Nitrato-complexes of Iridium. Part 2.[1] $M_2[Ir(NO_3)_6]$ (M = K, Rb, or Cs)

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Potassium, rubidium, and caesium hexanitratoiridate(IV) salts have been prepared by reactions of the corresponding hexabromoiridate(IV) compounds with dinitrogen pentaoxide. Solution properties, vibrational spectra, magnetic properties, and *X*-ray powder diffraction data are reported and the behaviour of the potassium salt in acetonitrile and 100% nitric acid solutions has been investigated by electronic spectroscopy.

HEXAHALOGENO-COMPLEXES of iridium(IV) are relatively inert towards oxides of nitrogen. Thus N_2O_4 is unreactive towards both hexachloro- and hexabromoiridate(IV) compounds, but N_2O_5 will react with hexabromoiridates(IV). In the work reported here, the latter have proved useful in terms of reactivity and ease of removal of by-products in the synthesis of nitrato-complexes, and a detailed account of the synthesis and some properties of the complexes $M_2[Ir(NO_3)_6]$ (M = K, Rb, or Cs) is now presented.

A preliminary account [2] of the first isolation of the compounds $M_2[Ir(NO_3)_6]$ (M = K, Rb, or Cs) and $K_2[Pt(NO_3)_6]$ from reactions of the corresponding bromo-complexes with N_2O_5 and a detailed report [3] of an e.s.r. study on $K_2[Ir(NO_3)_6]$ have already been published.

EXPERIMENTAL

Reaction of Potassium Hexabromoiridate(IV) *with Dinitrogen Pentaoxide*.—Potassium hexabromoiridate(IV) (Johnson–Matthey, Ltd.) was added to freshly prepared dinitrogen pentaoxide at 195 K against a countercurrent of dry nitrogen and the reaction vessel was allowed to warm to room temperature. A reaction began immediately and the colour of the starting material changed from deep blue to dark red. When the reaction had ceased, excess of N_2O_5 was removed in a stream of dry nitrogen and the product was briefly evacuated at room temperature to remove final traces of nitrogen oxides. A dark red free-flowing powder remained, which was shown by analysis to be potassium hexanitratoiridate(IV), $K_2[Ir(NO_3)_6]$ {Found: K, 12.9; N, 12.95. $K_2[Ir(NO_3)_6]$ requires K, 12.15; N, 13.1%}.

Reaction of Rubidium Hexabromoiridate(IV) *with Dinitrogen Pentaoxide*.—Rubidium hexabromoiridate(IV) was prepared by a simple precipitation reaction between $K_2[IrBr_6]$ and $Rb_2[SO_4]$. This freshly prepared salt was dried at 110 °C *in vacuo* for 2 days to remove all traces of water. It was then treated with N_2O_5, as described above, to yield $Rb_2[Ir(NO_3)_6]$ {Found: N, 10.95. $Rb_2[Ir(NO_3)_6]$ requires N, 11.45%}.

Reaction of Caesium Hexabromoiridate(IV) *with Dinitrogen Pentaoxide*.—Caesium hexabromoiridate(IV) was prepared by a simple precipitation reaction between $K_2[IrBr_6]$ and CsCl. This freshly prepared salt was dried at 110 °C *in vacuo* for 2 days to remove all traces of water. It was then treated with N_2O_5, as described above, to yield $Cs_2[Ir(NO_3)_6]$ {Found: N, 9.80. $Cs_2[Ir(NO_3)_6]$ requires N, 10.1%}.

Apparatus.—Glass apparatus, used in these preparations and in manipulation of the oxides of nitrogen or 100% nitric acid, was degreased by immersion in an alcohol–potassium hydroxide bath, washed with water and acetone, and dried overnight at 120 °C. Reaction vessels were fitted with phosphoric oxide guard tubes to prevent ingress of moisture and ground-glass joints were sealed with either Kel-F grease or polytetrafluoroethylene sleeves.

Physical Measurements.—Infrared spectra were recorded as mulls on a Perkin-Elmer 521 spectrophotometer using Halocarbon or Nujol mulling agents and silver chloride windows. The i.r. spectrum of $K_2[Ir(NO_3)_6]$ in MeCN was recorded in a short path length (*ca.* 10 μm) solution cell fitted with silver chloride windows. Electronic spectra (solids) were recorded on a Unicam SP700 spectrophotometer using a diffuse-reflectance unit and on a Unicam SP800 instrument using matched 10-mm fused silica cells (solutions). Magnetic measurements were made at room temperature by the Gouy method. *X*-Ray powder data were obtained using a Philips *X*-ray powder diffractometer with an 11-cm camera and Cu-K_α radiation. An exposure time of 3 h was used for the potassium and rubidium salts and 7 h for the caesium salt. The films were measured and from these data values of sin θ, $\sin^2 \theta$, *D*, and 2 θ were calculated by computer.[4] The density of each of the compounds was measured as 3.48, 3.31, and 3.20 g cm^{-3} for the salts of K, Rb, and Cs respectively. For each compound values of 2 θ, formula weight, and density were introduced into a second computer program [5] designed to index the powder patterns.

Analysis.—Potassium was determined by flame photometry. Total nitrogen content was determined by a modified Kjeldahl method involving reduction of nitrogen to ammonia using Devarda's alloy and alkali. The ammonia evolved on steam distillation was collected in an excess of 2% boric acid solution, which was then titrated against standard hydrochloric acid using bromocresol green–methyl red as indicator. The compound under investigation was first hydrolysed by breaking a closed ampoule, containing a known weight, in a known volume of 2 mol dm^{-3} sodium hydroxide solution in a closed vessel. Aliquots of this solution were taken for the nitrogen determination.

RESULTS AND DISCUSSION

Both $K_2[Ir(NO_3)_6]$ and $Rb_2[Ir(NO_3)_6]$ are dark red hygroscopic solids which blacken and decompose on exposure to moist air. The salt $Cs_2[Ir(NO_3)_6]$ is red-purple in colour and also very hygroscopic.

The compounds dissolve in water giving an initially deep red solution which very rapidly turns purple with the precipitation of the hydrated dioxide. No solvent was found in which the compounds were stable over long periods of time, except those (*e.g.* CCl_4) in which they were insoluble, although orange-red solutions in acetonitrile were apparently stable for up to 15 min, after which a white solid was deposited. A similar white solid was deposited after a short time in a number of the other organic solvents investigated and was presumed to be the alkali-metal nitrate.

The behaviour of $[Ir(NO_3)_6]^{2-}$ in 100% HNO_3 was of particular interest since nitrato-complexes might be expected to be stable in this solvent. However, a solution of $K_2[Ir(NO_3)_6]$ changed colour over a period of 24 h (see below).

The lack of a suitable solvent and the involatility of the three $[Ir(NO_3)_6]^{2-}$ salts has so far precluded the growth of single crystals for *X*-ray studies.

TABLE 1

Infrared spectra (cm^{-1}) of potassium, rubidium, and caesium hexanitratoiridate(IV) salts and ammonium hexanitratocerate(IV)

$K_2[Ir(NO_3)_6]$	$Rb_2[Ir(NO_3)_6]$	$Cs_2[Ir(NO_3)_6]$	$K_2[Ir(NO_3)_6]$ (in CH_3CN)	$[NH_4]_2[Ce(NO_3)_6]$	Assignment †
				1 596w	
				1 545w	
1 571vs,br	1 562vs	1 566vs	1 557vs	1 520vs	$A_1[\nu_{sym}(NO^*)]$
1 545 (sh)	1 532 (sh)	1 554 (sh)	1 513 (sh)		
1 265vs,br	1 260vs	1 257vs	1 262s,sp	1 275s	$B_1[\nu_{asym}(NO_2)]$
931vs	926vs		959w,sp		
901vs	902vs	888s		1 030vs	} $A_1[\nu_{sym}(NO_2)]$
805m,sp	803m,sp			802s	$A_1[\delta_{sym}(NO_2)]$
793m,sp	793m,sp	793m,sp			
784m,sp	784m,sp				
770 (sh)	770w				
764m,sp	762w	760w,br			
741m,sp	746w	755w,br		740s	$B_1[\delta_{asym}(NO_2)]$
726m,sp	724 (sh)	725vw			
712m,sp	712m,sp	711vw	713m,sp		
		694m,sp			

† Bidentate nitrate, C_{2v}. O* denotes an unco-ordinated oxygen atom.

Vibrational Spectra.—The i.r. spectra of $K_2[Ir(NO_3)_6]$, $Rb_2[Ir(NO_3)_6]$, and $Cs_2[Ir(NO_3)_6]$ were recorded as mulls and that of $K_2[Ir(NO_3)_6]$ was also recorded in acetonitrile solution. The latter spectrum was, however, complicated by a slow reaction of the compound with the solvent. These compounds showed no apparent attack on mulling agents even after several hours exposure. Bands attributable to the compounds are presented in Table 1.

TABLE 2

Magnetic data (at 299 K) for $M^I_2[Ir(NO_3)_6]$ complexes *

	$10^6\chi_g$/ $cm^3\ mol^{-1}$	$10^3\chi_M^{corr.}$/ $cm^3\ mol^{-1}$	$\mu_{eff.}$/B.M.
$K_2[Ir(NO_3)_6]$	1.904	1.398	1.83
$Rb_2[Ir(NO_3)_6]$	1.754	1.479	1.88
$Cs_2[Ir(NO_3)_6]$	0.915	0.971	1.52

* $\chi_{gM} = \chi_{g9} \times$ relative molecular mass; 1 B.M. = 0.927×10^{-23} A m^2.

The previously reported e.s.r. results [3] for $K_2[Ir(NO_3)_6]$ in a host lattice of $K_2[Pt(NO_3)_6]$ provided unambiguous evidence for symmetrically bidentate nitrate groups, in spite of the unsymmetrical low-spin d^5 configuration of Ir^{IV}. The assignments in Table 1 therefore refer to this nitrate bonding mode.[6] The anion $[Ce(NO_3)_6]^{2-}$ has been shown by *X*-ray crystallography to contain bidentate nitrate groups only, the oxygen atoms taking up an essentially icosahedral arrangement around the Ce^{IV} ion.[7] The i.r. spectrum of $[NH_4]_2[Ce(NO_3)_6]$ is therefore included in Table 1 for the purpose of comparison. In all the spectra in this Table the characteristic bands of ionic nitrate (at 1 390br and 830sp cm^{-1}) are absent, as also is a band assignable to the ν_6 fundamental mode of the bidentate nitrate ligand, designated as $B_2[\pi(O_2NO^*)]$ (O* denotes unco-ordinated oxygen), which seldom appears in such systems.

A striking feature of the mull spectra of the three hexanitratoiridate(IV) salts is the extensive band splitting over the 650—1 000 cm^{-1} region, which is somewhat less pronounced for the caesium than for the potassium and rubidium salts. This type of splitting is also observed in the salts of Na^+, K^+, Rb^+, and Cs^+ with the $[Co(NO_3)_4]^{2-}$ anion, again becoming less marked on progressing from the sodium to the caesium salt.[8] Interpretation of these band splittings requires knowledge of presently unavailable crystal structures.

Unfortunately, it has not yet been possible to obtain satisfactory Raman spectra of the three hexanitratoiridate(IV) complexes.

Magnetic Properties.—The magnetic susceptibilities of the solid complexes are presented in Table 2. The values of χ_M and the effective magnetic moment, $\mu_{eff.}$, were corrected for diamagnetism. These values are consistent with the low-spin d^5 configuration of Ir^{IV} with one unpaired electron. The caesium salt has a lower moment than the potassium and rubidium analogues which, taken in conjunction with the i.r. spectra, may reflect a structural difference in the case of this salt.

Electronic Spectrum of Potassium Hexanitratoiridate(IV).—Table 3 summarises the data. The diffuse-reflectance spectrum, consisting of several intense broad features and a number of weaker shoulders, was resolved with the aid of a Du Pont Curve Resolver into seven peaks at the positions quoted in the Table. This spectrum has already been discussed elsewhere,[3] although the lack of intensity data makes analysis very difficult.

The reaction of the $[Ir(NO_3)_6]^{2-}$ anion with many solvents has already been mentioned and its behaviour in 100% HNO_3 and MeCN has been investigated. A solution of $K_2[Ir(NO_3)_6]$ in 100% HNO_3 is initially orange-red but turns purple over a period of 24 h. The slow change in the visible spectrum was monitored over this period; the peak at 25 600 cm^{-1} diminished in intensity and shifted to 24 500 cm^{-1} whilst that at 17 700 cm^{-1} increased in intensity and developed a shoulder at *ca.* 15 500 cm^{-1}. An isosbestic point at *ca.* 19 750 cm^{-1} indicated that a simple one-step reaction was occurring, most probably involving only two species. It can be seen from Table 3 that the bands at 17 700 and 15 500 cm^{-1} correspond closely to those found in the visible spectra of 100% nitric acid solutions of $Ir_3O(NO_3)_{10}$ {which is likely to dissociate as $[Ir_3O(NO_3)_9]^+$ and NO_3^-} and $IrBr_3$.[1] Thus it appears that in 100% nitric acid, both $[Ir(NO_3)_6]^{2-}$, initially present in solution, and $IrBr_3$ are slowly converted to the trinuclear purple cation $[Ir_3O(NO_3)_9]^+$. The bands at 24 600 and 17 600 cm^{-1} in solution (b) and at 25 600 and 17 700 cm^{-1} in solution (c) are taken to indicate the presence of both $[Ir(NO_3)_6]^{2-}$ and $[Ir_3O(NO_3)_9]^+$ in freshly prepared MeCN and 100% HNO_3 solutions. Furthermore, the spectra of solutions (d) and (f) may suggest an approach, with time, to an equilibrium between these two iridium nitrato-species in solutions of $K_2[Ir(NO_3)_6]$ or $IrBr_3$ in 100% nitric acid.

TABLE 3

Electronic spectral data (cm^{-1})

$K_2[Ir(NO_3)_6]$				$Ir_3O(NO_3)_{10}$	$IrBr_3$
(a) [a]	(b) in MeCN [b]	(c) in HNO_3 [c]	(d) in HNO_3 [d]	(e) in HNO_3 [e]	(f) in HNO_3 [f]
	42 100				
39 100					
	37 900				
32 900					
27 200					
24 600	24 600	25 600	24 500		24 000
21 800					
18 500					
	17 600	17 700w	17 700	18 000	17 850
			15 500 (sh)	15 500 (sh)	15 500 (sh)
10 600					

[a] Diffuse reflectance. [b] Fresh solution. [c] Fresh solution in 100% HNO_3. [d] Solution in 100% HNO_3 after 24 h. [e] Solution in 100% HNO_3; ref. 1. [f] Solution in 100% HNO_3 after 4 h.

X-Ray Powder Data.—A possible structural difference between $Cs_2[Ir(NO_3)_6]$ and the corresponding potassium and rubidium salts is suggested by the i.r. and magnetic data. So far as the *X*-ray powder patterns are concerned, that for $Rb_2[Ir(NO_3)_6]$ can be indexed on an orthorhombic cell with $a = 11.35$, $b = 14.60$, and $c = 17.86$ Å ($Z = 8$); the pattern for $Cs_2[Ir(NO_3)_6]$ can be indexed on an orthorhombic cell with $a = 6.71$, $b = 15.44$, and $c = 15.19$ Å ($Z = 4$); and the data for $K_2[Ir(NO_3)_6]$ suggest a cell of lower symmetry.

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