Equilibria in Complexes of *N*-Heterocyclic Molecules. Part 18.† A Covalently Hydrated Iridium(III) Complex, Bis(2,2′-bipyridyl)(2,2′-bipyridyl–water)iridium(III) Trichloride Trihydrate

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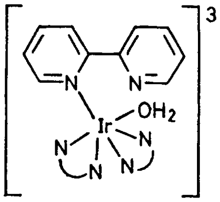
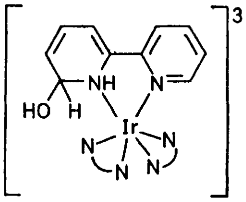
The compound $Ir(bipy)_3Cl_3{\cdot}4H_2O$ which had been previously suggested to contain a unidentate bipy ligand has now been shown by ^1H n.m.r. spectroscopy to contain the covalently hydrated complex cation $[Ir(bipy)_2(bipy{\cdot}H_2O)]^{3+}$. The site of attack at the pyridyl ring is discussed, as is the synthesis of several related iridium(III) complexes.

WHILE ligands such as 1,2-diaminoethane form[1-4] complexes in which they may behave either in a uni- or bi-dentate fashion, 2,2′-bipyridyl almost always displays bidentate bonding, not including bridging behaviour. In reactions involving the dissociation of one or more bipy ‡ ligands from a metal ion the bipy must be present as a unidentate ligand for at least a short time, but attempts to isolate complex compounds containing bipy in this configuration have been[5,6] unsuccessful. Recently, however, the preparation of a complex of bipy with Ir^{III} has been reported,[7] in which it was suggested that one bipy is a unidentate with the usual octahedral co-ordination sphere of Ir^{III} being completed by the oxygen atom of a water molecule as in (1). An alternative formulation such as (2) in which the water molecule is added across one of the bonds in a pyridyl residue was ruled out. Since we have previously found[8] that complexes like (2) are important in the chemistry of complex compounds of phen and bipy, it seemed worthwhile to investigate further the nature of the iridium(III) complex.



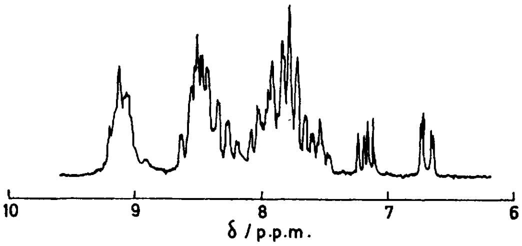
(1)



(2)

EXPERIMENTAL

The compound of stoicheiometric formula $Ir(bipy)_3(H_2O)_4Cl_3$ was made according to the published method[7] as far as was possible. This method of synthesis is discussed in greater detail in the next section. The yellow crystalline solid was dried *in vacuo* over silica gel (Found: C, 42.6; H, 3.7; N, 10.4. Calc. for $C_{30}H_{32}Cl_3IrN_6O_4$: C, 42.9; H, 3.8; N, 10.0%). The emission spectrum of the compound dissolved in 0.1 mol dm^{-3} HCl, recorded using a Perkin-Elmer MPF-4 instrument, and the absorption spectrum in the same solvent, recorded with a Beckman DK-2A ratio-recording spectrophotometer, were, within experimental error, the same as those reported by Watts *et al.*[7] Those workers do not give full i.r. details but do mention selected bands at 2 650s, 1 600vs, 1 310s, 1 292s, 1 274m, and 1 243s cm^{-1} for the compound. The grouping of the four bands between 1 320 and 1 240 cm^{-1} was, according to them, unique in a wide range of complexes by bipy with Ir^{III}. Using a Perkin-Elmer 257 grating i.r. spectrometer calibrated against polystyrene, the compound we have prepared gives four bands in this region at 1 311s, 1 292s, 1 275m, and 1 246s cm^{-1}. The light yellow perchlorate salt obtained by metathesis of the parent compound with propanolic $HClO_4$ gives four absorptions at 1 311s, 1 293s, 1 275m, and 1 244s cm^{-1}. The analytical figures together with all these results compel us to conclude that the compound we have obtained is identical to that previously reported. 100-MHz ^1H n.m.r. spectra were obtained with a Varian XL-100 pulsed Fourier-transform spectrometer with a ^2H lock at 35 °C.



100-MHz ^1H n.m.r. spectrum of $[Ir(bipy)_2(bipy{\cdot}H_2O)]^{3+}$ in $S(CD_3)_2O$ at 35 °C. The trace shown is the result of 272 accumulations

The salt $[Ir(bipy)_2Cl_2]Cl$ was prepared using the method of Martin and Waind[9] which was originally supposed to yield $Ir(bipy)_3Cl_3$. The compound made, which has the *cis* configuration,[10,11] gave an ^1H n.m.r. spectrum in $S(CD_3)_2O$ solution identical to that reported[11] previously.

RESULTS AND DISCUSSION

The 100-MHz ^1H n.m.r. spectrum of the compound is shown in the Figure. The spectrum is considerably different from that of a conventional tris(2,2′-bipyridyl)-metal complex which possesses D_3 symmetry, such as $[Ru(bipy)_3]^{2+}$. The most outstanding feature of the present spectrum is the appearance at higher field of a doublet and of a doublet of doublets coupled to it at 6.65 and 7.14 p.p.m. respectively. In free py, the signal at highest field is that of the β-proton[12] (7.27 p.p.m. in CCl_4) and the α doublet is observed at 8.57 p.p.m. A

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† Part 17, W. S. Walters, R. D. Gillard, and P. A. Williams, *Austral. J. Chem.*, in the press.

‡ bipy = 2,2′-Bipyridyl, phen = 1,10-phenanthroline, py = pyridine, $5NO_2$-phen = 5-nitro-1,10-phenanthroline.

similar set of results has been reported for free bipyridyl.[13] The highest-field signals are those of the 5- and 5'-protons which occur at 7.12 and 7.35 p.p.m. in CCl_4 and MeOH respectively. The 6,6' doublet is observed at 8.59 and 8.64 and the 2,2' doublet at 8.50 and 8.31 p.p.m. In complexes of phen and bipy with more than one ligand some or all of the protons α to nitrogen may be ring-shielded.[14] For example, in *cis*-$[Ir(bipy)_2Cl_2]^+$ the resonance for the shielded protons occurs[11] at 7.85 p.p.m. In tris complexes the frequencies for the shielded protons vary somewhat but are never higher than 7 p.p.m. A system comparable to the present one is the $[Os(bipy)_3]^{2+}$ cation whose 6- and 6'-protons are observed[11] at 7.52 p.p.m. It has also been stated[15] that the ^1H n.m.r. spectrum of $[Ir(bipy)_3]^{3+}$ 'strongly resembles the spectra of $[Os(bipy)_3]^{2+}$ and $[Fe(bipy)_3]^{2+}$' although the chemical shifts in that study were not quoted. The signal observed as a doublet for the present $[Ir(bipy)_3(OH_2)]^{3+}$ complex at 6.65 p.p.m. is at much higher field than for any of these complexes or for the free ligands.

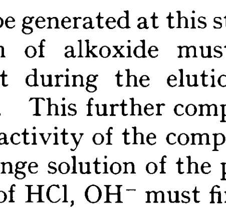
The spectrum indicates then that unidentate bipy is not present and in fact fits the formulation (2) of a covalently hydrated complex. In the only other ^1H n.m.r. study of a covalently hydrated metal complex of the bipy ligand,[16] the signal due to the proton at the newly tetrahedral carbon atom was observed at 6.77 p.p.m. However, in the related pseudo-base compounds of $5NO_2$-phen, signals at[17] 6.48 (OMe^- attack at the ligand) and[18] 6.5 p.p.m. (OH^- attack at the ligand) are observed.

Watts *et al.*[7] in their initial paper on the nature of this compound systematically eliminated all the possible stereochemistries except those shown in (1) and (2). Their final choice was made on the basis of the fact that, when $[Ir(bipy)_3(OH_2)]^{3+}$ is dissolved in aqueous acid and base, different emission spectra are obtained whereas when $[Ir(bipy)_3]^{3+}$ is dissolved in acid and base the same emission spectrum is obtained but is different to the former two. As a result they concluded that there was no evidence to support a 'facile equilibrium between the tris complex of Ir^{III} and a covalent hydrate.' This statement is undoubtedly correct. However, because there is no *facile* equilibrium, it is not to say that no equilibrium exists. Furthermore, the existence in some contexts of $[Ir(bipy)_3]^{3+}$ in the covalently hydrated form (2), $[Ir(bipy)_2(bipy{\cdot}H_2O)]^{3+}$, clearly explains some of the puzzling features of the compound.

The appearance of the band at 2 650 cm^{-1} in the i.r. spectrum of $[Ir(bipy)_2(bipy{\cdot}H_2O)]Cl_3{\cdot}3H_2O$ is consistent with the N–H stretch of the covalent hydrate. One strong piece of evidence in relation to this is the fact that no evidence for the diprotonated $[Ir(bipy)_2(OH_2)(Hbipy)]^{4+}$ complex could be found[7] at pH as low as 0. A single pK_a value was obtained (3.0 ± 0.1) whereas for the complex $[Ir(bipy)_2(OH_2)_2]^{3+}$ two pK_a values were found as expected. The covalently hydrated complex is expected to show only one pK_a value which we attribute to deprotonation at the N–H of the covalent hydrate.

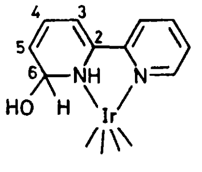
That the compound $Ir(bipy)_2(bipy{\cdot}H_2O)Cl_3{\cdot}3H_2O$ should be ***kinetically*** of different stability to $[Ir(bipy)_3]^{3+}$ may not be too surprising considering the complicated method by which the covalent hydrate species was prepared. In fact it is not possible to prepare the compound exactly as outlined in the experimental section of the study of Watts *et al.*[7] After passing the reaction mixture on to a column of Sephadex LH-20 prepared with 0.01 mol dm^{-3} methoxide in MeOH, the column is eluted with this same solvent. On the basis of the known[17] reaction of OMe^- at the ligand in $5NO_2$-phen complexes of Ru and with bipy complexes of Pt,[19] reaction with the iridium(III) complex at this stage is impossible to discount. The methanolic methoxide solution of the product (which is eluted *first* from the column) is evaporated to dryness and then dissolved in the minimum volume of boiling propan-1-ol which is 0.01 mol dm^{-3} in Na(OMe). This procedure is not possible to follow since an excess of Na(OMe) is present when the methanol is removed from the eluate. Propoxide must also be generated at this stage. In addition, the concentration of alkoxide must be considerably greater than that during the elution because of the volumes involved. This further complicates the picture with respect to reactivity of the complex towards OMe^-. When the hot orange solution of the product is acidified with a few drops of HCl, OH^- must first be generated as the alkoxide is destroyed and it may be at this point that the covalent hydrate is formed. It is also possible that a reactive intermediate is generated in the initial reaction. An interesting result is that when crude $[Ir(bipy)_2Cl_2]Cl$ obtained from the preparative method in ref. 9 is treated in the same fashion as the product of Watts *et al.* from the cation-exchange column, a small amount of covalent hydrate is formed. This suggests that the orange impurity in the crude $[Ir(bipy)_2Cl_2]Cl$ is an iridium(III) species which contains three bipy ligands per mol of Ir as was originally suggested.[9]

Unfortunately, the site of attack at the bipy ligand cannot be unambiguously assigned from the proton resonances. We were able[16] to do this with $Pt(bipy)(CN)_2{\cdot}H_2O$, (3), since the high-field peak was strongly coupled to the platinum atom. In square-planar complexes of phen and bipy the hydrogen atoms α to nitrogen are the most deshielded indicating that, on the basis of charge, the 6- and 6'-carbon atoms are the ones most susceptible to nucleophilic attack. As has been mentioned above, in octahedral complexes the picture is somewhat different. Three possible structures, (4)—(6),



(3)

can be envisaged for the attack of one water molecule at the complex to form the $[Ir(bipy)_2(bipy{\cdot}H_2O)]^{3+}$ cation. Attack at C^3 or C^5 can be excluded since the remaining proton must be at the nitrogen in order to explain the observed i.r. and acid-base data and results. For (4) the high-field doublet arises from H^6 and the high-field doublet of doublets from H^5. The doublet of doublets at 7.14 p.p.m. would be assigned to H^4 in structure (5) where attack at the ring is *para* to the co-ordinating nitrogen atom, and the doublet at high field to H^3. For the formulation (6), the high-field doublet is assigned to H^3 again and the doublet of doublets to H^4. On the basis of charge, the partial formula (4) would appear to be unlikely since the H^6 atoms are among the most shielded in octahedral complexes of this type. However, this simplistic view may not represent the electrophilicity of the carbon atoms involved. The carbon atoms attacked by OMe^- in $[Ru(5NO_2\text{-phen})_3]^{2+}$ are not those which are also bonded to the hydrogen atoms whose signals appear at lowest field.



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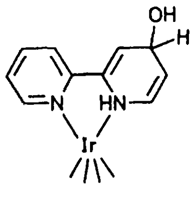

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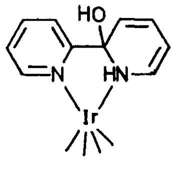

(6)

Both upfield signals integrate for one proton each while the complex signal group, arising from the C^3 protons, centred around 9.1 p.p.m. accounts for only five protons. The lowest-field signal of the next group of signals at 8.7 p.p.m. is not that of the missing H^3 proton since decoupling this signal collapses the doublets of doublets at 7.14 p.p.m. to a doublet whose coupling constant corresponds to that of the doublet at 6.65 p.p.m. The signal at 8.7 p.p.m. is thus the second triplet of the water-attacked ring. This assignment seems to rule out structure (5) because H^5 would have to be shifted downfield by *ca.* 100 Hz on attack at the ring. Of the remaining two possibilities, (6) has the same assignment as (5) and hence the above argument applies here also. Additionally, in this case H^3 must be assigned to the 6.65 p.p.m. doublet which seems shifted to an unusually high-field position. Therefore, although C^6 does not bond to the most deshielded proton, it appears that structure (4) best fits the decoupling experiments that could be undertaken, given the spectral complexity.

Finally, Watts *et al.*[7] have also noted in the i.r. spectrum of *cis*-$[Ir(bipy)_2(OH_2)_2]^{3+}$ an iminium N–H stretch at 2 650 cm^{-1}. They supposed that this also was due to the presence of a unidentate bipy moiety in this complex cation, at least in part. On the basis of our findings, however, it seems more likely that this complex is also covalently hydrated, although possibly to a different extent compared with the $[Ir(bipy)_2(bipy{\cdot}H_2O)]^{3+}$ ion. We shall report the results of a study on this and other related complexes of Ir^{III} in the near future.

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