

## 5 Artículos

- Artículo 1** García-Antón, Jordi; Pons, Josefina; Solans, Xavier; Font-Bardia, Mercè; Ros, Josep. “Synthesis of New Pd<sup>II</sup> Complexes Containing Thioether-Pyrazole Hemilabile Ligands. Structural Analysis by <sup>1</sup>H, <sup>13</sup>C NMR and Crystal Structures of [PdCl<sub>2</sub>(bddo)] and [Pd(bddo)](BF<sub>4</sub>)<sub>2</sub> [bddo = 1,8-Bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane]”. *Eur. J. Inorg. Chem.* **2002**, 3319-3327.
- Artículo 2** García-Antón, Jordi; Pons, Josefina; Solans, Xavier; Font-Bardia, Mercè; Ros, Josep. “Crystal Structure of [Pd(bddn)](BF<sub>4</sub>)<sub>2</sub> [bddn = 1,9-Bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithianonane]” En preparación.
- Artículo 3** García-Antón, Jordi; Pons, Josefina; Solans, Xavier; Font-Bardia, Mercè; Ros, Josep. “Synthesis of New Pd<sup>II</sup> Complexes Containing a Thioether-Pyrazole Hemilabile Ligand. Structural Analysis by <sup>1</sup>H, <sup>13</sup>C NMR and Crystal Structure of [PdCl(bdtp)]BF<sub>4</sub> [bdtp = 1,5-Bis(3,5-dimethyl-1-pyrazolyl)-3-thiapentane]”. *Eur. J. Inorg. Chem.* En prensa.
- Artículo 4** García-Antón, Jordi; Pons, Josefina; Solans, Xavier; Font-Bardia, Mercè; Ros, Josep. “Synthesis, Characterisation and X-Ray Crystal Structure of New Ni<sup>II</sup>, Pd<sup>II</sup> and Pt<sup>II</sup> Complexes of Tridentate Pyrazole Based Ligands with NOS-Donor Set”. *Eur. J. Inorg. Chem.* **2003**, 2992-3000.
- Artículo 5** García-Antón, Jordi; Pons, Josefina; Solans, Xavier; Font-Bardia, Mercè; Ros, Josep. “Synthesis, X-Ray Crystal Structure, and NMR Characterisation of Thiolate-Bridged Dinuclear Ni<sup>II</sup>, Pd<sup>II</sup> and Pt<sup>II</sup> Complexes of Didentate Ligands with NS-Donor Set”. *Inorg. Chim. Acta* En prensa.
- Artículo 6** García-Antón, Jordi; Pons, Josefina; Solans, Xavier; Font-Bardia, Mercè; Ros, Josep. “Reactivity of [PdCl(μ-med)]<sub>2</sub> with Monodentate or Bidentate Ligands. Structure of the Dinuclear Complexes [Pd(μ-med)(PPh<sub>3</sub>)]<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub> and [Pd(μ-med)(bpy)]<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub> [Hmed = 1-(2-mercaptoethyl)-3,5-dimethylpyrazole]”. En prensa.
- Artículo 7** García-Antón, Jordi; Mathieu, René; Lugan, Noël; Pons, Josefina; Ros, Josep. “Study of the coordination properties toward Rh<sup>I</sup> of N<sub>2</sub>S- (1,5-bis(3,5-dimethyl-1-pyrazolyl)-3-thiapentane) or N<sub>2</sub>S<sub>2</sub>- (1,8-bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane or 1,2-bis[3-(3,5-dimethyl-1-pyrazolyl)-2-thiapropyl]benzene ligand) donor ligands”. En preparación.



# Synthesis of New Pd<sup>II</sup> Complexes Containing Thioether–Pyrazole Hemilabile Ligands – Structural Analysis by <sup>1</sup>H and <sup>13</sup>C NMR Spectroscopy and Crystal Structures of [PdCl<sub>2</sub>(bddo)] and [Pd(bddo)](BF<sub>4</sub>)<sub>2</sub> [bddo = 1,8-Bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane]

Jordi García-Antón,<sup>[a]</sup> Josefina Pons,<sup>\*[a]</sup> Xavier Solans,<sup>[b]</sup> Mercè Font-Bardia,<sup>[b]</sup> and Josep Ros<sup>\*[a]</sup>

**Keywords:** Hemilabile ligands / N ligands / Palladium / S ligands

Treatment of the ligands 1,6-bis(3,5-dimethyl-1-pyrazolyl)-2,5-dithiahexane (bddh), 1,7-bis(3,5-dimethyl-1-pyrazolyl)-2,6-dithiaheptane (bddhp), 1,8-bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane (bddo) and 1,9-bis(3,5-dimethyl-1-pyrazolyl)-3,7-dithianonane (bddn) with [PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>] produces [PdCl<sub>2</sub>(L)] or [Pd<sub>2</sub>Cl<sub>4</sub>(L)] complexes, depending on the stoichiometry. Treatment of the complexes [PdCl<sub>2</sub>(bddo)] and [PdCl<sub>2</sub>(bddn)] with AgBF<sub>4</sub> gives [Pd(bddo)](BF<sub>4</sub>)<sub>2</sub> and [Pd(bddn)](BF<sub>4</sub>)<sub>2</sub>. These Pd<sup>II</sup> complexes have been characterised by elemental analyses, conductivity measurements, IR and <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy where possible. The X-ray structures of the complexes [PdCl<sub>2</sub>(bddo)] and

[Pd(bddo)](BF<sub>4</sub>)<sub>2</sub> have been determined. In [PdCl<sub>2</sub>(bddo)] the thioether–pyrazole ligand is coordinated through the azine nitrogen atoms to the metal atom, which completes its coordination with two chloride ions in a *trans* disposition. In [Pd(bddo)](BF<sub>4</sub>)<sub>2</sub> the metal atom is tetracoordinated by the two thioether sulfur atoms and the two azine nitrogen atoms of the pyrazole rings. Complexes [PdCl<sub>2</sub>(bddo)] and [PdCl<sub>2</sub>(bddn)] were obtained again when the complexes [Pd(bddo)](BF<sub>4</sub>)<sub>2</sub> and [Pd(bddn)](BF<sub>4</sub>)<sub>2</sub> were heated under reflux in a solution of Et<sub>4</sub>NCl in CH<sub>2</sub>Cl<sub>2</sub>/MeOH (1:1).

(© Wiley-VCH Verlag GmbH, 69451 Weinheim, Germany, 2002)

## Introduction

The chemistry of hemilabile ligands has been widely studied in recent years.<sup>[1]</sup> The term “hemilabile ligand”, introduced in 1979 by Jeffrey and Rauchfuss,<sup>[2]</sup> refers to polydentate chelates containing at least two types of bonding groups displaying different properties in substitution reactions (one labile and one inert). Thus, one group bonds strongly to a metal centre and the other group is weakly bonded and easily displaced by coordinating ligands. This makes them very attractive for catalytic purposes.

In recent years, we have studied and reported on the properties of hemilabile ligands based on the pyrazolyl group and on some other groups, containing N,<sup>[3]</sup> P<sup>[4]</sup> or O<sup>[5]</sup> atoms. This article is the initial part of a study of ligands containing pyrazolyl and thioether groups.

The literature describes the use of low molecular mass coordination compounds (with cations such as Ni<sup>II</sup>, Cu<sup>I</sup>, Cu<sup>II</sup>, Co<sup>II</sup>, Zn<sup>II</sup>, Cd<sup>II</sup> and Ag<sup>I</sup>) with ligands of this kind for

the modelling of metalloprotein-active centres in the bio-inorganic field.<sup>[6–9]</sup> Our goal is to extend these studies to include the potential hemilabile capability of ligands that coordinate Pd<sup>II</sup>.

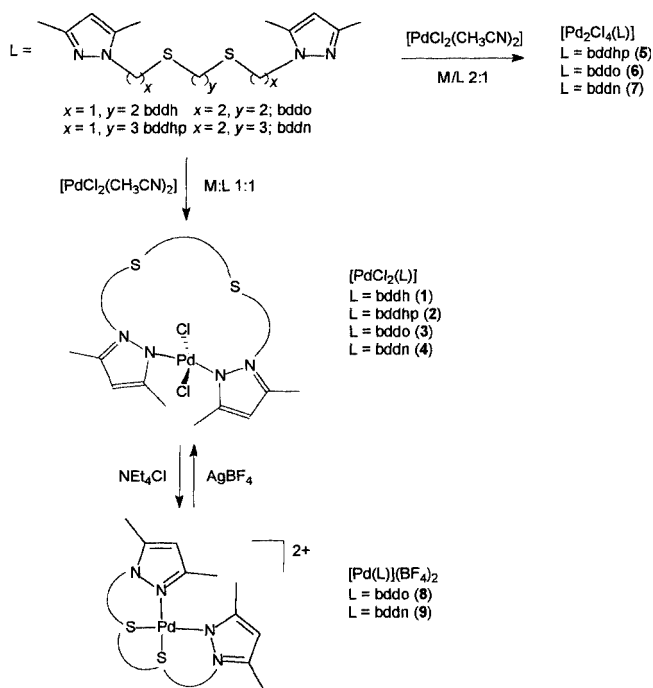
Here we report the synthesis of the ligand 1,7-bis(3,5-dimethyl-1-pyrazolyl)-2,6-dithiaheptane (bddhp). We have also studied the reactivity towards Pd<sup>II</sup> of the previously described ligands 1,6-bis(3,5-dimethyl-1-pyrazolyl)-2,5-dithiahexane (bddh),<sup>[6]</sup> 1,8-bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane (bddo)<sup>[7]</sup> and 1,9-bis(3,5-dimethyl-1-pyrazolyl)-3,7-dithianonane (bddn)<sup>[8]</sup> (Scheme 1). We have isolated the following complexes: [PdCl<sub>2</sub>L] with L = bddh (**1**), L = bddhp (**2**), L = bddo (**3**) and L = bddn (**4**), and [Pd<sub>2</sub>Cl<sub>4</sub>L] with L = bddhp (**5**), L = bddo (**6**) and L = bddn (**7**). Treatment of **3** and **4** with AgBF<sub>4</sub> affords [Pd(bddo)](BF<sub>4</sub>)<sub>2</sub> (**8**) and [Pd(bddn)](BF<sub>4</sub>)<sub>2</sub> (**9**). NMR studies and the X-ray crystal structures of **3** and **8** are also presented.

## Results and Discussion

The pyrazole ligands bddh, bddo and bddn were synthesised as described in the literature.<sup>[6–8]</sup> The bddh ligand was further purified by chromatography (silica gel 60) with methanol/dichloromethane (1:9) as eluent; bddo and bddn were purified by extraction (CHCl<sub>3</sub>/H<sub>2</sub>O/NaOH).

<sup>[a]</sup> Departament de Química, Facultat de Ciències, Universitat Autònoma de Barcelona, 08193 Bellaterra-Cerdanyola, Barcelona, Spain  
Fax: (internat.) + 34-93/581-3101  
E-mail: Josefina.Pons@uab.es

<sup>[b]</sup> Cristal·lografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona, Martí i Franquès s/n, 08028 Barcelona, Spain



Scheme 1

Ligand bddhp, not previously reported in the literature, was prepared by a synthetic route similar to that used for the ligand bddh.<sup>[6a]</sup> Treatment of 2-(hydroxymethyl)-3,5-dimethylpyrazole with thionyl chloride gave 2-(chloromethyl)-3,5-pyrazolium chloride. This compound, on treatment with 1,3-propanedithiol in the presence of sodium hydroxide, yielded the desired product. The ligand bddhp was characterised by elemental analysis, mass spectrometry and IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

Complexes  $[PdCl_2L]$  [ $L =$  bddh (1), bddhp (2), bddo (3) and bddn (4)] were obtained by treatment of the corresponding ligand either with  $[PdCl_2(CH_3CN)_2]$  or with  $[PdCl_2(COD)]$  in a 1:1 M/L ratio. Complexes  $[Pd_2Cl_4L]$  [ $L =$  bddhp (5), bddo (6) and bddn (7)] were obtained by use of a 2:1 M/L ratio.

Treatment of 3 and 4 with  $AgBF_4$  gave compounds of formula  $[PdL](BF_4)_2$  [ $L =$  bddo (8) and bddn (9)]. In contrast, use of the same reaction conditions with complexes 1 and 2 gave decomposition products. When complexes 8 and 9 were heated under reflux in a solution of  $Et_4NCl$  in  $CH_2Cl_2/MeOH$  (1:1) for 24 h, complexes 3 and 4 were obtained again.

The elemental analyses of products 5, 6 and 7 are consistent with the formulas  $[Pd_2Cl_4L]$ . The low solubilities of the complexes were sufficient for their conductivity and <sup>1</sup>H NMR spectra to be measured, but their <sup>13</sup>C NMR spectra could not be recorded.

Conductivity values in acetonitrile for complexes 1–4, and in DMSO for complexes 5–7, are in agreement with non-electrolyte natures (Table 4). Conductivity values in methanol for complexes 8 and 9 are in agreement with 2:1 electrolytes. The reported values for  $10^{-3}$  M solutions of

non-electrolyte complexes are lower than  $120 \Omega^{-1}cm^2mol^{-1}$  or  $50 \Omega^{-1}cm^2mol^{-1}$  in acetonitrile or DMSO, respectively, while the range of conductivity values for  $10^{-3}$  M solutions of 2:1 electrolyte compounds in methanol is between 160 and  $220 \Omega^{-1}cm^2mol^{-1}$ .<sup>[10]</sup>

The IR spectra of all complexes are similar to those of the ligands, the most characteristic bands being those attributable to the pyrazolyl group:  $\nu(C=C)$  and  $\nu(C=N)$  between  $1564$ – $1554$   $cm^{-1}$  and  $\delta(C-H)_{oop}$  between  $820$  and  $778$   $cm^{-1}$ . The  $\nu(B-F)$  band at  $1061$   $cm^{-1}$  is characteristic for 8 and 9.<sup>[11]</sup>

The IR spectra of the complexes in the  $500$ – $100$   $cm^{-1}$  region were also studied. Complexes  $[PdCl_2L]$  (1–4) show two well-defined bands corresponding to  $\nu(Pd-Cl)$  at  $340$ – $326$   $cm^{-1}$  and  $\nu(Pd-N)$  at  $473$ – $448$   $cm^{-1}$ . For the  $[Pd_2Cl_4L]$  complexes 5–7, three bands can be observed. One of these can be assigned to  $\nu(Pd-N)$  at  $459$ – $452$   $cm^{-1}$ . The number and energy of the other two bands are consistent with the presence of terminal ( $366$ – $360$   $cm^{-1}$ ) and bridging ( $335$ – $299$   $cm^{-1}$ )  $Pd-Cl$  bonds. For complexes 8 and 9 the  $\nu(Pd-N)$  and  $\nu(Pd-S)$  bands can be attributed to the signals appearing between  $461$ – $456$  and  $238$ – $247$   $cm^{-1}$ , respectively.<sup>[12]</sup>

## NMR Experiments

The <sup>1</sup>H and <sup>13</sup>C NMR spectra of complexes 1–4, 8 and 9 show the signals of coordinated ligands. NMR spectroscopic data are shown in the Exp. Sect. NMR spectra of compounds 3, 4, 8 and 9 were studied in more detail.

Study of the  $S-CH_2-CH_2-N$  fragment (in 3 and 4) as an AA'XX' system gave a set of coupling constants for each compound. These constants were consistent with the simulated spectra for compounds 3 and 4, obtained with the aid of the *g* NMR program.<sup>[13]</sup> All these results are reported in Table 1. Figure 1 shows the experimentally determined and simulated spectra for 3.

Table 1. <sup>1</sup>H NMR results: chemical shifts (ppm) and <sup>1</sup>H,<sup>1</sup>H coupling constants (Hz) for 3 and 4 in  $CDCl_3$

Compound	3	4
$\delta(CH_2)$ (6)	4.93	4.89
$\delta(CH_2)$ (7)	3.08	3.14
$^2J(6a,6b)$	–12.28	–12.87
$^2J(7a,7b)$	–12.28	–14.32
$^3J(6a,7a) = ^3J(6b,7b)$ ,	4.81, 13.01	4.87, 12.39
$^3J(6a,7b) = ^3J(6b,7a)$		

The Karplus equation cannot be used directly to calculate the dihedral angle between adjacent hydrogen atoms if the ethylenic fragments are  $\alpha$ -substituted by heteroatoms (O, S, NR). In such cases, coupling constants are dependent on the electronegativity of the  $\alpha$ -heteroatom substituent as well as on the dihedral angle.<sup>[14]</sup> Here, we have used a program based on the Karplus equation but which takes account of the electronegativity of the fragments connected

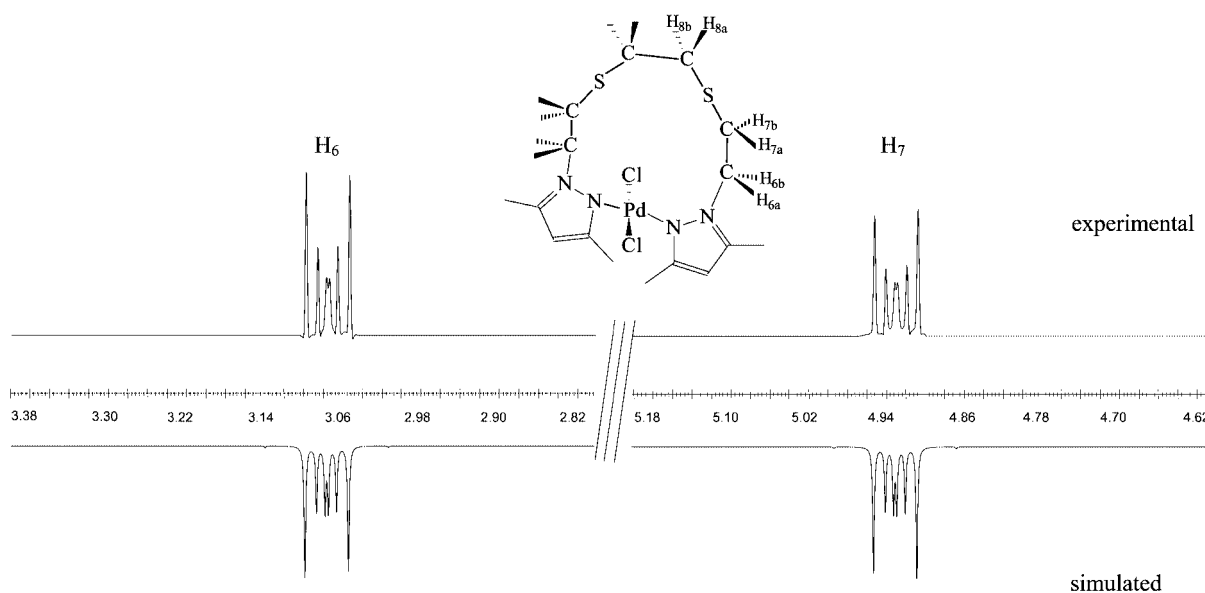


Figure 1. The 400-MHz <sup>1</sup>H NMR and the simulated *g* NMR spectra for the NCH<sub>2</sub>CH<sub>2</sub>S fragment of [PdCl<sub>2</sub>(bddo)] (**3**)

to the two carbon atoms involved.<sup>[15]</sup> Although this program was designed for organic molecules, in our case it works correctly when our ligands are coordinated to Pd<sup>II</sup>. By use of this program, the dihedral angles corresponding to the observed adjacent coupling constants (<sup>3</sup>*J*<sub>6a,7a</sub> = 4.81 and 4.87 Hz for **3** and **4**, respectively) are 51° and 52° for **3** and **4**, respectively. These values are in both cases consistent with an *anti* conformation (Figure 2).

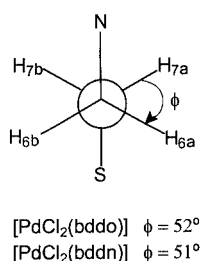


Figure 2. Dihedral angles for the NCH<sub>2</sub>CH<sub>2</sub>S fragment of [PdCl<sub>2</sub>(bddo)] (**3**)

The two different chains [S–(CH<sub>2</sub>)<sub>2</sub>–N and S–(CH<sub>2</sub>)<sub>*x*</sub>–S; *x* = 2 for **8** and *x* = 3 for **9**] were studied separately. HMQC spectra were used to assign the signals of protons H<sub>6</sub>, H<sub>7</sub> and H<sub>8</sub> for **8** and H<sub>6</sub>, H<sub>7</sub>, H<sub>8</sub> and H<sub>9</sub> for **9** (Figure 3). Simulated <sup>1</sup>H NMR spectra of both chains were obtained by use of the *g* NMR program.<sup>[13]</sup> The coupling constants are reported in Table 2.

Because of the symmetry of **8**, the two CH<sub>2</sub> units in the S–CH<sub>2</sub>–CH<sub>2</sub>–S fragment are equivalent. The two protons of each CH<sub>2</sub>, though, are diastereotopic and can be assigned to the two doublets found at  $\delta = 3.52$  and 4.04 ppm. The signal of H<sub>8</sub> for the S–(CH<sub>2</sub>)<sub>3</sub>–S chain in compound **9** is superposed on that of H<sub>7</sub> and could not be further studied.

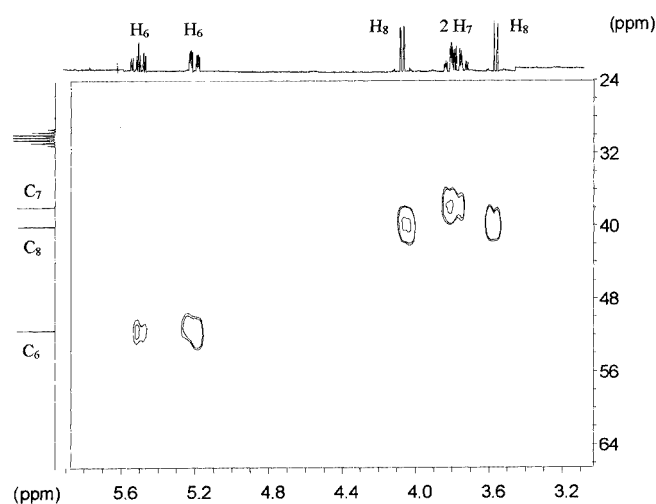


Figure 3. The 250-MHz 2D HMQC spectrum of [Pd(bddo)](BF<sub>4</sub>)<sub>2</sub> (**8**)

Table 2. <sup>1</sup>H NMR results: chemical shifts (ppm) and <sup>1</sup>H,<sup>1</sup>H coupling constants (Hz) for **8** and **9** in [D<sub>6</sub>]acetone

Compound	<b>8</b>	<b>9</b>
$\delta$ (H) (6 <i>R</i> ), $\delta$ (H) (6 <i>S</i> )	5.19, 5.50	5.23, 5.58
$\delta$ (H) (7 <i>S</i> ), $\delta$ (H) (7 <i>R</i> )	3.72, 3.78	3.52, 3.92
$\delta$ (H) (8 <i>R</i> ), $\delta$ (H) (8 <i>S</i> )	3.52, 4.04	3.53
$\delta$ (H) (9 <i>R</i> ), $\delta$ (H) (9 <i>S</i> )	–	2.70
<sup>2</sup> <i>J</i> (6 <i>R</i> ,6 <i>S</i> )	–13.56	–8.80
<sup>2</sup> <i>J</i> (7 <i>R</i> ,7 <i>S</i> )	–13.70	–4.40
<sup>3</sup> <i>J</i> (6 <i>R</i> ,7 <i>R</i> ), <sup>3</sup> <i>J</i> (6 <i>S</i> ,7 <i>S</i> )	2.11, 3.17,	2.92, 10.28,
<sup>3</sup> <i>J</i> (6 <i>R</i> ,7 <i>S</i> ), <sup>3</sup> <i>J</i> (6 <i>S</i> ,7 <i>R</i> )	3.84, 12.45	15.24, 15.52
<sup>2</sup> <i>J</i> (8 <i>R</i> ,8 <i>S</i> )	–8.04	–

For complexes **8** and **9**, the two protons of each CH<sub>2</sub> group in the S–CH<sub>2</sub>–CH<sub>2</sub>–N chain are diastereotopic, thus giving rise to four groups of signals, each attributable to a single hydrogen atom. This happens because of the rigid conformation of the ligand when it is complexed. In this way, each group of signals can be assigned as a double doublet. In **8**, the two signals of lower  $\delta$  value appear partially superimposed. Figure 4 shows the experimental and the simulated spectra for **8**.

### Crystal Structure of [PdCl<sub>2</sub>(bdo)] (**3**)

The structure of **3** (Figure 5) consists of discrete [PdCl<sub>2</sub>(bdo)] units. The palladium atom is coordinated by two pyrazole nitrogen and two chlorine atoms in a distorted square-planar geometry. The tetrahedral distortion can be observed in the mean separation [ $\pm 0.174(3)$ ] of the atoms coordinated to the Pd atom in relation to the mean plane. Tetrahedral distortion of the square-planar geometry can

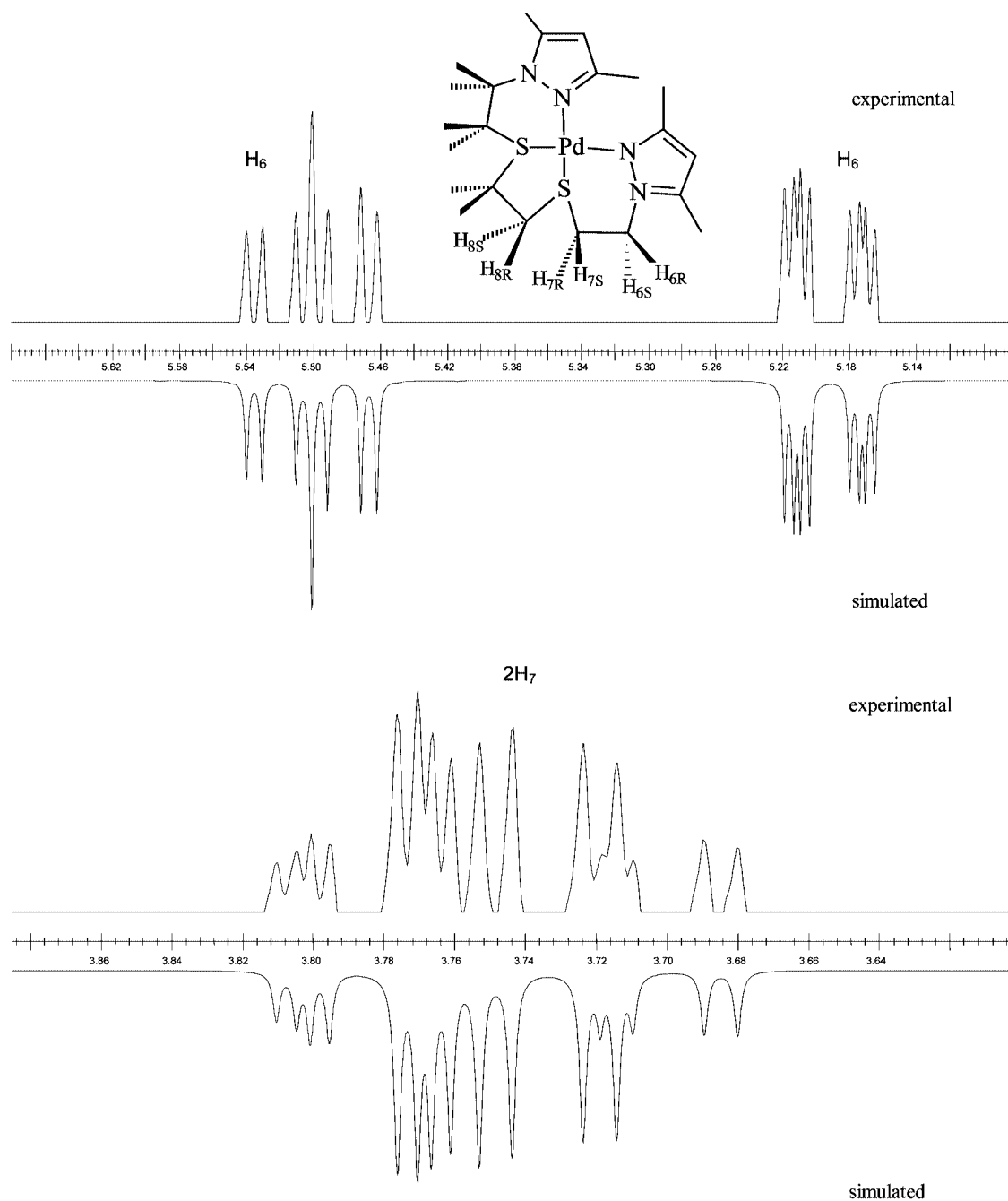


Figure 4. The 400-MHz <sup>1</sup>H NMR and the simulated *g* NMR spectra for the H<sub>6</sub> and H<sub>7</sub> protons of the NCH<sub>2</sub>CH<sub>2</sub>S fragment of [Pd(bdo)](BF<sub>4</sub>)<sub>2</sub> (**8**)

also be observed in the angles Cl(1)–Pd–Cl(2) and N(1)–Pd–N(3), of 172.47(4) and 168.65(9)°, respectively. The dihedral angle between the planes N(1)–Pd–Cl(1) and N(3)–Pd–Cl(2) is 13.5(1)°.

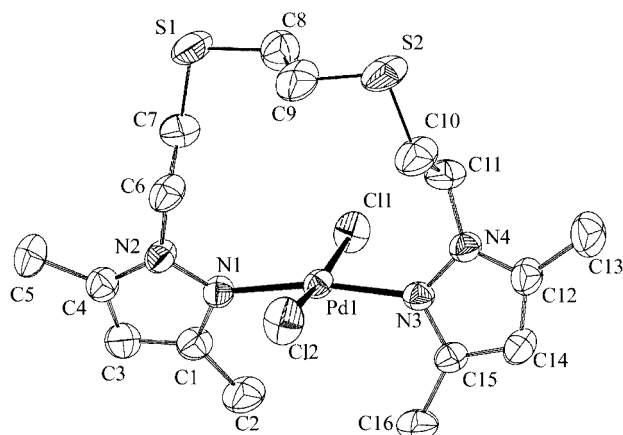


Figure 5. ORTEP drawing of [PdCl<sub>2</sub>(bddo)] (**3**, 273 K determination) showing all non-hydrogen atoms and the atom-numbering scheme; 50% probability amplitude displacement ellipsoids are shown

The pyrazolyl groups are *trans* to each other. The PdN<sub>2</sub>Cl<sub>2</sub> core (containing pyrazole nitrogen atoms and terminal chloride ions) is found in 11 complexes described in the literature (seven of the complexes found had *trans* geometry and five were *cis*).<sup>[16]</sup> Both the Pd–N and the Pd–Cl bond lengths in **3** are of the same order as those found in the literature.<sup>[17]</sup> The palladium atom does not interact with the sulfur atoms, the Pd–S distances being 5.02(8) and 5.16(8) Å, respectively. The SCH<sub>2</sub>CH<sub>2</sub>S bridging segment is disordered in the crystal.

The structure of **3** is similar to that found for the complex [CuCl<sub>2</sub>(bddo)],<sup>[7b]</sup> but the copper complex shows greater distortion of the square-planar geometry. This can be observed in the dihedral angle between the planes N(1)–Cu–Cl(1) and N(3)–Cu–Cl(2), which is 27°. Table 3 lists some selected bond lengths and angles for this complex.

Table 3. Selected bond lengths (Å) and angles (°) for **3** and **8**, with estimated standard deviations (e.s.d.) in parentheses

<b>3</b>		<b>8</b>	
Pd(1)–N(1)	2.027(3)	Pd(1)–N(1)	2.027(4)
Pd(1)–N(3)	2.017(3)	Pd(1)–N(4)	2.030(4)
Pd(1)–Cl(1)	2.292(1)	Pd(1)–S(1)	2.246(1)
Pd(1)–Cl(2)	2.287(1)	Pd(1)–S(2)	2.247(1)
N(1)–Pd(1)–Cl(1)	90.98(9)	N(1)–Pd(1)–N(4)	97.4(2)
N(1)–Pd(1)–Cl(2)	90.03(9)	N(1)–Pd(1)–S(2)	86.2(1)
N(3)–Pd(1)–Cl(1)	91.38(9)	N(4)–Pd(1)–S(1)	86.8(1)
N(3)–Pd(1)–Cl(2)	89.08(9)	S(1)–Pd(1)–S(2)	89.78(6)
N(1)–Pd(1)–N(3)	168.65(9)	N(1)–Pd(1)–S(1)	175.4(1)
Cl(1)–Pd(1)–Cl(2)	172.47(4)	N(4)–Pd(1)–S(2)	175.2(1)

## Crystal Structure of [Pd(bddo)](BF<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (**8**)

The structure of **8** (Figure 6) consists of cationic units of [Pd(bddo)]<sup>2+</sup>, BF<sub>4</sub><sup>–</sup> anions and solvent molecules (H<sub>2</sub>O). Two nitrogen atoms of the pyrazolyl groups and two thioether groups coordinate the palladium atom in a slightly distorted square-planar geometry. The pyrazolyl groups are *cis* to each other. The tetrahedral distortion of the square-planar geometry can be observed in the mean separation of the atoms linked to Pd from the mean plane, which is ±0.050(3) Å. The dihedral angle between the planes N(1)–Pd–N(4) and S(1)–Pd–S(2) is 3.79(9)°. Some selected bond lengths and bond angles for this complex are listed in Table 3.

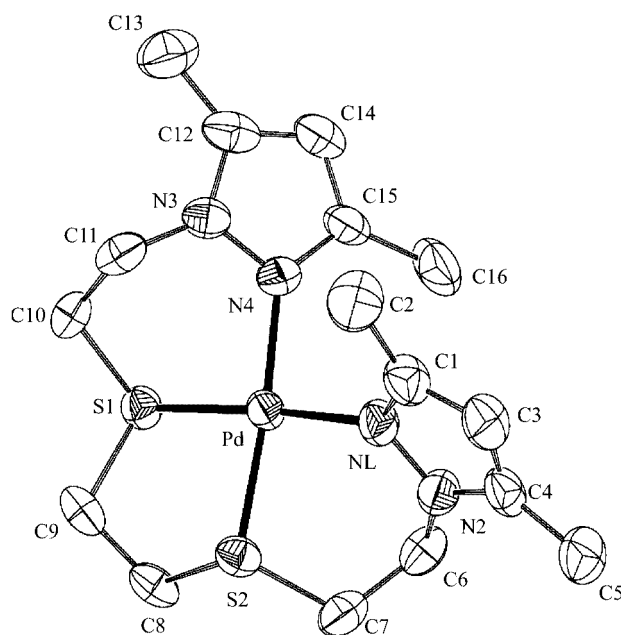


Figure 6. ORTEP drawing of [Pd(bddo)](BF<sub>4</sub>)<sub>2</sub> (**8**, 273 K determination) showing all non-hydrogen atoms and the atom-numbering scheme; 50% probability amplitude displacement ellipsoids are shown

The PdN<sub>2</sub>S<sub>2</sub> core (N in aromatic amine and S thioether) is found in five complexes in the literature.<sup>[18]</sup> The Pd–N and Pd–S distances in complex **8** are of the same order as those found in the literature for this kind of complexes.<sup>[17]</sup>

Ligand bddo acts as a tetradentate chelate and forms two Pd–N–N–C–C–S six-membered rings and one Pd–S–C–C–S five-membered ring. All of these have half-chair configurations. For the six-membered rings the N(4)–Pd–S(1) and N(1)–Pd–S(2) bite angles are 86.8(1) and 86.2(1)°, respectively. For the five-membered ring, the S(1)–Pd–S(2) bite angle is 89.75(6)°. These bite angles are similar to those reported in the literature for [Pd(pdto)](ClO<sub>4</sub>)<sub>2</sub> [pdto = 1,8-bis(2-pyridyl)-3,6-dithiaoctane] (N–Pd–S bite angles are 86.9 and 87.2° and the S–Pd–S bite angle is 89.4°).<sup>[18d]</sup> This is the only compound with a PdN<sub>2</sub>S<sub>2</sub> core similar to that presented in this paper, with two six-membered rings and one five-membered ring.

The half-chair distortions in the six-membered rings are  $\Delta C_S(\text{Pd}) = 10.9(4)^\circ$  and  $17.0(4)^\circ$  and  $\Delta C_S[\text{S}(1)-\text{C}(10)] = 11.95(5)^\circ$ ,  $\Delta C_S[\text{S}(2)-\text{C}(7)] = 14.0(6)^\circ$  for  $\text{Pd}-\text{S}(1)-\text{C}(10)-\text{C}(11)-\text{N}(3)-\text{N}(4)$  and  $\text{Pd}-\text{S}(2)-\text{C}(7)-\text{C}(6)-\text{N}(2)-\text{N}(1)$ , respectively.

## Conclusion

We have shown that thioether–pyrazole  $\text{N}_2\text{S}_2$  ligands can coordinate  $\text{Pd}^{\text{II}}$  centres in different ways. Treatment of  $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$  with these ligands gave complexes in which the  $\text{Pd}^{\text{II}}$  centre is bonded to two pyrazole rings and two chloride ions in a *trans* disposition. Abstraction of the chloride components in **3** and **4** with  $\text{AgBF}_4$  gave complexes **8** and **9** with the  $\text{Pd}^{\text{II}}\text{N}_2\text{S}_2$  core. These kinds of complexes were not obtained with *bddh* and *bddhp* ligands, probably because of the imposed geometry of the hypothetical  $\text{PdNNCS}$  metallacycle, which would induce steric hindrance between the methyl groups of the pyrazole rings. The  $\text{Cl}_2\text{N}_2$  and  $\text{N}_2\text{S}_2$  coordination modes of  $\text{Pd}^{\text{II}}$  can be interconverted. Thus, if **8** and **9** are heated under reflux in solutions with  $\text{Et}_4\text{NCl}$ , **3** and **4** are formed again. This reactivity is confirmation of the hemilabile behaviour of these thioether–pyrazole ligands in the complexation of  $\text{Pd}^{\text{II}}$ .

## Experimental Section

**Generals Remarks:** Preparations were performed by use of conventional vacuum line and Schlenk techniques. All reagents were commercial grade materials and were used without further purification. Acetonitrile and dichloromethane were dried and distilled by standard methods and deoxygenated in the vacuum line in advance. Samples of  $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]^{[19]}$  and  $[\text{PdCl}_2(\text{COD})]^{[20]}$  were prepared as described in the literature. 1,6-Bis(3,5-dimethyl-1-pyrazolyl)-2,5-dithiahexane (*bddh*),<sup>[6a]</sup> 1,8-bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane (*bddo*)<sup>[7a]</sup> and 1,9-bis(3,5-dimethyl-1-pyrazolyl)-3,7-dithianonane (*bddn*)<sup>[8]</sup> were prepared according to the published methods. Analyses (C, H, N, S) were performed in our analytical laboratory with a Carlo Erba CHNS EA-1108 instrument. Conductivity measurements were performed at room temperature in  $10^{-3}$  M acetonitrile, DMSO or methanol solutions, with the aid of a Crison micro CM 2200 conductimeter. Infrared spectra were recorded as KBr pellets or polyethylene mulls under nitrogen over the 4000–100  $\text{cm}^{-1}$  range. The  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  NMR and HMQC spectra were obtained either with Bruker 250-MHz or 400-MHz instruments. Chemical shifts ( $\delta$ ) were determined relative to internal TMS and are given in ppm. Mass spectra were obtained with an HP 5989A apparatus.

**1,7-Bis(3,5-dimethyl-1-pyrazolyl)-2,6-dithiaheptane (*bddhp*):** 2-(Chloromethyl)-3,5-pyrazolium chloride<sup>[6a]</sup> (720 mg, 3.98 mmol) and 1,3-propanedithiol (0.20 mL, 1.97 mmol) were dissolved in dry DMF (6 mL) and the mixture was then heated to 90 °C. After the mixture had been maintained at this temperature for 15 min, sodium hydroxide (500 mg, 12.1 mmol), dissolved in water (7 mL), was added dropwise. Heating was stopped; after 15 min, additional water (7 mL) was added. After cooling to room temperature, the reaction mixture was extracted four times with  $\text{CHCl}_3$  (15 mL). The collected organic layers were dried with anhydrous sodium sulfate and removed under vacuum. The product was purified by

chromatography (silica gel 60) with methanol/dichloromethane (1:9) as eluent to give a white solid. Yield: 0.46 g (72%). M.p. 30–32 °C. IR (NaCl,  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 2918$  [ $\nu(\text{C}-\text{H})_{\text{al}}$ ], 1558 [ $\nu(\text{C}=\text{C})$ ,  $\nu(\text{C}=\text{N})$ ], 1455 [ $\delta(\text{CH}_3)_{\text{as}}$ ], 1378 [ $\delta(\text{CH}_3)_{\text{s}}$ ], 779 [ $\delta(\text{C}-\text{H})_{\text{oop}}$ ].  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$  solution):  $\delta = 1.76$  (q,  $^3J = 7$  Hz, 2 H,  $\text{CH}_2-\text{CH}_2-\text{CH}_2$ ), 2.22 (s, 6 H, *Me*), 2.31 (s, 6 H, *Me*), 2.67 (t,  $^3J = 7$  Hz, 4 H,  $\text{S}-\text{CH}_2-\text{CH}_2$ ), 5.05 (s, 4 H, *pz-CH}\_2-\text{S}*), 5.86 (s, 2 H, *pz-CH*) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$  solution, 63 MHz):  $\delta = 11.6$  (*Me*), 13.9 (*Me*), 29.4 ( $\text{CH}_2-\text{CH}_2-\text{CH}_2$ ), 30.3 ( $\text{S}-\text{CH}_2-\text{CH}_2$ ), 50.3 (*pz-CH}\_2-\text{S}*), 106.9 (*pz-CH*), 139.4 (*pz-C*), 148.1 (*pz-C*) ppm. MS (CI,  $\text{NH}_3$ ):  $m/z$  (%) = 325 (100) [ $\text{MH}^+$ ].  $\text{C}_{15}\text{H}_{24}\text{N}_4\text{S}_2$  (324): calcd. C 55.52, H 7.45, N 17.27, S 19.76; found C 55.21, H 7.25, N 16.96, S 19.71.

### Synthesis of the $\text{Pd}^{\text{II}}$ Complexes

**Complexes  $[\text{PdCl}_2\text{L}]$  with  $\text{L} = \text{bddh}$  (**1**), *bddhp* (**2**), *bddo* (**3**) and *bddn* (**4**):** A solution of  $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$  or  $[\text{PdCl}_2(\text{COD})]$  (0.36 mmol) in dichloromethane (30 mL) was added to a solution of the appropriate ligand (0.36 mmol) in dichloromethane (10 mL). After the mixture had been stirred for 12 h, most of the solvent was removed under vacuum. Diethyl ether was then added to induce precipitation. The resulting precipitate was then filtered and washed with diethyl ether, yielding the desired compound.

**Complex 1:** IR (KBr,  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 2951$  [ $\nu(\text{C}-\text{H})_{\text{al}}$ ], 1562 [ $\nu(\text{C}=\text{C})$ ,  $\nu(\text{C}=\text{N})$ ], 1462 [ $\delta(\text{CH}_3)_{\text{as}}$ ], 1380 [ $\delta(\text{CH}_3)_{\text{s}}$ ], 778 [ $\delta(\text{C}-\text{H})_{\text{oop}}$ ]. IR (polyethylene,  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 459$  [ $\nu(\text{Pd}-\text{N})_{\text{as}}$ ], 326 [ $\nu(\text{Pd}-\text{Cl})$ ].  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$  solution):  $\delta = 2.35$  (s, 6 H, *Me*), 2.85 (s, 6 H, *Me*), 3.96 (s, 4 H,  $\text{S}-\text{CH}_2-\text{CH}_2-\text{S}$ ), 5.96 (s, 2 H, *pz-CH*), 5.98 (s, 4 H, *pz-CH}\_2-\text{S}*) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$  solution):  $\delta = 12.5$  (*Me*), 16.3 (*Me*), 31.6 ( $\text{S}-\text{CH}_2-\text{CH}_2-\text{S}$ ), 48.8 (*pz-CH}\_2-\text{S}*), 108.9 (*pz-CH*), 144.8, 152.5 (*pz-C*) ppm.

**Complex 2:** IR (KBr,  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 3130$  [ $\nu(\text{C}-\text{H})_{\text{ar}}$ ], 2923 [ $\nu(\text{C}-\text{H})_{\text{al}}$ ], 1559 [ $\nu(\text{C}=\text{C})$ ,  $\nu(\text{C}=\text{N})$ ], 1464 [ $\delta(\text{CH}_3)_{\text{as}}$ ], 1381 [ $\delta(\text{CH}_3)_{\text{s}}$ ], 800 [ $\delta(\text{C}-\text{H})_{\text{oop}}$ ]. IR (polyethylene,  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 448$  [ $\nu(\text{Pd}-\text{N})_{\text{as}}$ ], 338 [ $\nu(\text{Pd}-\text{Cl})$ ].  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$  solution):  $\delta = 2.38$  (s, 6 H, *Me*), 3.01 (s, 6 H, *Me*), 3.13 (m, 2 H,  $\text{CH}_2-\text{CH}_2-\text{CH}_2$ ), 3.22 (m, 4 H,  $\text{S}-\text{CH}_2-\text{CH}_2$ ), 5.84 (s, 4 H, *pz-CH}\_2-\text{S}*), 6.02 (s, 2 H, *pz-CH*) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$  solution):  $\delta = 12.7$  (*Me*), 16.4 (*Me*), 27.2 ( $\text{CH}_2-\text{CH}_2-\text{CH}_2$ ), 31.4 ( $\text{S}-\text{CH}_2-\text{CH}_2$ ), 48.3 (*pz-CH}\_2-\text{S}*), 109.7 (*pz-CH*), 144.6, 151.4 (*pz-C*) ppm.

**Complex 3:** IR (KBr,  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 3129$  [ $\nu(\text{C}-\text{H})_{\text{ar}}$ ], 2918 [ $\nu(\text{C}-\text{H})_{\text{al}}$ ], 1557 [ $\nu(\text{C}=\text{C})$ ,  $\nu(\text{C}=\text{N})$ ], 1469 [ $\delta(\text{CH}_3)_{\text{as}}$ ], 1393 [ $\delta(\text{CH}_3)_{\text{s}}$ ], 820 [ $\delta(\text{C}-\text{H})_{\text{oop}}$ ]. IR (polyethylene,  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 453$  [ $\nu(\text{Pd}-\text{N})_{\text{as}}$ ], 340 [ $\nu(\text{Pd}-\text{Cl})$ ].  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$  solution):  $\delta = 2.28$  (s, 6 H, *Me*), 2.95 (s, 6 H, *Me*), 3.08 (m, 4 H,  $\text{CH}_2-\text{CH}_2-\text{S}$ ), 3.20 (s, 4 H,  $\text{S}-\text{CH}_2-\text{CH}_2-\text{S}$ ), 4.93(m, 4 H, *pz-CH}\_2-\text{CH}\_2*), 5.94 (s, 2 H, *pz-CH*) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$  solution):  $\delta = 12.1$  (*Me*), 15.5 (*Me*), 30.8 ( $\text{S}-\text{CH}_2-\text{CH}_2-\text{S}$ ), 34.0 ( $\text{CH}_2-\text{CH}_2-\text{S}$ ), 51.1 (*pz-CH}\_2-\text{CH}\_2*), 108.8 (*pz-CH*), 142.9, 150.6 (*pz-C*) ppm.

**Complex 4:** IR (KBr,  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 3126$  [ $\nu(\text{C}-\text{H})_{\text{ar}}$ ], 2917 [ $\nu(\text{C}-\text{H})_{\text{al}}$ ], 1554 [ $\nu(\text{C}=\text{C})$ ,  $\nu(\text{C}=\text{N})$ ], 1469 [ $\delta(\text{CH}_3)_{\text{as}}$ ], 1390 [ $\delta(\text{CH}_3)_{\text{s}}$ ], 789 [ $\delta(\text{C}-\text{H})_{\text{oop}}$ ]. IR (polyethylene,  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 473$  [ $\nu(\text{Pd}-\text{N})_{\text{as}}$ ], 335 [ $\nu(\text{Pd}-\text{Cl})$ ].  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$  solution):  $\delta = 2.28$  (s, 6 H, *Me*), 2.97 (s, 6 H, *Me*), 1.72 (q, 2 H,  $\text{CH}_2-\text{CH}_2-\text{CH}_2$ ), 2.84 (t, 4 H,  $\text{CH}_2-\text{CH}_2-\text{CH}_2$ ), 3.14 (m, 4 H,  $\text{CH}_2-\text{CH}_2-\text{S}$ ), 4.89 (m, 4 H, *pz-CH}\_2-\text{CH}\_2*), 5.94 (s, 2 H, *pz-CH*) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$  solution):  $\delta = 12.1$  (*Me*), 15.6 (*Me*), 29.5, 29.6, 30.6 (*pz-CH}\_2-\text{CH}\_2-\text{S}*,  $\text{CH}_2-\text{CH}_2-\text{CH}_2$ ,  $\text{CH}_2-\text{CH}_2-\text{CH}_2$ ), 50.7 (*pz-CH}\_2-\text{CH}\_2*), 108.8 (*pz-CH*), 143.1, 150.9 (*pz-C*) ppm.

**Complexes  $[\text{Pd}_2\text{Cl}_4\text{L}]$  with  $\text{L} = \text{bddhp}$  (**5**), *bddo* (**6**) and *bddn* (**7**):** A solution of  $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$  (0.36 mmol) in dichloromethane



(30 mL) was added to a solution of the appropriate ligand (0.18 mmol) in dichloromethane (10 mL). After the mixture had been stirred for 12 h, a precipitate had formed. This precipitate was filtered off, washed with diethyl ether and dried under vacuum, yielding the desired compound. No Pd<sup>II</sup> complex of this stoichiometry with bddh as ligand could be isolated.

**Complex 5:** IR (KBr, cm<sup>-1</sup>):  $\tilde{\nu}$  = 3129 [ν(C–H)<sub>ar</sub>], 2967 [ν(C–H)<sub>al</sub>], 1564 [ν(C=C)], 1463 [ν(C=N)],  $\delta$ (CH<sub>3</sub>)<sub>as</sub>, 1392 [ $\delta$ (CH<sub>3</sub>)<sub>s</sub>], 808 [ $\delta$ (C–H)<sub>oop</sub>]. IR (polyethylene, cm<sup>-1</sup>):  $\tilde{\nu}$  = 452 [ν(Pd–N)<sub>as</sub>], 366 [ν(Pd–Cl)], 335 [ν<sub>B</sub>(Pd–Cl)]. <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO solution):  $\delta$  = 2.16 (s, 6 H, *Me*), 2.34 (s, 6 H, *Me*), 2.69 (br, 2 H, CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>), 2.97 (br, 4 H, S–CH<sub>2</sub>–CH<sub>2</sub>), 5.67 (br, 4 H, pz–CH<sub>2</sub>–S), 5.97 (s, 2 H, pz–CH).

**Complex 6:** IR (KBr, cm<sup>-1</sup>): 3120 [ν(C–H)<sub>ar</sub>], 2967 [ν(C–H)<sub>al</sub>], ν(C=C), 1554 [ν(C=N)], 1467 [ $\delta$ (CH<sub>3</sub>)<sub>as</sub>], 1395 [ $\delta$ (CH<sub>3</sub>)<sub>s</sub>], 797 [ $\delta$ (C–H)<sub>oop</sub>]. IR (polyethylene, cm<sup>-1</sup>): 456 [ν(Pd–N)<sub>as</sub>], 367 [ν(Pd–Cl)], 322 [ν<sub>B</sub>(Pd–Cl)]. <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO solution):  $\delta$  = 2.36 (s, 6 H, *Me*), 2.43 (s, 6 H, *Me*), 2.79 (br, 4 H, CH<sub>2</sub>–CH<sub>2</sub>–S), 4.23 (br, 4 H, S–CH<sub>2</sub>–CH<sub>2</sub>–S), 4.92 (br, 4 H, pz–CH<sub>2</sub>–CH<sub>2</sub>), 6.19 (s, 2 H, pz–CH) ppm.

**Complex 7:** IR (KBr, cm<sup>-1</sup>):  $\tilde{\nu}$  = 3126 [ν(C–H)<sub>ar</sub>], 2958 [ν(C–H)<sub>al</sub>], 1560 [ν(C=C)], ν(C=N), 1470 [ $\delta$ (CH<sub>3</sub>)<sub>as</sub>], 1400 [ $\delta$ (CH<sub>3</sub>)<sub>s</sub>]. IR (polyethylene, cm<sup>-1</sup>):  $\tilde{\nu}$  = 459 [ν(Pd–N)<sub>as</sub>], 360 [ν(Pd–Cl)], 319 [ν<sub>B</sub>(Pd–Cl)]. <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO solution):  $\delta$  = 2.25 (s, 6 H, *Me*), 2.80 (s, 6 H, *Me*), 2.05 (br, 2 H, CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>), 2.42 (br, 4 H, CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>), 4.50 (br, 4 H, CH<sub>2</sub>–CH<sub>2</sub>–S), 4.90 (br, 4 H, pz–CH<sub>2</sub>–CH<sub>2</sub>), 6.20 (s, 2 H, pz–CH) ppm.

**Complexes [Pd(bddo)](BF<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (**8**) and [Pd(bddn)](BF<sub>4</sub>)<sub>2</sub> (**9**):** A solution of AgBF<sub>4</sub> (0.86 mmol) was added dropwise with vigorous stirring to a solution of [PdCl<sub>2</sub>(L)] (L = bddo or bddn, 0.43 mmol) in dichloromethane (10 mL) and methanol (10 mL). The reaction was carried out in the dark to prevent reduction of Ag<sup>I</sup> to Ag<sup>0</sup>. After 5 min, stirring was stopped, and AgCl was filtered off. When the volume of the resultant solution had been reduced to roughly 5 mL, the product precipitated as a yellow solid. This solid was filtered and washed with dichloromethane.

**Complex 8:** IR (KBr, cm<sup>-1</sup>):  $\tilde{\nu}$  = 3141 [ν(C–H)<sub>ar</sub>], 2956 [ν(C–H)<sub>al</sub>], 1553 [ν(C=C)], ν(C=N), 1470 [ $\delta$ (CH<sub>3</sub>)<sub>as</sub>], 1395 [ $\delta$ (CH<sub>3</sub>)<sub>s</sub>], 1061 [ν(B–F)], 791 [ $\delta$ (C–H)<sub>oop</sub>]. IR (polyethylene, cm<sup>-1</sup>):  $\tilde{\nu}$  = 461 [ν(Pd–N)<sub>as</sub>], 238 [ν(Pd–S)]. <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]acetone):  $\delta$  = 1.99 (s, 6 H, *Me*), 2.52 (s, 6 H, *Me*), 3.72/3.78/5.19/5.50 (pz–CH<sub>2</sub>–CH<sub>2</sub>), 6.26 (s, 2 H, pz–CH) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, [D<sub>6</sub>]acetone):  $\delta$  = 11.9 (*Me*), 13.3 (*Me*), 31.4 (S–CH<sub>2</sub>–CH<sub>2</sub>), 48.3 (pz–CH<sub>2</sub>–CH<sub>2</sub>–S), 109.0 (pz–CH), 147.0, 152.1 (pz–C) ppm.

**Complex 9:** IR (KBr, cm<sup>-1</sup>):  $\tilde{\nu}$  = 3129 [ν(C–H)<sub>ar</sub>], 2985–2928 [ν(C–H)<sub>al</sub>], 1549 [ν(C=C)], ν(C=N), 1472 [ $\delta$ (CH<sub>3</sub>)<sub>as</sub>], 1393 [ $\delta$ (CH<sub>3</sub>)<sub>s</sub>], 1061 [ν(B–F)], 810 [ $\delta$ (C–H)<sub>oop</sub>]. IR (polyethylene, cm<sup>-1</sup>):  $\tilde{\nu}$  = 456 [ν(Pd–N)<sub>as</sub>], 247 [ν(Pd–S)]. <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]acetone):  $\delta$  = 1.85 (s, 6 H, *Me*), 2.52 (s, 6 H, *Me*), 3.52/3.92/5.23/5.58 (pz–CH<sub>2</sub>–CH<sub>2</sub>), 6.24 (s, 2 H, pz–CH) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, [D<sub>6</sub>]acetone):  $\delta$  = 11.3 (*Me*), 12.7 (*Me*), 22.8 (CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>), 31.2 (pz–CH<sub>2</sub>–CH<sub>2</sub>), 36.4 (CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>), 49.9 (pz–CH<sub>2</sub>–CH<sub>2</sub>), 108.9 (pz–CH), 146.1, 152.1 (pz–C) ppm.

Tables 1 and 2 show coupling constants for complexes **3**, **4**, **8** and **9**; Table 4 shows other analytical and physical data for all complexes.

**X-ray Crystallographic Study:** Crystals of compounds **3** and **8** suitable for X-ray diffraction experiments were obtained by crystallisation from CH<sub>2</sub>Cl<sub>2</sub> and MeOH, respectively. The data for **3** were collected with an Enraf–Nonius CAD<sub>4</sub> four-circle diffractometer, by the  $\Omega/2\theta$  scan technique. The data for **8** were collected with an MAR345 diffractometer with an image plate detector, by the  $\phi$ -scan technique. Both crystals were subjected to graphite-monochromated Mo–K $\alpha$  radiation. The structures were solved by direct methods with the SHELXS 97 computer program<sup>[21]</sup> and refined by full-matrix, least squares with the SHELXL 97 program.<sup>[22]</sup> All hydrogen atoms were computed and refined by use of a riding model. The final *R* (on *F*) factor and  $\omega R$  (on *F*<sup>2</sup>) values, as well as the numbers of parameters refined and other details concerning the refinement of the crystal structure are presented in Table 5. CCDC-185048 (**3**) and -185049 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cam-

Table 4. Physical and analytical data for complexes **1**–**9**

Compound	Yield (%)	Analysis <sup>[a]</sup> N	C	H	S	Conductivity ( $\Omega^{-1}$ cm <sup>2</sup> mol <sup>-1</sup> )
[PdCl <sub>2</sub> (bddh)] ( <b>1</b> )	77	(11.49) 11.27	(34.47) 34.35	(4.55) 4.43	(13.15) 13.40	80 <sup>[b]</sup>
[PdCl <sub>2</sub> (bddhp)] ( <b>2</b> )	74	(11.16) 10.88	(35.90) 35.85	(4.82) 4.69	(12.78) 13.07	89 <sup>[b]</sup>
[PdCl <sub>2</sub> (bddo)] ( <b>3</b> )	96	(10.86) 10.98	(37.25) 37.03	(5.08) 5.33	(12.43) 12.57	96 <sup>[b]</sup>
[PdCl <sub>2</sub> (bddn)] ( <b>4</b> )	98	(10.57) 10.32	(38.53) 38.36	(5.33) 5.34	(12.10) 12.47	74 <sup>[b]</sup>
[Pd <sub>2</sub> Cl <sub>4</sub> (bddhp)] ( <b>5</b> )	80	(8.25) 8.05	(26.53) 26.42	(3.56) 3.33	(9.44) 9.25	27 <sup>[c]</sup>
[Pd <sub>2</sub> Cl <sub>4</sub> (bddo)] ( <b>6</b> )	87	(8.08) 7.81	(27.72) 27.49	(3.78) 3.88	(9.25) 9.59	29 <sup>[c]</sup>
[Pd <sub>2</sub> Cl <sub>4</sub> (bddn)] ( <b>7</b> )	83	(7.92) 7.58	(28.87) 28.72	(3.99) 3.95	(9.07) 8.86	23 <sup>[c]</sup>
[Pd(bddo)](BF <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O ( <b>8</b> )	89	(8.80) 8.61	(30.19) 30.03	(4.43) 4.36	(10.07) 10.39	163 <sup>[d]</sup>
[Pd(bddn)](BF <sub>4</sub> ) <sub>2</sub> ( <b>9</b> )	90	(8.86) 8.69	(32.28) 31.89	(4.46) 4.36	(10.14) 10.02	175 <sup>[d]</sup>

<sup>[a]</sup> Calculated analytical values are given in parentheses. <sup>[b]</sup> 10<sup>-3</sup> M in acetonitrile. <sup>[c]</sup> 10<sup>-3</sup> M in DMSO. <sup>[d]</sup> 10<sup>-3</sup> M in MeOH.

Table 5. Crystallographic data for crystal structures **3** and **8**

Compound	<b>3</b>	<b>8</b>
Empirical formula	C <sub>16</sub> H <sub>26</sub> Cl <sub>2</sub> N <sub>4</sub> PdS <sub>2</sub>	C <sub>16</sub> H <sub>28</sub> B <sub>2</sub> F <sub>8</sub> N <sub>4</sub> OPdS <sub>2</sub>
Formula mass [g·mol <sup>-1</sup> ]	515.83	636.56
Temperature [K]	293(2)	293(2)
Crystal system	monoclinic	orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> bca
Unit cell dimensions		
<i>a</i> [Å]	8.821(8)	14.219(1)
<i>b</i> [Å]	28.22(1)	16.493(1)
<i>c</i> [Å]	9.305(2)	20.834(1)
β [°]	112.62(3)	90
Volume [Å <sup>3</sup> ]	2138(2)	4885.9(5)
<i>Z</i>	4	8
<i>D</i> <sub>calcd.</sub> [g cm <sup>-3</sup> ]	1.602	1.736
μ [mm <sup>-1</sup> ]	1.320	1.009
<i>F</i> (000)	1048	2576
Crystal size [mm]	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.2
θ range [°]	2.48 to 29.99	2.13 to 25.01
Reflections collected:		
total, independent, <i>R</i> <sub>int</sub>	6539, 6168, 0.0578	17711, 3987, 0.0438
Data/restraints/parameters	6118/0/263	3987/0/295
<i>a</i> <sup>[a]</sup>	0.0285	0.0829
Final <i>R</i> 1, <i>wR</i> 2	0.0313, 0.0631	0.0398, 0.1259
<i>R</i> 1 (all data), <i>wR</i> 2	0.0946, 0.0762	0.0657, 0.1343
Residual electron density [e <sup>-</sup> Å <sup>-3</sup> ]	+0.433, -0.426	+0.694, -0.709

<sup>[a]</sup> The function minimised was  $\sum w(|F_o|^2 - |F_c|^2)^2$ , where  $w = [\sigma^2(I) + (aP)^2]^{-1}$ , and  $P = (|F_o|^2 + 2|F_c|^2)/3$ .

bridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

## Acknowledgments

Support by the Ministerio de Educación y Cultura of Spain (Project BQU2000-0238 and grant to J. G.) is gratefully acknowledged.

- [1] <sup>[1a]</sup> A. Bader, E. Lindner, *Coord. Chem. Rev.* **1991**, *108*, 27. <sup>[1b]</sup> C. S. Slone, D. A. Weinberger, C. A. Mirkin, *Prog. Inorg. Chem.* **1999**, *48*, 233.
- [2] <sup>[2a]</sup> J. C. Jeffrey, and T. B. Rauchfuss, *Inorg. Chem.* **1979**, *18*, 2658. <sup>[2b]</sup> S. Borns, R. Kadyrov, D. Heller, W. Baumann, A. Spannenberg, R. Kempe, J. Holz, A. Börner, *Eur. J. Inorg. Chem.* **1998**, 1291. <sup>[2c]</sup> P. Jutzi, T. Redeker, *Eur. J. Inorg. Chem.* **1998**, 663. <sup>[2d]</sup> I. Moldes, E. de la Encarnación, J. Ros, A. Alvarez-Larena, J. F. Piniella, *J. Organomet. Chem.* **1998**, *556*, 165.
- [3] <sup>[3a]</sup> R. Mathieu, G. Esquiús, N. Lugan, J. Pons, J. Ros, *Eur. J. Inorg. Chem.* **2001**, 2683. <sup>[3b]</sup> G. Esquiús, J. Pons, R. Yáñez, J. Ros, *J. Organomet. Chem.* **2001**, *619*, 14. <sup>[3c]</sup> G. Esquiús, J. Pons, R. Yáñez, J. Ros, X. Solans, M. Font-Bardía, *J. Organomet. Chem.* **2000**, *605*, 226. <sup>[3d]</sup> G. Esquiús, J. Pons, R. Yáñez, J. Ros, X. Solans, M. Font-Bardía, *Acta Crystallogr.* **2002**, *C58*, 133.
- [4] R. Tribó, J. Pons, R. Yáñez, J. F. Piniella, A. Álvarez-Larena, J. Ros, *Inorg. Chem. Commun.* **2000**, *3*, 545.
- [5] A. Boixassa, J. Pons, A. Virgili, X. Solans, M. Font-Bardía, J. Ros, *Inorg. Chim. Acta*, accepted.
- [6] <sup>[6a]</sup> W. G. Haanstra, W. L. Driessen, J. Reedijk, R. Fröhlich, B. Krebs, *Inorg. Chim. Acta* **1991**, *185*, 175. <sup>[6b]</sup> W. G. Haanstra, W. L. Driessen, R. A. G. de Graaff, J. Reedijk, Y. F. Wang, C. H. Stam, *Inorg. Chim. Acta* **1991**, *186*, 215.
- [7] <sup>[7a]</sup> W. G. Haanstra, W. L. Driessen, J. Reedijk, U. Turpeinen, R. Hämmäläinen, *J. Chem. Soc., Dalton Trans.* **1989**, 2309.

- <sup>[7b]</sup> W. G. Haanstra, W. A. J. W. van der Donk, W. L. Driessen, J. Reedijk, J. S. Wood, M. G. B. Drew, *J. Chem. Soc., Dalton Trans.* **1990**, 3123.
- [8] W. G. Haanstra, W. A. J. W. van der Donk, W. L. Driessen, J. Reedijk, M. G. B. Drew, J. S. Wood, *Inorg. Chim. Acta* **1990**, *176*, 299.
- [9] <sup>[9a]</sup> W. G. Haanstra, W. L. Driessen, M. van Roon, A. L. E. Stoffels, J. Reedijk, *J. Chem. Soc., Dalton Trans.* **1992**, 481. <sup>[9b]</sup> R. Burth, H. Vahrenkamp, *Inorg. Chim. Acta* **1998**, *282*, 193. <sup>[9c]</sup> P. Gosh, M. Wood, J. B. Bonano, T. Hascall, G. Parkin, *Polyhedron* **1999**, *18*, 107.
- [10] <sup>[10a]</sup> W. J. Geary, *Coord. Chem. Rev.* **1971**, *7*, 81. <sup>[10b]</sup> L. K. Thompson, F. L. Lee, E. J. Gabe, *Inorg. Chem.* **1988**, *27*, 39.
- [11] <sup>[11a]</sup> E. Pretsch, T. Clerc, J. Seibl, W. Simon, *Tables of Determination of Organic Compounds. <sup>13</sup>C NMR, <sup>1</sup>H NMR, IR, MS, UV/Vis, Chemical Laboratory Practice*, Springer-Verlag, Berlin, Germany, **1989**. <sup>[11b]</sup> D. H. Williams, I. Fleming, *Spectroscopic Methods in Organic Chemistry*, McGraw-Hill, London, UK, **1995**.
- [12] <sup>[12a]</sup> R. J. H. Clark, G. Natile, U. Belluco, L. Cattalini, C. Filipin, *J. Chem. Soc. A* **1970**, 659. <sup>[12b]</sup> K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley and Sons, New York, USA, **1986**.
- [13] P. H. M. Budzelaar, *g NMR ver. 4.0*, IvorySoft, Cherwell Scientific, Oxford, UK, **1997**.
- [14] <sup>[14a]</sup> J. Elguero, A. Fruchier, *An. Quim.* **1974**, *70*, 141. <sup>[14b]</sup> I. Akorta, J. Elguero, A. Fruchier, D. J. Macquarrie, A. Virgili, *J. Organomet. Chem.* **2001**, *625*, 148.
- [15] C. M. Cerda-García-Rojas, L. G. Zepeda, P. Joseph-Nathan, *Tetrahedron Comput. Methodol.* **1990**, *3*, 113.
- [16] <sup>[16a]</sup> V. M. Agre, N. P. Kozlova, V. K. Trunov, L. G. Makarevich, O. V. Ivanov, *Koord. Khim.* **1979**, *5*, 1406. <sup>[16b]</sup> V. M. Agre, N. P. Kozlova, V. K. Trunov, V. M. Oziomko, E. S. Zaitseva, *Koord. Khim.* **1980**, *6*, 948. <sup>[16c]</sup> V. I. Sokol, M. A. Porai-Koshits, T. O. Vardosanidze, V. N. Voropaev, E. S. Dominina, G. G. Skvortsova, *Koord. Khim.* **1983**, *9*, 539. <sup>[16d]</sup> A. A. Watson, D.

- A. House, P. J. Steel, *J. Organomet. Chem.* **1986**, *311*, 387. <sup>[16c]</sup>  
G. Minghetti, M. A. Cinellu, A. L. Bandini, G. Banditelli, F. Demartin, M. Manassero, *J. Organomet. Chem.* **1986**, *315*, 387. <sup>[16f]</sup>  
C. Cheng, J. Lain, Y. Wu, S. Wang, *Acta Crystallogr.* **1990**, *C46*, 208. <sup>[16g]</sup>  
A. Chandrasekaran, S. S. Krishnamurthy, M. Nethaji, *Inorg. Chem.* **1993**, *32*, 6102. <sup>[16h]</sup>  
A. T. Baker, J. K. Crass, M. Maniska, D. C. Craig, *Inorg. Chim. Acta* **1995**, *230*, 225. <sup>[16i]</sup>  
C. M. Hartshorn, P. J. Steel, *Chem. Commun.* **1997**, 541. <sup>[16j]</sup>  
S. Tsuji, D. C. Swenson, R. F. Jordan, *Organometallics* **1999**, *18*, 4758.
- <sup>[17]</sup> F. H. Allen, O. Kennard, *Chem. Des. Autom. News* **1993**, *8*, 31.
- <sup>[18]</sup> <sup>[18a]</sup> H. Nikol, H. Bürgi, K. I. Hardcastle, H. B. Grey, *Inorg. Chem.* **1995**, *34*, 6319. <sup>[18b]</sup>  
A. J. Blake, Y. V. Roberts, M. Schröder, *J. Chem. Soc., Dalton Trans.* **1996**, 1885. <sup>[18c]</sup>  
F. Contu, F. Demartin, F. A. Devillanova, A. Garau, F. Isaia, V. Lippolis, A. Salis, G. Verani, *J. Chem. Soc., Dalton Trans.* **1997**, 4401. <sup>[18d]</sup>  
S. V. Kolotilov, E. A. Goresnik, V. V. Pavlishuk, K. B. Yatsimirskii, *Zh. Neorg. Khim.* **2000**, *45*, 967.
- <sup>[19]</sup> S. Komiya, *Synthesis of Organometallic Compounds: A Practical Guide*, John Wiley and Sons, New York, USA, **1997**.
- <sup>[20]</sup> F. A. Cotton, *Inorg. Synth.* **1972**, *13*, 52.
- <sup>[21]</sup> G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467.
- <sup>[22]</sup> G. M. Sheldrick, *SHELXS 97, SHELXL 97, CIFTAB – Program for Crystal Structure Analysis (Release 97–2)*, Institut für Anorganische Chemie der Universität, Tammanstraße 4, 3400 Göttingen, Germany, **1998**.

Received June 5, 2002  
[102296]



---

# STRUCTURE OF {[1,9-BIS(3,5-DIMETHYL-1-PYRAZOLYL- $\kappa^2N,N'$ )-3,7-DITHIA- $\kappa^2S,S'$ -NONANE]PALLADATE(II)}TETRAPHENYLBORATE

**Jordi García-Antón, Josefina Pons, Josep Ros**

*Departament de Química, Universitat Autònoma de Barcelona, E-08193-Bellaterra, Cerdanyola, Spain*

**Xavier Solans and Mercè Font-Bardía**

*Departament de Cristal·lografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona, Gran Via 585, E-08007, Barcelona, Spain*

---

The crystal structure of the title compound, {[1,9-Bis(3,5-dimethyl-1-pyrazolyl- $\kappa^2N,N'$ )-3,7-dithia- $\kappa^2S,S'$ -nonane]}palladate(II)}tetraphenylborate [Pd(bddn)](BF<sub>4</sub>)<sub>2</sub> has been solved. The molecule has a C<sub>2</sub> symmetry and consists of a mononuclear palladium(II) complex. Two nitrogen atoms of the pyrazolyl groups and two thioether groups coordinate the palladium atom in a slightly distorted square-planar geometry.

## Comment

The coordination chemistry of hemilabile ligands has been widely studied in recent years. Braunstein *et al.* (2001) published an extensive review completing those presented by Slone *et al.* (1999) and Bader *et al.* (1991). In our group, bidentate ligands containing two donor centres of different strengths have been prepared, N,N' (Mathieu *et al.* 2001), N,P (Esquiús *et al.* 2002), and N,S (García-Antón *et al.* 2002). Recently we have presented the crystal structure of complex {[1,8-bis(3,5-dimethyl-1-pyrazolyl- $\kappa^2N,N'$ )-3,6-dithia- $\kappa^2S,S'$ -octane]}palladate(II)}tetraphenylborate. Thus, as a continuation of our investigations we now present the X-ray crystal structure of a mononuclear palladium(II) complex with 1,9-bis(3,5-dimethyl-1-pyrazolyl)-3,7-dithianonane (**bddn**).

**Experimental**

A solution of AgBF<sub>4</sub> (0.86 mmol) was added dropwise with vigorous stirring to a solution of [PdCl<sub>2</sub>(1,9-bis(3,5-dimethyl-1-pyrazolyl)-3,7-dithianonane)] (0.43 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) and CH<sub>3</sub>OH (10 ml). The reaction was carried out in the dark to prevent reduction of Ag(I) to Ag(0). After 5 min, stirring was stopped, and AgCl was filtered off. When the volume of the resultant solution had been reduced to roughly 5 mL, the product precipitated as a yellow solid. This solid was filtered and washed with dichloromethane. Crystals of (I) were obtained by evaporation of a methanol solution.

**Table 1.** Crystallographic data for [Pd(bddn)](BF<sub>4</sub>)<sub>2</sub>.

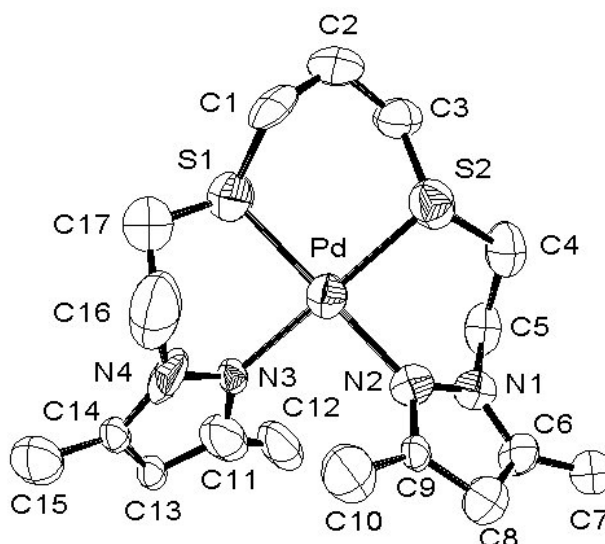
Compound	[Pd(bddn)](BF <sub>4</sub> ) <sub>2</sub>
empirical formula	C <sub>17</sub> H <sub>28</sub> B <sub>2</sub> F <sub>8</sub> N <sub>4</sub> PdS <sub>2</sub>
molecular mass, g	632.57
temperature, K	293(2)
crystal system	monoclinic
space group	P21/c
unit cell dimensions	
<i>a</i> , Å	11.7590(10)
<i>b</i> , Å	18.6500(10)
<i>c</i> , Å	11.8800(10)
β, deg	111.29
volume, Å <sup>3</sup>	2427.5(3)
<i>Z</i>	4
<i>D</i> <sub>calcd.</sub> , g cm <sup>-3</sup>	1.731
μ, mm <sup>-1</sup>	1.012
<i>F</i> (000)	1272
crystal size (mm)	0.1 x 0.1 x 0.2
θ range, deg	3.02 to 24.97
reflexions collected:	
total, independent, <i>R</i> <sub>int</sub>	9639, 1538, 0.0933
data / restraints / parameters	1538, 139, 260
<i>a</i> *	0.0754
final <i>R</i> 1, <i>wR</i> 2	0.0410, 0.0997
<i>R</i> 1 (all data), <i>wR</i> 2	0.0822, 0.1099
residual electron density, e Å <sup>-3</sup>	+0.323, -0.302

\* The function minimized was  $\sum w(|F_o|)^2 - |F_c|^2)^2$ , where  $w = [\sigma^2(I) + (aP)^2P]^{-1}$ , and  $P = (|F_o|^2 + 2|F_c|^2)/3$

**Table 2.** Selected bond lengths (Å) and bond angles (°) for [Pd(bddn)](BF<sub>4</sub>)<sub>2</sub> with estimated standard deviations (e.s.d.s.) in parentheses.

[Pd(bddn)](BF <sub>4</sub> ) <sub>2</sub>	
Pd-N(2)	2.022(9)
Pd-N(3)	2.045(14)
Pd-S(1)	2.280(4)
Pd-S(2)	2.289(3)
N(2)-Pd-S(1)	176.7(4)
N(3)-Pd-S(1)	85.8(4)
N(2)-Pd-N(3)	94.0(5)
N(2)-Pd-S(2)	86.7(3)
N(3)-Pd-S(2)	178.8(3)
S(1)-Pd-S(2)	93.54(13)

**Figure 1.** ORTEP drawing of [Pd(bddn)](BF<sub>4</sub>)<sub>2</sub> (273 K determination) showing all non hydrogen atoms and the atom numbering scheme. 50% probability amplitude displacement ellipsoids are shown.



Bader, A. & Lindner, E. (1991). *Coord. Chem. rev.* **108**, 27-110.

Braunstein, P. & Naud, F. (2001). *Angew. Chem. Int. Ed.* **40**, 680-699.

Esquiú, G., Pons, J., Yáñez, R., Ros, J., Mathieu, R., Donnadieu, B. & Lugan, N. (2002). *Eur. J. Inorg. Chem.* 2999-3006.

García-Antón, J., Pons, J., Solans, X., Font-Bardia, M. & Ros, J. (2002). *Eur. J. Inorg. Chem.* 3319-3327.

Mathieu, R., Esquiú, G., Lugan, N., Pons, J. & Ros, J. (2001). *Eur. J. Inorg. Chem.* 2683-2688.

Slone, C.S., Weinberger, D.A. & Mirkin, C.A. (1999). *Prog. Inorg. Chem.* **48**, 233-250.



# Synthesis of New Pd<sup>II</sup> Complexes Containing a Thioether-Pyrazole Hemilabile Ligand – Structural Analysis by <sup>1</sup>H, <sup>13</sup>C NMR Spectroscopy and Crystal Structure of [PdCl(bdtp)]BF<sub>4</sub> (bdtp = 1,5-Bis(3,5-Dimethyl-1-pyrazolyl)-3-thiapentane)

Jordi García-Antón,<sup>[a]</sup> Josefina Pons,<sup>\*[a]</sup> Xavier Solans,<sup>[b]</sup> Mercè Font-Bardia,<sup>[b]</sup> and Josep Ros<sup>\*[a]</sup>

**Keywords:** Palladium / N,S ligands / Hemilabile ligands

Treatment of the ligand 1,5-bis(3,5-dimethyl-1-pyrazolyl)-3-thiapentane (bdtp) with [PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>] led to a [PdCl<sub>2</sub>(bdtp)] complex. Subsequent treatment of this complex with AgBF<sub>4</sub> gave [PdCl(bdtp)](BF<sub>4</sub>). These Pd<sup>II</sup> complexes were characterised by elemental analysis, conductivity measurements, IR spectroscopy, and <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. Complex [PdCl<sub>2</sub>(bdtp)] was again obtained when the complex [PdCl(bdtp)](BF<sub>4</sub>) was heated under reflux in a solution of NEt<sub>4</sub>Cl in CH<sub>2</sub>Cl<sub>2</sub>/MeOH (1:1). Ligand bdtp

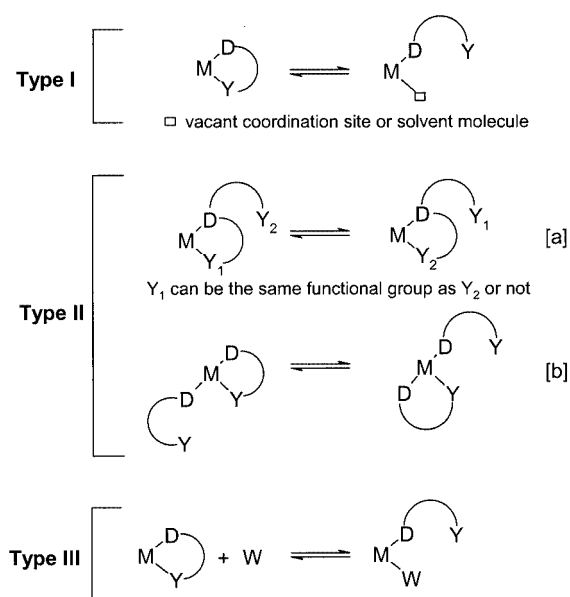
in complexes **1** and **2** exhibited a hemilabile character. The X-ray structure of the complex [PdCl(bdtp)](BF<sub>4</sub>) was determined. The metal atom is tricoordinated by the two azine nitrogen atoms and one thioether sulfur atom of the thioether-pyrazole ligand, its coordination (distorted square planar) being completed with one chloride ion.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2003)

## Introduction

The chemistry of hemilabile ligands in coordination and organometallic chemistry has been widely studied in recent years due to their potential application in catalysis. In particular, bidentate ligands containing two donor centres of different strengths with respect to substitution (labile Y and inert D) have been reviewed in recent reports and articles.<sup>[1]</sup> According to the review by P. Braunstein and F. Naud<sup>[1a]</sup> there are three types of hemilability. In type I hemilability, the labile donor group coordinates and decoordinates from the metal centre spontaneously. In type II, there is intramolecular competition between donor groups of the same ligand (a) or between donor groups of two identical ligands (b). Finally, in type III, the hemilabile character is due to the presence of an external reagent (Scheme 1 shows these types of hemilability for mononuclear complexes).

In recent years, we have studied and reported on the properties of hemilabile ligands based on the pyrazolyl group and on some other groups containing N,<sup>[2]</sup> P<sup>[3]</sup> or



Scheme 1

O<sup>[4]</sup> atoms. This paper continues the study of the potential hemilability of ligands containing pyrazolyl and thioether groups.<sup>[5]</sup>

The bonding properties of this family of ligands are also well documented,<sup>[6]</sup> especially the synthesis and structural characterisation of complexes of Co<sup>II</sup>,<sup>[7]</sup> Zn<sup>II</sup>,<sup>[8]</sup> Cd<sup>II</sup>,<sup>[8]</sup> Cu<sup>I</sup> [7,9] and Ag<sup>I</sup> [7] with 1,5-bis(3,5-dimethylpyrazol-1-yl)-3-thi-

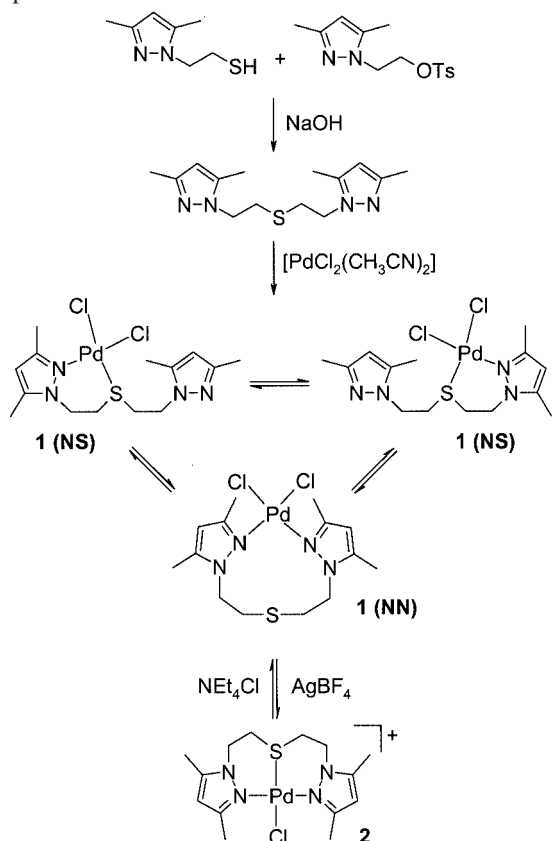
<sup>[a]</sup> Departament de Química, Facultat de Ciències, Universitat Autònoma de Barcelona, 08193 Bellaterra, Cerdanyola, Barcelona, Spain  
Fax: (internat.) +34-935-813101  
E-mail: Josefina.Pons@uab.es

<sup>[b]</sup> Cristallografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona, Martí i Franquès s/n, 08028 Barcelona, Spain

Supporting information for this article is available on the WWW under <http://www.eurjic.org> or from the author.

apentane (bdtp). The ligand acts in a tridentate manner (NSN) in all these complexes except  $[\text{ZnCl}_2(\text{bdtp})]$ , in which it behaves in a bidentate fashion (NN).

In this paper, we report on the study of the coordination of the ligand  $\text{bdtp}^{[10]}$  with  $\text{Pd}^{\text{II}}$ , and the isolation of the complex  $[\text{PdCl}_2(\text{bdtp})]$  (**1**). Treatment of this complex with  $\text{AgBF}_4$  gives  $[\text{PdCl}(\text{bdtp})](\text{BF}_4)$  (**2**) (Scheme 2). NMR spectroscopic studies and the X-ray crystal structure of **2** are also presented.



Scheme 2

## Results and Discussion

Although ligand 1,5-bis(3,5-dimethylpyrazol-1-yl)-3-thiapentane (bdtp) has previously been reported in the literature,<sup>[10]</sup> in this paper we describe an alternative synthetic route. Treatment of 1-(2-mercaptoethyl)-3,5-dimethylpyrazole and 1-[2-(*p*-tolylsulfonyloxy)ethyl]-3,5-dimethylpyrazole in the presence of sodium hydroxide in water gave the desired product (Scheme 2). The ligand bdtp was characterised by elemental analysis, mass spectrometry, IR spectroscopy, and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy.

Complex  $[\text{PdCl}_2(\text{bdtp})]$  (**1**) was obtained by treatment of the ligand with  $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$  in a 1:1 M/L ratio. Treatment of **1** with one equivalent of  $\text{AgBF}_4$  gave a compound of formula  $[\text{PdCl}(\text{bdtp})](\text{BF}_4)$  (**2**). Both products were yellow and gave satisfactory C, H, N and S elemental analyses. When complex **2** was heated under reflux in a solution of  $\text{Et}_4\text{NCl}$  in  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (1:1) for 24 hours, complex **1** was again obtained.

Conductivity data in acetonitrile are in agreement with a non-electrolyte nature for compound **1** ( $37 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ) and 1:1 electrolyte for compound **2** ( $123 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ). The reported values for  $10^{-3} \text{M}$  solutions of non-electrolyte compounds are lower than  $120 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$  and between  $120\text{--}160 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$  for 1:1 electrolyte compounds in acetonitrile.<sup>[11]</sup>

According to IR data for compound **1**, the Pd atom is coordinated to nitrogen atoms [ $\nu(\text{Pd-N})$   $456 \text{cm}^{-1}$ ], two chlorine atoms in a *cis* arrangement [two bands are observed,  $\nu(\text{Pd-Cl})$   $367$  and  $336 \text{cm}^{-1}$ ] and to sulfur atoms [ $\nu(\text{Pd-S})$   $280 \text{cm}^{-1}$ ]. In compound **2** only one band for  $\nu(\text{Pd-Cl})$  ( $334 \text{cm}^{-1}$ ) was observed as well as  $\nu(\text{Pd-N})$  ( $450 \text{cm}^{-1}$ ) and  $\nu(\text{Pd-S})$  ( $256 \text{cm}^{-1}$ ) bands.<sup>[12]</sup>

## NMR Experiments

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compounds **1** and **2** were recorded in  $\text{CDCl}_3$  and  $\text{CD}_2\text{Cl}_2$ , respectively, and show the signals of the coordinated ligands. NMR spectroscopic data are reported in the Exp. Sect.

The  $^1\text{H}$  NMR spectrum of **1** in solution at 298 K shows sharp resonances for the CH and  $\text{CH}_3$  groups of the pyrazolyl cycles, but poorly defined broad bands for the  $\text{N-CH}_2\text{-CH}_2\text{-S}$  chain. This suggests a fluxional process occurring in solution, which was studied carrying out a variable temperature  $^1\text{H}$  NMR study in  $\text{CDCl}_3$  (Figure 1). Lowering of the temperature induces a progressive broadening and splitting of the signal corresponding to the CH group of the pyrazolyl rings until 233 K where three well-defined signals are observed at  $\delta = 5.90$ , 5.82 and 5.77 ppm. The two signals at lower  $\delta$  integrate for one H atom each, while the signal at  $\delta = 5.90$  ppm integrates for two H atoms. This suggests that at 298 K there is a fluxional process in which the thioether-pyrazole ligand alternates the *N,N* and *N,S* bidentate coordinations (in the ratio of approximately 1:1). At 233 K, where both species can be observed, the *N,N* coordination shows only one signal for the CH group of the pyrazolyl rings,<sup>[5a]</sup> whereas in the *N,S* coordination mode the pyrazolyl groups are not equivalent (coordinated and free pyrazolyl groups) and there is one signal for each.

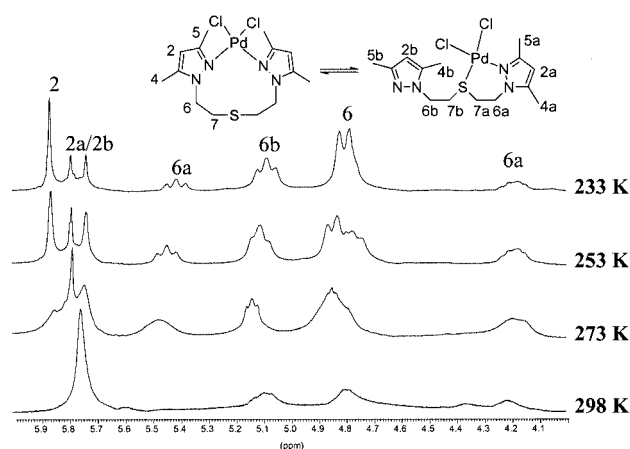


Figure 1. Numbering of complex  $[\text{PdCl}_2(\text{bdtp})]$  and 400 MHz  $^1\text{H}$  NMR variable temperature experiments for 2-H and 6-H

Ill defined broad bands corresponding to the methylenic groups of the N-CH<sub>2</sub>-CH<sub>2</sub>-S chain at 298 K become assignable signals at 233 K. Thus, if we focus on 6-H (7-H is superimposed with other signals) at 233 K, four groups of signals can be attributed to the methylene functionalities directly linked to the pyrazolyl group in the NN and NS isomers. One of them (at  $\delta = 4.84$  ppm) can be attributed to the CH<sub>2</sub> of the NN isomer (6-H, Figure 1), as it integrates for four H atoms. The signal at  $\delta = 5.12$  ppm can be assigned to the CH<sub>2</sub> of the open arm of the NS isomer (6b-H). It integrates for two H atoms and resembles a triplet. Finally, signals at  $\delta = 4.21$  and 5.45 ppm can be assigned to the CH<sub>2</sub> group in the chelating arm of the NS isomer (6a-H), as they integrate for one H atom each. The rigid conformation of this arm in this isomer leads to the two hydrogens of this CH<sub>2</sub> group becoming diastereotopic, and therefore they have different chemical displacements. Although they are not completely defined, these signals resemble those observed for complexes found in the literature with similar Pd-N-N-C-C-S rings.<sup>[5]</sup>

The <sup>13</sup>C NMR spectrum, at room temperature, of complex **1** also shows broad bands. This is consistent with the fluxional process explained for the <sup>1</sup>H NMR spectra.

From the structure of complex **2** it can be seen that the two protons of each CH<sub>2</sub> moiety in the S-CH<sub>2</sub>-CH<sub>2</sub>-N chains are diastereotopic, thus leading to four groups of signals which can be associated to a single hydrogen atom in each chain. This happens because of the rigid conformation of the ligand when complexed. Thus, each group of signals can be assigned as doublets of doublets of doublets (Figure 2). The HMQC spectrum allowed us to assign the two doublets of doublets of doublets of lower  $\delta$  to 7-H and the ones at higher  $\delta$  to 6-H.

Study of the S-CH<sub>2</sub>-CH<sub>2</sub>-N fragment (in, **2**) as an AA'XX' system gave a set of coupling constants (Table 1). These constants were consistent with the simulated spectra obtained with the aid of the g NMR program.<sup>[13]</sup>

Table 1. <sup>1</sup>H NMR results: chemical shifts (ppm, CD<sub>2</sub>Cl<sub>2</sub>) and <sup>1</sup>H,<sup>1</sup>H coupling constants (Hz) for **2**

$\delta$ H (6S)	4.92	<sup>2</sup> J(6R,6S)	-15.9
$\delta$ H (6R)	5.20	<sup>2</sup> J(7R,7S)	-14.8
$\delta$ H (7R)	2.97	<sup>3</sup> J(7R,6S)	2.5
$\delta$ H (7S)	3.78	<sup>3</sup> J(7S,6S)	3.2
		<sup>3</sup> J(7R,6R)	12.1
		<sup>3</sup> J(7S,6R)	1.6

In the NOESY spectrum it can be seen that the methyl group at  $\delta = 2.40$  ppm shows an NOE interaction with the doublet of doublets of doublets at  $\delta = 4.92$  ppm, but not with the one at  $\delta = 5.20$  ppm. From the X-ray structure of **2** (Figure 3), it can be observed that the nearest proton to the CH<sub>3</sub>(5) moiety is 6S-H and therefore it should be the one with the NOE interaction. This information leads us to assign 6S-H to the doublet of doublets of doublets at  $\delta = 4.92$  ppm and 6R-H to the signal at  $\delta = 5.20$  ppm.

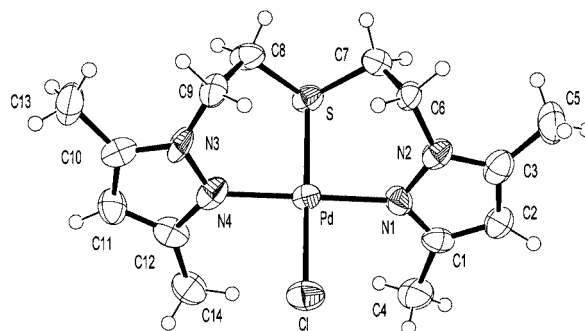


Figure 3. ORTEP drawing of [PdCl(bdtp)]<sup>+</sup> cation (293 K determination). 50% probability amplitude displacement ellipsoids are shown

The coupling constants enabled us to differentiate 7R-H and 7S-H. These coupling constants agree with the confor-

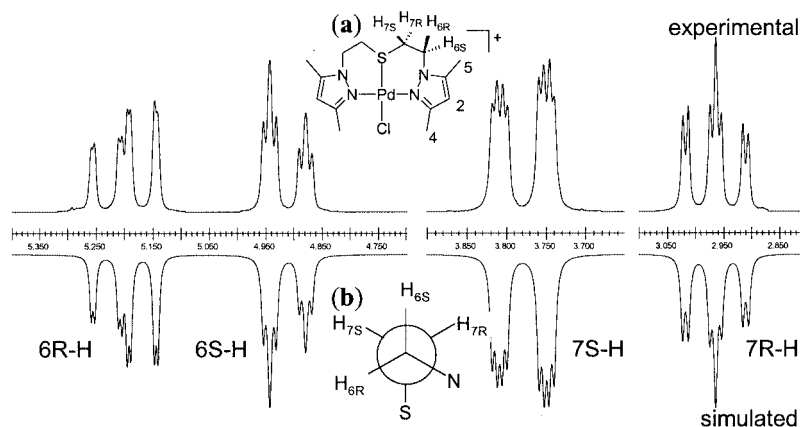


Figure 2. The 250 MHz <sup>1</sup>H NMR and the simulated g NMR spectrum for the NCH<sub>2</sub>CH<sub>2</sub>S fragment of [PdCl(bdtp)](BF<sub>4</sub>) including (a) the numbering and (b) the dihedral angles for the NCH<sub>2</sub>CH<sub>2</sub>S fragment

mation of the S–CH<sub>2</sub>–CH<sub>2</sub>–N chain as seen in Figure 2, which has been corroborated by an X-ray crystal study. Geminal <sup>2</sup>*J* and ca. 180° <sup>3</sup>*J* coupling constants have significantly higher values than ca. 30° and ca. 60° <sup>3</sup>*J* coupling constants.<sup>[14]</sup> Thus, 7*R*-H should correspond to the doublet of doublets of doublets at δ = 2.97 ppm and 7*S*-H to the one at δ = 3.78 ppm.

### Crystal Structure of [PdCl(bdtp)](BF<sub>4</sub>) (2)

The molecular structure of compound **2** consists of discrete [PdCl(bdtp)]<sup>+</sup> cations and BF<sub>4</sub><sup>−</sup> anions (Figure 3), packed according to normal van der Waals forces.

The cation complex is mononuclear. The Pd<sup>II</sup> ion is coordinated to the bdtp ligand by its three donor atoms via two pyrazole nitrogens and one thioether sulfur, along with one chlorine atom. The PdN<sub>2</sub>SCl core (S thioether) is found in three complexes in the literature.<sup>[15]</sup> Some selected bond lengths and bond angles for this complex are listed in Table 2.

Table 2. Selected bond lengths (Å) and bond angles (°) for **2** with estimated standard deviations (e.s.d.s.) in parentheses

Pd–N1	2.004(7)
Pd–N4	2.040(7)
Pd–S	2.308(2)
Pd–Cl	2.291(2)
N1–Pd–S	90.5(2)
N4–Pd–S	88.5(2)
N1–Pd–N4	176.6(3)
N1–Pd–Cl	89.8(2)
N4–Pd–Cl	91.5(2)
S–Pd–Cl	175.18(8)

The Pd–N bond lengths [2.004(7) Å and 2.040(7) Å], the Pd–S bond length [2.308(2) Å] and the Pd–Cl bond length [2.291(2) Å] can be regarded as normal compared with the distances found in the literature.<sup>[16]</sup> The coordination geometry is square planar with a tetrahedral distortion, as can be deduced from the bond angles and the mean separation [0.0765 Å] of the atoms coordinated to the Pd atom in relation to the mean plane that contains these four atoms and the Pd atom. The dihedral angle between the planes N1–Pd–Cl and N4–Pd–S is 5.85°. Ligand bdtp acts as a tridentate chelate and forms two Pd–N–N–C–C–S six-membered rings with a boat conformation, sharing an edge (Pd–S). The boat distortions in the six-membered rings are ΔC<sub>S</sub>[(S–C7)] = 12.4(6)° and ΔC<sub>S</sub>[(N1–N2)] = 14.8(10)° for Pd–N1–N2–C6–C7–S and ΔC<sub>S</sub>[(S–C8)] = 4.0(6)° and ΔC<sub>S</sub>[(N3–N4)] = 5.2(9)° for Pd–N4–N3–C9–C8–S, respectively [see Equation (1)].

$$\Delta C_S = \sqrt{\frac{\sum_{i=1}^m (\phi_i + \phi'_i)^2}{m}} \quad (1)$$

*m* = equivalent torsion angles

Φ<sub>*i*</sub>+Φ<sub>*i*</sub>' = torsion angles related to the considered plane<sup>[17]</sup>

The nitrogen-thioether bite angles of the ligand are 90.5(2)° and 91.5(2)°, respectively, which are similar to the corresponding bite in the [Co(NO<sub>3</sub>)<sub>2</sub>(bdtp)] and [CuBr(bdtp)] complexes.<sup>[7]</sup>

### Conclusions

The thioether-pyrazole ligand bdtp can coordinate Pd<sup>II</sup> centres in different ways. In this paper we describe all the possible polydentate coordinations in mononuclear complexes: two bidentate coordinations (NN and NS) and a tridentate coordination (NSN). Furthermore, we have demonstrated the hemilabile properties of this ligand when coordinated to Pd<sup>II</sup>. In complex **1** the ligand alternates the NN and NS coordination types at room temperature, which would be type II hemilability.<sup>[1a]</sup>

Complex **2** (where ligand bdtp uses NSN coordination) is obtained from **1** by treatment with AgBF<sub>4</sub>. When **2** is heated under reflux in a solution of Et<sub>4</sub>NCl in CH<sub>2</sub>Cl<sub>2</sub>/MeOH (1:1), **1** is obtained once again. This could be considered as type III hemilability.

### Experimental Section

**Generals Remarks:** Preparations were performed using usual vacuum line and Schlenk techniques. All reagents were commercial grade materials and were used without further purification. Acetonitrile and dichloromethane were dried and distilled by standard methods and previously deoxygenated in the vacuum line.

Samples of [PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>] were prepared as described in the literature.<sup>[18]</sup>

Analyses (C,N,H,S) were performed in our analytical laboratory on a Carlo Erba CHNS EA-1108 instrument. Conductivity measurements were performed at room temperature in ca. 10<sup>−3</sup> M acetonitrile solutions employing a Crison, micro CM 2200 conductometer. Infrared spectra were recorded from KBr pellets or polyethylene mulls in the range 4000–100 cm<sup>−1</sup> under a nitrogen atmosphere. The <sup>1</sup>H NMR, <sup>13</sup>C{<sup>1</sup>H} NMR and HMQC spectra were obtained either on a Bruker 250 MHz or Bruker 400 MHz instrument. Chemical shifts (δ) were determined relative to internal TMS and are given in ppm. A mass spectrum was obtained with an Esquire 3000 ion trap mass spectrometer from Bruker Daltonics.

**Synthesis of the Ligand 1,5-bis(3,5-dimethyl-1-pyrazolyl)-3-thiapentane (bdtp):** Although the synthesis of the ligand bdtp had been previously reported in the literature,<sup>[10]</sup> here, we describe an alternative synthetic route. A solution of 1-(2-mercaptoethyl)-3,5-dimethylpyrazole (2.00 g, 12.8 mmol), 1-[2-(*p*-tolylsulfonyloxy)ethyl]-3,5-dimethylpyrazole (3.77 g, 12.8 mmol) and of sodium hydroxide (0.53 g, 12.9 mmol; 97% of water (25 mL) was refluxed for five hours. After cooling to room temperature, the reaction mixture was extracted three times with CHCl<sub>3</sub> (15 mL). The collected organic layers were dried with anhydrous sodium sulfate and removed under vacuum to give a white solid. Yield: 2.17 g (61%). M.p.: 80.3–80.9 °C. C<sub>14</sub>H<sub>22</sub>N<sub>4</sub>S (278.42): calcd. C 60.39, H 7.96, N 20.12, S 11.52; found C 60.20, H 7.73, N 20.41, S 11.23. IR (KBr, cm<sup>−1</sup>): ν(C–H)<sub>al</sub> = 2924, ν(C=C), ν(C=N) 1550, δ(CH<sub>3</sub>)<sub>as</sub> = 1481–1436, δ(CH<sub>3</sub>)<sub>s</sub> 1302, δ(C–H)<sub>oop</sub> = 800–775. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 2.22 (s, 6 H, Me), 2.27 (s, 6 H, Me), 2.84

(t,  $^3J = 6.9$  Hz, 4 H, pz-CH<sub>2</sub>-CH<sub>2</sub>-S), 4.10 (t,  $^3J = 6.9$  Hz, 4 H, pz-CH<sub>2</sub>-CH<sub>2</sub>-S), 5.79 (s, 2 H, pz-CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 63 MHz):  $\delta = 11.4$  (Me), 13.7 (Me), 32.5 (pz-CH<sub>2</sub>-CH<sub>2</sub>-S), 48.7 (pz-CH<sub>2</sub>-CH<sub>2</sub>-S), 105.3 (pz-CH), 139.5 (pz-C), 148.1 (pz-C) ppm. MS (ESI):  $m/z$  (%) = 279 (72) [M + H<sup>+</sup>], 301 (100) [M + Na<sup>+</sup>].

**Synthesis of [PdCl<sub>2</sub>(bdtp)] (1):** A solution of [PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>] (0.097 g, 0.374 mmol) in dichloromethane (15 mL) was added to a solution of bdtp (0.105 g, 0.378 mmol) in dichloromethane (10 mL). After the mixture had been stirred for 12 h, most of the solvent was removed under vacuum. Diethyl ether was then added to induce precipitation. The resulting precipitate was then filtered and washed with diethyl ether, yielding the desired compound. Yield: 0.157 g (92%). Conductivity ( $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ ,  $9.98 \cdot 10^{-4}$  M in acetonitrile): 37. C<sub>14</sub>H<sub>22</sub>Cl<sub>2</sub>N<sub>4</sub>PdS (455.74): calcd. C 36.90, H 4.87, N 12.29, S 7.04; found C 36.58, H 4.92, N 12.11, S 6.93. IR (KBr, cm<sup>-1</sup>):  $\nu(\text{C-H})_{\text{al}} = 2920$ ,  $\nu(\text{C}=\text{C})$ ,  $\nu(\text{C}=\text{N})$  1557,  $\delta(\text{CH}_3)_{\text{as}} = 1467-1420$ ,  $\delta(\text{CH}_3)_{\text{s}} = 1313$ ,  $\delta(\text{C-H})_{\text{oop}} = 788$ . IR (polyethylene, cm<sup>-1</sup>):  $\nu(\text{Pd-N})_{\text{as}} = 456$ ,  $\nu(\text{Pd-Cl}) = 336$ , 367,  $\nu(\text{Pd-S}) = 280$  cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 233 K): (For simplicity we have used the numeration as in Figure 1; peaks from 2.20 ppm to 2.69 ppm are not integrated because they are superimposed with other signals, although these peaks all together integrate the expected 31 H atoms.)  $\delta$  (isomer N,N) = 2.24, 2.55 [s, Me (4/5)], 2.69 [br., pz-CH<sub>2</sub>-CH<sub>2</sub>-S (7)], 4.84 [br., 4 H, pz-CH<sub>2</sub>-CH<sub>2</sub>-S (6)], 5.91 [s, pz-CH (2)].  $\delta$  (isomer N,S) = 2.25, 2.56 [s, Me (4a/b, 5a/b)], 2.20 [br., pz-CH<sub>2</sub>-CH<sub>2</sub>-S (7b)], 2.85 [br., 1 H, pz-CH<sub>2</sub>-CHH-S (7a)], 3.37 [br., 1 H, pz-CH<sub>2</sub>-CHH-S (7a)], 4.21 [br., 1 H, pz-CHH-CH<sub>2</sub>-S (6a)], 5.12 [br., 2 H, pz-CH<sub>2</sub>-CH<sub>2</sub>-S (6b)], 5.45 [br., 1 H, pz-CHH-CH<sub>2</sub>-S (6a)], 5.77, 5.83 [s, 1H each, pz-CH (2a/2b)]. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 63 MHz, 298 K):  $\delta = 12.3$  (br., Me), 15.3 (br., Me), 29.9 (br., pz-CH<sub>2</sub>-CH<sub>2</sub>-S), 49.8 (br., pz-CH<sub>2</sub>-CH<sub>2</sub>-S), 108.2 (br., pz-CH), 143.6 (br., pz-C), 150.7 (br., pz-C).

**Synthesis of [PdCl(bdtp)]BF<sub>4</sub> (2):** A solution of AgBF<sub>4</sub> (0.063 g, 0.324 mmol) in methanol (2 mL) was added dropwise with vigorous stirring to a solution of **1** (0.149 g, 0.327 mmol) in dichloromethane (5 mL) and methanol (5 mL). The reaction was carried out in the dark to prevent reduction of Ag<sup>I</sup> to Ag<sup>0</sup>. After five minutes, stirring was stopped, and AgCl was filtered off through a pad of Celite. When the volume of the resultant solution had been reduced to roughly 5 mL, the product precipitated as a yellow solid. This solid was filtered and dried under vacuum. Yield: 0.146 g (89%). Conductivity ( $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ ,  $9.87 \cdot 10^{-4}$  M in acetonitrile): 123. C<sub>14</sub>H<sub>22</sub>BClF<sub>4</sub>N<sub>4</sub>PdS (507.09): calcd. C 33.16, H 4.37, N 11.05, S 6.32; found C 33.45, H 4.40, N 10.93, S 6.12. IR (KBr, cm<sup>-1</sup>):  $\nu(\text{C-H})_{\text{ar}} = 3014$ ,  $\nu(\text{C-H})_{\text{al}} = 2967-2923$ ,  $\nu(\text{C}=\text{C})$ ,  $\nu(\text{C}=\text{N})$  1554,  $\delta(\text{CH}_3)_{\text{as}} = 1468-1423$ ,  $\delta(\text{CH}_3)_{\text{s}} = 1319$ ,  $\nu(\text{B-F}) = 1049$ ,  $\delta(\text{C-H})_{\text{oop}} = 817$ . IR (polyethylene, cm<sup>-1</sup>):  $\nu(\text{Pd-N})_{\text{as}} = 450$ ,  $\nu(\text{Pd-Cl}) = 334$ ,  $\nu(\text{Pd-S}) = 256$ . <sup>1</sup>H NMR (250 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 2.40$  (s, 6 H, Me), 2.70 (s, 6 H, Me), 2.97 (ddd, 2 H, pz-CH<sub>2</sub>-CHH), 3.78 (ddd, 1 H, pz-CH<sub>2</sub>-CHH), 4.92 (ddd, 1 H, pz-CHH-CH<sub>2</sub>), 5.20 (ddd, 1 H, pz-CHH-CH<sub>2</sub>), 6.08 (s, 2 H, pz-CH) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (63 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 12.2$  (Me), 15.7 (Me), 39.8 (S-CH<sub>2</sub>-CH<sub>2</sub>), 51.2 (pz-CH<sub>2</sub>-CH<sub>2</sub>), 109.3 (pz-CH), 145.1, 154.1 (pz-C).

**Synthesis of [PdCl<sub>2</sub>(bdtp)] (1) from [PdCl(bdtp)](BF<sub>4</sub>):** A solution of **2** (0.053 g, 0.104 mmol) and NEt<sub>4</sub>Cl (0.033 g, 0.199 mmol) in a mixture (1:1) of dichloromethane and methanol (20 mL) was refluxed for 24 hours. After cooling to room temperature, the reaction mixture was extracted three times with 15 mL of CHCl<sub>3</sub>. The collected organic layers were dried with anhydrous sodium sulfate

and removed in vacuo to yield the desired product. Yield: 0.038 g (80%).

**X-ray Crystallographic Study:** Suitable crystals of compound **2** were obtained by crystallisation from CH<sub>2</sub>Cl<sub>2</sub>. Data were collected on an Enraf-Nonius CAD4 four-circle diffractometer, using the  $\omega/2\theta$  scan technique. The crystals were collected with graphite-monochromated Mo-K $\alpha$  radiation. 2977 reflections were measured in the range  $2.11^\circ < \theta < 29.98$ . 1529 reflections were assumed as observed applying the condition  $I > 2\sigma(I)$ . Three reflections were measured every two hours as orientation and intensity control and significant intensity decay was not observed. Lorentz-polarisation but no absorption corrections were performed. The structure was solved by direct methods using the SHELXS 97 computer program and refined by the full-matrix least-squares method with a SHELXL 97 computer program.<sup>[19]</sup> All hydrogen atoms were computed and refined with an overall isotropic temperature factor using a riding model. The final  $R$  (on  $F$ ) factor and  $wR$  (on  $F^2$ ) values, as well as the numbers of parameters refined and other details concerning the refinement of the crystal structure are presented in Table 3.

Table 3. Crystallographic data of **2**

Empirical formula	C <sub>14</sub> H <sub>22</sub> BClF <sub>4</sub> N <sub>4</sub> PdS
Molecular mass, g	507.08
Temperature, K	293(2)
Crystal system	monoclinic
Space group	C <sub>c</sub>
Unit cell dimensions	
<i>a</i> , Å	5.138(8)
<i>b</i> , Å	30.957(6)
<i>c</i> , Å	12.355(3)
$\beta$ , deg	92.87(7)
<i>V</i> , Å <sup>3</sup>	1963(3)
<i>Z</i>	4
<i>D</i> <sub>calcd.</sub> , g cm <sup>-3</sup>	1.716
$\mu$ , mm <sup>-1</sup>	1.230
<i>F</i> (000)	1016
Crystal size (mm)	0.1 × 0.1 × 0.2
$\theta$ range, deg	2.11 to 29.98
Reflections collected:	2977, 2977, 0.0134
total, independent, $R_{\text{int}}$	
Data/restraints/parameters	2977, 2, 235
$a^{[a]}$	0.0095
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub>	0.0337, 0.0492
<i>R</i> <sub>1</sub> (all data), <i>wR</i> <sub>2</sub>	0.1430, 0.0656
Residual electron density, e <sup>-</sup> Å <sup>-3</sup>	+0.774, -0.777

[a] The function minimized was  $\sum w(|F_o|^2 - |F_c|^2)^2$ , where  $w = [\sigma^2(I) + (aP)^2]^{-1}$ , and  $P = (|F_o|^2 + 2|F_c|^2)/3$ .

CCDC-208981 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223-336-033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

## Acknowledgments

Support by the Spanish Ministerio de Educación y Cultura (Project BQU2000-0238 and a grant to J.G.) is gratefully acknowledged.

[1] [a] P. Braunstein, F. Naud, *Angew. Chem. Int. Ed.* **2001**, *40*, 680. [1b] C. S. Slone, D. A. Weinberger, C. A. Mirkin, *Prog.*

- Inorg. Chem.* **1999**, *48*, 233. <sup>[1c]</sup> A. Bader, E. Lindner, *Coord. Chem. Rev.* **1991**, *108*, 27.
- [2] <sup>[2a]</sup> R. Mathieu, G. Esquiús, N. Lugañ, J. Pons, J. Ros, *Eur. J. Inorg. Chem.* **2001**, 2683. <sup>[2b]</sup> G. Esquiús, J. Pons, R. Yáñez, J. Ros, *J. Organomet. Chem.* **2001**, *619*, 14. <sup>[2c]</sup> G. Esquiús, J. Pons, R. Yáñez, J. Ros, X. Solans, M. Font-Bardía, *J. Organomet. Chem.* **2000**, *605*, 226. <sup>[2d]</sup> G. Esquiús, J. Pons, R. Yáñez, J. Ros, X. Solans, M. Font-Bardía, *Acta Crystallogr., Sect. C* **2002**, *58*, 133. <sup>[2e]</sup> G. Esquiús, J. Pons, R. Yáñez, J. Ros, R. Mathieu, B. Donnadieu, N. Lugañ, *Eur. J. Inorg. Chem.* **2002**, 2999.
- [3] <sup>[3a]</sup> R. Tribó, J. Pons, R. Yáñez, J. F. Piniella, A. Álvarez-Larena, J. Ros, *Inorg. Chem. Commun.* **2000**, *3*, 545. <sup>[3b]</sup> G. Esquiús, J. Pons, R. Yáñez, J. Ros, R. Mathieu, B. Donnadieu, N. Lugañ, *J. Organomet. Chem.* **2003**, *667*, 126. <sup>[3c]</sup> R. Tribó, J. Ros, J. Pons, R. Yáñez, A. Álvarez-Larena, J. F. Piniella, *J. Organomet. Chem.*, in press.
- [4] <sup>[4a]</sup> A. Boixassa, J. Pons, A. Virgili, X. Solans, M. Font-Bardía, J. Ros, *Inorg. Chim. Acta* **2002**, *340*, 49. <sup>[4b]</sup> A. Boixassa, J. Pons, X. Solans, M. Font-Bardía, J. Ros, *Inorg. Chim. Acta* **2003**, *346*, 151. <sup>[4c]</sup> A. Boixassa, J. Pons, X. Solans, M. Font-Bardía, J. Ros, *Inorg. Chim. Acta*, manuscript accepted.
- [5] <sup>[5a]</sup> J. García-Antón, J. Pons, X. Solans, M. Font-Bardía, J. Ros, *Eur. J. Inorg. Chem.* **2002**, 3319. <sup>[5b]</sup> J. García-Antón, J. Pons, X. Solans, M. Font-Bardía, J. Ros, *Eur. J. Inorg. Chem.*, manuscript accepted.
- [6] <sup>[6a]</sup> E. Bouwman, W. L. Driessen, J. Reedijk, *Coord. Chem. Rev.* **1990**, *143*. <sup>[6b]</sup> M. Di Varia, F. Mani, *J. Chem. Soc., Dalton Trans.* **1985**, 2327. <sup>[6c]</sup> P. K. Byers, A. J. Canty, *Inorg. Chim. Acta* **1985**, *104*, L13. <sup>[6d]</sup> W. G. Haanstra, Van der Donk, W. L. Driessen, J. Reedijk, M. G. B. Drew, J. S. Wood, *Inorg. Chim. Acta* **1990**, *176*, 299. <sup>[6e]</sup> W. G. Haanstra, Van der Donk, A. J. W. Wilfred, W. L. Driessen, J. Reedijk, J. S. Wood, M. G. B. Drew, G. B. Michael, *J. Chem. Soc., Dalton Trans.* **1990**, 3123. <sup>[6f]</sup> W. G. Haanstra, W. L. Driessen, R. A. G. De Graaff, J. Reedijk, Y. F. Wang, C. H. Stam, *Inorg. Chim. Acta* **1991**, *186*, 215. <sup>[6g]</sup> W. G. Haanstra, W. L. Driessen, J. Reedijk, *Acta Crystallogr., Sect. C* **1992**, *48*, 14. <sup>[6h]</sup> F. Meyer, A. Jacobi, L. Zsolnai, *Chem. Berichter/Receuil* **1997**, *130*, 1441. <sup>[6i]</sup> H. Cheng, J. K. Dutra, S. M. Sakya, *PCT Int. Appl.* **2001**, 93pp. <sup>[6j]</sup> U. Heinemann, B. W. Krueger, H. Gayer, F. Maurer, C. Boie, R. Ebert, U. Wachendoff-Neumann, U. Mauler-Machnik, *Eur. Pat. Appl.* **2003**, 32pp.
- [7] W. G. Haanstra, W. L. Driessen, M. van Roon, A. L. E. Stoffels, J. Reedijk, *Chem. Soc., J. Chem. Soc., Dalton Trans.* **1992**, 481.
- [8] P. Ghosh, M. Wood, J. B. Bonanno, T. Hascall, G. Parkin, *Polyhedron* **1999**, *18*, 1107.
- [9] A. L. E. Stoffels, W. G. Haanstra, W. L. Driessen, J. Reedijk, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1419.
- [10] T. N. Sorrell, M. R. Malachowski, *Inorg. Chem.* **1983**, *22*, 1883.
- [11] <sup>[11a]</sup> W. J. Geary, *Coord. Chem. Rev.* **1971**, *7*, 81. <sup>[11b]</sup> L. K. Thompson, F. L. Lee, E. J. Gabe, *Inorg. Chem.* **1988**, *27*, 39.
- [12] <sup>[12a]</sup> R. J. H. Clark, G. Natile, U. Belluco, L. Cattalini, C. Filipin, *J. Chem. Soc.* **1970**, 659. <sup>[12b]</sup> K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. John Wiley & Sons, New York, **1986**.
- [13] P. H. M. Budzelaar, *g NMR – version 4.0*, IvorySoft, Cherwell Scientific, Oxford, UK, **1997**.
- [14] <sup>[14a]</sup> E. Pretsh, T. Clerc, J. Seibl, W. Simon, *Tables of Determination of Organic Compounds. <sup>13</sup>C NMR, <sup>1</sup>H NMR, IR, MS, UV/Vis, Chemical Laboratory Practice*. Springer-Verlag, Germany, **1989**. <sup>[14b]</sup> D. H. Williams, I. Fleming, *Spectroscopic Methods in Organic Chemistry*. McGraw-Hill, UK, **1995**.
- [15] <sup>[15a]</sup> B. T. Khan, S. Shamsuddin, K. Venkatasubramanian, *Polyhedron* **1992**, *11*, 671. <sup>[15b]</sup> U. Heinzel, R. Mattes, *Inorg. Chim. Acta* **1992**, *194*, 157. <sup>[15c]</sup> B. Chak, A. McAuley, T. W. Whitcombe, *Inorg. Chim. Acta* **1996**, *246*, 349.
- [16] <sup>[16a]</sup> D. B. Grotjahn, D. Combs, S. Van, G. Aguirre, F. Ortega, *Inorg. Chem.* **2000**, *39*, 2080. <sup>[16b]</sup> D. B. Grotjahn, S. Van, D. Combs, A. A. Lev, C. Schneider, C. D. Incarvito, K. Lam, G. Rossi, A. L. Rheingold, M. Rideout, C. Meyer, G. Hernandez, L. Mejorado, *Inorg. Chem.* **2003**, *42*, 3347.
- [17] W. L. Drax, C. M. Weeks, D. C. Roher, *Topics in Stereochemistry* (Eds. E. L. Eliel, Allinger), John Wiley & Sons, New York, **1976**.
- [18] S. Komiya, *Synthesis of Organometallic Compounds: A Practical Guide*, John Wiley & Sons, New York, **1997**.
- [19] G. M. Sheldrick, *SHELXS 97, SHELXL 97, CIFTAB-Program for Crystal Structure Analysis* (Release 97–2), Institut für Anorganische Chemie der Universität, Tammanstraße 4, 3400 Göttingen, Germany, **1998**.

Received March 24, 2003

## FULL PAPER

# Synthesis, Characterisation, and X-ray Crystal Structure of New Ni<sup>II</sup>, Pd<sup>II</sup>, and Pt<sup>II</sup> Complexes of Tridentate Pyrazole-Based Ligands with an NOS-Donor Set

Jordi García-Antón,<sup>[a]</sup> Josefina Pons,<sup>\*[a]</sup> Xavier Solans,<sup>[b]</sup> Mercè Font-Bardia,<sup>[b]</sup> and Josep Ros<sup>\*[a]</sup>

**Keywords:** Nickel / N ligands / O ligands / Palladium / Platinum / S ligands

Treatment of the ligands 1-(3-thia-5-hydroxypentyl)-3,5-dimethylpyrazole (thpd) and 1-(3-thia-6-hydroxyhexyl)-3,5-dimethylpyrazole (thhd) with [PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>], [PtCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>], and NiCl<sub>2</sub>·6H<sub>2</sub>O produces the complexes [MCl<sub>2</sub>(L)] [M = Pd, L = thpd (**1**), thhd (**2**); M = Pt, L = thpd (**3**), thhd (**4**); M = Ni, L = thpd (**5**), thhd (**6**)], which have been characterised by elemental analyses, conductivity, IR, electronic spectra, and NMR spectroscopy (when possible). The crystal structures of **2**, **3**, and **4**, determined by single-crystal X-ray diffraction, each consist of discrete [MCl<sub>2</sub>(L)] units. Each M<sup>II</sup> atom is coordinated by the pyrazolyl nitrogen and

the thioether sulfur from the ligand and two *cis* chloride ions in a square-planar geometry. Crystallisation of [NiCl<sub>2</sub>(thpd)] in non-anhydrous alcohols yields [NiCl(H<sub>2</sub>O)<sub>2</sub>(thpd)]Cl ([**7**]Cl), the crystal structure of which was determined by single-crystal X-ray diffraction to reveal nickel atoms coordinated by two water molecules, one chloride ion and one thpd ligand (coordinating via all three donor atoms, N, S, and O) in a skew-trapezoidal bipyramid (distorted octahedral) geometry.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2003)

## Introduction

The coordination chemistry of chelating ligands containing mixed functionalities is of continued importance.<sup>[1]</sup> In particular, the chemistry of ligands that contain both inert and labile groups has received considerable attention.<sup>[2]</sup> Jeffrey and Rauchfuss first introduced the term “hemilabile ligand” in 1979<sup>[3]</sup> to describe polydentate chelates that contain at least two different types of bonding groups — a hard and a soft donor group<sup>[4]</sup> — making them attractive for catalytic purposes.

Our group has previously synthesised and characterised pyrazolic ligands with two donor groups, in particular N–N(amine),<sup>[5]</sup> N–P,<sup>[6]</sup> N–O,<sup>[7]</sup> and N–S.<sup>[8]</sup> Our next goal is to study the coordinative properties of ligands with three donor groups.

Here, we report the synthesis and full characterisation of two new ligands, 1-(3-thia-5-hydroxypentyl)-3,5-dimethylpyrazole (thpd), and 1-(3-thia-6-hydroxyhexyl)-3,5-dimethylpyrazole (thhd), the three different donor atoms in this case being nitrogen, sulfur, and oxygen. The com-

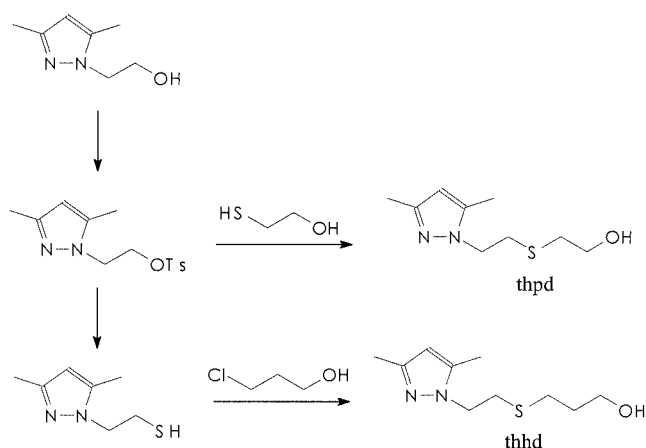
plexation of these ligands with [MCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>] (M = Pd<sup>II</sup>, Pt<sup>II</sup>) and NiCl<sub>2</sub>·6H<sub>2</sub>O is also reported, to give the complexes: [MCl<sub>2</sub>(L)] [M = Pd, L = thpd (**1**), thhd (**2**); M = Pt, L = thpd (**3**), thhd (**4**); M = Ni, L = thpd (**5**), thhd (**6**)]. Treatment of **5** with non-anhydrous alcohols produces [NiCl(H<sub>2</sub>O)<sub>2</sub>(thpd)]Cl ([**7**]Cl). These complexes have been characterised by elemental analyses, conductivity, IR spectroscopy and, when possible, <sup>1</sup>H NMR, <sup>13</sup>C{<sup>1</sup>H} NMR, and <sup>195</sup>Pt{<sup>1</sup>H} NMR spectroscopy. The X-ray crystal structures of complexes **2**, **3**, **4**, and [**7**]Cl are also presented.

## Results and Discussion

The ligands 1-(3-thia-5-hydroxypentyl)-3,5-dimethylpyrazole (thpd) and 1-(3-thia-6-hydroxyhexyl)-3,5-dimethylpyrazole (thhd), not previously reported, were synthesised to initiate a new study of pyrazole-based ligands with N1 alkyl substituents containing two different donor atoms (in this case O and S). In this respect, 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)ethyl 4-methylbenzenesulfonate<sup>[9]</sup> on treatment with 2-mercaptoethanol gave thpd and 1-(2-mercaptoethyl)-3,5-dimethylpyrazole<sup>[10]</sup> on treatment with 3-chloro-1-propanol gave thhd (Scheme 1). These ligands were characterised by elemental analysis, MS spectrometry, and infrared, <sup>1</sup>H NMR and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy.

<sup>[a]</sup> Departament de Química, Facultat de Ciències, Universitat Autònoma de Barcelona, 08193 Bellaterra-Cerdanyola, Barcelona, Spain  
Fax: (internat.) + 34-93/581-3101  
E-mail: Josefina.Pons@uab.es

<sup>[b]</sup> Cristal·lografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona, Martí i Franquès s/n, 08028 Barcelona, Spain



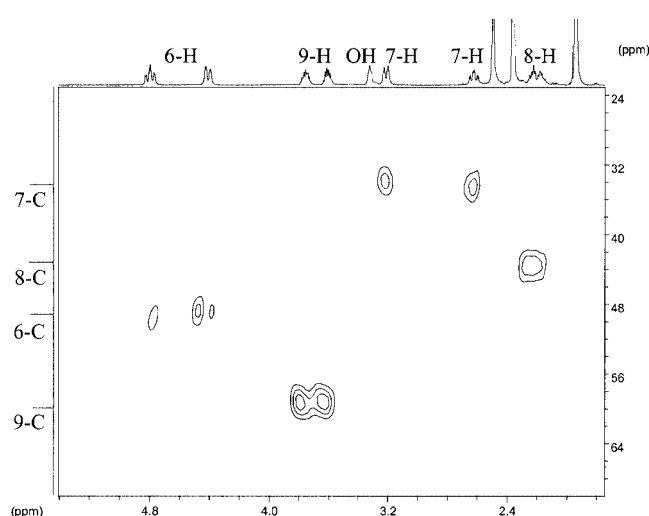
Scheme 1

Treatment of thpd and thhd with  $[\text{MCl}_2(\text{CH}_3\text{CN})_2]$  ( $\text{M} = \text{Pd}^{\text{II}}$  [11] and  $\text{Pt}^{\text{II}}$  [12]) produced four chloro complexes whose elemental analyses agree with the formula  $[\text{MCl}_2(\text{L})]$  ( $\text{M} = \text{Pd}$ ,  $\text{L} = \text{thpd}$  (**1**),  $\text{L} = \text{thhd}$  (**2**);  $\text{M} = \text{Pt}$ ,  $\text{L} = \text{thpd}$  (**3**),  $\text{L} = \text{thhd}$  (**4**)). Conductivity values in acetonitrile for complexes **1–4** reveal a non-electrolyte nature [ $1.8\text{--}6.4 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ ]. The reported values for  $10^{-3} \text{ M}$  solutions of non-electrolyte complexes are lower than  $120 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$  in acetonitrile.<sup>[13]</sup>

The IR spectra of the complexes **1–4** are similar to those of the ligands, the most characteristic bands being those attributable to the pyrazolyl group,  $\nu(\text{C}=\text{C})$  and  $\nu(\text{C}=\text{N})$  between  $1553$  and  $1548 \text{ cm}^{-1}$  and  $\delta(\text{C-H})_{\text{oop}}$  between  $828$  and  $785 \text{ cm}^{-1}$ .<sup>[14]</sup>

Suitable single crystals for X-ray structure determination were obtained by recrystallisation from methanol for **2–4**.

<sup>1</sup>H and <sup>13</sup>C NMR spectra of **1–4**, recorded in  $[\text{D}_3]\text{acetonitrile}$ , show the signals of the coordinated ligands (data are reported in the Exp. Sect.). HMQC spectra at  $253 \text{ K}$  were used to assign the proton signals (e.g. for **3** in Figure 1).

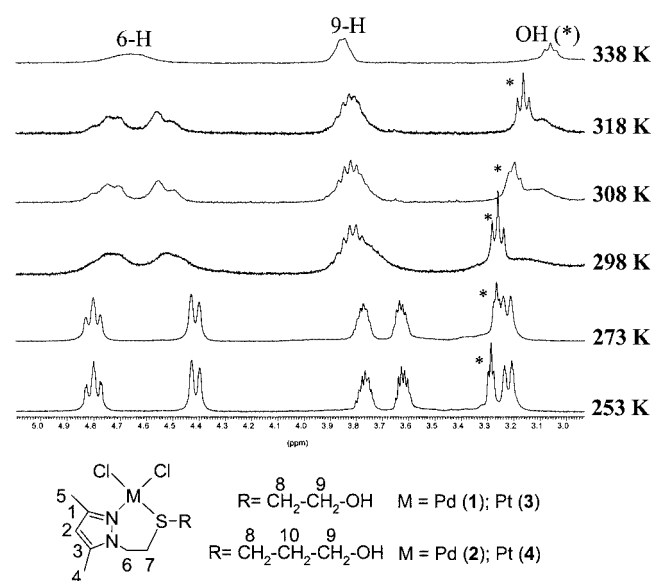
Figure 1. 250 MHz 2D HMQC spectrum of **3** at  $253 \text{ K}$ 

The <sup>1</sup>H NMR spectra of complexes **1–4** at  $298 \text{ K}$  show sharp resonances for the CH and CH<sub>3</sub> groups of the pyrazolyl cycles. For **1** and **2**, only one broad band can be attributed to each CH<sub>2</sub> in the S-(CH<sub>2</sub>)<sub>2</sub>-N and S-(CH<sub>2</sub>)<sub>x</sub>-OH ( $x = 2$  for **1** and  $x = 3$  for **2**) chains, whereas at  $253 \text{ K}$ , the two protons of each CH<sub>2</sub> (in both chains) can be assigned to two different signals (although some of the signals are partially superposed and are given as a single multiplet in the Exp. Sect.). These two signals for each CH<sub>2</sub> are due to the rigidity of these chains, at  $253 \text{ K}$ , giving rise to two diastereotopic hydrogens for each CH<sub>2</sub>.

At  $298 \text{ K}$ , for complexes **3** and **4**, two broad bands can be assigned to each CH<sub>2</sub> in the S-(CH<sub>2</sub>)<sub>2</sub>-N chain but only one signal for each CH<sub>2</sub> in the S-(CH<sub>2</sub>)<sub>x</sub>-OH ( $x = 2$  for **3** and  $x = 3$  for **4**) chain. At  $253 \text{ K}$ , signals attributable to the CH<sub>2</sub> in the S-(CH<sub>2</sub>)<sub>2</sub>-N chain become well-defined multiplets and the CH<sub>2</sub> corresponding to the S-(CH<sub>2</sub>)<sub>x</sub>-OH chain show two well-defined signals for each of them (but, as for the Pd<sup>II</sup> complexes, some of these signals are superposed and are given as a single multiplet in the Exp. Sect.).

The broad bands for **1–4** at  $298 \text{ K}$  arise from fluxional processes that involve the S-(CH<sub>2</sub>)<sub>2</sub>-N and S-(CH<sub>2</sub>)<sub>x</sub>-OH ( $x = 2$  for **1**, **3** and  $x = 3$  for **2**, **4**) chains. This led us to record variable-temperature spectra for **1–4** (spectra for 6-H, 9-H and the alcohol group for **3** are shown in Figure 2). The two different chains [S-(CH<sub>2</sub>)<sub>2</sub>-N and S-(CH<sub>2</sub>)<sub>x</sub>-OH] were studied separately.

For the S-(CH<sub>2</sub>)<sub>2</sub>-N chain, the two CH<sub>2</sub> signals coalesce to one at  $273$  and  $293 \text{ K}$  for complexes **1** and **2**, respectively, whereas **3** and **4** required heating to  $338$  and  $345 \text{ K}$ , respectively, to bring about coalescence. These temperature coalescences and the separation of the two signals attributed to each CH<sub>2</sub> correspond to  $\Delta G^\ddagger$  values of ca.  $55$ ,  $59$ ,  $66$ , and  $68 \text{ kJ}\cdot\text{mol}^{-1}$  for **1–4**, respectively.<sup>[15]</sup>

Figure 2. Numbering scheme for the complexes **1–4** and <sup>1</sup>H NMR variable-temperature experiments for 6-H and 9-H in **3**



The  $\Delta G^\ddagger$ s are consistent with a chelate ring-flipping process due to the rocking of the pyrazolyl cycle around the M–N bond without any metal–ligand bond breaking.<sup>[5e,7c]</sup> At higher temperatures, with ring-flipping, the two hydrogens of each CH<sub>2</sub> are interconverted and only one signal can be observed. These energy values could also be consistent with a mechanism that implies an inversion of the sulfur atom configuration.<sup>[16,17]</sup>

For the S–(CH<sub>2</sub>)<sub>x</sub>–OH chains ( $x = 2$  for **1** and **3** and  $x = 3$  for **2** and **4**) the rigidity could be attributed to hydrogen bonds that occur only at low temperatures. This would explain why the hydrogens of these chains appear as diastereotopic at 253 K. Definitive evidence for O–H···Cl interactions in the solid state is given by the X-ray analyses of **2–4**. The existence of these interactions in solution was proved by the variable-temperature spectra of the alcohol group (example for **3** in Figure 2) in which the chemical shift of the alcohol group varied with temperature (from  $\delta = 3.23$  and 2.78 ppm at 298 K to  $\delta = 3.36$  and 3.03 ppm for **1** and **2**, respectively and from  $\delta = 3.06$  and 2.83 ppm at 338 K to  $\delta = 3.29$  and 3.09 at 253 K for **3** and **4**, respectively). The R–OH resonances shift to lower fields with decreasing temperature, as expected for this kind of process.<sup>[18]</sup>

For the S–(CH<sub>2</sub>)<sub>x</sub>–OH chains the two CH<sub>2</sub> signals coalesce at 298 K for complexes **1–4**, which, together with the separations of the two signals, corresponds to  $\Delta G^\ddagger$ s of ca. 61 kJ·mol<sup>-1</sup> for **1** and **3** and ca. 63 and 66 kJ·mol<sup>-1</sup> for **2** and **4**, respectively.<sup>[15]</sup>

Additional <sup>195</sup>Pt{<sup>1</sup>H} NMR experiments for complexes **3** and **4** at 298 K revealed only one band for each complex ( $\delta = -2868$  ppm for **3** and  $-2879$  ppm for **4**). This suggests that all of the bands in the <sup>1</sup>H NMR spectra belong to only one complex, as expected from the data obtained with the variable-temperature experiments.

Treatment with NiCl<sub>2</sub>·6H<sub>2</sub>O led to the isolation of one complex for each ligand. Their elemental analyses agree with the formula [NiCl<sub>2</sub>(L)] [L = thpd (**5**) and thhd (**6**)]. The molar conductivities in absolute ethanol are consistent with non-electrolyte complexes [14.3–18.7 Ω<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>]. Reported values for 10<sup>-3</sup> M solutions of non-electrolyte complexes in absolute ethanol are lower than 35 Ω<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>.<sup>[13]</sup> The IR spectra (4000–400 cm<sup>-1</sup>) of complexes **5** and **6** are similar to those of the ligands.<sup>[14]</sup> Additional spectra in the region 500–100 cm<sup>-1</sup> present well-defined bands corresponding to  $\nu(\text{Ni–N})$  (450, 461 cm<sup>-1</sup>),  $\nu(\text{Ni–Cl})$  (368, 387 cm<sup>-1</sup>), and  $\nu(\text{Ni–S})$  (328, 344 cm<sup>-1</sup>) bands for **5** and **6**, respectively, and a band attributable to  $\nu(\text{Ni–O})$  at 498 cm<sup>-1</sup> for **5** and 520 cm<sup>-1</sup> for **6**.<sup>[19]</sup>

Electronic spectra of the complexes **5** and **6** measured in absolute ethanol show a single d–d band at 422 nm ( $\epsilon = 55$  mol<sup>-1</sup>cm<sup>-1</sup>L) for **5** and 414 nm ( $\epsilon = 75$  mol<sup>-1</sup>cm<sup>-1</sup>L) for **6** that can be attributed to the <sup>3</sup>E'(F)→<sup>3</sup>E''(P) transition, which is characteristic for pentacoordinate Ni<sup>II</sup> complexes.<sup>[20]</sup> It was not possible to obtain single crystals of these complexes.

When **5** was dissolved in methanol or ethanol it reacted with the water in the solvent to give a complex that was

obtained as suitable single crystals for X-ray structure determination. This complex {[NiCl(H<sub>2</sub>O)<sub>2</sub>(thpd)]Cl (**[7]Cl**)} has an IR spectrum with bands that can be attributed to water molecules not observed for complex **5**. The electronic spectrum of complex **[7]Cl** was measured in ethanol and shows two bands in the visible region at 731 ( $\epsilon = 4$  mol<sup>-1</sup>cm<sup>-1</sup>L) and 403 nm ( $\epsilon = 10$  mol<sup>-1</sup>cm<sup>-1</sup>L), which can be attributed to <sup>3</sup>A<sub>2g</sub>→<sup>3</sup>T<sub>1g</sub>(F) and <sup>3</sup>A<sub>2g</sub>→<sup>3</sup>T<sub>1g</sub>(P) transitions, respectively, these being characteristic for octahedral Ni<sup>II</sup> complexes.<sup>[20]</sup> An equivalent complex with thhd could not be isolated.

### Crystal Structure of [MCl<sub>2</sub>(L)] [M = Pd, L = thhd (**2**); M = Pt, L = thpd (**3**), thhd (**4**)]

The structure of **2** consists of discrete [PdCl<sub>2</sub>(thhd)] units (Figure 3), while **3** and **4** consist of discrete [PtCl<sub>2</sub>(L)] (L = thpd and thhd, respectively) units (Figures 4 and 5, respectively). Crystallographic data for complexes **2** and **4** indicate that they are isostructural.

The metal atom of each structure is surrounded by an identical *core* composed of the nitrogen and thioether sulfur from the pyrazole ligand and two chlorine atoms. The metal atoms have a slightly distorted square-planar geometry, with the chloride ions in a *cis* arrangement. A small tetrahedral distortion can be observed in the mean separation of the atoms linked to the metal cation in relation to the mean plane [ $\pm 0.065(4)$  Å for **2**,  $\pm 0.001(3)$  Å for **3**, and  $\pm 0.050(3)$  Å for **4**].

Some selected bond lengths and bond angles are listed in Table 1. There are two complexes in the literature with a PdCl<sub>2</sub>NS *core* (terminal chloride ion, pyrazolic nitrogen, and thioether sulfur). For complex **2**, Pd–Cl, Pd–N, and

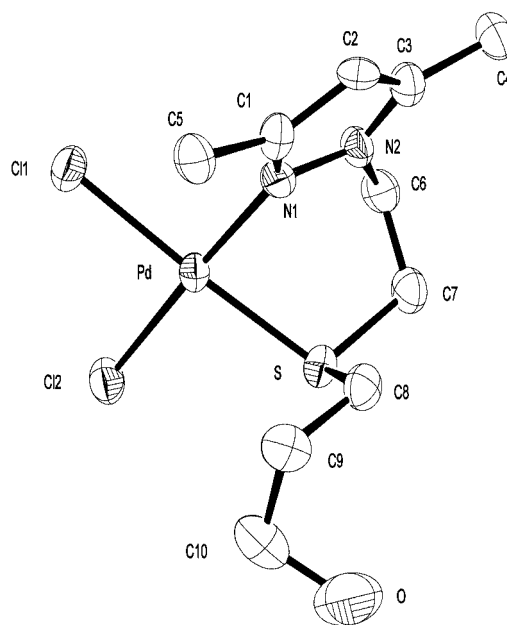


Figure 3. ORTEP drawing of [PdCl<sub>2</sub>(thhd)] (**2**, 293 K determination) showing all non-hydrogen atoms and the atom-numbering scheme; 50% probability amplitude displacement ellipsoids are shown

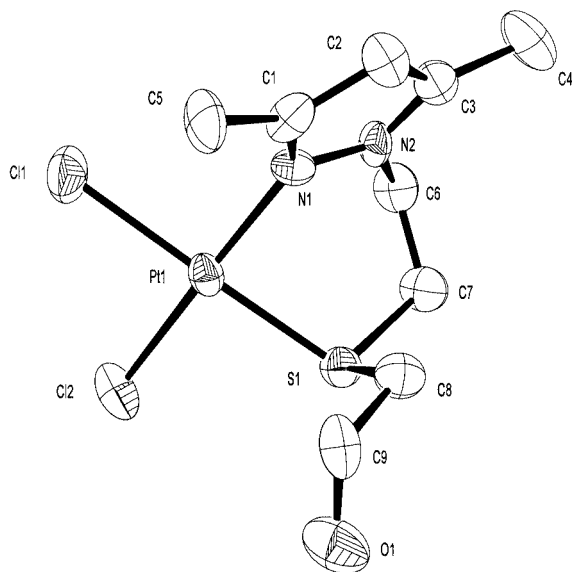


Figure 4. ORTEP drawing of [PtCl<sub>2</sub>(thpd)] (**3**, 293 K determination) showing all non-hydrogen atoms and the atom-numbering scheme; 50% probability amplitude displacement ellipsoids are shown

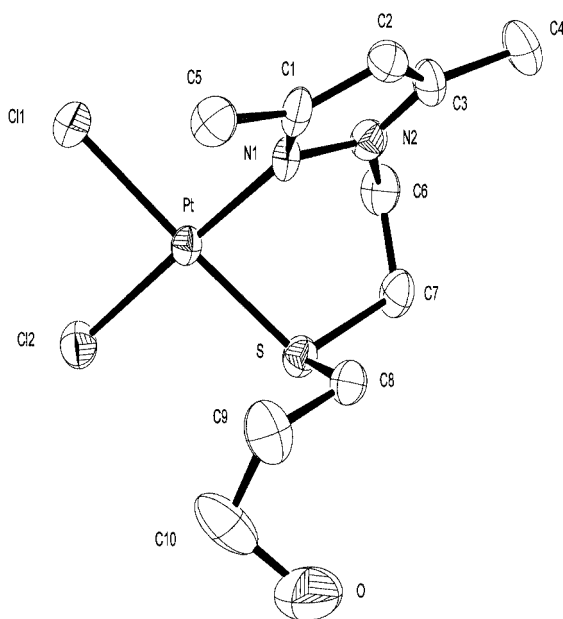


Figure 5. ORTEP drawing of [PtCl<sub>2</sub>(thhd)] (**4**, 293 K determination) showing all non-hydrogen atoms and the atom-numbering scheme; 50% probability amplitude displacement ellipsoids are shown

Pd–S bond lengths are similar to those found for the two reported complexes.<sup>[21]</sup>

No structural data for complexes with a PtCl<sub>2</sub>NS core (terminal chloride ion, pyrazolic nitrogen, and thioether sulfur) have been reported, although two structures with a PtCl<sub>2</sub>NS core (aromatic amine) have been described<sup>[22]</sup> in addition to five complexes with a PtN<sub>2</sub>Cl<sub>2</sub> core (terminal chloride and pyrazolic nitrogen) have been described.<sup>[23]</sup> For complexes **3** and **4**, the Pt–S,<sup>[22]</sup> Pt–N,<sup>[23]</sup> and

Pt–Cl<sup>[24]</sup> bond lengths are of the same order as those found in the literature.

The thpd and thhd ligands act as bidentate chelates, and form one M–S–C–C–N–N six-membered ring in each complex, all of which have a boat conformation. Bite angles are 86.9(1)° for N(1)–Pd–S in **2** and 87.7(1)° and 87.5(3)° for N(1)–Pt–S in **3** and **4**, respectively. For complex **2** this bite angle is similar to those reported for [Pd(bddo)](BF<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O [bddo = 1,8-bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane], 88.8(2) and 86.2(1)°,<sup>[8a]</sup> and [Pd(pdto)](ClO<sub>4</sub>)<sub>2</sub> [pdto = 1,8-bis(2-pyridyl)-3,6-dithiaoctane], 86.9° and 87.2°.<sup>[25]</sup>

Distortion of the boat conformation in six-membered rings is observed in ΔC<sub>s</sub> [for **2** ΔC<sub>s</sub>(Pd) = 6.8(4)° and ΔC<sub>s</sub>(S–C7) = 11.0(5)°; for **3** ΔC<sub>s</sub>(Pt) = 16.0(9)° and ΔC<sub>s</sub>(S–C7) = 16.3(10)°; and for **4** ΔC<sub>s</sub>(Pt) = 6.1(3)° and ΔC<sub>s</sub>(S–C7) = 13.7(4)°; Φ<sub>1</sub>+Φ<sub>1</sub>' = torsion angles related to the considered plane;<sup>[26]</sup> *m* = equivalent torsion angles].

$$\Delta C_s = \sqrt{\frac{\sum_{i=1}^m (\phi_i + \phi_i')^2}{m}}$$

Complexes **2–4** contain intermolecular hydrogen bonds between Cl and OH (Table 2). Complexes **2** and **4** yield infinite chains parallel to the crystallographic vector *b*, whereas the chains for complex **3** are parallel to the crystallographic vector *c* (an example for **4** is given in Figure 6).

#### Crystal Structure of [NiCl(H<sub>2</sub>O)<sub>2</sub>(thpd)]Cl ([7]Cl)

The structure of [7]Cl consists of cationic units of [NiCl(H<sub>2</sub>O)<sub>2</sub>(thpd)]<sup>+</sup> and chloride anions (Figure 7). The ligand is coordinated to the metallic centre by the nitrogen, sulfur, and oxygen atoms. Nickel(II) completes its coordination with one chloride ion and two water molecules in a skew-trapezoidal bipyramid (distorted octahedral) geometry (Cl1, N1, O2, O3, and Ni atoms being in a plane) with angles at Ni<sup>II</sup> in the range 83.68(8)–96.90(9)° and 168.32(6)–176.16(7)°. Water molecules are arranged *trans* to the sulfur and the nitrogen atoms, and the chloride ion is *trans* to the alcohol group.

Some selected bond lengths and bond angles are listed on Table 3. No other complex with a NiClNO<sub>3</sub>S core appears in the literature. The Ni–O, Ni–OH<sub>2</sub>, Ni–S, Ni–Cl, and Ni–N bond lengths are of the same order as those found for Ni–O(alcohol),<sup>[27]</sup> Ni–OH<sub>2</sub> (complexes containing two water molecules),<sup>[28]</sup> Ni–S(thioether),<sup>[9,27a,29]</sup> Ni–Cl(terminal),<sup>[27b,28d,29b,29d,30]</sup> and Ni–N(pyrazole)<sup>[9,27–30]</sup> bond lengths, respectively.

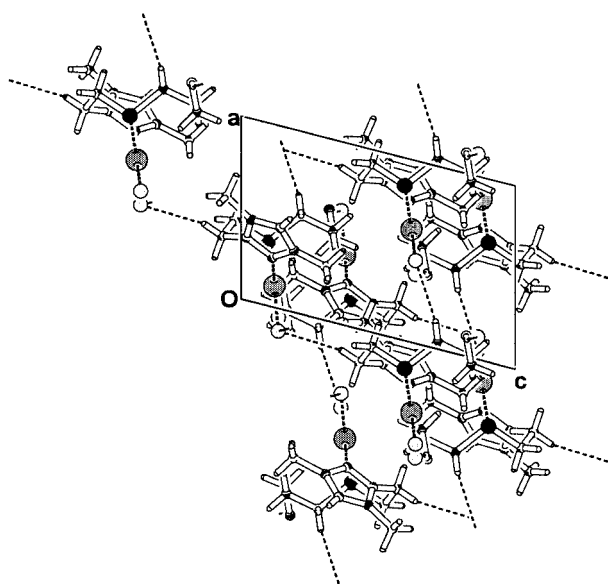
The thpd ligand acts as a tridentate chelate and forms one Ni–S–C–C–O five-membered ring with an envelope conformation [C9 being ±0.457(4) Å out of the plane formed by the other four atoms] and one Ni–N–N–C–C–S six-membered ring with a boat conformation. Distortion of the boat in the six-membered ring is observed in ΔC<sub>s</sub>(Ni) = 13.2(2)° and ΔC<sub>s</sub>(S–C7) = 55.9(2)°.

Table 1. Selected bond lengths (Å) and angles (°) for 2–4 with estimated standard deviations (e.s.d.s) in parentheses

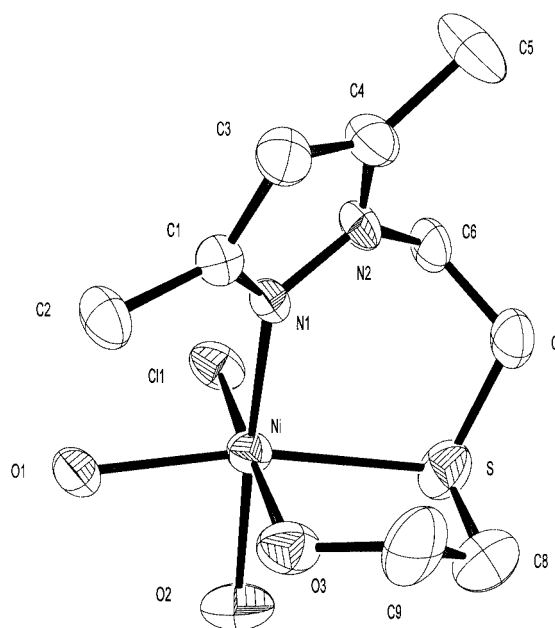
2		3		4	
Pd–N(1)	2.001(5)	Pt–N(1)	2.024(8)	Pt–N(1)	2.002(3)
Pd–S	2.279(2)	Pt–S	2.260(3)	Pt–S	2.2588(10)
Pd–Cl(2)	2.280(2)	Pt–Cl(2)	2.311(3)	Pt–Cl(2)	2.2909(11)
Pd–Cl(1)	2.326(2)	Pt–Cl(1)	2.321(4)	Pt–Cl(1)	2.3263(10)
N(1)–Pd–S	86.91(14)	N(1)–Pt–S	87.5(3)	N(1)–Pt–S	87.72(10)
N(1)–Pd–Cl(2)	176.03(13)	N(1)–Pt–Cl(2)	177.1(2)	N(1)–Pt–Cl(2)	177.69(10)
S–Pd–Cl(2)	90.49(6)	S–Pt–Cl(2)	90.73(16)	S–Pt–Cl(2)	90.84(4)
N(1)–Pd–Cl(1)	91.58(13)	N(1)–Pt–Cl(1)	91.7(3)	N(1)–Pt–Cl(1)	91.18(10)
S–Pd–Cl(1)	175.91(5)	S–Pt–Cl(1)	177.46(11)	S–Pt–Cl(1)	176.41(4)
Cl(1)–Pd–Cl(2)	91.21(6)	Cl(1)–Pt–Cl(2)	89.98(14)	Cl(1)–Pt–Cl(2)	90.37(4)

Table 2. Distances and angles related to hydrogen bonding

Compound	D–H	H···A	D···A	D–H···A
<b>2</b>				
O–H(10)···Cl(1)	0.82(8)	2.43(8)	3.235(8)	165(4)
<b>3</b>				
O–H(10)···Cl(2)	0.82(9)	2.40(9)	3.214(12)	174(6)
<b>4</b>				
O–H(10)···Cl(1)	0.82(4)	2.44(4)	3.235(5)	164(2)
[7]Cl				
O(1)–H(10)···Cl(2)	0.78(3)	2.44(3)	3.110(4)	145(2)
O(2)–H(20)···Cl(2)	0.78(2)	2.42(2)	3.148(4)	157(3)
O(3)–H(30)···Cl(2)	0.66(4)	2.42(4)	3.077(4)	173(4)

Figure 6. Partial view of the infinite chain formed by the different units of [PtCl<sub>2</sub>(thhd)] (4) bonded by hydrogen bonds

For the six-membered ring, the N(1)–Ni–S bite angle is 93.12(8), while for the five-membered ring the S–Ni–O(3) bite angle is 83.68(8)°. The N–Ni–S bite angle is greater and the S–Ni–O is similar to those reported in the literature for [Ni<sub>3</sub>(bdnol)Cl<sub>3</sub>(EtOH)]·3EtOH (N–Ni–S bite angles are 89.991° and 91.634° and S–Ni–O bite angles are 82.177° and 84.090°) and [Ni<sub>2</sub>(bdnol)Cl<sub>3</sub>]·MeCN

Figure 7. ORTEP drawing of [NiCl(H<sub>2</sub>O)<sub>2</sub>(thpd)]<sup>+</sup> ([7]<sup>+</sup>, 293 K determination) showing all non-hydrogen atoms and the atom-numbering scheme; 50% probability amplitude displacement ellipsoids are shown

[bdnol = 1,9-bis(3,5-dimethyl-1-pyrazolyl)-3,7-dithia-5-nonanol] (N–Ni–S bite angles are 91.514° and 91.755° and S–Ni–O bite angles are 83.952° and 84.016°).<sup>[29b]</sup>

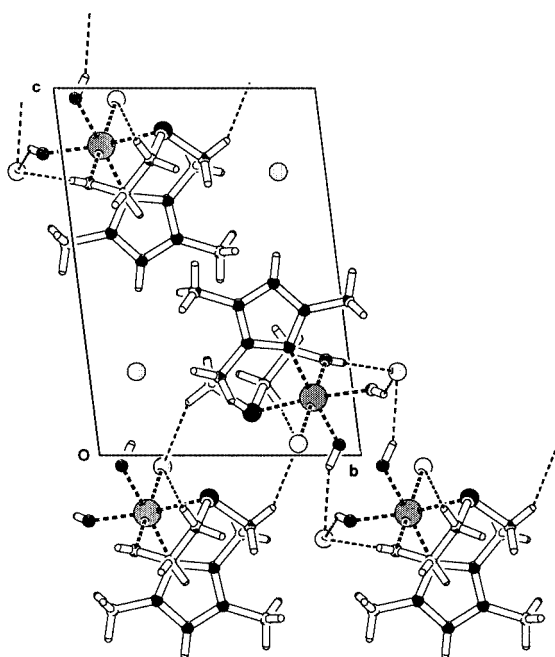
This complex contains three types of hydrogen bonds, intramolecular O(1)–H(10)···Cl(2) and intermolecular O(2)–H(20)···Cl(2) and O(3)–H(30)···Cl(2). The O(2)–H(20)···Cl(2) bonding yields a four-membered circuit and O(3)–H(30)···Cl(2) furnishes infinite chains parallel to the crystallographic vector *a* (Table 2, Figure 8).

## Conclusion

The structures of the chlorocomplexes presented here were originally investigated to discover the configuration of the new potentially tridentate N, O, S ligands 1-(3-thia-5-hydroxypentyl)-3,5-dimethylpyrazole (thpd) and 1-(3-thia-6-hydroxyhexyl)-3,5-dimethylpyrazole (thhd) when com-

Table 3. Selected bond lengths (Å) and angles (°) for [7]<sup>+</sup> with estimated standard deviations (e.s.d.s) in parentheses

[7] <sup>+</sup>	
Ni–O(1)	2.060(3)
Ni–N(1)	2.082(2)
Ni–O(2)	2.121(2)
Ni–O(3)	2.114(2)
Ni–Cl(1)	2.3881(12)
Ni–S	2.408(2)
O(1)–Ni–N(1)	96.90(9)
O(1)–Ni–O(3)	90.38(10)
N(1)–Ni–O(3)	86.83(9)
O(1)–Ni–O(2)	84.46(11)
N(1)–Ni–O(2)	172.78(9)
O(3)–Ni–O(2)	86.03(9)
O(1)–Ni–Cl(1)	91.58(8)
N(1)–Ni–Cl(1)	96.22(7)
O(3)–Ni–Cl(1)	176.16(7)
O(2)–Ni–Cl(1)	90.88(7)
O(1)–Ni–S	168.32(6)
N(1)–Ni–S	93.12(8)
O(3)–Ni–S	83.68(8)
O(2)–Ni–S	85.10(9)
Cl(1)–Ni–S	93.81(6)

Figure 8. Partial view of the infinite 3D-structure formed by the different units of [NiCl(H<sub>2</sub>O)<sub>2</sub>(thpd)]Cl ([7]Cl) bonded by hydrogen bonds

plexed to group 10 metals. These ligands present different coordination environments, depending on the metal ion, as observed in the X-ray structures. Hence, coordination is N, S for Pd<sup>II</sup> and Pt<sup>II</sup>, but N, S, O for Ni<sup>II</sup>. NMR studies proved very useful in determining the configuration of ligands in the complexes. These results will enable the study of the hemilabile behaviour of these novel N, O, S ligands when coordinated to transition metals.

## Experimental Section

**Generals Remarks:** Preparations were performed using the usual vacuum line and Schlenk techniques. All reagents were commercial grade and were used without further purification. Acetonitrile was dried and distilled by standard methods and deoxygenated in the vacuum line.

2-(3,5-Dimethyl-1*H*-pyrazol-1-yl)ethyl 4-methylbenzenesulfonate<sup>[9]</sup> and 1-(2-mercaptoethyl)-3,5-dimethylpyrazole<sup>[10]</sup> were prepared according to published methods, as were samples of [PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>]<sup>[11]</sup> and [PtCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>]<sup>[12]</sup>

Analyses (C, N, H, S) were performed in our analytical laboratory on a Carlo Erba CHNS EA-1108 instrument. Conductivity measurements were performed at room temperature in 10<sup>-3</sup> M absolute ethanol or acetonitrile solutions employing a Crison, micro CM 2200 conductimeter. Infrared spectra were recorded as KBr pellets or polyethylene mulls in the range 4000–100 cm<sup>-1</sup> under a nitrogen atmosphere. Electronic spectra in solution were run on a Kontron-Uvikon 860 in acetonitrile between 750 and 350 nm. The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR and HMQC spectra were obtained either on a Bruker AC-250 MHz or a Bruker 500 MHz instrument. <sup>195</sup>Pt{<sup>1</sup>H} NMR spectra were obtained on a Bruker Advance DRX 250 MHz instrument. <sup>1</sup>H and <sup>13</sup>C chemical shifts (δ) were determined relative to internal TMS and are given in ppm. <sup>195</sup>Pt chemical shifts (δ) are relative to external 0.1 mol·dm<sup>-3</sup> Na<sub>2</sub>PtCl<sub>6</sub> and are given in ppm. Mass spectra were obtained on a HP 5989A apparatus.

### Synthesis of 1-(3-Thia-5-hydroxypentyl)-3,5-dimethylpyrazole (thpd)

A solution of 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)ethyl 4-methylbenzenesulfonate (6.26 g, 21.3 mmol), mercaptoethanol (1.50 mL, 21.2 mmol) and sodium hydroxide (0.94 g, 22.8 mmol) in distilled water (30 mL) was refluxed for 5 h. After cooling to room temperature, the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 25 mL). The collected organic layers were dried with anhydrous sodium sulfate and removed in vacuo to give a brown oil that was then washed with diethyl ether to afford the desired product as a white solid. Yield: 2.70 g (61%). M.p.: 46.6–47.5 °C. C<sub>9</sub>H<sub>16</sub>N<sub>2</sub>OS (200.1) C 53.97, H 8.00, N 13.99, S 16.04; found C 54.17, H 7.93, N 14.10, S 15.91. IR (KBr, cm<sup>-1</sup>): ν(O–H) 3221, ν(C–H)<sub>al</sub> 2943, ν(C=C), ν(C=N) 1549, δ(CH<sub>3</sub>)<sub>as</sub> 1456, δ(CH<sub>3</sub>)<sub>s</sub> 1386, δ(C–H)<sub>oop</sub> 792. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub> solution): δ = 2.20 (s, 3 H, Me), 2.25 (s, 3 H, Me), 2.60 (t, <sup>3</sup>J = 6 Hz, 2 H, CH<sub>2</sub>–CH<sub>2</sub>–OH), 2.95 (t, <sup>3</sup>J = 7 Hz, 2 H, pz-CH<sub>2</sub>–CH<sub>2</sub>), 3.28 (b, 1 H, OH), 3.69 (t, <sup>3</sup>J = 6 Hz, 2 H, CH<sub>2</sub>–CH<sub>2</sub>–OH), 4.14 (t, <sup>3</sup>J = 7 Hz, 2 H, pz-CH<sub>2</sub>–CH<sub>2</sub>), 5.79 (s, 1 H, pz-CH) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (63 MHz, CDCl<sub>3</sub> solution): δ = 11.2 (Me), 13.5 (Me), 32.1 (pz-CH<sub>2</sub>–CH<sub>2</sub>), 35.6 (CH<sub>2</sub>–CH<sub>2</sub>–OH), 48.5 (pz-CH<sub>2</sub>–CH<sub>2</sub>), 61.2 (CH<sub>2</sub>–CH<sub>2</sub>–OH), 105.3 (pz-CH), 147.9 (pz-C) ppm. MS (CI, NH<sub>3</sub>): *m/z* (%) = 201 [MH<sup>+</sup>] (33%), 115 [pz-(CH<sub>2</sub>)<sub>2</sub>-S<sup>+</sup>] (21), 109 [pz-CH<sub>2</sub><sup>+</sup>] (88), 97 [pzH<sup>+</sup>] (100).

### 1-(3-Thia-6-hydroxyhexyl)-3,5-dimethylpyrazole (thhd)

A mixture of 1-(2-mercaptoethyl)-3,5-dimethylpyrazole (2.72 g, 17.4 mmol) and 3-chloro-1-propanol (1.50 mL, 17.4 mmol) in THF (40 mL) and sodium hydroxide (0.70 g, 17.0 mmol) in distilled water (30 mL) were refluxed for 4.5 h. After cooling to room temperature, the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 25 mL) and the collected organic layers were dried with anhydrous sodium sulfate and removed in vacuo. The brown oil thus formed was then washed with diethyl ether and the desired product precipitated as a white solid. Yield: 2.24 g (60%). M.p.: 53.7–54.1 °C. C<sub>10</sub>H<sub>18</sub>N<sub>2</sub>OS (214.1) C 56.04, H 8.46, N 13.07, S 14.91; found C 55.83, H 8.21, N 12.82, S 14.73. IR (KBr, cm<sup>-1</sup>): ν(O–H) 3298, ν(C–H)<sub>al</sub> 2913,

$\nu(\text{C}=\text{C})$ ,  $\nu(\text{C}=\text{N})$  1553,  $\delta(\text{CH}_3)_{\text{as}}$  1446,  $\delta(\text{CH}_3)_{\text{s}}$  1386,  $\delta(\text{C}-\text{H})_{\text{oop}}$  778.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$  solution):  $\delta$  = 1.80 (qt, 2 H,  $^3J$  = 6 Hz,  $\text{CH}_2-\text{CH}_2-\text{OH}$ ), 2.20 (s, 3 H, *Me*), 2.26 (s, 3 H, *Me*), 2.55 (t,  $^3J$  = 6 Hz, 2 H, *S-CH}\_2-\text{CH}\_2-\text{CH}\_2*), 2.92 (t,  $^3J$  = 7 Hz, 2 H, *pz-CH}\_2-\text{CH}\_2*), 3.70 (t,  $^3J$  = 6 Hz, 2 H,  $\text{CH}_2-\text{CH}_2-\text{OH}$ ), 4.15 (t,  $^3J$  = 7 Hz, 2 H, *pz-CH}\_2-\text{CH}\_2*), 5.78 (s, 1 H, *pz-CH*) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (63 MHz,  $\text{CDCl}_3$  solution):  $\delta$  = 11.2 (*Me*), 13.5 (*Me*), 28.6 ( $\text{CH}_2-\text{CH}_2-\text{CH}_2$ ), 32.1, 32.2 (*pz-CH}\_2-\text{CH}\_2*, *S-CH}\_2-\text{CH}\_2-\text{CH}\_2*), 48.5 (*pz-CH}\_2-\text{CH}\_2*), 61.2 ( $\text{CH}_2-\text{CH}_2-\text{OH}$ ), 105.2 (*pz-CH*), 139.3, 147.9 (*pz-C*) ppm. MS (CI,  $\text{NH}_3$ ): *m/z* [%]: 215 [ $\text{MH}^+$ ] (5%), 115 [ $\text{p}(\text{CH}_2)_2\text{S}^+$ ] (22), 109 [ $\text{p}(\text{CH}_2)_2^+$ ] (59), 97 [ $\text{p}(\text{CH}_2)_2^+$ ] (100).

**Synthesis of [PdCl<sub>2</sub>(L)] [L = thpd (1), L = thhd (2)] and [PtCl<sub>2</sub>L] [L = thpd (3), L = thhd (4)]:** A solution of [PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>] (0.101 g, 0.389 mmol) or [PtCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>] (0.075 g, 0.215 mmol) in acetonitrile (20 mL) was added dropwise to an equimolar solution of thpd or thhd in acetonitrile (10 mL). The resulting solution was stirred for 12 h, after which the acetonitrile was evaporated and the solid residue washed with chloroform (2 × 2 mL) and then dried under vacuum. The palladium complexes were orange solids, and the platinum complexes yellow solids.

**Complex 1:** Yield: 0.180 (99%). Conductivity ( $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ ,  $1.01 \cdot 10^{-3}$  M in acetonitrile): 1.8. C<sub>9</sub>H<sub>16</sub>Cl<sub>2</sub>N<sub>2</sub>OPdS (377.52) C 28.61, H 4.24, N 7.42, S 8.50; found C 28.23, H 4.11, N 7.13, S 8.26. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{O}-\text{H})$  3386,  $\nu(\text{C}-\text{H})_{\text{al}}$  2984–2937,  $\nu(\text{C}=\text{C})$ ,  $\nu(\text{C}=\text{N})$  1549,  $\delta(\text{CH}_3)_{\text{as}}$  1468,  $\delta(\text{CH}_3)_{\text{s}}$  1402,  $\delta(\text{C}-\text{H})_{\text{oop}}$  785. IR (polyethylene,  $\text{cm}^{-1}$ ):  $\nu(\text{Pd}-\text{N})$  467,  $\nu(\text{Pd}-\text{Cl})$  340–335,  $\nu(\text{Pd}-\text{S})$  292.  $^1\text{H}$  NMR (500 MHz, [D<sub>3</sub>]acetonitrile, 253 K):  $\delta$  = 2.09 (b, 2 H,  $\text{CH}_2-\text{CH}_2-\text{OH}$ ), 2.27 (s, 3 H, *Me*), 2.54 (s, 3 H, *Me*), 2.60 (b, 1 H, *pz-CH}\_2-\text{CHH}*), 3.20 (b, 1 H, *pz-CH}\_2-\text{CHH}*), 3.36 (t, 1 H, OH), 3.71 (b, 1 H,  $\text{CH}_2-\text{CHH}-\text{OH}$ ), 3.83 (b, 1 H,  $\text{CH}_2-\text{CHH}-\text{OH}$ ), 4.70 (b, 1 H, *pz-CHH}-\text{CH}\_2*), 4.84 (b, 1 H, *pz-CHH}-\text{CH}\_2*), 6.05 (s, 1 H, *pz-CH*) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (63 MHz, [D<sub>3</sub>]acetonitrile, 298 K):  $\delta$  = 11.9 (*Me*), 15.4 (*Me*), 35.1, 42.6 (*pz-CH}\_2-\text{CH}\_2*,  $\text{CH}_2-\text{CH}_2-\text{OH}$ ), 49.8 (*pz-CH}\_2-\text{CH}\_2*), 60.5 ( $\text{CH}_2-\text{CH}_2-\text{OH}$ ), 109.2 (*pz-CH*) ppm.

**Complex 2:** Yield: 0.180 (96%). Conductivity ( $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ ,  $9.97 \cdot 10^{-4}$  M in acetonitrile): 4.1. C<sub>10</sub>H<sub>18</sub>Cl<sub>2</sub>N<sub>2</sub>OPdS (391.62) C 30.64, H 4.60, N 7.15, S 8.20; found C 30.74, H 4.73, N 7.10, S 7.96. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{O}-\text{H})$  3462,  $\nu(\text{C}-\text{H})_{\text{ar}}$  3123,  $\nu(\text{C}-\text{H})_{\text{al}}$  2975–2921,  $\nu(\text{C}=\text{C})$ ,  $\nu(\text{C}=\text{N})$  1548,  $\delta(\text{CH}_3)_{\text{as}}$  1463,  $\delta(\text{CH}_3)_{\text{s}}$  1393,  $\delta(\text{C}-\text{H})_{\text{oop}}$  828. IR (polyethylene,  $\text{cm}^{-1}$ ):  $\nu(\text{Pd}-\text{N})$  462,  $\nu(\text{Pd}-\text{Cl})$  343–329,  $\nu(\text{Pd}-\text{S})$  307.  $^1\text{H}$  NMR (500 MHz, [D<sub>3</sub>]acetonitrile, 253 K):  $\delta$  = 1.82 (b, 1 H, *S-CHH}-\text{CH}\_2-\text{CH}\_2*), 2.21 (b, 1 H, *S-CHH}-\text{CH}\_2-\text{CH}\_2*), 2.05 (b,  $\text{CH}_2-\text{CH}_2-\text{CH}_2$ ), – this peak could not be integrated because it is too close to the solvent signal –2.39 (s, 3 H, *Me*), 2.51 (s, 3 H, *Me*), 2.51 (b, 1 H, *pz-CH}\_2-\text{CHH}*), 3.03 (b, 1 H, OH), 3.24 (b, 1 H, *pz-CH}\_2-\text{CHH}*), 3.52 (b, 1 H,  $\text{CH}_2-\text{CHH}-\text{OH}$ ), 3.58 (b, 1 H,  $\text{CH}_2-\text{CHH}-\text{OH}$ ), 4.73 (b, 1 H, *pz-CHH}-\text{CH}\_2*), 4.92 (b, 1 H, *pz-CHH}-\text{CH}\_2*), 6.11 (s, 1 H, *pz-CH*) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (63 MHz, [D<sub>3</sub>]acetonitrile, 298 K):  $\delta$  = 12.0 (*Me*), 15.3 (*Me*), 32.3 ( $\text{CH}_2-\text{CH}_2-\text{CH}_2$ ), 35.2, 37.6 (*pz-CH}\_2-\text{CH}\_2*, *S-CH}\_2-\text{CH}\_2-\text{CH}\_2*), 49.8 (*pz-CH}\_2-\text{CH}\_2*), 60.4 ( $\text{CH}_2-\text{CH}_2-\text{OH}$ ), 109.3 (*pz-CH*), 145.0, 153.0 (*pz-C*) ppm.

**Complex 3:** Yield: 0.080 (98%). Conductivity ( $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ ,  $1.07 \cdot 10^{-3}$  M in acetonitrile): 5.3. C<sub>9</sub>H<sub>16</sub>Cl<sub>2</sub>N<sub>2</sub>OPtS (466.29) C 23.16, H 3.43, N 6.00, S 6.88; found C 23.03, H 3.48, N 6.02, S 6.73. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{O}-\text{H})$  3420,  $\nu(\text{C}-\text{H})_{\text{al}}$  2974–2924,  $\nu(\text{C}=\text{C})$ ,  $\nu(\text{C}=\text{N})$  1553,  $\delta(\text{CH}_3)_{\text{as}}$  1470,  $\delta(\text{CH}_3)_{\text{s}}$  1409,  $\delta(\text{C}-\text{H})_{\text{oop}}$  791. IR (polyethylene,  $\text{cm}^{-1}$ ):  $\nu(\text{Pd}-\text{N})$  496,  $\nu(\text{Pd}-\text{Cl})$  327,  $\nu(\text{Pd}-\text{S})$  303.  $^1\text{H}$  NMR (500 MHz, [D<sub>3</sub>]acetonitrile, 253 K):  $\delta$  = 2.24 (b, 2 H,

$\text{CH}_2-\text{CH}_2-\text{OH}$ ), 2.38 (s, 3 H, *Me*), 2.50 (s, 3 H, *Me*), 2.62 (b, 1 H, *pz-CH}\_2-\text{CHH}*), 3.22 (b, 1 H, *pz-CH}\_2-\text{CHH}*), 3.29 (t, 1 H, OH), 3.62 (m, 1 H,  $\text{CH}_2-\text{CHH}-\text{OH}$ ), 3.76 (m, 1 H,  $\text{CH}_2-\text{CHH}-\text{OH}$ ), 4.53 (m, 1 H, *pz-CHH}-\text{CH}\_2*), 4.72 (m, 1 H, *pz-CHH}-\text{CH}\_2*), 6.08 (s, 1 H, *pz-CH*) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (63 MHz, [D<sub>3</sub>]acetonitrile, 298 K):  $\delta$  = 12.0 (*Me*), 15.0 (*Me*), 34.6 (*pz-CH}\_2-\text{CH}\_2*), 43.5 ( $\text{CH}_2-\text{CH}_2-\text{OH}$ ), 49.5 (*pz-CH}\_2-\text{CH}\_2*), 60.2 ( $\text{CH}_2-\text{CH}_2-\text{OH}$ ), 108.8 (*pz-CH*), 144.2 (*pz-C*) ppm.  $^{195}\text{Pt}\{^1\text{H}\}$  NMR (53.8 MHz, [D<sub>3</sub>]acetonitrile, 298 K):  $\delta$  = –2868 ppm.

**Complex 4:** Yield: 0.083 (98%). Conductivity ( $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ ,  $9.85 \cdot 10^{-4}$  M in acetonitrile): 6.4. C<sub>10</sub>H<sub>18</sub>Cl<sub>2</sub>N<sub>2</sub>OPtS (480.31) C 24.98, H 3.75, N 5.83, S 6.69; found C 25.25, H 3.81, N 6.11, S 6.62. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{O}-\text{H})$  3477,  $\nu(\text{C}-\text{H})_{\text{ar}}$  3124,  $\nu(\text{C}-\text{H})_{\text{al}}$  2977–2924,  $\nu(\text{C}=\text{C})$ ,  $\nu(\text{C}=\text{N})$  1549,  $\delta(\text{CH}_3)_{\text{as}}$  1466,  $\delta(\text{CH}_3)_{\text{s}}$  1397,  $\delta(\text{C}-\text{H})_{\text{oop}}$  828. IR (polyethylene,  $\text{cm}^{-1}$ ):  $\nu(\text{Pd}-\text{N})$  493,  $\nu(\text{Pd}-\text{Cl})$  322,  $\nu(\text{Pd}-\text{S})$  305.  $^1\text{H}$  NMR (500 MHz, [D<sub>3</sub>]acetonitrile, 253 K):  $\delta$  = 1.86 (b, *S-CHH}-\text{CH}\_2-\text{CH}\_2*), 2.31 (b, *S-CHH}-\text{CH}\_2-\text{CH}\_2*), 1.93 (b,  $\text{CH}_2-\text{CH}_2-\text{CH}_2$ ), last three peaks could not be integrated because they were too close to the solvent signal; 2.39 (s, 3 H, *Me*), 2.51 (s, 3 H, *Me*), 2.56 (b, 1 H, *pz-CH}\_2-\text{CHH}*), 3.09 (b, 1 H, OH), 3.28 (b, 1 H, *pz-CH}\_2-\text{CHH}*), 3.51 (m,  $\text{CH}_2-\text{CH}_2-\text{OH}$ ), 3.55 (m,  $\text{CH}_2-\text{CH}_2-\text{OH}$ ), last two peaks integrate together 2 H, 4.50 (m, 1 H, *pz-CHH}-\text{CH}\_2*), 4.82 (m, 1 H, *pz-CHH}-\text{CH}\_2*), 6.12 (s, 1 H, *pz-CH*) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (63 MHz, [D<sub>3</sub>]acetonitrile, 298 K):  $\delta$  = 11.5 (*Me*), 14.4 (*Me*), 31.3 ( $\text{CH}_2-\text{CH}_2-\text{CH}_2$ ), 34.4 (*pz-CH}\_2-\text{CH}\_2*), 38.0 (*S-CH}\_2-\text{CH}\_2-\text{CH}\_2*), 49.0 (*pz-CH}\_2-\text{CH}\_2*), 59.6 ( $\text{CH}_2-\text{CH}_2-\text{OH}$ ), 108.3 (*pz-CH*), 143.6, 152.5 (*pz-C*) ppm.  $^{195}\text{Pt}\{^1\text{H}\}$  NMR (53.8 MHz, [D<sub>3</sub>]acetonitrile, 298 K):  $\delta$  = –2879 ppm.

**Synthesis of [NiCl<sub>2</sub>(L)] with L = thpd (5), L = thhd (6):** NiCl<sub>2</sub>·6H<sub>2</sub>O (0.546 mmol) in a mixture absolute ethanol (10 mL) and triethylorthoformate (2 mL) was added dropwise, under vigorous stirring, to a solution of thpd or thhd (0.546 mmol) in absolute ethanol (10 mL). The solution turned from initial green to yellow. After 12 h of stirring, the solvent was evaporated and the desired product obtained as a pale green solid.

**Complex 5:** Yield: 0.176 g (98%). Conductivity ( $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ ,  $1.02 \cdot 10^{-3}$  M in absolute ethanol): 18.7. C<sub>9</sub>H<sub>16</sub>Cl<sub>2</sub>N<sub>2</sub>NiOS (329.9) C 32.77, H 4.89, N 8.49, S 9.72; found C 32.68, H 5.06, N 8.20, S 9.43. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{O}-\text{H})$  3269,  $\nu(\text{C}-\text{H})_{\text{al}}$  2947,  $\nu(\text{C}=\text{C})$ ,  $\nu(\text{C}=\text{N})$  1555,  $\delta(\text{CH}_3)_{\text{as}}$  1469,  $\delta(\text{CH}_3)_{\text{s}}$  1401,  $\delta(\text{C}-\text{H})_{\text{oop}}$  724. IR (polyethylene,  $\text{cm}^{-1}$ ):  $\nu(\text{Ni}-\text{O})$  498,  $\nu(\text{Ni}-\text{N})$  450,  $\nu(\text{Ni}-\text{Cl})$  368,  $\nu(\text{Ni}-\text{S})$  328. UV/Vis (absolute ethanol,  $1.03 \cdot 10^{-3}$  M),  $\lambda(\epsilon)$ : 422 nm ( $55\text{ mol}^{-1}\text{cm}^{-1}\text{L}$ ).

**Complex 6:** Yield: 0.182 (97%). Conductivity ( $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ ,  $9.87 \cdot 10^{-4}$  M in absolute ethanol): 14.3. C<sub>10</sub>H<sub>18</sub>Cl<sub>2</sub>N<sub>2</sub>NiOS (343.9) C 34.89, H 5.23, N 8.14, S 9.33; found C 34.66, H 5.17, N 7.86, S 9.07. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{O}-\text{H})$  3250,  $\nu(\text{C}-\text{H})_{\text{al}}$  2922,  $\nu(\text{C}=\text{C})$ ,  $\nu(\text{C}=\text{N})$  1558,  $\delta(\text{CH}_3)_{\text{as}}$  1465,  $\delta(\text{CH}_3)_{\text{s}}$  1387,  $\delta(\text{C}-\text{H})_{\text{oop}}$  728. IR (polyethylene,  $\text{cm}^{-1}$ ):  $\nu(\text{Ni}-\text{O})$  520,  $\nu(\text{Ni}-\text{N})$  461,  $\nu(\text{Ni}-\text{Cl})$  387,  $\nu(\text{Ni}-\text{S})$  344. UV/Vis (absolute ethanol,  $9.76 \cdot 10^{-4}$  M),  $\lambda(\epsilon)$ : 414 nm ( $75\text{ mol}^{-1}\text{cm}^{-1}\text{L}$ ).

**Synthesis of [NiCl(H<sub>2</sub>O)<sub>2</sub>(thpd)]Cl ([7]Cl):** Complex 5 (0.056 g, 0.170 mmol) was dissolved in ethanol or methanol. After 12 h, the solvent was evaporated and complex [7]Cl precipitated as bright green crystals.

**Complex [7]Cl:** Yield: 0.060 g (97%). Conductivity ( $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ ,  $1.07 \cdot 10^{-3}$  M in absolute ethanol): 41.3. C<sub>9</sub>H<sub>20</sub>Cl<sub>2</sub>N<sub>2</sub>NiO<sub>3</sub>S (365.94) C 29.54, H 5.51, N 7.66, S 8.76; found C 29.60, H 5.46, N 7.72, S 8.56. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{O}-\text{H})_{\text{water}}$  3318,  $\nu(\text{O}-\text{H})_{\text{alcohol}}$  3238,

Table 4. Crystallographic data for 2–4

Compound	2	3	4
Empirical formula	C <sub>10</sub> H <sub>18</sub> Cl <sub>2</sub> N <sub>2</sub> OPdS	C <sub>9</sub> H <sub>16</sub> Cl <sub>2</sub> N <sub>2</sub> OPtS	C <sub>10</sub> H <sub>18</sub> Cl <sub>2</sub> N <sub>2</sub> OPtS
Molecular mass	391.62	466.29	480.31
Temperature, K	293(2)	293(2)	293(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	Cc	<i>P</i> 2 <sub>1</sub> / <i>n</i>
Unit cell dimensions			
<i>a</i> , Å	7.6360(10)	15.21(2)	7.6520(10)
<i>b</i> , Å	15.9160(10)	8.205(4)	15.9520(10)
<i>c</i> , Å	11.8370(10)	11.720(7)	11.8190(10)
β, deg	104.343(2)	111.59(8)	104.2740(10)
Volume, Å <sup>3</sup>	1393.8(2)	1360(2)	1398.1(2)
<i>Z</i>	4	4	4
<i>D</i> <sub>calcd.</sub> , Mg·m <sup>-3</sup>	1.866	2.277	2.282
μ, mm <sup>-1</sup>	18.50	10.85	10.55
<i>F</i> (000)	784	880	912
Crystal size (mm)	0.1 × 0.1 × 0.2	0.2 × 0.2 × 0.1	0.1 × 0.1 × 0.3
θ range, deg	3.15 to 31.51	2.87 to 30.03	2.19 to 31.58
Reflexions collected: total, independent, <i>R</i> <sub>int</sub>	3500, 1559, 0.0273	2015, 2015, 0.0153	8103, 3162, 0.0333
Data/restraints/parameters	1559/0/161	2015/2/145	3162/0/154
Weighting coef. <i>a</i> , <i>b</i> <sup>[a]</sup>	0.0522, 4.4364	0.0469, 0	0.0576, 0
Final <i>R</i> 1, <i>wR</i> 2	0.0359, 0.0954	0.0302, 0.0715	0.0281, 0.0787
<i>R</i> 1 (all data), <i>wR</i> 2	0.0388, 0.0982	0.0348, 0.0730	0.0369, 0.0815
Residual electron density, e <sup>-</sup> ·Å <sup>-3</sup>	+0.425, -0.451	+0.717, -0.743	+0.671, -0.622

[a] The function minimised was  $\sum w(|F_o|^2 - |F_c|^2)^2$ , where  $w = [\sigma^2(I) + (aP)^2 + bP]^{-1}$ , and  $P = (|F_o|^2 + 2|F_c|^2)/3$ .

Table 5. Crystallographic data for [7]Cl

Compound	[7]Cl
Empirical formula	C <sub>9</sub> H <sub>20</sub> Cl <sub>2</sub> N <sub>2</sub> NiO <sub>3</sub> S
Molecular mass	365.94
Temperature, K	293(2)
Crystal system	triclinic
Space group	<i>P</i> 1̄ ( <i>n</i> ° 2)
Unit cell dimensions	
<i>a</i> , Å	7.206(3)
<i>b</i> , Å	8.611(8)
<i>c</i> , Å	12.661(5)
α, deg	95.97(5)
β, deg	104.97(3)
γ, deg	93.60(5)
Volume, Å <sup>3</sup>	751.6(8)
<i>Z</i>	2
<i>D</i> <sub>calcd.</sub> , Mg·m <sup>-3</sup>	1.617
μ, mm <sup>-1</sup>	17.86
<i>F</i> (000)	380
Crystal size (mm)	0.1 × 0.1 × 0.2
θ range, deg	2.74 to 30.20
Reflexions collected: Total, independent, <i>R</i> <sub>int</sub>	4333, 4333, 0.0099
Data/restraints/parameters	4333/0/184
Weighting coef. <i>a</i> , <i>b</i> <sup>[a]</sup>	0.0198, 0
Final <i>R</i> 1, <i>wR</i> 2	0.0357, 0.0610
<i>R</i> 1 (all data), <i>wR</i> 2	0.1029, 0.0726
Residual electron density, e <sup>-</sup> ·Å <sup>-3</sup>	+0.421, -0.347

[a] The function minimised was  $\sum w(|F_o|^2 - |F_c|^2)^2$ , where  $w = [\sigma^2(I) + (aP)^2 + bP]^{-1}$ , and  $P = (|F_o|^2 + 2|F_c|^2)/3$ .

$\nu(\text{C-H})_{\text{al}}$  2957–2928,  $\nu(\text{C=C})$ ,  $\nu(\text{C=N})$  1558,  $\delta(\text{CH}_3)_{\text{as}}$  1467,  $\delta(\text{CH}_3)_{\text{s}}$  1386,  $\delta(\text{C-H})_{\text{oop}}$  728. IR (polyethylene, cm<sup>-1</sup>):  $\nu(\text{Ni-O})$  499,  $\nu(\text{Ni-N})$  454,  $\nu(\text{Ni-Cl})$  368,  $\nu(\text{Ni-S})$  322. UV/Vis (absolute ethanol, 1.02·10<sup>-3</sup> M),  $\lambda(\epsilon)$ : 731 nm (4 mol<sup>-1</sup>cm<sup>-1</sup>L), 403 nm (10 mol<sup>-1</sup>cm<sup>-1</sup>L).

**X-ray Crystallographic Study:** Suitable crystals for X-ray diffraction experiments of compounds 2–4 and [7]Cl were obtained by crystallisation from methanol. Data for 2 and 4 were collected on a MAR345 diffractometer with an Image Plate detector, using the *s*-scan technique. Data for 3 and [7]Cl were collected on an Enraf–Nonius CAD4 four-circle diffractometer, using the omega/2θ scan technique. All crystal data were collected using graphite-monochromated Mo-*K*<sub>α</sub> radiation. The structures were solved by direct methods using the SHELXS-97 computer program<sup>[31]</sup> and refined by full-matrix least-squares method with a SHELXL-97.<sup>[32]</sup>

Five H atoms in structure [7]Cl were located from a difference synthesis and refined with an overall isotropic temperature factor. Thirteen Hs for [7]Cl and all hydrogen atoms for structures 2–4 were computed and refined using a riding model. The final *R* (on *F*) factor and ω*R* (on *F*<sup>2</sup>) values, as well as the numbers of parameters refined and other details concerning the refinement of the crystal structure, are presented in Tables 4 and 5.

CCDC-199097 (2), -199096 (3), -199095 (4), and -199098 ([7]Cl) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

## Acknowledgments

Support by the Spanish Ministerio de Educación y Cultura (Project BQU2000-0238 and a grant to J. G.) is gratefully acknowledged.

[1] C. S. Slone, D. A. Weinberger, C. A. Mirkin, *Prog. Inorg. Chem.* **1999**, 48, 233.

[2] A. Bader, E. Lindner, *Coord. Chem. Rev.* **1991**, 108, 27.

[3] J. C. Jeffrey, T. B. Rauchfuss, *Inorg. Chem.* **1979**, 18, 2658.

[4] [4a] E. Bouwman, W. L. Driessen, J. Reedijk, *Coord. Chem. Rev.* **1990**, 104, 143. [4b] P. Braunstein, F. Naud, *Angew. Chem. Int. Ed.* **2001**, 40, 680.

- [5] [5a] R. Mathieu, G. Esquiús, N. Lugan, J. Pons, J. Ros, *Eur. J. Inorg. Chem.* **2001**, 2683. [5b] G. Esquiús, J. Pons, R. Yáñez, J. Ros, *J. Organomet. Chem.* **2001**, 619, 14. [5c] G. Esquiús, J. Pons, R. Yáñez, J. Ros, X. Solans, M. Font-Bardía, *J. Organomet. Chem.* **2000**, 605, 226. [5d] G. Esquiús, J. Pons, R. Yáñez, J. Ros, X. Solans, M. Font-Bardía, *Acta Crystallogr., Sect. C* **2002**, 58, 133. [5e] G. Esquiús, J. Pons, R. Yáñez, J. Ros, R. Mathieu, B. Donnadieu, N. Lugan, *Eur. J. Inorg. Chem.* **2002**, 2999.
- [6] [6a] R. Tribó, J. Pons, R. Yáñez, J. F. Piniella, A. Álvarez-Larena, J. Ros, *Inorg. Chem. Commun.* **2000**, 3, 545. [6b] G. Esquiús, J. Pons, R. Yáñez, J. Ros, R. Mathieu, B. Donnadieu, N. Lugan, *J. Organomet. Chem.* **2003**, 667, 126. [6c] R. Tribó, J. Ros, J. Pons, R. Yáñez, A. Álvarez-Larena, J. F. Piniella, *J. Organomet. Chem.* in press.
- [7] [7a] A. Boixassa, J. Pons, A. Virgili, X. Solans, M. Font-Bardía, J. Ros, *Inorg. Chim. Acta* **2002**, 340, 49. [7b] A. Boixassa, J. Pons, X. Solans, M. Font-Bardía, J. Ros, *Inorg. Chim. Acta* **2003**, 346, 151. [7c] A. Boixassa, J. Pons, J. Ros, R. Mathieu, N. Lugan, manuscript submitted to *J. Organomet. Chem.*
- [8] [8a] J. García-Antón, J. Pons, X. Solans, M. Font-Bardía, J. Ros, *Eur. J. Inorg. Chem.* **2002**, 3319. [8b] J. García-Antón, J. Pons, X. Solans, M. Font-Bardía, J. Ros, *Inorg. Chim. Acta* accepted.
- [9] W. G. Haanstra, W. L. Driessen, J. Reedijk, U. Turpeinen, R. Hämäläinen, *J. Chem. Soc., Dalton Trans.* **1989**, 2309.
- [10] E. Bouwman, P. Evans, R. A. G. de Graaf, H. Kooijman, R. Poinsot, P. Rabu, J. Reedijk, A. L. Spek, *Inorg. Chem.* **1995**, 34, 6302.
- [11] S. Komiyama, *Synthesis of Organometallic Compounds: A Practical Guide*, John Wiley & Sons, New York, USA, **1997**.
- [12] F. A. Cotton, *Inorganic Synthesis* **1972**, 13, 52.
- [13] [13a] W. J. Geary, *Coord. Chem. Rev.* **1971**, 7, 81. [13b] L. K. Thompson, F. L. Lee, E. J. Gabe, *Inorg. Chem.* **1988**, 27, 39.
- [14] [14a] E. Pretsch, T. Clerc, J. Seibl, W. Simon, *Tables of Determination of Organic Compounds. <sup>13</sup>C NMR, <sup>1</sup>H NMR, IR, MS, UV/Vis, Chemical Laboratory Practice*. Springer-Verlag, Berlin, Germany, **1989**. [14b] D. H. Williams, I. Fleming, *Spectroscopic Methods in Organic Chemistry*. McGraw-Hill, London, UK, **1995**.
- [15] H. Friebolin *Basic One- and Two-Dimensional NMR Spectroscopy* Wiley-VCH Verlag GmbH, Weinheim, Germany, **1998**.
- [16] E. W. Abel, S. K. Bhargava, K. Orrell, *Prog. Inorg. Chem.* **1994**, 32, 1.
- [17] N. Durán, P. González-Duarte, A. Lledós, T. Parella, J. Sola, G. Ujaque, W. Clegg, K. A. Fraser, *Inorg. Chim. Acta* **1997**, 265, 89.
- [18] J. Llop, C. Masalles, C. Viñas, F. Teixidor, R. Sillanpää, R. Kivekäs, *Dalton Trans.* **2003**, 556.
- [19] [19a] R. J. H. Clark, G. Natile, U. Belluco, L. Cattalini, C. Filipin, *J. Chem. Soc., (A)* **1970**, 659. [19b] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. John Wiley and Sons, New York, USA, **1986**.
- [20] [20a] D. Sutton, *Electronic Spectra of Transition Metal Complexes*. McGraw Hill, London, UK, **1975**. [20b] J. C. Bailar, H. J. Emeleus, S. R. Nyttorm, A. F. T. Dickenson, *Comprehensive Inorganic Chemistry*, Pergamon Press, London, UK, **1973**. [20c] F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry* 5th ed., John Wiley and Sons, New York, USA, **1975**. [20d] N. F. Curtis, Y. M. Curtis, *Inorg. Chem.* **1965**, 4, 804.
- [21] D. B. Grotjahn, D. Combs, S. Van, G. Aguirre, F. Ortega, *Inorg. Chem.* **2000**, 39, 2080.
- [22] [22a] A. C. Aiub, N. R. Basso, O. L. Casagrande Jr., J. Dupont, M. Horner, A. J. Bortoluzzi, C. Maichle-Mossmeyer, *J. Coord. Chem.* **1996**, 40, 35. [22b] N. K. Skvortsov, N. F. Chernov, O. M. Trofimova, V. K. Belskii, V. M. Svetlichnaya, M. G. Voronkov, *Zh. Obshch. Khim.* **1994**, 64, 54.
- [23] [23a] R. G. Raptis, J. F. Fackler Jr., *Acta Crystallogr., Sect. C (Cr. Str. Commun.)* **1991**, 47, 1180. [23b] G. B. Onca, V. Moreno, M. Font-Bardía, X. Solans, J. M. Pérez, C. Alonso, *J. Inorg. Biochem.* **1999**, 75, 205. [23c] J. A. Broomhead, L. M. Rendina, M. Sterns, *Inorg. Chem.* **1992**, 31, 1880. [23d] M. A. Cirellu, S. Stoccoro, G. Minghetti, A. L. Bandini, G. Banditelli, B. Bovio, *J. Organomet. Chem.* **1989**, 372, 311. [23e] K. Sakai, Y. Tomita, K. Goshima, M. Ohminato, T. Tsuboruma, K. Matsumoto, K. Ohmura, K. Kawakami, *Inorg. Chim. Acta* **2000**, 297, 64.
- [24] F. H. Allen, O. Kennard, *Chem. Des. Autom. News* **1993**, 8, 31.
- [25] S. V. Kolotilov, E. A. Goreschnik, V. V. Pavlishuk, K. B. Yatsimirkii, *Zh. Neorg. Khim.* **2000**, 45, 967.
- [26] W. L. Drax, C. M. Weeks, D. C. Roher, *Topics in Stereochemistry* (Eds.: E. L. Eliel and N. L. Allinger), John Wiley and Sons, New York, **1976**.
- [27] [27a] M. Konrad, F. Meyer, A. Jacobi, P. Kircher, P. Rutsch, L. Zlonai, *Inorg. Chem.* **1999**, 38, 4559. [27b] F. Paap, E. Bouwman, W. L. Driessen, R. A. G. de Graaf, J. Reedijk, *J. Chem. Soc., Dalton Trans.* **1985**, 737. [27c] Y. Sun, P. Cheng, S. Yan, Z. Jiang, D. Liao, P. Shen, *Inorg. Chem.* **2000**, 3, 289. [27d] L. Siegfried, T. A. Kaden, F. Meyer, P. Kircher, H. Pritzkow, *J. Chem. Soc., Dalton Trans.* **2001**, 2310. [27e] J. Casabó, J. Pons, K. S. Siddiqi, F. Teixidor, E. Molins, C. Miravittles, *J. Chem. Soc., Dalton Trans.* **1989**, 1401. [27f] B. S. Hammes, C. J. Carrano, *Inorg. Chem.* **1999**, 38, 3562. [27g] T. C. Higgs, C. J. Carrano, *Inorg. Chem.* **1997**, 36, 298. [27h] M. Mikuriya, K. Nakadera, T. Kotera, *Bull. Chem. Soc., Jpn.* **1996**, 69, 399. [27i] B. Hommerich, H. Schwoppe, D. Volkmer, B. Krebs, *Z. Anorg. Allg. Chem.* **1999**, 625, 75. [27j] S. Sheu, M. Tien, M. Cheng, T. Ho, S. Peng, Y. Lin, *J. Chem. Soc., Dalton Trans.* **1995**, 3503.
- [28] [28a] L. Rosenberg, L. K. Thompson, E. J. Gabe, F. L. Lee, *J. Chem. Soc., Dalton Trans.* **1986**, 625. [28b] N. Saha, A. Saha, S. Chaudhuri, T. C. W. Mak, T. Banerjee, P. Roychoudhury, *Polyhedron* **1992**, 11, 2341. [28c] M. Malecka, A. Rybarczyk-Pirek, T. A. Olszak, K. Malinowska, J. Ochocky, *Acta Crystallogr., Sect. C (Cr. Str. Commun.)* **2001**, 57, 513. [28d] J. Pons, A. Chadghan, J. Casabó, A. Álvarez-Larena, J. F. Piniella, X. Solans, M. Font-Bardía, J. Ros, *Polyhedron* **2001**, 20, 1029. [28e] A. Podder, B. P. Mukhopadhyay, N. Saha, A. Saha, B. Stensland, *J. Crystallogr. Spectrosc. Res.* **1989**, 19, 71. [28f] L. Pan, N. Ching, X. Huang, J. Li, *Chemistry-A European Journal* **2001**, 7, 4431. [28g] M. A. Masood, D. J. Hodgson, *Inorg. Chem.* **1994**, 33, 3038.
- [29] [29a] F. Paap, W. L. Driessen, J. Reedijk, A. L. Spek, *Inorg. Chimica. Acta* **1988**, 150, 57. [29b] E. Bouwman, P. Evans, H. Kooijman, J. Reedijk, A. L. Spek, *J. Chem. Soc., Chem. Commun.* **1993**, 1746. [29c] S. Chiou, P. Ge, C. G. Riordan, L. M. Liabile-Sands, A. L. Rheingold, *Chem. Commun.* **1999**, 159. [29d] M. Konrad, F. Meyer, K. Heinze, L. Zsolnai, *J. Chem. Soc., Dalton Trans.* **1998**, 199.
- [30] [30a] I. A. Krol, V. M. Agre, V. K. Trunov, O. I. Ivanov, *Koord. Khim.* **1979**, 5, 1569. [30b] S. Buchler, F. Meyer, A. Jacobi, P. Kircher, L. Zsolnai, *Z. Naturforsch., Teil B* **1999**, 54, 1295. [30c] C. W. Reinmann, A. D. Mighell, F. A. Mauer, *Acta Crystallogr.* **1967**, 23, 135. [30d] R. B. Helmholtz, W. Hinrichs, J. Reedijk, *Acta Crystallogr., Sect. C (Cr. Str. Commun.)* **1987**, 43, 226. [30e] F. Meyer, U. Ruschewitz, P. Schober, B. Antelmann, L. Zsolnai, *J. Chem. Soc., Dalton Trans.* **1998**, 1181.
- [31] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, 46, 467.
- [32] G. M. Sheldrick, *SHELXS-97, SHELXL-97, CIFTAB-Program for Crystal Structure Analysis (Release 97-2)*, Institut für Anorganische Chemie der Universität, Tammanstraße 4, 3400 Göttingen, Germany, **1998**.

Received January 16, 2003







ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Inorganica Chimica Acta xxx (2003) 1–8

Inorganica  
Chimica Acta

www.elsevier.com/locate/ica

## Synthesis, X-ray crystal structure, and NMR characterisation of thiolate-bridged dinuclear Ni(II), Pd(II) and Pt(II) complexes of didentate ligands with NS-donor set

Jordi García-Antón<sup>a</sup>, Josefina Pons<sup>a,\*</sup>, Xavier Solans<sup>b</sup>, Mercè Font-Bardia<sup>b</sup>,  
Josep Ros<sup>a,\*</sup>

<sup>a</sup> Departament de Química, Facultat de Ciències, Universitat Autònoma de Barcelona, 08193-Bellaterra-Cerdanyola, Barcelona, Spain

<sup>b</sup> Cristal·lografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona, Martí i Franquès s/n, 08028 Barcelona, Spain

Received 29 January 2003; accepted 16 April 2003

### Abstract

Thiolate-bridged dinuclear nickel(II), palladium(II) and platinum(II) complexes with *N*-(2-mercaptoethyl)-3,5-dimethylpyrazole (Hmed), [MCl(med)]<sub>2</sub> (M = Ni (**1**), Pd (**2**), Pt (**3**)), have been synthesised and characterised by elemental analyses, conductivity, IR, electronic spectra and NMR spectroscopies. The crystal structure of **2** was determined by a single-crystal X-ray diffraction method. The structure consists of thiolate-bridged dinuclear units. Each Pd(II) atom is coordinated by a pyrazolic nitrogen, one chlorine and two bridging sulfur atoms. When the synthesis of complex **1** was carried out in acetonitrile and in the presence of oxygen, [NiCl<sub>3</sub>(Hdeds)] (**4**) was formed (deds = 1,1'-(dithiodiethylene)bis(3,5-dimethylpyrazole)). The crystal structure of this complex was also determined by single-crystal X-ray diffraction method. The structure consists of nickel(II) ions coordinated by three chloride ions and one pyrazolic nitrogen atom. Ligand deds is the result of the oxidation of *N*-(2-mercaptoethyl)-3,5-dimethylpyrazole (Hmed).

© 2003 Elsevier Science B.V. All rights reserved.

**Keywords:** Nickel; Palladium; Platinum; Dinuclear; N,S ligands

### 1. Introduction

The known tendency of thiolate ligands to give highly insoluble neutral complexes of polymeric nature has led to new synthetic strategies [1] and thus has enabled the obtaining of structural information on metal-thiolate complexes [2].

Discrete first-row transition-metal complexes featuring central M(μ<sub>2</sub>-SR)<sub>x</sub>M cores (x = 1–3) have come under increased investigation in the past several years [3]. There are several M(μ<sub>2</sub>-SR)<sub>x</sub>M type complexes [4], most of which have been studied in attempts to mimic

the bonding, spectral and redox properties of bioinorganic compounds [1a,5,6,7].

The Ni(μ<sub>2</sub>-SR)<sub>x</sub>Ni has attracted much attention to model the active site of the nickel-enzymes [8], in particular for the hydrogenases, metalloenzymes which catalyse H<sub>2</sub> = 2H<sup>+</sup> + 2e<sup>-</sup>. Only recently, however, it has been established that the active site contained a dimetallic substructure [9].

Pt(μ<sub>2</sub>-SR)<sub>x</sub>Pt complexes have been ascribed as anti-tumor drugs [10]. However, their inactivation is thought probably to be due to the bonding of platinum atoms to sulfur-containing biomolecules [11].

In recent years, we have studied and reported the synthesis and characterisation of ligands *N*-alkylaminopyrazole [12], *N*-hydroxyalkylpyrazole [13], *N*-phosphinopyrazole [14] and more recently ligands containing pyrazolyl and thioether groups [15].

\* Corresponding authors. Tel.: +34-93-581 2895; fax: +34-93-581 3101.

E-mail address: josefina.pons@uab.es (J. Pons).

In the present paper, we describe the examination of dinuclear Ni(II), Pd(II) and Pt(II) complexes of the ligand with NS-donor set *N*-(2-mercaptoethyl)-3,5-dimethylpyrazole (Hmed). The reactivity of dinuclear Ni(II) complex in acetonitrile with the HCl formed in the reaction mixture in the presence of oxygen, leads to a new mononuclear Ni(II) complex with a NiCl<sub>3</sub>N core. Thiolate ligands med<sup>-</sup> are oxidised to disulfide 1,1'-(dithiodiethylene(bis(3,5-dimethylpyrazole)) (deds) in this reaction (Fig. 1).

NMR studies of complexes 1–3 and the X-ray crystal structures of 2 and 4 are also presented.

## 2. Results and discussion

### 2.1. Synthesis and spectroscopic properties of the complexes

The *N*-(2-mercaptoethyl)-3,5-dimethylpyrazole (Hmed) (Fig. 2) was synthesised according to a procedure previously described by Bouwman et al. [16]. Complexes [M(med)Cl]<sub>2</sub> (M = Ni(II) (1), Pd(II) (2) and Pt(II) (3)) were obtained by reaction of the ligand Hmed with NiCl<sub>2</sub>·6H<sub>2</sub>O, [PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>] [17] or [PtCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>] [18], respectively. Reaction of Hmed with NiCl<sub>2</sub>·6H<sub>2</sub>O always gave a secondary product (4) in very small quantities. This compound (4) was formulated as [NiCl<sub>3</sub>(Hdeds)] being deds 1,1'-(dithiodiethylene)bis(3,5-dimethylpyrazole), the product of oxidation of med<sup>-</sup>. Complex [NiCl<sub>3</sub>(Hdeds)] (4) was obtained directly by treatment of NiCl<sub>2</sub>·6H<sub>2</sub>O with Hmed in acetonitrile, in the presence of oxygen.

Elemental analyses of products 1–4 are consistent with the proposed molecular formula. Conductivity values in acetonitrile for all complexes are in agreement with a non-electrolyte nature of complexes. The reported values for 10<sup>-3</sup> M solutions of non-electrolyte complexes in acetonitrile are lower than 120 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> [19].

The main difference among IR spectra of complexes 1–3 and the IR spectrum of the free ligand is the absence of the ν(S–H) band found at 2543 cm<sup>-1</sup>. This happens because ligand Hmed acts as a thiolate when complexed. Complexes 1–3 present one band between 1550–1554

cm<sup>-1</sup> which is characteristic of ν(C=C) and ν(C=N) absorption bands of pyrazole rings. However, complex 4 shows two absorption bands in this region (1592 and 1554 cm<sup>-1</sup>), which were assigned to the protonated and complexed pyrazolyl groups, respectively [20].

The IR spectra of complexes in the region 500–100 cm<sup>-1</sup> were also studied [21]. Complexes 1–3 show three well-defined bands corresponding to ν(M–S) at 366–315 cm<sup>-1</sup>, ν(M–Cl) at 388–333 cm<sup>-1</sup> and ν(M–N) at 513–450 cm<sup>-1</sup>. For complex 4 only two bands were assigned for ν(Ni–Cl) at 375 cm<sup>-1</sup> and ν(Ni–N) at 484 cm<sup>-1</sup>.

Electronic spectra of the complexes 1 and 4 were measured in acetonitrile. Complex 1 shows two intense ligand-to-metal charge transfer bands at 524 nm (ε = 411 mol<sup>-1</sup> cm<sup>-1</sup>) and 416 nm (ε = 1010 l mol<sup>-1</sup> cm<sup>-1</sup>) [22]. Electronic spectrum of complex 4 exhibits one d–d band at 616 nm (ε = 215 l mol<sup>-1</sup> cm<sup>-1</sup>), which can be attributed to the <sup>3</sup>T<sub>1</sub>(F) → <sup>3</sup>T<sub>1</sub>(P) transition, characteristic for tetrahedral Ni(II) complexes. Absorption bands at 447 and 362 nm for 2 and 384 nm for 3 can be assigned to d–d and charge transfer transitions [23].

### 2.2. NMR experiments

<sup>1</sup>H and <sup>13</sup>C NMR spectra of compounds 1, 2 and 3 were recorded in CDCl<sub>3</sub> and show the signals of the coordinated ligands. NMR data are reported in the experimental section. From the structure of complexes 1, 2 and 3 it can be seen that the two protons of each CH<sub>2</sub> in the S–CH<sub>2</sub>–CH<sub>2</sub>–N chain are diastereotopic, thus leading to four groups of signals, which can be associated to a single hydrogen each. This happens because of the rigid conformation of the ligand when it is complexed. In this way, each group of signals can be assigned as doublets of doublets of doublets (Fig. 2).

HMQC spectra (Fig. 3) were used to assign protons H<sub>1R</sub> and H<sub>1S</sub> to the two doublets of doublets of doublets of lower δ and H<sub>2R</sub> and H<sub>2S</sub> to those of higher δ.

NOESY spectra (Fig. 4) allowed us to differentiate H<sub>2R</sub> from H<sub>2S</sub> and CH<sub>3</sub>(4) from CH<sub>3</sub>(7): the singlet that appears at 2.56 ppm shows NOE interaction only with H<sub>5</sub> and was assigned to CH<sub>3</sub>(4). The singlet at 2.29 ppm, besides having NOE interaction with H<sub>5</sub>, shows strong NOE interaction with the doublets of doublets of

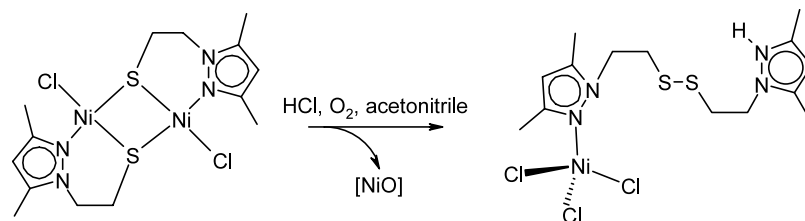


Fig. 1. Synthesis of [NiCl<sub>3</sub>(Hdeds)] (4).

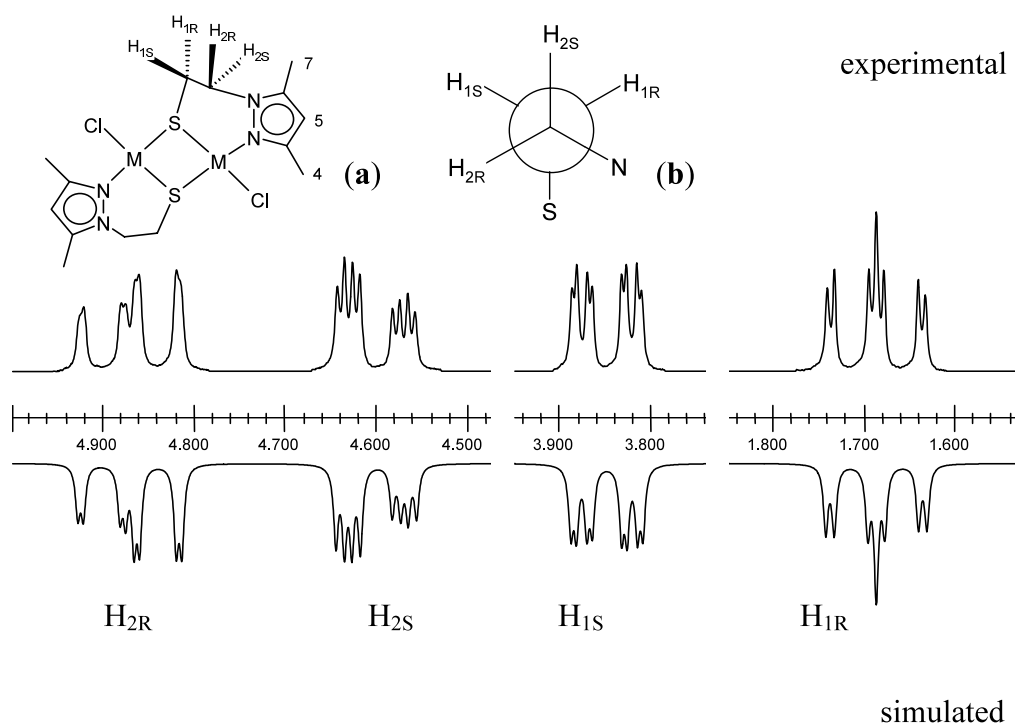


Fig. 2. The 400 MHz  $^1\text{H}$  NMR and gNMR simulated spectra for  $\text{NCH}_2\text{CH}_2\text{S}$  fragment of  $[\text{PdCl}(\text{med})]_2$  (**2**), including (a) the numbering and (b) the dihedral angles for the  $\text{NCH}_2\text{CH}_2\text{S}$  fragment of  $[\text{MCl}(\text{med})]_2$  ( $\text{M} = \text{Ni}$  (**1**),  $\text{Pd}$  (**2**) or  $\text{Pt}$  (**3**)).

doublets at 4.60 ppm and weak NOE interaction with the doublets of doublets at 4.87 ppm and was assigned to  $\text{CH}_3(7)$ . From the X-ray structure of **2**, it can be seen that the nearest proton to  $\text{CH}_3(7)$  is  $\text{H}_{2\text{S}}$  and therefore should have a stronger NOE interaction. This information leads us to assign it to the doublets of doublets at 4.60 ppm and  $\text{H}_{2\text{R}}$  to the signal at 4.87 ppm.

Coupling constants (obtained from the gNMR generated  $^1\text{H}$  NMR simulated spectra, Fig. 2) helped us to differentiate  $\text{H}_{1\text{R}}$  and  $\text{H}_{1\text{S}}$ . These coupling constants agree with the conformation of the  $\text{S}-\text{CH}_2-\text{CH}_2-\text{N}$  chain as seen in Fig. 2, which has been corroborated by a X-ray crystal study.

Geminal  $^2J$  and  $\approx 180^\circ$   $^3J$  coupling constants have significantly higher values than  $\approx 30^\circ$  and  $\approx 60^\circ$   $^3J$

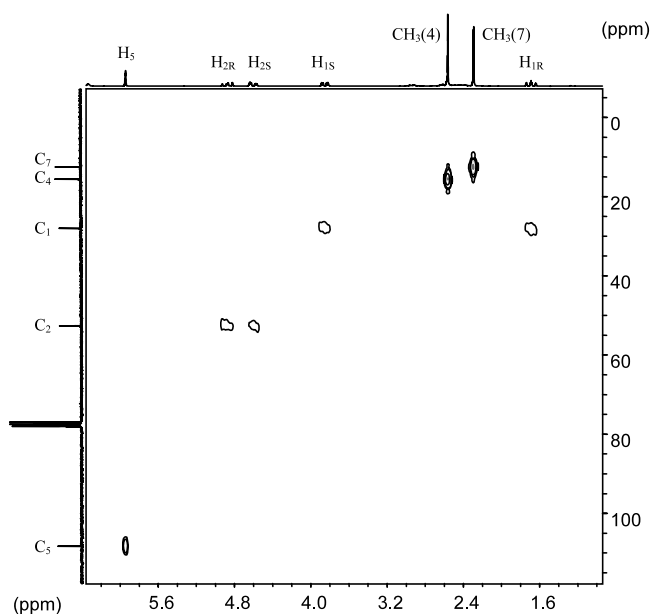


Fig. 3. The 250 MHz 2D HMQC spectrum of  $[\text{PdCl}(\text{med})]_2$  (**2**).

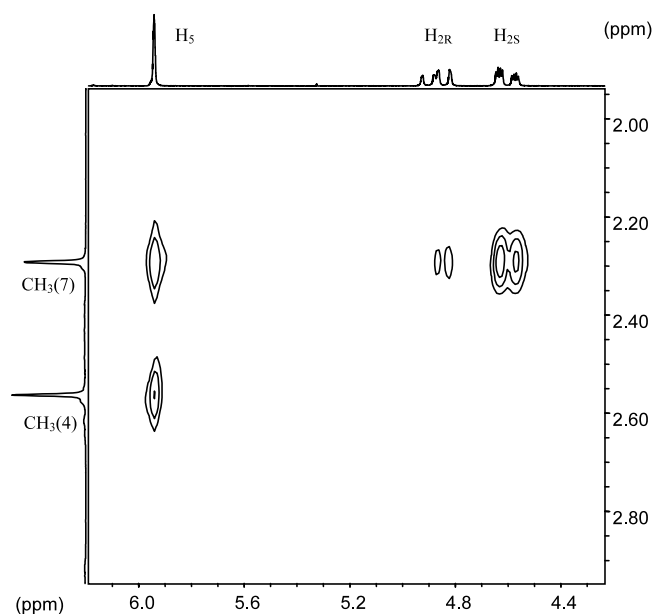


Fig. 4. The 250 MHz 2D NOESY spectrum of  $[\text{PdCl}(\text{med})]_2$  (**2**).

Table 1  
 $^1\text{H}$  NMR results: chemical shifts (ppm) and  $^1\text{H}$ – $^1\text{H}$  coupling constants (Hz)

Compound	1 (CDCl <sub>3</sub> )	2 (CDCl <sub>3</sub> )	3 (CDCl <sub>3</sub> )
$\delta$ H (2S)	4.49	4.60	4.27
$\delta$ H (2R)	5.60	4.87	5.00
$\delta$ H (1R)	0.75	1.69	1.67
$\delta$ H (1S)	2.63	3.85	3.97
$^2J$ (2R,2S)	–14.8	–15.4	–14.9
$^2J$ (1R,1S)	–13.2	–13.9	–13.7
$^3J$ (1R,2S)	2.2	2.2	2.1
$^3J$ (1S,2S)	3.7	4.4	4.0
$^3J$ (1R,2R)	11.7	11.7	11.6
$^3J$ (1S,2R)	1.5	1.5	1.8
$^3J$ (Pt,1R)	–	–	45.0
$^3J$ (Pt,1S)	–	–	49.8

coupling constants [24] (Fig. 2). Thus,  $\text{H}_{1\text{R}}$  should correspond to the doublets of doublets of doublets at 1.69 ppm and  $\text{H}_{1\text{S}}$  to the one at 3.85 ppm (Table 1).

### 2.3. Crystal and molecular structure of $[\text{Pd}(\text{med})\text{Cl}]_2$ (2)

The structure of **2** (Fig. 5) consists of dimeric  $[\text{Pd}(\text{med})\text{Cl}]_2$  units linked by van der Waals forces. Each palladium atom is coordinated by two thiolate-bridging sulfurs (in *anti* conformation), one pyrazole nitrogen and one chloride ion in a distorted square-planar geometry. Table 2 lists some selected bond distances and bond angles for this complex.

The largest deviations to the mean planes that contain the four donor atoms and the Pd atom are 0.052(1) Å in S(2) and –0.048(3) Å in N(3) for Pd(2) and 0.062(3) Å in N(2) and –0.068(1) in S(1) for Pd(1).

The two planar  $\text{PdClNS}_2$  units are joined via two bridging thiolate ligands forming a four-membered ring, which is CR-form with Pd··Pd and S··S distances 3.1174(4) and 2.910(1) Å, respectively. The dihedral angles between the planes Pd(1)–S(1)–Pd(2) and Pd(1)–S(2)–Pd(2) is 54.84(4)°. This dihedral angle is larger

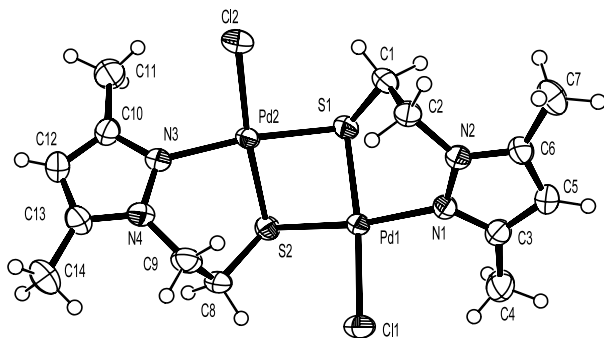


Fig. 5. ORTEP drawing of  $[\text{PdCl}(\text{med})]_2$  (**2**) (293 K determination) showing the atom numbering scheme. Fifty percent probability amplitude displacement ellipsoids are shown.

Table 2  
 Selected bond lengths (Å) and angles (°) for **2** and **4** with estimated standard deviations (e.s.d.s.) in parentheses

	<b>2</b>		<b>4</b>	
<i>Bond lengths</i>				
Pd(1)–N(1)	2.057(3)	Ni–N(1)	2.011(3)	
Pd(1)–S(1)	2.2804(10)	Ni–Cl(1)	2.2916(11)	
Pd(1)–S(2)	2.2807(9)	Ni–Cl(2)	2.2492(12)	
Pd(1)–Cl(1)	2.3379(10)	Ni–Cl(3)	2.2386(12)	
Pd(1)–Pd(2)	3.1175(4)			
Pd(2)–N(3)	2.056(3)			
Pd(2)–S(2)	2.2746(10)			
Pd(2)–S(1)	2.2864(10)			
Pd(2)–Cl(2)	2.3409(12)			
<i>Bond angles</i>				
N(1)–Pd(1)–S(1)	91.51(10)	N(1)–Ni–Cl(1)	104.79(9)	
N(1)–Pd(1)–S(2)	170.42(10)	N(1)–Ni–Cl(2)	105.13(9)	
S(1)–Pd(1)–S(2)	79.29(4)	N(1)–Ni–Cl(3)	119.41(9)	
N(1)–Pd(1)–Cl(1)	93.49(10)	Cl(1)–Ni–Cl(2)	105.29(5)	
S(1)–Pd(1)–Cl(1)	173.65(4)	Cl(1)–Ni–Cl(3)	105.21(5)	
S(2)–Pd(1)–Cl(1)	95.87(4)	Cl(2)–Ni–Cl(3)	115.67(5)	
N(3)–Pd(2)–S(2)	92.06(9)			
N(3)–Pd(2)–S(1)	171.24(9)			
S(2)–Pd(2)–S(1)	79.29(4)			
N(3)–Pd(2)–Cl(2)	93.20(9)			
S(2)–Pd(2)–Cl(2)	173.54(4)			
S(1)–Pd(2)–Cl(2)	95.52(4)			

than those found in the literature for dimeric complexes with  $\text{PdClNS}_2$  core [6c–6d].

Pd–N distances are smaller and Pd–Cl and Pd–S distances are similar to the ones found for related complexes [6]. However, Pd–N bond distances are of the same order as the ones found in the literature for complexes containing Pd–Npz (pz = pyrazole) [13,15].

The pyrazole–thiolate ligand acts as a bidentate chelate (as well as bridging ligand), forming two Pd–S–C–C–N–N rings. These two six-membered rings have boat conformation. Bite angles S(1)–Pd(1)–N(1) and N(3)–Pd(2)–S(2) are 91.5(1)° and 92.1(1)°, respectively.

The distortion of the boat in six-membered rings are  $\Delta C_S(\text{Pd1}) = 10.1(3)^\circ$ ,  $\Delta C_2(\text{S1}–\text{C1}) = 42.4(4)^\circ$  and  $\Delta C_S(\text{Pd2}) = 13.1(3)^\circ$ ,  $\Delta C_2(\text{S2}–\text{C8}) = 40.5(4)^\circ$  for Pd1–S1–C1–C2–N2–N1 and Pd2–S2–C8–C9–N4–N3, respectively.

### 2.4. Crystal and molecular structure of $[\text{NiCl}_3(\text{Hded})]$ (4)

The structure of **4** consists of discrete  $[\text{NiCl}_3(\text{Hded})]$  units, linked by hydrogen bonds (Fig. 6). Nickel atom is coordinated by three terminal chloride ions and one pyrazole nitrogen in a slightly distorted tetrahedral geometry.

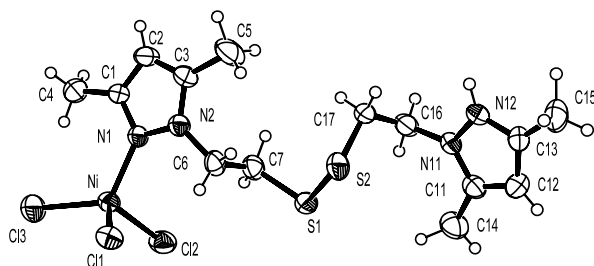


Fig. 6. ORTEP drawing of  $[\text{NiCl}_3(\text{Hdeds})]$  (**4**) (293 K determination) showing the atom numbering scheme. Fifty percent probability amplitude displacement ellipsoids are shown.

Ni–N and Ni–Cl distances are similar to those found in the literature for Ni(II) complexes containing pyrazolyl groups and at least one coordinated Cl atom [25].

The azine nitrogen in the uncoordinated pyrazole (N12) is protonated. The positive charge is cancelled out by the negative charge that is provided by the third chloride ion linked to Ni(II), forming a zwitterionic structure. Pyrazole N(12) atom is intermolecularly hydrogen bridged to Cl(1) atom from another molecule, thereby linking the molecules into a chain (the N(12)–H bond length is 0.86(4) Å and the contact parameters between N(12)–H and Cl(1) are: H···Cl(1), 2.30(4) Å; N(12)···Cl(1), 3.158(4) Å; symmetry code (i):  $x, y, 1+z$ ).

No other complex with  $\text{NiCl}_3\text{N}$  core (terminal Cl) has been fully described in the literature. Only one complex with this core (but with one bridged chloride ion) was found, but due to the poor quality of the crystal it could not be further described in the corresponding paper [26].

The most similar complex to the one presented here is a copper complex with  $\text{CuCl}_3\text{N}$  core (pyrazole nitrogen and terminal chloride):  $[\text{Cu}(\text{daeH})\text{Cl}_3]$  where  $\text{daeH} = N$ -(2-(3,5-dimethyl-1-pyrazolyl)ethyl)hydro-ethylammonium [27].

### 3. Experimental

#### 3.1. General methods

Preparations were performed using usual *vacuum* line and Schlenk techniques. All reagents were commercial grade materials and were used without further purification. Acetonitrile and dichloromethane were dried and distilled by standard methods and previously deoxygenated in the *vacuum* line.

*N*-(2-mercaptoethyl)-3,5-dimethylpyrazole was prepared according to the published methods [16].

Samples of  $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$  [17] and  $[\text{PtCl}_2(\text{CH}_3\text{CN})_2]$  [18] were prepared as described in the literature.

Analyses (C, N, H, S) were performed in our analytical laboratory on a Carlo Erba CHNS EA-1108 instrument. Conductivity measurements were performed at room temperature in  $10^{-3}$  M acetonitrile solutions employing a Crison, micro CM 2200 conductimeter. Infrared spectra were recorded from KBr pellets or polyethylene mulls in the range  $4000\text{--}100\text{ cm}^{-1}$  under a nitrogen atmosphere. Electronic spectra in solution were run on a Kontron-Uvikon 860 in acetonitrile between 750 and 350 nm. The  $^1\text{H}$  NMR,  $^{13}\text{C}\{^1\text{H}\}$  NMR, HMQC and NOESY spectra were obtained either on a Bruker 250 MHz or Bruker 400 MHz instrument. Chemical shifts ( $\delta$ ) were determined relative to internal TMS and are given in ppm.

#### 3.2. Synthesis

##### 3.2.1. Preparation of $[\text{Ni}(\text{med})\text{Cl}]_2$ (**1**)

To a solution of 0.345 g (2.21 mmol) of *N*-(2-mercaptoethyl)-3,5-dimethylpyrazole in 5 ml of absolute ethanol (light brown) and 2 ml of triethyl orthoformate was added dropwise a solution of 0.525 g (2.21 mmol) of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in absolute ethanol (green). Solution turned into dark brown colour and a precipitate of the same colour was formed. After stirring for 1 h, the precipitate was filtered off and dried in vacuum. Yield: 0.46 g (83%),  $\text{C}_{14}\text{H}_{22}\text{Cl}_2\text{N}_4\text{Ni}_2\text{S}_2$  (498.78): C 33.71, H 4.45, N 11.23, S 12.86; Found: C 34.06, H 4.46, N 11.24, S 12.53%. Conductivity ( $\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ ,  $1.06 \cdot 10^{-3}$  M in acetonitrile): 14.0, IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{C-H})_{\text{al}}$  2982–2921,  $\nu(\text{C=C})$ ,  $\nu(\text{C=N})$  1554,  $\delta(\text{CH}_3)_{\text{as}}$  1469–1421,  $\delta(\text{CH}_3)_{\text{s}}$  1310,  $\delta(\text{C-H})_{\text{oop}}$  774. IR (polyethylene,  $\text{cm}^{-1}$ ):  $\nu(\text{Ni-N})_{\text{as}}$  463,  $\nu(\text{Ni-Cl})$  388,  $\nu(\text{Ni-S})$  366. UV–Vis (acetonitrile,  $1.1 \cdot 10^{-3}$  M, nm),  $\lambda(\epsilon)$ : 524(411), 416(1010).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 2.19$  (s, 6H, Me), 2.74 (s, 6H, Me), 0.72/2.60/4.47/5.58 (4 ddd, 8H, pz- $\text{CH}_2$ - $\text{CH}_2$ ), 5.79 (s, 2H, pz-CH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 11.9$  (Me), 15.7 (Me), 24.7 (S- $\text{CH}_2$ - $\text{CH}_2$ ), 50.4 (pz- $\text{CH}_2$ - $\text{CH}_2$ ), 108.4 (pz-CH), 142.1, 152.8 (pz-C).

##### 3.2.2. Preparation of $[\text{Pd}(\text{med})\text{Cl}]_2$ (**2**) and $[\text{Pt}(\text{med})\text{Cl}]_2$ (**3**)

A solution of 0.100 g (0.39 mmol) of  $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$  (orange) or 0.076 g (0.22 mmol) of  $[\text{PtCl}_2(\text{CH}_3\text{CN})_2]$  (yellow) in 5 ml of dichloromethane was added dropwise to a solution containing (Pd: 0.061 g, 0.39 mmol; Pt: 0.034 g, 0.22 mmol) of *N*-(2-mercaptoethyl)-3,5-dimethylpyrazole in 5 ml of dichloromethane (light brown). After 12 h stirring, solvent was removed in vacuum. For Pd complex, the resulting precipitate was then filtered off and washed with diethyl ether, yielding the desired compound. Pt complex was further purified by chromatography (silica gel 60) using methanol-dichloromethane (1:9) as eluent to give the desired product as a yellow precipitate.

**2:** Yield: 0.112 g (98%),  $C_{14}H_{22}Cl_2N_4S_2Pd_2$  (594.23): C 28.30, H 3.73, N 9.43, S 10.76; Found: C 28.65, H 3.91, N 9.20, S 10.44%. Conductivity ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ,  $7.08 \times 10^{-4} \text{ M}$  in acetonitrile): 11.2, IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{C-H})_{\text{ar}}$  3119–3078,  $\nu(\text{C-H})_{\text{al}}$  2976–2918,  $\nu(\text{C}=\text{C})$ ,  $\nu(\text{C}=\text{N})$  1550,  $\delta(\text{CH}_3)_{\text{as}}$  1466–1422,  $\delta(\text{CH}_3)_{\text{s}}$  1312,  $\delta(\text{C-H})_{\text{oop}}$  814–771. IR (polyethylene,  $\text{cm}^{-1}$ ):  $\nu(\text{Pd-N})_{\text{as}}$  450,  $\nu(\text{Pd-Cl})$  360,  $\nu(\text{Pd-S})$  315. UV–Vis (acetonitrile,  $1.0 \times 10^{-3} \text{ M}$ , nm),  $\lambda$ : 447, 362.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 2.29$  (s, 6H, *Me*), 2.56 (s, 6H, *Me*), 1.69/3.85/4.60/4.87 (4 ddd, 8H, *pz-CH}\_2\text{-CH}\_2*), 5.94 (s, 2H, *pz-CH*).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 12.4$  (*Me*), 15.6 (*Me*), 28.0 (*S-CH}\_2\text{-CH}\_2*), 52.6 (*pz-CH}\_2\text{-CH}\_2*), 108.2 (*pz-CH*), 141.9, 152.4 (*pz-C*).

**3:** Yield: 0.044 g (52%),  $C_{14}H_{22}Cl_2N_4S_2Pt_2$  (771.54): C 21.79, H 2.87, N 7.26, S 8.32; Found: C 21.67, H 2.52, N 6.99, S 8.03%. Conductivity ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ,  $1.13 \times 10^{-3} \text{ M}$  in acetonitrile): 12.5, IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{C-H})_{\text{al}}$  2959–2853,  $\nu(\text{C}=\text{C})$ ,  $\nu(\text{C}=\text{N})$  1552,  $\delta(\text{CH}_3)_{\text{as}}$  1467–1416,  $\delta(\text{CH}_3)_{\text{s}}$  1302,  $\delta(\text{C-H})_{\text{oop}}$  801. IR (polyethylene,  $\text{cm}^{-1}$ ):  $\nu(\text{Pt-N})_{\text{as}}$  513,  $\nu(\text{Pt-Cl})$  330,  $\nu(\text{Pt-S})$  320. UV–Vis (acetonitrile,  $1.6 \times 10^{-3} \text{ M}$ , nm),  $\lambda$ : 384.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 2.23$  (s, 6H, *Me*), 2.54 (s, 6H, *Me*), 1.69/3.98/4.29/5.02 (4 ddd, 8H, *pz-CH}\_2\text{-CH}\_2*), 5.94 (s, 2H, *pz-CH*).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 12.3$  (*Me*), 14.9 (*Me*), 24.8 (*S-CH}\_2\text{-CH}\_2*), 51.1 (*pz-CH}\_2\text{-CH}\_2*), 107.7 (*pz-CH*), 141.1, 152.2 (*pz-C*).

### 3.2.3. Preparation of $[\text{NiCl}_3(\text{Hded})]$ (**4**)

A solution of 0.256 g (1.1 mmol) of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in 20 ml of acetonitrile (blue) was added dropwise to a solution of 0.168 g (1.1 mmol) of *N*-(2-mercaptoethyl)-3,5-dimethylpyrazole in 5 ml of acetonitrile and 2 ml of triethyl orthoformate. Solution turned into dark brown colour (dimeric nickel(II) complex). In presence of oxygen, and after 3 days, solution turned into blue turquoise and a pale yellow precipitate was formed (nickel oxide). Precipitate was filtered off and then solvent was evaporated to give the desired product. Yield: 0.24 g (96%),  $C_{14}H_{23}Cl_3N_4NiS_2$  (476.54): C 35.29, H 4.86, N 11.76, S 13.46; Found: C 35.56, H 4.94, N 11.83, S 13.52%. Conductivity ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ,  $1.01 \times 10^{-3} \text{ M}$  in acetonitrile): 21.4, IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{C-H})_{\text{ar}}$  3129,  $\nu(\text{C-H})_{\text{al}}$  2967–2920,  $\nu(\text{C}=\text{C})$ ,  $\nu(\text{C}=\text{N})$  1592, 1554,  $\delta(\text{CH}_3)_{\text{as}}$  1462–1427,  $\delta(\text{CH}_3)_{\text{s}}$  1292,  $\delta(\text{C-H})_{\text{oop}}$  815–833. IR (polyethylene,  $\text{cm}^{-1}$ ):  $\nu(\text{Ni-N})_{\text{as}}$  484,  $\nu(\text{Ni-Cl})$  375. UV–Vis (acetonitrile,  $9.8 \times 10^{-4} \text{ M}$ , nm),  $\lambda(\epsilon)$ : 616(215).

### 3.3. X-ray crystal structure analyses

Suitable crystals for X-ray diffraction experiments of compounds **2** and **4** were obtained by crystallisation from  $\text{CH}_2\text{Cl}_2$  and acetonitrile, respectively. Data were collected on a MAR345 diffractometer with Image Plate detector, using  $\phi$ -scan technique. Both crystals were

Table 3  
Crystallographic data for **2** and **4**

Compound	<b>2</b>	<b>4</b>
Empirical formula	$C_{14}H_{22}Cl_2N_4Pd_2S_2$	$C_{14}H_{23}Cl_3N_4NiS_2$
Molecular mass (g)	594.18	476.54
Temperature (K)	293(2)	293(2)
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
Unit cell dimensions		
<i>a</i> (Å)	8.649(1)	10.545(1)
<i>b</i> (Å)	10.484(1)	10.488(1)
<i>c</i> (Å)	11.946(1)	10.944(1)
$\alpha$ (°)	104.685(1)	82.961(2)
$\beta$ (°)	95.166(1)	71.510(1)
$\gamma$ (°)	95.912(1)	64.282(2)
<i>V</i> Å <sup>3</sup>	1034.64(2)	1034.0(2)
<i>Z</i>	2	2
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.907	1.531
$\mu$ (mm <sup>-1</sup> )	2.202	1.532
<i>F</i> (0 0 0)	584	492
Crystal size (mm)	0.1 × 0.1 × 0.2	0.1 × 0.1 × 0.2
$\theta$ Range (°)	3.03–31.50	1.96–24.89
Reflexions collected:		
Total, independent, <i>R</i> <sub>int</sub>	9823, 5922, 0.0266	5688, 3146, 0.0287
Data/restraints/parameters	5381, 0, 243	3146, 0, 297
<i>ab</i> *	0.0413, 2.6258	0.0487, 1.3308
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub>	0.0370, 0.0902	0.0392, 0.0969
<i>R</i> <sub>1</sub> (all data), <i>wR</i> <sub>2</sub>	0.0487, 0.0975	0.0577, 0.1061
Residual electron density (e Å <sup>-3</sup> )	+0.756, -0.843	+0.310, -0.398

\* The function minimized was  $\sum w(|F_o|^2 - |F_c|^2)^2$ , where  $w = [\sigma^2(I) + (aP)^2 + bP]^{-1}$ , and  $P = (|F_o|^2 + 2|F_c|^2)/3$ .

collected with graphite-monochromated Mo K $\alpha$  radiation. The structures were solved by direct methods using the SHELXS 97 computer program [28] and refined by full-matrix least-squares method with a SHELXL 97 computer program [29].

All hydrogen atoms were computed and refined using a riding model. The final *R* (on *F*) factor and  $\omega R$  (on *F*<sup>2</sup>) values, as well as the numbers of parameters refined and other details concerning the refinement of the crystal structure are presented in Table 3.

## 4. Conclusion

The ligand *N*-(2-mercaptoethyl)-3,5-dimethylpyrazole (Hmed) reacts with Ni(II), Pd(II) and Pt(II) ions to give new thiolate bridged dinuclear compounds. These complexes contain the anionic [med]<sup>-</sup> ligand in a chelating form, which induces a rigid conformation of the ethylenic fragment. NMR studies have shown to be very useful in the determination of the configuration of ligands in these complexes. This study represent an important addition to the series of similar structures established with  $M(\mu_2\text{-SR})_2M$  cores. Ni(II) complex

[NiCl(med)]<sub>2</sub> can be oxidised in acetonitrile solution leading to a new complex with an unique NiCl<sub>3</sub>N core.

We expect to find further exciting reactivity of **2** with other substrates to permit study of the hemilabile character of the ligand.

## 5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 196720 (**2**), CCDC 196721 (**4**). These data can be obtained free of charge at [www: http://www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223-336-033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

## Acknowledgements

Supports by the Ministerio de Educación y Cultura of Spain (Project BQU2000-0238 and grant to J.G.) are gratefully acknowledged.

## References

- [1] (a) S. Brooker, *Coord. Chem. Rev.* 222 (2001) 33; (b) J.G. Wright, M.J. Natan, F.M. McDonnell, D.M. Ralston, T.V. O'Halloran, *Prog. Inorg. Chem.* 38 (1990) 323; (c) P.J. Blower, J.R. Dilworth, *Coord. Chem. Rev.* 76 (1987) 121; (d) R.H. Holm, *Chem. Rev.* 10 (1981) 455.
- [2] (a) J. Arnold, *Prog. Inorg. Chem.* 43 (1995) 353; (b) M.G. Kanatzidis, D. Coucovanis, *J. Am. Chem. Soc.* 108 (1986) 337; (c) I.G. Dance, *Polyhedron* 5 (1986) 1037; (d) A.D. Watson, C.h. Pulla Rao, J.R. Dorfman, R.H. Holm, *Inorg. Chem.* 24 (1985) 2820; (e) K.S. Hagen, R.H. Holm, *Inorg. Chem.* 23 (1984) 418; (f) D. Coucovanis, *Acc. Chem. Res.* 14 (1981) 201.
- [3] (a) T. Beissel, T. Glaser, F. Kesting, K. Wieghardt, B. Nuber, *Inorg. Chem.* 35 (1996) 3936; (b) T. Beissel, F. Birkelbach, E. Bill, T. Glaser, F. Kesting, C. Krebs, T. Weyhermüller, K. Wieghardt, C. Butzlaff, A.X. Trautwein, *J. Am. Chem. Soc.* 118 (1996) 12376.
- [4] (a) B. Krebs, E. Henkel, *Angew. Chem., Int. Ed. Engl.* 30 (1991) 769; (b) I.G. Dance, R.G. Garbutt, M.L. Scudder, *Inorg. Chem.* 29 (1990) 1571.
- [5] di(thiolate)-bridged Ni/Ni systems see: (a) S. Brooker, G.B. Caygill, P.D. Croucher, T.C. Davidson, D.L.J. Clive, S.R. Magnson, S.P. Cramer, C.Y. Ralston, *J. Chem. Soc., Dalton Trans.* (2000) 3113. (b) S. Brooker, P.D. Croucher, T.C. Davidson, G.S. Dunbar, C.U. Beck, S. Subramanian, *Eur. J. Inorg. Chem.* (2000) 169. (c) B. Kersting, G. Steinfeld, J. Hausmann, *Eur. J. Inorg. Chem.*, (1999) 179. (d) C.A. Grapperhaus, J.A. Bellefeuille, J.H. Reibenspies, M.Y. Darensbourg, *Inorg. Chem.* 38 (1999) 3698. (e) S.C. Davies, D.L. Hughes, S. Longhurst, *Acta Crystallogr., Sect. C (Cr. Str. Commun.)* 55 (1999) 1436. (f) C.B. Allan, G. Davidson, S.B. Choudhury, Z. Gu, K. Bose, R.O. Day, M.J. Maroney, *Inorg. Chem.* 37 (1998) 4166. (g) S. Brooker, P.D. Croucher, T.C. Davidson, G.S. Dunbar, A.J. McQuillan, G.B. Jameson, *Chem. Commun.* (1998) 2131. (h) B. Kersting, D. Siebert, *Inorg. Chem.* 37 (1998) 3820. (i) C.R. Commas, K.L. Jantzi, J.I. Wirgau, T.C. Stauffer, J.W. Kampf, P.D. Boyle, *Inorg. Chem.* 37 (1998) 5851. (j) E. Bouwman, R.K. Henderson, A.K. Powell, J. Reedijk, W.J.J. Smeets, A.L. Spek, N. Veldman, S. Wocadlo, *J. Chem. Soc., Dalton Trans.* (1998) 3495. (k) N.F. Curtis, O.P. Gladhikh, S.L. Heath, K.R. Morgan, *Aust. J. Chem.* 51 (1998) 49. (l) S. Brooker, P.D. Croucher, F.M. Roxburgh, *J. Chem. Soc., Dalton Trans.* (1996) 3031. (m) S.B. Choudhury, M.A. Pressler, S.A. Mirza, R.O. Day, M.J. Maroney, *Inorg. Chem.* 33 (1994) 4831. (n) A.J. Atkins, A.J. Blake, M. Schroder, *Chem. Commun.* (1993) 1062. (o) M. Mikuriya, M. Handa, S. Shigematsu, S. Funaki, T. Fujii, H. Okawa, K. Toriumi, T. Koshihara, H. Terauchi, *Bull. Chem. Soc. Jpn* 66 (1993) 1104. (p) M. Mikuriya, S. Kida, I. Murase, *Bull. Chem. Soc. Jpn* 60 (1987) 1180. (q) T.B. Vance, L.B. Warner, K. Seff, *Inorg. Chem.* 16 (1977) 2106.
- [6] di(thiolate)-bridged Pd/Pd systems see: (a) G. Sánchez, J.L. Serrano, M.C. Ramírez de Arellano, J. Pérez, G. López, *Polyhedron* 19 (2000) 1395 (b) B. Kersting, *Eur. J. Inorg. Chem.* 37 (1998) 1071. (c) H. Barrera, J.M. Viñas, M. Font-Altaba, X. Solans, *Polyhedron* 4 (1985) 2027. (d) X. Solans, M. Font-Altaba, J.L. Briand, J. Sola, J. Suades, H. Barrera, *Acta Crystallogr., Sect C (Cr. Str. Commun.)* 39 (1983) 1653.
- [7] di(thiolate)-bridged Pt/Pt systems see: (a) K.A. Mitchell, C.M. Jensen, *Inorg. Chem.* 34 (1995) 4441. (b) K.A. Mitchell, C.M. Jensen, *Inorg. Chem.* 32 (1993) 2608. (c) M. Capdevila, W. Clegg, P. González-Duarte, I. Mira, *J. Chem. Soc., Dalton Trans.* (1992) 173. (d) J.A. Ayllón, P. González-Duarte, C. Miravittles, E. Molins, *J. Chem. Soc., Dalton Trans.* (1990) 1793. (e) C.E. Briant, C.J. Gardner, T.S.A. Hor, N.D. Howells, D.M.P. Mingos, *J. Chem. Soc., Dalton Trans.* (1984) 2645.
- [8] M. Mirukiya, M. Handa, S. Shigematsu, S. Funaki, T. Fujii, H. Okawa, K. Toriumi, T. Koshihara, H. Teranchi, *Bull. Chem. Soc. Jpn* 66 (1993) 1104.
- [9] A. Volbeda, M.H. Charon, C. Piras, E.C. Hatchikion, M. Frey, J.C. Fontecilla-Camps, *Nature* 373 (1995) 580.
- [10] (a) I.H. Krakoff, *Cancer Treat. Rep.* 63 (1979) 1523; (b) M. Dentro, F.C. Luft, N.M. Yum, S.D. Williams, L.H. Einhorn, *Cancer* 41 (1978) 1274; (c) K.A. Mitchell, C.M. Jensen, *Inorg. Chem.* 34 (1995) 4441.
- [11] (a) E.L.M. Lempers, J. Reedijk, *Inorg. Chem.* 29 (1990) 1880; (b) C. Dedon, R.F. Borch, *Biochem. Pharmacol.* 36 (1978) 1955.
- [12] (a) G. Esquiús, J. Pons, R. Yáñez, J. Ros, R. Mathieu, B. Donnadiu, N. Lugan, *Eur. J. Inorg. Chem.* (2002) 2999; (b) R. Mathieu, G. Esquiús, N. Lugan, J. Pons, J. Ros, *Eur. J. Inorg. Chem.* (2001) 2683; (c) G. Esquiús, J. Pons, R. Yáñez, J. Ros, *J. Organomet. Chem.* 619 (2001) 14; (d) G. Esquiús, J. Pons, R. Yáñez, J. Ros, X. Solans, M. Font-Bardía, *J. Organomet. Chem.* 605 (2000) 226; (e) G. Esquiús, J. Pons, R. Yáñez, J. Ros, X. Solans, M. Font-Bardía, *Acta Crystallogr. C58* (2002) 133.
- [13] (a) A. Boixassa, J. Pons, A. Virgili, X. Solans, M. Font-Bardía, *J. Ros, Inorg. Chim. Acta* 340 (2002) 49; (b) A. Boixassa, J. Pons, X. Solans, M. Font-Bardía, *J. Ros, Inorg. Chim. Acta* 346 (2003) 151.
- [14] R. Tribó, J. Pons, R. Yáñez, J.F. Piniella, A. Álvarez-Larena, *J. Ros, Inorg. Chem. Commun.* 3 (2000) 545.
- [15] J. García-Antón, J. Pons, X. Solans, M. Font-Bardía, *J. Ros, Eur. J. Inorg. Chem.* (2002) 3319.

- [16] E. Bouwman, P. Evans, R.A.G. de Graaf, H. Kooijman, R. Poinsot, P. Rabu, J. Reedijk, A.L. Spek, *Inorg. Chem.* 34 (1995) 6302.
- [17] S. Komiya, *Synthesis of Organometallic Compounds: A Practical Guide*, Wiley, New York, USA, 1997.
- [18] F.A. Cotton, *Inorganic Synthesis* 13 (1972) 52.
- [19] (a) W.J. Geary, *Coord. Chem. Rev.* 7 (1971) 81;  
(b) L.K. Thompson, F.L. Lee, E.J. Gabe, *Inorg. Chem.* 27 (1988) 39.
- [20] (a) E. Pretsh, T. Clerc, J. Seibl, W. Simon, *Tables of Determination of Organic Compounds. <sup>13</sup>C-NMR, <sup>1</sup>H-NMR, IR, MS, UV/VIS*, Chemical Laboratory Practice, Springer, Berlin, Germany, 1989;  
(b) D.H. Williams, I. Fleming, *Spectroscopic Methods in Organic Chemistry*, McGraw-Hill, London, UK, 1995.
- [21] (a) R.J.H. Clark, G. Natile, U. Belluco, L. Cattalini, C. Filippin, *J. Chem. Soc. (A)* (1970) 659;  
(b) K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, USA, 1986.
- [22] (a) M.A. Halcrow, E. Christon, *Chem. Rev.* 94 (1994) 2421;  
(b) B. Kersting, G. Steinfeld, J. Hausmann, *Eur. J. Inorg. Chem.* (1999) 179;  
(c) M. Handa, M. Mikuriya, Z.J. Zhong, H. Okawa, S. Kida, *Bull. Chem. Soc. Jpn* 61 (1988) 3883.
- [23] (a) D. Sutton, *Electronic Spectra of Transition Metal Complexes*, McGraw-Hill, London, UK, 1975;  
(b) J.C. Bailar, H.J. Emeleus, S.R. Nyttorm, A.F.T. Dickenson, *Comprehensive Inorganic Chemistry*, Pergamon Press, London, UK, 1973.
- [24] E. Pretsh, T. Clerc, J. Seibl, W. Simon, *Tables of Determination of Organic Compounds. <sup>13</sup>C-NMR, <sup>1</sup>H-NMR, IR, MS, UV/VIS*, Chemical Laboratory Practice, Springer, Berlin, Germany, 1989.
- [25] F.H. Allen, O. Kennard, *Chem. Des. Autom. News* 8 (1993) 31.
- [26] S. Buchler, F. Meyer, A. Jacobi, P. Kircher, L. Zsolnai, *Z. Naturforsch* 54b (1999) 1295.
- [27] W.L. Driessen, R.M. de Vos, A. Etz, J. Reedijk, *Inorg. Chim. Acta* 235 (1995) 127.
- [28] G.M. Sheldrick, *Acta Crystallogr.* A46 (1990) 467.
- [29] G.M. Sheldrick, *SHELXS 97, SHELXL 97, CIFTAB-Program for Crystal Structure Analysis (Release 97-2)*, Institut für Anorganische Chemie der Universität, Tammanstraße 4, 3400 Göttingen, Berlin, Germany, 1998.