



Cite this: *Chem. Commun.*, 2015, 51, 1222

Received 20th November 2014,  
Accepted 28th November 2014

DOI: 10.1039/c4cc09271f

[www.rsc.org/chemcomm](http://www.rsc.org/chemcomm)

$[\text{HIr}^{\text{IV}}\text{W}_6\text{O}_{24}]^{7-}$ , representing the first Ir-containing Anderson–Evans-type polyanion and the first structurally characterized  $\text{Ir}^{\text{IV}}$ -based polyoxometalate, has been isolated as its hydrated sodium salt and characterized by single-crystal X-ray diffraction, mass spectrometry, and IR, UV-Vis and EPR spectroscopy. Cyclic voltammetry indicates that the  $\text{Ir}^{\text{IV}}$  ions in  $[\text{HIrW}_6\text{O}_{24}]^{7-}$  can undergo reversible one-electron reduction and oxidation, resulting in  $\text{Ir}^{\text{III}}$  and  $\text{Ir}^{\text{V}}$  derivatives.

The chemistry of polyoxometalates (POMs) incorporating noble metals represents a rapidly developing area, the interest in which is driven by various fundamental and applied aspects.<sup>1</sup> Members of this class demonstrate a range of promising properties, in particular, catalytic activity in water splitting<sup>2,3</sup> and oxidation of various organic substrates.<sup>4</sup> We stress, though, that the number of publications on POM complexes of Ru and Pd by far exceeds those dedicated to all remaining noble metals (Pt, Au, Ir, Os and Rh) taken together. In particular, the chemistry of Ir-containing POMs for a long time has been limited to various POM-supported  $\text{Ir}^{\text{I}}$ - and  $\text{Ir}^{\text{III}}$ -organometallic complexes (e.g.  $[\text{Ir}^{\text{I}}(1,5\text{-COD})]^+$ ,  $[\text{Ir}^{\text{III}}(\text{Cp}^*)]^{2+}$  etc.),<sup>5</sup> some of which, e.g.  $[(1,5\text{-COD})\text{Ir}^{\text{I}}\text{Nb}_3\text{P}_2\text{W}_{15}\text{O}_{62}]^{8-}$ , are pre-catalysts for cycloalkene oxygenation with  $\text{O}_2$ .<sup>5b-d</sup> Recently a number of Keggin and Wells–Dawson type POMs with covalently grafted heteroleptic cyclo-metalated  $\text{Ir}^{\text{III}}$ -complexes exhibiting effective charge separation

between the  $\text{Ir}^{\text{III}}$ -based chromophore and the POM unit were reported.<sup>6</sup> The first reliably characterized iridium-containing POM incorporating no organometallic fragments,  $[(\text{Ir}^{\text{III}}\text{Cl}_4)(\text{P}_2\text{W}_{20}\text{O}_{72})]^{15-}$ , was reported as late as in 2009 by Hill's group and identified as a water oxidation catalyst.<sup>3</sup> Two years later, the synthesis, characterization and reactivity of Keggin-type complexes  $[\text{PW}_{11}\text{O}_{39}\text{Ir}^{\text{III}}\text{L}]^{n-}$  ( $n = 4$  or 5; L =  $\text{H}_2\text{O}$ , OH,  $\text{CH}_3$ , Cl, SCN) were reported.<sup>7</sup> Yet, POMs incorporating  $\text{Ir}^{\text{IV}}$  centers, which are of interest as promoters or intermediates in oxidation reactions, remain unknown. For this oxidation state, we expect Ir-containing polyoxotungstates or molybdates to adopt the Anderson–Evans structure, in analogy to known  $\text{Rh}^{\text{III}}$ ,<sup>8</sup>  $\text{Pt}^{\text{IV}}$ ,<sup>9,10</sup> and even  $\text{Pd}^{\text{IV}}$  derivatives.<sup>11</sup>

We report the preparation of  $[\text{HIr}^{\text{IV}}\text{W}_6\text{O}_{24}]^{7-}$  ( $\text{IrW}$ ), the first polyoxometalate incorporating  $\text{Ir}^{\text{IV}}$ , and its characterization by single-crystal X-ray analysis, mass spectrometry, IR, UV-Vis and EPR spectroscopy, as well as cyclic voltammetry.

$\text{IrW}$  assembles in condensation reactions of *in situ*-formed  $\text{Ir}^{\text{IV}}$  hydroxo complexes with tungstate ions in aqueous acetate media. In a first step,  $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$  was dissolved in a  $\text{CH}_3\text{COONa}$  solution and the pH of the reaction mixture was adjusted to 12 with 6 M NaOH. Heating of the solution led to a gradual color change from brown-green to blue and then to purple. Previous studies on alkaline solutions of hexachloroiridate(III) have shown that the processes in such reaction systems include substitution of  $\text{Cl}^-$  ligands in the inner coordination sphere of the  $\text{Ir}^{\text{III}}$  ions by  $\text{OH}^-$  groups and the subsequent oxidation of thus formed hydroxo-oxo complexes of  $\text{Ir}^{\text{III}}$  in air.<sup>12</sup> During the reaction, the color change of the  $\text{Ir}^{\text{IV}}$ -containing solutions from blue to purple is apparently caused by (not well-defined) oligomerization processes. Another hypothesis postulates transformation of the blue superoxo dimeric  $[(\text{OH})_5\text{Ir}^{\text{IV}}(\mu\text{-O}_2^-)\text{Ir}^{\text{IV}}(\text{OH})_5]^{3-}$  species into the purple  $[(\text{OH})_4\text{Ir}^{\text{IV}}(\mu\text{-O}_2^{2-})(\mu\text{-OH})\text{Ir}^{\text{IV}}(\text{OH})_5]^{3-}$  complex, based on UV-Vis and EPR studies of 3 M KOH solutions of  $[\text{IrCl}_6]^{3-}$ .<sup>12f</sup> Next, the solution of the *in situ*-formed  $\text{Ir}^{\text{IV}}$  hydroxo complexes was added dropwise to a solution containing the lacunary  $[\text{B}-\alpha\text{-PW}_9\text{O}_{34}]^{9-}$  polyanion under careful control of pH kept strictly between 6 and 7 by addition of diluted nitric acid.

<sup>a</sup> Nikolaev Institute of Inorganic Chemistry SB RAS, 630090 Novosibirsk, Russia.  
E-mail: caesar@niic.nsc.ru; Fax: +7 383-330-94-89; Tel: +7 383-316-58-45

<sup>b</sup> Novosibirsk State University, 630090 Novosibirsk, Russia

<sup>c</sup> Peter Grünberg Institute – PGI 6, Forschungszentrum Jülich, D-52425 Jülich, Germany. E-mail: paul.koegerler@ac.rwth-aachen.de

<sup>d</sup> Institute of Inorganic Chemistry, RWTH Aachen University, D-52074 Aachen, Germany

<sup>e</sup> Central Institute for Engineering, Electronics and Analytics – ZEA 3, Forschungszentrum Jülich, D-52425 Jülich, Germany

<sup>†</sup> Electronic supplementary information (ESI) available: Crystallographic data in CIF format; details on synthesis, crystallographic and electrochemical studies; crystal packing in  $\text{Na}\text{-IrW}$ , bond valence sum values; mass spectrometry; IR and UV-Vis spectra. See DOI: 10.1039/c4cc09271f

<sup>‡</sup> These authors contributed equally.



$[\text{B}-\alpha\text{-PW}_9\text{O}_{34}]^{9-}$  is unstable in solution and acts as a source of free  $\text{WO}_4^{2-}$  species, which effectively assemble and condense around  $\text{Ir}^{\text{IV}}$ , resulting in **IrW**. This is conceptually similar to the controlled formation of  $\text{Mn}^{\text{III}}$  species by slow hydrolysis of  $[\text{Mn}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4\text{O}_{12}]$  in the synthesis of Mn-substituted polyoxotungstates.<sup>13</sup> It should be noted that both monoprotonated and non-protonated forms of  $[\text{Ir}^{\text{IV}}\text{W}^{\text{VI}}\text{O}_{24}]^{8-}$  (**IrW'**) can be isolated as the hydrated sodium salts  $\text{Na}_6\text{H}[\text{Ir}^{\text{IV}}\text{W}^{\text{VI}}\text{O}_{24}]\cdot26\text{H}_2\text{O}$  (**Na-IrW**) and  $\text{Na}_8[\text{Ir}^{\text{IV}}\text{W}^{\text{VI}}\text{O}_{24}]\cdot26\text{H}_2\text{O}$  (**Na<sub>8</sub>-IrW'**), respectively. The exact protonation state depends on the final pH of the reaction mixture.

Thus, pure **Na-IrW** crystals form when the final pH of the reaction mixture before crystallization is set within the range of 6.1–6.5. At higher final pH (7.0–7.5) crystals of **Na<sub>8</sub>-IrW'** form as a byproduct to **Na-IrW**. No crystals could be isolated at pH > 7.6 where one could expect formation of pure **Na<sub>8</sub>-IrW'**. We herein focus on the monoprotonated species and provide structural data for **Na<sub>8</sub>-IrW'** in the ESI.<sup>†</sup>

Our attempts to rationalize the synthetic procedure by reacting  $\text{Ir}^{\text{IV}}$  solutions directly with  $\text{Na}_2\text{WO}_4$  at various ratios were not successful and resulted in formation of the paratungstate salt  $\text{Na}_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}]\cdot25\text{H}_2\text{O}$  as the main product, as established *via* single-crystal X-ray measurements and IR spectroscopy. We conjecture that an initial excess of  $\text{Ir}^{\text{IV}}$  ions coupled with the gradual release of  $\text{WO}_4^{2-}$  species into the reaction medium are key to successful preparation of **IrW**. Alternatively, **IrW** can be prepared by prolonged heating of  $\text{K}_2[\text{IrF}_6]$  with  $\text{Na}_2\text{WO}_4$  in water at neutral pH, however, this reaction is not very well reproducible and the **IrW** salts could be isolated only in a low yield ( $\leq 10\%$ ).

The compound  $\text{Na}_6\text{H}[\text{Ir}^{\text{IV}}\text{W}^{\text{VI}}\text{O}_{24}]\cdot26\text{H}_2\text{O}$  (**Na-IrW**) crystallizes in the triclinic space group  $P\bar{1}$ . The **IrW** polyanions display an Anderson–Evans-type ring structure comprising a central  $\text{Ir}^{\text{IV}}\text{O}_6$  octahedron surrounded by six distorted edge-sharing  $\text{W}^{\text{VI}}\text{O}_6$  octahedra (Fig. 1). All metal centers in the  $\text{IrW}_6$  core define a single plane and form a virtually regular Ir-centered  $\text{W}_6$  hexagon ( $\text{W}\cdots\text{W}$ : 3.223–3.345 Å;  $\text{Ir}\cdots\text{W}$ : 3.234–3.316 Å). **IrW** has idealized  $D_{3d}$  symmetry and thus belongs to the A-type family of polyanions with Anderson–Evans structure which is typical for  $[\text{M}'\text{W}_6\text{O}_{24}]^{n-}$  heteropolyoxotungstates. In contrast, some of the polyoxomolybdates  $[\text{M}'\text{Mo}_6\text{O}_{24}]^{n-}$  may also adopt a bent conformation with  $C_{2v}$  symmetry (usually referred as a B-type Anderson–Evans structure), which was *e.g.* found in

$[\text{H}_4\text{PtMo}_6\text{O}_{24}]^{4-}$ <sup>9a,c–e</sup>  $[\text{H}_2\text{SbMo}_6\text{O}_{24}]^{5-}$  (ref. 14) and hepta-molybdate  $[\text{Mo}_7\text{O}_{24}]^{6-}$  ions.<sup>15</sup>

There are three types of oxygen atoms in **IrW**:  $\mu_3\text{-O}$  linking  $\text{Ir}^{\text{IV}}$  and two  $\text{W}^{\text{VI}}$  centers ( $\text{Ir}-\text{O}$ : 1.994(5)–2.022(5) Å;  $\text{W}-\text{O}$ : 2.142(5)–2.293(5) Å),  $\mu_2\text{-O}$  bridging two  $\text{W}^{\text{VI}}$  ions ( $\text{W}-\text{O}$ : 1.923(5)–1.987(5) Å) and terminal O atoms ( $\text{W}=\text{O}$ : 1.735(5)–1.747(5) Å). The average  $\text{Ir}-\text{O}$  bond length in **IrW** of 2.004 Å is comparable with that of 2.013 Å observed in the only structurally characterized  $\text{Ir}^{\text{III}}$ -containing all-inorganic polyoxotungstate  $[(\text{Ir}^{\text{III}}\text{Cl}_4)\text{P}_2\text{W}_{20}\text{O}_{72}]^{15-}$ ,<sup>3</sup> and with that in  $\text{Ir}^{\text{IV}}$  oxides, *e.g.*  $\text{CaIrO}_3$  (2.057 Å).<sup>16</sup> The  $\text{W}-\text{O}$  distances in **IrW** are similar to the  $\text{W}-\text{O}$  bond lengths in other  $[\text{XW}_6\text{O}_{24}]^{n-}$  species ( $\text{X} = \text{Pt}^{\text{IV}}$ ,  $\text{Te}^{\text{IV}}$ ,  $\text{Mn}^{\text{IV}}$ ,  $n = 8$ ;  $\text{X} = \text{Sb}^{\text{V}}$ ,  $n = 7$ ).<sup>10,17</sup> Bond valence sum calculations (Table S2, ESI<sup>†</sup>) suggest a disorder of a proton over two inversion center related  $\mu_3\text{-O}$  atoms (O123) in **IrW**. The second proton, which should be present in the structure of **Na-IrW** from the charge balance considerations (only six  $\text{Na}^+$  counter-cations were found both in X-ray diffraction and elemental analyses of **Na-IrW**), is either highly disordered over the terminal oxygens of the **IrW** polyanions (BVS 1.60–1.67) or, more likely, is associated with an oxygen of a co-crystallized water molecule, *i.e.* as a  $\text{H}_3\text{O}^+$  cation. In the crystal lattice of **Na-IrW** the  $\text{Na}^+$  counter-cations and the crystal water molecules assemble in the parallel infinite zig-zag  $\{\text{Na}_6(\mu_2\text{-H}_2\text{O})_{10}(\text{H}_2\text{O})^t\}_{14}^{6n+}$  chains. The **IrW** polyanions are packed between the chains (see ESI<sup>†</sup> for details) and form an extended net of hydrogen bonds with the H atoms of the  $\text{H}_2\text{O}$  molecules (Fig. S1 and Table S4, ESI<sup>†</sup>).

The oxidation state of the iridium center ( $\text{Ir}^{\text{IV}}$ ,  $5d^5$ ,  $S = 1/2$ ) was further confirmed by the characteristic EPR signal around  $g = 2$  (Fig. 2). The complexity of the powder spectrum indicates the strong contribution of quadrupole as well as hyperfine coupling ( $I = 3/2$  for  $^{191}\text{Ir}$  [natural abundance 37%] and  $^{193}\text{Ir}$  [63%]), similar to what has been observed for iridium(IV) impurities displaying a tetragonally distorted octahedral environment in  $\text{MgO}$  and  $\text{CaO}$  matrices.<sup>18</sup> Unfortunately, low distortion of the iridium coordination sphere in **IrW** leads to a small split between  $g$  values, and the resulting overlap of the various components in our powder X-band spectrum precludes direct determination of the hyperfine and quadrupole coupling constants, while the large number of variables renders an exhaustive search of the parameter space impracticable.

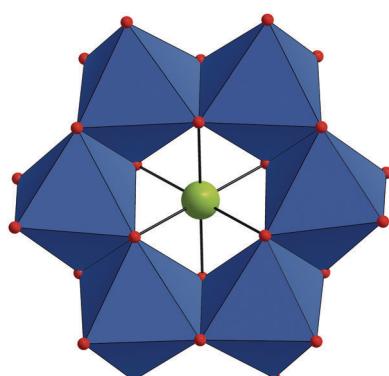


Fig. 1 Structure of **IrW**. Color code:  $\text{WO}_6$ , blue octahedra; Ir, green; O, red.

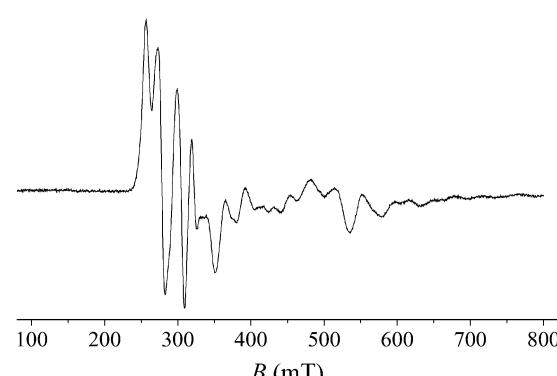


Fig. 2 Powder X-band EPR spectrum of **Na-IrW** at 110 K.



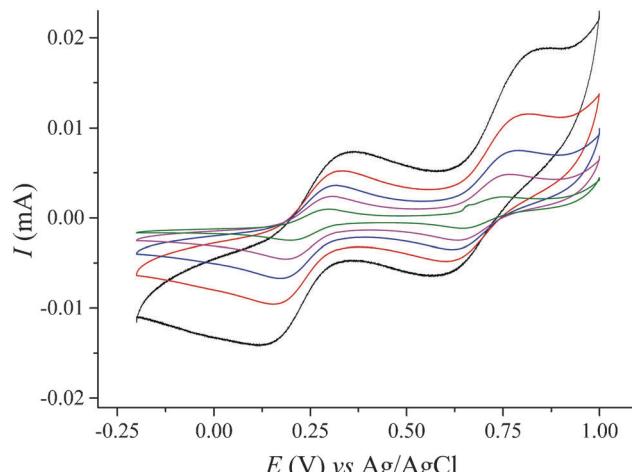


Fig. 3 CV of 1.3 mM **Na–IrW** solution in 2 M NaOAc medium (pH 6.1) at different scan rates: 10 mV s<sup>-1</sup> (green), 25 mV s<sup>-1</sup> (pink), 50 mV s<sup>-1</sup> (blue), 100 mV s<sup>-1</sup> (red), 250 mV s<sup>-1</sup> (black) vs. Ag/AgCl.

The ESI mass spectrum obtained by ionization of **Na–IrW** solution in H<sub>2</sub>O/MeOH is very complex and exhibits signals which could be assigned for the doubly negatively charged ion pairs {Na<sub>4</sub>H<sub>2</sub>[Ir<sup>IV</sup>W<sub>6</sub><sup>VI</sup>O<sub>24</sub>]}<sup>2-</sup> and {Na<sub>3</sub>H<sub>3</sub>[Ir<sup>IV</sup>W<sub>6</sub><sup>VI</sup>O<sub>24</sub>]}<sup>2-</sup> as well as sets of signals corresponding to various decomposition products, *e.g.* [HWO<sub>4</sub>]<sup>-</sup>, [HW<sub>2</sub>O<sub>7</sub>]<sup>-</sup>, Na<sub>x</sub>H<sub>5-x</sub>[IrW<sub>5</sub>O<sub>20</sub>]<sup>2-</sup> *etc.* (see ESI†). While it confirms the existence of the intact polyanions in aqueous solutions the obtained data do not answer the question if the partial decomposition starts to occur already in the solution or only happens during the ionization process. The stability of the polyanions in aqueous solution as well as aqueous acetate media with different pH has been further checked by UV-vis spectroscopy (see ESI† for details). Electrochemistry studies of **IrW** in aqueous CH<sub>3</sub>COONa solution at pH 6.1 (see ESI†) produce typical voltammograms (Fig. 3) that show two quasi-reversible redox couples with the corresponding peak potentials  $E_{1/2}$  located at 0.245 V ( $\Delta E = 0.190$  V at 100 mV s<sup>-1</sup>) and 0.700 V ( $\Delta E = 0.200$  V) *vs.* Ag/AgCl reference electrode (0.441 V and 0.896 V *vs.* SHE, respectively). These waves are attributed to the Ir<sup>III</sup>/Ir<sup>IV</sup> and Ir<sup>IV</sup>/Ir<sup>V</sup> redox transformations within the polyanion [IrW<sub>6</sub>O<sub>24</sub>]<sup>n-</sup>. The observed Ir<sup>III</sup>/Ir<sup>IV</sup> potential value is similar to 0.18 V found for the Ir<sup>III</sup>/Ir<sup>IV</sup> transition in [PW<sub>11</sub>O<sub>39</sub>Ir<sup>III</sup>(H<sub>2</sub>O)]<sup>4-</sup>, and the Ir<sup>IV</sup>/Ir<sup>V</sup> couple is close to the potential of irreversible oxidation of the Ir centers in the same POM 0.75 V (*vs.* Ag/AgCl).<sup>7a</sup> The significant shift to lower potentials as compared with the Ir<sup>III</sup>/Ir<sup>IV</sup> couple observed in the hexachloroiridates (0.669 V *vs.* Ag/AgCl<sup>19</sup>) is consistent with the stabilization of higher oxidation states of transition metals generally observed in the oxygen environment provided by polyoxometalates. The relative broadness of the waves could be due to uncompensated solution resistance but this can be ruled out since no change was observed upon increase of the electrolyte concentration. A deviation from reversibility is to be also excluded by the fact that the peak currents for the both processes remain proportional to the square root of the scan rate (Fig. S11, ESI†), indicating diffusion-controlled electrode

reactions for scan rates up to 1 V s<sup>-1</sup>.<sup>20</sup> The diffusion coefficient  $D = 2.62 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup> calculated for [Ir<sup>IV</sup>W<sub>6</sub>O<sub>24</sub>]<sup>7-</sup> according to Randles–Sevcik equation<sup>21</sup> compares well to the values reported for other polyoxotungstates.<sup>22</sup> The broadness of the redox waves reflects the co-existence of multiple protonation states at pH = 6.1. This is supported by significant narrowing of the waves when the pH decreases to 4.3 (Fig. S12, ESI†), as well as by isolation of the non-protonated form, **IrW'**, at pH > 6.5 (*vide supra*). Detailed studies of the protonation phenomena are underway. The redox couples associated with reduction of tungsten(vi) centers in **IrW** are not accessible, which is typical for W<sup>VI</sup> centers in POMs possessing two terminal *cis*-oxo ligands.<sup>23</sup>

In summary, the identified synthetic path leading to new Ir<sup>IV</sup>-based polyoxotungstate with Anderson–Evans structure, [Ir<sup>IV</sup>W<sub>6</sub>O<sub>24</sub>]<sup>7-</sup>, comprises the use of *in situ*-formed Ir<sup>IV</sup> oxohydroxo complexes and tungstate ions gradually released in solution. The **IrW** polyanion is the first example of a structurally characterized Ir<sup>IV</sup>-containing POM as well as the first Ir-based POM with Anderson–Evans structure. The Ir<sup>IV</sup> oxidation state in **IrW** has been directly confirmed by EPR spectroscopy and the cyclic voltammetry measurements showed the possibility of reversible oxidation and reduction of the Ir<sup>IV</sup> ions in **IrW** resulting in Ir<sup>V</sup> and Ir<sup>III</sup> species. Our results suggest existence of a rich Ir<sup>IV</sup>-POM and possibly even Ir<sup>V</sup>-POM chemistry that we are planning to elucidate.

PK appreciates EU financial support (ERC Starting Grant MOLSPINTRON, no. 308051). The work has been supported by RFBR grant No. 13-03-00012 (to MNS). Support by President fellowship to SAA is gratefully acknowledged.

## Notes and references

- (a) P. Putaj and F. Lefebvre, *Coord. Chem. Rev.*, 2011, **255**, 1642; (b) N. V. Izarova, M. T. Pope and U. Kortz, *Angew. Chem., Int. Ed.*, 2012, **51**, 9492.
- See for example: (a) M. N. Sokolov, S. A. Adonin, P. A. Abramov, D. A. Mainichev, N. F. Zakharchuk and V. P. Fedin, *Chem. Commun.*, 2012, **48**, 6666; (b) H. J. Lv, Y. V. Geletii, C. C. Zhao, J. W. Vickers, G. B. Zhu, Z. Luo, J. Song, T. Q. Lian, D. G. Musaev and C. L. Hill, *Chem. Soc. Rev.*, 2012, **41**, 7572; (c) A. Sartorel, M. Bonchio, S. Campagna and F. Scandola, *Chem. Soc. Rev.*, 2013, **42**, 2262 and references therein.
- R. Cao, H. Ma, Y. V. Geletii, K. I. Hardcastle and C. L. Hill, *Inorg. Chem.*, 2009, **48**, 5596.
- See for example: (a) C. N. Kato, A. Shinohara, N. Moriya and K. No-miya, *Catal. Commun.*, 2006, **7**, 413; (b) L. D. Dingwall, C. M. Corcoran, A. F. Lee, L. Olivi, L. M. Lynam and K. Wilson, *Chem. Commun.*, 2008, 53; (c) R. Neumann and D. Barats, *Adv. Synth. Catal.*, 2010, **352**, 293; (d) M. N. Sokolov, S. A. Adonin, E. V. Peresypkina, P. A. Abramov, A. I. Smolentsev, D. I. Potemkin, P. V. Snytnikov and V. P. Fedin, *Inorg. Chim. Acta*, 2013, **394**, 656 and references therein.
- (a) See ref. 1a the references therein and; (b) N. Mizuno, D. K. Lyon and R. G. Finke, *J. Catal.*, 1991, **128**, 84; (c) N. Mizuno, H. Weiner and R. G. Finke, *J. Mol. Catal. A: Chem.*, 1996, **114**, 15; (d) H. Weiner, A. Trovarelli and R. G. Finke, *J. Mol. Catal. A: Chem.*, 2003, **191**, 253; (e) G. Modugno, A. Monney, M. Bonchio, M. Albrecht and M. Carraro, *Eur. J. Inorg. Chem.*, 2014, 2356.
- (a) B. Matt, J. Moussa, L. M. Chamoreau, C. Afonso, A. Proust, H. Amouri and G. Izzet, *Organometallics*, 2012, **31**, 35; (b) B. Matt, X. Xiang, A. L. Kaledin, N. N. Han, J. Moussa, H. Amouri, S. Alves, C. L. Hill, T. Q. Lian, D. G. Musaev, G. Izzet and A. Proust, *Chem. Sci.*, 2013, **4**, 1737; (c) B. Matt, J. Fize, J. Moussa, H. Amouri, A. Pereira, V. Artero, G. Izzet and A. Proust, *Energy Environ. Sci.*, 2013, **6**, 1504.
- (a) M. N. Sokolov, S. A. Adonin, D. A. Mainichev, C. Vicent, N. F. Zakharchuk, A. M. Danilenko and V. P. Fedin, *Chem. Commun.*,



2011, **47**, 7833; (b) M. N. Sokolov, S. A. Adonin, P. L. Sinkevich, C. Vicent, D. A. Mainichev and V. P. Fedin, *Dalton Trans.*, 2012, **41**, 9889; (c) M. N. Sokolov, S. A. Adonin, P. L. Sinkevich, C. Vicent, D. A. Mainichev and V. P. Fedin, *Z. Anorg. Allg. Chem.*, 2014, **640**, 122.

8 (a) G. A. Barbieri, *Atti Accad. Lincei*, 1914, **23**, 334; (b) Y. Ozawa, Y. Hayashi and K. Isobe, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1991, **47**, 637; (c) G. Z. Kaziev, S. H. Quinones, V. K. Bel'skii, V. E. Zavodnik and I. V. Osminkina, *Russ. J. Inorg. Chem.*, 2002, **47**, 14.

9 For  $\text{PtMo}_6$  see for example: (a) U. Lee and Y. Sasaki, *Chem. Lett.*, 1984, 1297; (b) U. Lee, *Bull. Korean Chem. Soc.*, 1988, **9**, 256; (c) K.-M. Park and U. Lee, *Chem. Lett.*, 1989, 1943; (d) U. Lee and Y. Sasaki, *Bull. Korean Chem. Soc.*, 1994, **15**, 37; (e) H.-C. Joo, K.-M. Park and U. Lee, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1994, **50**, 1659; (f) U. Lee, H.-C. Joo and K.-M. Park, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2010, **66**, i25.

10 For  $\text{PtW}_6$  see: (a) U. Lee, A. Kobayashi and Y. Sasaki, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1983, **39**, 817; (b) U. Lee, H. Ichida, A. Kobayashi and Y. Sasaki, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1984, **40**, 5; (c) U. Lee and Y. Sasaki, *Taehan Hwahakhoe Chi*, 1987, **31**, 118; (d) R. E. Marsh and I. Bernal, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1995, **51**, 300; (e) U. Lee, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2002, **58**, 130; (f) U. Lee, S.-J. Jang, H.-C. Joo and K.-M. Park, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2003, **59**, i116; (g) U. Lee and H.-C. Joo, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2004, **60**, i33; (h) U. Lee, H.-C. Joo and K.-M. Park, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2004, **60**, i55; (i) U. Lee and H.-C. Joo, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2004, **60**, i86.

11 S. Angus-Dunne, R. C. Burns, D. C. Craig and G. A. Lawrence, *Z. Anorg. Allg. Chem.*, 2010, **636**, 727.

12 (a) J. M. P. Cabral, *J. Inorg. Nucl. Chem.*, 1964, **26**, 1657; (b) J. C. Chahg and C. S. Garner, *Inorg. Chem.*, 1965, **4**, 209; (c) A. A. El-Awady, E. J. Bounsell and C. S. Garner, *Inorg. Chem.*, 1967, **6**, 79; (d) D. A. Fine, *Inorg. Chem.*, 1969, **8**, 1014; (e) S. E. Castillo-Blum, D. T. Richens and A. G. Sykes, *Inorg. Chem.*, 1989, **28**, 954; (f) D. A. Pankratov, P. N. Komozin and Y. M. Kiselev, *Russ. J. Inorg. Chem.*, 2011, **56**, 1794.

13 X. Fang, P. Kögerler, Y. Furukawa, M. Speldrich and M. Luban, *Angew. Chem., Int. Ed.*, 2011, **50**, 5212.

14 A. Ogawa, H. Yamato, U. Lee, H. Ichida, A. Kobayashi and Y. Sasaki, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1988, **44**, 1879.

15 I. Lindqvist, *Acta Crystallogr.*, 1950, **3**, 159.

16 M. Sugahara, A. Yoshisa, A. Yoneda, T. Hashimoto, S. Sakai, M. Okube, A. Nakatsuka and O. Ohtaka, *Am. Mineral.*, 2008, **93**, 1148.

17  $\text{SbW}_6$ : (a) U. Lee and Y. Sasaki, *Bull. Korean Chem. Soc.*, 1987, **8**, 1; (b) H. Naruke and T. Yamase, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1992, **48**, 597; (c) H. Naruke, N. Kajitani and T. Konya, *J. Solid State Chem.*, 2011, **184**, 770;  $\text{MnW}_6$ : (d) V. S. Sergienko, V. N. Molchanov, M. A. Porai Koshits and E. A. Torchennkova, *Koord. Khim.*, 1979, **5**, 936; (e) A. L. Nolan, R. C. Burns, G. A. Lawrence and D. C. Craig, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2000, **56**, 729; (f) A. V. Oreshkina, G. Z. Kaziev, S. H. Quinones, A. I. Stash and P. A. Shipilova, *Russ. J. Coord. Chem.*, 2011, **37**, 845;  $\text{TeW}_6$ : (g) K. J. Schmidt, G. J. D. Schrobilgen and J. F. Sawyer, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1986, **42**, 1115.

18 A. Raizman and J. T. Suss, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1980, **22**, 1141.

19 P. George, I. H. Hanania and D. H. Irvine, *J. Chem. Soc.*, 1957, 3048.

20 A. M. Bond, *Broadening Electrochemical Horizons*, Oxford University Press, 2003.

21 A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, John Wiley & Sons, New York, 1980.

22 See for example: (a) C. Rong and F. C. Anson, *Inorg. Chem.*, 1994, **33**, 1064; (b) G. Bernardini, A. G. Wedd, C. Zhao and A. M. Bond, *Dalton Trans.*, 2012, **41**, 9944.

23 (a) D. H. Brown and J. A. Mair, *J. Chem. Soc.*, 1958, 2597; (b) P. Souchay and R. Contant, *Bull. Soc. Chim. Fr.*, 1973, 3287; (c) S. C. Termes and M. T. Pope, *Transition Met. Chem.*, 1978, **3**, 103.

