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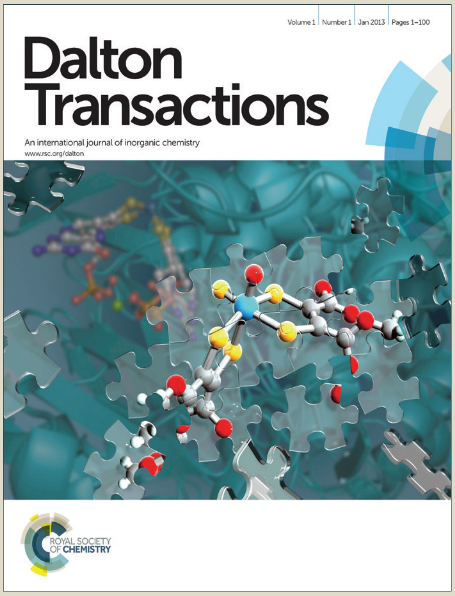

Complexation of Metal Carbonyl Units with $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ and $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$: Insights into the Chiral "Twisted-sandwich" Dimeric Structures

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Abstract: Several polyoxometalate-supported metal carbonyl complexes, $K_7Na_3P_2W_{23}O_{80}\{Re(CO)_3\}_2\cdot 38H_2O$ (**1**), $(C_3H_{10}N)_8Na_2P_2W_{23}O_{80}\{Re(CO)_3\}_2\cdot 10H_2O$ (**1a**) and $(C_3H_{10}N)_6HNa_3P_2W_{23}O_{80}\{Mn(CO)_3\}_2\cdot 6H_2O$ (**2**), have been prepared from the dimerization of the monovacant Keggin $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ with metal carbonyl complexes $[M(CO)_3]^+$ (M = Re, Mn) in acidic aqueous solutions. The resulting "twisted-sandwich" architectures are chiral, but their crystalline solids are racemic. A detailed investigation involving syntheses, crystal structures, and electrochemistry is presented.

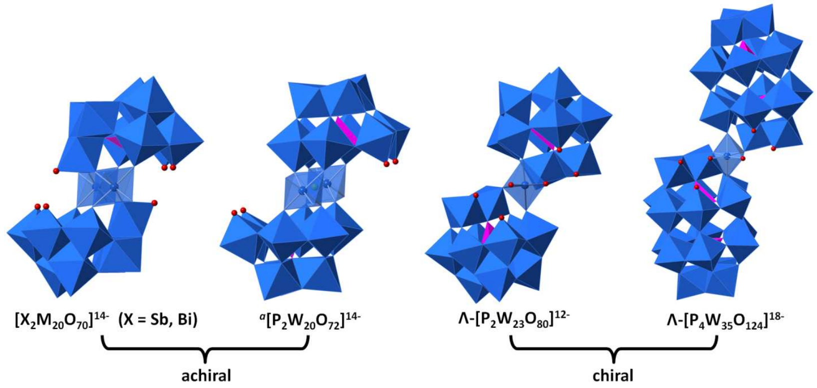
Introduction

Polyoxometalate (POM)-based organometallic derivatives have been widely used for development of materials and catalysis.[1] These inorganic-organic hybrids can combine the advantages of POMs (i.e. oxidative and thermal stability, multi-electron redox activity), and organometallic complexes (i.e. chirality, magnetism, catalytic activity and visible-light absorptivity). Chiral POMs are of considerable interest in context with pharmaceuticals, catalysis, and other areas where chirality is both common and functionally critical. Chiral POMs are difficult to make; most are synthesized as racemic mixtures. Enantiopure POM derivatives are rare, but can be accessed by functionalizing with organic/organometallic units.[2] To date the majority of these hybrid POMs involve organo-tin/germanium/ruthenium complexes with phenyl or alkyl ligands.[3] POM-supported metal carbonyl complexes (PSMCs) were relatively less studied. PSMCs were originally used to mimic metal carbonyl derivatives deposited onto solid-oxide surfaces. Some of the latter are stable and efficient heterogeneous catalysts for hydrogenation and hydrocarbonation in industry.[4] The molecular-level structures, especially short-range orders and precise interface configurations, can only be partially characterized (i.e. EXAFS), because these materials are heterogeneous in nature. From several vantages, POMs are molecular representations of metal oxides; thus we and others (see Table 1) have used POM derivatives as homogeneous tractable analogues of metal oxide-supported organometallic species. This study focuses on the interaction between metal carbonyl units and the POM surfaces at an atomic level.

In addition, the $[M(CO)_n]^+$ in PSMCs can act as face-directed cations to mediate the crystallization process,[5] one point addressed in this study, and they can be catalytically active. For example, $[(Ph_3P)_2Rh(CO)(CH_3CN)]_4[SiW_{12}O_{40}]$ catalyzes the hydroformylation of olefins.[6] In addition, PSMCs can exhibit visible-light-induced photo-redox activity as in the complex, $K_{15}Na[P_4W_{35}O_{124}\{Re(CO)_3\}_2]$ (**3**).[7] Hence, the development of PSMCs is a growing area of technical interest. The PSMCs investigated in this article are based on the monovacant POM ligands, $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ and $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$.

Results and Discussion

Synthesis and Crystal Structures. Table 1 summarizes all the PSMCs to date.[6-8] The majority are the Lindqvist-type derivatives (Entries #2,3,6,7,8 and 10). A few are Keggin and Dawson POMs (especially the defect forms). Most of these hydrid compounds have been made by one-pot hydrothermal methods. Recently, we successfully bound $[M(CO)_3]^+$ (M = Re, Mn) on the vacant sites of Krebs-type "slipped-sandwich" POMs, $[X_2W_{20}O_{70}]^{14-}$ (X = Sb, Bi), through a facile method (Entry #13).[9] One target reactive POM ligand for construction of PSMCs is the rare phosphorus-centered "slipped-sandwich" analogue, $[P_2W_{20}O_{72}]^{14-}$ (Scheme 1). We note, however, that the polytungstates, $[P_2W_{19}O_{69}(OH_2)]^{14-}$, $[P_2W_{20}O_{70}(OH_2)_2]^{10-}$ and $[P_2W_{21}O_{71}(OH_2)_3]^{6-}$ have been reported.[10] In 2009, an Ir(III)-substituted POM, $[(IrCl_4)KP_2W_{20}O_{72}]^{14-}$, in which an $[IrCl_4]^-$ group is bound to an external position of $[P_2W_{20}O_{72}]^{14-}$ was published.[11] Recently, Kirschhock *et al.* reported a one-step conversion of $[PW_{12}O_{40}]^{3-}$ to $[P_2W_{20}O_{72}]^{14-}$.[12] It is noteworthy that $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ and $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ usually capture transition metals to form one of three types of complexes: 1) conventional 1:1 monomeric species, $[PW_{11}O_{39}M(H_2O)]^{n-}$ and $[P_2W_{17}O_{61}M(H_2O)]^{n-}$,[13] 2) achiral 2:2 dimeric $[\{PW_{11}O_{39}M(\mu\text{-}OH)\}_2]^{n-}$ and $[\{P_2W_{17}O_{61}M(\mu\text{-}OH)(H_2O)\}_2]^{n-}$,[14] and 3) chiral 2:1 dimers, $[(PW_{11}O_{39})_2M(H_2O)]^{n-}$ and $[(P_2W_{17}O_{61})_2M]^{n-}$.[15] Organometallic derivatives of these POMs are known.[3f, 10d, 16] The recent synthesis of **3** demonstrates that the defect polyanion, $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$, undergoes a dimerization process with $[Re(CO)_3]^+$ to generate a "twisted-sandwich" structure (Entry #14).[7] We thus attempted to investigate the reactivity between metal carbonyl groups and monovacant POMs in this study.



Scheme 1. Representative "slipped" and "twisted" sandwich polytungstate ligands. WO_6: blue octahedra; XO_3 or XO_4 (X = Sb Bi, P): purple tetrahedra. Oxygen atoms in the coordinating sites are red balls. [a] One K^+ resides at the inversion center.

Table 1. Summary of PSMCs

	Formulas	Conditions	Comments	Refs
1	$[\{CpFe(CO)_2Sn\}SiW_{11}O_{39}]^{5-}$ $[\{CpFe(CO)_2Sn\}_2PW_{10}O_{38}]^{5-}$ and related compounds	$CpFe(CO)_2SnCl_3$ reacted with POMs or Na_2WO_4/NaH_2PO_4 in one-pot; precipitates isolated upon addition of K^+ or TBA/TMA	Early examples of PSMCs; no crystal structures; characterized by FTIR, ^{31}P and ^{183}W NMR	8a, b
2	$[(OC)_3M(Nb_2W_4O_{19})]^{3-}$ (M = Re and Mn) $[\{(CO)_2Rh\}_5(Nb_2W_4O_{19})_2]^{3-}$ $[\{(CO)_2Rh\}_3(Nb_2W_4O_{19})_2]^{5-}$ $[\{(CO)_2Ir\}_2H(Nb_2W_4O_{19})_2]^{5-}$	$[M(CO)_3(CH_3CN)_3](PF_6)$ (M = Re, Mn) or $[Rh(CO)_2Cl]_2$ refluxed with $TBA_4(Nb_2W_4O_{19})$; CO bubbled into $TBA_5[\{(C_8H_{12})Ir\}_2H(Nb_2W_4O_{19})_2]$ in CH_3CN	Disordered crystal structures for Re/Mn compounds; no X-ray structures for Rh/Ir complexes; ^{17}O and ^{183}W NMR	8c-e
3	$[\{CpTi(Mo_5O_{18})\}Mn(CO)_3]^{2-}$ $[\{CpTi(W_5O_{18})\}_2Ru_2(CO)_4]^{4-}$	$[Mn(CO)_3(CH_3CN)_3](PF_6)$ reacted with $[CpTi(Mo_5O_{18})(MoO_2Cl)]$ in CH_3CN; $[(CH_3CN)_6Ru_2(CO)_4](PF_6)_2$ reacted with $TBA_3[CpTiW_5O_{18}]$ in CH_2Cl_2	Bifunctional POM-supported organometallic compounds; no crystal structures; ^{17}O NMR and FTIR	8f, g
4	$[(Ph_3P)_2Rh(CO)(CH_3CN)]_n[XM_{12}O_{40}]$ (X = Si, P; M = W, Mo; n = 3,4)	$H_4SiW_{12}O_{40}$ precipitated with $[(Ph_3P)_3Rh(CO)]^+[HC(SO_2CF_3)_2]^-$ from EtOH/MeCN	Ion pairs; no crystal structures; EXAFS study; heterogeneous catalysts for hydroformylation of olefins	6
5	$[Re(CO)_3P_2W_{15}Nb_3O_{62}]^{8-}$ $[Ir(CO)_2P_2W_{15}Nb_3O_{62}]^{8-}$ $[Rh(CO)_2P_2W_{15}Nb_3O_{62}]^{8-}$	$[Re(CO)_3(CH_3CN)_3](BF_4)$ reacted with $TBA_9P_2W_{15}Nb_3O_{62}$ in CH_3CN; CO bubbled into a solution of $[M(1,5\text{-}COD)P_2W_{15}Nb_3O_{62}]^{8-}$ (M = Ir and Rh)	PSMCs based on Dawson POMs; no crystal structures; ^{31}P and ^{183}W NMR, FTIR	8h
6	$[M_6O_{19}\{M'(CO)_3\}_n]^{(8-n)-}$ (M = Nb, Ta; M' = Mn, Re; n = 1, 2)	$[M(CO)_3]^+$ reacted with $K_7HNb_6O_{19}$ and $K_8Ta_6O_{19}$ by hydrothermal methods in autoclave	X-ray structures determined; ^{17}O NMR and FTIR	8i
7	$[Mo_2O_5(OMe)_5\{M(CO)_3\}_2]^-$ (M = Re and Mn) $[Mo_2O_4(OMe)_6\{Mn(CO)_3\}_2]$ $[Mo_2O_6(OMe)_4\{Re(CO)_3\}_2]^{2-}$ $[Mo_2O_4\{RC(CH_2O)_3\}_2\{Mn(CO)_3\}_2]$ (R = Me and CH_2OH) and the related	$[M(CO)_3]^+$ reacted with $TBA_2Mo_2O_7$ in MeOH; *w/o* $RC(CH_2OH)_3$ (R = Me, CH_2OH)	Crystal structures determined; isolobal analogy between d^0-*fac*-$\{MoO_2X\}$ (X = O, OR, Cl) and d^6-*fac*-$\{M(CO)_3\}$	8j
8	$[M(CO)_3(H_2O)\{Mo_5O_{13}\text{-}(OMe)_4(NO)\}]^{2-}$ (M = Re, Mn), $[Na\{Mo_5O_{13}(OMe)_4(NO)\}_2\{Mn(CO)_3\}_2]^{3-}$ and the other similar compounds	$[M(CO)_3]^+$ reacted with $TBA_2[Na(MeOH)\text{-}\{Mo_5O_{13}(OMe)_4(NO)\}]$ in MeOH	X-ray structures determined; $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ is a multifunctional ligand	8k
9	$[SiW_{11}O_{39}Ru(CO)]^{6-}$	$Ru(acac)_3$ reacted with $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$ under hydrothermal conditions in autoclave	No single-crystal structure; powder XRD, ^{13}C NMR and FTIR; photo-redox chemistry	8l
10	$[(H_2W_8O_{30})\{M(CO)_3\}_2]^{8-}$ $[(H_2Mo_8O_{30})\{M(CO)_3\}_2]^{8-}$ (M = Re, Mn)	One-pot synthesis of $[M(CO)_3]^+$ with Na_2WO_4 ,or $[Mo_7O_{24}]^{6-}$, in H_2O/CH_3COOH	X-ray structures obtained; Lindqvist isopolyoxotungstate supported metal carbonyl derivatives	8m, n
11	$[Mn(CO)_3(A\text{-}\alpha\text{-}H_2XW_9O_{34})]^{8-}$ (X = Si, Ge)	$[Mn(CO)_3]^+$ reacted with $[\gamma\text{-}XW_{10}O_{36}]^{8-}$ (X = Si, Ge) in H_2O/CH_3CN solution at neutral pH	X-ray structures determined; crystal formation due to the degradation of $[\gamma\text{-}XW_{10}O_{36}]^{8-}$	8p
12	$[Mn(CO)_3(CH_3CN)_3]_3[XM_{12}O_{40}]$, $[Mn(CO)_3(CH_3CN)_3]_3[X_2M_{18}O_{40}]$ (X = P, As, Si, Ge; M = W, Mo)	$[Mn(CO)_3]^+$ interacts with plenary Dawson/Keggin POMs in H_2O/CH_3CN	X-ray structures determined; Ion pairs	8o
13	$[X_2W_{20}O_{70}\{M(CO)_3\}_2]^{12-}$ (X = Sb, Bi; M = Re, Mn)	$[M(CO)_3]^+$ reacted with Krebs-type $[X_2W_{22}O_{74}(OH)_2]^{12-}$ (X = Sb, Bi) in water	X-ray structures obtained; *fac*-$[M(CO)_3]^+$ and *fac*-$[TM(H_2O)_3]^{2+/3+}$ (TM = Co, Cu, Zn,	8q

			Fe) shown to be topologically equivalent units.	
14	$[P_4W_{35}O_{124}\{M(CO)_3\}_2]^{16-}$ $[P_2W_{23}O_{80}\{M(CO)_3\}_2]^{10-}$ (M = Re, Mn)	$[M(CO)_3]^+$ (M = Re, Mn) reacted with $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ or $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ in water at pH 2 ~ 2.5	Defect Dawson or Keggin PSMCs; X-ray structures; visible-light activity; charge-transfer study	7 and in this article
15	$[P_2W_{17}O_{61}\{Re(CO)_3\}_3\{ORb(H_2O)\}(\mu_3\text{-}OH)]^{9-}$	$[Re(CO)_3]^+$ reacted with $[P_4W_{35}O_{124}\{Re(CO)_3\}_2]^{16-}$ in water at pH 5 ~ 6	The first molecular analogue of solid-oxide supported metal carbonyl clusters; electronic structure and dynamics study.	17

Cp = cyclopentadienyl; TBA = tetrabutylammonium; TMA = tetramethylammonium; COD = 1,5-cyclooctadiene; acac = acetylacetonate

Reaction of $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ with solvated $[Re(CO)_3]^+$, or $[Mn(CO)_3]^+$ in acidic solutions (pH < 4), readily forms the "twisted-sandwich" PSMCs, $[P_2W_{23}O_{80}\{M(CO)_3\}_2]^{10-}$ (M = Re, Mn). We propose the following self-assembly pathway. The starting solutions become reddish upon heating, a characteristic feature indicating the formation of W-O-M bonds.[7] As shown in Figure 1b, the four terminal oxygen atoms in $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ formed by removing the $W{=}O^{4+}$ unit are separated by a diagonal distance of ~ 4.2 Å (Figure 1), thus $[M(CO)_3]^+$ cannot bond to three of them directly. $[M(CO)_3]^+$ is likely to bind to O(1) and O(2) (or the symmetry-equivalent O(1') and O(2')), because the distances between them are ~ 2.7 Å, while the distances of O(1)-O(1') and O(2)-O(2') are ~ 3.1 Å. The resulting di-coordinated intermediates are chiral building blocks. They lead to chirality in each dimeric product polyanion with racemic configurations in the solid state. The third coordination site is occupied by an extra $[WO_2]^{2+}$ unit which derives from degraded POM precursors. As shown in Figure 1c, the resulting oxygen triangle (sides: 2.72 – 2.78 Å), constructed from the central oxygen, O(1) and O(2) (or O(1') and O(2')), is similar to that in the Krebs dimers. Upon decreasing the pH (<4), the solution colors become darker indicating an ongoing dimerization process (Figure 1d). In our trials, the three crystals are prepared at pH ~ 2-2.5. An acidic pH is critical; the yield is very low at higher pH (>6).

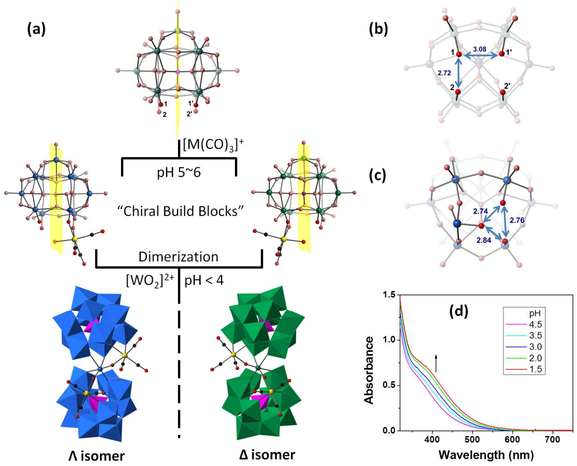


Fig. 1. (a) Scheme of proposed synthetic pathways of **1** and **2**. Color code: O, red; C, black; P and PO_4, violet; Re or Mn, yellow; W and WO_6, blue or green. The yellow rectangles represent the mirror planes in $[\alpha\text{-}PW_{11}O_{39}]^{7-}$. (b) Representative distances (unit: Å) of the four terminal oxygens in $[\alpha\text{-}PW_{11}O_{39}]^{7-}$. (c) The trigonal coordination sites (Å). (d) UV-vis absorption spectra of **1**. The first spectrum was recorded after 0.5 hr of reaction. Spectra thereafter were recorded upon titration.

The structure of **1** shows an ideal C_2 symmetry with only one ^{31}P NMR peak (Figures 1a and 2a). The bond distances of Re-O and C-O are in the range of 1.87 to 1.91 Å and 1.16 to 1.20 Å respectively, which are consistent to other PSMCs.[6-8, 8o-q] The structure can be regarded as the dimerization of two $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ polyanions with an extra $[WO_2]^{2+}$ unit as the rotating center. This structural feature is similar to that in some organo-ruthenium-substituted POMs.[18] The central W atom resides in a distorted octahedral cage, and the four neighboring metals $\{ReW_3\}$ are almost in the same plane (± 1°; see the green planes in Figure 3a). The chirality derives from two $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ units staggered relative to one another around the central W atom, i.e. a torsion angle of ± 48.5° between the two green planes (Figure 3a). However, unlike $[Hf(PW_{11}O_{39})_2]^{11-}$ which crystallizes in a chiral space group,[2, 15e, 19] **1** crystallizes in the centrosymmetric space group $P\overline{1}$. Thus, **1** is racemic (Λ- and Δ- forms of two enantiomers in a 1:1 ratio) in the solid state. A much higher yield (~70%) can be achieved using trimethylammonium (TMA). The resulting **1a** crystallizes in the orthorhombic space group *Pbca*. The crystal quality is inferior to **1**, which probably results from a shorter crystallization time, highly disordered TMA cations, a high symmetry space group and a very large unit cell volume. Figures 4a and 4b show the ordered atomic positions of the Λ- and Δ- forms assembled in the unit cell.

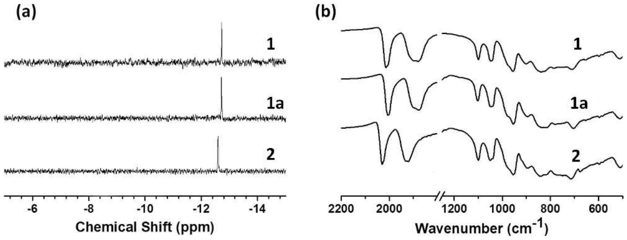


Fig 2. (a) ^{31}P NMR of **1** (D_2O), **1a** (D_2O with LiCl) and **2** (D_2O with LiCl), with respect to 85% H_3PO_4 (0 ppm). (b) FTIR spectra of **1**, **1a** and **2** (KBr pellets).

A similar racemic structure is also observed in **2** ($[Mn(CO)_3]^+$ in place of $[Re(CO)_3]^+$). There is only one ^{31}P peak (Figure 2a). The Mn-C and C-O bond distances are in the range of 1.80 to 1.83 Å and 1.12 to 1.16 Å respectively. The twist angle is ±44.1°. Compound **2** crystallizes in a monoclinic, *C*2/c space group (Figure 4c). Compound **3** also shows the "twisted-sandwich" structure (±44.1°) but with a larger Dawson-derived ligand in place of the Keggin-derived ligand (Figure 3b). The structure is similar to $[Ce_2(H_2O)_8(P_2W_{17}O_{61})_2]^{14-}$.[20] Both compounds crystallize in the centrosymmetric space group, triclinic $P\overline{1}$ (Figure 4d).

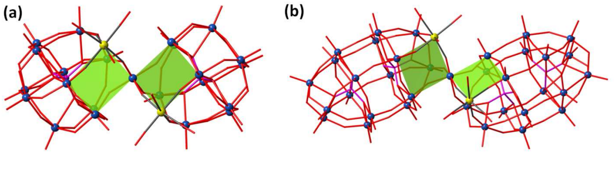


Fig. 3. X-ray structures of Λ-**1** (a) and Λ-**3** (b) in ball-and-stick modes. Color code: C, gray; O, red; Re/Mn, yellow; W, blue. The green planes illustrate the torsion angles and relative positions of two POM ligands.

Because these complexes show C_2 symmetry and each $\{M(CO)_3\}^+$ unit has local C_{3v} symmetry, the FTIR spectra show two symmetric and one anti-symmetric IR-active CO stretching modes (Figure 2b). Compounds **1** and **1a** have lower C-O frequencies relative to **2**, which is consistent with the stronger M-to-CO dπ-π^* back bonding as Re(I) is more electron donating than Mn(I). The C-O bond strength is consistent with the C-O bond length (Table 2).

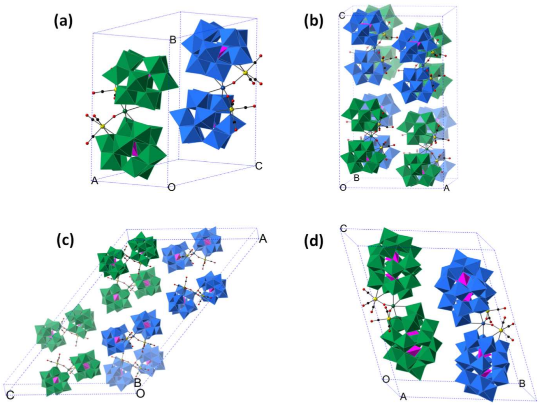


Fig. 4. The packing arrangements of Λ- (blue) and Δ- (green) isomers in the single unit cells of crystal structures of (a) **1**, (b) **1a**, (c) **2** and (d) **3**. Color code: O, red; C, black; PO_4, violet; Re or Mn, yellow; WO_6, blue or green.

Electrochemical Studies. The cyclic voltammetry (CV) of **1** in negative region shows two well-resolved reversible peaks with $E_{1/2}$ at -0.64 and -0.84 V, respectively (Figure 5a). The voltammetric pattern, similar to those of $[\alpha\text{-}PW_{11}O_{39}]^{7-}$-based POMs, i.e. $[M(PW_{11}O_{39})_2]^{11-}$ (M = lanthanide and actinide elements), can be assigned to W(VI/V) reductions.[15a, 15f] The anodic peak currents, $i_{p,a}$, are proportional to the square root of the scan rate, $v^{1/2}$ ($R^2 = 0.996$), indicating that the redox processes of **1** are diffusion-controlled (Figure 5b). The CV of **2** in the positive potential region shows a quasi-reversible peak ($E_{pc} = 0.71$ and $E_{pa} = 0.82$ V) assigned to the oxidation of Mn centers (Figure 5c). In the negative region, reduction of W centers follows a similar pattern as in **1**, however the waves are poorly resolved. The redox processes are diffusion-controlled but with a linear dependence between $i_{p,a}$ and $v^{1/2}$ ($R^2 = 0.966$). This dependence is experimentally less well-defined than for **1** which likely reflects the hydrolytic instability of this complex.

Table 2. Crystal structure data for compounds **1**, **1a** and **2**

	1	**1a** [a]	**2**
Empirical formula	$C_6H_{76}O_{124}K_7Na_3P_2Re_2W_{23}$	$C_{30}H_{100}N_8O_{96}Na_2P_2Re_2W_{23}$	$C_{24}H_{74}N_6O_{93}KNa_3Mn_2P_2W_{23}$
T [K]	173(2)	173(2)	173(2)
M_r [g mol^{-1}]	7137.93	6817.77	6443.04
Crystal system	Triclinic	Orthorhombic	Monoclinic
Space group	$P\bar{1}$	*Pbca*	*C*2/*c*
a [Å]	13.0794(4)	23.0635(18)	57.054(8)
b [Å]	19.8716(6)	26.1690(19)	13.2708(18)
c [Å]	21.3258(6)	38.199(3)	36.998(5)
α [°]	76.506(2)	90	90
β [°]	84.428(2)	90	127.936(2)
γ [°]	82.631(2)	90	90
V [Å^3]	5332.3(3)	23055(3)	22094(5)
Z	2	8	8
ρ_{calcd} [g cm^{-3}]	4.263	3.752	3.939
μ [mm^{-1}]	27.390	25.064	24.313
Reflection collected	64578	90059	108179
Independent refl. (R_{int})	32520 (0.0413)	21865 (0.1409)	26360 (0.0570)
Goodness-of-fit	1.075	1.056	1.033
R_1 [I>2σ(I)]	0.0530	0.1000	0.0366
wR_2	0.1166	0.2082	0.0798
R_1 (all data)	0.0803	0.1951	0.0502
wR_2 (all data)	0.1358	0.2679	0.0868
Largest diff. peak and hole [e Å^3]	4.748, -5.419	5.050, -3.344	3.646, -2.483
Selective bond lengths (Å), bond angles (°) and CO stretching vibrations (cm^{-1})			
P-O^b	1.52-1.56	1.50-1.59	1.50-1.55
M-O^b	2.07-2.15	1.99-2.20	1.97-2.03
M-C^c	1.88-1.91	1.71-1.90	1.80-1.83
C-O^c	1.16-1.20	1.20-1.23	1.13-1.16
M-C-O^c	176-180	172-179	174-179
C-O stretching	2013, 1900, 1879	2005, 1897, 1877	2031, 1930, 1921

$R_1 = \Sigma\,||F_0|-|F_c||/\Sigma|F_0|$; $wR_2 = \{\Sigma[w(F_0^2-F_c^2)^2/\Sigma w(F_0^2)^2]\}^{1/2}$

[a] Refined with constraints. [b] Oxygen from POMs (M = Re or Mn). [c] Carbon and oxygen from carbonyl groups.

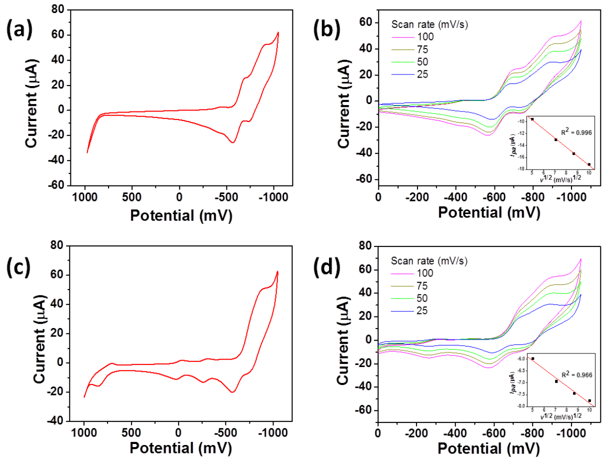


Fig. 5. CVs of (a) **1** and (c) **2** at scan rate of 100 mV s^{-1} and in the range of +1.1 to -1.1 V. Also shown CVs of (b) **1** and (d) **2** at scan rates of 25, 50, 75 and 100 mV s^{-1} in the range of 0 to -1.1 V. The insets illustrate the correlation between selected anodic peak currents and the square root of scan rates.

Conclusions

We have thoroughly investigated the coordination chemistry of metal tricarbonyl precursors and monovacant Keggin/Dawson POMs, [α-$PW_{11}O_{39}$]$^{7-}$ and [α_2-$P_2W_{17}O_{61}$]$^{10-}$. Three POM-supported metal carbonyl complexes (PSMCs) have been prepared and their structural, spectroscopic and electrochemical properties established. All the PSMCs published to date have been tabulated. This article provides more convenient syntheses and a novel POM scaffold, named the "twisted-sandwich". In these new PSMCs, each polyanion is chiral, but they exist as a racemic enantiomeric pair in the unit cells. Given that PSMCs are potentially attractive for catalysis, the resolution of these enantiomeric pairs would be of interest.

Experimental Section

Materials and Instrumentation. All chemicals were reagent grade and used as supplied. The Keggin and Dawson polyoxometalate precursors Na_7[α-$PW_{11}O_{39}$] and K_{10}[α_2-$P_2W_{17}O_{61}$] were prepared according to the literature.[21] The low-valent complexes $M(CO)_3(CH_3CN)_3(BF_4)$ (M = Re, Mn) were made following known methods but using $AgBF_4$ in place of $AgClO_4$.[22] The purities of these compounds were analyzed by ^{1}H NMR, ^{31}P NMR and FT-IR spectroscopy.

The FT-IR spectra were acquired on a Thermo Nicolet 6700 spectrometer with KBr pellets (2%). UV-vis spectra were collected using an Agilent 8453 spectrophotometer equipped with a diode-array detector interfaced with an Agilent 89090A cell temperature controller unit. ^{31}P NMR spectra (162.13 MHz) in D_2O were measured on a Varian INOVA 400 spectrometer with respect to 85% H_3PO_4 (0 ppm) as an internal standard. Elemental analyses were performed by Galbraith Lab Inc., Knoxville, TN (K, Mn, Na, P, Re, W) and Atlantic Microlab Inc., Norcross, GA (C, H, N).

$K_7Na_3P_2W_{23}O_{80}\{Re(CO)_3\}_2\cdot 38H_2O$ (1). $Na_7PW_{11}O_{39}$ (0.1 mmol, 286 mg) and $Re(CO)_3(CH_3CN)_3BF_4$ (0.1 mmol, 48 mg) were dissolved in 15 mL of hot water. The mixtures were heated at ~70 °C for 0.5 h, during which the solution slowly became orange-red. The solution was then cooled to room temperature and the pH was adjusted to ~2.5 by addition of 1.0 M HCl. The solution became dark red in color and was filtered. KCl (200 mg) was added to the above solution in small portions. Plate-shaped single crystals suitable for X-ray diffraction were collected after slow evaporation for *ca*. 3 weeks. Yield: 45 mg (13% based on P). FTIR (2500 – 400 cm^{-1}): 2013 (s), 1900 (s), 1879 (s), 1099 (s), 1046 (s), 956 (s), 903 (m), 838 (s), 785 (w), 743 (w), 708 (w), 653 (w), 598 (w), 513 (w). Electronic spectral data (350 – 700 nm, in H_2O): $\varepsilon_{400\ nm}$ ~ 1.1×10^4 M^{-1}cm^{-1}. ^{31}P NMR: -12.7 ppm. Anal. Calcd. for $C_6H_{76}O_{124}K_7Na_3P_2Re_2W_{23}$: K, 3.8; Na, 0.97; P, 0.87; Re, 5.2; W, 59.2. Found: K, 3.8; Na, 1.1; P, 0.83; Re, 5.1; W, 59.5.

$(C_3H_{10}N)_8Na_2P_2W_{23}O_{80}\{Re(CO)_3\}_2\cdot 10H_2O$ (1a). The preparation was similar to that for **1** but with trimethylammonium bromide (~100 mg) substituted for KCl. Large block-shaped crystals suitable for X-ray diffraction measurements formed overnight and were separated by filtration, washed, dried and analyzed. Yield: 240 mg (70% based on P). FTIR (2500 – 400 cm^{-1}): 2006 (s), 1900 (s), 1876 (s), 1099 (s), 1103 (s), 1047 (s), 954 (s), 895 (m), 835 (s), 817 (s), 781 (w), 703 (s), 654 (w), 595 (w), 513 (w). Electronic spectral data (350 – 700 nm, in H_2O): $\varepsilon_{400\ nm}$ ~ 1.1×10^4 M^{-1}cm^{-1}. ^{31}P NMR: -12.7 ppm. Anal. Calcd. for $C_{30}H_{100}N_8O_{96}Na_2P_2Re_2W_{23}$: C, 5.28; H, 1.47; N, 1.64; Na, 0.67. Found: C, 5.26; H, 1.46; N, 1.65; Na, 0.70.

$(C_3H_{10}N)_6KNa_3P_2W_{23}O_{80}\{Mn(CO)_3\}_2\cdot 7H_2O$ (2). $Mn(CO)_5Br$ (0.1 mmol, 27 mg) and $AgNO_3$ (0.1 mmol, 17 mg) were dissolved in 1 mL of methanol. The mixtures were stirred in the dark at room temperature for ~2 hrs and then filtered. The filtrate containing the *in situ* formed $[Mn(CO)_3]^+$ precursors was then added to an aqueous solution (15 mL) of $Na_7PW_{11}O_{39}$ (0.1 mmol, 286 mg). The mixtures were stirred in the dark at ~50 °C for another ~2 hrs and then filtered. HCl (1 M) was added dropwise until the final pH was ~2.5. Trimethylammonium bromide (~20 mg) and KCl (100 mg) was then added and the solution was filtered again. The solution was kept in the dark for slow evaporation. Black-red crystals in large block shapes were collected after ~2 weeks. Yield: 150 mg (45% based on P). FTIR (2500 – 400 cm^{-1}): 2031 (s), 1930 (s), 1921 (s), 1099 (s), 1049 (s), 955 (s), 895 (m), 841 (m), 823 (w), 767 (w), 750 (w), 714 (s), 677 (w), 598 (w), 582 (w), 509 (m). Electronic spectral data (350 – 700 nm, in H_2O): $\varepsilon_{400\ nm}$ ~ 9.7×10^3 M^{-1}cm^{-1}. ^{31}P NMR: -12.6 ppm. Anal. Calcd. for $C_{24}H_{74}N_6O_{93}KNa_3Mn_2P_2W_{23}$: C, 4.47; H, 1.15; N, 1.30; K, 0.61; Na, 1.0; Mn, 1.7; P, 0.96; W, 65.6. Found: C, 4.46; H, 1.13; N, 1.27; K, 0.68; Na, 0.96; Mn, 1.5; P, 0.89; W, 65.4.

Crystallography. X-ray analysis was performed on a Bruker D8 SMART APEXII CCD sealed tube diffractometer. Diffraction intensities were measured using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 173(2) K. Structure solution, refinement, graphics were generated using SHELXTL-97 software.[23] The largest residual electron density for each structure was located close to the W atoms and was most likely due to imperfect absorption corrections frequently encountered in heavy-metal atom structures. Crystal data collection and refinement parameters are given in Table 2. CCDC-917606 (**1**), 917607 (**1a**), 917608 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Electrochemistry. Cyclic voltammograms (CVs) were obtained at room temperature using a BAS CV-50W potentiostat in the standard three-electrode configuration. A glassy-carbon disk and a platinum wire were used as the working and counter electrodes, respectively. The reference was a Ag/AgCl (3 M NaCl) (BASi) electrode. All reported reduction potentials are relative to this reference. CVs were performed in 20 mM sodium acetate buffer (pH = 4) with 0.2 M $LiClO_4$ as supporting electrolyte.

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Entry for the Table of Contents

Text:

Capturing $[M(CO)_3]^+$ (M = Re, Mn) by $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ or $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ leads to polyoxometalate-supported metal carbonyl complexes with chiral “twisted-sandwich” structures.