An Electron Spin Resonance Study of the Bonding in Potassium Hexanitratoiridate(IV)

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Electron spin resonance measurements on $K_2[Ir(NO_3)_6]$ have yielded the following parameters: $g = -1.12$, $A(^{193}Ir) = 221 \times 10^{-4}$ cm^{-1}, $A(^{191}Ir) = 180 \times 10^{-4}$ cm^{-1}, $f_\pi = 0.38$. There is considerable delocalisation of the metal *d*-electrons into π^* orbitals on the nitrate group, being up to three times that found for the corresponding halogen complexes. A qualitative molecular-orbital bonding scheme is presented which describes the bonding between the metal and the bidentate nitrate ligands.

THE classic paper by Owen and Stevens[1] in 1953 reported the first observation of superhyperfine coupling to ligands in the hexachloroiridate(IV) anion. This was the first unambiguous experimental evidence that the metal *d*-electrons moved in molecular orbitals over the whole complex and showed that there were π-bonds in addition to the σ-bonds. Recently,[2] the corresponding hexanitrato-complex has been prepared, and this paper describes the results of electronic and e.s.r. spectral studies on this complex, $K_2[Ir(NO_3)_6]$.

By analogy with the $[Ce(NO_3)_6]^{2-}$ and $[Th(NO_3)_6]^{2-}$ anions of known structure,[3] and in keeping with the clear preference of nitrate to co-ordinate *via* two oxygens as revealed by recent *X*-ray crystallographic studies,[4] $[Ir(NO_3)_6]^{2-}$ is expected to incorporate bidentate nitrate groups, so disposed as to generate overall T_h symmetry of the anion. The presence of bidentate nitrate groups in $[Ir(NO_3)_6]^{2-}$ is supported by both i.r. and Raman spectroscopic evidence. $K_2[Pt(NO_3)_6]$, Possessing a spherically symmetrical d^6 configuration, is anticipated to have symmetrically bidentate nitrate groups and has been shown by *X*-ray powder photography to be isomorphous with $K_2[Ir(NO_3)_6]$.[2]

Our results show that there is very considerable π-bonding in this molecule, being up to three times that found in the corresponding halogeno-complexes.

EXPERIMENTAL

E.s.r. spectra were recorded at *X*-band frequencies using Varian E3 and V-4504 spectrometers. Powdered samples of 1% $K_2[Ir(NO_3)_6]$ in $K_2[Pt(NO_3)_6]$ were used and prepared from the solid-state reaction of 1% $K_2[IrBr_6]$ in $K_2[PtBr_6]$ with N_2O_5. Single crystals of the complex were impossible to prepare. Diffuse reflectance spectra were measured on a Unicam SP 800 spectrophotometer.

RESULTS

E.s.r. Spectra.—At 77 K, the spectrum consisted of a complex set of features around $g = 2$, together with a group of isotropic absorptions around $g = 1.1$. Analysis of the former showed that the signals were due to the NO_2 molecule and were, in fact, identical to those obtained by Atkins *et al.*[5] for NO_2 trapped in ice, and arose from traces of NO_2 present from the decomposition of N_2O_5. The absorptions around $g = 1.1$ consisted of two isotropic quartets, an outer set attributed to ^{193}Ir ($I = 3/2$, 61.5%, $\beta_N = 0.17$) and an inner set attributed to ^{191}Ir ($I = 3/2$, 38.5%, $\beta_N = 0.16$) at

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[1] J. Owen and K. W. H. Stevens, *Nature*, 1953, **171**, 836.

[2] B. Harrison, N. Logan, and J. B. Raynor, *J.C.S. Chem. Comm.*, 1974, 202.

[3] T. A. Beineke and J. Delgaudio, *Inorg. Chem.*, 1968, **7**, 715; S. Scavnicar and B. Prodic, *Acta Cryst.*, 1964, **18**, 698.

[4] C. C. Addison, N. Logan, S. C. Wallwork, and C. D. Gardner, *Quart. Rev.*, 1971, **25**, 289.

[5] P. W. Atkins, N. Keen, and M. C. R. Symons, *J. Chem. Soc.*, 1962, 2873.

field positions 5 132, 5 373, 5 852, and 6 414 and 5 253, 5 450, 5 802, and 6 269 G, respectively (Figure 1). The field positions of each line were corrected by the use of the Breit–Rabi equation to yield $g = 1.12$, $A(^{193}\text{Ir}) = 221 \times 10^{-4}\ \text{cm}^{-1}$, and $A(^{191}\text{Ir}) = 180 \times 10^{-4}\ \text{cm}^{-1}$. The line widths varied in the range 2—3 G and showed no sign of asymmetry or superhyperfine structure. Several additional very weak isotropic lines were observed close to the main absorptions all of which could be attributed to the same species in very small abundance in a slightly different environment. At room temperature, no spectra were observable.

Optical Spectra.—The diffuse reflectance spectrum consisted of several intense broad features and a number of weaker shoulders. Since the $n \rightarrow \pi^*$ absorption of NO_3^-, which consists of an intense and very broad band [6] extending from *ca.* 31 000 to 38 000 cm^{-1}, is likely to be present, it was subtracted from the spectrum. The remaining spectrum was then associated with the iridium chromophore and comprised various charge-transfer bands and internal transitions between levels split by spin-orbit coupling. With the aid of a Du Pont Curve Resolver, the spectrum was decomposed into six rather broad absorptions at 39 100, 32 900, 27 200, 24 600, 21 800, and 18 500 cm^{-1}. In addition, there was a well resolved but weak peak at 10 600 cm^{-1}.

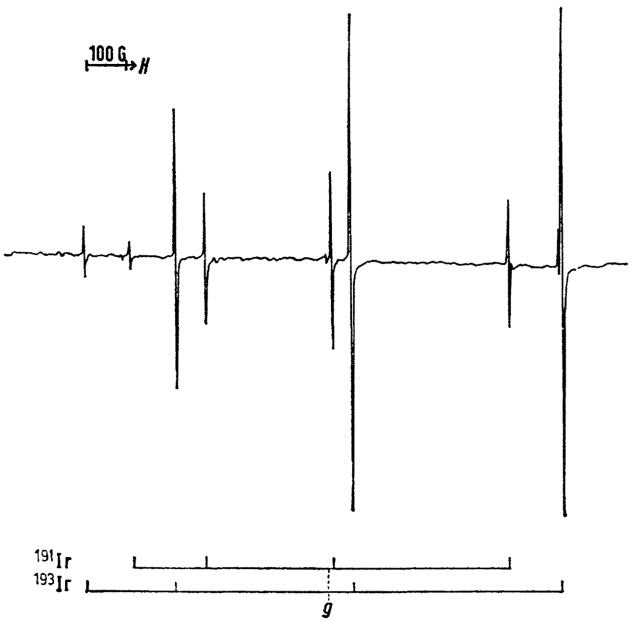

FIGURE 1 E.s.r. spectrum of $K_2[Ir(NO_3)_6]$ in $K_2[Pt(NO_3)_6]$ at 77 K

DISCUSSION

Optical Spectrum.—The lack of intensity data for the optical spectrum makes analysis of the spectrum very difficult. Had intensity data been available, these would have assisted in assigning charge-transfer transitions and some of the transitions associated with the excited sub-shell configuration $t_g{}^4e_g$. Only five of the ten terms of the first excited configuration $t_g{}^4e_g$ are admixed into the ground state. These terms and their energies, relative to the ground state $t_g{}^5$, are as follows: [7]

$$\begin{aligned} E_1 &= \Delta - 3B - C \\ E_2 &= \Delta + 12B - C \\ E_3 &= \Delta + 2B - C \\ E_4 &= \Delta - 5B - 4C \\ E_5 &= \Delta + 3B - 4C \end{aligned} \qquad (1)$$

where Δ is the ligand-field splitting and B and C are the Racah parameters.

The strong absorption at 18 500 cm^{-1} is most probably charge-transfer absorption ($2t_u \rightarrow 3t_g$) since Jorgensen [8] has estimated the optical electronegativities of Ir^{IV} and $(NO_3)^-(\pi)$ as *ca.* 2.4 and 3.0 respectively. The transition $1t_u \rightarrow 3t_g$ (E_c) cannot be assigned with great certainty, but since it is likely to be at least 5 000 cm^{-1} larger than the $2t_u \rightarrow 3t_g$ transition, then it could be at *ca.* 23 500 cm^{-1}. Since the overall number and distribution of bands in $[Ir(NO_3)_6]^{2-}$ is the same as in $[IrCl_6]^{2-}$ and $[IrBr_6]^{2-}$, differing only in their position in the wavenumber scale, then analysis by analogy with the hexahalides is valid. The multiplet of bands between 21 800 and 27 200 cm^{-1} may thus be assigned to transition between spin-orbit levels. Estimates [9] of the ligand-field parameters which fit the optical spectra and compare well with those for related work [10] are as follows: $\Delta = 30\,000 \pm 2\,000$, $B = 300 \pm 50$, $C = 1\,200 \pm 200$ cm^{-1}. Using these values the energies of the excited states E_1 to E_5 are as follows: 27 900, 32 400, 29 400, 23 700, and 26 100 cm^{-1}, respectively.

E.S.R. Parameters.—In the following analysis, we will use the equations for cubic symmetry since the d-orbitals in T_h point-group transform as t_g and e_g with the five d-electrons in t_g. The spin Hamiltonian of the ground-state doublet for Ir^{4+} in a cubic field is given by

$$\mathscr{H} = g\beta H \cdot S + AS \cdot I \qquad (2)$$

The g-tensor. To zeroth order, the value of g is negative and is given by Stevens [11] as:

$$g = -\frac{4k_{\pi\pi} + 2}{3} \qquad (3)$$

However, a large number of excited configurations can be obtained by taking a bonding electron and placing it in one of the empty antibonding orbitals. Furthermore, spin-orbit coupling mixes some of these excited configurations into the ground state. Thornley [7] has shown that these spin-orbit contributions are very significant and are essential for the full analysis of the g and hyperfine parameters. Charge-transfer influences the parameters to a lesser extent. The equation for g then becomes

$$g = -\frac{4k_{\pi\pi} + 2}{3} - \frac{k_{\sigma\pi} 8\zeta_{\sigma\pi}}{3E_1} - \frac{4k_{\sigma\pi}}{E_2}\left(6B + \frac{\zeta_{\sigma\pi}}{3}\right) + \frac{4k_{\sigma\pi}}{E_3}(2B + \zeta_{\sigma\pi}) - \frac{8k_{ab}\zeta_{ab}}{3E_c} \qquad (4)$$

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[6] C. C. Addison and D. Sutton, *J. Chem. Soc.* (*A*), 1966, 1524.

[7] J. H. M. Thornley, *J. Phys.* (*C*), 1968, **1**, 1024.

[8] C. K. Jorgensen, ' Oxidation Numbers and Oxidation States,' Springer-Verlag, Berlin, 1969, p. 146.

[9] C. K. Jorgensen, personal communication.

[10] C. K. Jorgensen, *Mol. Phys.*, 1959, **2**, 309.

[11] K. W. H. Stevens, *Proc. Roy. Soc.*, 1953, **A219**, 542.

where $k_{\pi\pi}$ and $k_{\sigma\pi}$ are orbital reduction factors associated with π and σ bonding orbitals. k_{ab} Is the orbital reduction factor associated with the orbitals involved with charge transfer ($\pi t_g \rightarrow 5dt_g$). $\zeta_{\sigma\pi}$ and ζ_{ab} Are spin-orbit coupling constants between the metal t_g and e_g orbitals and the ligand p and metal d orbitals, respectively. Assuming $k_{\sigma\pi} = k_{\pi\pi}$, $k_{ab} = f_\pi^{\frac{1}{2}}$, where f_π is the covalency parameter (the fraction of transferred electron in each orbital). $\zeta_{\sigma\pi} \approx \zeta'\mathrm{Ir}^{4+} \approx 2\,000$ cm^{-1} (neglecting ζ_{ligand}), where ζ' is the effective spin-orbit coupling constant for the $5d$ electrons of Ir^{4+}.[7] This is a rough value for initial calculations. Furthermore, $k_{\pi\pi} = 1 - 2f_\pi$ and $\zeta_{ab} = 2f_\pi\zeta'$.

Now, substituting $g = -1.12$ and the calculated values of B, E_1, E_2, E_3, and E_c into equation (4), we get $f_\pi = 0.41$ and $k_{\pi\pi} = 0.18$. If this rough value of $k_{\pi\pi}$ is now used to get a better value of ζ' ($= k_{\text{free ion}}$), then the new value of ζ' will equal $0.18 \times 5\,000 \approx 900$ cm^{-1}. Using this value, and recycling the calculation, then final self-consistent values are $\zeta' = 1\,250$ cm^{-1}, $f_\pi = 0.38$, and $k_{\pi\pi} = 0.24$. This compares with $f_\pi = 0.33$ using equations to zeroth-order only. Electron transferences of this magnitude are not common, and represent three times the covalency found in the halogeno complexes.

E.s.r. of Ir$^{\text{IV}}$ octahedral complexes

Species	g	A(Ir)/10^{-4} cm^{-1}	f_π/%	Ref.
$K_2[Ir/PtF_6]$ (trig.)	1.506 (z) 2.042 (x, y)	25.5 (z) 32.3 (x, y)		a
$Cs_2[Ir/GeF_6]$ (cubic)	1.853	27.2	8.1—11.5 [c]	a
$K_2[Ir/PtCl_6]$ (cubic)	1.79			
$[NH_4]_2[Ir/PtCl_6]$ (cubic)	1.786	26.3	8.0—14.1 [c]	a
$Cs_2[Ir/ZrCl_6]$ (cubic)	1.7617	29 [100], 26 [111]		e
$Na_2[Ir/PtCl_6]\cdot 6H_2O$ (tet.)	1.050 (z) 2.168 (x) 2.078 (y)	24.9 (z) 25.5 (x, y)		a
$K_2[Ir/PtBr_6]$ (cubic + dist.)	1.60 (z) 1.87 (x, y)		7.5—14.1 [c,d]	a
$Na_2[Ir/PtBr_6]\cdot 6H_2O$ (tet.)	0.75 (z) 2.25 (x) 2.21 (y)	25.5 (x, y)		a
Ir^{4+} in MgO (cubic)	1.7385	26.7 (^{193}Ir) 25.0 (^{191}Ir)	6.7	b
$K_2[Ir/Pt(NO_3)_6]$ (cubic)	1.12	221 (^{193}Ir) 180 (^{191}Ir)	38	This work

[a] Ref. 7. [b] J. T. Suss, W. Low, and M. Foguel, *Phys. Letters*, 1970, **33A**, 14. [c] The first value deduced from A values, the second from g values, by Thornley, ref. 7. [d] Estimated parameters for cubic symmetry. [e] S. Maniv and A. Gabay, *J. Magnetic Resonance*, 1974, **13**, 148.

The hyperfine tensor. The hyperfine coupling is given by the following expression:

$$2P\left[-\frac{4}{7}+\frac{\kappa}{6}-\frac{4\zeta_{\sigma\pi}}{3E_1}-\frac{16}{7E_2}\left(6B+\frac{\zeta_{\sigma\pi}}{3}\right)+\frac{16}{7E_3}\left(2B+\zeta_{\sigma\pi}\right)-\frac{2\zeta_{\sigma\pi}}{7E_4}+\frac{2\zeta_{\sigma\pi}}{21E_5}-\left(\frac{4}{7}-\frac{\kappa}{6}\right)\frac{2\zeta_{ab}\beta_\pi}{E_c}\right] \quad (5)$$

where β_π is the orbital coefficient of the metal π-bonding molecular orbitals and is taken as 0.6. κ and P Have their usual significance. P Has been calculated [12] using Hartree–Foch calculations of Basch and Gray [13] to be 30.57×10^{-4} cm^{-1}. The sign of the experimental hyperfine splittings is not determined experimentally, and both possibilities are considered. Using positive and negative values respectively, $\kappa = +24.0$ and -16.2. These values are numerically considerably larger than found in earlier work.[14,15] The positive value could imply considerable mixing of s-orbitals with the orbitals containing the unpaired electron. This is not possible in this point group. Alternatively, an inner-shell polarisation mechanism could account for it. The large delocalisation onto the ligands implies that the $5d$ orbital is effectively expanded so that more of the filled $5s$ orbital would be inside the $5d$ orbital thus making κ more negative. However, associated lowering of the effective charge on the metal ion will allow the filled s-orbitals to expand, thus reducing the electron density at the nucleus and hence making κ less negative.[16] κ Could even be positive since it is the difference between large positive and negative numbers associated with contributions from filled $1s$, $2s$, $3s$, $4s$, and $5s$ orbitals. Since κ is known to be positive for the hexahalogenoiridates (*ca.* +6.44 or +1.46 depending upon whether A is positive or negative), then a larger positive value for $[Ir(NO_3)_6]^{2-}$ is entirely reasonable. We thus take A to be positive and $\kappa = +24.0$. Furthermore, A for the hexahalides is also probably positive since κ for the nitrato-complex is nearly four times that for the halogeno-complex (taking $\kappa = 6.44$) and correlates well with the threefold increase in covalency. In the foregoing analysis, numerous assumptions have been made which could alter the value of f_π calculated, although many of the potential errors are self cancelling. One of the most difficult parameters to assess is a suitable value for P. Only one value is available, and this has been used. However, it is known that P varies with actual charge on the metal, and this is difficult to esti-

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[12] B. A. Goodman and J. B. Raynor, *J. Inorg. Nuclear Chem.*, 1970, **32**, 3406.

[13] H. Basch and H. B. Gray, *Theor. Chim. Acta*, 1966, **4**, 367.

[14] J. H. E. Griffiths and J. Owen, *Proc. Roy. Soc.*, 1954, **A226**, 96.

[15] E. Cipollini, J. Owen, J. H. M. Thornley, and C. Windsor, *Proc. Phys. Soc.*, 1962, **79**, 1083.

[16] A. J. Freeman and R. E. Watson in ' Magnetism,' eds. G. T. Rado and H. Suhl, Academic Press, New York, 1965, IIA, p. 168.

mate. Analysis of the metal hyperfine tensor is thus less reliable than analysis of the g-tensor. Nevertheless, it would seem reasonable to conclude that the nitrato-complex is about three times more covalent than the halogeno-complexes, and also that the g-value reduction is perhaps the most reliable indicator of the total covalency. The Table summarises the e.s.r. data for this and related complexes.

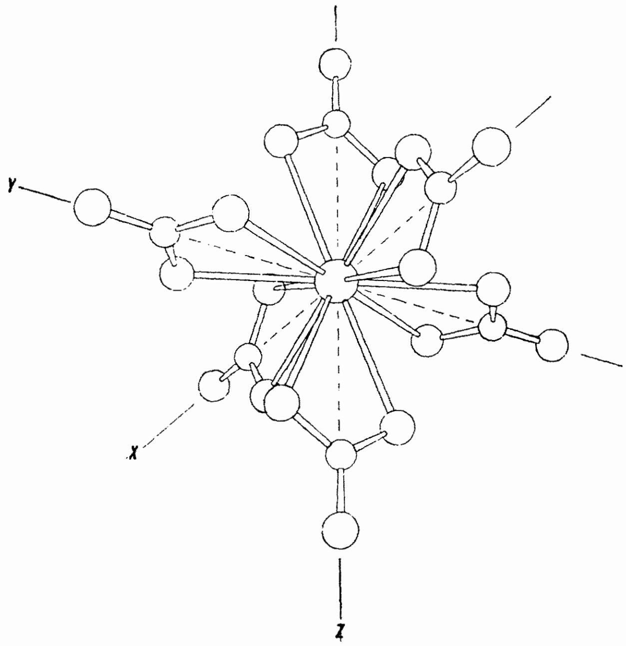

FIGURE 2 Axis notation for $[Ir(NO_3)_6]^{2-}$

Ligand hyperfine tensor. With so much back bonding to the nitrate ligand, the ligand is beginning to resemble NO_3^{2-}. Hyperfine coupling to nitrogen might have been expected and it is perhaps surprising that none is detected. In cubic symmetry for a t_g^5 ground state, the powder spectrum will, however, be isotropic. In NO_3^{2-}, the large isotropic hyperfine coupling arises from a small deformation of the nominally planar ligand (13° out of planarity) which gives some s-character to the orbital containing the electron.[17] Although there is extensive delocalisation in $K_2[Ir(NO_3)_6]$, there is insufficient to cause sufficient bending in the ligand which would lead to a detectable hyperfine coupling to nitrogen because most of the delocalised electron would be on the two oxygens nearest the iridium. Nitrogen hyperfine coupling would probably be observed in a single-crystal study, but such crystals have not yet been isolated.

In concluding the analysis of the e.s.r. parameters, our assumption of cubic symmetry is justified by the isotropic spectrum.[18] Any static distortion would have resulted in an anisotropic spectrum. In fact, in our system of $K_2[Ir(NO_3)_6]$ in a host lattice of $K_2[Pt(NO_3)_6]$, e.s.r. results provide unambiguous evidence for symmetrically bidentate nitrate groups. Since the X-ray powder spectra of $K_2[Ir(NO_3)_6]$ and $K_2[Pt(NO_3)_6]$ show that they are isomorphous, then we conclude that both complexes have symmetrically bonded bidentate nitrates.

Dynamic Jahn–Teller Effects.—The equations and arguments presented above have assumed that the metal is centred exactly in T_h symmetry. Since the ground state has orbital degeneracy (^2T_g), then the system is liable to a Jahn–Teller distortion. However, in a cubic system, with a T_g ground state, any distortion is going to be small. Whether or not the distortion is static or dynamic depends upon the relative magnitudes of the zero point energy of the associated vibrations and the energy barrier separating equivalent configurations. Since our e.s.r. spectrum is isotropic at 77 K, then any distortion is not static, and we must consider the possibility of a dynamic Jahn–Teller effect. As Ham[19] has shown, it is possible to get a small but significant

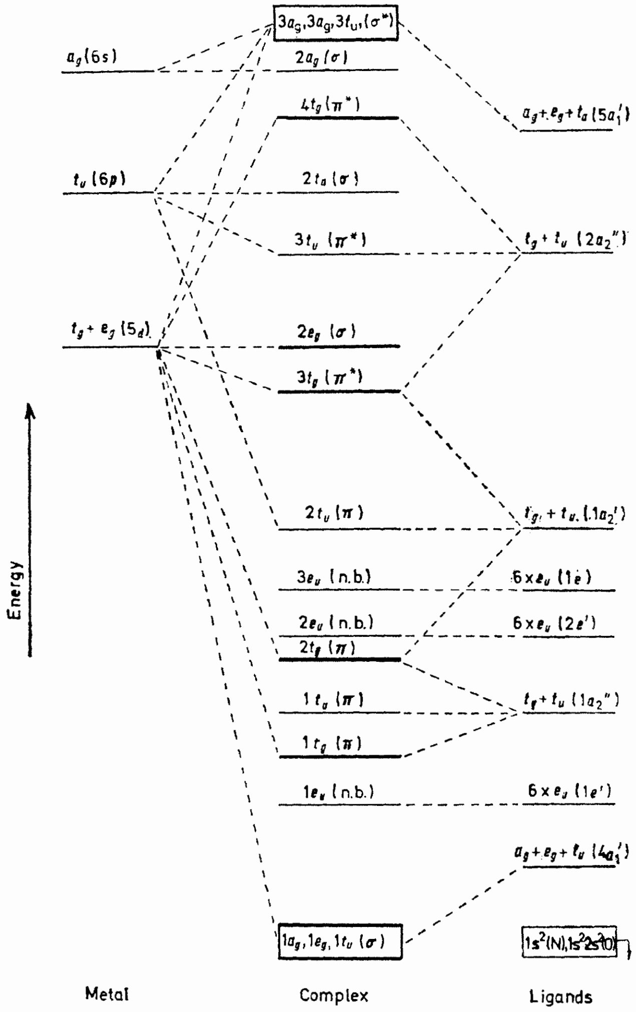

FIGURE 3 Qualitative molecular-orbital energy-level diagram for $[M(NO_3)_6]^{n-}$ with T_h point group

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[17] P. W. Atkins and M. C. R. Symons, *J. Chem. Soc.*, 1962, 4794.

[18] A. Abragam and B. Bleaney, 'Electron Paramagnetic Resonance of Transition Metal Ions,' Clarendon Press, Oxford, 1970, p. 481.

[19] F. S. Ham, *Phys. Rev.*, 1965, **138A**, 1727.

quenching of both spin and orbital angular momenta with a net effect upon the *g*-factor similar to that caused by covalency. Thus the measured value of the orbital reduction factor *k* can include contributions due to both covalency and the dynamic Jahn–Teller effect. The result is that the actual covalency may be less than that calculated using the equations of Thornley. The effects cannot be separated with the available experimental data. It is possible that the very narrow linewidths observed arise from inefficient spin-lattice relaxation associated with the dynamic Jahn–Teller effect.

Whilst this effect may modify the amount of π-backbonding described above, it does not invalidate the general conclusion that considerable π-backbonding is present in the ion.

The Bonding in $[Ir(NO_3)_6]^{2-}$.—In order to give a realistic picture of the bonding between the metal and the symmetrically bidentate nitrate groups, we must consider the molecular orbitals formed between metal atomic orbitals and the nitrate molecular orbitals of appropriate symmetry. The nitrate molecular orbitals have been given by Walsh.[20] We consider each in turn and see how they transform in T_h symmetry in $M(NO_3)_6$. Figure 3 is a qualitative molecular-orbital diagram where the ligand molecular orbitals are given in increasing order of energy. Their symmetry in T_h point group is given, together with their local symmetry in D_{3h} point group. Orbitals with symmetry e_u are non-bonding; so also are the $1t_u(\pi)$, $2t_u(\pi)$, $3t_u(\pi)$, and $2t_u(\sigma)$ since the amount of overlap between the appropriate metal and the ligand orbitals is negligible. We are thus left with a set of deep seated σ-bonding molecular orbitals ($1a_g$, $1e_g$, $1t_u$) and the corresponding set of σ-antibonding molecular orbitals ($3a_g$, $3e_g$, $3t_u$). The only other molecular orbitals to be considered are the $1t_g$ and $2t_g$ π-bonding and the $3t_g$ and $4t_g$ π-antibonding molecular orbitals. Figure 4 gives a pictorial representation of some of these molecular orbitals.

It is immediately apparent that the σ-bonds consist of three-centre bonds between the metal and two oxygen atoms. The same is true of the π-bonds: the $1t_g$ and $2t_g$ molecular orbitals are filled and represent the π-bonding between the metal and two oxygen atoms on each nitrate group and are also three-centre. In the case of Ir^{IV}, the five extra electrons are in the $3t_g$ molecular orbital which is largely π^* and has considerable ligand character. Hence it is not surprising that e.s.r. results show that up to two electrons are delocalised onto the ligands.

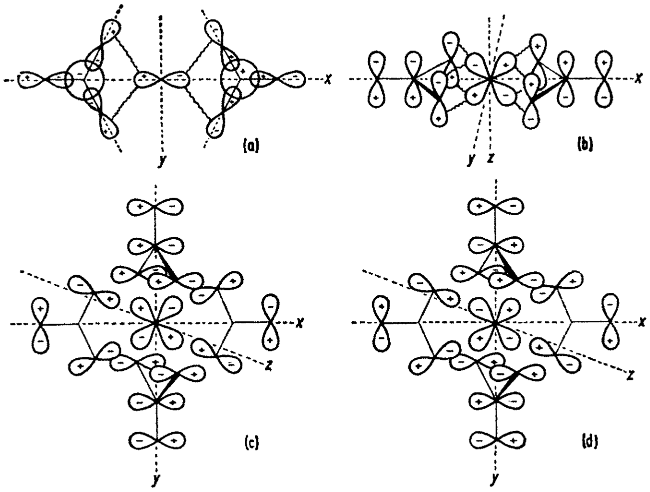

FIGURE 4 Representation of some of the molecular orbitals in $[M(NO_3)_6]^{n-}$: (a) $1t_u$ (σ), showing a metal p_x orbital interacting with ligand $4a_1'$ orbitals in the *xy* plane; (b) $1t_g$ (π), showing a metal d_{xz} orbital interacting with ligand $1a_2''$ orbitals in the *xy* plane; (c) $2t_g$ (π), showing a metal d_{xy} orbital interacting with ligand $1a_2'$ orbitals in the *xy* plane along the *x*-axis and $1a_2''$ orbitals in the *yz* plane along the *y*-axis; (d) $3t_g$ (π^*), showing a metal d_{xy} orbital interacting with ligand $1a_2'$ orbitals in the *xy* plane along the *x*-axis and $2a_2''$ orbitals in the *yz* plane along the *y*-axis.

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[20] A. D. Walsh, *J. Chem. Soc.*, 1953, 2301.