Nature of the '$[Ir(bpy)_2(H_2O)(bpy)]^{3+}$' (bipy = 2,2'-bipyridine) Cation. Monodentate or Covalently Hydrated Bipyridine Ligand? *X*-Ray Crystal Structure of the Perchlorate Salt

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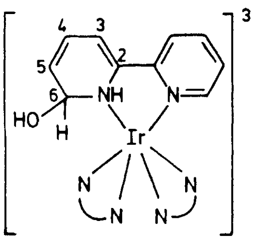
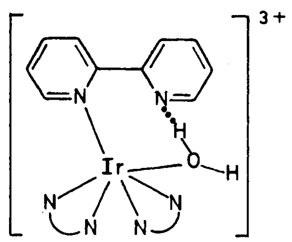
Summary A single-crystal *X*-ray structural study of the ClO_4^- salt of the title cation demonstrates that this species contains *neither* a monodentate *nor* a covalently hydrated bipyridine ligand; all three bipyridine ligands are chelated to iridium(III) but one bipyridine ligand is ligated *via* the nitrogen of one ring and the C(3) carbon of the other ring, reminiscent of orthometallated compounds.

THE nature of the compound(s) containing three 2,2'-bipyridine (bpy) ligands per iridium atom has been the subject of a controversial debate[1–5] since the first report by Flynn and Demas[6] of the successful preparation of the $[Ir(bpy)_3]^{3+}$ cation. This species was formulated to have all three bipyridine ligands ligated to iridium(III) *via* the nitrogen atoms as shown by ^{13}C n.m.r. spectroscopy (D_3 symmetry; *five* well resolved ^{13}C resonances). Later, Watts and his co-workers[1] identified another complex also containing three bipyridine ligands per Ir but having distinct absorption and emission spectral properties, as well as different photophysical characteristics (*e.g.* pH titration of the emission) from $[Ir(bpy)_3]^{3+}$. Of the various possibilities, including a six-co-ordinate Ir^{III} bound to two bidentate bpy ligands and one 'covalently hydrated' bpy, complex (**1**),[4]



(1)



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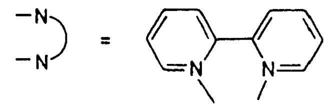

the complex was described[2] as a six-co-ordinate Ir^{III} bound to two (bidentate) bpy ligands, one monodentate bpy, and one water molecule, complex (**2**). The appearance of an immonium N–H stretching band in the i.r. spectrum (ν 2650 cm^{-1}) of the acidic form of (**1**) or (**2**), and the disappearance of the band in the basic form were cited[1] as evidence for such a formulation. One source of the controversy about the composition of the title compound in solution appears to rest on the ^1H n.m.r. spectrum which consists (in $[^2H_6]$-dimethyl sulphoxide) of broad multiplets at δ *ca.* 9·2, 8·4, and 7·8 [*vs.* $SiMe_4$] in addition to a doublet at δ 6·65 and a doublet of doublets at δ 7·14.[3–5] Gillard and his co-workers[4] interpreted this as evidence for the existence of a covalent hydrate and assigned the δ 6·65 doublet to the proton on the tetrahedral carbon C(6) of (**1**). In contrast, the two upfield multiplets are absent in DCl–D_2O solutions;[5] also, the completely proton-decoupled ^{13}C n.m.r. spectrum consists of 25 peaks in the region 120—160 p.p.m. downfield from $SiMe_4$ and no other resonance appears upfield of 120 p.p.m.[5] where signals from covalently hydrated carbon atoms are expected to be found.[7] These data preclude the existence of (**1**) and were taken as being consistent with (**2**).[5] This debate has led us to investigate the detailed nature of the title compound in the solid state as part of our systematic studies into the behaviour of polypyridyl complexes.

A crystal of the perchlorate salt of the title cation with dimensions 0·3 × 0·2 × 0·2 mm was chosen for this study. *Crystal data:* monoclinic, space group $P2_1/c$; $a = 16{\cdot}619(10)$, $b = 16{\cdot}200(6)$, $c = 13{\cdot}550(6)$ Å, $\beta = 108{\cdot}74(4)°$; $Z = 4$ for $[Ir(bpy)_2(Hbpy)]\,(ClO_4)_3{\cdot}H_2O$, $D_c = 1{\cdot}88$, $D_m = 1{\cdot}86$ g cm^{-3} (by flotation). Of the 3218 reflections collected, 2376 reflections with $I > 3\sigma(I)$ were used to solve the structure by Patterson methods and Fourier techniques. Block-diagonal matrix, least-squares refinement of all non-hydrogen atoms with anisotropic thermal parameters reduced the final discrepancy index to 4·4%.†

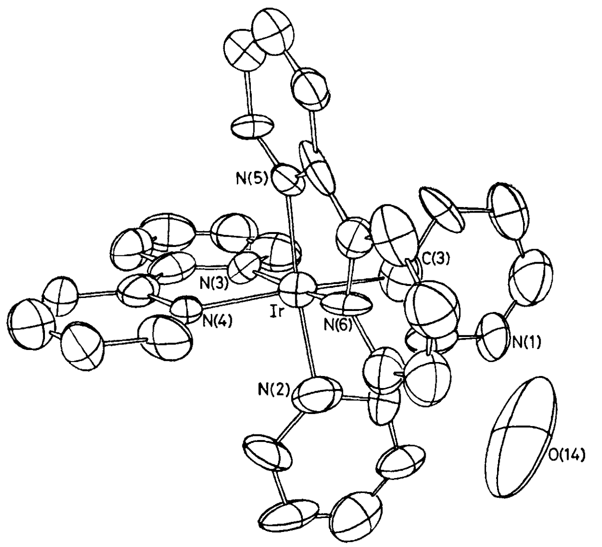

FIGURE. Structure of the $[Ir(bpy)_2(Hbpy)]^{3+}$ cation with the water molecule; the ClO_4^- anions have been omitted for clarity.

The structure of the Λ enantiomer of $[Ir(bpy)_2(Hbpy)]^{3+}$ with the water molecule is shown in the Figure. The structure about iridium consists of three *chelated* bipyridine ligands but, as noted below, one of the bpy ligands is bound *via* a carbon atom; the mean iridium–ligand donor atom distance is 2·05(4) Å. Intraligand N–Ir–N angles range from 78·2 to 80·8°, comparable to bond angles in $Cu(bpy)_3^{2+}$ and $Cu(phen)_3^{2+}$ (ref. 8) (phen = 1,10-phenanthroline), and $Cu(terpy)_2^{2+}$ (ref. 9) and $Cr(terpy)_2^{3+}$ (ref. 10) (terpy = 2,2′,2″-terpyridine), but slightly smaller than those found in $Fe(phen)_3^{2+}$ (82·9°).[11] There are seven ClO_4^- anions about the $[Ir(bpy)_2(Hbpy)]^{3+}$ cation within 3·1–3·3 Å of a non-hydrogen atom. Six of these ClO_4^- ions have oxygens wedged in pockets in the structure such that in the solid state the cation and ClO_4^- form tight ion-pairs.[10]

Several features of the full structure are noteworthy. First, there is *no* evidence for a monodentate bipyridine ligand in the structure. Also, there is *no* evidence for a covalently hydrated bipyridine ligand; the closest approach of the water oxygen to a bipyridine non-hydrogen atom is 2·75 Å, about 1·3 Å longer than the expected C–O distance (*ca.* 1·4 Å) if a carbon atom were covalently hydrated. The water oxygen is also 2·56 Å from a ClO_4^- oxgen and 3·03 Å from the nearest non-hydrogen atom of the other pyridyl ring of the same bpy ligand. These distances indicate that the water molecule is hydrogen bonded not only to the ClO_4^- anion[10] but also to a bipyridine ring atom.

It is difficult to reconcile these data with those that have caused the controversy over the nature of the title compound, if the bipyridines were all ligated *via* the nitrogen donor atoms, since the compound we have studied behaves in solution[1,2,12] differently from the tris-NN′-chelated $[Ir(bpy)_3]^{3+}$ cation. However, the data of Watts,[1,2] DeArmond,[3] and Gillard[4] can be understood if one pyridyl ring of a bpy ligand were bonded to iridium *via* the C(3) carbon as in structure (**3**), shown in the protonated form

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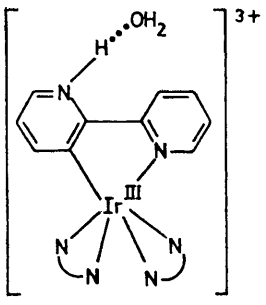
† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



(3)

(pK 3·0[1]). This is not unreasonable since iridium[13] and other metals[14] are known to form cyclometallated species with organic substrates, and also in view of the conditions used[1,3,4] to prepare the complex. The appearance of the i.r. band at 2650 cm^{-1} is consistent with an N–H stretching band in (**3**). Observation of only one pK value (3·0[1]) and one pK^* value (3·5[2]) is in keeping with the expectation for (**3**). Of particular importance, it is clear that a ^{13}C n.m.r. spectrum of (**3**) would show more than five ^{13}C resonances[5] and also that (**3**) would have a more complicated ^{1}H n.m.r. spectrum[3–5] than the simple tris-NN′-chelated $[Ir(bpy)_3]^{3+}$ cation. Additionally, the observed N–O distance of 2·75 Å is symptomatic of hydrogen bonding between the water molecule and the nitrogen atom.[15] This is reminiscent of the tightly held water molecule in the hydrates of 2,2′-bipyridine and 1,10-phenanthroline.[16] We wish to point out that our X-ray data do not identify the interchanged C(3) carbon and nitrogen atom; only the hydrogen-bonded water molecule (Figure) affords the clue as to the position of the unco-ordinated free nitrogen. Also, our data do not exclude the possibility that the iridium may be bonded to both C(3) and C(3′) carbons of the bipyridyl ligand.

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