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A New Family of Layered Molybdenum(V) Cobalto-Phosphates Built up of $[H_{14}(Mo_{16}O_{32})Co_{16}(PO_4)_{24}(H_2O)_{20}]^{10-}$ Wheels

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Metal – oxo cluster compounds exhibit unusual topological properties, and are attractive in view of their use in various fields ranging from catalysis to medicine.[1] Self-assembly processes involving Mo^V lead to a structurally diverse family of well-defined ring-shaped nanoparticles or clusters,[2] and it has been shown recently that such compounds can be connected in several different ways to design extended solids.[3] An alternative way to this step-by-step aggregation process for the design of oxomolybdenum frameworks is the one-pot hydrothermal method. Hydrothermal synthesis of fully reduced molybdenum phosphates has thus been extensively used to prepare solid-state materials. The octahedral coordination of the metal centers combined with the tetrahedral geometry of the phosphate groups is at the origin of a large variety of structures, ranging from one-dimensional polymers to three-dimensional open frameworks.[4] Among these materials, to our knowledge, the only examples of molybdenum phosphates that incorporate first-row transition metals are based on the same building unit, namely the well-characterized $[P_4Mo_6O_{25}(OH)_3]^{3-}$ ion.[5] We describe here the synthesis, structure, and magnetic properties of the new two-dimensional cobaltomolybdenum phosphate **1**, which is constructed from unprecedented large structural groups containing sixteen Co^{II} and sixteen Mo^V ions. These groups are linked by four dicobalto bridges. The related compound **2** has been also isolated and characterized by X-ray diffraction. The structure of **2** contains the same basal units connected by four tetrahedral Co^{II} centers.

$[(Mo_2O_4)_8(HPO_4)_{14}(PO_4)_{10}\{Co_{22}Cl_2(H_2O)_{42}\}] \cdot 28\,H_2O$ **1**

$[(Mo_2O_4)_8(HPO_4)_{14}(PO_4)_{10}\{Co_{19}Na_4(H_2O)_{34}\}] \cdot 14\,H_2O$ **2**

Reaction of sodium molybdate with Mo metal as reducing agent, phosphoric acid, and Co^{II} chloride under hydrothermal conditions gave, for a starting pH of 2.0, red parallelepiped crystals of **1** in good yield and, for an initial pH of 3.9 and a smaller amount of Co^{II}, dark purple crystals of the related compound **2**. A single-crystal structure determination of **1**[6] revealed a two-dimensional network. The structure can be described as building groups containing sixteen molybdenum centers and four tetramers of cobalt that form a wheel with a diameter of 19 Å with overall C_{4v} symmetry (Figure 1 a). Valence bond summations have been applied on all atoms to confirm the valence of the metal atoms and to locate water molecules and fourteen terminal hydroxo groups of the

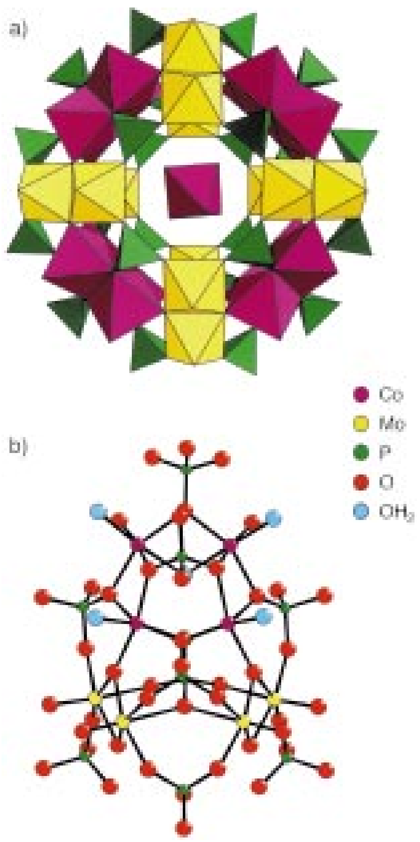

Figure 1. a) Polyhedral representation of the building unit in **1** and **2**; b) ball-and-stick side view of one quarter of the building unit showing the tetramers of Co^{II} and Mo^V.

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phosphato ligands.[7] On this basis, the wheel is anionic with the general formula $[(Mo_2O_4)_8(HPO_4)_{14}(PO_4)_{10}Co_{16}(H_2O)_{20}]^{10-}$. The arrangement of the sixteen Mo^V centers can be described as four tetramers linked together through phosphato groups, leading to an hexadecamer of Mo^V centers. Each Mo tetramer (Figure 1 b) is formed by two $\{Mo_2(\mu\text{-}O)_2\}$ dimers, a common structural arrangement among Mo^V-containing compounds that results from the tendency of the Mo^V ions to form diamagnetic Mo–Mo pairs.[4] The four molybdenum atoms are bridged by three phosphato groups through a μ_3-oxygen and six μ_2-oxygen atoms. Two phosphato groups connect a tetramer of Mo centers to two tetramers of Co centers. A tetramer of cobalt centers (Figure 1 b) consists of four distorted edge-shared octahedra, the metal centers forming almost a square with angles and edges in the range of 89.28–90.59° and 3.16–3.37 Å, respectively. The Co^{II} centers are bridged through six phosphato groups and a water molecule. The coordination sphere of each Co^{II} center is completed by a terminal water molecule and an oxygen atom arising from the $\{Mo_2(\mu\text{-}O)_2\}$ groups. A noteworthy feature in the structure of **1** is the presence of an isolated $[Co^{II}(H_2O)_6]^{2+}$ octahedron enclosed in the wheel (Figure 1 a), the Co^{II} center is located at an inversion center. This encapsulated Co^{II} monomer is stabilized by hydrogen bonding ($d_{O\cdots O} = 2.696$–2.830 Å) between the oxygen atoms of the water molecules and μ_2-oxygen atoms of the phosphate groups surrounding the $[Co^{II}(H_2O)_6]^{2+}$ octahedron. Each wheel is connected to four other wheels by four cobalt dimers through phosphato groups (Figure 2 a). While two of them are the dimeric entities $\{Co_2(H_2O)_6(\mu\text{-}PO_4)_2(PO_4)_2\}$, the two other dimers $\{Co_2(H_2O)_4(\mu\text{-}PO_4)_2(PO_4)_2(\mu\text{-}Cl)_2\}$ have been found disordered over two positions. In the latter species, the chloride ions are *trans* to the μ-phosphato ligand, and are shared with cobalt ions of the wheel. Notably, attempts to synthesize a chlorine-free analogue of **1** have been so far unsuccessful. The connection of the wheels through dimeric Co^{II} octahedra produces the layer structure depicted in Figure 2 a. Finally, a $Co^{II}(H_2O)_5$ group is attached to the inorganic layer through an oxygen atom of a phosphate.

The structure of the building block of compound **2** is analogous to that for compound **1**. Nevertheless, the nature of the groups connecting the wheels are different, leading to a drastic change of the two-dimensional structure. In **2**, each wheel is connected to four other wheels by four cobalt monomers in a distorted tetrahedral environment, which imposes a nonplanar arrangement. The angle between two adjacent building groups, which was calculated considering the geometry of the $\{CoO_4\}$ linker, is 81.2(3)° (Figure 2 b).

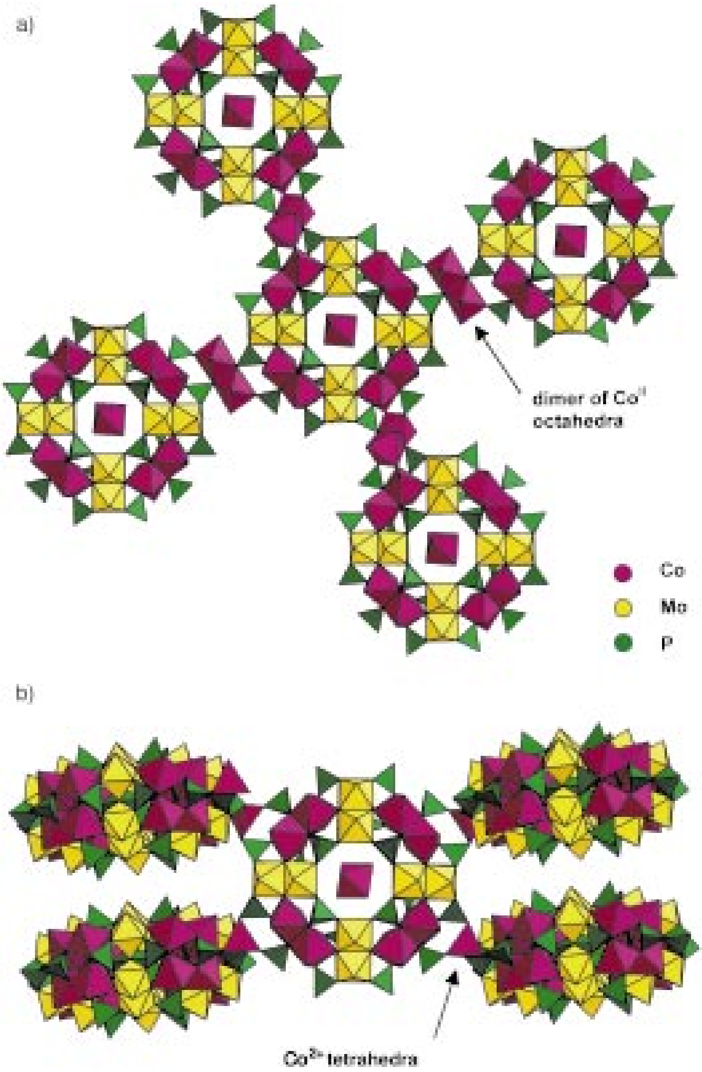

Figure 2. View of the connecting scheme between the building groups in a) **1** and b) **2**.

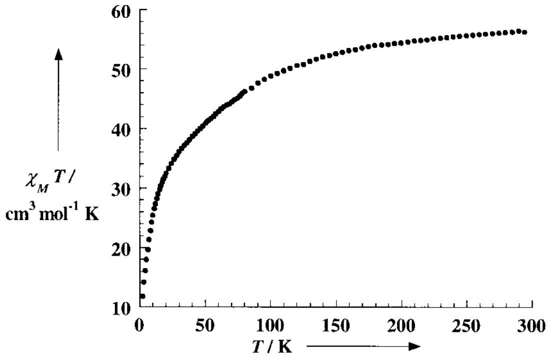

Figure 3. Plot of the dependence of $\chi_M T$ on temperature for **1**.

The magnetic behavior of a microcrystalline sample of compound **1** was studied in the range 2–300 K, and the result is shown in Figure 3 in the form of a plot of $\chi_M T$ versus T (where χ_M is the magnetic susceptibility per unit of **1**).[8] The curve exhibits a continuous decrease upon cooling from 300 K ($\chi_M T = 55.54$ cm^{3}mol^{-1}K, $g = 2.32$) to 2 K ($\chi_M T = 11.75$ cm^{3}mol^{-1}K). As a result of the pairing of the d^1 electrons in the Mo^V dimers, the only magnetically active species in **1** are the Co^{II} ions. As high-spin octahedral Co^{II} ions possess the orbitally degenerate ground state $^4T_{1g}$, spin-orbit coupling leads to a value of $\chi_M T$ for 22 Co^{II} ions at room temperature greater than expected for the spin-only case ($\chi_M T = 41.25$ cm^{3}mol^{-1}K). Nevertheless, the low-temperature $\chi_M T$ value is significantly below the theoretical value calculated for isolated Co^{II} centers for any values of Δ/λ, where λ refers to the spin–orbit coupling parameter and Δ to the ligand-field splitting parameter.[9] This clearly indicates the presence of relatively strong antiferromagnetic Co^{II}–Co^{II}

interactions. This result differs from that previously found by Casañ-Pastor et al. for the tetrameric cobalto–polyoxometalate $[Co_4O_{14}(H_2O)_2(PW_9O_{27})_2]^{10-}$,[10] which displayed ferromagnetic coupling. This difference could be tentatively explained by the fact that the Co-O-Co angles are 90° and ~100° for this compound, and range between 94.9(2)° and 108.1(2)° for **1**, leading in this case to a nonorthogonality of the magnetic orbitals through the bridging oxygen atoms. Furthermore, due to the topology of the Co_4O_{16} groups, spin frustration phenomenon must not occur for **1** due to the long distances of the diagonals of the near square formed by the cobalt centers (4.61–4.63 Å compared to 3.16–3.37 Å for the side of the near square).

In summary, novel extended magnetic solids composed of cobalt(II) and molybdenum(V) phosphates based on a new and complex structural core have been obtained and characterized crystallographically. The versatility of Co^{II} ions, which can adopt both the octahedral and tetrahedral coordination, results in two different organizations of these building groups in the solid, which are controlled by the conditions used for the hydrothermal synthesis. In preliminary experiments, we have found that replacement of Co^{II} by other transition metals of the first row can lead to compounds presenting an isostructural building block, but with an arrangement specific to the metal center and the synthetic conditions. A structural and magnetic characterization of the whole family is in progress.

Experimental Section

1: A mixture of $Na_2MoO_4 \cdot 2H_2O$ (0.470 g, 1.94 mmol), Mo (0.030 g, 0.31 mmol), H_3PO_4 (8 M, 0.53 mL, 4.22 mmol), $CoCl_2 \cdot 6H_2O$ (0.804 g, 3.38 mmol), and water (4 mL) was stirred, and the pH adjusted to 2.0 with HCl (1 M). The resulting suspension was sealed in a 23 mL Teflon-lined reactor which was kept at 180 °C for 70 h. Red parallelepiped crystals of **1** were isolated as a single product by filtration and washed with water (30 % yield, based on total Mo). **1**: IR: $\tilde{\nu}$ = 566 (m), 588 (m), 769 (w), 920 (sh), 959 (s), 1018 (s), 1109 (s) cm^{-1}.

2: The analogous compound **2** was synthesized by a similar procedure starting from a mixture of $Na_2MoO_4 \cdot 2H_2O$ (0.470 g, 1.94 mmol), Mo (0.030 g, 0.31 mmol), H_3PO_4 (8 M, 0.53 mL, 4.22 mmol), $CoCl_2 \cdot 6H_2O$ (0.200 g, 0.84 mmol), and water (4 mL). Then, the pH was adjusted to 3.9. Dark purple parallepiped crystals were obtained in poor yield, mixed with an unidentified blue powder. **2**: IR: $\tilde{\nu}$ = 528 (m), 587 (m), 773 (m), 942 (sh), 970 (s), 1024 (s), 1076 (s) cm^{-1}.

Received: January 22, 2001 [Z16478]

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[6] Crystal data and structure refinement for **1**: a dark red crystal (0.26 × 0.20 × 0.06 mm) was analyzed with a Siemens SMART three-circle diffractometer equipped with a CCD two-dimensional detector using $Mo_{K\alpha}$ monochromated radiation ($\lambda = 0.71073$ Å). Triclinic, space group $P\bar{1}$, $a = 16.0238(5)$, $b = 17.6267(6)$, $c = 19.6432(7)$ Å, $\alpha = 109.285(1)$, $\beta = 113.379(1)$, $\gamma = 97.726(1)°$, $V = 4575.6(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.417$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 3.296$ mm^{-1}, $F(000) = 3232$, 32241 reflections measured, of which 22674 were independent, 1170 refined parameters, $R = 0.0522$, $wR_2 = 0.1541$. Crystal data and structure refinement for **2**: a dark purple crystal (0.20 × 0.10 × 0.10 mm) was analyzed. Monoclinic, space group $P2_1/n$, $a = 15.7711(2)$, $b = 17.01940(10)$, $c = 30.2699(4)$ Å, $\beta = 98.539(1)°$, $V = 8034.8(2)$ Å^3, $Z = 3$, $\rho_{calcd} = 2.677$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 3.541$ mm^{-1}, $F(000) = 6277$, 54435 reflections measured, of which 20850 were independent, 1094 refined parameters, $R = 0.0655$, $wR_2 = 0.1612$. For **1** and **2**, data reduction was performed with the SAINT software. The absorption correction was based on multiple and symmetry-equivalent reflections in the data set using the SADABS program based on the method of Blessing. The structures were solved by direct methods and refined by full-matrix least-squares using the SHELX-TL package. As crystal structures show disorder in the range of water molecules, the exact formula and molecular weight have been established considering data from thermogravimetic studies. For **2**, a disorder has been found on two phosphato groups, occupying two different sites with a ratio ⅔:⅓. Further details on the crystal structure investigations 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 numbers CSD-411682 (**1**) and CSD-411686 (**2**).

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