Structure of Tris(2,2′-bipyridyl)ruthenium(II) Hexafluorophosphate, $[Ru(bipy)_3][PF_6]_2$; *X*-Ray Crystallographic Determination

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Summary Analysis of Ru–N bond lengths based on an *X*-ray crystallographic determination of the molecular structure of $[Ru(bipy)_3]^{2+}$ and on reactivity patterns of various $[Ru(bipy)_3]^{n+}$ species suggests that members of the series have similar structures; this similarity may be important in the development of new solar energy catalysts.

The $[Ru(bipy)_3]^{2+}$ ion (bipy = 2,2′-bipyridyl) can be regarded as a model compound whose photo-accessible excited state can cause the dissociation of water into hydrogen and oxygen. For example, it has been possible to set up photoelectrochemical cells utilizing the $[Ru(bipy)_3]^{2+}$ photoexcited state to generate reactive species which drive reactions leading to the production of hydrogen[1] and oxygen.[2] Reactive species such as $[Ru(bipy)_3]^{+}$ and $[Ru(bipy)_3]^{3+}$ can be obtained from the excited state of $Ru[(bipy)_3]^{2+}$ by reductive and oxidative quenching, respectively.

The excited state behaviour of the complex ion $[Ru(bipy)_3]^{2+}$ has been the subject of many recent reports, most of them appearing since the 1972 discovery of Gaffney and Adamson[3] that electron transfer takes place from an excited state of this ion. These studies include determinations of electrode potentials for oxidation,[4] $*[Ru(bipy)_3]^{2+} \rightarrow [Ru(bipy)_3]^{3+} + e^-$ (0·8—1·1 V), and for reduction,[5] $*[Ru(bipy)_3]^{2+} + e^- \longrightarrow [Ru(bipy)_3]^+$ (0·6—1·0 V), and determinations of rates of electron transfer reactions in which $*[Ru(bipy)_3]^{2+}$ is used as an oxidant[5,6] or as a reductant.[3,4,7] Studies of environmental factors include reactivities of $*[Ru(bipy)_3]^{2+}$ in monolayer assemblies,[8] micelles,[9] and polyelectrolytes.[9] Photogalvanic cells designed to utilize the excited state properties of $*[Ru(bipy)_3]^{2+}$ as the driving force in electrochemical processes have also been constructed.[10]

In order to obtain structural information on the various species involved, information which is crucial to an understanding of the above phenomena, we have determined the molecular structure of the complex ion $[Ru(bipy)_3]^{2+}$ by means of an *X*-ray diffraction study of a crystal of the hexafluorophosphate salt.† The $[Ru(bipy)_3]^{2+}$ cation, with crystallographic symmetry D_3–32, has octahedral co-ordination with a propeller-like arrangement of ligands around Ru; the geometry of one of the two enantiomers in the crystal is shown in the Figure, together with bond lengths and bond angles.

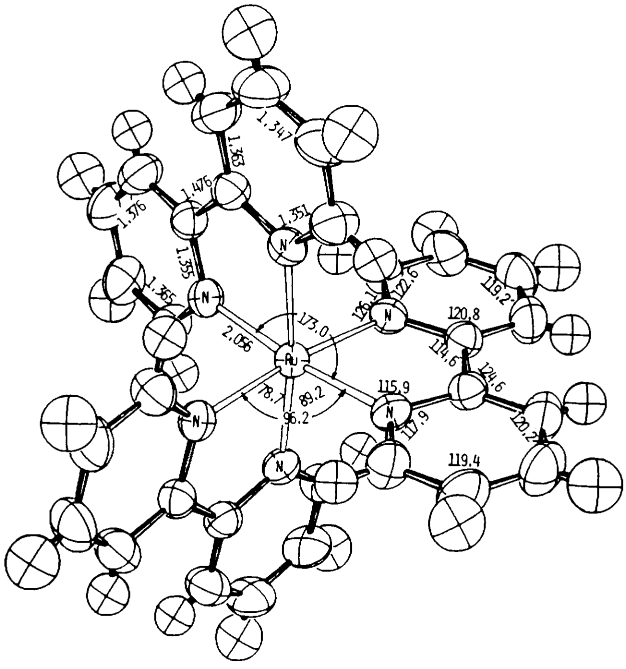

FIGURE. The structure of the tris(2,2′-bipyridyl)ruthenium(II) dication. The co-ordination polyhedron about Ru is approximately a regular octahedron. Rotations of 120° about the view direction relate the three ligand molecules, and 180° rotations about axes in the plane of the drawing relate the two halves of each ligand molecule. Each symmetry-unique bond length (Å) and bond angle (degrees) is labelled once. Atoms are represented by ellipsoids including 50% probability of thermal displacement.

The Ru–N bond length of 2·056(6) Å is somewhat shorter than the corresponding bond lengths in two Ru^{III} complexes: 2·104(4) Å[11] in $[Ru(NH_3)_6]^{3+}$ and 2·08(2) Å (average)[12]‡ in $[(bipy)_2(NO_2)Ru^{III}–O–Ru^{III}(NO_2)(bipy)_2]^{2+}$. The shorter bond length in the Ru^{II} complex is contrary to an expected increase in bond length resulting from a larger ionic radius of Ru^{II}. The bond length decrease suggests that, in the $[Ru(bipy)_3]^{2+}$ ion, there is considerable π bonding between the delocalized π^* orbitals on the bipyridyl ligands and the t_{2g} orbitals of the Ru^{II} core; in the Ru^{III} complexes this π bonding is reduced or absent because the energy of the *d* orbitals of Ru^{III} is lowered, leading to less extensive overlap of the t_{2g} set with the ligand π^* orbitals. The similarity of bond lengths in the analogous *ortho*-phenanthroline complexes of iron, $[Fe(phen)_3]^{2+}$ and $[Fe(phen)_3]^{3+}$ (1·98 [13] and 1·97 Å,[14] respectively) suggests that a similar explanation holds there also.

The small change in the Ru–N bond length implies that there is little or no Franck–Condon barrier to electron transfer between $[Ru(bipy)_3]^{2+}$ and $[Ru(bipy)_3]^{3+}$, and consequently electron exchange should take place readily. Indeed, the self-exchange rate constant for the $[Ru(bipy)_3]^{2+,3+}$ couple has been reported[15] to be $1·2 \times 10^9$ l mol^{-1} s^{-1} (ionic strength 1·0 M, H_2O, 25 °C), a value which is near the diffusion-controlled upper limit. This is in contrast to cases[16] in which the reduced and oxidized species have significantly different bond lengths.

The self-exchange rate constant for the $[Ru(bipy)_3]^{1+,2+}$ couple is also quite large,§ $\gg 10^8$ l mol^{-1} s^{-1}. Thus, we infer that there can be little Franck–Condon barrier in this case as well, and that the Ru–N bond length for $[Ru(bipy)_3]^+$ is near that in the higher-valent species. The added electron in the $[Ru(bipy)_3]^+$ ion has been assigned to a ligand π^* orbital;[17] if this assignment is accepted, it appears that occupancy of this orbital does not greatly perturb the structure. Since the π^* ligand orbital is also the one occupied[18] by the promoted electron in excited $*[Ru(bipy)_3]^{2+}$, we may further infer that this excited species has a structure not greatly perturbed from that of the ground state ion. Studies of luminescence from $*[Ru(bipy)_3]^{2+}$ support this conclusion.[19] Thus, it is suggested that all members of the series $[Ru(bipy)_3]^+$, $[Ru(bipy)_3]^{2+}$, $*[Ru(bipy)_3]^{2+}$, and $[Ru(bipy)_3]^{3+}$ have similar structures.

Two consequences of possible importance to systems for homogeneous catalysis follow. First, the part of the excitation free energy in the Marcus–Hush[20] theory of electron transfer kinetics arising from inner-sphere rearrangement effects is small. Thus, in designing procedures for altering catalytic properties, one can focus on the remaining terms, which involve outer-sphere rearrangement effects and the work required to bring the reactants together. The environmental studies cited[8,9] above fall into

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† *Crystal data:* $Ru(C_{10}H_8N_2)_3(PF_6)_2$, hexagonal, centrosymmetric space group $P\bar{3}c$, $Z = 2$, $a = 10·760(1)$, $c = 16·391(3)$ Å. Integrated reflections measured diffractometrically with Nb-filtered Mo-K_α radiation were corrected for absorption. The structure was solved directly with the program MULTAN-78. Least-squares refinement with 1034 non-zero weighted observations led to a final discrepancy index $R_F = 0·044$. Bond lengths and angles in the cation are given in the Figure. The fluorophosphate ion is of octahedral symmetry C_3–3, with two independent P–F distances of 1·54 and 1·57 Å. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ The eight Ru–N(bipy) bond lengths range from 2·061 to 2·100 Å; the average is 2·08 Å, from ref. 12.

§ The exchange rate was estimated from data in ref. 5a.

this category. Secondly, the ground-state energy manifolds for the four Ru complex ions are displaced nearly vertically along the energy axis; such a configuration may be important and perhaps necessary if a practical electron transfer homogeneous catalyst is to be developed. It is interesting to note that potential photo-electron-transfer catalysts receiving the most attention are ruthenium and iron tris-bipyridyl complexes.[21] Currently, we are studying properties of binuclear ruthenium complexes containing bipyridyl ligands and bipyridyl-like bridging ligands such as 2,3-bis(2′-pyridyl)quinoxaline.

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[1] B. Durham, W. J. Dressick, and T. J. Meyer, *J.C.S. Chem. Comm.*, 1979, 381.

[2] S. O. Kobayashi, N. Furuta, and O. Simamura, *Chem. Letters*, 1976, 503.

[3] H. Gaffney and A. W. Adamson, *J. Amer. Chem. Soc.*, 1972, **94**, 8238.

[4] C. R. Bock, T. J. Meyer, and D. G. Whitten, *J. Amer. Chem. Soc.*, 1975, **97**, 2909.

[5] C. Creutz and N. Sutin, (a) *Inorg. Chem.*, 1976, **15**, 496; (b) *J. Amer. Chem. Soc.*, 1976, **98**, 6384.

[6] C. D. Jonah, M. S. Matheson, and D. Meisel, *J. Amer. Chem. Soc.*, 1978, **100**, 1449; C. P. Anderson, D. J. Salmon, R. C. Young, and T. J. Meyer, *ibid.*, 1977, **99**, 1980.

[7] C. T. Lin, W. Boettcher, M. Chon, C. Creutz, and N. Sutin, *J. Amer. Chem. Soc.*, 1976, **98**, 6536; J. N. Demas and A. W. Adamson, *ibid.*, 1973, **95**, 5159; T. J. Meyer, *Accounts Chem. Res.*, 1978, **11**, 94.

[8] G. L. Gains, Jr., P. E. Behnken, and S. J. Valenty, *J. Amer. Chem. Soc.*, 1978, **100**, 6549; S. J. Valenty and G. L. Gains, *ibid.*, 1977, **99**, 1285; G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsch, and D. G. Whitten, *ibid.*, 1976, **98**, 2337; 1977, **99**, 4947.

[9] D. Meisel and M. S. Matheson, *J. Amer. Chem. Soc.*, 1977, **99**, 6577.

[10] B. Durham and T. J. Meyer, *J. Amer. Chem. Soc.*, 1978, **100**, 6286; C. T. Lin and N. Sutin, *J. Phys. Chem.*, 1976, **80**, 97; W. D. K. Clark and N. Sutin, *J. Amer. Chem. Soc.*, 1977, **99**, 4676.

[11] H. C. Stynes and J. A. Ibers, *Inorg. Chem.*, 1971, **10**, 2304.

[12] D. W. Phelps, E. M. Kahn, and D. J. Hodgson, *Inorg. Chem.*, 1975, **14**, 2486.

[13] A. Zalkin, D. H. Templeton, and T. Ueki, *Inorg. Chem.*, 1973, **12**, 1641.

[14] J. Baker, L. M. Englehardt, B. N. Figgis, and A. H. White, *J.C.S. Dalton*, 1975, 530.

[15] F. R. Keene, R. C. Young, and T. J. Meyer, *J. Amer. Chem. Soc.*, 1977, **99**, 2468.

[16] Compare the self-exchange rate constant of 10^8 l mol^{-1} s^{-1} for the $[Fe(phen)]^{2+,3+}$ couple, taken from M. W. Deitrich and A. Wahl, *J. Chem. Phys.*, 1963, **38**, 1591, with 10^{-12} l mol^{-1} s^{-1} for the $[Co(NH_3)_6]^{2+,3+}$ couple, taken from D. R. Stranks, *Discuss. Faraday Soc.*, 1960, **29**, 116. According to refs. 13 and 14, Δ(Fe–N) is 0·01 Å whereas Δ(Co–N) according to ref. 11 is *ca.* 0·18 Å.

[17] N. E. Tokel-Takvoryan, R. E. Hemingway, and A. J. Bard, *J. Am. Chem. Soc.*, 1973, **95**, 6582.

[18] R. W. Harrigan and G. A. Crosby, *J. Chem. Phys.*, 1973, **59**, 3468; R. W. Harrigan, G. D. Hager, and G. A. Crosby, *Chem. Phys. Letters*, 1973, **21**, 487.

[19] G. D. Hager and G. A. Crosby, *J. Amer. Chem. Soc.*, 1975, **97**, 7031; G. D. Hager, R. J. Watts, and G. A. Crosby, *ibid.*, p. 7037; K. W. Hipps and G. A. Crosby, *ibid.*, p. 7042.

[20] R. A. Marcus, *Ann. Rev. Phys. Chem.*, 1964, **15**, 155; N. S. Hush, *Trans. Faraday Soc.*, 1961, **57**, 557.

[21] D. G. Whitten, J. Mercer-Smith, T. K. Foreman, and R. H. Schmehl, 30th Southeastern Regional American Chemical Society Meeting, Symposium on Solar Energy, Abstract 412, Savannah, Georgia, November 8—10, 1978.