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$[(Co(H_2O)_4)_2(H_2W_{12}O_{42})]_n^{6n-}$: A Novel Chainlike Heteropolyanion Formed by Paradodecatungstate and Cobalt(II) Ions

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Introduction

Heteropolyanions with the general formula $[X_xM_mO_y]^{q-}$ (M = W, Mo, Nb, V, ...; X = Si, P, B, Co, Fe, Cu, ...), known for well over a century, constitute a large fundamental class of inorganic compounds that in recent years have become of increasing interest and relevance to several disciplines due to their topological and electronic versatility.[1] Most of them have discrete clusterlike structures of definite sizes and shapes formed by closed and highly symmetrical networks of MO_6 octahedra sharing edges, corners, or faces.

Structures of extended heteropolyanions showing chain- or layerlike networks have been observed very rarely.[2,3] Taking advantage of the ability of polyanions to act as ligands, it is possible to form cation−polyanion complexes of increasing nuclearities which may exhibit low-dimensional structures. This is the case of the complex formed from the heteropolyanion $[UMo_{12}O_{42}]^{8-}$ and Th^{4+}, in which the polyanion acts as a hexadentate ligand forming chains of UMo_{12} units[2] linked by Th^{4+}. A second example[3] is provided by the complex formed from the isopolyanion $[Mo_8O_{27}]^{6-}$ and Eu^{3+}. In this case, two adjacent Mo_8O_{27} units are linked by two Eu^{3+} ions to give an infinite chain.

We report here a novel example of an extended heteropolyanion showing a chainlike structure: the cobalt-containing heteropolyanion $[(Co(H_2O)_4)_2(H_2W_{12}O_{42})]_n^{6n-}$. To our knowledge, this is the first example in which the paradodecatungstate $[H_2W_{12}O_{42}]^{10-}$ ion acts as a ligand.

Experimental Section

Preparation of $K_6[Co(H_2O)_4]_2[H_2W_{12}O_{42}]\cdot 14H_2O$. This compound was obtained as an insoluble pink material during the preparation of salts of the substituted Keggin anion $[CoCoW_{11}O_{40}]^{8-}$ following Baker's procedure.[4] By recrystallization of the impure potassium salt of the Keggin anion in acid solution (pH = 5.50), pink-purple needle-like crystals of this compound were deposited after several days and separated mechanically from the olive green crystal cubes of $[K_8(CoCoW_{11}O_{40})]\cdot 17H_2O$. Thermogravimetric analysis (Perkin-Elmer TGA 7) was used for the determination of water of crystallization (7.2%). Anal. Found (calcd): K, 6.52 (6.46); W, 60.68 (60.79); Co, 3.19 (3.28); H, 1.36 (1.28). Characteristic IR absorption data, ν/cm^{-1} (KBr): 3399 vs, 1628 s, 937 s, 876 m, 699 m, 527 w, 495 m, 422 w.

Table 1. Crystallographic Data for $K_6[Co(H_2O)_4]_2[H_2W_{12}O_{42}]\cdot 14H_2O$

fw	3629.01	space gp	$P2_1/n$
a, Å	14.990(5)	T, °C	20
b, Å	10.352(7)	wavelength, Å	0.710 73
c, Å	18.760(5)	μ(Mo Kα), cm^{-1}	252.62
β, deg.	93.08(3)	$R(F)^a$	0.027
V, Å^3	2907.1	$R_w(F)^b$	0.038
Z	2		

[a] $R = \sum[|F_o| - |F_c|]/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. $w = 4F_o^2/[\sigma^2(|F_o|) - (0.06|F_o|^2)]$.

X-ray Crystal Structure Determination. A crystal of approximate dimensions 0.2 × 0.2 × 0.4 mm^3 was mounted on an Enraf-Nonius CAD4 diffractometer equipped with graphite-crystal-monochromated Mo Kα radiation (λ = 0.710 73 Å). The cell constants and an orientation matrix for data collection were obtained from least-squares refinements, using the setting angles of 25 centered reflections in the range $10° < 2\theta < 18°$. The intensities were collected using the $\theta-2\theta$ scan mode. The measurement of three standard reflections every 60 min revealed no intensity fluctuations. One set of reflections was collected up to $2\theta = 52°$. The intensities were corrected for Lorentz−polarization effects, and an empirical absorption[5] was applied to isotropically refined data. The structure was solved by direct methods using MULTAN[6] and the solution developed using full-matrix least-squares refinement and difference Fourier syntheses. Anisotropic thermal parameters were refined for all non-hydrogens atoms, except one oxygen atom of the anion (O4), the four water molecules coordinated to the cobalt, and the disordered water molecule (two positions with occupancy factors 0.5), which are refined isotropically. Maximum features in final difference Fourier syntheses: +2.01/−0.47 (the two most intense peaks found in the final difference Fourier syntheses were less than 1.1 Å from W). Scattering factors and correction for anomalous dispersion were taken from ref 7. The drawings were made with ORTEP[8] and STRUPLO.[9] All calculations were performed with the MolEN programs[10] on a Digital Micro VAX 3100. Crystal data and positional atomic coordinates are given respectively in Tables 1 and 2.

Spectroscopic and Magnetic Measurements. IR spectra was recorded on a Perkin-Elmer 882 IR spectrophotometer. EPR spectra at 4 K where recorded with a Bruker ER 200D spectrometer equipped with a continuous-flow cryostat. The magnetic measurements were carried out with a magnetometer (905 VTS, SHE Corp.) equipped with a SQUID sensor.

Results and Discussion

The presence of insoluble "pink cobaltous tungstates" during the preparation of the cobalt(II)-containing anion $[CoCoW_{11}O_{40}]^{8-}$ was already noticed by Baker et al., but the identity and composition of this precipitate were unknown.[4] Single-crystal X-ray analysis allows us to identify this precipitate as the potassium salt of the polymeric anion $[(Co(H_2O)_4)_2(H_2W_{12}O_{42})]_n^{6n-}$. The structure of this anion is formed by paradodecatungstate ions $[H_2W_{12}O_{42}]^{10-}$ linked by Co^{2+} ions

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(1) (a) Pope, M. T.; Müller, A. *Angew. Chem.* **1991**, 103, 56. (b) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: Berlin, 1983. (c) Pope, M. T.; Müller, A. *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1994.

(2) Molchanov, V. N.; Tatjanina, I. V.; Torchenkova, E. A. *J. Chem. Soc., Chem. Commun.* **1981**, 93.

(3) Yamase, T.; Naruke, H. *J. Chem. Soc., Dalton Trans.* **1991**, 285.

(4) Baker, L. C. W.; McCutcheon, T. *J. Am. Chem. Soc.* **1956**, *78*, 4503.

(5) Walker, N.; Stuart, D. An Empirical Method for Correcting Diffractometer Data for Absorption Effects (DIFABS). *Acta Crystallogr.* **1983**, *A39*, 158.

(6) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data. Universities of York, England, and Louvain, Belgium, 1982.

(7) Cromer, D. T.; Waber, T. J. *International Table for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(8) Johnson, C. K. ORTEP II. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(9) Fisher, R. X. *J. Appl. Crystallogr.* **1985**, *18*, 258.

(10) K. C. Fair, *MolEN User's Manual. An Interactive Intelligent System for Crystal Structure Analysis*; Enraf-Nonius: Delft, The Netherlands, 1989.

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Table 2. Fractional Coordinates and Equivalent Isotropic Thermal Parameters

atom	x	y	z	B_{eq},[a] Å^2
W1	0.16565(4)	0.11394(6)	−0.14736(3)	0.93(1)
W2	0.04049(4)	−0.10113(7)	−0.23590(3)	1.03(1)
W3	−0.11683(4)	−0.23958(6)	−0.14494(3)	1.03(1)
W4	−0.07985(4)	0.12521(6)	−0.12137(3)	0.88(1)
W5	0.10762(4)	−0.20097(6)	−0.04950(3)	0.84(1)
W6	0.24036(4)	0.01405(7)	0.03385(3)	0.97(1)
Co	0.1510(2)	0.4652(3)	−0.1191(2)	2.66(6)
O1	−0.0684(7)	−0.044(1)	−0.1632(6)	1.3(2)
O2	−0.0932(7)	0.025(1)	−0.0152(6)	1.1(2)
O3	0.1182(8)	−0.084(1)	−0.1260(5)	1.1(2)
O4	−0.1121(7)	0.253(1)	−0.0504(5)	0.9(2)*
O5	−0.0074(7)	−0.259(1)	−0.1996(6)	1.4(2)
O6	−0.2123(7)	0.073(1)	−0.1154(6)	1.2(2)
O7	0.2347(7)	−0.135(1)	−0.0209(6)	1.4(2)
O8	0.2145(7)	0.114(1)	−0.0538(5)	1.1(2)
O9	0.1917(7)	0.172(1)	0.0789(5)	1.3(2)
O10	0.0794(8)	0.071(1)	−0.2265(6)	1.5(2)
O11	0.0371(7)	0.140(1)	−0.0980(6)	1.3(2)
O12	−0.0108(7)	−0.212(1)	−0.0597(5)	1.3(2)
O13	0.1343(7)	−0.172(1)	−0.2717(6)	1.7(2)
O14	−0.0328(7)	−0.082(1)	−0.3089(5)	1.3(2)
O15	−0.1213(8)	−0.403(1)	−0.1214(6)	1.7(2)
O16	−0.1893(8)	−0.236(1)	−0.2208(6)	1.8(2)
O17	−0.0966(8)	0.217(1)	−0.1983(6)	1.7(2)
O18	0.2588(7)	0.063(1)	−0.1898(6)	1.5(2)
O19	0.3539(8)	0.038(1)	0.0505(6)	2.0(3)
O20	0.1457(8)	−0.346(1)	−0.0836(6)	1.5(2)
O21	0.1642(8)	0.280(1)	−0.1614(6)	1.4(2)
O22	0.2756(7)	0.505(1)	−0.1463(5)	0.9(2)*
O23	0.201(1)	0.394(1)	−0.0196(7)	2.9(3)*
O24	0.1004(9)	0.531(1)	−0.2223(7)	2.3(2)*
O25	0.0242(9)	0.438(1)	−0.0826(7)	2.5(3)*
K1	−0.2024(3)	0.0332(5)	0.7129(3)	3.0(1)
K2	−0.3876(3)	0.1764(5)	0.8443(2)	3.1(1)
K3	−0.4673(3)	0.1998(5)	0.2075(3)	3.4(1)
O1w	−0.2936(9)	0.231(1)	0.1769(7)	2.9(3)*
O2w	0.224(1)	0.117(2)	0.4081(8)	4.3(4)*
O3w	0.368(1)	0.049(2)	0.2316(9)	4.7(4)*
O4w	0.891(1)	0.192(2)	0.618(1)	6.1(5)*
O5w	0.430(2)	0.176(3)	0.896(2)	11.5(9)*
O6w	0.539(2)	0.082(3)	0.076(2)	11.4(9)*
O7w	0.421(3)	0.725(5)	0.008(3)	9(1)*
O8w	0.398(3)	0.485(5)	−0.010(3)	8(1)*

[a] Starred values are for atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter: $B_{eq} = {}^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

to yield a polymer chain running parallel to the [010] direction (Figures 1 and 3).

In this salt, all the counterions are potassium ions (three crystallographically independent sites K1, K2, and K3) which are coordinated to three water molecules and to three oxygen atoms belonging to two paratungstate ions from two neighboring chains.

The structure of the paradodecatungstate ion $[H_2W_{12}O_{42}]^{10-}$ is similar to that reported for $(NH_4)_{10}[H_2W_{12}O_{42}]\cdot 10H_2O$.[11] This ion is centrosymmetric and consists of four corner-sharing groups of two types, each type containing three edge-sharing WO_6 octahedra (Figure 3) in which the W atoms define an equilateral triangle (angles of 59.61, 59.79, and 60.60°) or an angular open trimer (angle $W_{side}-W_{central}-W_{side}$ = 115.72°); in the triangular type the octahedra have one unshared oxygen, while in the angular type the octahedra have two unshared oxygens. The two open trimers are well separated (the minimal W−W distance is 5.72 Å). Tungsten−oxygen distances are divided into four groups: (i) tungsten−terminal oxygen, 1.72−1.75 Å; (ii) tungsten−oxygen linked to cobalt, 1.74 Å; (iii) tungsten−bridging oxygen, 1.79−2.21 Å; (iv) tungsten−internal oxygen common to three tungsten atoms, 1.89−2.32 Å. In the polymer chain this polyanion acts as a tetradentate ligand coordinating the cobalt(II) ions through the terminal oxygen atoms (Figure 2) of four nonadjacent WO_6 octahedra; two oxygens belong to the two opposite triangular units, and the other two, to two terminal octahedra of the angular trimers (see Figure 1).

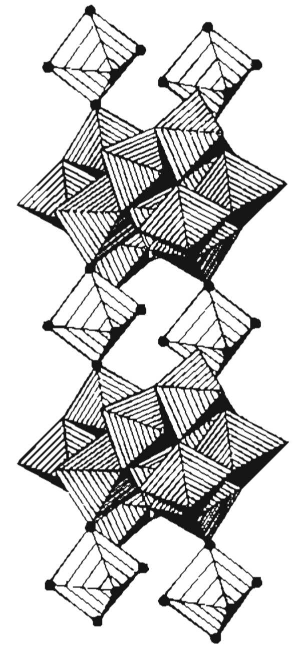

Figure 1. Polyhedral representation of the $[(H_2W_{12}O_{42})]^{10-}$ anion showing the coordination to the four cobalt(II) octahedral sites and the infinite chain along the [010] direction. Black points represent the oxygen atoms coordinated to cobalt(II).

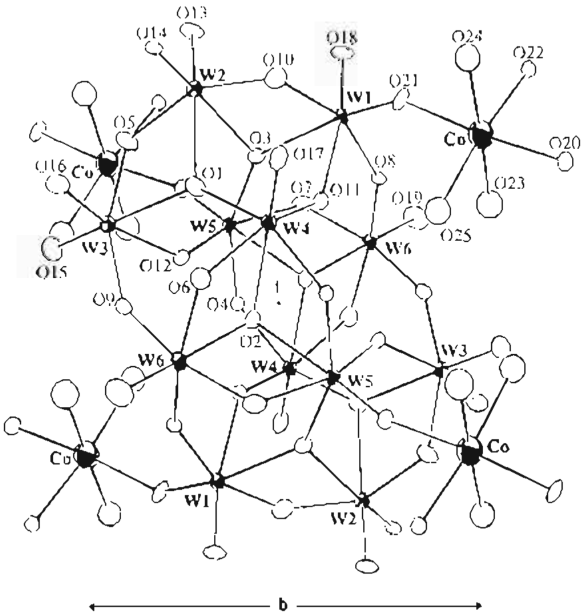

Figure 2. ORTEP drawing of the structure of the $K_6[Co(H_2O)_4]_2[H_2W_{12}O_{42}]\cdot 14H_2O$ with atomic numbering.

The coordination site of the cobalt ions is a distorted octahedron formed by two oxygen atoms in trans positions from two paratungstate groups and completed by four water molecules. The six cobalt−oxygen distances are close: Co−O = 2.07 Å and Co−OH_2 = 2.10 Å. In the chain the cobalt ions

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[11] Allmann, V. R. *Acta Crystallogr.* **1971**, *B27*, 1393. Evans, H. T.; Rollins, O. W. *Ibid.* **1976**, *B32*, 1565.

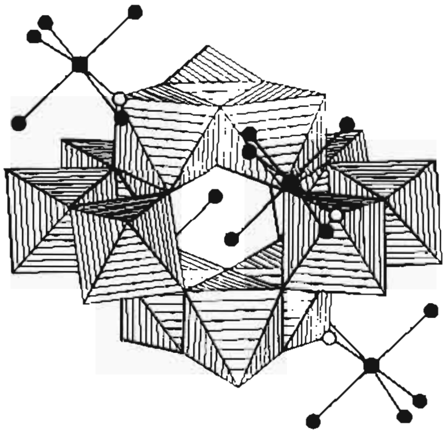

Figure 3. The paradodecatungstate ligand showing the coordination polyhedra and the four corner-sharing groups.

are well separated, with cobalt–cobalt distances longer than 4 Å. This fact leads to a good magnetic isolation of Co^{2+} as demonstrated by the magnetic measurements and EPR spectra. Thus, a nearly constant value of $\mu_{eff} = 4.2\ \mu_B$ is observed in the range of temperatures 4–300 K. On the other hand, powder EPR measurements at 4 K show a rhombic spectrum with signals at $g_1 = 6.0$, $g_2 = 4.2$, and $g_3 = 2.8$, which are close to those found in other octahedral CoO_6 chromophores.[12] Finally, it should be noted that the topology of the metal cations in the chain is similar to that reported for $[(Eu(H_2O)_6)_2(Mo_8O_{27})]$, since in both chains the polyoxometalate units are linked by two metal cations. However, the coordination mode of the polyoxometalate ligands is different. Thus, while the 9-coordinate europium ion is linked by two oxygen atoms of a Mo_8O_{27} unit and one oxygen atom of a neighbouring unit, in the title compound each cobalt ion is coordinated to two terminal oxygens belonging to two neighboring paratungstate ions.

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Supplementary Material Available: Tables listing detailed experimental data for X-ray diffraction, thermal parameters, and complete bond angles and bond lengths (4 pages). Ordering information is given on any current masthead page.

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[12] Bencini, A.; Gatteschi, D.; Melson, G. A. *Transition Met. Chem.* **1982**, *8*, 1.