An IrIV-containing polyoxometalate†

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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. Members of this class demonstrate a range of promising properties, in particular, catalytic activity in water splitting2,3 and oxidation of various organic substrates. 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 Ir4- and Ir6-organometallic complexes [e.g. {Ir[1,5-COD]}2, [Ir(Cp*)(μ2-Cl)] etc.], some of which, e.g. [(1,5-COD)Ir(NbP2W24O72)4]5−, are pre-catalysts for cycloalkene oxygenation with O2.5 Recently a number of a Keggin and Wells–Dawson type POMs with covalently grafted heteroleptic cyclooctatetraenate complexes exhibit effective charge separation between the IrIII-based chromophore and the POM unit were reported.6 The first reliably characterized iridium-containing POM incorporating no organometallic fragments, [{IrIII(O2CMe)2(C6H4)}2+][PF6]−, was reported as late as in 2009 by Hill’s group and identified as a water oxidation catalyst.3 Two years later, the synthesis, characterization and reactivity of Keggin-type complexes [PW11O39IrIII(L)]n− (n = 4 or 5; L = H2O, OH, CH3, Cl, SCN) were reported.7 Yet, POMs incorporating IrIV 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 RhIII,8 PtIV,9,10 and even PdIV derivatives.11

We report the preparation of [H2IrIVW6O24]7− (IrW), the first polyoxometalate incorporating IrIV, and its characterization by single-crystal X-ray analysis, mass spectrometry, IR, UV-Vis and EPR spectroscopy, as well as cyclic voltammetry.

IrW assemblies in condensation reactions of in situ-formed IrIV hydroxo complexes with tungstate ions in aqueous acetate media. In a first step, IrCl3·3H2O was dissolved in a CH3COONa 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 Cl− ligands in the inner coordination sphere of the IrIII ions by OH− groups and the subsequent oxidation of thus formed hydroxo–oxy complexes of IrIII in air.12 During the reaction, the color change of the IrIV-containing solutions from blue to purple is apparently caused by (not well-defined) oligomerization processes. Another hypothesis postulates transformation of the blue superoxo dimeric [{OH2IrIV(μ2-O2−)]IrIV(OH)5}3− species into the purple [{OH2IrIV(μ2-O2−)]IrIV(OH)5}3− complex, based on UV-Vis and EPR studies of 3 M KOH solutions of IrCl6]3−.13 Next, the solution of the in situ-formed IrIV hydroxo complexes was added dropwise to a solution containing the lacunary [B-α-PW10O40]8− polyanion under careful control of pH kept strictly between 6 and 7 by addition of diluted nitric acid.

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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. Members of this class demonstrate a range of promising properties, in particular, catalytic activity in water splitting and oxidation of various organic substrates. 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 Ir4- and Ir6-organometallic complexes [e.g. {Ir[1,5-COD]}2, [Ir(Cp*)(μ2-Cl)] etc.], some of which, e.g. [(1,5-COD)Ir(NbP2W24O72)4]5−, are pre-catalysts for cycloalkene oxygenation with O2. Recently a number of a Keggin and Wells–Dawson type POMs with covalently grafted heteroleptic cyclooctatetraenate complexes exhibit effective charge separation between the IrIII-based chromophore and the POM unit were reported. The first reliably characterized iridium-containing POM incorporating no organometallic fragments, [{IrIII(O2CMe)2(C6H4)}2+][PF6]−, was reported as late as in 2009 by Hill’s group and identified as a water oxidation catalyst. Two years later, the synthesis, characterization and reactivity of Keggin-type complexes [PW11O39IrIII(L)]n− (n = 4 or 5; L = H2O, OH, CH3, Cl, SCN) were reported. Yet, POMs incorporating IrIV 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 RhIII, PtIV, and even PdIV derivatives.

We report the preparation of [H2IrIVW6O24]7− (IrW), the first polyoxometalate incorporating IrIV, and its characterization by single-crystal X-ray analysis, mass spectrometry, IR, UV-Vis and EPR spectroscopy, as well as cyclic voltammetry.

IrW assemblies in condensation reactions of in situ-formed IrIV hydroxo complexes with tungstate ions in aqueous acetate media. In a first step, IrCl3·3H2O was dissolved in a CH3COONa 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 Cl− ligands in the inner coordination sphere of the IrIII ions by OH− groups and the subsequent oxidation of thus formed hydroxo–oxy complexes of IrIII in air. During the reaction, the color change of the IrIV-containing solutions from blue to purple is apparently caused by (not well-defined) oligomerization processes. Another hypothesis postulates transformation of the blue superoxo dimeric [{OH2IrIV(μ2-O2−)]IrIV(OH)5}3− species into the purple [{OH2IrIV(μ2-O2−)]IrIV(OH)5}3− complex, based on UV-Vis and EPR studies of 3 M KOH solutions of IrCl6]3−. Next, the solution of the in situ-formed IrIV hydroxo complexes was added dropwise to a solution containing the lacunary [B-α-PW10O40]8− polyanion under careful control of pH kept strictly between 6 and 7 by addition of diluted nitric acid.
has idealized

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\]

define a single plane and form a virtually regular Ir-centered W\(_6\) octahedron surrounded by six distorted edge-sharing \(\text{IrIVO}_6\) octahedra. At neutral pH, however, this reaction is not very well reproducible.

6.1–6.5. At higher final pH (7.0–7.5) crystals of the reaction mixture before crystallization is set within the range of structural data for \(\text{Na}_6\text{IrW}_6\text{O}_{24}\) \(\text{Na}^-\text{IrW}^+\text{Na}^-\text{IrW}^+\) (Na–IrW\(^+\)) can be isolated as the hydrated sodium salts Na\(_6\)[H\(_3\)Ir\(_3\)W\(_6\)O\(_{24}\)]26H\(_2\)O (Na–IrW) and Na\(_3\)[Ir\(_2\)W\(_6\)O\(_{24}\)]26H\(_2\)O (Na\(_3\)–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\(_6–IrW\) form as a byproduct to Na–IrW. No crystals could be isolated at pH > 7.6 where one could expect formation of pure Na\(_6–IrW\)\(^+\). We herein focus on the monoprotonated species and provide structural data for Na\(_6–IrW\)\(^+\) in the ESI†.

Our attempts to rationalize the synthetic procedure by reacting Ir\(^{IV}\) solutions directly with Na\(_2\)WO\(_4\) at various ratios were not successful and resulted in formation of the paratungstate salt Na\(_8\)[H\(_2\)Ir\(_3\)W\(_6\)O\(_{24}\)]25H\(_2\)O as the main product, as established via single-crystal X-ray measurements and IR spectroscopy. We conjecture that an initial excess of Ir\(^{IV}\) ions coupled with the gradual release of WO\(_4^{2–}\) species into the reaction medium are key to successful preparation of IrW. Alternatively, IrW can be prepared by prolonged heating of K\(_2\)[Ir\(_6\)] with Na\(_2\)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 (< 10%).

The compound Na\(_6\)[H\(_3\)Ir\(_3\)W\(_6\)O\(_{24}\)]26H\(_2\)O (Na–IrW) crystallizes in the triclinic space group \(\text{P}1\). The IrW polyanions display an Anderson–Evans-type ring structure comprising a central Ir\(^{IV}\) octahedron surrounded by six distorted edge-sharing W\(_6\)O\(_{24}\) octahedra (Fig. 1). All metal centers in the IrW\(_6\) core define a single plane and form a virtually regular Ir-centered W\(_6\) hexagon (W – W: 3.223–3.345 Å; Ir – 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 \([\text{MWO}_6\text{Ir}_3]^{3–}\) heteropolyoxotungstates. In contrast, some of the polyoxomolybdates \([\text{M}^\text{III}\text{Mo}_6\text{O}_{24}]^{3–}\) may also adopt a bent conformation with \(C_2\) symmetry (usually referred as a B-type Anderson–Evans structure), which was e.g. found in \([\text{H}_4\text{PtMo}_6\text{O}_{24}]^{3–}\), \([\text{H}_2\text{SbMo}_6\text{O}_{24}]^{3–}\) (ref. 14) and heptamolybdate \([\text{Mo}_6\text{O}_{24}]^{6–}\) ions.\(^{15}\)

There are three types of oxygen atoms in IrW: \(\mu_2\)-O linking Ir\(^{IV}\) and two W\(^{VI}\) centers (Ir–O: 1.994(5)–2.022(5) Å; W–O: 2.142(5)–2.293(5) Å), \(\mu_3\)-O bridging two W\(^{VI}\) ions (W–O: 1.923(5)–1.987(5) Å) and terminal O atoms (W–O: 1.735(5)–1.747(5) Å). The average Ir–O bond length in IrW of 2.004 Å is comparable with that of 2.013 Å observed in the only structurally characterized Ir\(^{III}\)-containing all-inorganic polyoxotungstate \([\text{Ir}^{\text{III}}\text{Cl}_4]\text{P}_2\text{W}_{20}\text{O}_{72}]^{15–}\),\(^{3,5}\) and with that in Ir\(^{IV}\) oxides, e.g. CaIrO\(_4\) (2.057 Å).\(^{16}\) The W–O distances in IrW are similar to the W–O bond lengths in other \([\text{XW}_6\text{O}_{24}]^{3–}\) species (X = Pt\(^{IV}\), Te\(^{IV}\), Mn\(^{IV}\), n = 8; X = Sb\(^{V}\), n = 7).\(^{10,17}\) Bond valence sum calculations (Table S2, ESI†) suggest a disorder of a proton over two inversion center related \(\mu_3\)-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 Na\(^+\) co-precipitations 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 H\(_2\)O\(^–\) cation. In the crystal lattice of Na–IrW the Na\(^+\) counterions and the crystal water molecules assemble in the parallel infinite zig-zag \([\text{Na}_6(\mu_2-H_2O)_{10}(H_2O)_{16})_{6n}\) chains. The IrW polyanions are packed between the chains (see ESI† for details) and form an extended net of hydrogen bonds with the H atoms of the H\(_2\)O molecules (Fig. S1 and Table S4, ESI†).

The oxidation state of the iridium center (Ir\(^{IV}\), \(5d^5\), \(S = 1/2\)) 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 \(^{191}\)Ir [natural abundance 37%] and \(^{195}\)Ir [63%]), similar to what has been observed for iridium\(^{IV}\) impurities displaying a tetragonally distorted octahedral environment in MgO and CaO matrices.\(^{18}\) 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.
The ESI mass spectrum obtained by ionization of Na–IrW solution in H₂O/MeOH is very complex and exhibits signals which could be assigned for the doubly negatively charged ion pairs [Na₄H₂Ir(V)W₆O₂₄]²⁻ and [Na₃H₃Ir(V)W₆O₂₄]³⁻ as well as sets of signals corresponding to various decomposition products, e.g. [HWO₄]⁻, [HW₂O₇]⁻, Na₄H₂[Ir(V)W₅O₂₀]²⁻ 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 their acid–base behavior with different pH has been further checked by UV–vis spectroscopy (see ESI† for details). Electrochemistry studies of IrW in aqueous CH₃COONa solution at pH 6.1 (see ESI†) produce typical voltammograms (Fig. 3) that show two quasi-reversible redox couples with the corresponding peak potentials E₁/₂ located at 0.245 V (ΔE = 0.190 V at 100 mV s⁻¹) and 0.700 V (ΔE = 0.200 V) vs. Ag/AgCl reference electrode (0.441 V and 0.896 V vs. SHE, respectively). These waves are attributed to the Ir⁴⁺/Ir⁵⁺ and Ir⁵⁺/Ir⁴⁺ redox transformations within the polyanion [Ir(V)W₆O₂₄]⁻. The observed Ir⁴⁺/Ir⁵⁺ potential value is similar to 0.18 V found for the Ir⁴⁺/Ir⁵⁺ transition in [PW₄O₁₁]³⁻ and the Ir⁵⁺/Ir⁴⁺ couple is close to the potential of irreversible oxidation of the Ir centers in the same POM 0.75 V (vs. Ag/AgCl). The significant shift to lower potentials as compared with the Ir⁴⁺/Ir⁵⁺ couple observed in the hexachloroiridates (0.669 V vs. Ag/AgCl) 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 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⁻¹. The diffusion coefficient D = 2.62 × 10⁻⁶ cm² s⁻¹ calculated for [Ir(V)W₆O₂₄]⁷⁻ according to Randles–Sevcik equation compares well to the values reported for other polyoxotungstates.22 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, IrW⁷⁻, 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 W⁶⁺ centers in POMs possessing two terminal cis-oxo ligands.23

In summary, the identified synthetic path leading to new Ir⁵⁺-based polyoxotungstate with Anderson–Evans structure, [Ir(V)W₆O₂₄]⁷⁻, comprises the use of in situ-formed Ir⁵⁺ oxo-hydroxo complexes and tungstate ions gradually released in solution. The IrW polyanion is the first example of a structurally characterized Ir⁵⁺-containing POM as well as the first Ir-based POM with Anderson–Evans structure. The Ir⁵⁺ 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 Ir⁵⁺ ions in IrW resulting in Ir⁵⁺ and Ir⁴⁺ species. Our results suggest existence of a rich Ir⁵⁺-POM and possibly even Ir⁴⁺-POM chemistry that we are planning to elucidate.

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Notes and references


