Inorganica Chimica Acta, *177* (1990) 107–114

The preparative and structural chemistries of hexahalogeno and trichlorostannato complexes of iridium

Richard K. Coll, Jack E. Fergusson*, Bruce R. Penfold, Douglas A. Rankin and **Ward T. Robinson**
Department of Chemistry, University of Canterbury, Christchurch (New Zealand)

(Received March 6, 1990; revised June 20, 1990)

Abstract

In a study of Ir(III) and Ir(IV) halogeno complexes it was found that oxidation of Ir(III) to Ir(IV) occurs readily, even in the presence of reducing agents such as tin(II) halides and from solutions containing predominantly the trivalent oxidation state. The three cubic (*Fm*3*m*) hexahalogenoiridates(IV) complexes; oxonium hexabromoiridate(IV), $(H_3O)_2[IrBr_6]$, $a = 1027.4(3)$ pm, Ir–Br = 251.5(1) pm; ammonium hexabromoiridate(IV), $(NH_4)_2[IrBr_6]$, $a = 1044.0(2)$ pm, Ir–Br = 254.9(3) pm; and caesium hexachloroiridate(IV), $Cs_2[IrCl_6]$, $a = 1021.19(8)$ pm, Ir–Cl = 233.2(2) pm, were isolated from the solutions, and their single crystal and molecular structures determined. The iridium(III) and rhodium(III) trichlorostannato complexes $A_3[IrCl_5(SnCl_3)]$ for $A = K^+$, NH_4^+, and $Rb_3[RhCl_3(SnCl_3)_3]$ have been prepared. The single crystal X-ray structure has been determined for $K_3[IrCl_5(SnCl_3)]$. The complex and the isomorphous NH_4^+ salt belong to the orthorhombic crystal system $a = 958.73(13)$, $b = 951.70(15)$, $c = 784.80(9)$ pm, with space group $Pmn2_1$. The molecule has *m* symmetry and the Ir–Cl bond length for the chlorine atom bound opposite the $SnCl_3^-$ ligand is longer at 243.8(3) pm compared with the other Ir–Cl bond lengths which lie in the range 233.9(3)–237.6(2) pm. The Ir–Sn bond length of 249.6(1) pm is relatively short compared with other reported values.

Introduction

The facile redox chemistry of Ir(III)/Ir(IV) halogeno species has led to the isolation of Ir(IV) complexes from solutions considered to contain Ir(III) [1]. In the present study both the oxonium and ammonium complexes, $(H_3O)_2[IrBr_6]$ and $(NH_4)_2[IrBr_6]$, were obtained from a HBr solution after passing a solution of $K_3[IrBr_6]$ down an acidified ion-exchange column [1]. Crystals of the salts were obtained after the addition of NH_4Br and $SnBr_2$ in an attempt to prepare Ir(III)/Sn(II) complexes according to procedures described in the literature [2]. The features of the preparative reactions have been investigated and the crystal and molecular structure of the oxonium complex determined. The structure solution of the ammonium salt was determined but it did not refine well. The caesium hexachloro salt $Cs_2[IrCl_6]$ was also obtained, as outlined previously [1] from aerial oxidation of an Ir(III) solution, and its structure determined.

The preparations of trichlorostannato complexes of rhodium and iridium were also achieved and it appears that the $SnCl_3^-$ ligand exerts a *trans* effect. The complexes $A_3[IrCl_5(SnCl_3)]$ for $A = K^+$, NH_4^+, and $Rb_3[RhCl_3(SnCl_3)_3]$ have been prepared and the crystal structure determined for $K_3[IrCl_5(SnCl_3)]$. Unit cell data and precession photography indicate that the ammonium salt is isomorphous with the potassium salt.

Experimental

Preparations

Oxonium and ammonium hexabromoiridates(IV)

Potassium hexabromoiridate(III) (0.2 g) dissolved in distilled water (50 ml) was passed slowly down an acidified cation exchange column (Dowex 50W-X8). The stoichiometric amount of ammonium bromide (0.075 g) dissolved in 2 M hydrobromic acid (5 ml) was added to the effluent. The volume of the solution was then reduced to near dryness by heating, and the residue taken up in hot reagent grade concentrated hydrobromic acid (20 ml). To this solution was added $SnBr_2$ (0.14 g) dissolved in 2 M hydrobromic acid (5 ml). The solution which was pale green in colour was left in air in a desiccator

---

*Author to whom correspondence should be addressed.

over potassium hydroxide pellets. After several weeks small dark octahedral shaped crystals appeared (0.03 g) and were collected and washed with acetone and diethylether and air dried. Under the microscope the crystals appeared homogeneous, however, the infrared spectrum suggested a mixture of oxonium and ammonium salts. Separate crystals of oxonium hexabromoiridate(IV), $(H_3O)_2[IrBr_6]$ and ammonium hexabromoiridate(IV), $(NH_4)_2[IrBr_6]$ were picked from the product, and the structure of the former was determined from single crystal X-ray analyses.

A solution of the oxonium complex in water (0.001 M) had a pH of 2.6, and the ammonium complex had a pH of 2.7, whereas the pH of a solution of $K_2[IrBr_6]$ under the same conditions was 4.9. This supports the existence of the acidic cations H_3O^+ and NH_4^+.

Caesium hexachloroiridate(IV)

The potassium salt $K_2[IrCl_6]$ (0.2 g) dissolved in a minimum of water was added to an acidified ion-exchange resin. To the effluent was added CsCl or $CsCO_3$ dissolved in the minimum amount of water to give a cation:anion ratio of 2:1. A red product precipitated immediately. Small quantities of the compound were also obtained as red crystals produced from atmospheric oxidation of solutions used in the preparation of the caesium hexachloroiridium(III) complex [1].

Potassium and ammonium pentachloro(trichlorostannato)iridate(III)

The complexes were prepared by a method similar to that employed by Antonov *et al.* [2] to obtain salts of the type $A_3[RhCl_n(SnCl_3)_{6-n}]$. The complex $(NH_4)_3[IrCl_6]$ (0.13 g) was dissolved in reagent grade concentrated HCl (10 ml) and $SnCl_2 \cdot 2H_2O$ (0.12 g), dissolved in reagent grade HCl (10 ml), was added. The solution was heated for 10 min on a water bath, potassium oxalate (0.04 g) was added and the solution heated for a further 10 min. The solvent volume was reduced to > 10 ml and the hot solution allowed to cool at atmospheric pressure. Small thin plate shaped dichroic red–green crystals of $(NH_4)_3[IrCl_5(SnCl_3)]$ appeared overnight. The potassium salt $K_3[IrCl_5(SnCl_3)]$ was similarly prepared but no oxalate was used.

Rubidium trichlorotris(trichlorostannato)rhodate(III)

The complex $Rb_3[RhCl_3(SnCl_3)_3]$ was prepared in a manner similar to that used for $K_3[IrCl_5(SnCl_3)]$, but using $RhCl_3 \cdot xH_2O$ as the starting material.

Reaction chemistry

A blue–purple solution of $K_2[IrBr_6]$ (0.001 M) with a typical $[IrX_6]^{2-}$ (d^5) UV–Vis absorption spectrum (d–d bands at 511.3, 543.2 and 583.1 nm, and a broad band with its highest absorption at 674.9 nm [3]) turned pale green in reagent grade 2 M HBr on the addition of 2.5 mol of $SnBr_2$ at room temperature. Within a short period (minutes to 1–2 h) the solution in air had reverted to the blue–purple colour with the same UV–Vis spectrum as the starting material, except for a reduction in intensity of 39%. Addition of more $SnBr_2$ (2.5 mol) produced the pale green solution again, and this also changed back to the blue–purple solution over a similar time span. The green solution had a UV–Vis spectrum similar to that of Ir(III) (d^6) halogeno complexes [3].

The reactions were repeated, this time using HBr purified from free Br_2. The pale green solution obtained on the first addition of the tin dibromide did not in this case revert to the Ir(IV) solution.

In a chloro system the trichlorostannato complexes were isolated using similar reactions. The addition of $SnCl_2 \cdot 2H_2O$ to solutions of $A_3[IrCl_6]$ produced a solution which was lighter in colour, and which had a UV–Vis spectrum different from that of the starting material. The crystalline materials obtained from these reactions had infrared spectra that were also different to the starting material. These spectra were characterized by the appearance of new absorbances in the low frequency region of the spectrum (K^+ 345 cm^{-1}, NH_4^+ 340 cm^{-1}).

Single crystal data collection

Oxonium hexabromoiridate(IV)

A dark octahedral shaped crystal was placed on a Nicolet R3m four circle diffractometer using graphite monochromated Mo Kα radiation and a low temperature (123 K) nitrogen gas stream. Cell parameters and standard deviations were obtained from the least-squares refinement of 25 accurately centred reflections. The data collection was carried out using ω-scans. Three check reflections were monitored regularly and indicated no instability or movement of the crystal. There were 111 unique reflections observed with an intensity greater than 3σ and these were used in the structure solution and refinement.

Caesium hexachloroiridate(IV)

Using Zr filtered Mo Kα radiation on a Hilger and Watts four circle diffractometer, 1560 reflections were collected using the θ–2θ scan technique in the positive octant of reciprocal space ($h, k, l \geq 0$) out to a Bragg angle of 45°. Equivalent reflections were averaged for use in the initial structure solution. A total of 187 reflections with an intensity greater than 3σ were used in the final structure refinement.

Potassium pentachloro(trichlorostannato)iridate(III)

The intensities of 1031 reflections were measured in the positive octant of reciprocal space using the ω-scan technique. Of these, 863 were unique with an intensity greater than 3σ and were used in the least-squares refinement.

Structure solution and refinement

Oxonium hexabromoiridate(IV)

The data were treated for Lorentz and polarization effects. The position of the iridium atom was deduced directly from the Patterson map and a subsequent difference map indicated that there were no tin atoms present but only bromine and oxygen. Atom positions were taken from the $Cs_2[IrCl_6]$ structure and R dropped to 0.08. Weighted least-squares refinement using absorption corrected data (empirical absorption correction; minimum transmission = 0.521, maximum transmission = 0.958) and anisotropic thermal parameters for all atoms led to a final R of 0.0317 and R_w of 0.0237. The goodness of fit was 1.314, and the final difference map showed no anomalous peaks. No attempt was made to locate the hydrogen atoms and it is evident from the symmetry of the oxygen site that they must be disordered. Substitution of N for O in the refinement gave a much poorer fit. The final electron density difference map showed no anomalies and the residual peaks in the difference Fourier are concentrated around the heavy atoms and are most likely to be associated with residual anisotropy.

Caesium hexachloroiridate(IV)

A trial least-squares refinement using coordinates reported for $K_2[PtCl_6]$ [4] give $R = 0.065$. Corrections were made for absorption using an analytical method based on the method of De Meulenaer and Tompa [5], and the chlorine atoms were assigned anisotropic thermal parameters. It was necessary to correct for extinction. Final least-squares refinement gave $R = 0.020$ ($R_w = 0.021$) for 187 reflections.

Ammonium hexabromoiridate(IV)

A study of the ammonium complex confirmed it was isomorphous with the oxonium salt, but the structure did not refine well. However, both the cell constant and Ir–Br bond length were obtained with good standard deviations.

Potassium pentachloro(trichlorostannato)iridate(III)

The systematic absences were consistent with two space groups; *Pmmn* and *Pmn*2_1. Attempts to solve the structure in the space group *Pmmn* were unsuccessful, and the structure was solved in *Pmn*2_1. The data were treated for Lorentz and polarization effects and the position of the iridium atom deduced from the Patterson map. The resulting difference map indicated that there were two atoms attached to the iridium with Ir–L bond lengths of *c.* 2.50 Å. It was thought that these were both tin atoms but the refinement did not proceed satisfactorily. However, replacing one of the tin atoms with chlorine resulted in an R value of 0.1699. The remaining atoms were located from difference maps and the application of an empirical absorption correction (based on an empirical method using a thin plate model; maximum transmission = 0.776, minimum transmission = 0.201), led to an R of 0.0475. Using a weighted least-squares refinement and assigning anisotropic thermal parameters to all atoms led to a final R of 0.251, a weighted R of 0.254, with a goodness of fit of 0.852. The origin of the polar space group *Pmn*2_1 can lie anywhere along the intersection of the mirror plane and the glide plane, and hence was defined by fixing the z coordinate of the iridium atom.

The crystal data and experimental parameters for the data collections are given in Table 1, and the atom positions and thermal parameters for the iridium(IV) complexes in Tables 2 and 3. The atomic coordinates and temperature factors for $K_3[IrCl_5(SnCl_3)]$ are given in Tables 4 and 5. All the programs used for the data reduction and structure solution are included in the SHELXTL (version 4.0) program package [6].

Results and discussion

Preparations

The isolation of the Ir(IV) complexes $(H_3O)_2[IrBr_6]$ and $(NH_4)_2[IrBr_6]$ from the reactions involving Sn(II) was unexpected. It appears that free dibromine in the HBr is the principal oxidizing agent [1], and when the reaction is open to the air production of more dibromine maintains the reaction. A number of reaction conditions were investigated and these, together with reactions reported in the literature, are outlined in Table 6. It is apparent that the formation of Ir(IV) in the acid solutions is easily achieved with the oxidizing agents Br_2, O_2 and Cl_2, even in the presence of reducing agents such as SnX_2 and $C_2O_4^{2-}$. For reactions in HBr, the presence of dioxygen leads to the formation of dibromine from the bromine ion and this is the reason for the continuing oxidation. Air bubbled through HBr, with and without $SnBr_2$ present, produces dibromine as demonstrated from the similarity of the UV–Vis

TABLE 1. Crystal data and experimental parameters for iridium complexes

	$(H_3O)_2[IrBr_6]$	$Cs_2[IrCl_6]$	$K_3[IrCl_5(SnCl_3)]$
Crystal data			
Formula weight	709.671	670.72	711.82
Crystal system	cubic	cubic	orthorhombic
Space group	*Fm3m*	*Fm3m*	$Pmn2_1$
a (pm)	1027.38(28)	1021.19(8)	[a]
Volume ($pm^3 \times 10^6$)	1084.39(89)	1064.93	716.11(17)
F(000)	1213	1156	640
μ (cm^{-1})	341.28	215.1	133.45
Experimental parameters			
Temperature (°C)	−150	22	−110
Radiation	Mo Kα	Mo Kα	Mo Kα
Scan range (°)	2.2	0.5 & 0.6	2.0
Scan speed (°/min)	4.88	4.88	4.88
Crystal dimensions (mm^3)	$0.1 \times 0.14 \times 0.16$	$0.20 \times 0.20 \times 0.20$	$0.40 \times 0.24 \times 0.02$
Crystal volume (mm^3)	0.0015	0.016915	0.002
Calculated density (g cm^{-3})	4.54	4.18	3.30
Measured density (g cm^{-3})	>3.31	>3.31	>3.31
Molecules per unit cell	4	4	2
Molarity (°)	0.3	0.20	0.28
Reflections used in refinement	111	187	863
Ratio observations to variables	19:1	26:1	12.5:1
Range of transmission factors	0.521–0.958	0.1894–0.1160	0.201–0.776

[a] $a = 958.73(13)$, $b = 951.70(15)$, $c = 784.80(9)$ pm. Cell dimensions for NH_4^+ salt: $a = 959.3(3)$, $b = 949.5(2)$, $c = 783.2(2)$ pm.

TABLE 2. Atom positions for $(H_3O)_2[IrBr_6]$ and $Cs_2[IrCl_6]$[a]

Atom	*x*	*y*	*z*	*U*
$(H_3O)_2[IrBr_6]$				
Ir	0	0	0	19.9(2)
Br	2448(1)	0	0	27.6(2)
O(1)	2500	2500	2500	15.3(12)
$Cs_2[IrCl_6]$				
Ir	0	0	0	
Br	25	25	25	
O(1)	2283(1)	0	0	

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor. Atom coordinates $\times 10^4$. Temperature factors $\times 10^3$.

spectrum of the reaction mixture and Br_2 dissolved in pure HBr. In some preparations, the stannous bromide was heated together with the iridium(IV) hexabromo complex under a dinitrogen atmosphere giving the Ir(III) complex in solution. However, when crystallization was carried out in open vessels some oxidation involving dioxygen occurred giving both Ir(III) and Ir(IV) products.

A number of redox reactions are possible all with favourable potentials.

$$2[IrBr_6]^{2-} + Sn^{2+} \longrightarrow 2[IrBr_6]^{3-} + Sn^{4+}$$

$E = +0.87$ V

$$2[IrBr_6]^{3-} + Br_2 \longrightarrow 2[IrBr_6]^{2-} + 2Br^-$$

$E = +0.05$ V

$$4[IrBr_6]^{3-} + O_2 + 4H^+ \longrightarrow 4[IrBr_6]^{2-} + 2H_2O$$

$E = +0.24$ V

$$Sn^{2+} + Br_2 \longrightarrow Sn^{4+} + 2Br^-$$

$E = +0.92$ V

$$4Br^- + O_2 + 4H^+ \longrightarrow 2Br_2 + 2H_2O$$

$E = +0.16$ V

An E_h–pH diagram for some of the half reactions is given in Fig. 1. It is apparent from the diagram that in acid solutions up to a pH 3 to 4, dioxygen is able to oxidize Br^- and $[IrX_6]^{3-}$. Dibromine can oxidize $[IrX_6]^{3-}$, and O_2, Br_2, and $[IrX_2]^{2-}$ can oxidize $SnBr_2$ over a wide pH range as the E_h–pH line for Sn^{4+}/Sn^{2+} lies at $E_h = 0.02$ V. Therefore it is not surprising that the Ir(IV) hexabromo anion is produced. Presumably its existence will depend on the relative amounts of the oxidizing and reducing agents in solution. In addition the Ir(IV) halogeno complexes are generally less soluble than Ir(III) complexes and could crystallize out first from a mixture of both oxidation states. Both the oxonium and the ammonium Ir(IV) salts crystallize out of solution, as shown by the infrared spectrum. Since the crystals of the two salts have the same morphology when

TABLE 3. Thermal parameters for $(H_3O)_2[IrBr_6]$ and $Cs_2[IrCl_6]$ [a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
$(H_3O)_2[IrBr_6]$						
Ir	19.9(3)	19.9(3)	19.9(3)	0	0	0
Br	15.8(4)	33.4(4)	33.4(4)	0	0	0
O	15.3(2)	15.3(2)	15.3(2)	0	0	0
$Cs_2[IrCl_6]$						
Ir	18.4(1)					
Br	29.2(1)					
O	20.9(4)	30.5(7)	30.5	0	0	0

[a] Anisotropic temperature factors in $pm^2 \times 10$; the anisotropic temperature factor exponent takes the form: $-2\pi^2(h^2a^*U_{11}^2 + k^2b^*U_{22}^2 .... + 2klb^*c^*U_{23} \cos \alpha)$.

TABLE 4. Atomic coordinates for $K_3[IrCl_5(SnCl_3)]$ [a]

Atom	x	y	z	U
Ir	0	3102(1)	−6582(0)	11.4(1)
Sn	5000(0)	9060(1)	−9781(1)	12.4(2)
Cl(1)	5000(0)	8148(3)	−4148(4)	18.9(10)
Cl(2)	7522(2)	3122(2)	−6637(5)	20.2(6)
Cl(3)	0	5292(4)	−8196(5)	18.3(9)
Cl(4)	0	4367(4)	−3981(5)	20.9(9)
Cl(5)	8114(2)	661(3)	−2848(3)	22.3(6)
Cl(6)	0	−1431(4)	−5696(5)	22.3(10)
K(1)	0	−1407(7)	24(9)	60.5(19)
K(2)	7587(3)	3733(3)	−679(4)	36.0(9)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor. Atom coordinates $\times 10^4$. Temperature factors $\times 10^3$.

viewed under a microscope it is a matter of chance as to which crystalline complex is selected for single crystal X-ray analysis.

For the hexachloro complex in HCl, where aerial oxidation of Cl^- does not occur, the oxidant appears to be dioxygen under the acid conditions used in the reaction [1].

$$4[IrCl_6]^{3-} + O_2 + 4H^+ \longrightarrow 4[IrCl_6]^{2-} + 2H_2O$$

$$E = +0.21 \text{ V}$$

In the presence of excess Sn(II) and oxalate however, it is possible to isolate the trichlorostannato complexes.

Description and discussion of the structures

The three iridium(IV) compounds all have the hexachloroplatinate(IV) structure, with the iridium atom on a special position with site symmetry $4/mm$, and there is one distinct crystallographic Ir–X (X = Cl, Br) bond per structure. The Ir–Br bond lengths are 251.5(1) and 254.9(3) pm for the oxonium and ammonium salts, respectively, and the Ir–Cl bond length is 233.2(2) pm. The Ir–Cl bond length is typical of the values reported in other studies for hexachloro–Ir(IV) complexes e.g. 230.7(8) pm [11], and generally a little shorter than the bond lengths for hexahalogeno–Ir(III) complexes (Ir(III)–Cl range of values 232.7(3)–238.7(3) pm [12, 13]). There does not appear to be any other Ir(IV)–Br bond lengths reported, and the values obtained are a little longer than the Ir(III)–Br bond lengths in hexabromo

TABLE 5. Thermal parameters for $K_3[IrCl_5(SnCl_3)]$ [a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ir	12.3(2)	9.4(2)	11.9(2)	0(2)	0(0)	0(0)
Sn	13.5(4)	11.0(4)	12.8(4)	0(3)	0(0)	0(0)
Cl(1)	25.2(7)	17.6(18)	13.9(15)	6.3(12)	0(0)	0(0)
Cl(2)	15.4(9)	18.9(11)	26.2(11)	1.0(10)	−1.8(15)	0(1)
Cl(3)	23.2(15)	12.8(15)	18.9(16)	4.4(13)	0(0)	0(0)
Cl(4)	26.9(16)	19.7(18)	15.9(14)	−0.5(1)	0(0)	0(0)
Cl(5)	20.1(10)	26.1(12)	20.8(10)	1.8(9)	4.5(10)	−0.1(1)
Cl(6)	25.2(18)	13.2(16)	28.3(20)	−0.6(15)	0(0)	0(0)
K(1)	56.2(28)	64.6(36)	60.8(35)	−6.6(30)	0(0)	0(0)
K(2)	37.3(14)	33.4(16)	37.2(16)	1.8(11)	−6.0(10)	2.0(12)

[a] Anisotropic temperature factors in $pm^2 \times 10$.

TABLE 6. Reactions involving $[IrX_6]^{2-}$ and $[IrX_6]^{3-}$

Starting material	Reaction conditions[a]	Products	Evidence[b]	Reference
$[IrBr_6]^{3-}$	Pure $HBr/SnBr_2/O_2$	$[IrBr_6]^{2-}$, $[IrBr_6]^{3-}$	UV–Vis	this work
	$HBr/SnBr_2/O_2$	$[IrBr_6]^{2-}$, $[IrBr_6]^{3-}$	UV–Vis, XRS	this work
	HBr/O_2	$[IrBr_6]^{2-}$, $[IrBr_6]^{3-}$	UV–Vis	7
$[IrBr_6]^{2-}$	$HBr/SnBr_2/O_2$	$[IrBr_6]^{2-}$	UV–Vis	this work
	Pure $HBr/SnBr_2/O_2$	$[IrBr_6]^{2-}$, $[IrBr_6]^{3-}$	UV–Vis	this work
	Pure HBr/Xs $SnBr_2/O_2$	$[IrBr_6]^{2-}$, $[IrBr_6]^{3-}$	UV–Vis	this work
	$HBr/SnBr_2/N_2$	$[IrBr_6]^{2-}$, $[IrBr_6]^{3-}$	UV–Vis	this work
	Pure 4 M $HBr/N_2/SnBr_2$	$[IrBr_6]^{2-}$, $[IrBr_6]^{3-}$	UV–Vis	this work
	Pure 4 M HBr/Xs $SnBr_2$, O_2/C_2O_4	$[IrBr_6]^{2-}$, $[IrBr_6]^{3-}$	UV–Vis, XRS	this work
	$HBr/C_2O_4^{2-}/O_2$	$[IrBr_6]^{2-}$, $[IrBr_6]^{3-}$	UV–Vis	8
	$HBr/SnBr_2/O_2$	$[IrBr_6]^{2-}$	UV–Vis	this work
$[IrCl_6]^{3-}$	$HCl/SnCl_2/O_2$	$[IrCl_4(SnCl_3)_2]^{3-}$	UV–Vis, XRS, IR	9
	$HBr/SnBr_2/O_2$	$[IrBr_6]^{2-}$	UV–Vis	this work
	$HCl/Heat/Cl_2$	$[IrCl_6]^{2-}$	UV–Vis	10
	HCl/Xs $SnCl_2/O_2$	$[IrCl_6]^{2-}$, $[IrCl_6]^{3-}$	UV–Vis	this work
	$HCl/SnCl_2/O_2/C_2O_4^{2-}$	$[IrCl_4(SnCl_3)_2]^{3-}$	UV–Vis, XRS, IR	9
	HCl/O_2	$[IrCl_6]^{2-}$	UV–Vis	8
	$HCl/SnCl_2/O_2$	$[IrCl_6]^{2-}$, $[IrCl_6]^{3-}$	UV–Vis, XRS	this work
	Pure $HBr/SnBr_2/O_2$	$[IrBr_6]^{2-}$, $[IrBr_6]^{3-}$	UV–Vis, XRS	this work
	H_2O/Br_2	$[IrX_6]^{2-}$	UV–Vis	8
	4 M HCl/Xs $SnCl_2/O_2$	$[IrCl_6]^{2-}$, $[IrCl_6]^{3-}$	UV–Vis, XRS	this work
	Pure 4 M HBr/Xs $SnBr_2/O_2$	$[IrBr_6]^{2-}$, $[IrBr_6]^{3-}$	UV–Vis	this work
	HBr/O_2	$[IrBr_6]^{2-}$, $[IrBr_6]^{3-}$	UV–Vis	7
$[IrCl_6]^{2-}$	Pure HBr/Br_2	$[IrBr_6]^{2-}$, $[IrBr_6]^{3-}$	UV–Vis	7, 8

[a] Pure HBr = HBr free of Br_2, Xs = excess, O_2 = carried out in air. [b] XRS = X-ray structure.

complexes reported previously (Ir(III)–Br range of values 248.6(5)–251.2(4) pm [12]).

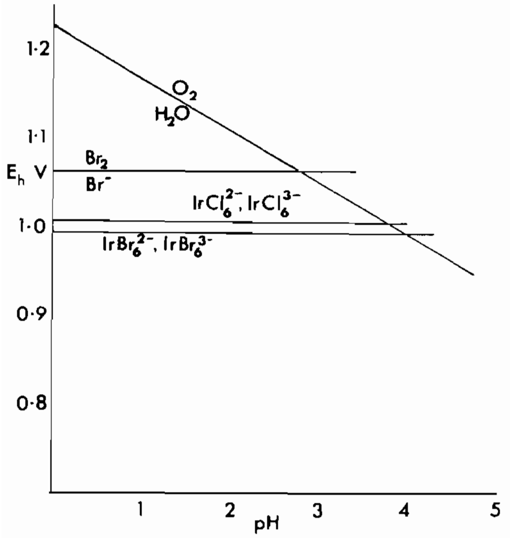

Fig. 1. The E_h–pH diagram for the systems O_2/H_2O, Br_2/Br^-, $IrCl_6^{2-}/IrCl_6^{3-}$ and $IrBr_6^{2-}/IrBr_6^{3-}$.

It is expected that the Ir(IV)–X bond length would be somewhat shorter than the Ir(III)–X bond length, by virtue of a greater effective nuclear charge on Ir(IV). This is found to be the case for Ru(IV)–Cl (231.8(2) pm) in $K_2[RuCl]_6$ [14] compared with Ru(III)–Cl (237.2(2)–238.4(2) pm) in $[Al(H_2O)_6][RuCl_6]\cdot 4H_2O$ [15]. The fact that for related compounds the Ir(III)–X and Ir(IV)–X bond lengths are similar and even tending to be longer in the Ir(IV) bromo case suggests that the effective nuclear charges of Ir(III) and Ir(IV) are similar. This may be a factor which promotes the facile redox chemistry of IrX_6^{2-}/IrX_6^{3-}. It is likely that the Ir–Br bond has some π character and this would be more significant for iridium(III) than iridium(IV), producing a shorter bond. Nikol'skii *et al.* [16] have shown that there is substantial π component in the M–Cl bond for complexes of the type $[M(NO)Cl_5]^{2-}$. This effect is likely to be similar or even greater for M–Br bonds.

Whereas oxonium salts are relatively common, isolation of crystalline oxonium halogeno complexes is rather rare. Complexes $(H_3O)_2[MX_6]$ are known for M/X = Os/I [17], Pt/Cl [18], In/F [19] and hexachloro iridate(IV), osmate(IV) and platinate(IV) acids are commercially available. Oxonium complexes are frequently isomorphous to ammonium complexes. In the present work the oxonium and ammonium cations are in competition with each other and it appears that both salts crystallize at the same time. This is not unexpected as the effective cation sizes would be similar, and they would participate about equally in hydrogen bonding if that is an important factor.

The structure of $K_3[IrCl_5(SnCl_3)]$ is shown in Fig. 2 and selected bond lengths and angles are listed in Table 7. The five chlorine atoms and the trichlorostannato ligand are coordinated to the iridium atom, with the coordination around the iridium atom being close to octahedral. There are only small deviations from ideal symmetry. The molecule has *m* symmetry with the iridium, the tin and four of the chlorine atoms lying on the mirror plane. Although many platinum metal complexes containing trichlorostannato ligands are known, there have been few X-ray structural determinations reported. Structures have been reported for iridium organometallic complexes [20, 21], containing one trichlorostannato ligand. The X-ray structures of halogeno complexes containing trichlorostannato ligands have been reported for osmium and ruthenium [22–25]. The Ir–Sn bond length found in the present work of 249.6(1) pm is short compared with that reported for other iridium complexes; 264.2(2) [20], and 258.67(6) [21] pm. Farrugia *et al.* [22, 23] found that the Ru–Sn bond length was shorter when the $SnCl_3^-$ ligand was opposite the chlorine atom compared with being opposite another $SnCl_3^-$ ligand, suggesting that a π-bonding component may be a significant factor in the length of the M–Sn bond. A similar effect was seen in the osmium complex $(NH_4)[OsCl(SnCl_3)_5]$ [24]. There is a considerable spread reported in the length of Sn–Cl bonds, viz. 234.0(4)–242(2) pm, and the bond lengths obtained in this determination are within this range. Most of the reported values lie at the top end of the range, however, whereas the values obtained here are in general short compared with most reported values [20–26].

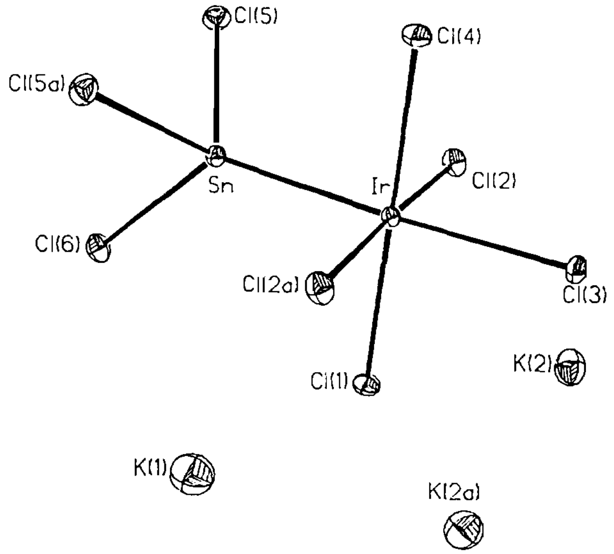

Fig. 2. Perspective view of the structure of $K_3[IrCl_5(SnCl_3)]$.

TABLE 7. Selected bond lengths (pm) and angles (°) for $K_3[IrCl_5(SnCl_3)]$

Bond	Length	Bond	Length
Ir–Sn	249.6(1)	Ir–Cl(1)	233.9(3)
Ir–Cl(2)	237.6(2)	Ir–Cl(3)	243.8(3)
Ir–Cl(4)	237.0(4)	Ir–Cl(5)	237.5(3)
Sn–Cl(6)	236.9(4)		
Bond system	**Angle**	**Bond system**	**Angle**
Cl(1)–Ir–Cl(4)	180.0(0)	Cl(1)–Ir–Cl(2)	89.3(1)
Cl(1)–Ir–Cl(3)	89.3(1)	Cl(3)–Ir–Sn	176.8(1)
Cl(1)–Ir–Sn	93.9(1)	Cl(5)–Ir–Sn	117.0(1)
Cl(6)–Sn–Ir	127.9(1)	Cl(5)–Sn–Cl(6)	95.0(1)

A further feature of the structure is the variation in the Ir–Cl bond lengths. The Ir–Cl bond length for the chlorine atom that is bound opposite the $SnCl_3^-$ ligand is long at 243.8(4) pm compared with the other Ir–Cl bonds in the complex; 233.9(3)–237.6(2) pm, and the Ir–Cl bond lengths obtained for the Ir(III) complex $K_3[IrCl_6]$; 2.352(5)–237.3(4) pm [14]. This feature has been observed in other structures [22–24], and this together with the short Ir–Sn bond length suggests that again both σ and π components are important in the Ir–Sn bond. It is interesting that the monotrichlorostannato–iridium complex was isolated under the same conditions from which bis- and tris-trichlorostannato rhodium complexes were formed [2]. In view of the X-ray structure this is somewhat surprising, as the short Ir–Sn bond and the long *trans* Ir–Cl bond suggests that the $SnCl_3^-$ ligand exerts a considerable *trans* effect. This may explain why no *trans* bis-trichlorostannato complex was formed.

Supplementary material

Tables of thermal parameters and observed and calculated structure factors are available from the authors on request.

Acknowledgement

The authors acknowledge grants for equipment from the New Zealand Universities Grants Committee.

References

1 J. E. Fergusson and D. A. Rankin, *Aust. J. Chem., 36* (1983) 863.

2 P. G. Antonov, Yu. N. Kukushikin, V. I. Anufriev, L. N. Vasil'ev and L. V. Konovalov, *Russ. J. Inorg. Chem., 24* (1979) 231.

3 C. K. Jørgensen, *Absorption Spectra and Chemical Bonding in Complexes,* Addison Wesley, Reading, MA, U.S.A., 1962.

4 J. D. H. Donnay and H. M. Ondik, *Crystal Data Determinative Tables,* Vol. 2, *Inorganic Compounds,* US Dept. Commerce, NBS and JCPDS, 3rd edn., U.S.A., 1973.

5 J. De Meulenaer and H. Tompa, *Acta Crystallogr., 19* (1965) 1014.

6 G. M. Sheldrick, *SHELXTL User Manual,* Revision 4, Nicolet XRD Corp., Cupertina, CA, 1981.

7 J. E. Fergusson and D. A. Rankin, *Aust. J. Chem., 36* (1983) 863.

8 D. A. Rankin, *Ph.D. Thesis,* University of Canterbury, 1978.

9 R. K. Coll and J. E. Fergusson, unpublished results.

10 D. A. Fine, *J. Inorg. Nucl. Chem., 32* (1970) 2731.

11 A. J. Lindop, *J. Phys. C., Solid State Phys., 3* (1970) 1984.

12 D. A. Rankin, B. R. Penfold and J. E. Fergusson, *Aust. J. Chem., 36* (1983) 871.

13 R. K. Coll, J. E. Fergusson, B. R. Penfold, D. A. Rankin and W. T. Robinson, *Aust. J. Chem., 40* (1987) 2115.

14 J.-P. Deloume, R. Faure and G. Thomas-David, *Acta Crystallogr., Sect. B, 35* (1979) 558.

15 T. E. Hopkins, A. Zalkin, D. H. Templeton and M. G. Adamson, *Inorg.Chem., 8* (1969) 2421.

16 A. B. Nikol'skii, V. I. Baranovskii, N. V. Ivanova and O. V. Sizova, *Russ. J. Inorg. Chem., 19* (1974) 145.

17 J. E. Fergusson, B. H. Robinson and W. R. Roper, *J. Chem. Soc.,* (1962) 2113.

18 R. D. Gillard and G. Wilkinson, *J. Chem. Soc.,* (1964) 1640.

19 E. N. Deichman and Zh. A. Britsyna, *Russ. J. Inorg. Chem., 9* (1964) 444.

20 P. Porta, H. M. Powell, R. J. Mawby and L. M. Venanzi, *J. Chem. Soc. A,* (1967) 455.

21 M. R. Churchill and L. G. Lin, *J. Am.Chem. Soc., 96* (1974) 76.

22 L. J. Farrugia, B. R. James, C. R. Lassigne and E. J. Wells, *Can. J. Chem., 60* (1982) 1304.

23 L. J. Farrugia, B. R. James, C. R. Lassigne and E. J. Wells, *Inorg. Chim. Acta, 53* (1981) L261.

24 T. S. Khodashova, M. A. Porai-Kishits, V. P. Nikolaev and V. N. Shchurkina, *J. Struct. Chem., 21* (2) (1980) 220.

25 B. Czeska, F. Weller and K. Dehnicke, *Z. Anorg. Allg. Chem., 498* (1983) 121.

26 G. Consiglio, F. Morandini, G. Ciani, A. Soroni and M. Kretschmer, *J. Am. Chem. Soc., 105* (1983) 1391.