Inorg. Chem. **2004**, *43*, 2689–2694

Inorganic Chemistry
Article

A New Heptanuclear Cobalt(II) Cluster Encapsulated in a Novel Heteropolyoxometalate Topology: Synthesis, Structure, and Magnetic Properties of $[Co_7(H_2O)_2(OH)_2P_2W_{25}O_{94}]^{16-}$

Juan M. Clemente-Juan, Eugenio Coronado,* Alicia Forment-Aliaga, José R. Galán-Mascarós, Carlos Giménez-Saiz, and Carlos J. Gómez-García

Instituto de Ciencia Molecular, Universidad de Valencia, C/Doctor Moliner 50,
46100 Burjassot, Spain

Received December 26, 2003

The synthesis and the structural and magnetic characterization of a novel heptanuclear cobalt cluster encapsulated in a heteropolyoxotungstate is reported. This complex shows how it is possible to control the nuclearity of the Co clusters formed in a tungstate solution by slightly changing the synthetic conditions, and the relevance of pH in this regard. This heptanuclear complex $[Co_7(H_2O)_2(OH)_2P_2W_{25}O_{94}]^{16-}$ (**Co**$_7$) crystallizes in the triclinic space group $P\bar{1}$ ($a = 12.3403(6)$ Å, $b = 22.5966(11)$ Å, $c = 23.2645(12)$ Å, $\alpha = 68.7830(11)°$, $\beta = 83.7981(12)°$, $\gamma = 78.5423(13)°$, $V = 5922.4(5)$ Å^3, $Z = 2$) and is formed by six CoO_6 octahedra from two Co_3 trimers sustained by Keggin trivacant fragments held together by the bridge $[CoW_7O_{26}(OH)_2]$, which contains one tetrahedral CoO_4 unit. The magnetic properties of the complex are discussed on the basis of the coexistence of ferro- and antiferromagnetic interactions and fitted according to an anisotropic exchange model in the low-temperature regime.

Introduction

The current interest of polyoxometalates in molecular magnetism is related to the ability of this class of inorganic compounds to provide excellent examples of magnetic clusters. These metal-oxide clusters have shown to be especially valuable for the study of magnetic interactions in discrete systems because many of their diamagnetic structures permit the inclusion of well-isolated magnetic clusters with various nuclearities and definite topologies and geometries.[1] Thanks to the rigidity imposed by the heteropoly ligands, this family of complexes constitutes a unique example in coordination chemistry wherein the sign, intensity, and nature of the exchange interaction can be tuned with ease. They are between the small molecular systems and the bulk state and can serve as model systems for in-depth understanding of the magnetic exchange interactions.[2]

A good example of this ability is provided by the complexes obtained from the lacunary trivacant Keggin ligands $[XW_9O_{34}]^{n-}$ or Wells−Dawson ligands $[X_2W_{15}O_{56}]^{n-}$ and divalent or trivalent paramagnetic transition-metal ions. In these, magnetic clusters with nuclearities comprised between 3 and 9 can be created.[3−7,11,12] Most of them show ferromagnetic interactions, or a coexistence of ferromagnetic and antiferromagnetic interactions, together with large

---

* Author to whom correspondence should be addressed. E-mail: eugenio.coronado@uv.es.

(1) (a) Müller, A.; Peters, F.; Pope, M. T.; Gatteschi, D. *Chem. Rev.* **1998**, *98*, 239−271. (b) Clemente-Juan, J. M.; Coronado, E. *Coord. Chem. Rev.* **1999**, *193−195*, 361−394.

(2) (a) Gatteschi, D. *Adv. Mater.* **1994**, *6*, 635−645. (b) *Magnetic Molecular Materials*; Gatteschi, D., Kahn, O., Miller, J. S., Palacio, F., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991.

(3) Gómez-García, C. J.; Coronado, E.; Ouahab, L. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 649−651.

(4) Clemente-Juan, J. M.; Andres, H.; Borrás-Almenar, J. J.; Coronado, E.; Güdel, H. U.; Aebersold, M.; Kearly, G.; Büttner, H.; Zolliker, M. *J. Am. Chem. Soc.* **1999**, *121*, 10021−10027.

(5) Clemente-Juan, J. M.; Coronado, E.; Galán-Mascarós, J. R.; Gómez-García, C. J. *Inorg. Chem.* **1999**, *38*, 55−63.

(6) (a) Finke, R. G.; Droege, M. W.; Domaille, P. J. *Inorg. Chem.* **1987**, *26*, 3886−3896. (b) Andres, H.; Clemente-Juan, J. M.; Aebersold, M.; Güdel, H. U.; Coronado, E.; Büttner, H.; Kearly, G.; Melero, J.; Burriel, R. *J. Am. Chem. Soc.* **1999**, *121*, 10028−10034.

(7) (a) Weakley, T. J. R. *J. Chem. Soc., Chem. Commun.* **1984**, 1406−1407. (b) Galán-Mascarós, J. R.; Gómez-Garc×c1a, C. J.; Borrás-Almenar, J. J.; Coronado, E. *Adv. Mater.* **1994**, *6*, 221−223.

(8) (a) Baker, L. C. W.; McCutcheon, T. P. *J. Am. Chem. Soc.* **1956**, *78*, 4503−4510. (b) Andres, H.; Aebersold, M.; Güdel, H. U.; Clemente-Juan, J. M.; Coronado, E.; Büttner, H.; Kearley, D.; Zolliker, M. *Chem. Phys. Lett.* **1998**, *289*, 224−230.

(9) Clemente-Juan, J. M.; Coronado, E.; Gaita-Ariño, A.; Giménez-Saiz, C.; Chaboussant, G.; Güdel, H. U.; Burriel, R.; Mutka, H. *Chem.−Eur. J.* **2002**, *8*, 5701−5708.

(10) Tourné, C. M.; Tourné, G. F.; Zonnevijlle, F. *J. Chem. Soc., Dalton Trans.* **1991**, 143−155.

(11) Andres, H.; Clemente-Juan, J. M.; Basler, R.; Aebersold, M.; Güdel, H. U.; Borrás-Almenar, J. J.; Gaita-Ariño, A.; Coronado, E.; Büttner, H.; Janssen, S. *Inorg. Chem.* **2001**, *40*, 1943−1950.

10.1021/ic0354872 CCC: \$27.50

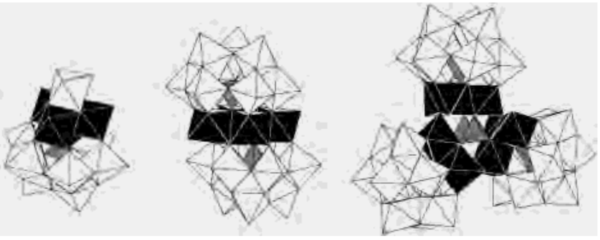

Figure 1. (From left to right) Structure of the polyanions: $[Ni_3(H_2O)_3(PW_{10}O_{39})H_2O]^{2-}$ (**Ni$_3$**), $[Ni_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ (**Ni$_4$**), and $[Ni_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]^{16-}$ (**Ni$_9$**), highlighting the NiO_6 (black) and PO_4 (gray) polyhedra.

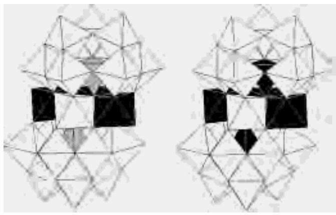

Figure 2. Structure of the polyanions $[Co_3W(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ (**Co$_3$W**) and $[Co_3W(H_2O)_2(CoW_9O_{34})_2]^{12-}$ (**Co$_5$**), highlighting the CoO_n (black) and ZnO_4 (gray) polyhedra.

magnetic anisotropies. Thus, by reaction of the trivacant Keggin ligand $[PW_9O_{34}]^{n-}$ with Ni(II), a complete family of magnetic clusters with nuclearities 3, 4, and 9 were obtained: $[Ni_3(H_2O)_3(PW_{10}O_{39})H_2O]^{2-}$ (**Ni$_3$**),[3] $[Ni_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ (**Ni$_4$**),[4] and $[Ni_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]^{16-}$ (**Ni$_9$**).[5] These molecular complexes are formed by 1, 2, or 3 $[PW_9O_{34}]^{n-}$ ligands (Figure 1). The Co(II) analogues with nuclearities 4 (**Co$_4$**)[6] and 9 (**Co$_9$**)[7] are also known. With this interesting magnetic ion other related magnetic clusters with nuclearities 2 (**Co$_2$**),[8] 3 (**Co$_3$W**),[10,9] and 5 (**Co$_5$**)[11] have also been reported. The former (**Co$_2$**) comes from the substitution in the Keggin structure of one of the tungstens by octahedral Co(II) and of the central heteroatom by tetrahedral Co(II), while **Co$_3$W** and **Co$_5$** exhibit the typical M_4 structure (M = Cr, Mn, Fe, Co, Ni, Cu, and Zn)[12] in which one of the M positions is occupied by W and the tetrahedral site of the $[XW_9O_{34}]^{n-}$ ligand is occupied by Zn(II) or Co(II) (Figure 2). Still, the Co(II) analogue of the **Ni$_3$** has not been synthesized yet. In an attempt to prepare this compound, we have obtained crystals of a novel structural type of polyoxometalate that contains an unprecedented magnetic cluster with seven exchange-coupled cobalt(II) ions. Here, we describe the synthesis, structure, and magnetic properties of this new magnetic compound.

Experimental Section

Synthesis: $K_7Na_7[Co_7(H_2O)_2(OH)_2P_2W_{25}O_{94}]Co(H_2O)_4 \cdot 13H_2O$ (Co$_7$). A solution of 1.29 g (5.18 mmol) of $Co(OOCCH_3)_2 \cdot 4H_2O$ in 35 mL of water was added to 60 mL of an aqueous solution containing 5.4 g (16.37 mmol) of $Na_2WO_4 \cdot 2H_2O$ and 0.22 g (1.55 mmol) of Na_2HPO_4 with pH ajusted to 5.4 with acetic acid. The resulting dark purple solution (pH = 5.5) was refluxed for 2 h and hot-filtered, and then 2.24 g of $K(OOCCH_3)$ was added to the filtrate while hot. After several days a mixture of red purple cubic-shaped crystals of Co_4 (≈12% yield) and violet platelike crystals of Co_7 (≈18% yield) were collected by filtration and separated by hand.

Table 1. Crystal and Structure Refinement Data for $K_7Na_7[Co_7(H_2O)_2(OH)_2P_2W_{25}O_{94}]Co(H_2O)_4 \cdot 13H_2O$ (**Co$_7$**)

empirical formula	$H_{40}Co_8K_7Na_7O_{115}P_2W_{25}$
M_w	7444.58
T (K)	293(2)
λ (Å)	0.71069
space group	$P\bar{1}$
a (Å)	12.3403(6)
b (Å)	22−5966(11)
c (Å)	23.2645(12)
α (deg)	68.7830(11)
β (deg)	83.7981(12)
γ (deg)	78.5423(13)
V (Å^3)	5922.4(5)
Z	2
ρ_{calc} (g cm^{-3})	4.125
μ (mm^{-1})	25.659
F(000)	6532
2θ range (deg)	3.16−61.14
reflections/unique	71658/35662
R_{int}	0.1983
reflections [$I > 2\sigma(I)$]	12282
parameters	910
final R indices for $I > 2\sigma(I)$	R1^a = 0.0615, wR2^b = 0.1156

[a] $R1 = \sum(F_o - F_c)/\sum(F_o)$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0161)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.

X-ray Data Collection and Structure Refinement. A violet, platelike single crystal with dimensions 0.29 × 0.05 × 0.02 mm^3 was mounted on a glass fiber for indexing and intensity data collection at room temperature on a Siemens SMART CCD diffractometer equipped using graphite monochromated Mo Kα radiation (λ = 0.71069 Å) with a nominal distance of 4.0 cm. Of the 71658 reflections collected (2θ = 61.14°), 35662 unique reflections (R_{int} = 0.198) were considered observed ($I > 2\sigma(I)$). An empirical absorption correction was applied by using the SADABS program[13] based on the Laue symmetry of the reciprocal space. Direct methods were used to solve the structure and to locate the heavy atoms (SIR97).[14] Then, the remaining atoms were found from successive difference maps and refined against F^2 with a full-matrix least-squares agorithm using SHELXL-97[15] and the WinGX (1.64) software package.[16] The final cycle of refinement, including the atomic coordinates, anisotropic thermal parameters (all metal atoms and phosphorus), and isotropic thermal parameters (all oxygen atoms), converged at R1 = 0.0615 and wR2 = 0.1156 [$I > 2\sigma(I)$]. In the final difference map the deepest hole was −3.226 e Å^{-3} and the highest peak 5.215 e Å^{-3}. Crystallographic data are summarized in Table 1. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-413578.

---

(12) (a) Weakley, T. J. R.; Evans, H. T.; Showell, J. S.; Tourné, G. F.; Tourné, C. M. *J. Chem. Soc., Chem. Commun.* **1973**, 139−140. (b) Evans, H. T.; Tourné, C. M.; Tourné, G. F.; Weakley, T. J. R. *J. Chem. Soc., Dalton Trans.* **1986**, 2699−2705. (c) Weakley, T. J. R.; Finke, R. G. *Inorg. Chem.* **1990**, *29*, 1235−1241. (d) Gómez-Garc×c1a, C. J.; Borrás-Almenar, J. J.; Coronado, E.; Ouahab, L. *Inorg. Chem.* **1994**, *33*, 4016−4022.

(13) Sheldrick, G. M. *SADABS*; Siemens Analytical X-Ray Instrument Division: Madison, WI, 1995.

(14) Altomare, A.; Burla, M. C.; Camali, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. SIR97. *J. Appl. Crystallogr.* **1999**, *32*, 115−119.

(15) Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.

(16) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837−838.

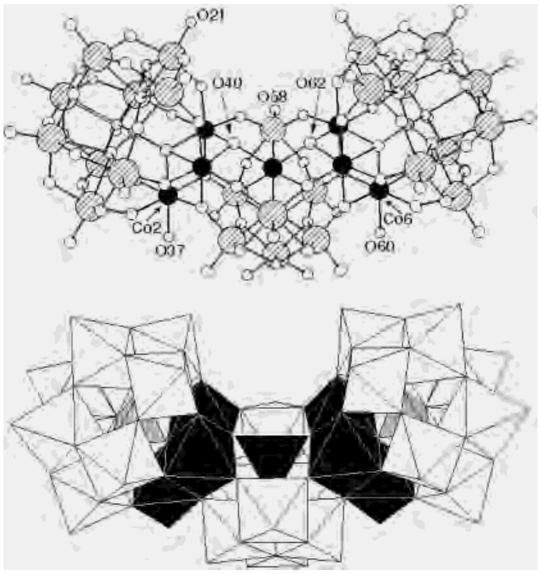

Figure 3. Structure of the $[Co_7(H_2O)_2(OH)_2P_2W_{25}O_{94}]^{16-}$ polyanion (**Co**$_7$).

Magnetic Properties. Variable temperature susceptibility measurements were carried out in the temperature range 2−300 K at a magnetic field of 0.1 T on a polycrystalline sample with a magnetometer (Quantum Design MPMS-XL-5) equipped with a SQUID sensor. The susceptibility data were corrected from the diamagnetic contributions as deduced by using Pascal's constant tables.

Results and Discussion

Synthesis and Structure. The use of the Keggin trivacant fragment $[PW_9O_{34}]^{9-}$ as a ligand has shown to provide a variety of well-insulated magnetic clusters of different topologies and nuclearities but with predictable magnetic properties. The key parameter in these syntheses has been the pH, while the relative amount of reagents determines the yields more than the species formed. Thus, crystals of **Ni**$_3$, **Ni**$_4$, and **Ni**$_9$ have been respectively isolated at pHs of 6.5, 6.9, and 7.5 from an aqueous mixture containing $[PW_9O_{34}]^{9-}$ and Ni(II).[5] The trend seems to be that at lower pH the equilibria are displaced toward the lower nuclearities. This trend is maintained in Co(II) where **Co**$_4$ and **Co**$_9$ are obtained at pHs of 6.5 and 7.1. However, the trinuclear Co(II) analogue to **Ni**$_3$ has not been obtained so far. In this work we have carefully studied the influence of the pH in the reaction between $[PW_9O_{34}]^{9-}$ and Co(II). We observed that at pH < 5 the monosubstituted species is obtained $[Co(H_2O)PW_{11}O_{39}]^{5-}$ (**Co**$_1$), while at pH > 6 **Co**$_4$ is the predominant species. When the pH was ajusted to 5.4, a mixture of crystals of the **Co**$_4$ salt and of a new phase were collected. The novel phase appeared as violet plate-shaped crystals clearly distinguishable from the purple cubic-shaped crystals of the **Co**$_4$ salt and can be easily separated by hand (**Co**$_7$/**Co**$_4$ ratio 3/2).

According to the X-ray diffraction analysis, this phase can be formulated as $K_7Na_7[Co_7(H_2O)_2(OH)_2P_2W_{25}O_{94}]Co(H_2O)_4\cdot 13H_2O$ (**Co**$_7$). This salt crystallizes in the triclinic space group $P\bar{1}$ (Table 1). The structure exhibits the presence of an unprecedented magnetic polyoxometalate (Figure 3) formed by the condensation of two Keggin structures, B-α-$[Co_3PW_9O_{40}]$ and a novel bridging cluster $[CoW_7O_{26}(OH)_2]$ (Figure 4). The Keggin subunits are formed by the trivacant $[PW_9O_{34}]^{9-}$ phosphotungstate ligand and three edge-sharing CoO_6 octahedra. The coordination around the cobalt ions is completed by two hydroxo bridges, which are shared with the central bridging unit, and two terminal water molecules. The central cluster contains a CoO_4 tetrahedron and seven edge-sharing WO_6 octahedra. This tetrahedron is formed by two bridging oxygens from the central structure $[W_7O_{26}]$ and by two OH bridging groups from the two Co_3O_{13} triads (Figure 3). Focusing on the heptameric magnetic cluster $[Co_7O_{24}(H_2O)_2(OH)_2]$, we observe that it is constituted by two triangular Co_3O_{12} units, connected to each other by sharing corners with a central CoO_4 tetrahedron (Figure 6).

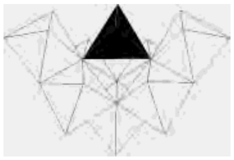

Figure 4. Structure of the bridging fragment $[CoW_7O_{26}(OH)_2]$ in the $[Co_7(H_2O)_2(OH)_2P_2W_{25}O_{94}]^{16-}$ polyanion (**Co**$_7$).

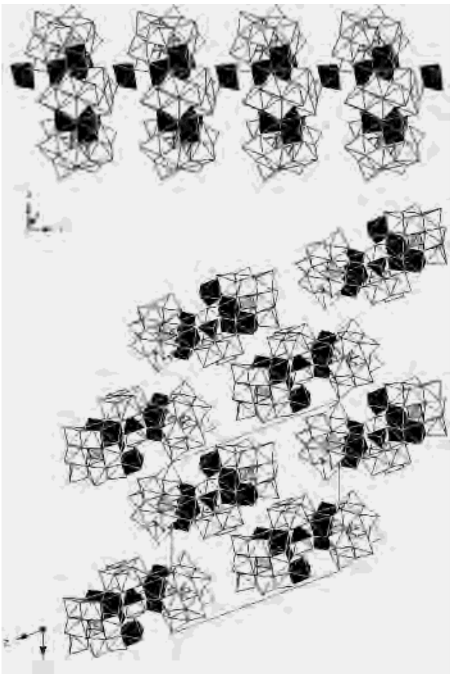

Figure 5. View of the $\{[Co_7(H_2O)_2(OH)_2P_2W_{25}O_{94}]Co(H_2O)_4\}_\infty$ chains (top) in the salt $K_7Na_7[Co_7(H_2O)_2(OH)_2P_2W_{25}O_{94}]Co(H_2O)_4\cdot 13H_2O$ (**Co**$_7$) and their packing on the *bc* plane (bottom).

The crystal packing reveals that the polyoxometalates are not discrete but form chains running parallel to the direction of the *a* axis (Figure 5). Every polyanion is linked to the two nearest polyanions via an octahedral CoO_6 unit acting as a bridge. This cobalt is coordinated to four water molecules, a bridging oxygen from a Keggin unit, and a bridging oxygen from the tetrahedral CoW_7 unit. Still, from the magnetic point of view the heptameric cluster core Co_7O_{28} is expected to be insulated since the diamagnetic tungstate framework keeps this cluster well-separated from the peripheral CoO_6 linker. In fact, these superexchange

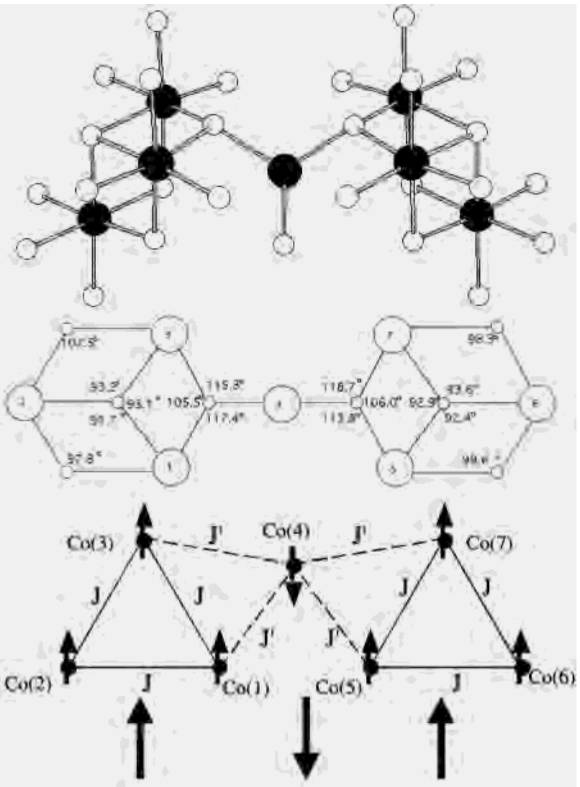

Figure 6. Structure magnetic cluster $[Co_7O_{28}]$ in the $[Co_7(H_2O)_2(OH)_2P_2W_{25}O_{94}]^{16-}$ polyanion (top), connectivity diagram (center), and exchange scheme (bottom). Distances (Å): $d(1-2) = 3.223$; $d(1-3) = 3.297$; $d(2-3) = 3.218$; $d(5-7) = 3.313$; $d(5-6) = 3.242$; $d(6-7) = 3.226$; $d(4-1) = 3.467$; $d(4-3) = 3.432$; $d(4-7) = 3.468$; $d(4-5) = 3.431$.

pathways involve at least O−W−O bridges and rather long cobalt-to-cobalt distances (minimum distance of 5.64 Å, Co3−Co8, with the rest over 6.5 Å), so they are expected to be negligible compared to the superexchange promoted by the oxo Co−O−Co bridges inside the Co_7 clusters.

Bond-valence sum calculations have been made to confirm the protonated oxygens in the structure. There are only two terminal oxygen ligands, O37 and O60, which are bonded to Co (Co2 and Co6); these terminal ligands are water molecules as indicated by these calculations (the bond valences for oxygens O37 and O60 are 0.33 and 0.29, respectively, indicating diprotonation). Using the same method allows the identification of the μ_3-bridging oxygens between the tetrahedral Co and the triads as OH groups; the bond valences for these O40 and O62 are 1.17 both. The eighth Co which connects one cluster to another has four terminal oxygens, O99, O100, O101, and O102, which correspond to four water molecules, as indicated by the bond-valence sum calculations (0.31, 0.29, 0.26, and 0.20, respectively).

A similar structural motif has been recently reported in the series of clusters of general formula $[(M_3XW_9O_{34}(H_2O))_2(XW_6O_{26})]^{17-}$ (M = Mn(II), Co(II), Ni(II); X = P(V), As(V)),[17,18] including a mix-metal tungstophosphate containing Ni(II) and Mn(II), $[(Ni_2MnPW_9O_{34}(H_2O))_2(PW_6O_{26})]^{17-}$ In these cases the tetrahedral positions are occupied by diamagnetic As(V) or P(V), instead of paramagnetic centers. Structurally, the bridging cluster $[CoW_7O_{26}(OH)_2]$ in our polyoxometalate has one extra tungsten atom compared to the $[XW_6O_{26}]$ frameworks. Moreover, these derivatives contain isolated clusters while the **Co_7** compound can be described as polyoxometalate infinite chains linked by external Co(II) ions.

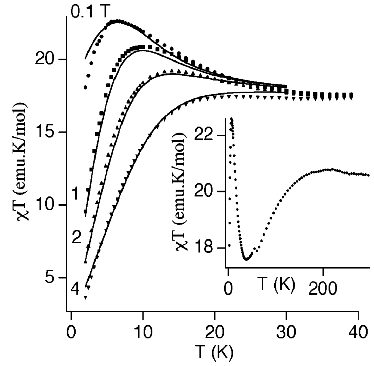

Figure 7. Thermal behavior of $\chi_m T$ for the salt $K_7Na_7[Co_7(H_2O)_2(OH)_2P_2W_{25}O_{94}]Co(H_2O)_4{\cdot}13H_2O$ (**Co_7**) at different fields: 0.1, 1, 2, and 4 T. The solid lines represent the best fitting with the anisotropic model used.

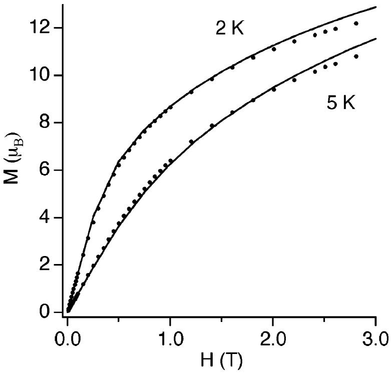

Figure 8. Magetization vs field for the salt $K_7Na_7[Co_7(H_2O)_2(OH)_2P_2W_{25}O_{94}]Co(H_2O)_4{\cdot}13H_2O$ (**Co_7**) at 2 and 5 K. The solid lines represent the best fitting with the anisotropic model used.

Magnetic Properties. The magnetic behavior of **Co_7** is displayed in Figure 7 as a plot of the product $\chi_m T$ vs T and in Figure 8 as a plot of the isothermal magnetization vs H measured from 0 to 5 T at 2 and 5 K. At room temperature $\chi_m T$ has a value of 20.5 emu K mol^{-1} and it slightly decreases upon cooling and reaches a minimum of 17.6 emu K mol^{-1} at ca. 35 K. Below this temperature, $\chi_m T$ shows an increase and reaches a maximum of 22.6 emu K mol^{-1} at 6 K followed by a sharp decrease at lower temperatures. The exchange network of this cobalt(II) cluster involves two kinds of exchange pathways, namely, J and J'. J accounts for the interactions between the octahedral Co's located inside each Co_3 triangle and J' for the interactions occurring between octahedral and tetrahedral cobalt ions (Figure 6). The former kind of interaction is well-documented in polyoxometalate chemistry and has shown to be ferromagnetic as it involves edge-sharing CoO_6 octahedra leading to angles Co−O−Co close to 90°, which favors the orthogonality of the magnetic orbitals (Figure 6). In contrast, the second kind of interaction

---

(17) Mbomekalle, I. M.; Keita, B.; Nierlich, M.; Kortz, U.; Berthet, P.; Nadjo, L. *Inorg. Chem.* **2003**, *42*, 5143−5152.

(18) Ritorto, M. D.; Anderson, T. M.; Neiwert, W. A.; Hill, C. L. *Inorg. Chem.* **2004**, *43*, 44−49.

occurs between octahedral and tetrahedral Co ions sharing a common OH ligand. As the bridging angle Co−O−Co is around 120°, the antiferromagnetic exchange pathways are dominant and J' is expected to be antiferromagnetic (Figure 6). In a qualitative way this simple picture allows one to describe Co_7 as a ferrimagnetic cluster in which the magnetic moments of the two ferromagnetic Co_3 clusters are oriented in parallel due to the antiferromagnetic coupling with the spin $S = {}^3/_2$ of the central cobalt.

Let us now analyze the experimental results using a quantitative approach. High-spin octahedral Co(II) is an orbitally degenerate ion with a $^4T_1$ ground electronic term. Because of spin−orbit coupling and the low-symmetry crystal field, this term splits into six Kramers doublets. At low temperature (below 30−40 K) only the lowest Kramers doublet is significantly populated so that the exchange interaction between two octahedral Co(II) ions can be conveniently described by assuming a coupling between these fully anisotropic Kramers doublets with fictitious spins $^1/_2$. The tetrahedral Co(II) ion has a $^4A_2$ ground state, which can be described as a spin-only $S = {}^3/_2$.[19] Expressing the spin anisotropy of octahedral Co(II) in terms of an exchange anisotropy, the Hamiltonian that describes the exchange interaction within the **Co**$_7$ cluster can be written as

$$H = -2 \sum_{\alpha=x,y,z} \{J_\alpha[\hat{S}_1^\alpha\hat{S}_2^\alpha + \hat{S}_1^\alpha\hat{S}_3^\alpha + \hat{S}_2^\alpha\hat{S}_3^\alpha + \hat{S}_5^\alpha\hat{S}_6^\alpha + \hat{S}_5^\alpha\hat{S}_7^\alpha + \hat{S}_6^\alpha\hat{S}_7^\alpha] + J'_\alpha[\hat{S}_1^\alpha\hat{S}_4^\alpha + \hat{S}_3^\alpha\hat{S}_4^\alpha + \hat{S}_4^\alpha\hat{S}_5^\alpha + \hat{S}_4^\alpha\hat{S}_7^\alpha]\} \quad (1)$$

where $S_1 = S_2 = S_3 = S_5 = S_6 = S_7 = {}^1/_2$, $S_4 = {}^3/_2$, J_α are the exchange components between the octahedral oxo-coordinated Co(II) ions, and J'_α are the exchange components between the octahedral and tetrahedral oxo-coordinated Co(II) ions.

In this model we are neglecting a possible zero-field splitting of the $^4A_2$ in the slightly distorted tetrahedral site. Furthermore, the encapsulated Co_7O_{28} magnetic unit is shielded from its surrounding and we can thus neglect any intercluster exchange interaction (see above). The presence of the eighth external octahedral Co(II) contribution has been taken into account by adding the Curie constant of a distorted octahedric Co(II) with $S = {}^1/_2$ and a typical g value of 4.33. In eq 1 the subscripts 1, 2, 3, 4, 5, 6, and 7 refer to the Co(II) ions in Figure 6. To evaluate the magnetic properties, the exchange Hamiltonian in eq 1 has been expressed in terms of irreducible tensor operators (ITOs) and solved by means of a general numerical formalism which is valid for any spin cluster. These calculations have been supported by an efficient computing program that allows to treat spin clusters formed by an arbitrary number of magnetic sites, N, with spins S_1, S_2, ..., S_N where each local spin S_i can have a different value.[20] In this model we have considered an isotropic tetrahedral Co(II) with an isotropic g_{T_d} value, which has been fixed to 2. On the other hand, an axial anisotropy has been assumed for the effective spin of octahedral Co(II) leading to axial J and g parameters. Finally, the exchange anisotropy has been assumed to be equal for J and J'. With these assumptions the number of parameters used in the fitting procedure has been reduced to 5. We have fitted only the low-temperature region, wherein the population of higher Kramers doublets of octahedral Co(II) ion is negligible. The set of parameters that provides the best fit is reported in Table 2.

Table 2. Magnetic Parameters for **Co**$_7$

parameters	estimated value	comments
J_z	9.0 cm^{-1}	F exchange
J'_z	−4.7 cm^{-1}	AF exchange
$J_{xy}/J_z = J'_{xy}/J'_z$	0.52	
g_z	5.2	Co(II) ions: 1,2,3,5,6,7
g_{xy}	4.7	Co(II) ions: 1,2,3,5,6,7
g_{T_d}	2	Co(II) ions: 4

This model reproduces the low-temperature magnetic behavior of the polyoxometalate compound (see Figure 7). The validity of the anisotropic exchange model developed here is further confirmed by the low-temperature behavior of the magnetization as a function of the external magnetic field (Figure 8). The parameters deduced from susceptibility analysis provide a good description of this experiment. Although the large number of parameters and the limited information provided by the magnetic measurements prevent one from obtaining accurate values of the exchange parameters, it is remarkable to observe that this model leads to the expected trends for the magnetic interactions. Thus, the exchange interaction between octahedral Co(II) ions is positive and therefore ferromagnetic, while that describing the interaction between octahedral and tetrahedral Co(II) ions is negative and therefore antiferromagnetic. Furthermore, magnetic measurements have also shown to be sensitive to the presence of anisotropy. In fact, a fully isotropic exchange model is completely unable to reproduce the experiments.

Finally, the nature and magnitude of the exchange parameters of the title compound are similar to those previously reported for the analogous cobalt clusters encapsulated by polyoxometalates (Table 3). Thus, the ferromagnetic coupling, $J = 9.0$ cm^{-1}, is in the range of values reported for the edge-sharing O_h−O_h interaction in the other POM complexes (from 8.4 to 12.9 cm^{-1}), in full agreement with the rigidity imposed by the polyoxotungstate framework (the Co(O_h)−Co(O_h) distances and Co(O_h)−O−Co(O_h) angles are very close in all these compounds). On the other hand, the exchange interaction between octahedral and tetrahedral oxo-coordinated Co(II) ions (O_h−T_d interaction) has been found to be antiferromagnetic and anisotropic, as in the other related compounds **Co**$_2$ and **Co**$_5$. Still, this exchange interaction is weaker in **Co**$_7$ (−4.7 cm^{-1}, compared to −17.9 cm^{-1} in **Co**$_2$ and −10 cm^{-1} in **Co**$_5$). Such a difference has a structural origin. In fact, in **Co**$_7$ the number of octahedral Co ions that are connected to the central Co(T_d) is larger than in the other two cases (four compared to one in **Co**$_2$ and three in **Co**$_5$). Further, the angles Co(O_h)−O−Co(T_d) are smaller in **Co**$_7$ and closer to the orthogonality value (ca. 114°, compared to 125° in **Co**$_2$ and 123° in **Co**$_5$).

---

[19] Carlin, R. L. *Magnetochemistry*; Springer: Berlin, 1986.

[20] (a) Borrás-Almenar, J. J.; Clemente-Juan, J. M.; Coronado, E.; Tsukerblat, B. S. *Inorg. Chem.* **1999**, *38*, 6081−6088. (b) Borrás-Almenar, J. J.; Clemente-Juan, J. M.; Coronado, E.; Tsukerblat, B. S. *J. Comput. Chem.* **2001**, *22*, 985−991.

Table 3. Magnetic Characterization of Magnetic Clusters Containing Co(II) Coordinated by Polyoxotungstate Ligands[a]

polyoxometalate (magnetic cluster)	S_i	parameters (cm^{-1})	comments	connectivity[c]
$[\text{Co(H}_2\text{O)CoW}_{11}\text{O}_{39}]^{8-}$ ($\mathbf{Co_2O_9}$)	$^3/_2$ and "1/2"[b]	$J_z = -17.9$, $J_{xy}/J_z = 0.33$	AF anisotropic exchange	O_h-T_d
$[\text{WCo}_3(\text{H}_2\text{O})_2(\text{ZnW}_9\text{O}_{34})_2]^{10-}$ ($\mathbf{Co_3O_{14}}$)	"$^1/_2$"	$J_z = 10$, $J_y = 10.5$, $J_x = 1.7$	F anisotropic exchange	O_h-O_h
$[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$ ($\mathbf{Co_4O_{16}}$)	"$^1/_2$"	$J_z = 12$, $J'_z = 19$, $J_{xy}/J_z = 0.60$	F anisotropic exchange	O_h-O_h
$[\text{WCo}_3(\text{H}_2\text{O})_2(\text{CoW}_9\text{O}_{34})_2]^{12-}$ ($\mathbf{Co_5O_{18}}$)	$^3/_2$ and "$^1/_2$"	$J_z = 12.9$, $J'_z = -10$, $J_{xy}/J_z = 0.43$, $J'_{xy}/J'_z = 0.33$	coexistence of F and AF anisotropic exchange	O_h-O_h, O_h-T_d
$([\text{Co}_7(\text{H}_2\text{O})_2(\text{OH})_2\text{P}_2\text{W}_{25}\text{O}_{94}]^{16-}$ ($\mathbf{Co_7O_{28}}$)	$^3/_2$ and "$^1/_2$"	$J_z = 9$, $J'_z = -4.7$, $J_{xy}/J_z = 0.52$	coexistence of F and AF anisotropic exchange	O_h-O_h, O_h-T_d
$[\text{Co}_9(\text{OH})_3(\text{H}_2\text{O})_6(\text{HPO}_4)_2(\text{PW}_9\text{O}_{34})_3]^{16-}$ ($\mathbf{Co_9O_{36}}$)	"$^1/_2$"	$J_z = 8.4$, $J'_z = -12$, $J_{xy}/J_z = 0$, $J'_{xy}J'_z = 0$	coexistence of F and AF anisotropic exchange, Ising	O_h-O_h

[a] S_i are the local spin values of the interacting metal centers. (F = ferromagnetic; AF = antiferromagnetic). [b] Effective spin for octahedral Co(II). [c] All O_h-T_d polyhedra are sharing vertexes and all O_h-O_h polyhedra are sharing edges, except in the $\mathbf{Co}_9$ cluster where octahedra are sharing both vertexes and edges.

Conclusion

In this work we have reported a novel heteropolyanion which encapsulates an heptanuclear magnetic cluster of Co(II). The molecular complex, $\mathbf{Co}_7$, represents a new member in the series of cobalt(II) clusters based on the well-known $[\text{PW}_9\text{O}_{34}]^{9-}$ trivacant ligand. Two main points deserve to be emphasized: (i) From the structural point of view a novel magnetic polyoxometalate formed by two reconstituted PW_9Co_3 Keggin fragments united through a bridging polyoxotungstate framework $[\text{CoW}_7\text{O}_{26}(\text{OH})_2]^{10-}$ has been reported. This is the first time that this central unit has been found to work as a building block in magnetic heteropolyoxotungstates. Interestingly, in the solid state these molecular polyanions are linked together through a common Co(II) ion to form a chain structure. (ii) From the magnetic point of view $\mathbf{Co}_7$ exhibits an unprecedented magnetic topology leading to a ferrimagnetic cluster. In this system two ferromagnetic Co_3 clusters have their magnetic moments ferromagnetically oriented thanks to the antiferromagnetic coupling established between these clusters and the central spin $S = {}^3/_2$ coming from the tetrahedral Co(II). This example is one of the very few cases of polyoxometalate-based magnetic clusters with coexistence of ferro- and antiferromagnetic interactions and exchange anisotropy.

Acknowledgment. This work was supported by the European Union (TMR Molnanomag) and the Ministerio de Ciencia y Tecnología (Projects MAT2001-3507 and BQU-2002-01091). J.M.C.-J., J.R.G.-M., and C.G.-S. thank the MCyT for a Ramón y Cajal contract. A.F.-A. thanks the Universitat de València for a predoctoral fellowship.

Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0354872