Chelated heteroatoms in polyoxometalates and the topological equivalence of {Co^{III}(en)} to type II *cis*-dioxometal centers. Synthesis and structure of [{Co(en)(μ-OH)$_2$Co(en)}{PW$_{10}$O$_{37}$Co(en)}$_2$]$^{8-}$ and [K⊂{Co(en)WO$_4$}{WO(H$_2$O)}(PW$_9$O$_{34}$)$_2$]$^{12-}$

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The first examples of polyoxometalate structures that incorporate embedded chelated heteroatoms point to new possibilities for stereochemical control of applications.

The connection between Werner-type coordination complexes and polyoxometalates may be traced back to the work of Baker and colleagues in the 1960's[1] and has opened up the extensive field of so-called transition metal substituted polyoxometalates (TMSP) as well as a variety of "sandwich" structures. These complexes have received intense investigation, especially in the laboratories of Hill and Neumann,[2] as robust and versatile oxidation catalysts ("inorganic metalloporphyrins", *etc.*). In all of these complexes each of the embedded transition metal cations has a single coordination site that commonly bears a monodentate sigma-donor ligand, and the {ML}$^{n+}$ group may therefore be viewed as a replacement for a type I[3] {MO$_{terminal}$}$^{4+}$ center in a parent polyoxometalate structure.†

In the course of our search for *resolvable* chiral polyoxometalate architectures we have been exploring the possibility of incorporating chelated metal centers into polyanion structures. We report here the first examples of what promises to be an extensive field of discrete complexes which can be clearly distinguished from the numerous known examples of network solids that incorporate metal chelates as linkers[4] and from symmetrical polyoxometalate anions that bear *surface-attached* metal chelates and organometallic groups.[5]

The title anions were isolated as sodium–potassium salts from reaction between K[Co(en)(CO$_3$)$_2$][6] and Na$_9$[A-PW$_9$O$_{34}$][7] followed by acidification to release carbon dioxide.‡ A minor product, Na$_{6.5}$K$_{5.5}$[K⊂{Co(en)WO$_4$}WO(H$_2$O)(PW$_9$O$_{34}$)$_2$]·19H$_2$O (anion **1**) forms first as purple blocks, followed by green Na$_7$K$_5$[{Co(en)(μ-OH)$_2$Co(en)}{PW$_{10}$O$_{37}$Co(en)}$_2$]·20H$_2$O (anion **2**). Both products were subjected to spectroscopic and single crystal X-ray structural analysis.§

Anion **1** (Fig. 1a) has a sandwich-type structure based on two [A-PW$_9$O$_{34}$]$^{9-}$ moieties¶ linked by two (structurally distinct) tungsten atoms and a {Co(en)} group. The polytungstate framework bears some similarity to that of [P$_2$W$_{19}$O$_{69}$(H$_2$O)]$^{14-}$ reported by Tourné and Tourné,[8] but the sandwiched *trans*-{OW(H$_2$O)} group in **1** has the water ligand directed *outside* the anion, whereas in the Tourné anion the coordinated water is *inside*. The additional sandwiched atoms in **1** (Fig. 1b) form an

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unprecedented edge-shared combination of {Co(en)O$_4$} and WO$_6$ octahedra. A potassium cation occupies the remaining vacancy in the sandwich belt, as is often observed in such structures. Although the anion has overall C_1 symmetry, the usual fluxional behavior of the ethylenediamine ligand effectively confers mirror symmetry.

The major product, anion **2**, has a centrosymmetric structure that is analogous to the long-known *meso*-[(en)$_2$Co(μ-OH)$_2$Co(en)$_2$]$^{4+}$ cation,[9] with the chiral [PW$_{10}$O$_{37}$Co(en)]$^{6-}$ group functioning as a bidentate ligand in place of one ethylenediamine on each cobalt atom. The tungstocobaltophosphate moiety can be viewed as a derivative of the well-known lacunary anion α-[PW$_{11}$O$_{39}$]$^{7-}$ in which {Co(en)}$^{3+}$ has replaced one of the (type-II[3]) *cis*-[WO$_2$]$^{2+}$ groups that surround the lacuna, see Fig. 2. The robust attachment of the two cobalt atoms to the polytungstate framework is shown by the significant elongation of formerly W⋯O terminal bonds (∼ 1.72 Å) to W⋯O(Co) (W⋯O, ∼ 1.80 Å). The tungsten-183 NMR spectrum of aqueous solutions of **2** (Fig. 3) is consistent with the solid-state structure. Ten lines are expected although three had very similar chemical shifts and were unresolved: δ/ppm, +85.9 (2W), +77.7 (2W), +51.0
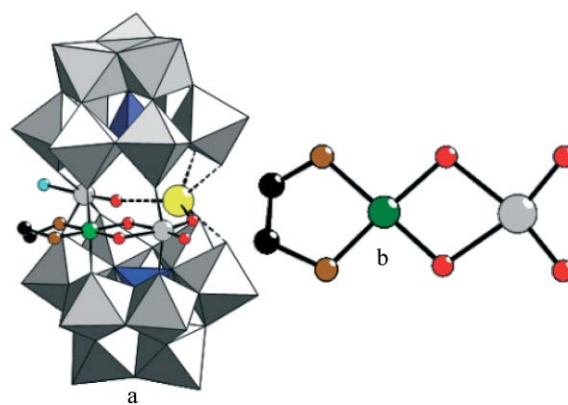

Fig. 1 (a) Composite polyhedral and ball-and-stick representation of the structure of anion **1**. Broken lines denote K⋯O interatomic distances between 2.6 and 3 Å. (b) View of atoms forming the "planar" belt of the anion. Color code: W (gray), Co (green), K (yellow), N (brown), C (black), O (red), H$_2$O (pale blue), PO$_4$ (dark blue), WO$_6$ (white). Bond distances: C–C 1.56(4); C–N 1.44(4), 1.56(3); Co–N 1.98(2), 1.93(2); Co–O$_b$ 1.976(17), 1.902(15); W–O$_b$ 2.173(16), 2.154(16); W–O$_t$ 1.751(19), 1.74(2). O$_t$ are the terminal oxygen atoms and O$_b$ are the bridging oxygen shared by Co and W.
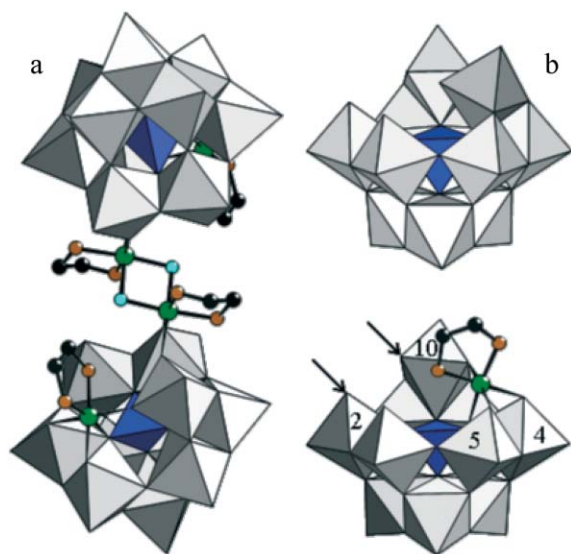
Fig. 2 (a) Composite polyhedral and ball-and-stick representation of the structure of anion **2**. (b) Structure of $[PW_{10}O_{37}\{Co(en)\}]^{6-}$ ligand illustrating its similarity to lacunary $[PW_{11}O_{39}]^{7-}$ (shown above). Arrows denote points of attachment to $\{(en)Co(\mu\text{-}OH)_2Co(en)\}$ core. The four WO_6 octahedra linked to cobalt atoms are labeled. Color code as in Fig. 1, except OH (pale blue). Selected interatomic distances (Å), range [average]: W–O$_{terminal}$, 1.703(16)–1.748(16) [1.72(2)]; W–O(Co), 1.784(13)–1.833(15) [1.81(2)]; Co–O(W), 1.886(14)–1.924(13) [1.91(2)]; Co–O(H), 1.902(12), 1.926(12); Co–O(P,W,W), 1.989(13).
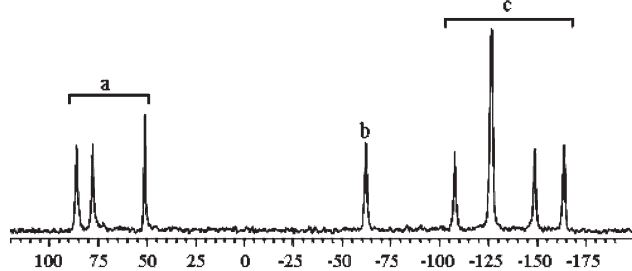

Fig. 3 Tungsten-183 NMR spectrum of anion **2**.

(2W), −62.4 (2W), −108.1 (2W), −126.8 (6W), −149.0 (2W), −164.0 (2W). Positive tungsten chemical shifts are rarely observed for diamagnetic polytungstates, and the three low-field resonances, labeled **a** in Fig. 3, are provisionally attributed to the three tungsten atoms (W4, W5, W10, Fig. 2b) in WO_6 octahedra that share *two* vertices with cobalt atoms, and the resonance at −62.4 ppm (**b**) to the tungsten (W2) in an octahedron that shares a single vertex with cobalt.

Both anions exhibit ligand-field transitions of Co^{III} at ~ 600 nm[I] attributed to $^1A_{1g} \rightarrow {}^1T_{1g}$ (the T$_{2g}$ transition is obscured by charge transfer absorption). Transitions from both types of cobalt centers in anion **2** are resolved. Since the absorption maximum for the Werner dicobalt cation is 525 nm,[9b] we attribute the shoulder at 535 nm to the corresponding cobalt in **2**, and the maximum at 619 nm to the cobalt attached to the tungstophosphate group. In addition these complexes present several new features. (1) They are the first examples of polyoxometalates that incorporate *embedded* chelated heteroatoms, and they thus open a broad range of new

steric and chiral possibilities for polyoxotungstate and -molybdate structures that we are currently exploring, (2) they are the first redox-stable examples of tungstocobaltates incorporating octahedral low-spin Co(III) centers, and (3) they demonstrate the structural equivalence of a monochelated transition metal to the type II *cis*-MO$_2$ building block common to many polyoxometalates.

Notes and references

† Examples of polyhapto ligands have also been observed in such complexes, *e.g.* $[PW_{11}O_{39}Ti(\eta^5\text{-}C_5H_5)]^{4-}$ [R. K. C. Ho, W. G. Klemperer, *J. Am. Chem. Soc.*, 1978, **100**, 6772–6774] and $[PW_{11}O_{39}Ru(\eta^2\text{-}HOOCCH:CHCOOH)]^{5-}$ [C. Rong, M. T. Pope, *J. Am. Chem. Soc.*, 1992, **114**, 2932–2938].

‡ To a solution of 0.86 g (3.15 mmol) of K[Co(en)(CO$_3$)$_2$] in 20 mL of warm (30–40 °C) water was added 5.0 g (2.1 mmol) of Na$_9$[A-PW$_9$O$_{34}$]·7H$_2$O and the pH of the slurry was carefully lowered to 6.0 by the addition of 2 M HCl. At pH 6.5 the tungstophosphate dissolved completely and CO$_2$ was evolved. The resulting clear blue-green solution was allowed to stand in an open beaker and after 1–2 days purple crystals (0.29 g) of **1** were deposited and were filtered off. Anal. Calcd (Found for C$_2$H$_{48}$CoK$_{6.5}$N$_2$Na$_{6.5}$P$_2$O$_{90}$W$_{20}$) Na, 2.6 (2.9); K, 4.4 (4.6); Co, 1.0 (0.95); P, 1.0 (1.0). λ_{max}, 581 nm; $\delta(^{31}P)$, −10.8 ppm. Green crystals of **2** began to appear after a week and were harvested after two weeks. Yield 2.23 g (43% based on tungsten). Anal. Calcd (Found for C$_8$H$_{72}$Co$_4$K$_5$N$_8$Na$_7$P$_2$O$_{96}$W$_{20}$) Na, 2.6 (2.6); K, 3.2 (3.2); Co, 3.8 (3.8); P, 1.0 (0.9). λ_{max}, 535 sh, 619 nm; $\delta(^{31}P)$, −7.48 ppm.

§ Analyses were performed on a Bruker-Siemens SMART CCD diffractometer equipped with a Mo anode and graphite monochromator, $\lambda(K_\alpha)$ 0.71073 Å. Crystals were mounted on a glass fiber and placed in a nitrogen stream at 173 K. Following application of routine Lorentz and polarization corrections, an empirical absorption correction was used, based on measured intensities of equivalent reflections at different φ and ω values. All structures were solved using direct methods and refined against $|F^2|$ over all independent reflections. The SMART, SAINT, SHELX-97, and XSEED software were used to solve and refine the data sets. Atoms heavier than oxygen, except disordered sodium cations, were refined anisotropically. Hydrogen atoms were not refined or calculated. As is frequently noted in large polyoxometalate structures there is extensive disorder of the cations and water molecules, to the extent that some of the cations and many of the water molecules cannot even be observed. In order to determine the occupancy of any disordered cations their atomic displacement parameters were first set to be comparable to the corresponding non-disordered atoms and their occupancies were refined. Then the occupancy numbers were held fixed and their atomic displacement factors were refined. **Crystal data.** C2CoK5.25N2O84P2W20, (anion **1**) M = 5399.19 g/mol, monoclinic, a = 16.245(3), b = 16.690(3), c = 35.129(6) Å, β = 93.090(3)°, V = 9510(3) Å^3, T = 182(2) K, space group $P2_1/c$ (no. 14), Z = 4, μ(Mo-Kα) = 24.611 mm^{-1}, 104976 reflections measured, 23072 unique (R_{int} = 0.1377). The final R_1 [$I > 2\sigma(I)$] was 0.0696. C8Co4K2N8Na3O96P2W20, (anion **2**) M = 5866.0 g/mol, triclinic, a = 11.696(2), b = 12.685(2), c = 20.359(4) Å, α = 103.378(3), β = 90.628(3), γ = 96.552(3)°, V = 2917.2(9) Å^3, T = 182(2) K, space group P-1 (no.2), Z = 1, μ(Mo-Kα) = 20.385 mm^{-1}, 32776 reflections measured, 13437 unique (R_{int} = 0.0720). The final R_1 [$I > 2\sigma(I)$] was 0.0752. CIF files for **1** and **2** are deposited with the Cambridge Crystallographic Data Centre. CCDC 278917, 278918. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b509756h

¶ Although the starting salt Na$_9$[A-PW$_9$O$_{34}$]·7H$_2$O contains the β-isomer of the anion, isomerization to the α framework has occurred in both products **1** and **2**. Such isomerization is commonly observed in syntheses of tungstophosphate complexes, see, *e.g.* U. Kortz, F. Hussain, M. Riecke, *Angew. Chem., Int. Ed.,* 2005, **44**, 3773–3777.

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