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COMMUNICATION

Novel octatungstate-supported tricarbonyl metal derivatives: $\{[H_2W_8O_{30}][M(CO)_3]_2\}^{8-}$ ($M = Mn^I$ and Re^I)†

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Three novel octatungstate-supported tricarbonyl metal derivatives have been synthesized and characterized, which represent the first examples of isopolyoxotungstates-supported carbonyl metal compounds.

Polyoxometalate(POM)-based carbonyl metal derivatives, as a peculiar class of organometallic oxides,[1] have attracted increasing attention owing to their unique structures and potential catalytic properties.[2] Particularly, the carbonyl manganese/rhenium derivatives of the POMs, with rich behaviors displayed by the d^6 carbonyl metal compounds and the POMs, are important. However, the carbonyl groups on metal carbonyl precursors are often unstable and easily decompose on heating or irradiation. To date, most of the known POM-based carbonyl manganese/rhenium compounds are heteropolyoxotungstates,[3] isopolyoxomolybdates,[4] and isopolyoxoniobates/isopolyoxotantalates.[5] Nevertheless, no investigation on the reactivity between isopolyoxotungstates (IPOTs) and d^6 carbonyl metal fragments has been made, the main reason is that the lower reactivity and the lower surface charge density of IPOTs means that thay do not tend to bond to organometallic units. Therefore, the synthesis of IPOTs that subsequently combine with d^6 carbonyl metal fragments to form novel aggregates remains very challenging in the POM-based organometallic chemistry. In order to obtain new IPOT-based carbonyl metal compounds, $Na_2WO_4{\cdot}2H_2O$ and $Mn(CO)_5Br$/$Re(CO)_5Br$ were selected as the starting materials. By changing the reaction parameters, it is expected that the construction of unprecedented IPOTs-based tricarbonyl metal aggregates with multidimensional structures will be possible. Based on above-mentioned considerations, we have devoted a great deal of effort to exploring this domain. In this communication, we report three novel octatungstate-supported tricarbonyl metal derivatives $H_6[Na(H_2O)_5]_2\{[H_2W_8O_{30}][Mn(CO)_3]_2\}{\cdot}13H_2O$ (**1**), $H_2[Na(H_2O)_5]_2$ $[Na(H_2O)_4]_2[Na(H_2O)_2]_2\{[H_2W_8O_{30}][Re(CO)_3]_2\}$ (**2**) and $[Na(H_2O)_5]_2$ $[Na_2(\mu_2\text{-}H_2O)_2(H_2O)_4]_2[Mn(H_2O)_2]\{[H_2W_8O_{30}][Mn(CO)_3]_2\}$ (**3**). Interestingly, **1**, **2** and **3** all consist of a $[H_2W_8O_{30}]^{10-}$ unit with two supporting $[M(CO)_3]^+$ ($M = Mn^I$ and Re^I) fragments, which are new examples for IPOT-supported carbonyl metal compounds. **1** and **2** exhibit isolated topologies whereas **3** displays a 1D chain architecture. **1**, **2** and **3** not only provide the first examples of IPOT-supported carbonyl metal compounds and enrich the structural diversity of POM-based organometallic compounds, but also realize the merging of carbonyl metal chemistry and IPOT chemistry.

Yellow crystals of **1–3** were prepared using similar methods, by reacting $Na_2WO_4{\cdot}2H_2O$ and $M(CO)_5Br$ ($M = Mn^I$, Re^I), and characterized by X-ray single-crystal diffraction, elemental analysis, IR spectroscopy, UV-vis spectroscopy, and electrochemistry. The phase purity of the bulk materials of these compounds were confirmed by comparison of their powder diffraction patterns with that calculated from their single crystal studies (Fig. S1†).‡Single-crystal X-ray diffraction analyses reveal that **1** and **2** are almost isomorphic with only slight differences in the bond lengths and bond angles regardless of Na^+ ions and water molecules. Only **1** is described here. **1** is a novel octatungstate-supported tricarbonyl manganese derivative and is composed of a $\{[H_2W_8O_{30}][Mn(CO)_3]_2\}^{8-}$ (**1a**) unit, two $[Na(H_2O)_5]^+$ cations, thirteen crystal water molecules and six protons. As shown in Fig. 1, **1a** is located at the crystallographic inversion center and can be viewed as two cubane $\{W_3MnO_4\}$ units with six supporting carbonyl groups connected by two WO_6 octahedra. Notably, the three W atoms in the cubane interconnect with each other by sharing μ_3-O, which is similar to the $\{Mo_3\}$ model.[6] Alternatively, **1a** can be also considered as an octatungstate $[H_2W_8O_{30}]^{10-}$ unit connecting two $[Mn(CO)_3]^+$ pendants by six μ_2-O atoms from the $[H_2W_8O_{30}]^{10-}$ unit. To our knowledge, the $[H_2W_8O_{30}]^{10-}$ polyoxoanion is very rare in polyoxotungstate chemistry.[7] This grafting fashion of a $[Mn(CO)_3]^+$ pendant capping to a POM unit *via* three bridging oxygen atoms is similar to the reported compounds.[3–5] In $[H_2W_8O_{30}]^{10-}$ unit, bond valence sum (BVS) definitely indicates that all the tungsten atoms are in the +6 oxidation state.[8] The $[H_2W_8O_{30}]^{10-}$ unit is built from two W_3O_{13} trimers bridged by two WO_6 octahedra in the corner-sharing mode. In **1** and **2**, the W–O distances are classified into three groups, 1.721(15)–1.773(18) Å and 1.69(2)–1.74(3) Å for W=O, 1.784(15)–2.219(14) Å and 1.78(3)–2.15(3) Å for W–(μ_2-O), and 1.989(13)–2.309(14) Å and

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† Electronic supplementary information (ESI) available: Discussion on the influences of the pH value on the stability of **1** and **3** in the mixed solution, electrochemical properties and related figures. CCDC reference numbers 809237, 809239 and 809238 for **1–3**, respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt11042j

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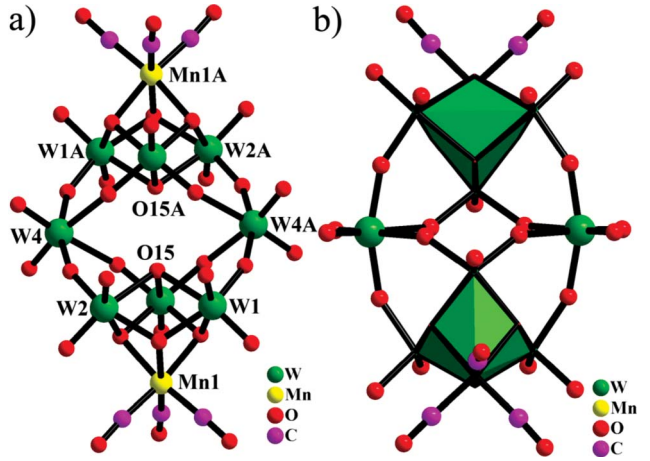

Fig. 1 (a) Ball-and-stick representation of **1a** in **1** with selected labelling scheme; (b) Combined polyhedral/ball-and-stick representation of **1a** in **1** with selected labelling scheme. Cyan octahedra: $\{W_3MnO_4\}$ cubanes. (The atoms with the suffix A is generated by the symmetry operation: A: $-2-x$, $-y$, $1-z$.)

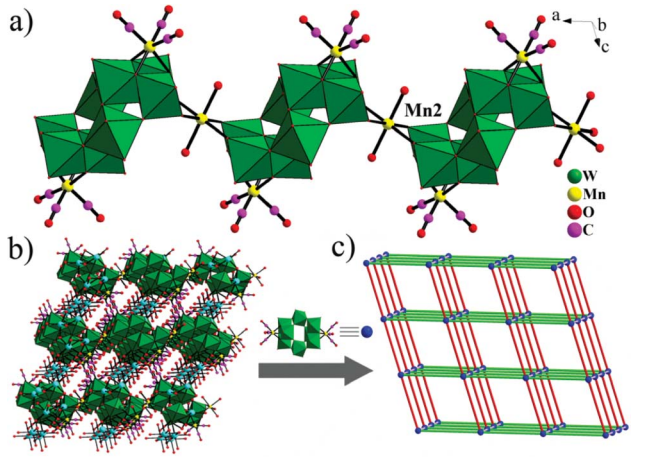

Fig. 2 (a) View of the 1D chain of **3**; (b) View of the 3D structure of **3**; (c) The 3D topology structure of **3**. Green octahedra: WO_6 units.

1.98(3)–2.28(2) Å for W–(μ_3-O), respectively. On the other hand, the supporting $[M(CO)_3]^+$ (M = Mn^I and Re^I) pendants inhabit in the MO_3C_3 octahedral geometry defined by three carbonyl ligands and three bridging oxygen atoms [Mn–O: 2.020(14)–2.083(15) Å, Re–O: 2.11(2)–2.15(3) Å]. As expected, the M–C distances in **2** are longer (av. Re–C 1.88 Å) than those in **1** (av. Mn–C 1.78 Å). BVS values of μ_3-O15 and μ_3-O15A atoms in the W_3O_{13} trimers of **1** are −1.25,[8] suggesting that both oxygen atoms are monoprotonated. Interestingly, to balance the charges of **1**, six protons should be added. These protons cannot be located crystallographically and are assumed to be delocalized over the whole structure, which is common in POM chemistry.[9] Furthermore, the Na atoms in **1** are six-coordinate octahedra formed by five water molecules and one terminal oxygen atom with the Na–O distances of 2.385(18) Å. The most intriguing feature of **1** is that each $[Na(H_2O)_5]^+$ cation in adjacent units joins together in the edge-sharing fashion forming a $[Na_2(H_2O)_8]^{4+}$ cluster with Na–O distances of 2.35(2)–2.47(2) Å. **1a** acts as a bidentate ligand connecting two $[Na_2(H_2O)_8]^{2+}$ clusters *via* terminal oxygen atoms to form a 1-D chainlike structure (Fig. S2†). Considering the role of Na^+ bridges, the main difference between **1** and **2** is that **1** is a 1D chain whereas **2** is a 2D sheet (Fig. S3–S4†).

Considering that **1a** can be linked by Na^+ ions, we expect to obtain multidimensional structures constructed by **1a** and transition metal bridges. Thus, we devoted ourselves to this subject. Finally, a 1D chain **3** was isolated. Adjacent **1a** in **3** link together by octahedral $[Mn(H_2O)_2]^{2+}$ cations to generate a 1D chain (Fig. 2a). In the structural unit of **3**, there are three crystallographically independent Na^+ ions. Both Na1 and Na2 ions are embedded in octahedral geometries with different coordination environments whereas the Na3 ion exhibits a square pyramid geometry. On one hand, two adjacent Na1 ions links each other by sharing two μ_2-OW atoms forming a type of $[Na_2(H_2O)_6]^{2+}$ dimeric clusters in the edge-sharing mode (Fig. S5a†). On the other hand, Na2 and Na3 ions join together by sharing one μ_3-O and two μ_2-OW atoms forming another type of $[Na_2(H_2O)_6]^{2+}$ dimeric clusters (Fig. S5b†), meanwhile the adjacent $[Na_2(H_2O)_6]^{2+}$ clusters are connected by two μ_2-OW bridges generating a $[Na_4(H_2O)_{10}]^{4+}$ tetrameric cluster in the corner-sharing mode (Fig. S5c†). Therefore, each **1a** in **3** acts as a decadentate ligand, coordinating to two $[Na_2(H_2O)_6]^{2+}$ clusters, two $[Na_4(H_2O)_{10}]^{4+}$ clusters and two $[Mn(H_2O)_2]^{2+}$ cations to construct an interesting 3D framework (Fig. 2). From the topological point of view, the 3D structure of **3** is a six-connected network with a 4^{15} topology, in which each $\{[H_2W_8O_{30}][Mn(CO)_3]_2\}^{8-}$ acts as a six-connected node (Fig. 2c).

As far as we know, the $\{[H_2W_8O_{30}][M(CO)_3]_2\}^{8-}$ (M = Mn^I, Re^I) clusters are prepared for the first time in the POM-based organometallic family. Obviously, each $[H_2W_8O_{30}]^{10-}$ cluster acts as a hexadentate ligand connecting two $[M(CO)_3]^+$ pendants with *fac*-d^6-$\{ML_3\}$ units which is common.[3–5] Simultaneously, each $[M(CO)_3]^+$ pendant is bonded to three μ_2-O atoms from the $[H_2W_8O_{30}]^{10-}$ unit and achieves the 18-electron configuration. Different from the reported compounds, **1** and **3** contain two *fac*-d^6-$\{ML_3\}$ units and even **3** forms a 1D structure *via* manganese bridges. To our knowledge, no POM-supported carbonyl metal derivative with an extended structure has been reported to date.

In order to investigate the properties of **1** and **3** in solution, the UV-vis spectra and cyclic voltammetric (CV) behaviors of **1** and **3** were monitored. UV-vis spectra of **1** and **3** (Fig. S7†) in the mixed solvent CH_3CN–H_2O (1 : 2, volume ratio) were measured in the range of 190–500 nm with two absorption bands centered at *ca.* 200 and 365 nm. The higher energy absorption bands are tentatively assigned to the $O_t \rightarrow W$ pπ–dπ charge-transfer transitions,[10] whereas the lower energy bands at *ca.* 365 nm are attributed to Mn (dπ) → CO (π^*) charge-transfer transitions.[11] The cyclic voltammetric (CV) behaviors of **1** and **3** in the mixed solvent CH_3CN–Na_2SO_4 (0.5 mol L^{-1}) (1 : 2, volume ratio) exhibit one pair of well-defined redox waves (Fig. S9†), which results from the cooperation of the redox processes of the W^{VI} atoms and $[Mn(CO)_3]^+$ pendants. Below 600 mV s^{-1}, the peak currents are proportional to the scan rates (Fig. S10†), indicating that the redox processes of **1** and **3** are surface-controlled.[12]

To study the stability of **1** and **3** in the mixed solvent CH_3CN–H_2O (1 : 2, volume ratio), both systems were monitored by *in situ* UV-vis studies. Both **1** and **3** remain stable for 6 h at room temperature in the dark (Fig. S11†). It is well known that POMs are commonly sensitive to pH, so systematic studies of *in situ* UV-vis spectra at different pH values in this mixed solution were

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also probed, which are further supported by the *in situ* CV curves of **1** and **3** in the mixed solvent CH_3CN–Na_2SO_4 (0.5 mol L^{-1}) (1 : 2, volume ratio). Take **1** for an example: with increasing pH value (Fig. S12a†), the absorption band at *ca.* 200 nm experiences a gradual hypsochromic shift whereas the absorbance become larger, indicating that **1a** may be gradually decomposed to WO_4^{2-} ions. Such a presupposition is supported by comparisons of UV-vis spectra between the alkaline solution (pH >7.5) of **1** and the alkaline solution of $Na_2WO_4{\cdot}2H_2O$ (Fig. S13a†). So, we assumed that the skeleton of **1** would be destroyed at pH higher than 7.5. In contrast, when the pH decreases (Fig. S12b†), the absorption band at *ca.* 200 nm experiences a gradual bathochromic shift and becomes weaker and weaker, meanwhile a new absorption band at *ca.* 260 nm appears assigned to the $O_{b,c} \rightarrow W$ charge transfer transitions, which shows that **1a** may be slowly transformed into a polymer of WO_4^{2-} ions upon addition of diluted HCl solution (Fig. S13b†). So, when the pH values are lower than 5.0 or higher than 7.5, the UV-vis spectra change strikingly, suggesting that the polyoxoanion have been polymerized or decomposed. The above analyses show that the pH range in which **1a** is stable in this mixed solution is about 5.0–7.5, which is further confirmed by the evolution of CV curves of **1** at different pH conditions (Fig. S14a, S14b†).

In summary, three octatungstate-supported tricarbonyl metal derivatives have been produced by the conventional method. These compounds all contain $\{[H_2W_8O_{30}][M(CO)_3]_2\}^{8-}$ (M = Mn^I and Re^I) units. Notably, $\{[H_2W_8O_{30}][M(CO)_3]_2\}^{8-}$ units were discovered for the first time. The preparations of **1–3** provide us with an effective and feasible way of designing novel IPOT carbonyl metal derivatives. In the following work, we will continue to investigate the pertinent synthetic chemistry by changing stoichiometric ratios and reactants to construct much more novel multidimensional structures of IPOT carbonyl metal derivatives. Furthermore, other carbonyl metal species will be introduced to our system. In addition, the catalytic activity of **1–3** will be evaluated in due course.

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Notes and references

‡ Crystal data: For **1**, $C_6H_{54}Mn_2Na_2O_{59}W_8$, Mr = 2697.15, Triclinic, $P\bar{1}$, a = 9.6124(8) Å, b = 12.1841(10) Å, c = 14.0241(11) Å, α = 71.5230(10)°, β = 87.4540(10)°, γ = 71.1410(10)°, V = 1471.1(2) Å^3, Z = 1, D_c = 3.044 g cm^{-3}, μ = 16.117 mm^{-1}, F(000) = 1226, GOF = 1.068. A total of 7069 reflections were collected, 5000 of which were unique (R_{int} = 0.0366). $R_1(wR_2)$ = 0.0689(0.1823) for 361 parameters and 5000 reflections [$I > 2\sigma(I)$]. For **2**, $C_6H_{48}Re_2Na_6O_{58}W_8$, Mr = 3029.55, Triclinic, $P\bar{1}$, a = 9.443(6) Å, b = 12.053(8) Å, c = 13.891(9) Å, α = 72.176(10)°, β = 88.395(10)°, γ = 71.095(11)°, V = 1419.4(16) Å^3, Z = 1, D_c = 3.540 g cm^{-3}, μ = 20.549 mm^{-1}, F(000) = 1352, GOF = 1.026. A total of 6446 reflections were collected, 4808 of which were unique (R_{int} = 0.0820). $R_1(wR_2)$ = 0.0892(0.2141) for 356 parameters and 4808 reflections [$I > 2\sigma(I)$]. For **3**, $C_6H_{50}Mn_3Na_6O_{60}W_8$, Mr = 2856.00, Triclinic, $P\bar{1}$, a = 11.184(4) Å, b = 11.519(4) Å, c = 12.269(4) Å, α = 98.291(5)°, β = 103.668(5)°, γ = 105.798(5)°, V = 1432.0(8) Å^3, Z = 1, D_c = 3.309 g cm^{-3}, μ = 16.802 mm^{-1}, F(000) = 1297, GOF = 1.027. A total of 7288 reflections were collected, 4993 of which were unique (R_{int} = 0.0210). $R_1(wR_2)$ = 0.0342(0.0882) for 377 parameters and 4993 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 Ka radiation (λ = 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.

1 P. Gouzerh and A. Proust, *Chem. Rev.*, 1998, **98**, 77.
2 (*a*) A. R. Siedle, C. G. Markell, P. A. Lyon, K. O. Hodgson and A. L. Roe, *Inorg. Chem.*, 1987, **26**, 219; (*b*) D. K. Lyon and R. G. Finke, *Inorg. Chem.*, 1990, **29**, 1787; (*c*) N. Mizuno, D. K. Lyon and R. G. Finke, *J. Catal.*, 1991, **128**, 84; (*d*) R. G. Finke, *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*, ed. M. T. Pope and A. Müller, Kluwer, Dordrecht, 1994, pp. 267; (*e*) N. Mizuno, H. Weiner and R. G. Finke, *J. Mol. Catal. A: Chem.*, 1996, **114**, 15; (*f*) K. Takahashi, M. Yamaguchi, T. Shido, H. Ohtani and K. Isobe, *J. Chem. Soc., Chem. Commun.*, 1995, 1301; (*g*) Y. Imada, T. Shido, R. Ohnishi, K. Isobe and M. Ichikawa, *Catal. Lett.*, 1996, **38**, 101.
3 (*a*) C. J. Besecker and W. G. Klemperer, *J. Am. Chem. Soc.*, 1980, **102**, 7598; (*b*) C. J. Besecker, V. W. Day, W. G. Klemperer and M. R. Thompson, *Inorg. Chem.*, 1985, **24**, 44; (*c*) T. Nagata, M. Pohl, H. Weiner and R. G. Finke, *Inorg. Chem.*, 1997, **36**, 1366.
4 (*a*) W. G. Day, M. F. Fredrich, M. R. Thompson, W. G. Klemperer, R.-S. Liu and W. Shum, *J. Am. Chem. Soc.*, 1981, **103**, 3597; (*b*) R. Villanneau, A. Proust, F. Robert and P. Gouzerh, *Chem.–Eur. J.*, 2003, **9**, 1982.
5 A. V. Besserguenev, M. H. Dickman and M. T. Pope, *Inorg. Chem.*, 2001, **40**, 2582.
6 Z.-X. Li, H. Ma, S.-L. Chen, Z.-D. Pan, Y.-F. Zeng, X.-L. Wang and X.-H. Bu, *Dalton Trans.*, 2011, **40**, 31.
7 (*a*) X. K. Fang and M. Luban, *Chem. Commun.*, 2011, **47**, 3066; (*b*) H. N. Miras, J. Yan, D.-L. Long and L. Cronin, *Angew. Chem.*, 2008, **120**, 8548, (*Angew. Chem., Int. Ed.*, 2008, **47**, 8420); (*c*) Y.-W. Li, Y.-G. Li, Y.-H. Wang, X.-J. Feng, Y. Lu and E.-B. Wang, *Inorg. Chem.*, 2009, **48**, 6752.
8 therein I. D. Brown and D. Altermatt, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1985, **41**, 244.
9 (*a*) P. Mialane, A. Dolbecq, L. Lisnard, A. Mallard, J. Marrot and F. Sécheresse, *Angew. Chem.*, 2002, **114**, 2504, (*Angew. Chem., Int. Ed.*, 2002, **41**, 2398); (*b*) H. An, E. Wang, D. Xiao, Y. Li, Z. Su and L. Xu, *Angew. Chem.*, 2006, **118**, 918, (*Angew. Chem., Int. Ed.*, 2006, **45**, 904); (*c*) E. M. Villa, C. A. Ohlin, E. Balogh, T. M. Anderson, M. D. Nyman and W. H. Casey, *Angew. Chem.*, 2008, **120**, 4922, (*Angew. Chem., Int. Ed.*, 2008, **47**, 4844).
10 J. Y. Niu and J. P. Wang, *Introduction of Heteropoly Compounds*, Henan University Press, Kaifeng, 2000.
11 (*a*) D. Burdinski, E. Bothe and K. Wieghardt, *Inorg. Chem.*, 2000, **39**, 105; (*b*) M. Busby, P. Matousek, M. Towrie, I. P. Clark, M. Motevalli, F. Hartl and A. Jr. Vlček, *Inorg. Chem.*, 2004, **43**, 4523; (*c*) S. Y. Reece and D. G. Nocera, *J. Am. Chem. Soc.*, 2005, **127**, 9448; (*d*) H. D. Batey, A. C. Whitwood and A. K. Duhme-Klair, *Inorg. Chem.*, 2007, **46**, 6516.
12 X. Wang, Y. Bi, B. Chen, H. Lin and G. Liu, *Inorg. Chem.*, 2008, **47**, 2442.

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