Nitrato-complexes of Iridium.   Part I. $Ir_3O(NO_3)_{10}$

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The new oxide nitrate of iridium(IV), $Ir_3O(NO_3)_{10}$, is prepared from dinitrogen pentoxide and iridium tribromide. The i.r. spectrum suggests its formulation as $[Ir_3O(NO_3)_9]^+NO_3^-$; its electronic spectra, X-ray powder pattern, room temperature magnetic moment, and chemical properties are discussed. A trinuclear structure involving pairs of nitrate bridges between octahedrally co-ordinated iridium atoms is suggested for the cation $[Ir_3O(NO_3)_9]^+$. The reaction between iridium tribromide and 100% nitric acid has also been studied.

TRINUCLEAR 'mixed-valence' oxy-anion complexes of iridium-(III) and -(IV) are known, the best characterised being the sulphato-species $K_{10}[Ir_3O(SO_4)_9]$ and M_4-$[Ir_3N(SO_4)_6(H_2O)_3]$ (M = K or NH_4).[1-5] The crystal structure of the anion in the NH_4^+ salt of the latter has been reported.[6] The nitrogen atom is situated at the centre of an equilateral triangle of iridium atoms and each pair of metal atoms is joined by double sulphate bridges. Octahedral co-ordination about iridium is completed by water molecules *trans* to the nitrogen. The arrangement of the nitrogen, iridium atoms, and water molecules is essentially planar. The presence of a π-bonding system involving the $2p_z$ orbital (perpendicular to this plane) of the nitrogen atom and iridium orbitals of suitable symmetry is supported by the short Ir–N distance (1·918 Å). The compound $K_{10}[Ir_3O(SO_4)_9]$ is therefore expected to incorporate both bridging and terminal (unidentate) sulphato-groups and a central oxygen atom. X-Ray crystallographic studies have revealed similar bridged acetato-systems in the complexes $[Cr_3O(OAc)_6(H_2O)_3]^+Cl^-,6H_2O$,[7] $[Mn_3O(OAc)_6^+OAc^-,HOAc]_n$ [8] (which also involves intermolecular bridging between trinuclear units by acetate groups), and $[Fe_3O(OAc)_6(H_2O)_3]^+$-ClO_4^-.[9]

We now report the preparation of a novel compound of empirical composition $Ir_3O(NO_3)_{10}$ which is believed on the basis of evidence discussed below, to be a structural analogue of the above sulphates and acetates.

EXPERIMENTAL

Reaction of Iridium Tribromide with Dinitrogen Pentoxide. —Hydrated iridium tribromide (Johnson–Matthey) was heated *in vacuo* at 110° for one week. The brown-green product was shown to be anhydrous by i.r. spectroscopy.

Iridium tribromide was added to freshly prepared dinitrogen pentoxide and the mixture was allowed to react overnight in a vessel vented to the atmosphere by a phosphoric oxide guard tube. On warming the mixture to room temperature the colour of the starting material changed from brown-green to purple and bromine was evolved. After reaction had ceased, the bulk of the residual dinitrogen pentoxide was removed in a stream of dry nitrogen. The product was then evacuated at room temperature for *ca.* 1 h to remove final traces of nitrogen oxides. A deep purple, free-flowing powder, containing no detectable bromide, remained. This was stored under an atmosphere of dry nitrogen and all further manipulations

were carried out in a dry box [Found: N, 11·45; Ir, 47·9. $Ir_3O(NO_3)_{10}$ requires N, 11·55; Ir, 47·55%].

Reaction of Iridium Tribromide with Nitric Acid.—Nitric acid (100%) was added to iridium tribromide in a tube vented to the atmosphere by a phosphoric oxide guard tube. The tribromide dissolved and the initially brown solution developed a purple colour which became more intense as the reaction proceeded. The excess of nitric acid was removed *in vacuo* but the product was a purple intractable gum which failed to solidify.

Physical Measurements.—I.r. spectra were recorded on a Perkin-Elmer 521 spectrometer using Halocarbon and Nujol mulling agents between silver chloride windows. Electronic spectra were recorded on a Unicam SP 800 spectrometer using 1·0-cm matched fused silica cells. X-Ray powder photographs were obtained using a Philips X-ray powder diffractometer with a 9-cm camera and Cu-K_α radiation. Magnetic measurements were made at room temperature by the Gouy method.

Iridium content was determined by reduction to the metal. Total nitrogen content was determined by the Dumas and Kjeldahl methods; the results were in good agreement.

RESULTS AND DISCUSSION

$Ir_3O(NO_3)_{10}$ is extremely deliquescent and rapidly hydrolysed to hydrated iridium dioxide, although stable for several weeks at room temperature in a dry atmosphere. On heating, no melting point was observed, but decomposition commenced at 70—75° yielding nitrogen dioxide and black iridium dioxide. Attempted sublimation by heating *in vacuo* proved unsuccessful.

The compound is insoluble in non-co-ordinating organic solvents but dissolves in organic oxygen- and nitrogen-donor solvents to give green solutions, which deposit brown-grey precipitates. Ethanol is oxidised to acetaldehyde and there is a vigorous reaction with diethyl ether.

The compound dissolves in 100% and 70% nitric acid and in concentrated sulphuric or phosphoric acid to give stable blue solutions. Dissolution in 2M-sodium hydroxide also yields an initially blue solution but hydrated iridium dioxide is deposited after a few minutes.

Infra red Spectrum.—The spectrum (Table 1 and Figure 1) is that expected for a covalent nitrate, but exhibits further features of particular interest, which are assigned

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[3] C. K. Jørgensen, *Acta Chem. Scand.*, 1959, **13**, 196.

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[5] D. R. Brown, M. B. Robin, J. D. E. McIntyre, and W. F. Peck, *Inorg. Chem.*, 1970, **9**, 2315.
[6] M. Ciechanowicz, W. P. Griffith, D. Pawson, A. C. Skapski, and M. J. Cleare, *Chem. Comm.*, 1971, 876.

as follows. Since no known unidentate nitrate group gives rise to an absorption above 1570 cm⁻¹, it is reasonable to assign the band at 1641 cm⁻¹ to the N–O stretching vibration (A_1) of a bidentate or bridging nitrate group bound to a fairly polarising metal ion. Furthermore,
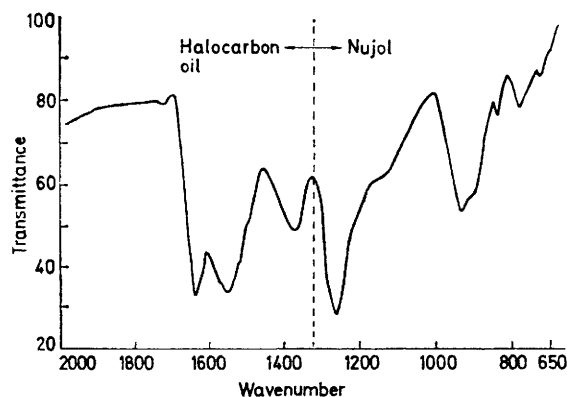

FIGURE 1   I.r. spectrum of $Ir_3O(NO_3)_{10}$

the appearance of the band at 1549 cm⁻¹ is suggestive of the presence of unidentate as well as bridging or bidentate nitrate groups.

Further bands of considerable significance occur at 1371 cm⁻¹ (s,br in Halocarbon oil) and 835 cm⁻¹ (m,sp

TABLE 1

The i.r. spectrum of $Ir_3O(NO_3)_{10}$ (cm⁻¹)

Nujol	Halocarbon oil	Nitrate assignment [a]
1641vs,br	1644vs,br	A_1 [ν(NO *)] bi
1549vs,br	1555vs,br	A' [ν$_{as}$(NO$_2$ *)] uni
	1371s,br	E' [ν$_d$(NO$_2$)] ion
1262vs,br		$\begin{cases} B_1 \text{ [ν}_{as}\text{(NO}_2\text{)] bi} \\ A' \text{ [ν}_s\text{(NO}_2\text{ *)] uni} \end{cases}$
934vs,br		$\begin{cases} A_1 \text{ [ν}_s\text{(NO}_2\text{)] bi} \\ A' \text{ [ν(NO)] uni} \end{cases}$
835m,sp	835m,sp	A_2'' [π(NO$_3$)] ion
782m	780m	$\begin{cases} A_1 \text{ [δ}_s\text{(NO}_2\text{)] bi} \\ A' \text{ [δ}_s\text{(NO}_2\text{ *)] uni} \end{cases}$
722w		$\begin{cases} B_1 \text{ [δ}_{as}\text{NO}_2\text{] bi} \\ A' \text{ [δ}_{as}\text{NO}_2\text{ *] uni} \\ E' \text{ [δ}_d\text{NO}_2\text{] ion} \end{cases}$

[a] ion = ionic, D_{3h}; uni = unidentate, C_s; bi = bidentate or bridging, C_{2v}.

* = Unco-ordinated oxygen atom(s).

in Nujol and Halocarbon oil). These have typical frequencies and characteristic shapes assignable to the E and A_2'' vibrational modes respectively of the nitrate ion. The i.r. spectrum of a solution of the compound in acetonitrile was also recorded. The nitrate bands observed resembled those in the mull spectra but evidence for co-ordination and/or reaction of the acetonitrile was also obtained.

Unfortunately, it has thus far proved impossible to obtain a satisfactory Raman spectrum of $Ir_3O(NO_3)_{10}$, either as the solid or in solution, because of its intense

absorption in the visible region and its reactivity towards useful solvents. In the light of i.r. evidence alone, however, it is tempting to formulate the compound as $[Ir_3^{IV}O(NO_3)_9]^+NO_3^-$ in which the cation may have the structure shown in Figure 2.

X-Ray Powder Photography.—X-Ray powder data for $Ir_3O(NO_3)_{10}$ was indexed (Table 2) initially by the

TABLE 2

X-Ray powder data for $Ir_3O(NO_3)_{10}$

d (Å)	$\sin^2 \theta_{obs}$	$\sin^2 \theta_{calc}$	Plane	Intensity
7·826	0·0097	0·0099	101 (011)	100
6·555	0·0138	0·0139	111	50
6·023	0·0164	0·0160	200 (020)	50
5·437	0·0211	0·0219	201 (021)	10
5·039	0·0234	0·0236	002	60
4·331	0·0317	$\begin{cases} 0·0320 \\ 0·0316 \end{cases}$	220 112	20
4·114	0·0351	0·0360	300 (030)	20
3·900	0·0391	0·0396	022 (202)	5
3·739	0·0425	0·0419	301 (031)	2
3·493	0·0487	0·0459	311 (131)	1
3·292	0·0548	0·0556	222	70
3·111	0·0614	0·0611	113	50
3·005	0·0656	0·0640	400 (040)	50
2·921	0·0741	0·0739	411 (141)	15
2·789	0·0764	0·0756	322 (232)	15
2·543	0·0919	0·0916	412 (142)	10
2·501	0·0950	$\begin{cases} 0·0944 \\ 0·0956 \end{cases}$	004 332	10
2·430	0·1007	0·1000	500 (050) (430, 340)	10
2·380	0·1049	$\begin{cases} 0·1040 \\ 0·1051 \end{cases}$	510 (150) 323 (233)	10
2·315	0·1109	0·1104	204 (024)	5
2·218	0·1208	0·1211	413 (143)	5
2·117	0·1326	0·1331	423 (243)	5
2·027	0·1446	0·1440	600 (060)	5
1·926	0·1602	0·1600	620 (260)	15
1·896	0·1654	0·1659	621 (261)	5
1·828	0·1779	0·1795	225	10
1·737	0·1970	0·1971	603 (063)	5
1·681	0·2103	0·2104	524 (254)	5
1·656	0·2168	$\begin{cases} 0·2164 \\ 0·2171 \end{cases}$	106 (016) 543 (453)	5
1·634	0·2226	0·2236	712 (172) (552)	10
1·595	0·2336	0·2331	633 (363)	2
1·551	0·2470	0·2475	505 (055) (435, 345)	2
1·533	0·2530	$\begin{cases} 0·2524 \\ 0·2531 \end{cases}$	316 (136) 713 (173) (553)	1
1·461	0·2785	0·2779	821 (281)	1
1·386	0·3095	0·3091	803 (083)	1
1·351	0·3257	$\begin{cases} 0·3251 \\ 0·3264 \\ 0·3251 \\ 0·3259 \end{cases}$	307 (037) 734 (374) 823 (283) 841 (481)	1
1·284	0·3605	$\begin{cases} 0·3611 \\ 0·3604 \end{cases}$	337 616 (166)	1
1·229	0·3935	$\begin{cases} 0·3931 \\ 0·3931 \end{cases}$	517 (157) 853 (583)	1

method of Lipson [10] in terms of a unit cell of tetragonal symmetry and dimensions $a = 12·19 \pm 0·15$ Å, $c = 10·03 \pm 0·15$ Å, $U = 1491 \pm 60$ Å³, $c/a = 0·8228$.

This indexing and the above parameters have now been confirmed using a specially adapted computer program [11] designed to index powder patterns other than monoclinic or triclinic.

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The density of $Ir_3O(NO_3)_{10}$ was determined by flotation and found to be $2 \cdot 738$ g cm^{-3}. If it is assumed that there are two molecules in the unit cell (which is a reasonable assumption in view of the small unit cell dimensions) the molecular weight is calculated to be 1230 ± 50 [$Ir_3O(NO_3)_{10}$ requires 1213].

Magnetic Properties.—$Ir_3O(NO_3)_{10}$ exhibits a magnetic moment (μ_{eff}) of $1 \cdot 24$ B.M. at 22 °C.

A simple MO approach to the question of energy levels and π-bonding in trinuclear iridium complexes was developed by Jørgensen and Orgel.[12] According to this
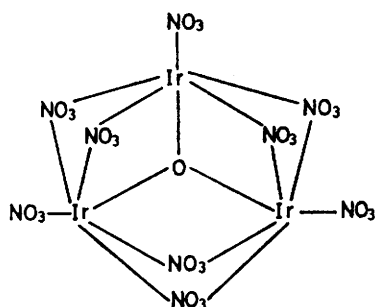

FIGURE 2 Proposed structure for $Ir_3O(NO_3)_9{}^+$

scheme and on the assumption that $Ir_3O(NO_3)_{10}$ incorporates three Ir^{IV} (d^5) centres (no evidence has been obtained for the presence of Ir^{III} in this compound), the presence of one unpaired electron is predicted on occupancy of 8 non-bonding orbitals by the 15 metal electrons. However, the observed magnetic moment is significantly lower than the 'spin-only' value for one unpaired electron. This may be indicative of intramolecular antiferromagnetism, which could be established by measurement of magnetic susceptibility over a range of temperature, as in the case of trinuclear Cr^{III} and Fe^{III} oxo-complexes containing acetato-bridges.[13]

Electronic Spectrum.—The electronic spectrum of $Ir_3O(NO_3)_{10}$ was measured in solution in 100% nitric

acid, concentrated sulphuric acid, and 2M-sodium hydroxide solution. A single absorption maximum was observed in each of these solvents at 18,000 (shoulder at 15,500), 17,700, and 17,800 cm^{-1} respectively. Other workers[14] have reported that an oxidised form of $K_{10}[Ir_3O(SO_4)_9]$ (also blue-purple in colour) has an absorption maximum at 17,550 cm^{-1}. According to the simple molecular orbital approach for trinuclear systems,[12] referred to above, the maximum in each of these spectra would be assigned to an π* ◄— n transition. A surprising feature was the apparent stability of Ir_3O-$(NO_3)_{10}$ in 2M-sodium hydroxide over short periods of time.

Although difficulty was experienced in isolating a solid product from the reaction between iridium tribromide and 100% nitric acid, the course of this reaction has been followed by observation of the electronic spectrum of the reaction mixture. The absorption band which developed was identical in position and profile to that observed for a solution of $Ir_3O(NO_3)_{10}$ in 100% nitric acid.

Further Reactions of Iridium and Some Iridium Compounds with Nitrogen Oxides and Nitric Acid.—Iridium metal was unreactive towards each of the following reagents: (*a*) pure liquid N_2O_4; (*b*) N_2O_4 diluted with appropriate organic donor solvents (*e.g.* MeCN); (*c*) pure solid N_2O_5; (*d*) 'liquid N_2O_5' (a mixture of N_2O_4, N_2O_5, and HNO_3); and (*e*) 70% HNO_3 (refluxed at the boiling point). The hexachloroiridates(IV) (M_2IrCl_6, M = K, Rb, Cs) were also found to be unreactive towards the above reagents. However, the hexabromoiridates(IV) (M_2IrBr_6, M = K, Rb, Cs) reacted with pure dinitrogen pentoxide to produce the corresponding hexanitrato-complexes. These compounds will be discussed in Part II.

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[13] A. Earnshaw, B. N. Figgis, and J. Lewis, *J. Chem. Soc. (A)*, 1966, 1656.

[14] S. I. Ginsberg, M. I. Yuz'ko, and L. G. Sal'skaya, *Russ. J. Inorg. Chem.*, 1963, **8**, 429.