equipped with a side arm with a septum through which gas and solution samples could be withdrawn for analysis. Typically, **1** was introduced as a solid, the flask was flushed with Ar, and solvent(s) and acid/base were transferred via syringe followed by three freeze/pump/thaw cycles. Carbon monoxide (6% methane as GC standard) was introduced and the reaction brought to temperature. Gas analyses were performed with 3 M × 4 mm column packed with Porapak Q with He carrier gas employing a thermal conductivity detector. Results are summarized in Table I.

Acknowledgment. The authors thank the Basic Science Division of the Department of Energy for generous support of this research under Grant DE-AT03-80ER10673. We also thank the National Science Foundation for the purchase of the Bruker WP-200 FTNMR spectrometer under Grant CHE 77-05926.

Registry No. 1, 56465-06-6; **2**, 91549-31-4; **3**, 91585-88-5; **5**, 91606-01-8; **6**, 91585-89-6; $[Me_4N][7]$, 91549-35-8; $[Me_3NH][7]$, 91549-37-0; [K(18-crown-6)][7], 91585-86-3; **8**, 91585-87-4; $[Me_3NH][7,8\text{-}C_2B_9H_{12}]$, 57409-10-6; $[Ru(CO)_3Cl_2]_2$, 22594-69-0; CO, 630-08-0.

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Spectroelectrochemical Studies on Tris(bipyridyl)iridium Complexes: Ultraviolet, Visible, and Near-Infrared Spectra of the Series $[Ir(bpy)_3]^{3+/2+/+/0}$

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Recently[1] we described the progression in absorption spectra for tris(bipyridyl)ruthenium(II), $[Ru(bpy)_3]^{2+}$ (I^{2+}) and its reduced analogues, $[Ru(bpy)_3]^+$ (I^+), $[Ru(bpy)_3]^0$ (I^0), and $[Ru(bpy)_3]^-$ (I^-). In each case we were able to assign all the observed bands in terms of characteristic electronic transitions involving noninteracting bpy^0 and bpy^- ligands (for I^+ and I^0) or discrete bpy^- ligands alone (I^-). We thus concluded that the complexes should be formulated with localized charge distributions, namely $[Ru^{II}(bpy^0)_3]^{2+}$, $[Ru^{II}(bpy^0)_2(bpy^-)]^+$, $[Ru^{II}(bpy^0)(bpy^-)_2]^0$, and $[Ru^{II}(bpy^-)_3]^-$. Parallel spectroelectrochemical studies on substituted Ru^{II}–bipyridyl complexes have recently appeared.[2]

Tris(bipyridyl)iridium(III) $[Ir(bpy)_3]^{3+}$ (II^{3+}), in common with I^{2+}, is a low-spin $d\pi^6$ complex. However, the tervalent complex II^{3+} has relatively facile ligand reductions, and, remarkably, six successive one-electron steps are observed. The pattern of electrode potentials for II^{3+} was noted by DeArmond et al.[3] to suggest a localized-charge model for the reduced complexes II^{2+}, II^+, etc. We now report confirmation of this interpretation using the spectroelectrochemical methods found to be definitive for I^{2+}.

There are marked differences in the electronic spectra of isoelectronic $[Ru(bpy)_3]^{2+}$ (I^{2+}) and $[Ir(bpy)_3]^{3+}$ (II^{3+}). Whereas for I^{2+} the visible spectral region is dominated by a metal-to-ligand charge-transfer (MLCT) transition, the first prominent absorption band of II^{3+} is an intraligand $\pi\pi^*$ transition at 32 200 cm^{-1},[4] the visible and near-infrared regions of the absorption spectrum being entirely featureless. The spectra of the intermediate complexes, I^+ and I^0, are complicated in the visible region due to superposition of the Ru^{II}–bpy^0 MLCT transition and characteristic bpy^- intraligand transitions. Thus we anticipated that $[Ir(bpy)_3]^{3+}$ and its reduced analogues would prove helpful in clarifying the visible spectral region, as the bpy^- intraligand transitions should emerge from a featureless background.

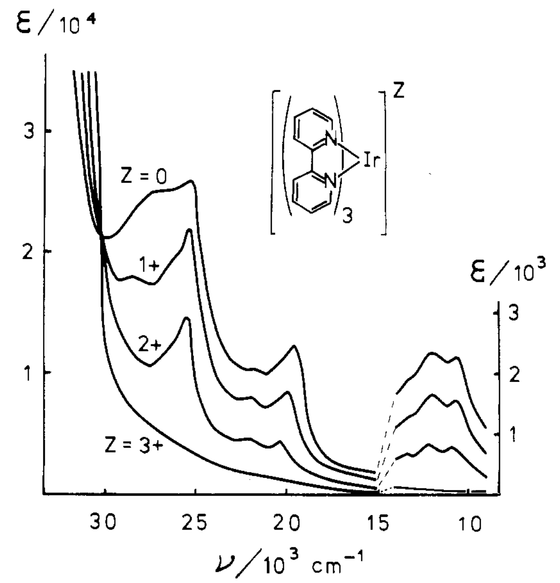

Figure 1. Absorption spectra for $[Ir(bpy)_3]^{3+/2+/+/0}$.

Results and Discussion

The reduced complexes $[Ir(bpy)_3]^{2+/+/0}$ were generated in turn in an optically transparent thin-layer electrode (OTTLE) cell, at −1.30, −1.45, and −1.60 V, respectively, vs. a nonaqueous Ag/Ag^+ reference electrode, and their spectra were measured in situ from 3500 to 33 000 cm^{-1}. In each case, after observation of the corresponding steady-state spectrum, the potential was set at −0.6 V and the spectrum was noted to return exactly to that of II^{3+} in its original concentration, thus establishing that no decomposition had occurred. In these circumstances, with strict exclusion of air, the entire series of iridium complexes proved neither solvent nor temperature sensitive, with invariant spectra in purified acetonitrile (at 30 and −40 °C), *N*,*N*-dimethylformamide, and dimethyl sulfoxide. Although $[Ir(bpy)_3]^-$ (II^-) is stable on a voltammetric time scale, it apparently decomposed on electrosynthesis. After generation of II^- and attempted regeneration of II^{3+} at either 15 or −40 °C, the original spectrum was not recovered, and further characterization of II^- (or II^{2-} and II^{3-}) was not pursued.

The successive spectra for $[Ir(bpy)_3]^{3+/2+/+/0}$ show crucial features in common with those for the ruthenium series. We see progressive growth of bands characterizing bpy^- and matching loss of the bpy^0 bands as the system is further reduced. A striking feature of Figure 1 is the maintenance of a pseudoisosbestic point relating four independent species. Thus, throughout the course of these reductions only the net interconversion of effectively isolated $Ir^{III}(bpy^0)$ and $Ir^{III}(bpy^-)$ chromophores is detected. This unequivocal observation justifies the consideration of extinction coefficients *per* ligand chromophore (see below) and establishes that the complexes should be formulated as shown in Table I. Assignment of

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[1] Heath, G. A.; Yellowlees, L. J.; Braterman, P. S. *J. Chem. Soc., Chem. Commun.* **1981**, 287. Elsewhere,[1,6,10] we have used symbols differently for such redox sequences, e.g., I, I^-, I^{2-}, I^{3-} for $[Ru(bpy)_3]^{2+/+/0/-}$, respectively.

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Table I. Absorption Spectra of Tris(bipyridyl) Complexes of Ruthenium(II) and Iridium(III): $\nu/10^3$ cm^{-1} ($\epsilon/10^4$ L mol^{-1} cm^{-1})

	transitions					
complex	$\pi \rightarrow \pi^*$, bpy^0	L → MCT, bpy$^{-\cdot}$	$\pi \rightarrow \pi^*$, bpy$^{-\cdot}$	M → L, bpy^0	$\pi \rightarrow \pi^*$, bpy$^{-\cdot}$	$\pi \rightarrow \pi^*$, bpy$^{-\cdot}$
$[Ru^{II}(bpy^0)_3]^{2+}$ (I^{2+})	35.0 (7.06)			22.1 (1.37)		
$[Ru^{II}(bpy^0)_2(bpy^-)]^+$ (I^+)	34.2 (5.12)		29.2 (1.74)	21.1 (1.25)	19.9 (1.35)	13.0 (0.09)
					18.9 (1.28)	11.5 (0.10)
						10.2 (0.09)
$[Ru^{II}(bpy^0)(bpy^-)_2]^0$ (I^0)	33.8 (4.00)		29.0 (2.50)	20.8 (sh)	19.5 (1.48)	12.9 (0.16)
					18.4 (1.46)	11.4 (0.19)
						10.1 (0.18)
$[Ru^{II}(bpy^-)_3]^-$ (I^-)			29.8 (3.82)		18.9 (1.56)	11.1 (0.26)
					18.0 (1.58)	9.9 (0.27)
$[Ir^{III}(bpy^0)_3]^{3+}$ (II^{3+})	32.2 (4.50)					
$[Ir^{III}(bpy^0)_2(bpy^-)]^{2+}$ (II^{2+})	32.5 (3.89)	obscured	25.6 (1.44)		22.2 (0.46)	13.4 (0.07)
					20.4 (0.44)	12.2 (0.08)
						10.8 (0.08)
$[Ir^{III}(bpy^0)(bpy^-)_2]^+$ (II^+)	32.8 (3.66)	28.6 (1.79)	25.4 (2.18)		22.0 (0.79)	13.1 (0.13)
					10.0 (0.83)	12.0 (0.16)
						10.7 (0.16)
$[Ir^{III}(bpy^-)_3]^0$ (II^0)		27.2 (2.51)	25.4 (2.54)		21.9 (1.04)	13.1 (0.19)
					19.6 (1.22)	11.9 (0.24)
						10.7 (0.23)

the various absorption bands follows directly from this. Table I also gives the absorption spectral data for the ruthenium series, including complete hitherto unpublished results for the near-infrared bands.

The visible spectral region around 20 000 cm^{-1} is indeed much simplified in the iridium complexes, compared to that of the corresponding (isoelectronic) ruthenium systems, because of the absence of a MLCT band. The growth of the visible $\pi\pi^*$ bpy$^-$ band upon reduction of II^{3+} is unambiguous, and the progression in intensity may be readily quantified. The measured extinction coefficient of the band at 20 000 cm^{-1} for $[Ir(bpy^0)_2(bpy^-)]^{2+}$ (II^{2+}) compares well with the similar absorption in Na$^+$ bpy$^-$,[5] and increases linearly from II^{2+} to II^0.

The higher energy $\pi\pi^*$ bpy$^-$ band observed here at 25 500 cm^{-1} is sharp and strongly resembles the analogous band in Na$^+$ bpy$^-$.[5] This is in accord with our earlier suggestion that the corresponding absorption in $[Ru(bpy)_3]^{+/0/-}$, which is considerably broadened, includes a M → L (bpy$^-$) transition.[1]

The near-infrared band also increases linearly in strength according to the number of bpy$^-$ ligands. The values of the extinction coefficients per reduced ligand agree closely with those for Na$^+$bpy$^-$ and for the ruthenium complexes, as does the structure within the band itself.

The simultaneous presence of discrete bpy^0 and bpy$^-$ ligands in II^{2+} and II^+ should be directly demonstrated by ligand-ligand intervalence charge-transfer (IVCT) transitions, as identified in isoelectronic I^+ and I^0.[6] We have confirmed that such a band is present in the absorption spectra of II^{2+} (ν = 3840 cm^{-1}, ϵ = 170 L mol^{-1} cm^{-1}) and II^+ (ν = 3840 cm^{-1}, ϵ = 300 L mol^{-1} cm^{-1}) in *N*,*N*-dimethylformamide and acetonitrile, but absent as expected in II^{3+} and II^0, which contain only bpy^0 and bpy$^-$ ligands, respectively.

The series II^{3+} to II^0, like the series I^{2+} to I^-, is best described by the localized model. The iridium system in fact clarifies the visible and near-ultraviolet spectra as there are no low-energy charge-transfer bands to mask the bpy$^-$ transitions. These observations put beyond doubt the character of the redox-active orbitals of these and many other $d\pi^6$ bipyridyl complexes. Electrons entering such orbitals are effectively trapped on the individual ligands, with negligible communication between the neighboring chelate rings. The thermal barrier to transposition of the electron is calculated to be approximately 1000 cm^{-1} ($^1/_4 h\nu_{IVCT}$).[7]

These spectroelectrochemical studies establish general diagnostic criteria for the presence of coordinated bpy$^-$. Exact band positions will depend on the central metal charge and on the nature of the accompanying ligands, but complexes thought to contain reduced, charge-localized, bipyridyl ligands must show (i) a near-infrared band near 10 000 cm^{-1} containing three peaks (or shoulders) separated by approximately 1000 cm^{-1} ($\epsilon \sim 10^3$/ligand), (ii) a visible doublet band near 20 000 cm^{-1} ($\epsilon \sim 5 \times 10^3$/ligand), and (iii) a near-ultraviolet band near 25 000 cm^{-1} ($\epsilon \sim 15 \times 10^3$/ligand). For example, the rich absorption spectra[5] of the series $[Fe(bpy)_3]^{2+/+/0/-}$ may be fully analyzed in terms of the familiar pattern of localized ligand-based reductions. In contrast, Schwarz and Creutz recently employed these criteria explicitly to establish that under pulse radiolysis $[Rh(bpy)_3]^{3+}$ is reduced to unstable $[R^{II}(bpy^0)_3]^{2+}$, rather than $[Rh^{III}(bpy^0)_2(bpy^-)]^{2+}$.[8]

It is notable that I^+ and II^{2+} are strictly analogous, with a common $M(d\pi^6)/(bpy^0)_2(bpy^-)$ configuration, whereas the optically excited states I* and II* differ fundamentally. Metal-centered oxidations of $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ occur at modest potentials, but oxidation of $[Ir(bpy)_3]^{3+}$ is inaccessible due to the increased core charge on iridium. Thus the additional nuclear proton drastically lowers the d-orbital manifold (more than the increased central ion charge stabilizes the ligand levels) so that in II^{3+} and II* the $d\pi$ levels fall below the ligand HOMO level. The contrasting natures of the equilibrated I* and II* states (MLCT and $L\pi\pi^*$, respectively) are confirmed by photoemission spectroscopy.[9]

Much attention focuses on I* since $[Ru(bpy)_3]^{2+}$ has been widely discussed as a prototype dye for photovoltaic cells. Flash photolysis absorption spectra[10,11] and resonance Raman studies[12] on I establish independently that an asymmetric charge distribution applies to the emitting state, I*, as well, viz. $^*[Ru^{III}(bpy^0)_2(bpy^-)]^{2+}$. Electrode potential correlations for numerous tris(bipyridyl)metalates have demonstrated that the ligand-orbital energies are strongly determined by central ion valency and surprisingly insensitive to d^n population.[13] Thus, in some respects $[Ir^{III}(bpy^0)_2(bpy^-)]^{2+}$ provides a better electronic structural model than $[Ru^{II}(bpy^0)_2(bpy^-)]^+$ for the ligand array in I*.

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

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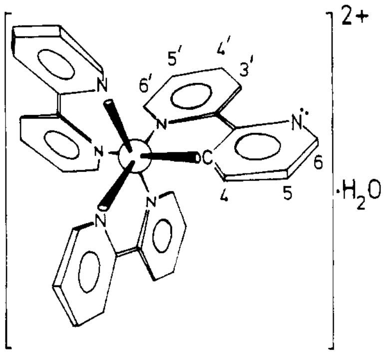
Received August 8, 1983

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