Inorganic Chemistry

Article

An Unusual Asymmetric Polyoxomolybdate Containing Mixed-Valence Antimony and Its Derivatives: $[Sb_4^VSb_2^{III}Mo_{18}O_{73}(H_2O)_2]^{12-}$ and $\{M(H_2O)_2[Sb_4^VSb_2^{III}Mo_{18}O_{73}(H_2O)_2]_2\}^{22-}$ (M = Mn^{II}, Fe^{II}, Cu^{II} or Co^{II})

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A new type of heteropolyanion containing mixed-valence antimony, $[Sb_4^VSb_2^{III}Mo_{18}O_{73}(H_2O)_2]^{12-}$ (**1a**), and its four derivatives, $\{M(H_2O)_2[Sb_4^VSb_2^{III}Mo_{18}O_{73}(H_2O)_2]_2\}^{22-}$ (M = Mn^{II}, Fe^{II}, Cu^{II}, or Co^{II}) (**2a**−**5a**), have been isolated as ammonium salt, and their structures were determined by single-crystal X-ray diffraction. The framework of the polyanion **1a** displays a curious asymmetric structure, and there exist six types of Sb coordination environments and seven types of {MoO$_6$} octahedra. The title compounds were also characterized by elemental analyses, IR, UV–vis, Raman spectra, and cyclic voltammgramms.

Introduction

Polyoxometalates (POMs) are an immense class of metal–oxygen cluster compounds formed in aqueous acidic solution by self-assembly which exhibit compositional diversity and structural versatility as well as potential applications in a variety of fields, including catalysis, analytic chemistry, medicine, and materials science.[1] Most of these structures contain fragments of several well-known polyoxoanions, such as Keggin anion $(XM_{12}O_{40})^{n-}$, Lindquist anion $(M_6O_{19}^{2-})$, and Dawson anion $((X_2M_{18}O_{62})^{n-}$, (M = Mo, W; X = Si, P, ...), or their monovacant and trivacant fragments which are the basis for numerous anions. To date, a large number of papers have been published that describe the synthesis and characterization of Sb(III)-containing polyoxotungstates based on the trivacant Keggin anion $SbW_9O_{33}^{9-}$, for example, dimeric $[Sb_2W_{22}O_{74}(OH)_2]^{12-}$, $[Sb_2W_{20}M_2O_{70}(H_2O)_6]^{(14-2n)-}$ $(M^{n+} = Fe^{3+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}),^{2}$ $[Fe_4(H_2O)_{10}(\beta-SbW_9O_{33})_2]^{6-},^{3}$ $[M_3(H_2O)_3(\alpha-SbW_9$-

$O_{33})_2]^{12-}$ (M = Cu^{2+}, Zn^{2+}),[4] $[(VO)_3(\alpha-SbW_9O_{33})_2]^{12-},^{5}$ $[(MnCl)_6(SbW_9O_{33})_2]^{12-},^{6}[\{Na(H_2O)_2\}_3\{M(C_3H_4N_2)\}_3(SbW_9$-$O_{33})_2]^{9-}$ (M = Ni^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}),[7] $[Cs_2Na(H_2O)_{10}Pd_3(\alpha$-$SbW_9O_{33})_2]^{9-},^{8}$ and $(C_{52}H_{60}NO_{12})_{12}[(Mn(H_2O))_3(SbW_9$-$O_{33})_2],^{9}$ four-meric $[Na_2Sb_4(H_2O)_4(SbW_9O_{33})_4]^{22-}$ ^{2} and $Ce_3Sb_4W_2O_8(H_2O)_{10}(SbW_9O_{33})_4^{19-},^{10}$ and six-meric $[Sb_6W_{65}$-$O_{217}(H_2O)_7]^{26-}$, which consists of four α-SbW$_9$O$_{33}$ and two β-SbW$_9$O$_{33}$ fragments which are linked together by a total of 11 WO$_6$ octahedra.[11] Nevertheless, there are very few reports about the compositions and structures of Sb-containing polyoxomolybdates. In 1982, Sasaki reported the first Sb-containing polyoxomolybdate, $[H_2Sb(V)Mo_6O_{24}]^{5-},^{12}$ with a structure analogous to the well-known heptamolybdate.

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Table 1. Crystallographic Data for **1–5**

compound	1	2	3	4	5
elemental composition	$H_{74}O_{86}N_{12}Mo_{18}Sb_6$	$H_{140}O_{172}N_{22}MnMo_{36}Sb_{12}$	$H_{140}O_{172}N_{22}FeMo_{36}Sb_{12}$	$H_{140}O_{172}N_{22}\ CuMo_{36}Sb_{12}$	$H_{140}O_{172}N_{22}\ CoMo_{36}Sb_{12}$
cryst dimens, mm	$0.21 \times 0.14 \times 0.12$	$0.28 \times 0.23 \times 0.15$	$0.35 \times 0.26 \times 0.20$	$0.26 \times 0.23 \times 0.16$	$0.12 \times 0.11 \times 0.08$
M, g mol^{-1}	4076.10	8171.05	8171.96	8179.66	8175.05
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	13.8137(6)	13.8612(9)	13.834(3)	13.7778(17)	13.8343(7)
b, Å	17.8810(7)	17.9531(12)	17.908(3)	17.945(2)	17.9604(11)
c, Å	19.7810(7)	19.8574(14)	19.789(4)	19.818(3)	19.8332(11)
α (deg)	69.542(2)	69.8010(10)	69.633(3)	69.621(2)	69.774(3)
β (deg)	82.375(2)	82.7290(10)	82.564(3)	82.432(2)	82.854(3)
γ (deg)	69.846(2)	69.3450(10)	69.733(2)	69.481(2)	69.451(3)
V, Å^3	4286.9(3)	4339.5(5)	4311.3(15)	4301.4(9)	4329.8(4)
Z	2	1	1	1	1
d calcd, g cm^{-1}	3.157	3.126	3.147	3.157	3.136
μ, cm^{-1}	4.516	4.672	4.570	4.681	4.655
total reflns	46766	22183	22711	22018	38721
indep reflns	21745 $R(\text{int}) = 0.0482$	15213 $R(\text{int}) = 0.0149$	15761 $R(\text{int}) = 0.0205$	15065 $R(\text{int}) = 0.0201$	15660 $R(\text{int}) = 0.0300$
parameters	966	977	973	978	983
GOF	1.042	1.047	1.132	1.242	1.153
$R1$ $(I > 2\sigma(I))$	0.0526	0.0414	0.0491	0.0460	0.0409
$wR2$ $(I > 2\sigma(I))$	0.1579	0.1264	0.1585	0.1539	0.1477
$R1$ (all data)	0.0890	0.0489	0.0612	0.0562	0.0539
$wR2$ (all data)	0.1825	0.1310	0.1660	0.1590	0.1605

More recently, the structures of two antimony-containing Keggin polyoxomolybdates, $[PSb^{III}(H_2O)Mo_{11}O_{39}]^{4-13}$ and $[Sb_4^VMo_{12}(OH)_6O_{48}]^{10-},^{14}$ have been reported. The former is the Sb^{III}-substituted Keggin anion, and the latter exhibits a central $Sb_4(OH)_6O_{14}$ core where all Sb^V atoms are coordinated octahedrally by six oxygen atoms. The synthesis and characterization of new Sb-containing polyoxomolybdates are interesting because the molybdenum oxides containing antimony often play an important role in heterogeneous oxidation catalysis,[15] and furthermore, exploring the possibility of incorporating both Sb(V) and Sb(III) into polyoxomolybdate frameworks could result in unprecedented structural features and novel properties. Herein we report the synthesis, structural, and some physico-chemical characterization of the first containing mixed-valence antimony polyoxomolybdate, $[Sb_4^VSb_2^{III}Mo_{18}O_{73}(H_2O)_2]^{12-}$ (**1a**), which can serve as a basic building block for larger polyoxomolybdates.

Experimental Section

Synthesis. All of the reagents for the preparation were used without further purification.

(NH$_4$)$_{12}$[Sb$_4^V$Sb$_2^{III}$Mo$_{18}$O$_{73}$(H$_2$O)$_2$]·11H$_2$O (1). (NH$_4$)$_6$Mo$_7$O$_{24}$· 4H$_2$O (1.6 g, 1.41 mmol) was dissolved in a solution of water (25 mL) and heated to 50 °C, then SbCl$_5$ (0.61 g, 2.0 mmol) and Sb$_2$O$_3$ (0.150 g, 0.51 mmol) dissolved in 25 mL of dilute HCl (0.3 M) solution were added dropwise, heated to 50 °C, adjusted to pH =

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3.0 below 70 °C, and kept at 60 °C for 20 min, and a small amount of precipitates was filtered off. The solution was allowed to cool to ambient temperature and filtered. After a few days, the colorless block crystals were formed and the yield was ca. 70% based on Mo. Anal. Calcd for $H_{74}Mo_{18}N_{12}O_{86}Sb_6$: Mo, 42.37; Sb, 17.92; N, 4.12; H, 1.83. Found: Mo, 43.1; Sb, 18.4; N, 4.16; H, 1.92. IR (cm^{-1}): 3424(vs), 3160(vs), 1616(s), 1402(s), 945(m), 891(vs), 777(s), 646(s), 461(m).

(NH$_4$)$_{22}$[Mn(H$_2$O)$_2$(Sb$_4^V$Sb$_2^{III}$Mo$_{18}$O$_{73}$(H$_2$O)$_2$)$_2$]·20H$_2$O (2). (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O (1.6 g, 1.41 mmol) was dissolved in a solution of water (25 mL) and heated to 50 °C, then SbCl$_5$ (0.31 g, 1 mmol) and Sb$_2$O$_3$ (0.30 g, 1 mmol) dissolved in 25 mL of dilute HCl (0.3 M) solution were added dropwise, heated to 50 °C, adjusted to pH = 3.0 below 70 °C, and kept at 60 °C for 20 min, and a small amount of precipitates was filtered off. Ten milliliters of aqueous solution dissolved in MnCl$_2$·6H$_2$O (0.08 g, 0.34 mmol) was added at stirring. The solution was allowed to cool to ambient temperature and filtered. After a few days, the orange block crystals were formed (yield ca. 68%). Anal. Calcd for $H_{148}MnN_{22}O_{176}Mo_{36}Sb_{12}$: Mo, 42.27; Sb, 17.88; Mn, 0.67; N, 3.77; H, 1.73. Found: Mo, 41.6; Sb, 17.6; Mn, 0.66; N, 3.71; H, 1.65. IR (cm^{-1}): 3425(vs), 3154(vs), 1614(s), 1401(s), 946(m), 903(vs), 777(s), 660(s), 479(m).

(NH$_4$)$_{22}$[Fe(H$_2$O)$_2$(Sb$_4^V$Sb$_2^{III}$Mo$_{18}$O$_{73}$)$_2$(H$_2$O)$_2$]·20H$_2$O (3). The preparation of **3** was similar to that of **2** except that FeSO$_4$·7H$_2$O (0.10 g, 0.36 mmol) was used. The crystals were dark-blue, and the yield was ca. 69% based on Mo. Anal. Calcd for $H_{140}O_{172}N_{22}FeMo_{36}Sb_{12}$: Mo, 42.26; Sb, 17.88; Fe, 0.68; N, 3.77; H, 1.73. Found: Mo, 42.1; Sb, 17.3; Fe, 0.71; N, 3.42, H, 1.82. IR (cm^{-1}): 3420(vs), 3161(vs), 1617(s), 1401(s), 948(m), 896(vs), 801(s), 647(s), 482(m).

(NH$_4$)$_{22}$[Cu(H$_2$O)$_2$(Sb$_4^V$Sb$_2^{III}$Mo$_{18}$O$_{73}$(H$_2$O)$_2$)$_2$]·20H$_2$O (4). The preparation of **4** was similar to that of **2** except that CuCl$_2$·2H$_2$O (0.06 g, 0.35 mmol) was used. The crystals were light-green, and the yield was ca. 65% based on Mo. Anal. Calcd for $H_{140}O_{172}N_{22}CuMo_{36}Sb_{12}$: Mo, 42.22; Sb, 17.86; Cu, 0.78; N, 3.77; H, 1.73. Found: Mo, 41.5; Sb, 17.5; Cu, 0.72; N, 3.51; H, 1.65. IR (cm^{-1}): 3447(vs), 3183(vs), 1623(s), 1401(s), 944(m), 896(vs), 772(s), 646(s), 479(m).

(NH$_4$)$_{22}$[Co(H$_2$O)$_2$(Sb$_4^V$Sb$_2^{III}$(H$_2$O)$_2$Mo$_{18}$O$_{73}$)$_2$]·20H$_2$O (5). The preparation of **5** was similar to that of **2** except that

CoCl$_2$·6H$_2$O(0.080 g, 0.34 mmol) was used. The crystals were pink, and the yield was ca. 73% based on Mo. Anal. Calcd for H$_{140}$O$_{172}$N$_{22}$CoMo$_{36}$Sb$_{12}$: Mo, 42.25; Sb, 17.87; Co, 0.72; N, 3.77; H$_2$O, 1.73. Found: Mo, 41.6; Sb, 17.6; Co, 0.66; N, 3.71; H, 1.78. IR (cm^{-1}): 3437(sh), 3130(vs), 1619(m), 1401(s), 940(w), 896(vs), 794(s), 654(s), 479(m).
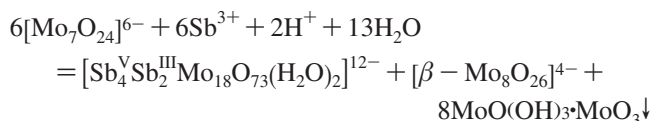
X-ray Crystallography. A selected crystal of the compounds **1–5** was mounted on a glass fiber capillary which was put on a BRUKER SMART APEX II CCD diffractometer equipped with graphite monochromatic radiation and used for data collection. Data were collected at 293(2) K using Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXTL-97) and refined by the full-matrix-block least-squares method on F^2. It was not possible to distinguish between H$_2$O and NH$_4^+$, and they were refined as oxygen atoms. All heavy atoms and framework oxygen atoms of polyanions were refined with anisotropic displacement parameters for **1–5**. The other atoms were refined isotropically. Hydrogen atoms were not included. The usual disorder of cations and solvent molecules makes it impossible to account for their total numbers by X-ray crystallography alone. As a result, elemental analysis was used to determine the total number of NH$_4^+$ cations and water molecules. Crystallographic data for the structural analysis have been deposited in the ICSD Inorganic Crystal Structure database. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldhafen, Germany (fax: (+49)7247–808–666); e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number 415721, 415759, 415760, 415761, and 415722 for **1–5**, respectively.

Physical Measurements. IR spectra were obtained on an EQUINOX55 IR spectrometer with KBr pellets. Raman spectrum measurements were performed using a laser Raman spectrophotometer (Jobin Yvon model Ramanor U-1000) at room temperature. Cyclic voltammetry was carried out at ambient temperature on a CHI680 system. A platinum disk with a surface area of 0.2 cm^2 was used as a working electrode, and a platinum wire served as the counter electrode. Reference electrode was a Ag/AgCl (3 M NaCl) electrode. Prior to each measurement, the working electrode was polished manually with a 0.25 μm diamond slurry and washed with distilled water in an ultrasonic bath. In the present study, the pH 3 media was made up of 0.2 M Na$_2$SO$_4$ + H$_2$SO$_4$. The support electrolytes were 0.2 M KCl. The solutions were deaerated thoroughly for at least 30 min with pure nitrogen and kept under a positive pressure of this gas during the experiments. All of the voltammetric measurements were made at 25 °C.

Results and Discussion

Syntheses. By using ammonium (NH$_4^+$) as counterions, the cluster polyanion **1a** and its derivatives were isolated as crystalline precipitates from an acidified Sb^{III}, Sb^V, and molybdate solution (pH = 3) at 50 °C in around 70% yield. There are three important affects on the formation and isolation of the title compounds, namely, the pH value of the solution, temperature, and counterions. When the pH value was changed to higher than 4 or lower than 2.5, we could not obtain the title compounds, suggesting that the overall structure of the polyanions collapsed. The temperature should not be higher than 80 °C, otherwise there were a lot of unknown precipitation. A lot of parallel experiments showed that it is necessary to use NH$_4^+$ as counterions for the crystallization and we could not obtain the title compounds in the form of sodium or potassium salts.

The compound **1** could also be prepared by reacting (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O and Sb$_2$O$_3$ at pH = 3 aqueous solution at 50–70 °C in only around 30% yield. During the process of reaction the color of solution changed to dark blue because the oxidation–reduction reactions took place, Sb^{III} + 2Mo^{VI} ↔ Sb^V + 2Mo^V, then Mo^V, Mo^{VI} and H$_2$O reacted to form molybdenum blue (MoO(OH)$_3$·MoO$_3$, blue powder precipitation), and besides, a small amount of (NH$_4$)$_4$(β-Mo$_8$O$_{26}$) was crystallized as byproduct, which was proved by IR spectrum and single-crystal X-ray diffraction. The title compounds and (NH$_4$)$_4$(β-Mo$_8$O$_{26}$) were easily distinguished by their different crystal shapes. The reaction can be expressed as follows:

$$6[Mo_7O_{24}]^{6-} + 6Sb^{3+} + 2H^+ + 13H_2O$$
$$= [Sb_4^VSb_2^{III}Mo_{18}O_{73}(H_2O)_2]^{12-} + [\beta - Mo_8O_{26}]^{4-} + 8MoO(OH)_3 \cdot MoO_3 \downarrow$$

Structures of [Mo$_{18}$Sb$^V_4$Sb$^{III}_2$O$_{73}$(H$_2$O)$_2$]$^{12-}$ (1a) and Its Derivatives {M(H$_2$O)$_2$[Sb$_4^V$Sb$_2^{III}$Mo$_{18}$O$_{73}$(H$_2$O)$_2$]$_2$}$^{22-}$ (M = Mn^{II}, Fe^{II}, Cu^{II}, or Co^{II}) (2a−5a). The cluster compounds **1–5** were characterized by single-crystal X-ray structure analyses, bond valence calculations (BVS), and elemental analyses to aid in the determination of the valence of molybdenum, transition-metal and antimony atoms, and protonation sites. The crystallographic data for the six compounds are given in Table 1.

X-ray crystallographic analysis of [Sb$_4^V$Sb$_2^{III}$Mo$_{18}$O$_{73}$(H$_2$O)$_2$]$^{12-}$ (**1a**) reveals that the cluster framework displays an unusual asymmetric structure with dimensions of 15 × 9 × 9 Å^3 (Figure 1), and the main body could be divided into two parallel planes (A and B) along the (1$\bar{1}$2) plane. Plane A consists of six Mo, three Sb, and oxo ligands, where six Mo and three Sb(VI) centers form a parallelogram and are arranged in three lines of three to form two {Mo$_3$} and one {Sb$_3$} groups (Figure 2A). Above plane A, two edge-sharing{Mo$_2$}pairswithMo···Modistancesof3.352(6)−3.366-(6) Å are attached to opposite sides, and a corner-sharing {Sb$_2$(III)} pair with Sb···Sb distances of 3.604(7) Å are inserted between two {Mo$_2$} pairs but are only connected with the left {Mo$_2$} pair via bridging oxygen atoms. Plane B locates below plane A and connects to plane A via bridging oxygen atoms. Plane B (Figure 2B) consists of six Mo, one Sb(1), and oxo ligands, and six Mo atoms are arranged in two lines of three to form two {Mo$_3$} units and one Sb(1) atom inserts between the left two Mo atoms. Below plane B, one edge-sharing {Mo$_2$} pair with Mo···Mo distances of 3.378(7) Å is attached to its left side.

Along the (011) plane, the polyanion can be viewed as composed of three approximate parallel ring fragments, C, D, and E (Figure 1). Ring C resembles a distorted Anderson structure despite the different connection fashions of bridging oxo ligands. Ring D consists of four Mo and two Sb(III), and a Sb(V) atom is inserted in the six-number ring. Fragment E is an eight-molybdenum ring composed of two distorted divacant Anderson fragments connected to each other.

The polyanion can also be viewed as a stacking composed of 18 {MoO$_6$} octahedra (their bond valence sums are
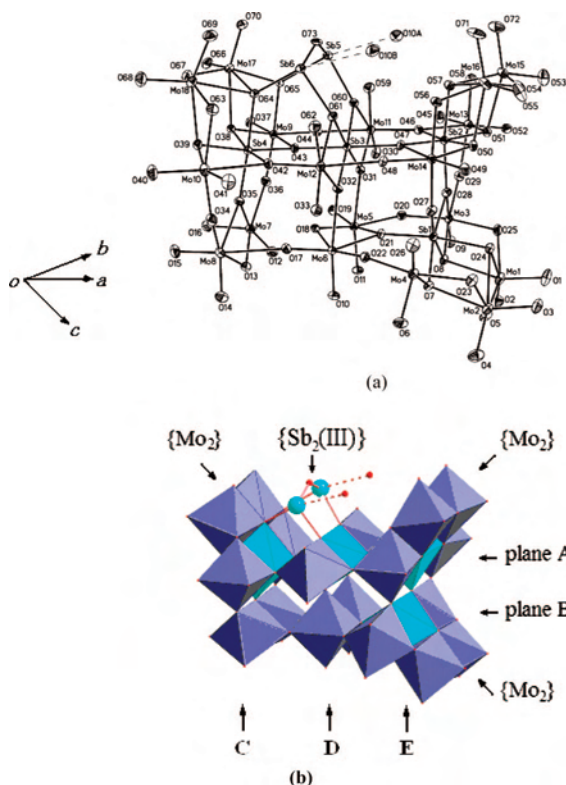
(a)

(b)

Figure 1. (a) ORTEP representation for $[Sb_4^VSb_2^{III}Mo_{18}O_{73}(H_2O)_2]^{12-}$ ion, with displacement ellipsoids shown at 30% probability level. All H atoms have been omitted for clarity; the polyanion has an unusual layer structure with a main body composed two parallel planes, A and B; above and below the planes, three edge-sharing {Mo₂} pairs and a corner-sharing distorted {Sb₂(III)} pair are attached. (b) Polyhedral representation showing the connectivity of the building blocks. Small red ball connected by the dotted line represents aqua-ligand oxygen atoms.
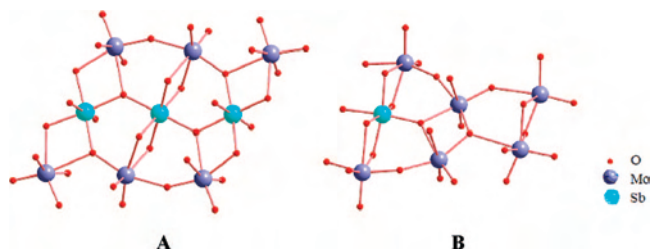

Figure 2. The connectivity of the atoms on planes A and B.

between 5.821 and 6.259, average 6.044), four {SbO₆} octahedra, and two {SbO₃} trigonal pyramids. The oxygen atoms can be classified into four groups according to their bonding arrangements: terminal oxygen (O_t), doubly oxygen (O_b), triply oxygen (O_c), and quadruply oxygen (O_a), and the molybdenum atoms within the cluster can be divided into seven types of {MoO₆} octahedra (Table S1) according to the further bonding partners of the oxygen atoms, which are all in the distorted octahedral environments coordinated by different types of oxygen atoms with a wide range of Mo–O bond lengths: Mo=O_d, 1.672(6)–1.725(6) Å, average 1.702(6) Å; Mo–O_b, 1.750(6)–2.078(6) Å, average 1.922(6) Å; Mo–O(μ_3), 2.002–2.535(6) Å, average 2.252(6) Å; Mo–O(μ_4), 2.379(6)–2.393(6) Å. It is noteworthy that {Mo(4)O₆} and {Mo(7)O₆} octahedra have a very long μ_2-O_{Mo2}–Mo distance (as long as 2.533 (Mo4–O27) and 2.589 Å (Mo7–O18)), which is much greater than the usual types

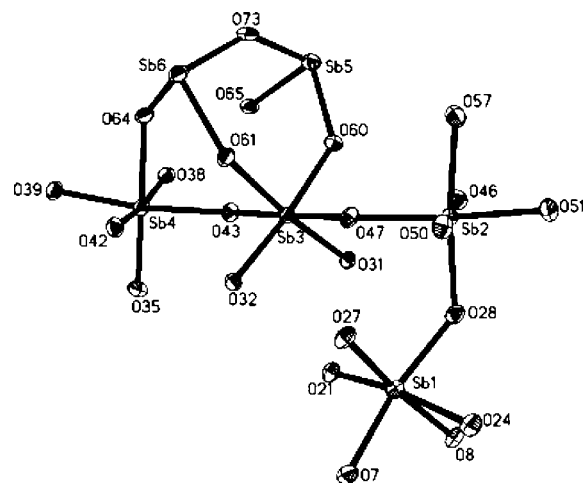**Figure 3.** The resulting {Sb₆O₂₄} core of $[Sb_4^VSb_2^{III}Mo_{18}O_{73}(H_2O)_2]^{12-}$.
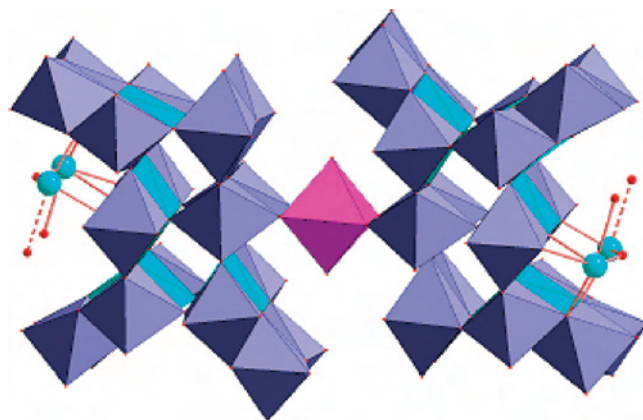
Figure 4. Polyhedral representation of the dimer $\{M(H_2O)_2[Sb_4^V-Sb_2^{III}Mo_{18}O_{73}(H_2O)_2]_2\}^{22-}$ (M = Mn^{II}, Fe^{II}, Cu^{II}, or Co^{II}).

of O–Mo bond lengths reported (less than 2.4 Å); therefore, only a weak interaction can be assumed between them, and the five-coordinated square pyramid {MoO₅} is also acceptable.

The resulting {Sb₆O₂₄} core of $[Sb_4^VSb_2^{III}Mo_{18}-O_{73}(H_2O)_2]^{12-}$ is shown in Figure 3. The coordination environments of the six Sb atoms in the polyanion are all different (Table S2), which results in a variety of Sb–O bonds with a wide range of Sb–O bond lengths in the polyanion. Sb(1)–Sb(4) are coordinated octahedrally by six oxygen atoms, and all have the bond valence sums +5. The coordination sphere of antimony(III) often defies a simple description.[16] Sb5 and Sb6 in the polyanion have three closer coordinated oxygen atoms, with the bond valence sums of 2.65 and 2.88, respectively, less than 3. The careful observation shows that there exists an aqua-ligand oxygen around Sb5 and Sb6 with Sb–O distances of 2.761(6) and 2.630(6) Å, respectively; the bond valences between them is 0.12 and 0.17, which markedly compensate the bond valence sums of Sb5 and Sb6 for the loss of +3; therefore, we can also describe the coordination spheres of Sb5 and Sb6 as [SbO₃(H₂O)], distorted Ψ-trigonal bipyramids (the lone pair

(16) (a) Sawyer, J. F.; Gillespie, R. J. *Prog. Inorg. Chem.* **1986**, *34*, 65 and references therein. (b) Adair, B. A.; Diaz de Delgado, G.; Delgado, J. M.; Cheetham, A. K. *J. Solid State Chem.* **2000**, *151*, 21.

Table 2. Selected Bond Distances (Å) for **1**–**5**

	1	2	3	4	5
Mo=O$_d$	1.672–1.725(6)	1.690–1.741(4)	1.677–1.732(6)	1.687–1.730(6)	1.677–1.733(6)
average	1.702	1.707	1.709	1.652	1.708
Mo−O(μ_2)	1.750–2.078(6)	1.782–2.080(4)	1.722–2.082(6)	1.779–2.078(6)	1.778−2.081(6)
average	1.921	1.925	1.918	1.925	1.926
Mo−O(μ_3)	1.935–2.533(6)	1.924–2.490(5)	1.939–2.506(6)	1.923–2.502(6)	1.920−2.476(6)
average	2.252	2.202	2.227	2.146	2.207
Mo−O(μ_4)	2.360, 2.361(7)	2.407, 2.395(5)	2.391, 2.403(6)	2.396, 2.392(6)	2.397, 2.410(6)
Sb−OH					
Sb−O(μ_2)	1.916, 1.962(7)	1.924, 1.948(5)	1.921, 1.957(5)	1.919, 1.954(5)	1.929, 1.947(5)
Sb−O(μ_3)	1.929, 2.087(6)	1.931–2.166(5)	1.924–2.119(5)	1.933–2.108(5)	1.930−2.186(5)
average	1.980	1.980	1.981	1.982	1.985
Sb−O(μ_4)	2.078, 2.053(6)	2.057, 2.055(5)	2.065, 2.048(5)	2.045, 2.076(5)	2.044, 2.063(5)
Sb−OH$_2$	2.761, 2.627(6)	2.503, 2.648(5)	2.704, 2.611(5)	2.704, 2.611(6)	2.493, 2.624(5)
M−O(W)		2.134, 2.226(5)	2.089, 2.201(6)	2.009, 2.327(6)	2.091, 2.150(6)
average		2.180	2.145	2.168	2.121
M−OH$_2$		2.070(7)	2.056(7)	1.973(6)	2.052(6)
Sb3···Sb3′		13.356	13.326	13.337	13.308

Table 3. Cathodic Peak Potentials (E_{cp}/V) and Anionic (E_{ap}/V) for the Starting Materials and **1**–**5**

compounds	E_{cp}			E_{ap}		
	I	II	III	I′	II′	III′
(NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O			−0.691			−0.324
SbCl$_5$(or Sb$_2$O$_3$)		−0.306			−0.093	
1	0.027	−0.428	−0.703	0.105		
2	0.106	−0.348	−0.657	0.197		−0.468
3	0.105	−0.340	−0.662	0.190		−0.459
4	0.140	−0.336	−0.660	0.310		−0.463
5	0.089	−0.357	−0.660	0.124	---	−0.467

occupies an equatorial position) and present the polyanion as $[Sb_4^VSb_2^{III}Mo_{18}O_{73}(H_2O)_2]^{12−}$.

The polyanion **1** demonstrates a high nucleophilicity and can act as a basic building block to form larger derivatives. It can be connected by a divalent transition-metal ion (Mn^{II}, Fe^{II}, Cu^{II}, or Co^{II}) to form a dimer, $\{M(H_2O)_2[Sb_4^VSb_2^{III}Mo_{18}O_{73}(H_2O)_2]_2\}^{22−}$ (M = Mn^{II}, Fe^{II}, Cu^{II}, Co^{II}) (Figure 4) in which the M^{II} ion is located at an inversion center of the dimer. The coordination sphere of the M^{II} center is completed by two terminal water molecules and four terminal oxygen atoms (O$_t$) of two polyanions. The valence sum for Mn^{II}, Fe^{II}, Cu^{II}, and Co^{II} are 2.15, 2.04, 2.17, and 2.00, respectively, implying the valence of all atom remains unchanged as reactants. The selective bond lengths of compounds **2**–**5** are also compared in Table 2.

Spectroscopy. The IR absorptions of all the compounds are very similar and show the O−H and N−H absorption bands as well as typical frequencies for Mo−O bonds. The characteristic absorptions of the polyanions below 1000 cm$^{−1}$ appear at ca. 946(s), 892(vs), 853(sh), 791(w), 778(s), 647(s), and 458(w), in which the peaks between 946(s), 892(vs), 853(sh), 791(w), and 778(s) are attributed to the absorption of υ(Mo−O$_d$), υ(O$_b$−Mo−O$_b$), and υ(Mo−O$_c$), and the peak at 647(s) cm$^{−1}$ is attributed to that of υ(Sb−O).[17] UV spectra of all the compounds have strong absorption bands in the region of 220−280 nm attributed to the charge transfer of Mo−O. Among the visible region, the compounds **2**–**5** all present one weak broad absorption band, and the maximum

absorption is respectively at ca. 695, 683, 704, and 693 nm for Mn^{II}, Fe^{II}, Cu^{II}, and Co^{II} compounds, attributed the d−d transfers of corresponding transition-metal ions. The Raman spectra of the mother compound **1** and the representative **2** of the dimers in solid and in aqueous solution (pH 3, 1 × 10$^{−3}$ M) were measured. For solid spectra, the absorptions of the two compounds are very similar, and the main characteristic absorptions appear at ca. 960(vs), 903 (s), and 870(s) cm$^{−1}$ compared with two weak absorptions at ca. 953(s) and 903(w) cm$^{−1}$ in solution. The two main characteristic absorptions of Raman spectra in the solid state and in solution are essentially consistent with the first two characteristic absorptions of IR spectra below 1000 cm$^{−1}$.

Cyclic Voltammogramms. Cyclic voltammetry was carried out in a pH = 3 aqueous solution in which the title compounds were formed and isolated. The cathodic and anionic peak potentials for the starting materials, (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O, SbCl$_5$, and the products **1**–**5**, are compared in Table 3. In the range of potentials extending from −1000 to 1000 mV, a couple of redox waves were observed both for (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O and SbCl$_5$, respectively. For (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O, E_{cp} and E_{ap} are located, respectively, at −0.691(III) and −0.324(III′) V, corresponding to the redox process of Mo(VI)/Mo(V). For SbCl$_5$, there is a strong reduction wave at −0.306(II) V, and its counterpart is weak at −0.093(II′) V, corresponding to the redox process of Sb(V)/Sb(III). The CV curves of the dimers **2**–**5** are similar and consist of three reduction waves, with E_{cp}, respectively, at ca. 0.1(I), −0.34(II), and −0.66(III) V, corresponding to only two anodic counterparts located at 0.19(I′) and −0.46(III′) V, respectively. For mother compound **1**, three reduction waves (0.027(I), −0.428(II), and −0.703(III) V) are more negative than those of the dimers **2**–**5**, and only one anodic counterpart appears at 0.105(I′) V. The first and last waves (I and III) are attributed to the redox processes of the Mo centers, and the second wave (II) is attributed to the redox process of the Sb centers. The redox processes occurring at the 3d transition metals in the heteropolyanions could not be observed for all compounds **2**–**5**. No attempt was made to ascertain quantitatively the number of electrons of each wave.

(17) (a) Nyquist, R. A.; Kagel, R. O. *Infrared Spectra of Inorganic Compounds (3800−45 cm⁻¹)*; Academic Press: New York and London, 1971. (b) Gilliam, S. J.; Jensen, J. O.; Banerjee, A.; Zeroka, D.; Kirkby, S. J.; Merrowa, C. N. *Spectrochim. Acta, Part A* **2004**, *60*, 425.

Conclusions

A novel type of heteropolyanion containing mixed-valence antimony, $[Sb_4{}^VSb_2{}^{III}Mo_{18}O_{73}(H_2O)_2]^{12-}$ (**1a**), and its several derivatives have been isolated as ammonium salt, and their structures were determined by X-ray crystallographic analysis. The framework of **1a** displays an unusual multilayer structure. It demonstrates a high nucleophilicity and can act as a basic building block to form larger derivatives, $\{M(H_2O)_2[Sb_4{}^VSb_2{}^{III}Mo_{18}O_{73}(H_2O)_2]_2\}^{22-}$ (M = Mn^{II}, Fe^{II}, Cu^{II}, or Co^{II}) (**2a**−**5a**). Polyanion **1a** contains an unprecedented mixed-valence six antimony and 18 molybdenum−oxo cluster, and therefore, these types of compounds are highly interesting for catalysis studies. A detailed investigation of the chemical and physical properties of the compounds is currently underway.