

## Octamolybdate-supported tricarbonyl metal derivatives: $[\{H_2Mo_8O_{30}\}\{M(CO)_3\}_2]^{8-}$ ( $M = Mn^I$ and $Re^I$ )<sup>†</sup>

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**Two novel octamolybdate-based tricarbonyl metal derivatives have been successfully synthesized and characterized, which represent the first two examples of tricarbonyl metal groups attached to a new  $\{Mo_8O_{30}\}$  building block.**

Although polyoxometalate (POM)-based organometallic (OM) derivatives are merely one of the class of organometallic oxides,<sup>1</sup> they have been receiving increasing interest not only for their rather specific structures, but for their potential applications in catalysis electro- and photo-chromism, magnetism and medicine.<sup>2</sup> Since the first POM-based OM compound was reported by Ho and Klemperer in 1978,<sup>3</sup> considerable attention has been directed toward POM-based organosilyl,<sup>4–6</sup> organo-germanium,<sup>4,5,7</sup> organo-tin,<sup>4,5,8</sup> and the noble organometallic (ruthenium, rhodium, palladium, platinum, iridium, *etc.*)<sup>1,5b,9</sup> derivatives in recent years. Till now, the organic moieties on the reported organometallic compounds mainly include cyclopentadienyl, phenyl and alkyl groups. Also noteworthy is the importance of the metal-carbonyl moiety  $M(CO)_n$  ( $M = Mn, Re$  or  $Ir$ ) in POM, which has become an important part of POMs.<sup>1,10</sup> But while carbonyl metal derivatives of POMs have attracted growing attention in recent years, the reports on new types of POM-based carbonyl metal derivatives are very rare mainly because most polyoxoanions have not enough charge density to combine with carbonyl metal groups, along with their dissolved incompatibility, the radiation or thermal

instability and the expensive prices of carbonyl metal compounds. At the present time, most of these reported derivatives are dominated by Lindqvist-type derivatives.<sup>10a,11</sup> The search for novel POM-based metal-carbonyl derivatives is still an interesting area of research, because only a detailed structural comprehension can help us further understand the rational synthetic process including the mechanism of formation. Very recently our group discovered the novel octatungstate-supported tricarbonyl metal polyanions  $[\{H_2W_8O_{30}\}\{M(CO)_3\}_2]^{8-}$  ( $M = Mn^I$  and  $Re^I$ ) with completely unprecedented structures.<sup>10f</sup>

Herein we present the first two examples of octamolybdate-supported tricarbonyl metal derivatives. Both clusters contain an  $[H_2Mo_8O_{30}]^{10-}$  framework that is grafted by two tricarbonyl metal fragments. These species were isolated as  $(NH_4)_4[H_4\{[H_2Mo_8O_{30}]-[Mn(CO)_3\}_2]\cdot 12H_2O$  (**1**) and  $(NH_4)_4[H_4\{[H_2Mo_8O_{30}]-[Re(CO)_3\}_2]\cdot 14H_2O$  (**2**). Furthermore, as part of our continuous work, we also get another octatungstate-supported tricarbonyl metal polyanion  $Na_8(H_2O)_{18}(CH_3COOH)_2[\{H_2W_8O_{30}\}\{Mn(CO)_3\}_2]\cdot 4H_2O$  (**3**).

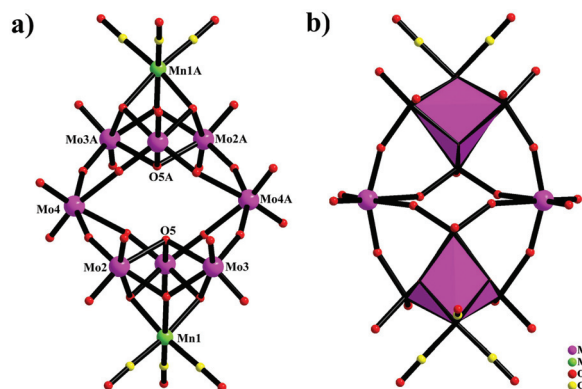
Red crystals of **1** and **2** were obtained by a similar reaction of  $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$  with  $Mn(CO)_5Br$  and  $Re(CO)_5Cl$  respectively, while **3** was prepared by reaction of  $Na_2WO_4\cdot 2H_2O$ ,  $ErCl_3\cdot 6H_2O$ ,  $CH_3COOH$  and  $Mn(CO)_5Br$ . The experimental XRPD pattern of the bulk products of **1** is in good agreement with that of the simulated XRPD pattern based on single-crystal X-ray diffraction, indicating the phase purity of the samples (Fig. S1 in the ESI<sup>†</sup>).

Single crystal X-ray diffraction analysis revealed that the polyanions in **1** and **2** are isostructural analogues (Tables S1 in the ESI<sup>†</sup>) and differ only in the heterometal centers  $M$  ( $M = Mn, 1; Re, 2$ ), see Fig. 1 and Fig. S2.† Therefore, only the structure of **1** is discussed here. **1** consists of an  $[\{H_2Mo_8O_{30}\}\{Mn(CO)_3\}_2]^{8-}$  (**1a**) unit, four  $NH_4^+$  cations, twelve crystal water molecules and four protons. **1a** is an analog to  $[\{H_2W_8O_{30}\}\{M(CO)_3\}_2]^{8-10f}$  reported by us recently and can be viewed as a triple-deck arrangement, that is, both the upper and bottom layers are composed of cubane  $\{Mo_3MnO_4\}$  subunits, which are linked through two corner-shared dimeric molybdate-

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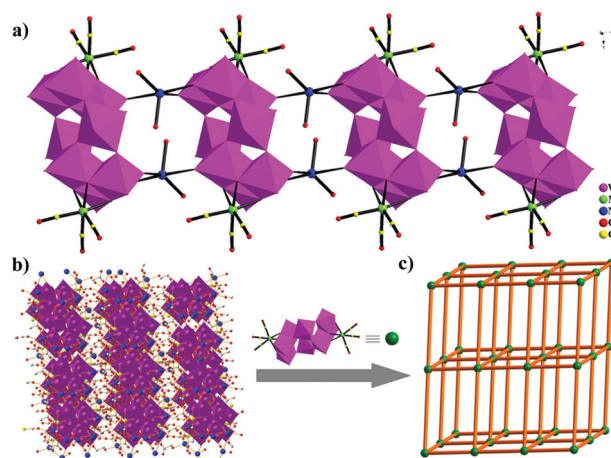
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† Electronic supplementary information (ESI) available: Comparison of the experimental and simulated XRPD patterns of **1**; ball-and-stick representations of **2**; combined ball-and-stick representation of  $Na^+$  cations; CVs, TG curves, IR spectra, UV-vis spectra, *in situ* UV-vis spectra, the aging of UV-vis and CVs of **1**; the BVS values of all the oxygen atoms except the lattice water molecules in **1–3**. CCDC 909647 (**1**), 909648 (**2**), 909649 (**3**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt32678g



**Fig. 1** (a) Ball-and-stick representation of **1a** in **1** with selected labelling scheme; (b) combined polyhedral/ball-and-stick representation of **1a** in **1** with selected labelling scheme. Pink octahedra:  $\{\text{Mo}_3\text{MnO}_4\}$  cubanes. (The atoms with the suffix A are generated by the symmetry operation: A:  $-x, 1 - y, -z$ .)

species. Notably, in the cubane  $\{\text{Mo}_3\text{MnO}_4\}$  subunit, three edge-sharing  $\{\text{MoO}_6\}$  octahedra are aggregated together by sharing four  $\mu_3\text{-O}$  atoms, which is similar to the  $\{\text{Mo}_3\text{O}_{13}\}$  model.<sup>11</sup> Alternatively, **1a** can also be described as two  $[\text{Mn}(\text{CO})_3]^+$  groups attached to the previously unreported isoctamolybdate fragment  $[\text{H}_2\text{Mo}_8\text{O}_{30}]^{10-}$ . Consistent with those described in the literature,<sup>10c,d,12</sup> each  $[\text{H}_2\text{Mo}_8\text{O}_{30}]^{10-}$  cluster acts as a hexadentate ligand connecting two  $[\text{Mn}(\text{CO})_3]^+$  pendants with *fac-d*<sup>6</sup>- $[\text{ML}_3]$  units which, in turn, is bonded to three  $\mu_2\text{-O}$  atoms from the  $[\text{H}_2\text{Mo}_8\text{O}_{30}]^{10-}$  unit and achieves the 18-electron configuration. It should be noted that the  $\{\text{Mo}_8\text{O}_{30}\}$  framework in **1a** is different from the previously common  $\{\text{Mo}_8\text{O}_{26}\}$  building block. In this way, it can be thought of as a new building block. Bond-valence sum (BVS) calculations clearly indicate that all the Mo atoms are in the +6 oxidation state (Tables S2–S5 in the ESI†).<sup>13</sup> Furthermore, the BVS values of all oxygen atoms in **1a** suggest that two protons are localized on  $\mu_3\text{-O5}$  and  $\mu_3\text{-O5A}$  atoms in the  $\text{Mo}_3\text{O}_{13}$  trimers and the other four protons should be added for the charge balance (Fig. S3a in the ESI†). However, these four protons can not be located crystallographically and are assumed to be delocalized over the whole structure, which is common in POM chemistry.<sup>14</sup> Interestingly, the BVS values of all oxygen atoms in **2a** indicate that six protons are localized on  $\mu_3\text{-O1}$ , O3, O7 and  $\mu_3\text{-O1A}$ , O3A, O7A atoms, respectively (Fig. S3b in the ESI†). The Mo–O distances in **1** and **2** get into three ranges, 1.691(3)–1.718(3) Å and 1.710(4)–1.736(4) Å for Mo=O<sub>t</sub>, 1.921(3)–2.310(3) Å and 1.783(3)–2.274(3) Å for Mo–( $\mu_2\text{-O}$ ), and 2.029(3)–2.281(3) Å and 2.053(3)–2.343(3) Å for Mo–( $\mu_3\text{-O}$ ), respectively. On the other hand, the environments of the two heterometal centers (M = Mn<sup>I</sup> and Re<sup>I</sup>) are similar. Each of them is ligated to three carbonyl ligands and three triply bridging oxygen atoms, displaying  $\text{MO}_3\text{C}_3$  octahedral geometry. Furthermore, the Re–C bond lengths in **2** range from 1.90 to 1.92 Å, while the C–O bond lengths range from 1.15 to 1.16 Å. **2** shows IR-active C–O stretching modes at 1891 and 2020  $\text{cm}^{-1}$ , respectively. These bond lengths and CO stretching frequencies are consistent with those observed for



**Fig. 2** (a) View of the 1D chain of **3**; (b) view of the 3D structure of **3**; (c) the 3D topology structure of **3**. Pink octahedra:  $\text{WO}_6$  units.

other Re(I) carbonyl complexes.<sup>10a,b,10f,10h</sup> This in turn suggests that the carbonyl metal groups are not affected before and after grafting with POMs. However, as expected, the M–C distances are longer in **2** (av. Re–C 1.911 Å) than in **1** (av. Mn–C 1.802 Å). In addition, it is important to point out that Gouzerh firstly reported POM-incorporating  $\{\text{Mn}(\text{CO})_3\}^+$  and  $\{\text{Re}(\text{CO})_3\}^+$  compounds and had also tried to obtain  $\text{Mo}_8$ -based carbonyl derivatives, but without success.<sup>10b</sup>

Unlike the previously reported clusters, and despite the close connection between the compositions of these clusters,<sup>10f</sup> **3** is composed of an  $[\{\text{H}_2\text{W}_8\text{O}_{30}\}\{\text{Mn}(\text{CO})_3\}_2]^{8-}$  (**3a**) anion, eight  $\text{Na}^+$  cations, two acetic acid molecules and twenty-two water molecules. In the structural unit of **3**, there are four crystallographically independent  $\text{Na}^+$  ions. Na1, Na2 and Na3 ions are embedded in octahedral geometries with different coordination environments whereas the Na4 ion exhibits a square pyramid geometry. On the one hand, Na1, Na2, Na3 and Na4 ions are connected in sequence forming a type of  $[\text{Na}_4(\text{H}_2\text{O})_9\text{-(CH}_3\text{COOH)}]^{4+}$  cluster (Fig. S4a in the ESI†). Wherein, Na1 and Na2 ions link each other by sharing one  $\mu_3\text{-O}$  and one  $\mu_2\text{-OW}$  atom in the edge-sharing mode, Na2 and Na3 ions join together by sharing two  $\mu_2\text{-OW}$  atoms in the edge-sharing mode, while Na3 and Na4 ions are connected by one  $\mu_2\text{-OW}$  bridge in the corner-sharing mode. On the other hand, the acetic acid molecule is attached to the Na3 ion through one  $\mu_2\text{-O}$  (Fig. S4b in the ESI†). Therefore,  $[\text{H}_2\text{W}_8\text{O}_{30}]^{10-}$  acts as a decadentate ligand, coordinating to two  $[\text{Na}_4(\text{H}_2\text{O})_9\text{-(CH}_3\text{COOH)}]^{4+}$  clusters and two  $[\text{Mn}(\text{H}_2\text{O})_2]^{2+}$  cations to construct an interesting 3D framework (Fig. 2). From the point of view of topology, the 3D structure of **3** is a six-connected network with a  $4^{15}$  topology, in which each **3a** acts as a six-connected node.

The UV-vis spectra of **1** and **3** were recorded in the mixed solvent  $\text{CH}_3\text{CN-H}_2\text{O}$  (1/2, v/v). Both display two similar absorption bands at ca. 200 and 365 nm for **1**, 218 and 366 nm for **3**, respectively (Fig. S6 in the ESI†). The higher one can be assigned to the charge transfer transitions of the  $\text{O}_t \rightarrow \text{W}$

$p\pi-d\pi$  charge-transfer transitions,<sup>15</sup> suggesting the presence of polyoxoanions; while the lower one can be assigned to Mn ( $d\pi$ )  $\rightarrow$  CO ( $\pi^*$ ) charge-transfer transitions which is not obvious resulting from the lower concentration,<sup>16</sup> indicating the existence of  $[\text{Mn}(\text{CO})_3]^+$ . It is noteworthy that the band at approximately 253 nm is also observed for **3**, attributed to the  $p\pi-d\pi$  charge-transfer transitions of  $\text{O}_b \rightarrow \text{W}$  bonds.<sup>17</sup> In addition, the results of *in situ* UV-vis of **1** and **3** indicate that they remain stable for at least 7 h at room temperature in the dark (Fig. S7 in the ESI†), which is further confirmed by the aging of cyclic voltammetric (CV) curves of **1** (Fig. S8 in the ESI†).

As is known, POMs are generally susceptible to pH, and thus systematic studies of *in situ* UV-vis spectra at different pH values in the aforementioned mixed solvent were also monitored, which are further supported by the *in situ* CV curves of **1** in the mixed solvent  $\text{CH}_3\text{CN}-\text{Na}_2\text{SO}_4$  ( $0.5 \text{ mol L}^{-1}$ ) ( $1/2$ , v/v). Considering that we have reported similar analogs,<sup>10f</sup> we only carry out this study on **1**. With the increase in pH value (Fig. S9a in the ESI†), the absorption band at ca. 200 nm experiences an inconspicuous blue shift whereas the absorbance becomes larger and larger, along with the advent of a weak absorption band at ca. 220 nm. Such variations might imply a stepwise decomposition process of polyoxoanions. And comparison between the UV-vis spectra of **1** and  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  (Fig. S10 in the ESI†) in the alkaline direction supports the assumption that the skeleton of **1** would be destroyed when pH is higher than 6.80. In contrast, when the pH decreases (Fig. S9b in the ESI†), the absorption band at ca. 200 nm experiences an obvious red shift and the absorbance increases first and then decreases. Meanwhile, Fig. S10† compares the CVs observed for **1** at different pH values, from which we can see that the CVs change strikingly when the pH values are lower than 4.0 or higher than 7.0. In the combination of the above analyses, we think that **1a** is stable between the pH 4.0 and 6.8 in this mixed solution.

The CV behaviors of **1** in the mixed solvent  $\text{CH}_3\text{CN}-\text{Na}_2\text{SO}_4$  ( $0.5 \text{ mol L}^{-1}$ ) ( $1/2$ , v/v) exhibit one pair of well-defined redox waves (Fig. S12 in the ESI†), which results from the cooperation of the redox processes of the  $\text{Mo}^{\text{VI}}$  atoms and  $[\text{Mn}(\text{CO})_3]^+$  pendants. Below  $300 \text{ mV s}^{-1}$ , the peak currents are proportional to the square root of the scan rates (Fig. S13 in the ESI†), indicating that the redox processes are probably diffusion-confined in a specific range of scan rates.<sup>18</sup> Furthermore, the electrocatalytic behaviors of  $\text{NO}_2^-$  by **1** were also investigated (Fig. S14 in the ESI†). Unfortunately, we found that the reduction peak currents of Mo and the corresponding oxidation peak currents basically remain unchanged with stepwise addition of modest amounts of nitrite, which implies that **1** hardly exhibits electrocatalytic activity towards the reduction of nitrite. Obviously, there is an irreversible oxidation that appears in the cyclic voltammograms as the nitrite is added, and this is expected for  $\text{NO}_2^-$ . This assumption is corroborated by the cyclic voltammograms of  $\text{CH}_3\text{CN}-\text{Na}_2\text{SO}_4$  ( $0.5 \text{ mol L}^{-1}$ ) ( $1/2$ , v/v) solution containing 0.0–5.0 mM  $\text{NaNO}_2$  in the absence of **1**.

In summary, **1–3** have been successfully synthesized by the conventional method. The anions of **1** and **2** present octamolybdate-supported tricarbonyl metal units  $[\{\text{H}_2\text{Mo}_8\text{O}_{30}\}\{\text{M}(\text{CO})_3\}_2]^{8-}$  ( $\text{M} = \text{Mn}$ , **1a**;  $\text{Re}$ , **2a**), while **3** is another new octatungstate-supported tricarbonyl metal derivative. Notably, the  $[\{\text{H}_2\text{Mo}_8\text{O}_{30}\}\{\text{M}(\text{CO})_3\}_2]^{8-}$  clusters have not been reported up to now in the POM-based organometallic family. The preparations of **1–3** provide us with an effective and feasible way of designing novel isopolyoxomolybdate (IPOM) and isopolyoxotungstate (IPOT) carbonyl metal derivatives. In the following work, we will continue to investigate the pertinent synthetic chemistry by changing reactants and their stoichiometric ratios so that we can construct much more novel structures of IPOM/IPOT-based carbonyl metal derivatives. Furthermore, other carbonyl metal species will be also introduced to our system.

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## Notes and references

† Crystal data: For **1**,  $\text{C}_6\text{H}_{16}\text{Mn}_2\text{Mo}_8\text{N}_4\text{O}_{48}$ ,  $M_r = 1819.82$ , triclinic, space group  $P\bar{1}$ ,  $a = 9.348(5)$ ,  $b = 11.652(6)$ ,  $c = 13.167(7)$  Å,  $\alpha = 110.481(7)^\circ$ ,  $\beta = 94.255(8)^\circ$ ,  $\gamma = 112.600(6)^\circ$ ,  $V = 1203.7(11)$  Å<sup>3</sup>,  $Z = 1$ ,  $\mu = 2.64 \text{ mm}^{-1}$ ,  $F(000) = 874$ ,  $\text{GOF} = 1.009$ . Of 6066 total reflections collected, 4185 were unique ( $R_{\text{int}} = 0.0190$ ).  $R_1(wR_2) = 0.0270(0.0736)$  for 307 parameters and 4185 reflections [ $I > 2\sigma(I)$ ]. For **2**,  $\text{C}_6\text{H}_{50}\text{Re}_2\text{Mo}_8\text{N}_4\text{O}_{50}$ ,  $M_r = 2118.39$ , monoclinic, space group  $P2(1)/n$ ,  $a = 10.570(3)$ ,  $b = 15.425(4)$ ,  $c = 15.933(4)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 91.290(4)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 2597.2(12)$  Å<sup>3</sup>,  $Z = 2$ ,  $\mu = 6.622 \text{ mm}^{-1}$ ,  $F(000) = 1988$ ,  $\text{GOF} = 1.041$ . Of 12 795 total reflections collected, 4557 were unique ( $R_{\text{int}} = 0.0289$ ).  $R_1(wR_2) = 0.0252(0.0686)$  for 316 parameters and 4557 reflections [ $I > 2\sigma(I)$ ]. For **3**,  $\text{C}_{10}\text{H}_{54}\text{Mn}_2\text{W}_8\text{Na}_8\text{O}_{62}$ ,  $M_r = 2931.10$ , triclinic, space group  $P\bar{1}$ ,  $a = 9.491(2)$ ,  $b = 12.290(3)$ ,  $c = 13.967(3)$  Å,  $\alpha = 71.437(3)^\circ$ ,  $\beta = 87.357(3)^\circ$ ,  $\gamma = 71.161(3)^\circ$ ,  $V = 1458.8(6)$  Å<sup>3</sup>,  $Z = 1$ ,  $\mu = 16.310 \text{ mm}^{-1}$ ,  $F(000) = 1336$ ,  $\text{GOF} = 1.031$ . Of 7422 total reflections collected, 5085 were unique ( $R_{\text{int}} = 0.0431$ ).  $R_1(wR_2) = 0.0653(0.1729)$  for 406 parameters and 5085 reflections [ $I > 2\sigma(I)$ ]. Intensity data were collected at 296(2) K on a Bruker Smart APEXII CCD diffractometer for **1–3** using graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å), respectively. Routine Lorentz and polarization corrections were applied and an absorption correction was performed using the SADABS program. Direct methods were used to solve the structure and refined by full-matrix least-squares on  $F^2$  using the SHELXTL-97 program package. All non-hydrogen atoms were refined anisotropically. A summary of the crystallographic data and structural refinements for **1–3** are summarized in Table S1. CCDC 909647 (1), CCDC 909648 (2), CCDC 909649 (3) contain the supplementary crystallographic data for this paper.

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