Experimental Section

$[Ir(bpy)_3](BF_4)_3$ was prepared by following a published method for $[Ir(bpy)_3](NO_3)_3$,[14] except that fluoroboric acid replaced nitric acid in the later stages, and the compound was then chromatographed repeatedly on Sephadex LH-20 as previously described.[15] The analytically pure product (λ_{max} 32 200 cm^{-1}, $\epsilon = 4.5 \times 10^4$ L mol^{-1} cm^{-1}, was checked by voltammetry (group of three equally intense reductions) and ^{13}C NMR (five resonances only) and showed no trace of the very common and persistent byproduct "hydroxytris(bipyridyl)iridium(III)"[16] ($\lambda_{max} = 32\,500$ cm^{-1}, $\epsilon = 3.6 \times 10^4$ L mol^{-1} cm^{-1}) or any other impurity.

Spectroelectrochemical data were collected as before,[1,6] by using a Metrohm E506 potentiostat and an OTTLE cell located directly in the beam of a Beckman 5270 spectrophotometer.

Acknowledgment. We thank Napier College of Commerce and Technology, Edinburgh, for access to this spectrometer, Johnson Matthey for a generous loan of iridium salts, and the SERC for financial support.

Registry No. II^{3+}, 16788-86-6; II^{2+}, 71818-70-7; II^{+}, 91549-50-7; II^0, 91549-51-8.

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Contribution from the Departments of Chemistry,
University of Glasgow, Glasgow G12 8QQ, U.K., and
University of Edinburgh, Edinburgh EH9 3JJ, U.K.

Solution Structure and Properties of the (2,2′-Bipyridinyl-C^3,N')bis(2,2′-bipyridine-N,N')iridium(III) Hydrate Ion, "Pseudo-$[Ir(bpy)_3(OH)]^{2+}$"

Paul S. Braterman,[†] Graham A. Heath,*[‡] Alan J. MacKenzie,[‡]
Brian C. Noble,[†] Robert D. Peacock,*[†] and Lesley J. Yellowlees[‡]

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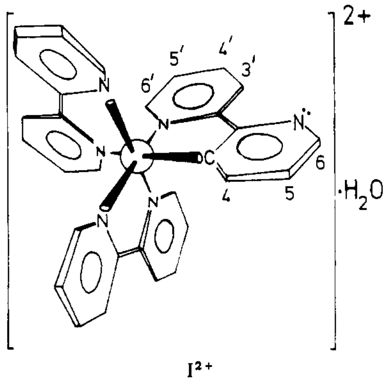
We report here comprehensive spectroscopic and electrochemical evidence that the pseudo-hydroxytris(2,2′-bipyridine)iridium(III) dication (I^{2+}) should be formulated with a 2,2′-bipyridinyl(1−)-C^3,N' ligand.



I^{2+}

The species "$[Ir(bpy)_3 \cdot H_2O]^{3+}$" ($I \cdot H^{3+}$) has properties very different from those of $[Ir(bpy)_3]^{3+}$, including reversible deprotonation to I^{2+}.[1] Both coordinatively aquated (with one monodentate bpy) and "covalently hydrated" structures have been advanced.[2] Recently, however, $I \cdot H^{3+}$ was suggested with considerable insight to be related to $[Ir(bpy)_3]^{3+}$ by rotation, ortho C-metalation (displacing H^+), and N-protonation of a single aromatic ring, accompanied by H-bonded association of H_2O.[3]

Table I. H^1 NMR Assignments for the C-Metalated Ring[a-c]

solvent	H_4	H_5	H_6
Me_2SO-d_6	6.60	7.09	8.44
Me_2CO-d_6	6.85	7.10	8.47
MeOH-d_4	7.33	7.52	8.70

[a] All δ values recorded at 360.13 MHz. [b] In MeOH, $J_{4,5} = 7.8$, $J_{5,6} = 5.3$, and $J_{4,6} = 1.3$ Hz. [c] Four further solvent-sensitive multiplets (at δ 7.66, 8.23, 8.37, and 8.73 in MeOH-d_4) complete the assignments to the unique ligand for $H_{5'}$, $H_{6'}$, $H_{4'}$, and $H_{3'}$, respectively.

Uncertainties remain because of the following: (i) Exact Ir/*o*-phenanthroline analogues of I^{2+} and $I \cdot H^{3+}$ have been reported,[4] although the suggested rearrangement is impossible for this rigid ligand. (ii) While the low-resolution X-ray data of $I \cdot H^{3+}$ establish that all three bipyridyl ligands are chelated and roughly planar, the identities of the donor atoms (N or C) are not clearly distinguished.[3] Also the position of the presumed water molecule, on which the inference of C-metalation was based, is very poorly defined.[3a] Thus, for example, C-metalation of *two* rings could not be excluded. (iii) Published ^1H and ^{13}C NMR spectra confirm low molecular symmetry but have not been satisfactorily assigned, even for salient features relating to the modified ligand.[2,5]

The 200- and 300-MHz ^1H NMR spectra of I^{2+} (which we have studied as its BF_4^- salt) are complex, but the maximum number of 23 separately detectable aromatic resonances are observed. We find that systematic comparison in MeOH-d_4, Me_2CO-d_6, and Me_2SO-d_6 allows convincing identification of the doublet-of-doublet signals for each of the three protons in the uniquely attached ring (Figure 1a). These resonances are distinguished by their particular solvent sensitivity, presumably due to dipolar interactions of the neighboring uncoordinated nitrogen atom, and their mutual coupling is confirmed by double-resonance techniques (see Table I).

In the 90-MHz ^{13}C NMR spectrum of I^{2+} in Me_2SO-d_6 (Figure 1b,c), we find signals representing 30 nonequivalent carbon atoms. Most strikingly, in a spectroscopic mode specific for non-H-bearing carbon atoms,[6] *seven* single resonances persist. Six of these resonances, in the range 154–162 ppm with respect to Me_4Si, correspond to the ring–ring bridging positions (cf. 155.7 ppm in $[Ir(bpy)_3]^{3+}$), while the seventh, standing apart at 140 ppm, is clearly due to the unique, presumably iridium-bound, carbon atom.

Electrochemical studies provide new insight into the electronic nature of the complex. Cyclic voltammetry of I^{2+} in dimethyl sulfoxide or acetonitrile shows two closely spaced

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[†] University of Glasgow.
[‡] University of Edinburgh.

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(6) The appropriate "quaternary-carbon-only" pulse sequence was suggested to the Edinburgh NMR laboratory by Dr. D. M. Doddrell of Griffith University, Queensland, Australia.

0020-1669/84/1323-3425$01.50/0

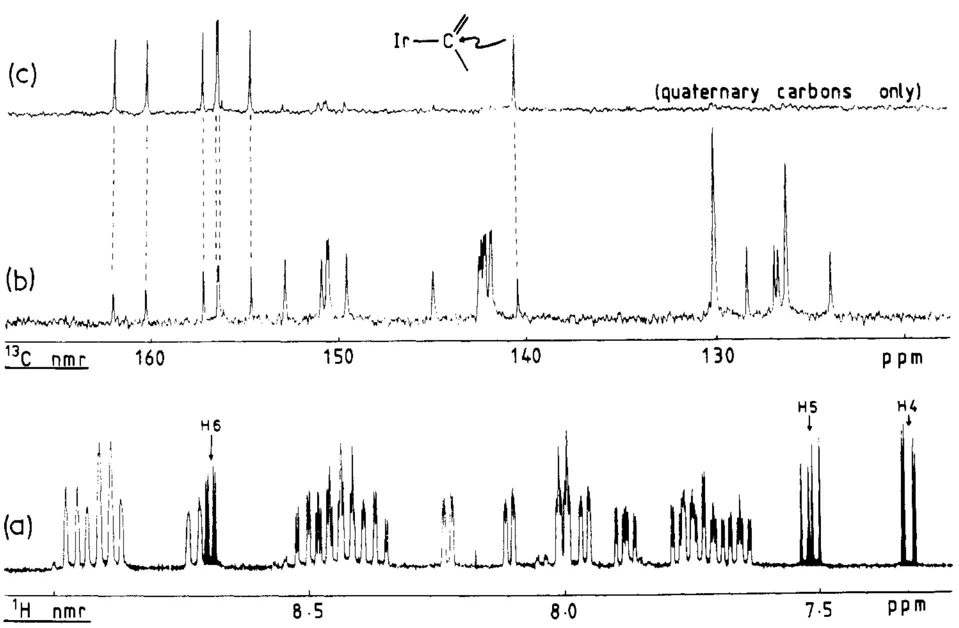

Figure 1. NMR spectra of I^{2+} in MeOH-d_4: (a) ^{1}H spectrum (360.13 MHz; line sharpened); (b) proton-decoupled ^{13}C spectrum (90.56 MHz); (c) proton-decoupled ^{13}C spectrum (90.56 MHz) for quaternary carbons only.

reversible reduction waves at −1.03 and −1.23 vs. SCE and two further waves, reversible and quasireversible, at −1.86 and −2.21 V, respectively. These reductions, also reported by Kahl et al.,[7] are characteristic of two and only two ordinary bipyridine ligands chelated to Ir(III). Moreover, the measured electrode potentials imply[8] the simultaneous presence of an effectively monoanionic neighboring ligand, represented by the chelated bipyridinyl group. Thus we note the first reduction potential is intermediate between that of $[Ir(bpy)_3]^{3+}$ (−0.82 V) and $[Ir(bpy)_2Cl_2]^+$ (−1.20 V), and the system is elegantly modeled by the further reductions of $[Ir(bpy)_2(bpy^-)]^{2+}$ at −1.00 and −1.20 V. I^{2+} also shows a new irreversible two-electron oxidation wave (E_p = +0.95 V), which we associate with the C-metalated ligand. It should be noted that the voltammetric behavior of I^{2+} is in marked contrast with Kahl's $[Ir(phen)_2(phen')(OH)]^{2+}$ (where phen represents bidentate and phen′ monodentate *o*-phenanthroline), for which three early reductions are reported.[4]

The electronic spectra of I^{2+}, I^+, and I^0 have been compared by using an optically transparent thin-layer electrolysis cell. I^{2+} and I^+ (but not I^0) both show the well-known[9] $\pi(6) \rightarrow \pi(7)$ transition of coordinated bpy around 33 000 cm^{-1}, with appropriately reduced intensity compared to $[Ir(bpy)_3]^{3+}$.[10] Equally, I^+ and I^0 (but not I^{2+}) show the characteristic absorptions of coordinated bpy$^-$ near 11 000, 20 000, and 26 000 cm^{-1} in accordance with the now familar pattern of localized reductions in $(d\pi)^6$ bpy complexes.[10,11] In addition, I^+ (but not I^0 or I^{2+}) shows a band at 5000 cm^{-1} (ϵ = 220 mol^{-1} dm^3 cm^{-1}) characteristic of ligand–ligand (bpy$^-$ → bpy) intervalence charge transfer.[12]

I^{2+} has been resolved into its optical isomers and shows an exciton couplet around 33 000 cm^{-1} readily assigned to a *cis*-M(bipy)$_2$ moiety.[9] Reduction to I^0, followed by reoxidation to I^{2+}, does not cause any loss of optical activity. These observations are, of course, consistent with successive ligand-based reductions at a kinetically inert Ir(III) center.

Collectively, these data demonstrate clearly that "pseudo-$[Ir(bpy)_3(OH)(BF_4)_2]$" contains a deprotonated N,C-bound ligand that is indeed physically and electronically unique and remains distinct from the accompanying normal bipyridine ligands in nonaqueous solution.[13]

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Registry No. $I^{2+}(BF_4^-)_2$, 91467-35-5; I^+, 91467-36-6; I, 91467-37-7.

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Contribution from the Department of Chemistry,
North Carolina State University,
Raleigh, North Carolina 27650

Molecular Orbital Study of the Substituent Effect on the Redox Properties of Disubstituted Bipyridines and Their Ruthenium(II) Complexes

Yasuhiko Ohsawa, Myung-Hwan Whangbo,*[†]
Kenneth W. Hanck,* and M. Keith DeArmond*

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In the electrochemical reduction of $[Ru(bpy)_3]^{2+}$ (**1**) (bpy = 2,2′-bipyridine) and its analogues with substituted 2,2′-bipyridines, six reduction waves can be observed.[1] Within the framework of simple molecular orbital (MO) theory, this is due to the fact that each bpy or its substituted analogue accepts up to two electrons in its lowest unoccupied MO level.[2] The six reduction waves found for **1** and [Ru(5,5′-

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[†] Camille and Henry Dreyfus Teacher-Scholar, 1980–1985.