A {Co₄O₄} Cubane Incorporated within a Polyoxoniobate Cluster
Zhijie Liang, Dongdi Zhang, Pengtao Ma, Jingyang Niu,* and Jingping Wang*[^a]
yellow crystals and purple crystals were obtained, respectively (see Scheme 1). Compound 1, however, can be crystallized without the need for organic ligands, in contrast to reports indicating an essential stabilizing role of organic ligands in the formation of TM-containing PONbs.\cite{20,24}

Bond valence sum (BVS) calculations for 1 indicate that the values for Co ions fall into the ranges 2.07–2.12 and 3.12–3.20 (Table S2 in the Supporting Information), confirming that both +2 and +3 oxidation states are in the compound, in good agreement with the results of X-ray photoelectron spectroscopy (XPS; Figure S1 in the Supporting Information).

Single-crystal X-ray diffraction analysis of the obtained black crystals shows that 1 crystallizes in the monoclinic space group P2/c. The gigantic polyanion 1a has dimensions of about 16×16×16 Å³ (Figure S2 in the Supporting Information). In the structure of 1a, [H₂CoO₆(Nb₂O₁₉)₆]^{18⁻} (Figure 1a), there is a [Co₈O₃₆]^{18⁻} core, whereas the oxidation state of the tetracoordinated cobalt is +2, which is defined by three terminal oxygen atoms from three [Nb₂O₁₉]^{6⁻} clusters and one oxygen atom from [CoO₆] cubane. As mentioned above, the reason that the presence of Co³⁺ centers in 1a is attributed to air oxidation. Interestingly, mixed-valent cobalt clusters are very rare among POMs.\cite{13} Furthermore, two protons should be added for charge-balance considerations and the BVS values of all oxygen atoms in 1a suggest that the protons delocalize over the entire architecture (Table S3 in the Supporting Information).

Furthermore, the overall architecture, exhibiting an approximate T₄ symmetry, can be considered an octanuclear [Co₈] cluster stabilized by four classical [Nb₂O₁₉]^{6⁻} building blocks (Figure 2). Four [Nb₂O₁₉]^{6⁻} units are bridged by four cobalt(II) ions. The total charge of 1a is 18⁻, which is balanced in the solid state by 12 potassium and 6 sodium counter cations. Notably, if each [Nb₂O₁₉]^{6⁻} units acts as a node, four [Nb₂O₁₉]^{6⁻} units are located in the four vertices of a tetrahedron. The [Co₈O₆] cubane resides in the center of this tetrahedron, while four Co²⁺ cations are situated outside it (Figure 1d). It differs from [Fe₈₄(PO₄)₆]^{14⁻}. The two sets of cobalt environments, Co₁, Co₁A, Co₂, Co₂A and Co₃, Co₃A, Co₄, Co₄A, each exhibit several tetrahedral geometries. Therefore, the structure incorporates three tetrahedra, which is unique in PONbs. Neighboring units link together forming a one-dimensional chain in the ab and bc plane [O78-K1-O40 98.1(2)°, O79-K15-O39 126.0(4)°], and then form a two-dimensional plane via a series of potassium–oxygen and sodium–oxygen bonds [O75-K7-O47 114.0(3)°, O35-K6-O11 113.5(3)°, O33-K8-O7 116.6(3)°; Na1–O9W 2.407(10) Å, K2–O11 2.825(8) Å; Figure S4 in the Supporting Information]. The formula is based on three different analytical methods, namely single-crystal X-ray diffraction, elemental analysis, and thermogravimetric analysis (TGA). The TGA indicated the presence of 39 water molecules in the crystal structure of 1a (Figure S5 in the Supporting Information).

Note that 1a resembles structurally the [Co₄(Nb₆)] cluster previously reported by our group.\cite{25} In the latter case, the structure is composed of six [Nb₂O₁₉]^{6⁻} blocks and a [Co₄] cluster containing a double-cubane core, [Co₄O₆(ΟH)]^{14⁻} and seven external Co ions. Six cobalt ions in this [Co₄] core are

![Figure 1](image1.png)

**Figure 1.** a) Ball-and-stick representation of 1a; b) simplified view of the [Co₆O₃₆] core; c) coordination geometry of the external Co³⁺ ions; d) polyhedral/ball-and-stick view of the linking model of [Co₆O₃₆] cubane, Co₆O₆, tetrahedron, and PONb. All hydrogens, potassium ions, sodium ions, and lattice water molecules are omitted for clarity.

![Figure 2](image2.png)

**Figure 2.** Representations of the various building blocks of 1a: polyhedral structure of the [Nb₂O₁₉]^{6⁻} unit and [Co₈].
connected to each [Nb$_6$O$_{19}$]$^{3-}$ unit by three bridging oxygen atoms, forming the main skeleton. Both 1 and (Co$_4$Nb$_{12}$) contain cubane cores and Lindqvist-type anions (Nb$_6$O$_{19}$), with the difference that the former contains mixed Co$^3+$ and Co$^5+$ ions and the latter contains only Co$^6+$ ions. The (Co$_4$Nb$_{12}$) cluster comprises two trigonal-antiprismatic fragments. However, 1 contains three tetrahedra. In addition, the types of coordination geometry for cobalt ions are markedly different.

The solid-state magnetic susceptibility of 1 was studied in the range of 2–300 K under an external magnetic field of 2000 Oe (Figure 3). The $\chi_mT$ value of 1 gradually declines with decreasing temperature and reaches a minimum of 2.30 emu mol$^{-1}$ K at 2 K. The effective moment $\chi_m$ decreases continuously with decreasing temperature, indicating the presence of antiferromagnetic exchange interactions, which is further confirmed by a negative Weiss constant $\theta = -9.16$ K derived by fitting the Curie–Weiss law to the magnetic data between 2 and 300 K (Figure S6 in the Supporting Information). Such antiferromagnetic coupling with a cubane core has been previously reported.\[1\] The value of $\chi_m$ increases from 0.03 emu mol$^{-1}$ at 300 K to 0.18 emu mol$^{-1}$ at 40 K, and then exponentially increases to reach a maximum of 1.15 emu mol$^{-1}$ at 2 K.

Based on the coordination pattern of the Co ions, Co$^5+$ ions represent $d^3$ high-spin centers whereas Co$^6+$ ions are $d^0$ low-spin (S = 0). The unpaired electrons will be on the Co$^5+$ centers. From the perspective of magnetism, therefore, compound 1 is effectively tetranuclear. This observation has also been previously reported.\[1\] When the $\chi_mT$ value of 9.12 emu mol$^{-1}$ K at room temperature (300 K) is compared with that of the spin-only value of 7.50 emu K mol$^{-1}$ for 4 non-interacting Co$^3+$ ions (S = 3/2) with $g = 2.0$, we can see that there is spin–orbit coupling.\[1\]

In summary, a novel tetrameric PONb has been successfully constructed by a new synthetic strategy. This is the first mixed-valence cobalt aggregate in PONb chemistry, and the second largest example of a Co-containing PONb. This synthetic strategy could potentially be extended beyond the synthesis of 1 to construct further novel frameworks based on other TMs.

Further possibilities for the assembly of nickel-, manganese-, and iron-containing PONbs are under consideration in our group.

**Experimental Section**

**Synthesis of 1**

Method 1: NH$_3$ (0.320 mL) was added to a stirred solution of CoCl$_2$·6H$_2$O (0.068 g, 0.284 mmol) in water (1.25 mL). The resulting solution was added dropwise to a stirred aqueous solution (10 mL) containing K$_2$HNb$_6$O$_{19}$·13H$_2$O (0.525 g, 0.385 mmol) and the pH value was adjusted to 12.00 by addition of NaOH solution (2 mol L$^{-1}$). The resulting suspension was transferred to a Teflon-lined autoclave and kept at 160°C for 22 h. After slow cooling to room temperature, a dark green solution was obtained, filtered, and then transferred to a straight glass tube. Diffusion between three phases produced black virgate-shaped crystals after two weeks. Yield: 10% (based on K$_8$Nb$_6$O$_{19}$·13H$_2$O).

Method 2: Same procedure as for method 1, except in the absence of NH$_3$. The pH value was adjusted to 12.50 by addition of NaOH solution (2 mol L$^{-1}$). Yield: 13% (based on K$_8$Nb$_6$O$_{19}$·13H$_2$O).

Method 3: 1,10-phenanthroline (0.033 g, 0.183 mmol) was added to a stirred solution of CoCl$_2$·6H$_2$O (0.090 g, 0.378 mmol) in water (0.833 mL). The resulting solution was added dropwise to a stirred aqueous solution (10 mL) containing K$_2$HNb$_6$O$_{19}$·13H$_2$O (0.667 g, 0.489 mmol) and the pH value was adjusted to 12.00 by addition of NaOH solution (2 mol L$^{-1}$). The resulting suspension was transferred to a Teflon-lined autoclave and kept at 160°C for 22 h. After slow cooling to room temperature, a dark green solution was obtained, filtered, and then transferred to a straight glass tube. Diffusion between three phases produced black virgate-shaped crystals after two weeks. Yield: 9% (based on K$_8$Nb$_6$O$_{19}$·13H$_2$O).

**Acknowledgements**

The authors gratefully acknowledge support from the National Natural Science Foundation of China and the Natural Science Foundation of Henan Province.

**Keywords**: cubanes - magnetism - mixed-valence - polyoxometalates - transition metals

**References**

