

A DFT Study of the Electronic Spectrum of the α -Keggin Anion $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$

Joan Miquel Maestre, Xavier Lopez, Carles Bo, and Josep-M. Poblet*

Departament de Química Física i Inorgànica and Institut d'Estudis Avançats, Universitat Rovira i Virgili 43005 Tarragona, Spain

Claude Daul

Institute de Chimie Inorganique et Analytique, Université de Fribourg, Perolles, CH-1700 Fribourg, Switzerland

Received October 15, 2001

Multiplet splittings for several excited configurations of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ were calculated using DFT methods. In agreement with the experimental interpretation of the spectrum the calculations found that the first strong band corresponds to Co d–d transitions, but it is worth noting that superposed to these transitions there are charge transfer transitions from cobalt to tungsten. The calculations also showed the importance of Jahn–Teller distortions in the excited states. With the exception of the consequences derived from a smaller splitting of d cobalt orbitals the d–d spectrum of $[\text{CoCl}_4]^{2-}$ is similar to that of the more complex Keggin anion. Finally, the energy of the bi-electronic transition ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})$ was estimated via an approximate procedure based on ligand field theory.

Introduction

The spectacular progress of computational transition-metal chemistry in the past decade is largely due to density functional theory (DFT) based methods.¹ These methods, however, have not been applied so extensively to excited states. In the mid-1970s, Messmer and Salahub and Ziegler et al. showed how multiplet splittings can be derived from single-determinant energies.² The idea is that, in symmetric molecules with degenerate orbitals, the particular multiplets arising from an open-shell configuration cannot, in general, be expressed by a single determinant and therefore density functional calculations do not directly give multiplet energies. It is possible, however, to formulate the energy of a particular state as the weighted sum of single-determinant energies. Following this line of thought Daul developed a system of programs that exploits symmetry to simplify the relationship between the multiplet and single-determinant energies.³ This method, which has been used with good results for atomic

and molecular systems,^{4–5} has been explained in detail and illustrated with several simple examples.³ Dickson and Ziegler used this method to make a complete theoretical interpretation of the electronic spectrum of the permanganate ion $[\text{MnO}_4]^-$.⁵ Our group is presently involved in the theoretical study of the electronic and magnetic properties of polyoxoanions,^{6–7} and here we report a study of the electronic spectrum of the α -Keggin anion $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ (Figure 1). For the sake of comparison, we have also carried out some calculations on the simpler ion $[\text{Co}^{\text{II}}\text{Cl}_4]^{2-}$ due to the high number of experimental data on this anion.^{8–9} There are also some theoretical studies that will allow comparison of our results.^{10–11}

* Author to whom correspondence should be addressed. E-mail: poblet@quimica.urv.es.

- (1) Davidson, E. R., Ed. *Chem. Rev.* **2000**, *100*, 351–818 (special issue on Computational Transition Metal Chemistry).
- (2) Messmer D.; Salahub D. *J. Chem. Phys.* **1976**, *65*, 779. Ziegler, T.; Rauk, A.; Baerends, J. E. *Theor. Chim. Acta* **1977**, *43*, 261.
- (3) Daul, C. *Int. J. Quantum Chem.* **1994**, *52*, 867.

- (4) Lannoo, M.; Baraff, G. A.; Schlüter, M. *Phys. Rev. B* **1981**, *24*, 943. Daul, C.; Güdel, J. Weber, H.-U. *J. Chem. Phys.* **1993**, *98*, 4023. Daul, C.; Baerends, E. J.; Vernooijs, P. *Inorg. Chem.* **1994**, *33*, 3538. Rosa, A.; Ricciardi, G.; Baerends, E. J.; Stufkens, D. J. *Inorg. Chem.* **1995**, *34*, 3425. Gilardoni, F.; Weber, J.; Bellafrourh, K.; Daul, C.; Güdel, H.-U. *J. Chem. Phys.* **1996**, *104*, 7624.
- (5) Dickson, R.; Ziegler, T. *Int. J. Quantum Chem.* **1996**, *58*, 681.
- (6) Maestre, J. M.; Lopez, X.; Bo, C.; Poblet, J. M.; Casañ-Pastor, N. *J. Am. Chem. Soc.* **2001**, *123*, 3749.
- (7) (a) Maestre, J. M.; Bo, C.; Poblet, J. M.; Casañ-Pastor, N.; Gomez-Romero, P. *Inorg. Chem.* **1998**, *37*, 3444. (b) Maestre, J. M.; Sarasa, J. P.; Bo, C.; Poblet, J.-M. *Inorg. Chem.* **1998**, *37*, 3071. (c) Lopez, X.; Maestre, J. M.; Bo, C.; Poblet, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 9571.

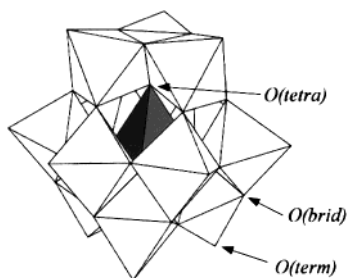


Figure 1. Polyhedral representation of an α -Keggin anion.

The spectrum of the α -Keggin anion $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ in solution has been measured by several groups.^{12–14} Matsuda and co-workers have also reported the solid-state spectrum of $\text{K}_6[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}$. The main features of the $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ spectrum are two strong bands originating near 7100 and 15000 cm^{-1} , a broad band centered at about 26000 cm^{-1} , and very strong bands around 38000 and 50000 cm^{-1} . It is well-known that the charge transfer bands in nonreduced Keggin anions appear in the near ultraviolet region (200–350 nm),¹⁵ and that these bands may be assigned to electronic

excitations from doubly occupied oxo orbitals to unoccupied d orbitals of the $\text{M}_{12}\text{O}_{36}$ cage. In a previous paper⁶ we demonstrated that the energy gap between these two sets of orbitals is independent of the central ion type. Therefore, we believe that the two bands in the region between 38000 and 50000 cm^{-1} can be unambiguously assigned to charge transfer ligand \rightarrow tungsten transitions.

Computational Details

All energies were computed by means of a DFT formalism that included gradient corrections for exchange and correlation. The formalism is based upon the local spin density approximation characterized by the electron gas exchange ($X\alpha$ with $\alpha = 2/3$) together with Vosko–Wilk–Nusair¹⁶ parametrization for correlation. Becke's nonlocal corrections to the exchange energy¹⁷ and Perdew's nonlocal corrections to the correlation energy¹⁸ were added. These calculations were carried out with the ADF program (version 2.3),¹⁹ using triple- ζ + polarization Slater basis sets to describe the valence electrons of O and Cl. For metal atoms, a frozen core composed of the 1s to 2sp shells for cobalt and 1s to 4spdf for tungsten was described by means of single Slater functions. ns and np electrons were described by double- ζ Slater functions, nd and (n + 1)s by triple- ζ functions, and (n + 1)p by a single orbital. These basis sets correspond to basis IV in the ADF standard basis library.^{20–21} Quasirelativistic corrections were used with the Pauli formalism and corrected core potentials. The quasirelativistic frozen core shells were generated using the auxiliary program DIRAC.¹⁹ The integration parameter in the molecular calculations, which determine the precision of the numerical integrals, was set to 6.0, quite a high value.

The multiplet energies were computed with the aid of the STAGEN program for determining the symmetry coefficients for wave functions and energies. All the determinantal energies were determined from a single set of orbitals, obtained by performing a spin-restricted calculation. The orbitals of a partially occupied configuration were equally occupied, with fractional occupations if necessary. This artificial state is referred as an *average occupied configuration*, or AOC.

All the calculations reported here considered only the ions without the crystal environment. This approximation is reasonable for the purpose of the present study since in a previous paper we showed that the crystal field is crucial for getting reasonable orbital energies, but the crystal environment does not necessarily modify either the ordering or the relative orbital energies of the cluster.⁷ Therefore, the relative energies of the different states reported here should not be altered if isotropic fields are included. For systems

- (8) Wiesner, J. R.; Srivastava, R. C.; Kennard, C. H.; DiVara, K.; Lingafelter, E. C. *Acta Crystallogr.* **1967**, *23*, 565. Stucky, G. D.; Folkers, J. B.; Kistenmacher, T. J. *Acta Crystallogr.* **1967**, *23*, 1064. Dunsmuir, J. T.; Lane, A. P. *J. Chem. Soc. A* **1971**, 2781. Gerloch, M.; Lewis, J.; Rickards, R. J. *J. Chem. Soc., Dalton Trans.* **1972**, 980. Clark, R. J.; Dunn, T. M. *J. Chem. Soc.* **1963**, 1198. Sabatini, A.; Sacconi, J. *J. Am. Chem. Soc.* **1964**, *86*, 17. Dunsmuir, J. T.; Lane, A. P. *J. Chem. Soc. A* **1971**, 404. Edwards, H. G. M.; Woodward, L. A.; Gall, M. J.; Ware, M. J. *Spectrochim. Acta, Part A* **1970**, *26A*, 287. Bird, B. D.; Cooke, E. A.; Day, P.; Orchard, A. F. *Philos. Trans. R. Soc. London, A* **1974**, *276*, 277. Hamer, N. K. *Mol. Phys.* **1963**, *6*, 257. Gale, R.; Godfrey, R. E.; Mason, S. F. *Chem. Phys. Lett.* **1976**, *38*, 441. Cotton, F. A.; Goodgame, M. *J. Am. Chem. Soc.* **1961**, *83*, 1777. Cotton, F. A.; Goodgame, D. M.; Goodgame, M.; Sacco, A. *J. Am. Chem. Soc.* **1961**, *83*, 4157. Cotton, F. A.; Goodgame, D. M.; Goodgame, M.; Sacco, A. *J. Am. Chem. Soc.* **1961**, *83*, 4690. Holm, R. H.; Cotton, F. A. *J. Chem. Phys.* **1959**, *31*, 788. Ferguson, J. *J. Chem. Phys.* **1960**, *32*, 528. Stephens, D. R.; Drickamer, H. G. *J. Chem. Phys.* **1961**, *35*, 429. Ferguson, J. *J. Chem. Phys.* **1963**, *39*, 116. Harada, M.; Sakatsume, S.; Tsujikawa, Y. *J. Phys. Soc. Jpn.* **1973**, *35*, 1234. Harada, M.; Tsujikawa, I. *J. Phys. Soc. Jpn.* **1974**, *37*, 1353. Harada, M.; Tsujikawa, I. *J. Phys. Soc. Jpn.* **1974**, *37*, 1359. Gale, R.; Godfrey, R. E.; Mason, S. F. *Chem. Phys. Lett.* **1976**, *38*, 446. Tsujikawa, I.; Harada, M. *Rev. Roum. Chim.* **1977**, *22*, 1305. Jha, N. K.; Saxena, A. *Inorg. Chim. Acta* **1977**, *22*, L21. Lever, A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier, Amsterdam, 1984. Schmidtke, H.-H.; Nover, J. *Inorg. Chim. Acta* **1995**, *240*, 231. Nover, J.; Schmidtke, H.-H. *Chem. Phys.* **1999**, *241*, 179.
- (9) Hipps, K. W.; Mazur, U. *J. Am. Chem. Soc.* **1987**, *109*, 3861. Hipps, K. W.; Mazur, U. *J. Phys. Chem.* **1987**, *91*, 5218.
- (10) Gerloch, M.; Lewis, J.; Rickards, R. J. *J. Chem. Soc., Dalton Trans.* **1972**, 980. Bird, B. D.; Cooke, E. A.; Day, P.; Orchard, A. F. *Philos. Trans. R. Soc. London, A* **1974**, *276*, 277. Ballhausen, C. J.; Jorgensen, C. K. *Acta Chem. Scand.* **1955**, *9*, 397. Orgel, L. E. *J. Chem. Phys.* **1955**, *23*, 1004. Ballhausen, C. J.; Liehr, A. D. *J. Mol. Spectrosc.* **1958**, *2*, 342. Hamer, N. K. *Mol. Phys.* **1963**, *6*, 257. Liehr, A. D. *J. Phys. Chem.* **1963**, *67*, 1314. Gale, R.; Godfrey, R. E.; Mason, S. F. *Chem. Phys. Lett.* **1976**, *38*, 441. Chandler, G. S.; Phillips, R. A. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 573. Brown, C. A.; Duer, M. J.; Gerloch, M.; McMeeking, R. F. *Mol. Phys.* **1988**, *64*, 793. Soudackov, A. V.; Tchougreeff, A. L.; Misurkin, Y. A. *Theor. Chim. Acta* **1992**, *83*, 389. Cassam-Chenaï, P.; Wolff, S. K.; Chandler, G. S.; Figgis, B. N. *Int. J. Quantum Chem.* **1996**, *60*, 667.
- (11) Johansen, H.; Andersen, N. *Mol. Phys.* **1986**, *58*, 965.
- (12) (a) Shimura, Y.; Tsuchida, R. *Bull. Chem. Soc. Jpn.* **1957**, *30*, 502. (b) Simmons, V. E. Ph.D. Thesis, Boston University, 1963. Rollins, O. W. *Inorg. Chem.* **1972**, *11*, 3114. (c) Nomiyama, K.; Kobayashi, R.; Miwa, M. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2983.
- (13) Kojima, K.; Matsuda, J. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 821.
- (14) Kojima, K.; Matsuda, J.; Kojima, N.; Ban, T.; Tsujikawa, I.; Kyoto, K.; Kyoto, S. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3213.

(15) See, for example: Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: Berlin, 1983; p 109.

(16) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

(17) Becke, A. D. *J. Chem. Phys.* **1986**, *84*, 4524; *Phys. Rev.* **1988**, *A38*, 3098.

(18) Perdew, J. P. *Phys. Rev.* **1986**, *B33*, 8882; **1986**, *B34*, 7406.

(19) *ADF 2.3 User's Guide*; Chemistry Department, Vrije Universiteit: Amsterdam, The Netherlands, 1997. Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41. Fonseca Guerra, C.; Visser, O.; Snijders, J. G.; te Velde, G.; Baerends, E. J. In *Methods and Techniques in Computational Chemistry: METECC-95*; Clementi, E., Corongiu, G., Eds.; STEF: Cagliari, Italy, 1995; p 305.

(20) Snijders, J. G.; Baerends, E. J.; Vernooijs, P. *At. Nucl. Data Tables* **1982**, *26*, 483. Vernooijs, P.; Snijders, J. G.; Baerends, E. J. *Slater type basis functions for the whole periodic system*; Internal Report, Free University of Amsterdam: Amsterdam, The Netherlands, 1981.

(21) Rosa, A.; Ricciardi, G.; Baerends, E. J.; Stufkens, D. J. *Inorg. Chem.* **1996**, *35*, 2886.

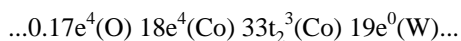
$[\text{Co}^{\text{II}}\text{Cl}_4]^{2-}$			$[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$		
	Orbital Composition			Orbital Composition	
4 a ₁	—	5.78 Co 80%	22 t ₁	— — —	3.04 W 61% O _{brid} 19%
			19 e	— —	2.73 W 65% O _{brid} 16%
5 t ₂	↑ ↑ ↑	2.33 Co 75%	33 t ₂	↑ ↑ ↑	2.55 Co 64% O _{tetra} 13%
2 e	↑ ↑	1.93 Co 84%	18 e	↑ ↑	1.87 Co 80% O _{tetra} 13%
1 t ₁	↑ ↑ ↑	0.00 Cl 99%	17 e	↑ ↑	0.00 O _{brid} 99%

Figure 2. Orbital energies computed at restricted level for $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ and for $[\text{Co}^{\text{II}}\text{Cl}_4]^{2-}$.

with short contacts between the anion and the counterions or the solvent, some of the conclusions reported here might not be directly applicable.

Results and Discussion

Ground-State Electronic Structure. A Keggin structure consists of an assembly of MO_6 octahedrons with a central tetrahedron, XO_4 , in which X is a main group element (P^{V} , Si^{IV} , etc.) or a transition-metal ion (Fe^{III} , Co^{II} , Co^{III} , etc.). Therefore, the $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ anion can also be viewed as a $\text{W}_{12}\text{O}_{40}$ cage that encapsulates a d^7 ion. Since the cobalt atom has a tetrahedral coordination, the five d cobalt orbitals split into two sets of e and t_2 symmetries in the α isomer. These two orbitals appear between the band of doubly occupied orbitals, which are formally delocalized over the oxo ligands, and the band of vacant orbitals, which are delocalized over the d shells of tungstens. The energy gap between these two bands is independent of the central ion (~ 2.8 eV in tungstates⁶). Figure 2 shows the relative energies of some frontier orbitals as well as their symmetries and percentage compositions (based on Mulliken population analysis). The 18e and 33 t_2 cobalt orbitals are shifted toward the tungsten band. Hence, while there is only 0.18 eV between 19e(W) and 33 t_2 (Co) orbitals, orbital 18e is 1.8 eV higher in energy than orbital 17e(O). According to the orbital diagram in Figure 2 the ground configuration in $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ is



For the sake of simplicity we will use $18e^433t_2^3$ or $e^4t_2^3$ to identify the ground configuration. Acerete et al.²² described the ground electronic state of α - $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ as a ${}^4\text{A}_2$, which corresponds to a $\text{Co}(\text{II}) d^7$ system with three unpaired electrons. Indeed, there are four electronic states associated with this configuration: the ${}^4\text{A}_2$ quadruplet, which is the ground state, and the ${}^2\text{E}$, ${}^2\text{T}_1$, and ${}^2\text{T}_2$ doublets, whose energies are relatively important with respect to the quadruplet, +1.49, +1.38, and +2.38 eV, respectively. We will limit the present study to the analysis of the electronic transitions allowed by the spin symmetry, and therefore for

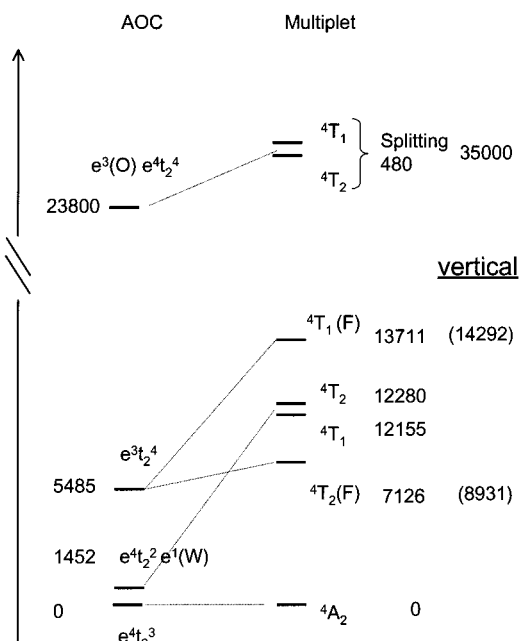


Figure 3. Multiplet energies (in cm^{-1}) for several configurations computed for optimal geometries in each configuration for $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$. All of the calculations were carried out with T_d symmetry. Vertical transition energies are also included for some states.

the excited configurations only the energies of the corresponding quadruplet states will be calculated.

The Co d–d Transitions. Associated with the excited configuration $e^3t_2^4$ there are two quadruplets of symmetries T_1 and T_2 at 13700 and 7100 cm^{-1} , respectively (Figure 3). These energies seem excessively high in comparison to the assignments made by Matsuda and co-workers, who proposed an excitation energy of 7830 cm^{-1} for the orbital-allowed transition ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ and of 4600 cm^{-1} for the forbidden transition ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$. Nomiya and co-workers^{12c} reported spectroscopic measures in nonaqueous solution for several Keggin anions and proposed, in particular, an excitation energy for the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ transition energy that was also in the region of 7800 cm^{-1} . They also alluded to the importance of Jahn–Teller distortions in the low-lying excited states. In order to quantify the role of the Jahn–Teller distortions in the spectrum of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ a series of calculations were carried out under the constraints of the D_{2d} symmetry group. The $e^3t_2^4$ configuration in the T_d symmetry splits in four configurations under D_{2d} .

In this symmetry, the lowest excited state is the quadruplet of symmetry B_2 which has an energy of 5300 cm^{-1} (Figure 4). This energy is in excellent agreement with the value of 4600 cm^{-1} predicted by Kojima and Matsuda for the forbidden transition. The next excited states, accessible through allowed transitions from the ground state ${}^4\text{B}_1$, range between 7700 and 11000 cm^{-1} , which is in good agreement with the presence of an intense, broad band in the near-infrared region (7000 and 9000 cm^{-1}) in the electronic spectrum measured by Matsuda and co-workers.

Table 1 shows selected geometrical parameters for T_d and D_{2d} geometries. Note that the geometry optimizations were carried out in the AOC configurations and the geometry obtained was used to evaluate the multiplet energies. Table

(22) Acerete, R.; Casañ-Pastor, N.; Bas-Serra, J.; Baker, L. C. W. *J. Am. Chem. Soc.* **1989**, *111*, 6049.

Table 1. Selected Geometrical Parameters for $[\text{CoCl}_4]^{2-}$ and $[\text{CoW}_{12}\text{O}_{40}]^{6-}$ Obtained from AOC Calculations^a

	T_d		D_{2d}				exptl
	$e^4t_2^3$	$e^3t_2^4$	$a_1^1b_1^2b_2^2e^2$	$a_1^2b_1^1b_2^1e^3$	$a_1^1b_1^2b_2^1e^3$	$a_1^2b_1^1b_2^2e^2$	
$[\text{CoCl}_4]^{2-}$							
Co–Cl	2.316	2.345	2.337	2.343	2.346	2.343	2.263
Cl–Co–Cl	109.47	109.47	98.89–115.01	124.45–102.54	113.36–107.56	100.15–114.33	107.22–110.61
$[\text{CoW}_{12}\text{O}_{40}]^{6-}$							
Co–O _{tetra}	1.866	1.882	1.857	1.861	1.878	1.877	1.895
O _{tetra} –Co–O _{tetra}	109.47	109.47	105.24–111.63	112.01–108.21	109.60–109.41	109.04–109.69	107.8–111.2
W–W	3.764–3.332	3.761–3.327	3.774–3.339	3.765–3.327	3.763–3.326	3.765–3.329	3.704av–3.267av
			3.759–3.321	3.778–3.336	.766–3.329	3.760–3.323	
O _{tetra} –W	2.226	2.213	2.206	2.243	2.217	2.215	2.13–2.18
			2.288	2.200		2.220	
W–O _{term}	1.788	1.787	1.787	1.783	1.786	1.785	1.68–1.73
			1.781	1.787		1.786	

^a Distances in angstroms and angles in degrees.

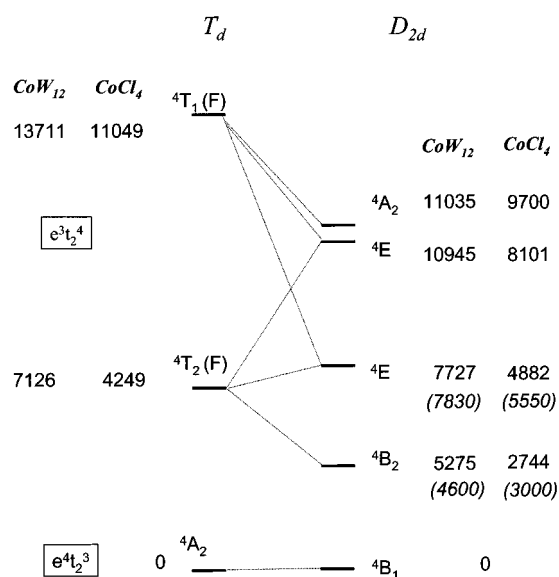


Figure 4. Multiplet splitting for the excited configuration $e^3t_2^4$ in the D_{2d} symmetry. The values in parentheses correspond to the experimental transition energies.

1 shows that under T_d symmetry the electronic transition increased the Co–O_{tetra} bond distance by 0.016 Å. The most remarkable variation that the Jahn–Teller distortion produces is found in the O_{tetra}–Co–O_{tetra} angle, which varies from -4.3° to 2.5° . The higher the distortion, the less stable the state is. On the other hand, the Jahn–Teller distortion does not modify the Co–O_{tetra} bond distances: in the four configurations studied, the Co–O_{tetra} is only modified as much as 0.012 Å. The W–W distances and W–O_{term} bonds also remain practically constant.

In the simpler cobalt(II) tetrachloride complex the cobalt ion is also under the effect of a tetrahedral field generated by the four ligands. In this case, however, the splitting of the e and t_2 orbitals is smaller because the field generated by the chlorine ligands is weaker. Hence, the energy gap between the two sets of d cobalt orbitals is 0.28 eV smaller than in the Keggin anion. This difference in the splitting can be easily rationalized if we consider that chloride ligands support lower negative charges and that the negative charges are further from the positive ion (see Table 1). As a matter of fact, the excitation energy for transferring one electron from the e to t_2 orbital was found at lower energies. The

multiplets 4T_2 and 4T_1 , associated with the excited $e^3t_2^4$ configuration, were computed to be at 4249 and 11049 cm^{-1} , respectively (Figure 4). These transitions are shifted $\sim 3000 \text{ cm}^{-1}$ toward the infrared region with respect to the spectrum predicted for the Keggin anion. The localization of the ${}^4A_2 \rightarrow {}^4T_1$ d–d band in $[\text{CoCl}_4]^{2-}$ in solution and in the gas phase has been known since the 1960s and appears in the region between 4400 and 6000 cm^{-1} . More recently, in 1987, Hipps and Mazur carried out inelastic electron tunneling spectroscopy (IETS) studies which enabled the electron forbidden ${}^4A_2 \rightarrow {}^4T_2$ transition (between 2000 and 4000 cm^{-1} and centered at 3000 cm^{-1}) to be assigned. Hipps and Mazur characterized the allowed electric dipole ${}^4A_2 \rightarrow {}^4T_1$ transition in both tunneling and FT-IR spectra, the band being centered at 5550 cm^{-1} between the 4450 and 7000 cm^{-1} regions.⁹ A comparison of the experimental and theoretical studies for d–d transitions in $[\text{CoCl}_4]^{2-}$ led to the conclusion that the theoretical calculations predict quite well the shift toward lower energies in relation to the Keggin anion but that the first allowed ${}^4A_2 \rightarrow {}^4T_1$ band is computed at excessively large energies (11000 cm^{-1} at the theoretical level compared to the measured values of $\sim 5500 \text{ cm}^{-1}$). This tendency had already been observed for the Keggin anion when the calculations were carried out in the T_d symmetry. For the ${}^4A_2 \rightarrow {}^4T_2$ transition the discrepancy between the DFT calculations and the experimental measure is visibly smaller ($\sim 1200 \text{ cm}^{-1}$).

As in $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$, a series of calculations were made under the restrictions of the D_{2d} symmetry group to analyze the Jahn–Teller effects on the excited $e^3t_2^4$ configuration of $[\text{CoCl}_4]^{2-}$. The results are completely in line with those found for the Keggin anion. In the D_{2d} symmetry the lowest multiplet arising from the excited configuration is the quadruplet 4B_2 , which is now computed at 2744 cm^{-1} above the ground state, a value that is in excellent agreement with the excitation energy reported by IETS (3000 cm^{-1}). The next state is a quadruplet of E symmetry with an energy of 4882 cm^{-1} . This energy is also concordant with the spectroscopic measures for the first allowed d–d transition. The next two quadruplets are at 8100 and 9700 cm^{-1} . All these energies are given in Figure 4, and the geometrical parameters are presented in Table 1. It is worth mentioning that under T_d symmetry the electronic transition increases the

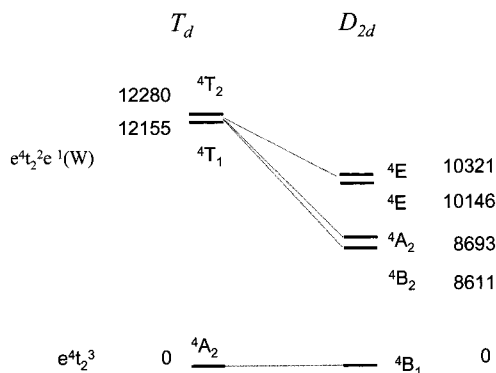


Figure 5. Multiplet splitting for the excited configuration $e^4t_2^2e^1(W)$ in the D_{2d} symmetry for $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$.

Co–Cl distance by 0.029 Å and that the Jahn–Teller distortion produces the same effects observed in the Keggin anion. The Co–Cl distances are not modified by more than 0.03 Å, and the Cl–Co–Cl angle is the parameter that varies most (from -10.6° to 15°). The distortion observed in $[\text{CoCl}_4]^{2-}$ is larger than in the Keggin anion because each tetrahedral oxygen is bonded to three W's inside the Keggin anion and therefore has less freedom.

The Charge Transfer Transitions. Although the AOC energies suggest that the excitation energies from d cobalt orbitals to unoccupied orbitals delocalized over the d shell of tungstens are very low, the calculations for multiplets in the T_d geometry yield energies of ~ 1.5 eV (~ 12000 cm^{-1}) for the two quadruplets arising from configuration $18e^4(\text{Co}) 33t_2^2(\text{Co}) 19e^1(\text{W})$ or $e^4t_2^2e^1(W)$ in the short formulation (see Figures 3 and 5). If the geometry is allowed to relax under the D_{2d} group, the excitation energy at ~ 1.5 eV splits into two signals at 8600 and 10000 cm^{-1} . According to these calculations, the band between 7000 and 9000 cm^{-1} in the experimental spectrum¹³ could be associated with the superposition of Co d–d excitations and Co \rightarrow W charge transfer transitions. It is worth noting that this possibility has never been mentioned previously. All Co–O_{tetra} bond distances are reduced (0.06 Å) upon excitation and D_{2d} geometry relaxation, whereas W–W interatomic distances are only slightly changed and W–O_{term} bonds are practically unmodified. The largest variation is found for the O_{tetra}–Co–O_{tetra} angle ($+5.2^\circ$ and -2.6°). The decrease in symmetry from T_d to D_{2d} is favored, in all cases, by the angular distortion and by the elongation of two pseudo-octahedral WO_6 .

One last series of calculations was carried out to analyze charge transfer excitations from oxo ligands to d cobalt orbitals. The O \rightarrow Co set of transitions includes several distinct excitations that may formally be associated with electronic excitations from terminal, bridging, or tetrahedral oxygens. The origin of this band may be estimated from the energy transition between the highest oxo orbital, 17e, which is formally delocalized over the valence shell of bridging oxygens. This transition is estimated to be approximately at 35000 cm^{-1} (Figure 3). Under D_{2d} symmetry, the energy of these transitions drops to 31000 cm^{-1} . This energy is higher than the experimental predictions, which suggested that the O \rightarrow Co transition starts at 26000 cm^{-1} .¹³

Approximate Treatment of Quadruplet States 4T_1 . A major shortcoming of multiplet treatment in the DFT framework is the lack of coupling between states of the same symmetry, such as ${}^4T_1(\text{F})$ and ${}^4T_1(\text{P})$. These states, arising from configurations $e^3t_2^4$ and $e^2t_2^5$, respectively, are mixed. Johansen and Andersen¹¹ previously studied this problem at the MCSCF/CI level in the $[\text{CoCl}_4]^{2-}$ system and found a considerable mixing of the two quadruplet states. The contribution of the $e^2t_2^5$ configuration to the lowest state was found to be 70.3% whereas the same configuration contributes 27.4% to the other state. The occupation numbers were $e^{2.27}t_2^{4.69}$ and $e^{2.70}t_2^{4.26}$, respectively.

We computed the energy of the quadruplet states for $[\text{CoCl}_4]^{2-}$ as well as for $[\text{CoW}_{12}\text{O}_{40}]^{6-}$. In both anions, the bielectronic excitation ${}^4A_2 \rightarrow {}^4T_1(\text{P})$ was found at lower energy than the monoexcitation ${}^4A_2 \rightarrow {}^4T_1(\text{F})$. In the Keggin anion, the ${}^4T_1(\text{P})$ appears at 12530 cm^{-1} above the ground state whereas the energy of the ${}^4T_1(\text{F})$ is 13711 cm^{-1} . For $[\text{CoCl}_4]^{2-}$, the corresponding energies of ${}^4T_1(\text{P})$ and ${}^4T_1(\text{F})$ are 7564 and 11049 cm^{-1} , respectively.

An approximate solution to this problem can be obtained by using ligand field theory to evaluate the necessary integrals.²³ We should mention that oxo ligands generate a weak field on the d^7 ion, and this means that the crystal field is lower than electron–electron repulsion. This situation arises when the crystal field is not strong enough to neglect electron–electron interactions and, consequently, states of the same symmetry will interact strongly. Defining Δ as the energy gap between orbitals e and t_2 and the Racah parameters as A, B, and C and referring the multiplet energies to the energy of the ground state 4A_2 , the matrix elements of the interaction matrix can be written as

4T_1	$e^3t_2^4 ({}^3T_1)$	$e^2 ({}^3A_2) t_2^5$
$e^3t_2^4 ({}^3T_1)$	$\Delta + 12B$	6B
$e^2 ({}^3A_2) t_2^5$	6B	$2\Delta + 3B$

Diagonalizing this matrix we directly get the energy for the transitions ${}^4A_2 \rightarrow {}^4T_1(\text{P})$ and ${}^4A_2 \rightarrow {}^4T_1(\text{F})$. According to the discussion in ref 23a, the multiplet energies calculated from the energies of the nonredundant single determinants in DFT can be set equal to the corresponding diagonal matrix elements above. Thus, a rough estimate of the two unknown parameters Δ and B can be easily obtained from the already computed DFT multiplet energies:

$$\Delta = E\{e^3t_2^4({}^3T_1); {}^4T_2\}$$

$$12B = E\{e^3t_2^4({}^3T_1); {}^4T_1\} - E\{e^3t_2^4({}^3T_1); {}^4T_2\}$$

The more the ligand field theory is appropriate, the more accurate is this approximate procedure. One major assumption of ligand field theory is that it only considers the metal atom and it does not take into account ligand effects. Thus, a major requirement for applying the above approximations

(23) (a) Ballhausen, C. J. *Introduction to ligand Field Theory*; McGraw-Hill: London, 1962. (b) Griffith, J. S. *The Theory of Transition Metal Ions*; University Press: Cambridge, 1961.

Table 2. State Energies, Crystal Field Parameters Δ and $12B$, and Crystal Field Transition Energies^a

	[CoW ₁₂ O ₄₀] ⁶⁻	[CoCl ₄] ²⁻
$ t_2^4(^3T_1)e^3;^4T_1\rangle$	13711	11049
$ t_2^4(^3T_1)e^3;^4T_2\rangle$	7126	4249
$ t_2^3e^4;^4A_2\rangle$	0	0
Δ	7126	4249
$12B$	6585	6800
$E(^4A_2 \rightarrow ^4T_1(P))$	18274	14050
$E(^4A_2 \rightarrow ^4T_1(F))$	11335	7197

^a All values in cm⁻¹.

is that the multiplets should have a pure metal character. The reader can observe in Figure 2 how the molecular orbitals involved, *e* and *t*₂, are quite localized on the cobalt center, the localization being somewhat higher in the [CoCl₄]²⁻ anion. The estimate for the electrostatic off-diagonal element $\langle e^3t_2(^3T_1);^4T_1|G|e^2(^3A_2)t_2^5;^4T_1\rangle = 6B$, where *G* is the electron–electron repulsion operator, is therefore acceptable.

Applying the procedure outlined above, we obtained the energies for ⁴T₁(P) and ⁴T₁(F) that are shown in Table 2. It is worth mentioning that the doubly excited state, ⁴T₁(P), appears now higher in energy than the singly excited state ⁴T₁(F), that is, we reproduce the correct order as obtained by MCSCF calculations.¹¹ For the Keggin anion, the transition to the ⁴T₁(P) is found at 18274 cm⁻¹. The experimental signal, on the other hand, was found at 15730 cm⁻¹. For [CoCl₄]²⁻, the computed value of 14050 cm⁻¹ compares quite well with the experimental signal at 14300 cm⁻¹. The results obtained for the [CoCl₄]²⁻ system were in better agreement with the experimental results because of the greater metal character of the molecular orbitals. The putative Jahn–Teller distortion in the e²t₂⁵ configuration is not expected to change these results significantly, since it only affects the *t*₂ orbital. The transition to the ⁴T₁(F) state is found at 11335 cm⁻¹ for the Keggin anion and at 7197 cm⁻¹ for the [CoCl₄]²⁻ anion.

Summary and Conclusions. Here, we report the first attempt to use DFT calculations to interpret the electronic spectrum of [Co^{II}W₁₂O₄₀]⁶⁻, a molecule with a rather complicated electronic structure. The calculations were carried out using the Δ SCF method proposed by Ziegler et al., a method that has been used to study several systems and which has provided good results. The study has been limited to transitions in which d orbitals of the Co atom take part. In complete agreement with the interpretation made on the basis of crystal field theory, the lowest excitation transition was found to correspond to the dipole forbidden ⁴A₂ → ⁴T₂ transition. In agreement with experimental assignments, the calculations suggest that the first strong band

(7000–9000 cm⁻¹) may be ascribed to Co d–d transitions, but it is worth noting that superposed to these transitions there are charge transfer transitions between d Co → W orbitals. The relatively low energy of these transitions is related to the small energy gap between the d Co orbital of symmetry *t*₂ and the unoccupied band of the d W orbitals. The calculations have also shown the importance of Jahn–Teller distortions in the excited configurations studied. Calculations were also carried out on the related [CoCl₄]²⁻ ion. With the exception of the consequences derived from a smaller splitting of d Co orbitals because of the weaker field generated by the Cl⁻ ligands, no significant differences were observed between the d–d spectra of [CoCl₄]²⁻ and of the more complex Keggin anion. The energies computed for the lowest electric dipole forbidden and electric dipole allowed transitions of 2700 and 4900 cm⁻¹ agree very well with the bands between 2000 and 4100 cm⁻¹ and between 4450 and 7000 cm⁻¹. This important coincidence comes about when Jahn–Teller distortions are considered for the excited states. There is less coincidence for the O → Co charge transfer band assigned to the band that originates at 26000 cm⁻¹ and which, according to our calculations, is shifted 5000 cm⁻¹ toward the UV region. This result, together with the low energies found for the excited configurations corresponding to the promotion of one electron from orbitals 33t₂(Co) to 19e(W), suggests that d Co orbitals are excessively shifted toward the d W band. And finally, the energy of the bielectronic transition ⁴A₂ → ⁴T₁(P) was estimated using an approximate procedure based on ligand field theory.

We should finally comment that in the present work we have been capable of reporting a semiquantitative analysis of the electronic spectrum of [Co^{II}W₁₂O₄₀]⁶⁻; nevertheless, we want to remark that the nice agreement between experimental and theoretical data should be viewed cautiously, since this agreement may be due to a cancellation of errors. We have explained, for example, that the Δ SCF method itself is unable to correctly describe states of the same symmetry, like the ⁴T₁(F) and ⁴T₁(P), because of the coupling between these two Co states. But, we must take into account that these two states may also mix with charge transfer states of the same symmetry and that similar couplings may occur in the quadruplets of symmetry T₂ or symmetry E in the D_{2d} structures.

Acknowledgment. All calculations have been carried out on workstations purchased with funds provided by the DGICYT of the Government of Spain and by the CIRIT of Generalitat of Catalunya (Grants PB98-0916-C02-02 and SGR99-0182).

IC0110676