Synthesis, Crystal Structure, and Properties of a Supramolecular Compound Based on Waugh-type Polyanion and Moroxydine

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A supramolecular compound $Na_3(HABOB)(H_2ABOB)[MnMo_9O_{32}]\cdot 5.5H_2O$ (ABOB = moroxydine) has been synthesized and characterized by elemental analyses, IR spectrum, diffuse reflectance spectrum, room temperature magnetic moment, single crystal X-ray diffraction, and TG analysis. It exhibits a two-dimensional, layered inorganic framework constructed from Waugh-type polyanions $[MnMo_9O_{32}]^{6-}$ and Na^+ ions linkers. Protonated ABOB molecules are hydrogen-bonded to the left- and right- handed $[MnMo_9O_{32}]^{6-}$ enantiomorphs to construct two kinds of infinite organic–inorganic hybrid chains.

Polyoxometalates (POMs), as early-transition-metal oxide clusters, have been attracting extensive interest in fields such as catalysis, ion exchange, electrochemistry, electrochromism, magnetism, and medicine for their enormous variety of structures and unique properties.[1] Most of the POMs belong to well-known structural types, such as the Keggin, Dawson, Anderson, or Lindqvist types. In contrast, much less research has been conducted in the field of Waugh-type POMs $[MMo_9O_{32}]^{6-}$ ($M = Mn^{IV}$ or Ni^{IV}).[2] Studies on them are still being in infancy.[3] Meanwhile, it is known that crystal engineering of supramolecular compounds employing POM building blocks and organic substrates is a rapidly developing area because these compounds may exhibit synergetic properties such as electrical, magnetic, and optical properties.[4] The nucleophilic characteristics of the POMs allow specific assembly with electrophilic organic substrates via electrostatic forces and OH···O or NH···O hydrogen-bonding interactions. Moroxydine is an effective antiviral medicine to influenza, chickenpox, and measles in the organoamine series. It is expected that the supramolecular interaction between moroxydine and POMs may exhibit synergistic pharmaceutical activity. Inspired by the aforementioned considerations, a supramolecular compound containing Waugh-type polyanion $[MnMo_9O_{32}]^{6-}$ and moroxydine, $Na_3(HABOB)(H_2ABOB)[MnMo_9O_{32}]\cdot 5.5H_2O$ (**1**) (ABOB = moroxydine),[5,14] has been synthesized.

The crystal structure determination[6] shows that compound **1** consists of three sodium ions, two protonated ABOB molecules, one $[MnMo_9O_{32}]^{6-}$ polyanion and lattice water molecules. The bond lengths and bond angles observed for the $[MnMo_9O_{32}]^{6-}$ polyanion indicate that its geometry is quite similar to that found in previously reported structure of ammonium 9-molybdomanganate.[2b] It is built around an octahedrally coordinated manganese atom. Three octahedral molybdenum atoms are arranged at the vertices of a triangle which is coplanar with the central MnO_6 octahedron, and another two groups of three molybdenum octahedra are placed above and below the middle layer of the four octahedra. It is noteworthy that the polyanion has two enantiomorphs, left- and right-handed, due to its ideal point symmetry D_3.[14] It has six coordination-active centers each being formed by a terminal oxygen atom of the middle layer MoO_6 octahedron and two terminal oxygen atoms of the Mo_3O_{13} triplet.

Compound **1** exhibits a two-dimensional (2D), layered inorganic framework built up of $[MnMo_9O_{32}]^{6-}$ polyanions with sodium ions as linkers (Figure 1). There are three crystallographically independent Na^+ ions. The Na(1) can coordinate to both of the two enantiomorphs. Its coordination polyhedron is formed by three terminal oxygen atoms from a coordination-active center of $[MnMo_9O_{32}]^{6-}$, two water molecules and a oxygen atom O(34) from ABOB, exhibiting an octahedron surrounding. The Na(2) connects two left-handed or two right-handed enantiomorphs $[MnMo_9O_{32}]^{6-}$ to form Chain 1 and 2, respectively. Chain 1 and 2 run parallel to each other alternately, which are further woven into a 2D layer by Na(3). Furthermore, the adjacent 2D layers pack along the *b* axis to form a 3D framework, with lattice water molecules and protonated ABOB molecules residing in the cavity.

From the geometry of compound **1**, we can see that only five coordination-active centers of $[MnMo_9O_{32}]^{6-}$ polyanion participate in bonding to the Na^+ ions.[14] So the $[MnMo_9O_{32}]^{6-}$ polyanion is a pentadentate ligand, leaving a coordination-active center vacant.

There exists notable hydrogen-bonding interactions between the $[MnMo_9O_{32}]^{6-}$ polyanions and five surrounding protonated ABOB molecules, namely, two ones containing O(34) and three other ones containing O(1) (Figure 2). The ones containing O(34) have special bonding mode: on one hand, it has two hydrogen-bonded nitrogen atoms N(7) and N(10) to the $[MnMo_9O_{32}]^{6-}$ anion, on the other hand, as discussed above, O(34) is coordinated to Na(1) of another $[MnMo_9O_{32}]^{6-}$ anion with the same handedness from the adjacent 2D layer. Then, because of the packing of 2D layers along the *b* axis, the same handed $[MnMo_9O_{32}]^{6-}$ polyanions are connected by ABOB molecules containing O(34) via hydrogen-bonding interactions to form two kinds of infinite organic–inorganic hybrid chains.[14]

The exact formula is established considering single crystal X-ray diffraction, elemental analyses, bond-valence-sum calculations, charge balance, and TG analysis. Bond-valence-sum cal-

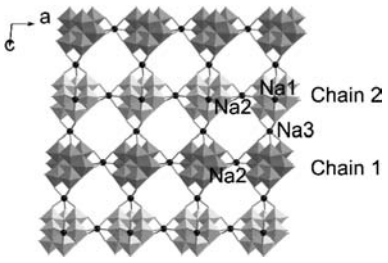

Figure 1. The 2D, layered inorganic framework of **1**.

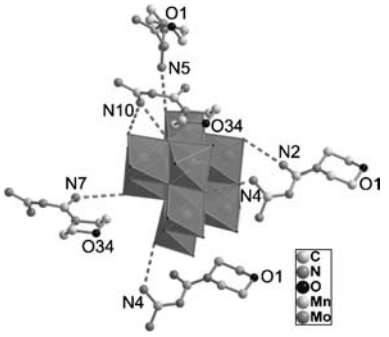

Figure 2. Drawing of hydrogen-bonding interactions.

culations[7] reveal that the central Mn atom is in +4 oxidation state, all the peripheral Mo atoms are in +6 oxidation state, and no O atoms are protonated. The overall charge of all Mn, Mo, Na, and O atoms in the formula obtained from the single crystal structure determination is thus −3. For the acidic synthetic condition of **1**, we presume that the ABOB molecules are protonated to meet the charge balance, with one monoprotonted and another diprotonted. The +4 oxidation state of central Mn atom has been observed in only a few polyoxometalates, including the series of heteropolyvanadomanganates(IV) with Mn:V = 1:13, 1:11(2:22), and 1:4(3:12),[8] hexatungstomanganate(IV) $[MnW_6O_{24}]^{8-}$,[9] and 12-niobmanganate(IV) $[MnNb_{12}O_{38}]^{12-}$.[10] The room-temperature magnetic moment of compound **1** is 3.93 BM, which is in good agreement with the value 3.88 BM calculated for a high-spin d^3 Mn^{IV} configuration. The content of crystallization water molecules is further confirmed by TG analysis.[14]

The diffuse reflectance spectrum[14] shows four absorption bands at 244, 286, 468, and 697 nm, exhibiting the characteristic peaks of precursor $[MnMo_9O_{32}]^{6-}$.[2c] The peaks at 244 and 286 nm are due to the charge-transfer transitions from ligands to metals $O_{b,c} \rightarrow Mo$ and $O_d \rightarrow Mo$, respectively. The peak at 468 nm is assigned to the first spin-allowed transition for a d^3 Mn^{IV} ion in octahedral coordination, $^4A_{2g}$ to $^4T_{2g}$, corresponding to the ligand-field splitting paramerer $\Delta = 21368\ cm^{-1}$, which is in agreement with the data $\Delta = 22500\ cm^{-1}$ given by Stratemeier et al.[11] and other rare data available for Mn^{IV} compounds. For instance, $\Delta \approx 21800\ cm^{-1}$ for $[MnF_6]^{2-}$,[12] while $\Delta = 21300\ cm^{-1}$ for Mn^{4+} doped into α-Al_2O_3.[13] The much weaker ruby band observed at 697 nm is most likely due to the spin-forbidden transition from $^4A_{2g}$ to ^2E_g according to Baker and Weakley.[2c]

In summary, we have successfully synthesized a supramolecular compound based on Waugh-type polyanion $[MnMo_9O_{32}]^{6-}$ and moroxydine. The hydrogen-bonding interactions in the compound enhance the stability of the structure. Compound **1** provides some insights into the interaction between organic substrates with $[MnMo_9O_{32}]^{6-}$ polyanion for the design of supramolecular compounds and flourishes the family of Waugh-type POMs. The synthesis of compound **1** also confirms the capacity of $[MnMo_9O_{32}]^{6-}$ to act as a precursor and building block for the construction of multidimensional materials. This work can also be extended into many other alternative electrophiles (e.g. transition metals and lanthanide metals ions), provided they have a sufficient affinity to the $[MnMo_9O_{32}]^{6-}$ precursor. The dimensionality of the materials could also be controlled by varying the number of the occupied coordination-active centers of the $[MnMo_9O_{32}]^{6-}$ polyanion. Additional experiments are ongoing and will be reported soon.

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References and Notes

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5 Supporting Information describes the synthesis of compound **1**. Anal. Calcd for $C_{12}H_{40}MnMo_9N_{10}Na_3O_{39.5}$ (%): C, 7.41; H, 2.07; N, 7.21%. Found: C, 7.49; H, 2.09; N, 7.18%. The selected IR (ν/cm^{-1}): 1677(w), 1645(w), 1627(w), 1515(m), 1368(w), 1309(w), 1107(w), 1004(w), 935(m), 893(m), 677(m), 598(w), 537(w), 493(w), 421(w).
6 Crystal data for $C_{12}H_{40}MnMo_9N_{10}Na_3O_{39.5}$ (**1**): $M_r = 1943.91$, monoclinic, space group $P2_1/c$, $a = 10.777(3)$, $b = 25.189(6)$, $c = 21.629(5)$ Å, $\beta = 94.988(4)^\circ$, $V = 5849(2)$ Å^3, $Z = 4$, $D_{calcd} = 2.208\ mg\ m^{-3}$, $\mu = 2.189\ mm^{-1}$, $F(000) = 3736$, λ(Mo Kα) = 0.71073 Å, $T = 293(2)$ K. 29873 reflections measured ($1.62^\circ < \theta < 25.00^\circ$), 10286 independent ($R_{int} = 0.0391$). $R_1 = 0.0460$, $wR_2 = 0.1338$ [$I > 2\sigma(I)$] and $S = 1.080$. CCDC: No. 626580.
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14 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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