Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

$[\mathrm{Co^{II}}_4\mathrm{Mo^{V}}_{12}\mathrm{O}_{28}(\mathrm{OH})_{12}(\mathrm{H_2O})_{12}]\cdot 12\mathrm{H_2O}$: facilitating single-crystal growth by deuteration

Arkady Ellern[a] and Paul Kögerler[b]*

[a]Ames Laboratory, Iowa State University, Ames, IA 50011, USA, and [b]Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1, 52074 Aachen, Germany
Correspondence e-mail: paul.koegerler@ac.rwth-aachen.de

Received 23 November 2011
Accepted 10 February 2012
Online 23 February 2012

The structure of the neutral heterometal oxide cluster dodecaaqua-di-μ_3-hydroxido-deca-μ_2-hydroxido-octacosaoxidotetracobalt(II)dodecamolybdenum(V) dodecahydrate, $[\mathrm{Mo_{12}O_{28}}(\mu_2\text{-OH})_{10}(\mu_3\text{-OH})_2\{\mathrm{Co(H_2O)_3}\}_4]$, is virtually identical to the previously reported $\mathrm{Ni^{II}}$ analogue $[\mathrm{Mo_{12}O_{28}}(\mu_2\text{-OH})_{10}(\mu_3\text{-OH})_2\{\mathrm{Ni^{II}(H_2O)_3}\}_4]$ [Müller, Beugholt, Kögerler, Bögge, Budko & Luban (2000). *Inorg. Chem.* **39**, 5176–5177], the first molecular magnet to exhibit signs of magnetostriction. The formation kinetics of the neutral cluster species, which is insoluble in water, can be significantly slowed by the use of deuterated reactants in order to grow single crystals of sufficient size for single-crystal X-ray diffraction studies using standard diffractometers. One half of the main cluster and six solvent water molecules constitute the asymmetric unit. The main cluster is located on a mirror plane.

Comment

Magnetically functionalized polyoxomolybdates present a structurally very diverse source of molecular spin polytopes featuring a wide range of magnetic phenomena. In these species, the redox-active, otherwise diamagnetic, molybdate structures serve as scaffolds into which (currently up to 30) magnetic transition metal cations can be integrated, resulting in magnetic characteristics ranging from molecular spin frustration and spin-glass transitions (Kögerler *et al.*, 2010) to magnetic metastability (Ritchie *et al.*, 2008) and charge-dependent exchange coupling (Botar *et al.*, 2009). The neutral polyoxomolybdate(V)-based cluster $[\mathrm{Mo_{12}O_{28}}(\mu_2\text{-OH})_{10}(\mu_3\text{-OH})_2\{\mathrm{Ni^{II}(H_2O)_3}\}_4]$ (= $\{\mathrm{Ni_4Mo_{12}}\}$), isolated as $\{\mathrm{Ni_4Mo_{12}}\}\cdot 14\mathrm{H_2O}$ (Müller *et al.*, 2000), represents the first molecular magnet featuring aspects of magnetostriction that were attributed to the 'non-innocent' ε-Keggin polyanion serving as a superexchange pathway between the $\mathrm{Ni^{II}}$ centres defining a nearly regular tetrahedron (Schnack *et al.*, 2006). In particular, both the exchange energies for the intramolecular antiferromagnetic coupling and the absorption intensities in the UV–vis spectroscopic range depend on the external magnetic field. In order to explore these effects in more detail, isostructural derivatives with other spin centres were targeted, though their characterization was hampered by the fact that the charge-neutral $\{M^{\mathrm{II}}{}_4\mathrm{Mo_{12}}\}$ clusters (where M is Co or Fe) are barely soluble in the aqueous reaction media, resulting in their immediate precipitation as microcrystalline products.

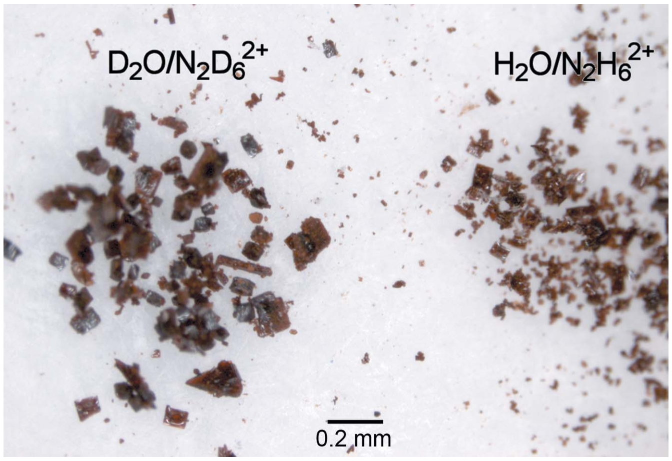

Figure 1
A microscope image comparing size distributions between crystalline material obtained using deuterated (left) and nondeuterated (right) educts in the synthesis of $\{\mathrm{Co_4Mo_{12}}\}\cdot 12\mathrm{H_2O}$.

We herein report that this problem in obtaining single crystals of the $\{\mathrm{Co^{II}}_4\mathrm{Mo_{12}}\}$ derivative suitable for X-ray diffraction studies can be overcome by utilizing deuterated reagents (in our case, $\mathrm{D_2O}$, deuterated ammonium molybdate and deuterated hydrazine sulfate). Apparently, the multiple condensation steps leading to the highly nucleophilic ε-Keggin polyanion $[\mathrm{H}_x\mathrm{Mo^V}_{12}\mathrm{O}_{40}]^{(20-x)-}$ are slowed down significantly, so that the formation of this proposed intermediate becomes the rate-determining step for the overall reaction and thus the growth of crystals. Under otherwise identical reaction conditions, this results in crystals with dimensions that are approximately one order of magnitude larger (Fig. 1).

The $\{\mathrm{Co_4Mo_{12}}\}$ cluster was isolated as the dodecahydrate, $[\mathrm{Mo^V}_{12}\mathrm{O}_{30}(\mu_2\text{-OH})_{10}\mathrm{H}_2\{\mathrm{Co^{II}(H_2O)_3}\}_4]\cdot 12\mathrm{H_2O}$ (= $\{\mathrm{Co_4Mo_{12}}\}\cdot 12\mathrm{H_2O}$). The cluster (Fig. 2) is virtually isostructural with the $\{\mathrm{Ni_4Mo_{12}}\}$ species and is of crystallographic C_s symmetry (atoms Co1, Co2, Mo4 and Mo5 define the mirror plane). $\{\mathrm{Co_4Mo_{12}}\}$ features a tenfold protonated ε-Keggin core anion, $[\mathrm{Mo^V}_{12}\mathrm{O}_{38}(\mu_3\text{-OH})_2]^{18-}$, built up from four edge-sharing $\{\mathrm{Mo_3}\}$ groups (each consisting of three edge-sharing $\mathrm{MoO_6}$ octahedra). Note that the T_d-symmetric ε-Keggin structure can be formally derived from the common α-Keggin isomer by rotating all four $\{\mathrm{Mo_3}\}$ groups by 60°. The ε-Keggin core comprises a central tetrahedral cavity defined by four μ_3-O-atom sites (atom O11 and its symmetry equivalents, and atoms O18 and O22), and two H atoms bind to the four μ_3-O sites. This double protonation is common to all known ε-Keggin structures lacking a central heteroanion template. Within the ε-Keggin framework, the Mo positions form six $\mathrm{Mo^V}_2$ groups with short Mo—Mo single bonds, with an average Mo—Mo

doi:10.1107/S0108270112006014

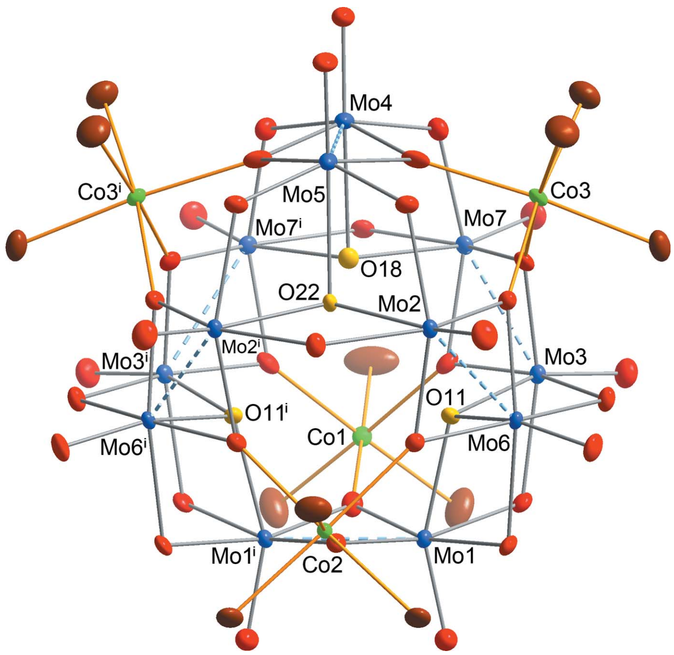

Figure 2
The structure of the $\{Co_4Mo_{12}\}$ cluster, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. (In the electronic version of the journal, Co atoms are green, Mo atoms are blue, μ_3-O atoms defining the central O_4 tetrahedron are yellow, O atoms of water ligands are brown and the remaining O atoms are red.) Short Mo$\cdots$Mo contacts are highlighted by dashed lines. H atoms were not located (see *Experimental*). [Symmetry code: (i) $x, -y + \frac{1}{2}, z$.]

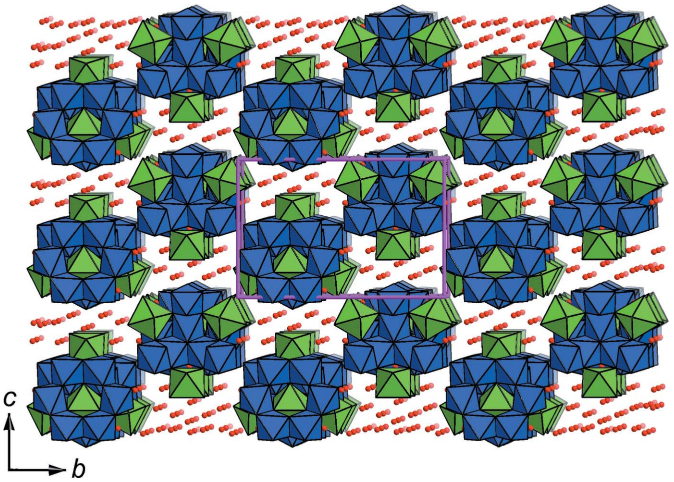

Figure 3
A packing diagram for $\{Co_4Mo_{12}\}\cdot 12H_2O$, viewed approximately along *a*, with the cell edge of one unit cell outlined. The neutral $\{Co_4Mo_{12}\}$ clusters are shown in a polyhedral representation and the O atoms of the solvent water molecules are drawn as small spheres.

separation of 2.586 (5) Å, but one longer distance for Mo4$\cdots$Mo5 of 2.9284 (15) Å. The Mo—Mo single bonds result in spin pairing; the analogous $\{Mo^{VI}{}_4Mo^{V}{}_{12}\}$-type tetracapped ε-Keggin cluster, in which four $Mo^{VI}O_3$ groups assume the positions of the $M^{II}(H_2O)_3$ groups in the $\{M^{II}Mo_{12}\}$ family, is diamagnetic (Müller *et al.*, 2000). Mo—Mo single bonds, with Mo—Mo distances ranging from 2.6 to 3.4 Å, are also found in face-sharing $Mo^{V}O_6$ dimers present, for example, in $\{Mo_{57}M_6\}$- or $\{Mo_{132}\}$-type polyoxomolybdates, where these $\{Mo^{V}{}_2\}$ dimers are diamagnetic as well (Müller *et al.*, 1999, 2001). The assignment of the oxidation state +V to all 12 Mo-atom positions is based on both charge-neutrality arguments and the observed absence of a magnetic moment of the ε-Keggin core, although the bond-valence sum for atom Mo5 of 5.816 is closer to +VI than +V. Note that the diamagnetism of the ε-Keggin core, which rules out a paramagnetic $\{Mo^{V}{}_{11}Mo^{VI}{}_1\}$ configuration, in both the title compound and the $\{Ni^{II}{}_4Mo^{V}{}_{12}\}$ analogue is evident from their high-temperature susceptibility once the contributions of the four M^{II} spin centres are subtracted.

In the title compound, four $[Co^{II}(H_2O)_3]^{2+}$ groups are each coordinated to three (nonprotonated) μ_2-oxide centres that interlink the Mo positions of the $\{Mo^{V}{}_2\}$ groups. This results in an octahedral $O_3Co^{II}(H_2O)_3$ coordination environment with all oxide and water ligands in *trans* orientations. The resulting Co—O bond lengths span very similar intervals: Co—(μ_2-O) = 2.015 (7)–2.072 (5) Å and Co—OH_2 = 2.027 (9)–2.118 (6) Å. This capping of the ε-Keggin core produces a near-regular Co_4 tetrahedron, in which the Co^{II} centres are coupled *via* –O—Mo—O– superexchange pathways. The Co$\cdots$Co distances range from 6.520 (2) to 6.707 (2) Å, compared with Ni$\cdots$Ni distances of 6.606 (5)–6.700 (5) Å in $\{Ni_4Mo_{12}\}$.

In the solid-state structure of $\{Co_4Mo_{12}\}\cdot 12H_2O$, the neutral cluster molecules are spaced apart by solvent water molecules (Fig. 3). The closest intermolecular Co$\cdots$Co distance in the solid state is 7.162 (2) Å [Co1 to Co3($x - 1, y, z$) of a neighbouring $\{Co_4Mo_{12}\}$ molecule], rendering intermolecular (dipole–dipole) magnetic coupling insignificant. Preliminary magnetic studies show that the octahedrally coordinated Co^{II} centres ($^4T_1, S = \frac{3}{2}$) in $\{Co_4Mo_{12}\}$ display pronounced single-ion ligand field and spin-orbit coupling effects (Speldrich *et al.*, 2011) and are antiferromagnetically coupled. From preliminary field-dependent magnetization studies, the first-level crossing fields (*i.e.* steps in the magnetization *versus* field curve at 0.5 K) occur at 1.5 and 7.1 T. This pronounced deviation from equidistant crossing fields, also observed in $\{Ni_4Mo_{12}\}$, is an initial indication that $\{Co_4Mo_{12}\}$ displays similar behaviour that could be caused by molecular magnetostriction.

Finally, we note that while the $\{Ni_4Mo_{12}\}\cdot 14H_2O$ compound originally reported (Müller *et al.*, 2000) crystallizes in the space group $C2/m$, we found that lowering the synthesis reaction temperature to 303 K (as required for the synthesis of the title compound, $\{Co_4Mo_{12}\}\cdot 12H_2O$) produces a derivative, $\{Ni_4Mo_{12}\}\cdot 12H_2O$, which also crystallizes in the space group $P2_1/m$ [a = 12.145 (2), b = 18.188 (3), c = 12.174 (2) Å and β = 93.030 (3)°] and otherwise exhibits a lattice construction identical to that of $\{Co_4Mo_{12}\}\cdot 12H_2O$.

Experimental

Ammonium molybdate, $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ (3.1 g, 2.5 mmol), and cobalt(II) acetate, $Co(CH_3COO)_2\cdot 4H_2O$ (11.2 g, 45 mmol), were dissolved in H_2O (250 ml) and acetic acid (50%, 40 ml) in a 500 ml Erlenmeyer flask. After the formation of a clear solution, hydrazinium sulfate (650 mg, 5.0 mmol) was added in small portions under vigorous stirring (pH *ca* 3.5). The flask was covered with Parafilm and kept in an oil bath at 303 K for 3 d. The precipitated $\{Co_4Mo_{12}\}\cdot 12H_2O$ was separated from the reaction solution by decanting and was washed several times with distilled water (yield 1.8 g; 69% based on Mo). IR (KBr pellet, ν, cm^{-1}): 3200 (*s*/*br*), 953 (*s*), 790 (*m*), 755 (*m*), 664 (*w*), 520 (*m*). Isolation of single crystals (brown plates) of sufficient size for single-crystal X-ray structure analysis required the use of D_2O, deuterated acetic acid, deuterated ammonium molybdate and deuterated hydrazine sulfate. As both H_2O and D_2O were present in the reaction mixture, it was not possible to determine the D:H ratio in the product (note that the formation of polyoxometalates in deuterated media generally results in products with H:D ratios that significantly deviate from the stochiometric H:D ratios of the reaction solutions). For simplicity, all H/D positions were therefore designated as H.

Crystal data

$[Co_4Mo_{12}O_{28}(OH)_{12}(H_2O)_{12}]\cdot 12H_2O$
M_r = 2471.48
Monoclinic, $P2_1/m$
a = 12.061 (3) Å
b = 18.151 (5) Å
c = 12.129 (3) Å
β = 93.403 (5)°
V = 2650.4 (12) $Å^3$
Z = 2
Mo $K\alpha$ radiation
μ = 4.09 mm^{-1}
T = 193 K
0.20 × 0.15 × 0.06 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) T_{min} = 0.62, T_{max} = 0.76
23238 measured reflections
6337 independent reflections
5163 reflections with $I > 2\sigma(I)$
R_{int} = 0.051

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.113
S = 1.12
6337 reflections
385 parameters
H-atom parameters not defined
$\Delta\rho_{max}$ = 1.80 e $Å^{-3}$
$\Delta\rho_{min}$ = −1.58 e $Å^{-3}$

During the structure solution and refinement, none of the expected H atoms were observed in a difference Fourier map and, therefore, they were not included in the refinement. The Mo centres are assumed to be Mo^V (see *Comment*) and each of the four Co centres binds to three terminal water ligands. At the very centre of the ε-Keggin cluster, a small cavity is defined by a tetrahedron of four μ_3-O atoms. As with all known ε-Keggin structures, two of them are expected to be protonated. To satisfy charge neutrality, the remaining ten H atoms are assigned to bridging O atoms on the cluster surface. The resulting formula and derived quantities were adjusted according to the analytical and physical properties of the compound.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2011); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

Work at the Ames Laboratory was supported by the Department of Energy Basic Energy Sciences under contract No. DE-AC02-07CH11358.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LG3073). Services for accessing these data are described at the back of the journal.

References

Botar, B., Ellern, A., Hermann, R. & Kögerler, P. (2009). *Angew. Chem. Int. Ed.* **48**, 9080–9083.

Brandenburg, K. (2011). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.

Bruker (2003). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA

Kögerler, P., Tsukerblat, B. & Müller, A. (2010). *Dalton Trans.* **39**, 21–36.

Müller, A., Beugholt, C., Kögerler, P., Bögge, H., Budko, S. & Luban, M. (2000). *Inorg. Chem.* **39**, 5176–5177.

Müller, A., Kögerler, P. & Dress, A. W. M. (2001). *Coord. Chem. Rev.* **222**, 193–218.

Müller, A., Kögerler, P. & Kuhlmann, C. (1999). *Chem. Commun.* pp. 1347–1358.

Ritchie, C., Ferguson, A., Nojiri, H., Miras, H. N., Song, Y. F., Long, D. L., Burkholder, E., Murrie, M., Kögerler, P., Brechin, E. K. & Cronin, L. (2008). *Angew. Chem. Int. Ed.* **47**, 5609–5612.

Schnack, J., Brüger, M., Luban, M., Kögerler, P., Morosan, E., Fuchs, E., Modler, R., Nojiri, H., Rai, R. C., Cao, J., Musfeldt, J. L. & Wei, X. (2006). *Phys. Rev. B*, **73**, 094401.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Speldrich, M., Schilder, H., Lueken, H. & Kögerler, P. (2011). *Isr. J. Chem.* **51**, 215–227.