New Nitrato-complexes, $M_2Ir(NO_3)_6$ (M=K, Rb, Cs) and $K_2Pt(NO_3)_6$, with Extensive Metal–Nitrate π-Bonding

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Summary New anhydrous hexanitrato-complexes of iridium(IV) and platinum(IV) have been prepared; e.s.r. measurements on $K_2Ir(NO_3)_6$ reveal a remarkably high ($f_\pi = 0{\cdot}38$) degree of iridium–nitrate π-bonding.

As part of a broad investigation[1] of the nitrate chemistry of iridium, the hitherto unknown series of alkali metal hexanitratoiridate(IV) salts, $M_2Ir(NO_3)_6$ (M = K, Rb, Cs), has been prepared from reactions of the corresponding hexabromoiridates(IV), M_2IrBr_6, with dinitrogen pentoxide. The analogous diamagnetic platinum salt, $K_2Pt(NO_3)_6$, has also been synthesised for the first time by a similar routes The complexes were characterised by analysis,‡ i.r. spectroscopy [the nitrate bands of $K_2Ir(NO_3)_6$ (1571s.b, 1545sh, 1265s.b, 931sh, 901s.b, 805m.sp, 793m.sp, 784m.sp, 770sh, 764m.sp, 741m.sp, 726m.sp, and 712m.sp, cm^{-1}) are typical and indicate that all the nitrate groups are bonding nominally in a bidentate fashion as observed[2,3] for $Ce(NO_3)_6^{2-}$ and $Th(NO_3)_6^{2-}$ which are of overall T_h symmetry] and *X*-ray powder diffraction [which shows that $K_2Ir(NO_3)_6$ and $K_2Pt(NO_3)_6$ are isomorphous]. The effective magnetic moments of the $M_2Ir(NO_3)_6$ salts at 299 K (M = K, 1·83; M = Rb, 1·88; M = Cs, 1·52 B.M.) are consistent with the expected low spin d^5 configuration of iridium(IV); detailed interpretation of these values will be attempted elsewhere.

The complex $K_2Ir(NO_3)_6$ is the nitrato-analogue of K_2IrCl_6, the e.s.r. data of which provided the original experimental evidence for π-interaction between a metal and a ligand.[4] Until now, little has been known quantitatively of the π-bonding capability of the nitrate ligand, and our e.s.r. measurements on $K_2Ir(NO_3)_6$ have now yielded significant information in this context.

The e.s.r. powder spectrum of a solid solution of $K_2Ir(NO_3)_6$ in $K_2Pt(NO_3)_6$ at 77 K consisted of two quartets of isotropic narrow lines (width 2—3 G) arising from interaction of the unpaired electron with the two magnetic nuclei of Ir (both have $I = \frac{3}{2}$) centred on $g = 1{\cdot}12$ and with $A(^{191}Ir) = 180 \times 10^{-4}\ cm^{-1}$ and $A(^{193}Ir) = 221 \times 10^{-4}\ cm^{-1}$ (after correction to second order). Analysis of the *g*-value using the equations of Thornley[5] yielded $f_\pi = 0{\cdot}38$. These

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‡ Satisfactory elemental analyses were obtained.

equations are valid despite the apparent reduced symmetry since in a T_h ligand field the *d*-orbitals split in the same way as for an O_h field. The low *g*-value is consistent with this large value of f_π and with the measured magnetic moment. The hyperfine coupling is surprisingly high (about eight times that found[4] in $IrCl_6^{2-}$). This is because the effect of the large delocalisation of the *d*-orbitals containing the unpaired electron alters the extent of polarisation of filled inner *s*-orbitals relative to each other in such a way as to make a dramatic change in A(Ir).[6] The argument is complex and lengthy, and will be presented in full elsewhere.

This large amount of π-bonding is equivalent to a net back-bonding of 1·9 electrons into the $2a_2^{n}(\pi^*)$ orbitals on the six NO_3^- (almost three times the π-bonding found[5] in K_2IrCl_6 where $f_\pi = 0{\cdot}14$) which in turn may cause some deformation of the nitrate ligand. Similar effects presumably occur in the diamagnetic platinum analogue.

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