■ Polyoxometalates | *Hot Paper* |

A {Co$_4$O$_4$} Cubane Incorporated within a Polyoxoniobate Cluster

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Abstract: A novel octacobalt-containing polyoxoniobate, $Na_6K_{12}[H_2Co_8O_4(Nb_6O_{19})_4]\cdot39H_2O$, has been prepared by a combination of hydrothermal and diffusion methods. The polyanion $[H_2Co_8O_4(Nb_6O_{19})_4]^{18-}$ incorporates a tetrameric assembly of Lindqvist-type $[Nb_6O_{19}]^{8-}$ fragments trapping a {Co$^{II}_4$Co$^{III}_4$} cluster which comprises a central {Co$^{III}_4$O$_4$} cubane core, surrounded by another four Co^{II} ions linkers. Furthermore, magnetic measurements show that the compound exhibits antiferromagnetic interactions.

The design and synthesis of novel transition metal (TM)-containing polyoxometalates (POMs), an important subclass of the POM family, is predominantly driven by attractive magnetic and photocatalytic properties.[1] However, the number of known polyoxoniobates (PONbs) is less than those of other POMs, owing to the basic nature of PONbs in aqueous media.[2,3] Generally, the synthetic strategy utilized to obtain TM-containing PONbs has involved choosing a metal that is base-soluble or protected by chelating ligands.[2b,4] Examples of this interesting type of PONb include copper-containing derivatives {Cu$_{24}$Nb$_{56}$}[5] and {Cu$_{25.5}$Nb$_{56}$},[5] {CuNb$_{11}$},[1b] titanium-containing derivatives {Ti$_{12}$Nb$_6$},[6a] {TiNb$_9$},[6b] and {Ti$_2$Nb$_8$},[6c] and vanadium-containing derivatives {V$_4$Nb$_6$},[4a] {V$_4$Nb$_{10}$},[7a] {V$_3$Nb$_{12}$},[4c,7b] {PV$_2$Nb$_{12}$},[7c] {V$_8$Nb$_8$},[7d] {PV$_6$Nb$_{12}$},[7e] and {VNb$_{14}$}.[7f] Some other TM-containing PONbs are also known, such as {MNb$_9$} (M = Co, Cr, Mn, Fe, Ni),[8a,b] {Cr$_2$Nb$_{10}$},[8c] {MnNb$_{10}$},[8d] {MNb$_{12}$} (M = Co, Mn, Ni),[9a,b] and {Co$_{14}$Nb$_{36}$}.[4b] Among the aforementioned TM-containing PONbs, titanium-substituted and vanadium-incorporating derivatives have been widely investigated. Moreover, the titanium and vanadium ions in the reported compounds are mostly of d^0 electron configuration. In contrast, incorporating TMs having d electrons may lead to interesting properties, such as magnetic and electro-optical properties. Whereas complexes of polyoxotungstates and polyoxomolybdates incorporating a larger number of Co ions have
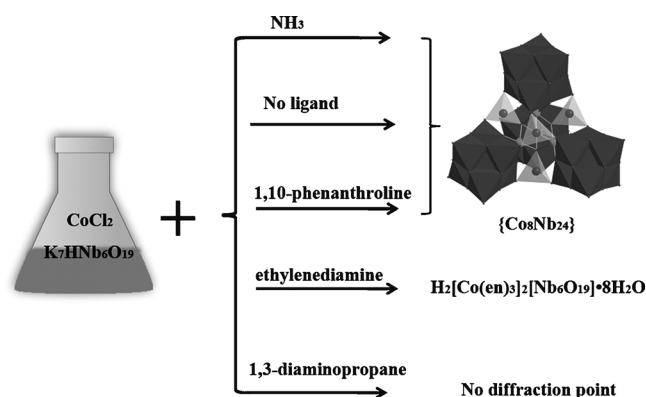
been reported (Table S1 in the Supporting Information), reports of Co analogues in PONbs are still very rare.

In the course of our ongoing investigation into large Nb–oxo clusters based on the Lindqvist-type anion $[Nb_6O_{19}]^{8-}$ and TM ions,[1b,4b,5] we present herein the tetrameric Co-containing PONb-based $Na_6K_{12}[H_2Co_8O_4(Nb_6O_{19})_4]\cdot39H_2O$ (**1**), which contains an octanuclear mixed-valent cluster including an appended {Co$^{III}_4$O$_4$} cubane motif. To our knowledge, compound **1** represents the first member of the mixed-valent PONb-based Co family. It was obtained by the hydrothermal reaction of $K_7HNb_6O_{19}\cdot13H_2O$ and $CoCl_2\cdot6H_2O$ with NH_3 in aqueous medium, followed by the diffusion method. Although hydrothermal and test tube diffusion method has been separately used in the syntheses of PONbs.[1b,4c,10] However, the combination is quite rare.

To investigate the source of Co^{3+} in the compound, $CoCl_2\cdot6H_2O$ was replaced in the reaction mixture by Co_3O_4. Unfortunately, no crystal was obtained. We speculated that a part of the Co^{2+} ions were oxidized to Co^{3+} ions as a result of air oxidation by vigorous stirring in the alkaline PONb solution during the reaction. The balanced chemical reaction for the formation of the polyanion $[H_2Co_8O_4(Nb_6O_{19})_4]^{18-}$ (**1a**) is given in Equation (1):

$$8\,[Co^{II}L_n] + 4\,[HNb_6O_{19}]^{7-} + O_2 + 6\,OH^- \rightarrow \\ [H_2Co_8O_4(Nb_6O_{19})_4]^{18-} + 8n\,L + 4\,H_2O \tag{1}$$
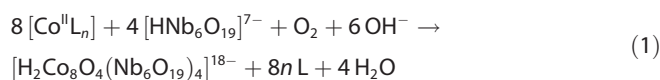
where ligand L = NH$_3$. To explore the role of the ligand and the influence on configuration, a series of experiments were carried out. Compound **1** could be formed by using 1,10-phenanthroline instead of NH$_3$ as the ligand (Scheme 1). However, when using ethanediamine or 1,3-diaminopropane as ligands,

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Scheme 1. The effect on experimental results of changing ligands.

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.[2b, 4]

Bond valence sum[11] (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 *P*2/*c*. The gigantic polyanion **1a** has dimensions of about 16×16 Å² (Figure S2 in the Supporting Information). In the structure of **1a**, $[H_2Co_8O_4(Nb_6O_{19})_4]^{18-}$ (Figure 1a), there is a {Co$_8$}
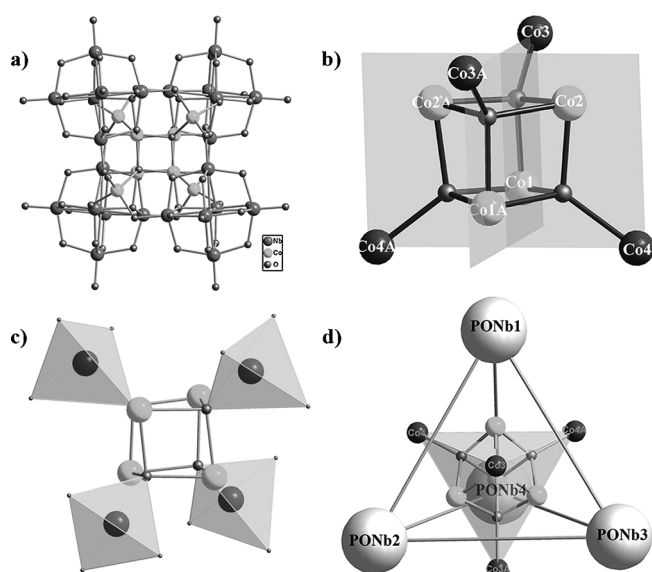

Figure 1. a) Ball-and-stick representation of **1a**; b) simplified view of the {Co$_8$O$_4$} core; c) coordination geometry of the external Co^{II} ions; d) polyhedral/ball-and-stick view of the linking model of {Co$^{III}_4$O$_4$} cubane, Co$^{II}_4$ tetrahedron, and PONb. All hydrogens, potassium ions, sodium ions, and lattice water molecules are omitted for clarity.

cluster (Figure S3 in the Supporting Information), which can be regarded as a distorted {Co$^{III}_4$O$_4$} cubane attached to four "outer" Co^{II} cations via the four oxygen atoms of {Co$^{III}_4$O$_4$} (Figure 1b,c). This distorted cubane-shaped, mixed-valent cobalt–oxo cluster, {Co$^{III}_4$O$_4$}, consists of four Co^{III} centers with four μ$_4$-O^{2-} anions acting as bridging ligands, which has already been reported for cobalt clusters.[12] In its simplest form, the extended cubane unit can therefore be regarded as a {Co$_8$O$_4$} core. Co1, Co1A, Co3, and Co3A lie in one plane. Co2, Co2A, Co4 and Co4A lie in the other plane. The {Co$_8$} cluster exhibits idealized C_{2v} symmetry (Figure 1b). The {Co$^{III}_4$O$_4$} cubane is distorted with Co-O-Co angles of 96.8(3)-98.3(3)°, O-Co-O angles of 81.7(3)–94.9(3)° and the Co–O distances fall into the range of 1.915(6)–1.955(6) Å. Interestingly, the four independent cobalt ions in **1a** display coordination geometries in two distinct

ways; the Co^{III} ions form distorted CoO$_6$ octahedra with three bridging oxygen atoms from the same $[Nb_6O_{19}]^{8-}$ cluster and three oxygen atoms from {Co$^{III}_4$O$_4$} cubane, whereas the oxidation state of the tetracoordinated cobalt is +2, which is defined by three terminal oxygen atoms from three $[Nb_6O_{19}]^{8-}$ clusters and one oxygen atom from {Co$_4$O$_4$} cubane. As mentioned above, the reason that the presence of Co^{III} centers in **1a** is attributed to air oxidation. Interestingly, mixed-valent cobalt clusters are very rare among POMs.[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 T_d symmetry, can be considered an octanuclear {Co$_8$} cluster stabilized by four classical $[Nb_6O_{19}]^{8-}$ building blocks (Figure 2). Four $[Nb_6O_{19}]^{8-}$ units are bridged by four cobalt(II)
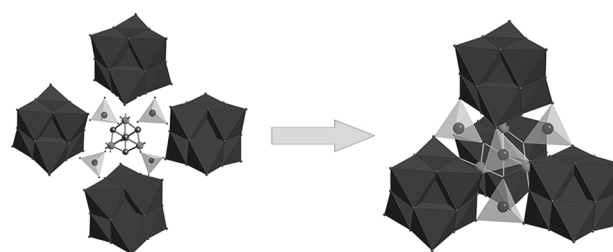

Figure 2. Representations of the various building blocks of **1a**: polyhedral structure of the $[Nb_6O_{19}]^{8-}$ unit and {Co$_8$}.

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 $[Nb_6O_{19}]^{8-}$ units acts as a node, four $[Nb_6O_{19}]^{8-}$ units are located in the four vertices of a tetrahedron. The {Co$^{III}_4$O$_4$} cubane resides in the center of this tetrahedron, while four Co^{II} cations are situated outside it (Figure 1d). It differs from $[Fe_{13.5}(PW_9)_4]$.[14] The two sets of cobalt environments, Co1, Co1A, Co2, Co2A and Co3, Co3A, Co4, Co4A, each exhibit severally 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-O1 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 {Co$_{14}$Nb$_{36}$} cluster previously reported by our group.[4b] In the latter case, the structure is composed of six $[Nb_6O_{19}]^{8-}$ blocks and a {Co$_{14}$} cluster that contains a double-cubane core, {Co$_7$O$_2$(OH)$_6$}$^{4+}$ and seven external Co ions. Six cobalt ions in this {Co$_7$} core are

connected to each $[Nb_6O_{19}]^{8-}$ unit by three bridging oxygen atoms, forming the main skeleton. Both **1** and {$Co_{14}Nb_{36}$} contain cubane cores and Lindqvist-type anions {Nb_6O_{19}}, with the difference that the former contains mixed Co^{II} and Co^{III} ions and the latter contains only Co^{II} ions. The {$Co_{14}Nb_{36}$} 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 $\chi_M T$ value of **1** gradually declines with

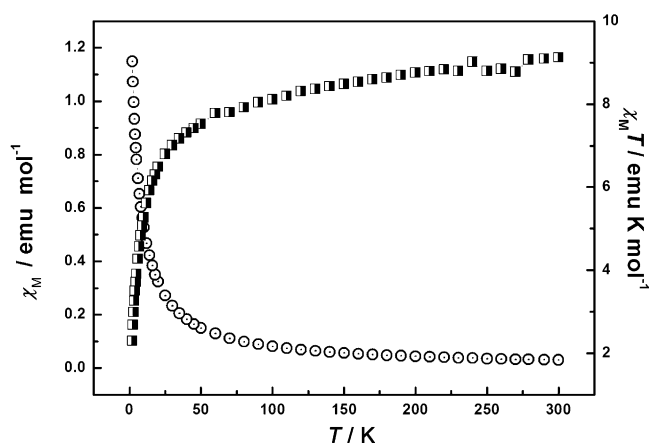**Figure 3.** Temperature dependence of the molar magnetic susceptibility χ_M and the product $\chi_M T$ for **1** between 2 and 300 K.

decreasing temperature and reaches a minimum of 2.30 emu mol^{-1} K at 2 K. The effective moment $\chi_M T$ 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.[15] The value of χ_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^{II} ions represent d^7 high-spin centers whereas Co^{III} ions are d^6 low-spin ($S = 0$). The unpaired electrons will be on the Co^{II} centers. From the perspective of magnetism, therefore, compound **1** is effectively tetranuclear. This observation has also been previously reported.[16] When the $\chi_M T$ 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^{II} ions ($S = 3/2$) with $g = 2.0$, we can see that there is spin–orbit coupling.[17]

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 $CoCl_2 \cdot 6H_2O$ (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 $K_7HNb_6O_{19} \cdot 13H_2O$ (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 $K_7[HNb_6O_{19}] \cdot 13H_2O$). IR (KBr pellet): 893, 870, 718, 537, 506 cm^{-1} (Figure S8 in the Supporting Information); elemental analysis (%) calcd for $K_{12}Na_6H_{80}Co_8Nb_{24}O_{119}$: Co 8.91, K 8.86, Na 2.61, Nb 42.12; found: Co 8.67, K 9.03, Na 2.34, Nb 41.65.

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 $K_7[HNb_6O_{19}] \cdot 13H_2O$).

Method 3: 1,10-phenanthroline (0.033 g, 0.183 mmol) was added to a stirred solution of $CoCl_2 \cdot 6H_2O$ (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 $K_7HNb_6O_{19} \cdot 13H_2O$ (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 $K_7[HNb_6O_{19}] \cdot 13H_2O$).

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