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Fusion of Coordination- and Polyoxometalate Chemistry – Chelated Cobalt(III) Centers as Structural Components of Polyoxomolybdates – $[\{Co(en)\}_4Mo_{10}O_{38}]^{4-}$ and Macrocyclic $[\{Co^{II}(H_2O)_2\}\{Co(en)\}_8\{Mo_{20}O_{76}\}]^{6-}$

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On the basis of the argument that a monochelated octahedral transition-metal unit is topologically analogous to the Type II (*cis*-dioxo) metal center frequently observed in the structures of many polyoxometalates, we report the synthesis and structural characterization of salts of two polyoxomolybdate anions demonstrating this principle, $[\{Co(en)\}_4Mo_{10}O_{38}]^{4-}$ (**1**) and $[\{Co^{II}(H_2O)_2\}\{Co(en)\}_8\{Mo_{20}O_{76}\}]^{6-}$ (**2**). Anion **1** has a structure of nominal C_s symmetry and consists of two blocks of seven edge-shared metal-centered octahedra linked by two corner-shared junctions (Co–O–Mo). The four octahedra which contain $\{Co(en)\}^{3+}$ instead of $\{MoO_2\}^{2+}$ are distributed unequally between the two blocks, three in one and the fourth in the other. The structure of **2** can be described as a chiral macrocyclic assembly (C_4 symmetry) of four identical blocks of seven octahedra as observed in the structure of **1**, but now containing two $\{Co(en)\}^{3+}$ per block. As in **1** the blocks are linked by corner-shared Co–O–Mo linkages. A *trans*-diaquacobalt(II) cation occupies the center of the anion. The opportunities provided by the introduction of chelated metal centers, especially those with unsymmetrical diamines, into new polyoxometalates include the generation of resolvable and optically stable structures that have so far eluded polyoxometalate chemists.

Introduction

The structures of the overwhelming majority of polyoxometalate anions are commonly described in terms of corner- and edge-sharing of MO_6 octahedra.[1] The outer surfaces of these anions contain MO_6 octahedra with either one unshared (terminal) oxygen, as is the case for the well-known Keggin structure, or two mutually *cis* unshared oxygen atoms, as in the Anderson–Evans anions, e.g. $[TeMo_6O_{24}]^{6-}$.[2] These structural features have been termed types I and II respectively,[3,4] and we have recently noted that a monochelated metal cation such as $\{Co(en)\}^{3+}$ is topologically equivalent to a type II metal center.[5] Because type II centers are considerably more common in polymolybdate structures than in polytungstates,[3,6] it seemed probable that multiple $\{Co(en)\}^{3+}$ groups could be incorporated as part of the framework of new polymolybdate structures. We report here two such structures as a proof-of-principle, and these point the way to new polyanion architectures and properties, not necessarily limited to molybdates.

Results and Discussion

Careful acidification of a solution containing potassium biscarbonatoethylenediaminecobaltate(III) and sodium molybdate simultaneously releases carbon dioxide and drives the polymerization of molybdate. The resulting green solution yields crystals of $K_3Na[\{Co(en)\}_4Mo_{10}O_{38}]\cdot 4H_2O$ (**1**). The structure of the anion of nominal C_s symmetry (Figure 1) consists of two blocks of seven edge-shared MX_6 octahedra linked by two vertices in order to conform to the Lipscomb criterion[4] for the MoO_6 octahedra. The four Co-centered octahedra are unevenly distributed between the two blocks. Although it is possible to imagine more symmetrical structures, it is interesting to note that the same anion is formed, and confirmed by a total of three structure determinations, from syntheses starting with $[Mo_7O_{24}]^{6-}$ as well as $[MoO_4]^{2-}$, and with Co/Mo ratios between 1:2.5 and 1:4. It is of further interest to note that if all octahedra were Mo-centered to give the hypothetical anion $[Mo_{14}O_{46}]^{4-}$ the two halves of the structure would be identical. We discuss this feature in more detail below.

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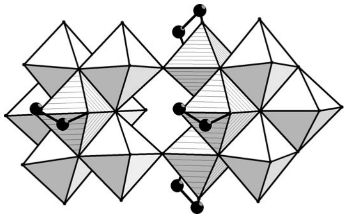

Figure 1. Polyhedral representation of the structure of the anion in **1**. MoO_6 octahedra (white), $Co(en)O_4$ octahedra (hatched), carbon atoms (black spheres). Selected average bond lengths [Å]: Mo–O(Co) 1.77; Co–O(Mo) 1.85; Mo–O(t) 1.69(3).

Crystals of a second product, $[Co^{II}(H_2O)_2\{Co^{III}(en)\}_8Mo_{20}O_{76}]^{6-}$ (**2**) were initially discovered in the mother liquor of a synthesis of **1** after several weeks. Structural and elemental analysis revealed a mixed-valence anion containing Co^{2+} as well as $\{Co(en)\}^{3+}$. It has subsequently been possible to prepare **2** in a more rational way (see Experimental Section) but currently in poor yield. Nevertheless, the structure of the anion in **2** (Figure 2) is of considerable novelty in polyoxometalate chemistry. The anion can be described as a chiral macrocyclic ligand surrounding a central "octahedral" Co atom. Bond-valence sums[7] for the central Co (2.14) and its *trans*-related unshared oxygen atoms (0.29, 0.34) identify divalent cobalt with two aqua ligands. Although no bond-valence parameters have yet been established for Co^{III}–O, N bonds, the average bond lengths observed for these in **2**, 1.922 Å (O) and 1.928 Å (N) are similar to those found for $[Co(en)(CO_3)_2]^-$, 1.913 and 1.938 Å respectively,[8] and are significantly shorter than the bonds to the central cobalt atom (2.014–2.154 Å). The cyclic polyoxometalate ligand, of nominal C_4 symmetry, is composed of four equivalent blocks of seven edge-shared octahedra, $5MoO_6$ and $2CoN_2O_4$, linked by Co–O–Mo vertices. The overall anion structure may be compared to that of a metalloporphyrin with two possible sites for ligand substitution, one of which is more crowded than the other; on the side of the anion shown in Figure 2 the separation between the central Co^{II} and the nearest carbon atom varies from 4.8–5.2 Å compared with 6.7–7.2 Å for the corresponding separation on the opposite side (Figure 3). It is of interest to note that both new polyoxoanions have the same empirical stoichiometry if the central Co^{II} atom is excluded, i.e.:

$$2[\{Co^{III}(en)\}_4Mo_{10}O_{38}]^{4-} + Co^{2+} + 2H_2O \rightarrow [Co^{II}(H_2O)_2\{Co^{III}(en)\}_8Mo_{20}O_{76}]^{6-}$$

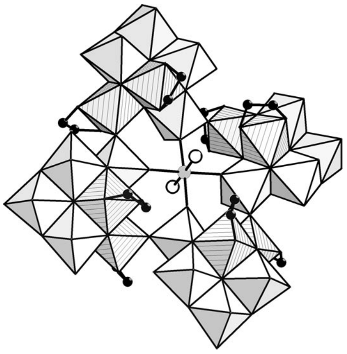

Figure 2. Polyhedral representation of the structure of the anion in **2**. Color scheme as in Figure 1 with central Co atom (gray sphere) and H_2O ligands (white spheres). Selected average bond lengths [Å]: Mo–O(Co^{III}) 1.78; Co^{III}–O(Mo) 1.92; Mo–O(Co^{II}) 1.75; Co^{II}–O(Mo) 2.09.

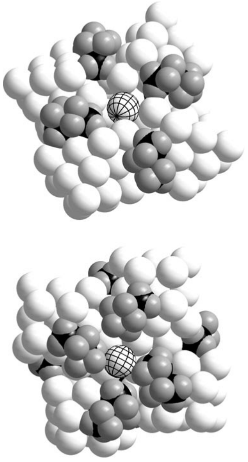

Figure 3. Space-filling representations of the structure of anion **2** viewed from the "open" (upper) and "crowded" (lower) sides. Key: cross-hatched sphere (central Co^{II} aqua ligand), white (oxygen), gray (hydrogen) black (nitrogen).

The structures of both **1** and **2** are based on the common "building block" of seven edge-shared metal-centered octahedra shown in Figure 4. Octahedra labeled 1, 2, 3, 4 and 6 in that Figure form a lacunary version of the Lindqvist structure $[M_6O_{19}]^{n-}$, observed for example in the lanthanide complexes $[Ln^{III}(W_5O_{18})]^{9-}$.[9] In anion **1**, "half" of the structure contains Co in octahedron 6, and the other "half" has Co in 5, 6 and 7. In anion **2** the cobalt cations occupy octahedra 5 (or 7) and 6. When Mo occupies octahedra 5 and/or 7 with three unshared vertices, one of "terminal" oxygen atoms becomes a bridging atom to cobalt, which allows the structure to conform to the Lipscomb criterion.

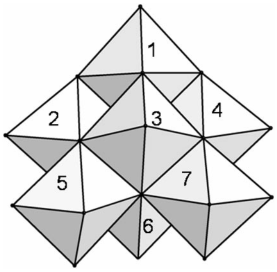

Figure 4. The structure of the common block of seven edge-shared MX_6 octahedra found in the structures of anions **1** and **2** is derived from a lacunary version of the Lindqvist structure (octahedra 1, 2, 3, 4, 6).

Conclusions

The introduction of $\{Co(en)\}^{3+}$ groups as topological analogs of *cis*-$\{MoO_2\}^{2+}$ units in polyoxomolybdate structures may easily be achieved through the use of bis(carbonato)diamminecobaltate(III) anions. The two new molybdocobaltate structures reported here have unprecedented polyoxometalate architectures and indicate that a larger and more varied field of such complexes should be accessible. The chiral macrocyclic ligand in **2** offers possibilities for new metal- and ligand-derivative chemistry. The broad range of bis(carbonato)cobaltate anions containing unsymmetrical and/or chiral diammine ligands provides opportunities to modify polyoxometalate structures via steric restraints and to generate chiral polyoxoanions that are resistant to facile racemization.

Experimental Section

Syntheses

Anion 1: A solution of $Na_2MoO_4·2H_2O$ (4.32 g, 17.8 mmol) in 40 mL water heated to 70 °C was treated with a solution of K[Co(en)$(CO_3)_2]·H_2O$[10] (2.00 g, 6.8 mmol) in 10 mL water and the clear mixture was carefully acidified with 6 M HCl (CO_2 evolution) to a final pH of 5.4 (color change from purple to green). Green crystals (0.9 g; 22% based on Mo) were harvested after 3 d and used for X-ray structural analysis. The filtrate deposited additional crystals upon standing for several days. $C_8H_{40}Co_4K_3Mo_{10}N_8NaO_{42}$ (2255.8): calcd. C 4.26, H 1.79, Co 10.45, K 5.20, Mo 42.53, N 4.97, Na 1.02, O 29.79, Mo/Co 2.50; found C 4.2, H 1.2, Co 10.3, K 4.8, Mo 42.5, N 4.9, Na 0.9, O 27.7, Mo/Co 2.54.[11] UV(aqueous solution): λ_{max} = 640 nm. IR: $\tilde{\nu}$ = 921 (vs), 899 (vs), 886 (vs), 842 (s), 720 (m), 631 (s) 541 (m).

The same anion (as confirmed by additional structure determinations) can be synthesized starting with solutions of ammonium or sodium heptamolybdate (no further acidification required in this case), and with Mo/Co ratios as high as 4:1.

Anion 2: $KCo(en)(CO_3)_2·H_2O$ (2.37 g, 8.0 mmol) and $Na_2MoO_4·2H_2O$ (4.84 g, 20.0 mmol) were added to 20 mL of warm (50 °C) water The pH of the resulting dark purple solution was carefully lowered from 9.2 to 6.5 using 2 M HCl (CO_2 evolution) and the resulting solution was stirred for 10 min. A solution of $CoCl_2·6H_2O$ (0.23 g, 1 mmol, 5 mL water) was added dropwise for 30 min maintaining the pH near 6 during the addition. The resulting cloudy solution was treated with saturated solutions of ammonium chloride and potassium chloride (1 mL each), the turbid solution was stirred for 2 h at 50 °C, cooled in a refrigerator and filtered. The dark green filtrate was allowed to stand at room temperature in an open beaker. Within a week green crystals of $K_{2.5}Na_{2.5}(NH_4)[Co(H_2O)_2Co_8(en)_8Mo_{20}O_{76}]·22H_2O$ were formed and harvested (yield 0.27 g; 6% based on Mo). $C_{16}H_{116}Co_9K_{2.5}Mo_{20}N_{17}Na_{2.5}O_{100}$ (4751.5): calcd. C 4.04, H 2.46, Co 11.16, K 2.06, Mo 40.38, N 5.01, Mo/Co 2.22; found C 4.1, H 2.8, Co 11.2, K 2.2, Mo 40.5, N 5.4, Mo/Co 2.26. An isostructural compound, confirmed by partial X-ray structural analysis, was synthesized using a solution of 0.16 g of $Cu(NO_3)_2·2.5H_2O$ in 5 mL water instead of $CoCl_2$ Yield 0.12 g. Elemental analyses were carried out by Kanti Labs Ltd., Mississauga, Ontario, Cnada.

Single-crystal X-ray analyses were performed with a Bruker-Siemens SMART CCD diffractometer equipped with a Mo anode and graphite monochromator, K_α wavelength 0.71073 Å. The crystals were mounted on a glass fiber and placed in a nitrogen stream at 173 K. An empirical absorption correction was applied, based on measured intensities of equivalent reflections at different ϕ and ω values.[12,13] The structures were solved by direct methods and refined against $|F^2|$ over all independent refections, using SMART, SAINT, SHELX-97, and X-SEED programs.[14–16] Structural Figures were generated by DIAMOND.[17] Atoms heavier than oxygen were refined anisotropically except for disordered sodium atoms. As is common in polyoxomolybdate structures there is extensive disorder of the cations and water molecules, to the extent that some of the cations cannot be located. In order to determine the occupancy of the disordered atoms their atomic displacement parameter factors were first set to be comparable to the corresponding non-disordered atoms and their occupancies were refined. The occupancy numbers were then held fixed and the atomic displacement factors refined. A summary of crystallographic data is presented in Table 1.[11]

CCDC-737233 (for **1**) and -737234 (for **2**) contain the supplementary crystallographic data for this paper. These data can be ob-

Table 1. Crystallographic data.

	1	**2**
Empirical formula	$C_8H_{54}Co_4K_3Mo_{10}N_8NaO_{53}$	$C_{16}H_{95.75}Co_9K_{1.25}Mo_{20}N_{18.5}Na_{2.25}O_{99.75}$
M_r	2446.00	4693.63
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	10.974(3)	16.911(2)
b [Å]	15.945(5)	18.813(2)
c [Å]	17.728(5)	23.064(3)
α [°]	86.834(5)	75.383(2)
β [°]	78.146(5)	75.542(2)
γ [°]	78.031(5)	71.066(2)
V [Å^3]	2969.7(15)	6602.6(14)
Z	2	2
ρ (calcd.) [Mg/m^3]	2.735	2.361
μ [mm]$^{-1}$	3.456	3.075
Crystal size [mm]	0.30 × 0.10 × 0.06	0.26 × 0.24 × 0.18
F(000)	2356	4502
T [K]	173(2)	173(2)
θ range [°]	1.17 to 30.54	1.86 to 28.34
Number of reflections	23745	69680
Independent reflections	14762 [R(int) = 0.0430]	29507 [R(int) = 0.0387]
R [$I > 2\sigma(I)$]	0.0936 ($R1$) 0.2492 (wR_2)	0.0526 (R_1) 0.1511 (wR_2)
R (all data)	0.1306 (R_1) 0.2822 (wR_2)	0.0760 (R_1) 0.1644 (wR_2)

tained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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[1] Recent reviews: a) *Polyoxometalate Molecular Science* (Eds.: J. J. Borrás-Almenar, E. Coronado, A. Müller, M. T. Pope), NATO SCIENCE SERIES: II, vol. 98, Kluwer Academic Publishers, Dordrecht **2003**; b) *Comprehensive Coordination Chemistry II* (Eds.: J. McCleverty, T. J. Meyer), Pergamon Press, Oxford **2004**, vol. 4, p. 635–678 (M. T. Pope), p. 679–759 (C. L. Hill), vol. 7, p. 1–56 (L. Cronin).

[2] H. T. Evans Jr., *J. Am. Chem. Soc.* **1948**, *70*, 1291–1292.

[3] M. T. Pope, *Inorg. Chem.* **1972**, *11*, 1973–1974.

[4] As first noted by W. N. Lipscomb, *Inorg. Chem.* **1965**, *4*, 132–134, structures containing MO_6 octahedra with *three* terminal oxygen atoms may not be stable, and there are very few, if any, authenticated examples.

[5] N. Belai, M. T. Pope, *Chem. Commun.* **2005**, 5760–5762.

[6] M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer Verlag, Berlin, **1983**, p. 140.

[7] I. D. Brown, D. Altermatt, *Acta Crystallogr., Sect. B* **1985**, *41*, 244–247.

[8] N. Belai, M. H. Dickman, M. T. Pope, *Acta Crystallogr., Sect. C* **2001**, *57*, 802–803.

[9] See, for example, T. Ozeki, T. Yamase, *Acta Crystallogr., Sect. B* **1994**, *50*, 128–134.

[10] Y. Kitamura, A. Shibata, *Inorg. Chim. Acta* **1993**, *203*, 37–42.

[11] Elemental analyses were made on a partially dehydrated version of the sample selected for the structure determination which revealed a mix of 12 ordered and disordered water molecules.

[12] R. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33–38.

[13] *SADABS Absorption Correction Method*, University of Göttingen, **1996**.

[14] *SAINT 4.050*, Siemens Analytical X-ray Instruments Inc., Madison, WI, **1996**.

[15] *SHELX-97 Structure Determination Software Programs*, Siemens Analytical X-ray Instruments Inc., Madison, WI, **1997**.

[16] *X-SEED*, http://x-seed.net.

[17] *DIAMOND version 3.2*, http://crystalimpact.com/diamond.

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