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Hydrogeniridate(VI) Anion and the Geometries of Tetrahedral Oxo-anions

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Supporting Information

ABSTRACT: The compound $KHIrO_4$, potassium hydrogentetraoxidoiridate(VI)(1−), crystallizes in a Scheelite-type structure containing discrete, slightly flattened, $[Ir(O_3OH)]^-$ tetrahedra—the first observation of a group 9 element in the 6+ oxidation state as an oxoanion.

The ability of the late second and third row transition metals to form high oxidation state compounds, particularly in combination with electron donating species such as F^-, O^{2-}, and N^{3-} is well-known. Examples of such compounds include the simple binary compounds $Os(VIII)O_4$[1] and $Ir(VI)F_6$;[2] complex oxides and oxido-, fluorido-, and nitrido- complex anions such as $Sr_2MgIr(VI)O_6$,[3] $K_2Os(OH)_4O_2$,[4] $KOsO_3N$,[5] and $Na_2Os(VI)O_4$;[6] and acid forms such as perrhenic acid hydrate, $HReO_4{\cdot}H_2O$.[7] The bonding in these high oxidation states often shows a significant degree of covalency with the formation of molecular anions, such as $[OsO_3N]^-$, $[Os(OH)_4O_2]^{2-}$, and $[ReO_4]^-$; these species are also often isomorphic with main group molecular anions such as $[I(OH)_4O_2]^-$, $[IO_4]^-$, and $[BrO_4]^-$.[8,9] While the discrete molecular anion chemistries of osmium and rhenium are reasonably well developed, that of iridium, particularly in its highest oxidation states, is sparse, even for Ir(IV) and Ir(V), and unknown for Ir(VI), except in fluorides.[2] Recent work by Walton and co-workers[10] has described a number of such hydroxy compounds of Ir(IV), such as $Sr_2Ir(OH)_8$ and $BaIr(OH)_6{\cdot}H_2O$, produced under oxidizing hydrothermal conditions (basic, nitrate-containing solutions); $BaIr(OH)_6{\cdot}H_2O$ is isostructural with $BaPt(OH)_6{\cdot}H_2O$ and contains discrete $[Ir(OH)_6]^{2-}$ octahedra.[10] The Ir(VI) oxidation state, in common with Re(VI) and Os(VI), has been stabilized in complex oxides with extended structures, especially of the double perovskite type, A_2MIrO_6.[3] Recently compounds of the stoichiometry "$Ln_2K_2Ir(VI)O_7$" (Ln = Nd, Sm) have been reported; however, bond valence calculations point to these being $Ln_2K_2Ir(V)O_6OH$, *vide infra*.[11] Similar compounds from the $(Ln,Sr)_{4-z}IrO_{7+\delta}$ series have also been reported, though XANES studies have confirmed that these materials contain Ir(V) and peroxide anions.[12] The coordination and crystal chemistry of iridium in IrX_n units, for Ir(III) to Ir(VI) and in various oxoiridates, have also been discussed.[13,14]

In order to obtain the highest oxidation states of iridium, as with Os, strongly oxidizing conditions are required, such as those developed under high pressures of oxygen or in the presence of strongly oxidizing species such as ClO_3^-. During recent attempts to generate Ir(V)/Ir(VI) complex oxides, equivalent to the superconducting MOs_2O_6 phases,[15,16] we have isolated a new potassium hydrogeniridate(VI) phase as single crystals and present here the structure of this unique iridium(VI) molecular anion compound. $KHIrO_4$ was obtained by the reaction of IrO_2, KO_2, and a small level of water heated inside a 1 cm diameter silica tube in which a gold tube containing Ag_2O had been placed (see Supporting Information). Several smallish single crystals, black tetragonal cuboids (Figure S1), were found in the reaction product. Single crystal X-ray diffraction data from two such crystals were collected and analyzed; full details of the structure solution are presented in the Experimental Section. $KHIrO_4$ crystallizes in the tetragonal space group $I4_1/a$; final refined coordinates are given in Table 1 and derived bond distances and angles of interest in Table 2. The structure consists of discrete, slightly flattened, $[Ir(O_3OH)]^-$ (hydrogeniridate or formally hydrogentetraoxidoiridate(VI)(1−)) tetrahedral anions separated by potassium ions; hydrogen positions are disordered among four oxygen atoms, and a weak hydrogen bond exists between neighboring hydrogeniridate(VI) anions, Figure 1. The Ir(VI)−O distance is 1.751(7) Å, and the slight flattening of the $[Ir(O_3OH)]^-$ tetrahedron, is similar to that observed for $[WO_4]^{2-}$ in $CaWO_4$, Table 2.

The derived bond lengths in combination with bond valence sums (BVS),[17−19] Table 2, demonstrate the oxidation state of the iridium as +6. No Ir(VI)−O BVS parameter is given in the literature, though the use of Ir(V) values (r_0 = 1.916, b = 0.37)[18] and those modified for bond softness (r_0 =1.898, b = 0.479[19]) produces BVSs considerably in excess of 5, at 6.25 and 5.45, respectively. Using estimated r_0 values for the Ir(VI)−O BVS parameter (taking those of W(VI) and Os(VI))[19]) gives BVSs of 6.05 and 6.18, respectively, confirming the Ir(VI) oxidation state in $KHIrO_4$. This assignment of the oxidation state of iridium as Ir(VI) is consistent with XANES data collected from a crystal of $KHIrO_4$ (Supporting Information), which showed a broad L_3 absorption edge centered at 11220.2(3)eV; however, such data cannot distingush oxidation states in high oxidation state compounds with signficant covalency, as reported previously, for example in the studies of manganates,[20] ferrates,[21] and iodates.[22] The oxygen BVS, obtained by summing contributions from Ir (1.37 v.u.), 1/4 × H (0.24 v.u.), and 2 × K (0.29 v.u.) is 1.90, supporting the final structural model and the presence of some OH groups;[19]

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Table 1. Refined Crystallographic Model for $KHIrO_4$[a]

atom	site/occ[b]	*x*	*y*	*z*	U_{eq}/Å^2
O	16*f*/1	0.7306(12)	0.6231(12)	0.0521(5)	0.0166(13)
H	16*f*/$^1/_4$	0.68(6)	0.50(4)	0.00(2)	0.03[c]
Ir	4*b*/1	0.5	0.75	0.125	0.0126(3)
K	4*a*/1	0.0	0.75	0.875	0.0108(8)

[a] Space group $I4_1/a$, $a = b = 5.6684(4)$, $c = 12.5666(14)$ Å. [b] Wyckoff site label and occupancy. [c] Fixed.

Table 2. Derived Bond Distances (Å) and Angles of Interest[a]

distance/angle	bond length (Å)/angle (deg)	bond valence sum
Ir−O	1.751(7) × 4	6.25/5.45[b]
K − O	2.765(7) × 4, 2.793(6) × 4	1.38/1.17
O···O	3.122(10)−3.240(10)	2.15/1.90
O−Ir−O	105.9(2) × 4, 116.9(4) × 2	

[a] Esds are given in parentheses. [b] Using published Ir(V) values from refs 18 and 19, respectively; see SI.

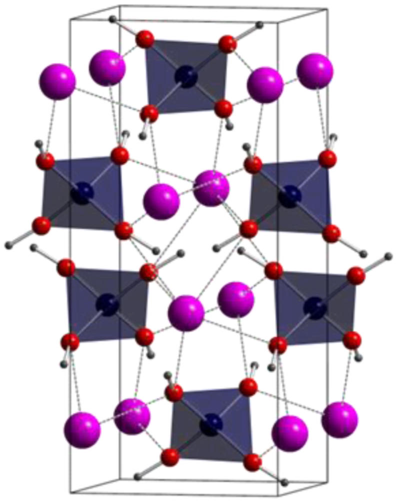

Figure 1. Structure of $KHIrO_4$. IrO_4 tetrahedra are shaded dark blue, oxygen, red spheres, potassium, magenta; and hydrogen, $^1/_4$ occupied sites, gray.

oxygen would be significantly underbonded without a contribition from hydrogen.

$KHIrO_4$ is isostructural with scheelite, $CaWO_4$ ($a = 5.62$, $c = 11.40$ Å) and other materials adopting this structure type such as $PbWO_4$, NH_4ReO_4 ($a = 5.892$, $c = 12.970$ Å), and $HReO_4\cdot H_2O$ ($a = 5.832$ $c = 12.938$ Å); of these only $HReO_4\cdot H_2O$ might contain a hydrogentetraoxidometallate anion. Other compounds containing hydrogentetraoxido anions, such as $CsHXO_4$, X = S and Se, adopt, at high temperatures, a closely related structure with disordering of the hydrogen position. These salts crystallize in $I4_1/amd$ with the $[HXO_4]^-$ anions rotated and aligned along the cell *a* and *b* lattice directions and show high proton conductivity above 450 K.[23] At low temperatures ordering of the $[HXO_4]^-$, X = S and Se, anions occurs with the formation of strong hydrogen bonds (O-(donor)−O(acceptor) = 2.55 Å) and a 4 orders of magnitude drop in proton conductivity.

Bond Lengths in Tetrahedral Oxoanions. The bond lengths of transition metal tetrahedral oxo-anions and neutral species were last reported and discussed in detail by Krebs and Hasse in 1976.[24] Since then further species in this family have been discovered and their structures reported. Also while this previous work limited discussion to transition metal compounds in oxidation numbers of five and above, it is possible to expand this analysis to main group species and also oxo-anions centered on an atom with an oxidation state of 4+. The Inorganic Chemical Structure Database[25] provides the data for this analysis as summarized in the Supporting Information, Table S1. Figure 2 plots the average or typical bond length in the $[XO_4]^{n-}$ species as a function of oxidation number; data are divided into five sets depending on the period or row of X. In general the expected variation, a decrease in bond length with increasing oxidation number, is observed. The variation may be fitted with a simple exponential, as in a bond valence sum analysis[17−19] or polynomial functions; over the data range considered a simple quadratic is sufficient, as used in Figure 2. The values for the 3d transition metals and their variation reflect that of the equivalent main group row elements, period 3. However, the values for the second and third row transition metals lie somewhat lower than might be expected in comparison with those in period 5 of the main group.

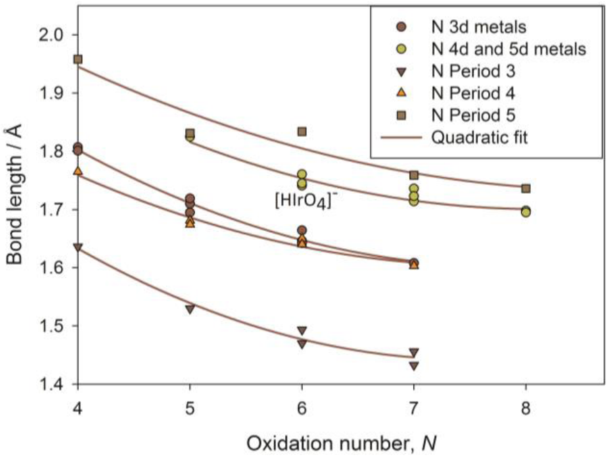

Figure 2. Variation of the X−O bond length in tetrahedral $[XO_4]^{n-}$ anions and XO_4 as a function of the X oxidation number, *N*. Data are divided into different main group periods and transition metal rows series depending on X; lines show least-squares quadratic fits to each series.

$KHIrO_4$ represents the first example of a molecular anion containing M(VI) from group 9. While some double perovskites, such as Sr_2MgIrO_6, contain Ir(VI), it seems unlikely, based on bond valence arguments, that the recently reported compounds "$Ln_2K_2IrO_7$" (Ln = Nd, Sm) contain Ir(VI).[11] Using the reported Ir−O distances the BVS calculations for iridium yield values near 5, and the O2 site produces a value near unity instead of the expected 2− (see Supporting Information). Therefore, it seems possible that these materials contain either a hitherto unidentified proton in an OH group at O2, especially as the synthesis was undertaken in a hydroxide melt,[11] or possibly a level of peroxide ion. This latter possibility is supported by the XANES work of Götzfried et al. and Ebbinghaus,[12] which contradicts that of Mugavero et al.[11] Furthermore, Choy et al.[26] report the Ir(V) and Ir(VI) L_3 absorption edges near 11214.2 and 11218.5 eV, respectively, in numerous complex iridium perovskites, significantly lower than the values of 11220.5 and 11221 eV extracted for Sr_2MgIrO_6 using the peak maximum.[11]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental methods. Synthesis, structure determination and XANES method and data. X-ray crystallographic data in CIF format (CSD 426539). Figure S1, photograph of a $KHIrO_4$ single crystal. Details of output from BVS calculations for $KHIrO_4$ and "$Ln_2K_2IrO_7$" (Ln=Nd, Sm). Table S1, M-O distances (Å) for oxotetrahedral anions used in Figure 2 of the main article. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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