

CoCl_4^{2-} complex in methanolic 4 M cobalt chloride solution exists in a regular tetrahedral coordination³⁵ and that the ZnCl_4^{2-} complex in aqueous solution also exists in a regular tetrahedral structure.³⁶ They have also investigated the structure of aqueous copper chloride at high concentrations.^{37,38} In a recent paper, Friedman et al. have discussed the complicated structure of aqueous nickel chloride solution in the high concentration range.³⁹

- (31) Ohtaki, H.; Maeda, M. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2197-2199.
 (32) Ohtaki, H.; Yamaguchi, T.; Maeda, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 701-708.
 (33) Ohtaki, H.; Yamaguchi, T.; Maeda, M. "Essays on Analytical Chemistry—In Memory of Professor Anders Ringbom"; Wänninen, E. Ed.; Pergamon Press: Oxford, 1977; pp 163-168.
 (34) Bol, W.; Gerrits, G. J. A.; van P. van Eck, C. L. *J. Appl. Crystallogr.* **1970**, *3*, 486.
 (35) Wertz, D. L.; Kruh, R. F. *J. Chem. Phys.* **1969**, *50*, 4313.
 (36) Wertz, D. L.; Bell, J. R. *J. Inorg. Nucl. Chem.* **1973**, *35*, 861-868.
 (37) Bell, J. R.; Tyvoll, J. L.; Wertz, D. L. *J. Am. Chem. Soc.* **1973**, *95*, 1456-1459.
 (38) Wertz, D. L.; Tyvoll, J. L. *J. Inorg. Nucl. Chem.* **1974**, *36*, 3713-3717.
 (39) Friedman, H. L.; Dudowicz, J. B. *Aust. J. Chem.* **1980**, *33*, 1889-1894.

As no data on structures of these metal ions in methanol are available, the configurations of the solvated methanol molecules around the ions are not clear. However, if octahedrally coordinated $\text{M}(\text{CH}_3\text{OH})_6^{2+}$ is assumed, it is possible that a change of coordination, from octahedral to tetrahedral structure, may occur in the course of the complex formation of both cobalt chloride and zinc chloride in methanol. In methanolic solution, ZnCl_4^{2-} must be tetrahedral as in aqueous solutions. For a more conclusive interpretation, further intensive studies on both thermodynamic parameters and structural analyses are necessary for various systems.

Acknowledgment. The authors wish to thank Professor Yukio Murakami for very helpful suggestions and Dr. Akio Ichimura for comments on the manuscript. H.D. thanks Associate Professor Masakazu Matsui of the Institute for Chemical Research, Kyoto University, for his helpful discussions.

Registry No. $\text{Co}(\text{ClO}_4)_2$, 13455-31-7; $\text{Ni}(\text{ClO}_4)_2$, 13637-71-3; $\text{Cu}(\text{ClO}_4)_2$, 13770-18-8; $\text{Zn}(\text{ClO}_4)_2$, 13637-61-1; Zn, 7440-66-6; Co, 7440-48-4; Ni, 7440-02-0; Cu, 7440-50-8.

Contribution from the Department of Chemistry, York University, Downsview, Toronto, Ontario, Canada M3J 1P3

Comparative Chemistry of Bipyrazyl and Bipyridyl Metal Complexes: Spectroscopy, Electrochemistry, and Photoanation

R. J. CRUTCHLEY and A. B. P. LEVER*

Received September 25, 1981

The photoanation of the bipyrazyl complex $\text{Ru}(\text{bpz})_3(\text{PF}_6)_2$, in acetonitrile containing chloride ion, leads to the formation of *cis*- $\text{Ru}(\text{bpz})_2(\text{CH}_3\text{CN})\text{Cl}^+$ (maximum quantum yield 0.37), *cis*- $\text{Ru}(\text{bpz})_2\text{Cl}_2$ (maximum quantum yield 0.001), and an unidentified mono(bipyrazyl)ruthenium(II) derivative. The mechanism of this reaction is discussed. Reaction of $\text{M}(\text{CO})_6$ ($\text{M} = \text{W}, \text{Mo}$) with bipyrazyl yields $\text{M}(\text{CO})_4\text{bpz}$. The electronic, vibrational, and ^1H NMR spectra and electrochemistry of these products were compared with those of their bipyridyl analogues. It is concluded that bipyrazyl is no better a π acceptor than bipyridyl because of weaker σ bonding leaving the metal ion more positively charged.

Introduction

We have recently reported¹ the photochemical properties of a new photocatalyst, the ruthenium(II) tris(bipyrazyl) dication, $\text{Ru}(\text{bpz})_3^{2+}$ (I). The charge-transfer excited state of this species has a redox couple (II^*/I), estimated to be ca. +1.3 V, thermodynamically sufficient to oxidize water at pH 7. We are currently directing our efforts into developing $\text{Ru}(\text{bpz})_3^{2+}$ for use as a photosensitizer in solar energy conversion schemes. In view of the importance of the tris(bipyridyl)ruthenium(II) cation, $\text{Ru}(\text{bpy})_3^{2+}$, as an energy conversion catalyst,² we have investigated some of the comparative chemistry of bipyridyl and bipyrazyl with a view to a greater understanding of both, but especially of the latter. We report, for the first time, the synthesis and characterization of $[\text{Ru}(\text{bpz})_2(\text{CH}_3\text{CN})\text{Cl}]^+[\text{PF}_6]^-$ (II) and $\text{Ru}(\text{bpz})_2\text{Cl}_2$ (III), both prepared by photoanation of the $\text{Ru}(\text{bpz})_3^{2+}$ cation in acetonitrile, and $\text{Mo}(\text{CO})_4\text{bpz}$ (IV) and $\text{W}(\text{CO})_4\text{bpz}$ (V) and compare their electrochemical and spectroscopic properties with those of their bipyridyl analogues.

Experimental Section

Bis(2-pyrazinecarboxylato)copper(II) was prepared by reaction of $\text{Cu}(\text{CO})_3$ with 2-pyrazinecarboxylic acid (purchased from Fisher and Aldrich, respectively), in aqueous solution. The copper complex was used without further purification in the preparation of 2,2'-bi-

pyrazine. $\text{Ru}(\text{Me}_2\text{SO})_4\text{Cl}_2^3$ and $\text{M}(\text{CO})_4\text{bpy}$, ($\text{M} = \text{Mo}$ or W)⁴ were prepared with use of literature methods. $\text{RuCl}_3 \cdot (1-3)\text{H}_2\text{O}$, $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, and $\text{W}(\text{CO})_6$ were all purchased from Alfa. Tetraethylammonium chloride monohydrate $[(\text{TEA})\text{Cl} \cdot \text{H}_2\text{O}]$ was purchased from Aldrich. All solvents used were reagent grade unless otherwise specified. The light source consisted of a focused 500-W tungsten halogen lamp. Light was passed through IR and 350-nm cutoff filters. Electronic and infrared spectra were recorded with a Perkin-Elmer Hitachi Model 340 microprocessor spectrometer and a Beckman IR 12 spectrometer, respectively. Conductivity data were obtained with a Wayne-Kerr conductivity bridge. All analyses were performed by Canadian Microanalytical Services Ltd. and agreed with the proposed formulations.

Preparation of 2,2'-Bipyrazine. This procedure is a much simplified version of an earlier preparation,⁵ which significantly improves the yield without reducing the purity of the product.

Bis(2-pyrazinecarboxylato)copper(II) (14 g) in a Pyrex boat was placed into a 1.2 m long Pyrex tube. The boat was heated under nitrogen atmosphere with a Meker burner, causing pyrolysis of the copper complex. Bipyrazine and pyrazine sublimed onto the sides of the Pyrex tube during pyrolysis, which was completed when the copper residue appeared reddish. After cooling, the boat was removed and air passed through the Pyrex tube to remove most of the pyrazine impurity. Bipyrazine was then washed out of the Pyrex tube with chloroform. The entire procedure was repeated several times to yield,

(1) Crutchley, R. J.; Lever, A. B. P. *J. Am. Chem. Soc.* **1980**, *102*, 7128.
 (2) Hann, R. A. *Chem. Br.* **1980**, *16*, 474.

(3) Evans, I. P.; Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 204.
 (4) Stiddard, M. H. B. *J. Chem. Soc.* **1962**, 4712.
 (5) Lafferty, J. J.; Case, F. H. *J. Org. Chem.* **1967**, *32*, 1591.

after evaporation of chloroform, 16 g of crude bipyrazine from 110 g of bis(2-pyrazinecarboxylato)copper(II). Recrystallization from toluene (300 mL) yielded pale yellow crystals of 2,2'-bipyrazine (12 g, 21%), mp 185 °C (lit.⁶ mp 190 °C).

Preparation of $\text{Ru}(\text{bpz})_3\text{Cl}_2 \cdot 3.5\text{H}_2\text{O}$. $\text{Ru}(\text{Me}_2\text{SO})_4\text{Cl}_2$ (1.0 g) and bpz (2.0 g) were refluxed together in water (70 mL) for 20 h. The reaction mixture was filtered and the filtrate evaporated to dryness. After it was washed with acetone and chloroform and again with acetone, the crude product (1.0 g) was dissolved in water (15 mL) and filtered. To the boiling filtrate was added slowly a 1:2 mixture of ethanol and propanol (50 mL). Orange, crystalline $\text{Ru}(\text{bpz})_3\text{Cl}_2 \cdot 3.5\text{H}_2\text{O}$ precipitated out as the solution cooled (0.8 g, 47%). Anal. C, H, N, Cl.

Preparation of $\text{Ru}(\text{bpz})_3(\text{PF}_6)_2 \cdot 1.5(\text{CH}_3)_2\text{CO}$. A solution of $\text{Ru}(\text{bpz})_3\text{Cl}_2 \cdot 3.5\text{H}_2\text{O}$ (2.0 g) in water (150 mL) was heated to boiling. To this was added an aqueous solution of 0.2 M KPF_6 (50 mL). A yellow precipitate immediately formed. The solution was allowed to cool to room temperature and then filtered. The crude product was washed with water and then dissolved in an acetone/ethanol solution (700 mL 6:1) and concentrated to 150 mL, yielding orange crystalline $\text{Ru}(\text{bpz})_3(\text{PF}_6)_2 \cdot 1.5(\text{CH}_3)_2\text{CO}$ (1.9 g, 70%). Anal. C, H, N.

Preparation of $[\text{Ru}(\text{bpz})_2(\text{CH}_3\text{CN})(\text{Cl})]^+[\text{PF}_6]^- \cdot 1/2\text{H}_2\text{O}$ (II). A solution of $\text{Ru}(\text{bpz})_3(\text{PF}_6)_2 \cdot 1.5(\text{CH}_3)_2\text{CO}$ (1.0 g) in CH_3CN (1500 mL) was irradiated ($\lambda > 350$ nm) and magnetically stirred. To this solution was added, slowly over 15 min, $(\text{TEA})\text{Cl} \cdot \text{H}_2\text{O}$ (0.193 g). The photoreaction takes approximately 4 h to be completed, after which the solution is a deep red. The acetonitrile was removed by solvent evaporation and the crude product digested in boiling *n*-PrOH. After filtration, the residue was dissolved in acetone (40 mL) and stored in a freezer for 2 days. This yielded dark red crystalline $[\text{Ru}(\text{bpz})_2(\text{CH}_3\text{CN})(\text{Cl})]^+[\text{PF}_6]^- \cdot 1/2\text{H}_2\text{O}$ (0.4 g, 58%). Anal. C, H, N, Cl.

Preparation of $\text{Ru}(\text{bpz})_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ (III). The procedure was as above except 0.3 g of $\text{Ru}(\text{bpz})_3(\text{PF}_6)_2 \cdot 1.5(\text{CH}_3)_2\text{CO}$ was used and 0.07 g of $(\text{TEA})\text{Cl} \cdot \text{H}_2\text{O}$ was added over 15 min. After a further 20 min, $(\text{TEA})\text{Cl} \cdot \text{H}_2\text{O}$ (4.93 g) was added and irradiation allowed to continue for 16 h. The solution at the end of the reaction is a deep purple. After filtration, the volume of the solution was reduced by evaporation to 80 mL, causing precipitation of the product. This was collected and washed with acetonitrile. Recrystallization from acetonitrile yielded purple microcrystals of $\text{Ru}(\text{bpz})_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ (0.07 g, 44%). Anal. C, H, N, Cl.

Preparation of $\text{Mo}(\text{CO})_4\text{bpz}$ (IV). $\text{Mo}(\text{CO})_6$ (0.83 g) and bpz (0.5 g) were refluxed under N_2 in toluene (150 mL) for 50 min. The solution was filtered hot, and to the filtrate was added hexane (700 mL). The hexane/toluene solution was placed in a freezer overnight, and upon filtration maroon needles of $\text{Mo}(\text{CO})_4\text{bpz}$ (0.8 g, 70%) were collected. Anal. C, H, N.

Preparation of $\text{W}(\text{CO})_4\text{bpz}$ (V). $\text{W}(\text{CO})_6$ (1.1 g) and bpz (0.5 g) were refluxed under N_2 in xylene (150 mL) for 1.75 h. The solution was filtered hot, and to the filtrate was added hexane (650 mL). The xylene/hexane solution was placed in a freezer overnight and then filtered, yielding brown needles of $\text{W}(\text{CO})_4\text{bpz}$ (0.9 g, 63%). Anal. C, H, N. $\text{Cr}(\text{CO})_4\text{bpz}$ is apparently unstable, and attempts to prepare it with the above method resulted in a brown insoluble product, which was not analyzed further. $\text{Ni}(\text{bpz})_3(\text{PF}_6)_2$ and $\text{Ni}(\text{bpy})_3(\text{ClO}_4)_2$ were prepared by literature methods.⁶

Quantum Yield Experiments. Spectroquality acetonitrile, purchased from Aldrich, and recrystallized and vacuum-dried $(\text{TEA})\text{Cl}$ ⁷ were used in these experiments. Irradiation of vacuum-degassed solutions of $\text{Ru}(\text{bpz})_3(\text{PF}_6)_2$ or $[\text{Ru}(\text{bpz})_2(\text{CH}_3\text{CN})(\text{Cl})]^+[\text{PF}_6]^-$, both 4.0×10^{-5} M, and $(\text{TEA})\text{Cl}$ (2.0×10^{-3} M) took place in a 1-cm quartz spectrophotometer cell under nitrogen. The light source was the same as that used to prepare the bis(bipyrazine)ruthenium complexes except the 350-nm cutoff filter was replaced with a 435.8 ± 7 nm interference filter for the photoanation of $\text{Ru}(\text{bpz})_3^{2+}$ or a 500 ± 7 nm interference filter for the photoanation of $[\text{Ru}(\text{bpz})_2(\text{CH}_3\text{CN})(\text{Cl})]^+$. Light intensity was monitored through ferrioxalate actinometry.⁸ Photolysis was interrupted periodically, and visible absorption spectra were recorded. In the dark, the spectrum of the photolysate remained constant for periods of several hours so that thermal reactions could be ignored.

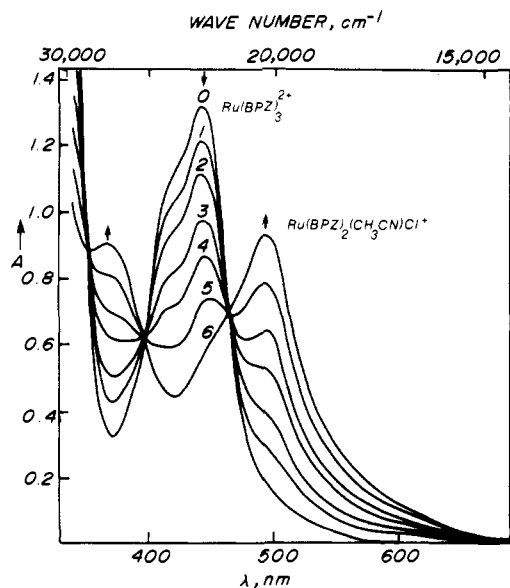


Figure 1. Sequential visible spectra illustrating irradiation ($\lambda = 435.8 \pm 7$ nm) of an acetonitrile solution of $\text{Ru}(\text{bpz})_3(\text{PF}_6)_2$, 8.6×10^{-5} M, and $(\text{TEA})\text{Cl}$, 2.0×10^{-4} M.

Quantum yields were calculated on the basis of the disappearance of $\text{Ru}(\text{bpz})_3^{2+}$ or $[\text{Ru}(\text{bpz})_2(\text{CH}_3\text{CN})(\text{Cl})]^+$, after the reaction was 25% completed.

¹H NMR. ¹H NMR spectra were recorded on a Varian EM-360 60-MHz NMR spectrometer at ambient temperature. Tetramethylsilane at 0.00 ppm or residual protons of dimethyl-*d*₆ sulfoxide at 2.50 ppm and chloroform-*d* at 7.25 ppm were used as internal references. Integration agrees with proton assignments shown in Table II.

Electrochemistry. Electrochemistry experiments were performed with a three-electrode system consisting of a platinum working electrode, a platinum counterelectrode, and a silver quasi-reference electrode. The silver quasi-reference electrode was calibrated during each experiment relative to the ferrocene/ferrocenium couple ($E_{1/2} = 0.310$ V vs. SCE in CH_3CN).⁹ Acetonitrile, used in the electrochemistry experiments, was vacuum distilled over P_2O_5 . Tetraethylammonium hexafluorophosphate (TEAH) was prepared by reacting $(\text{TEA})\text{Cl}$ with KPF_6 , purchased from Alfa, in aqueous solution. Crude TEAH was recrystallized twice from water and vacuum-dried at 120 °C for 24 h. Data were obtained by cyclic voltammetry with equipment and techniques previously described.¹⁰

Results and Discussion

Ruthenium Complexes and Photoanation. The long-term stability of a photocatalyst when exposed to light in aqueous or organic media is obviously of importance. $\text{Ru}(\text{bpz})_3(\text{PF}_6)_2$ (I) in acetonitrile is relatively stable when irradiated ($\lambda = 435.8 \pm 7$ nm). However, if Cl^- is added, photodecomposition occurs, resulting in an electronic spectrum typical of bis(diimine)ruthenium(II) complexes.¹¹ Figure 1 shows the visible spectrum of a typical photoanation experiment. The presence of isosbestic points at 350, 396, and 461 nm suggest only one photoproduct is being formed. Column chromatography on Sephadex LH-20 of a partially photolyzed acetonitrile solution of $\text{Ru}(\text{bpz})_3\text{Cl}_2$ separated unreacted $\text{Ru}(\text{bpz})_3^{2+}$ and only one ruthenium photoproduct as identified by their UV-vis spectra. In addition, photolyzed solutions of $\text{Ru}(\text{bpz})_3(\text{PF}_6)_2$ in the presence of Cl^- were extracted with hexane. The UV-vis spectrum before and after hexane extraction showed no change in the position of MLCT bands and a drop in intensity and a narrowing of ligand $\pi-\pi^*$ bands. The hexane extract was

(6) Lever, A. B. P.; Lewis, J.; Nyholm, R. S. *J. Chem. Soc.* **1964**, 1187.

(7) Unni, A. K. R.; Elias, L.; Schiff, H. I. *J. Phys. Chem.* **1963**, *67*, 1216.

(8) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.

(9) Mann, C. K.; Barnes, K. K. "Electrochemical Reactions in Non Aqueous Systems"; Marcel Dekker: New York, 1970.

(10) Lever, A. B. P.; Wilshire, J. P. *Inorg. Chem.* **1978**, *17*, 1145.

(11) Bryant, G. M.; Fergusson, J. E.; Powell, H. K. *J. Aust. J. Chem.* **1971**, *24*, 257.

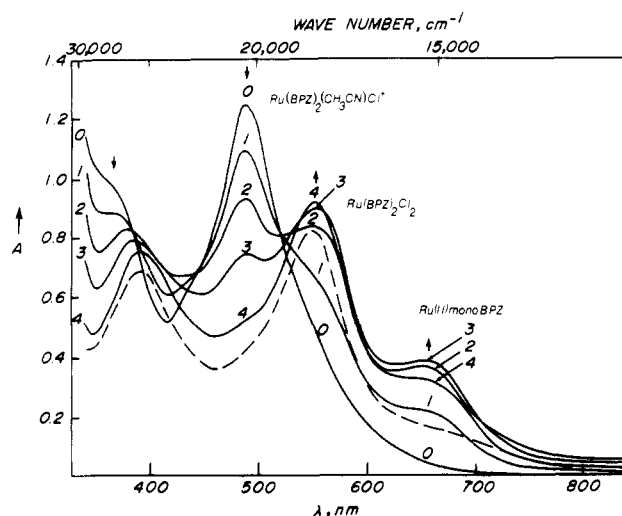


Figure 2. Sequential visible spectra (—) illustrating irradiation ($\lambda > 350$ nm) of an acetonitrile solution of $[\text{Ru}(\text{bpz})_2(\text{CH}_3\text{CN})(\text{Cl})][\text{PF}_6]$, 1.27×10^{-4} M, and $(\text{TEA})\text{Cl}$, 2.0×10^{-2} M, and spectrum (---) after 12 h in the dark. The secondary photolysis product has completely decomposed, and the spectrum is essentially that of $\text{Ru}(\text{bpz})_2\text{Cl}_2$.

Table I. Conductivity Data

complex ^a	molar conductivity, $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
$\text{Ru}(\text{bpz})_3(\text{PF}_6)_3$	385
$[\text{Ru}(\text{bpz})_2(\text{CH}_3\text{CN})(\text{Cl})][\text{PF}_6] \cdot 1/2 \text{H}_2\text{O}$	157
$\text{Ru}(\text{bpz})_2\text{Cl}_2 \cdot \text{H}_2\text{O}$	0
1:1 electrolyte ^b	120–160
2:1 electrolyte ^b	220–300
3:1 electrolyte ^b	340–420

^a 3.2×10^{-5} M in CH_3CN . ^b Geary, W. J. *Coord. Chem. Rev.* 1971, 7, 81.

evaporated, and the melting point and UV-vis spectrum of the residue indicated the product to be bipyrazine. The photoproduct was isolated, and its elemental analysis agrees with the formulation $[\text{Ru}(\text{bpz})_2(\text{CH}_2\text{CN})(\text{Cl})][\text{PF}_6]$ (II). The quantum yield is sensitive to $[\text{Cl}^-]$, being greatest when the $[\text{Cl}^-]$ is maximized.¹² We achieved a quantum yield as high as 0.37 for formation of complex II.

$[\text{Ru}(\text{bpz})_2(\text{CH}_3\text{CN})(\text{Cl})]^+$ is itself photoactive and as shown in Figure 2 can be irradiated ($\lambda > 350$ nm) to give $\text{Ru}(\text{bpz})_2\text{Cl}_2$ (III) (quantum yield 0.001) and an unstable ruthenium complex (VI) as yet unidentified. We believe this latter complex to be a mono(bipyrazyl)ruthenium(II) species (VI) due to its absorbance at 660 nm, which we assign to a MLCT transition, red shifted because of decreased coordination of bipyrazine ligands and increased coordination of Cl^- .¹¹ The stability of this mono(bipyrazyl) complex appears to decrease in the presence of oxygen and increasing $[\text{Cl}^-]$. The identities of the two major photoproducts, (II) and (III), were affirmed unequivocally by analysis, appropriate conductivity (Table I), NMR, and the essential identity of their electronic spectra with well-characterized bipyridyl analogues (see discussion below). They both have a cis configuration.

Jones and Cole-Hamilton¹³ reported the photoanation of the ruthenium(II) tris(bipyridyl) dication, $\text{Ru}(\text{bpy})_3^{2+}$, by Cl^- in acetonitrile. The only photoproduct, $[\text{Ru}(\text{bpy})_2(\text{CH}_3\text{CN})(\text{Cl})][\text{Cl}]$, was obtained with a maximum quantum yield of 0.01. In solvents of lower polarity such as acetone and CH_2Cl_2 , the only photoproduct formed was $\text{Ru}(\text{bpy})_2\text{Cl}_2$ with a slightly

greater quantum yield of 0.02.¹⁴ These facts are suggestive of an ion-paired mechanism for photoanation, and indeed, photoanation studies of $\text{Ru}(\text{bpy})_3^{2+}$ in DMF support this kind of mechanism.¹⁵

The mechanism of photoanation of $\text{Ru}(\text{bpz})_3^{2+}$, by analogy to that of $\text{Ru}(\text{bpy})_3^{2+}$, is believed to be dissociative, resulting in a five-coordinate intermediate with an end-bonded bipyrazine ligand. Complexes in nonaqueous solution associate with their counterions in ion pairs. Thus, as soon as the five-coordinate intermediate is formed, anation results from the Cl^- associated in the ion pair. Monodentate bipyridyl intermediates have been isolated and seen spectroscopically.^{16,17} However, these intermediates are unstable, and it is probable, in the case of $\text{Ru}(\text{bpz})_3^{2+}$, the buildup of a monodentate bipyrazyl complex is not seen spectroscopically because of its rapid re-formation to $\text{Ru}(\text{bpz})_3^{2+}$ or conversion to $[\text{Ru}(\text{bpz})_2(\text{CH}_3\text{CN})(\text{Cl})]^+$.

Van Houten and Watts¹⁶ examined the temperature dependence for the formation of monodentate bipyridyl complex, $[\text{Ru}(\text{bpy})_2(\text{bpy})(\text{Cl})]^+$, from $\text{Ru}(\text{bpy})_3^{2+}$ in 0.1 M HCl. They suggested that the photoanation reaction occurs via a ligand field state lying 10.4 kcal mol⁻¹ above the lowest level of the "triplet" charge-transfer state, which together with a further activation energy of 5.5 kcal mol⁻¹ gives a total apparent activation energy of 15.9 kcal mol⁻¹. Porter and Sparks¹⁸ have found the same activation energy for the racemization of $\text{Ru}(\text{bpy})_3^{2+}$. It is possible the greater photoanation quantum yield of $\text{Ru}(\text{bpz})_3^{2+}$ ($\phi = 0.37$) compared to that of $\text{Ru}(\text{bpy})_3^{2+}$ ($\phi = 0.01$)^{13,19} is due in part to a smaller energy separation between the photoactive ligand field state and the lowest level of the charge-transfer excited state. The photoanation of $\text{Ru}(\text{bpy})_3^{2+}$ in DMF is believed to proceed via ion multiplets: an ion-pair-formed $\text{Ru}(\text{bpy})_2(\text{DMF})(\text{A})^+$ and an ion-triplet-formed $\text{Ru}(\text{bpy})_2(\text{A})_2$ (A = anion ligand). However, it was noted by the authors¹⁵ that photoconversion occurred between the bis complexes. Moreover formation of the dithiocyanato complex was preceded by an induction period, a classic indication of secondary photolysis. The photoanation of $[\text{Ru}(\text{bpz})_2(\text{CH}_3\text{CN})(\text{Cl})]^+$ ²⁰ does not necessarily require an ion-multiplet mechanism but may simply result from the formation of cis- and trans-chloride intermediates. The existence of the mono(bipyrazyl) photoproduct VI suggests that photoanation of complex II proceeds via another monodentate bipyrazyl intermediate. This could, in principle, give rise to both cis- and trans-dichloro products. The trans isomer may be absent because of steric repulsion between H6 protons of opposing bipyrazine ligands. Before the trans intermediate could rearrange to the cis conformation, monodentate bipyrazyl is lost, forming the mono(bipyrazyl)ruthenium(II) complex. Further work is required on $[\text{Ru}(\text{bpz})_2(\text{CH}_3\text{CN})(\text{Cl})]^+$ photoanation in order to distinguish between possible mechanisms. Finally, $[\text{Ru}(\text{bpz})_2(\text{CH}_3\text{CN})(\text{Cl})]^+$ has no measurable luminescence at room temperature in acetonitrile, indicating the excited state is not populated to a great extent and/or is subject to self-quenching processes. Either possibility is expected to decrease

(14) Gleria, M.; Minto, F.; Beggiato, G.; Bortolus, P. *J. Chem. Soc., Chem. Commun.* 1978, 285.

(15) Hoggard, P. E.; Porter, G. B. *J. Am. Chem. Soc.* 1978, 100, 1457. Wallace, W. M.; Hoggard, P. E. *Inorg. Chem.* 1980, 19, 2141.

(16) Van Houten, J.; Watts, R. *J. Inorg. Chem.* 1978, 17, 3381.

(17) Durham, B.; Walsh, J. L.; Carter, C. L.; Meyer, J. *J. Inorg. Chem.* 1980, 19, 860.

(18) Porter, G. B.; Sparks, R. H. *J. Photochem.* 1980, 13, 123.

(19) This comparison should be treated with caution. The experimental conditions for the two measurements were not the same.

(20) Note that irradiation into the 443-nm band of $\text{Ru}(\text{bpz})_3^{2+}$ (in $\text{CH}_3\text{CN}/\text{Cl}^-$) leads only to formation of complex II, while irradiation into the 491-nm band of complex II leads to formation of complexes III and VI. Furthermore, irradiation ($\lambda > 350$ nm) of $\text{Ru}(\text{bpz})_2\text{Cl}_2$ in acetonitrile in the presence of 2.0×10^{-3} M $(\text{TEA})\text{Cl}$ will not form the mono(bipyrazyl) complex.

(12) At $[\text{Cl}^-] > 2.0 \times 10^{-3}$ M, $\text{Ru}(\text{bpz})_3\text{Cl}_2$ precipitates from solution.

(13) Jones, R. F.; Cole-Hamilton, D. J. *Inorg. Chim. Acta* 1981, 53, L3.

Table II. ^1H NMR Assignments^a

complex	H3	H5	H6	H3'	H5'	H6'	$J_{3,6}$	$J_{3',6'}$	$J_{5,6}$	$J_{5',6'}$
bpz ^b	9.53	8.84	8.84							
Ru(bpz) ₃ ²⁺	10.17	8.76	8.03				0.8		3.5	
<i>cis</i> -Ru(bpz) ₂ (CH ₃ CN)Cl ^{b,c}	10.20	9.20	9.85	10.04	8.52	8.14	0.8	0.8	3.2	3.2
<i>cis</i> -Ru(bpz) ₂ Cl ₂ ^b	10.15	9.08	9.61			7.97				
Mo(CO) ₄ bpz ^d	10.03	8.98	9.92	9.86	8.28	7.88	0.8	0.8	3.3	3.3
W(CO) ₄ bpz ^d				9.57	8.66	9.20		1.2		3.4
				9.60	8.60	9.29		1.3		3.4

^a All assignments are in δ referenced to Me₄Si, and all J values are in hertz. H3', H5', and H6' protons in the ring are trans to coordinated ligands other than bipyrazyl. ^b In Me₂SO-*d*₆. ^c CH₃CN methyl group at 2.43 ppm. ^d In CDCl₃ + 1% Me₄Si.

Table III. Vibrational Frequency (cm⁻¹) and Force Constant Data (mdyn/A) for (Bipyridyl)- and (Bipyrazyl)molybdenum and -tungsten Tetracarbonyls^a

complex	A ₁	B ₁	A ₁	B ₂	k_1	k_2	k_i	A ₁ (calcd)
Mo(bpy)(CO) ₄	2017 s	1909 vs	1878 sh	1829 s	13.87	15.45	0.37	1861
Mo(bpz)(CO) ₄	2021 s	1933 vs	1910 sh	1860 s	14.27	15.70	0.30	1887
W(bpy)(CO) ₄	2010 s	1899 vs	1873 sh	1826 s	13.84	15.31	0.37	1858
W(bpz)(CO) ₄	2018 s	1927 vs	1905 sh	1857 s	14.24	15.62	0.31	1885

^a Force constants are calculated according to the method and matrices in ref 28. The B₁, B₂ and higher energy A₁ frequencies were used as data. The lower energy A₁ frequency was calculated from the resulting force constants and is indicated in the final column. Bipyridyl frequency data are from ref 29. Our force constants differ slightly from those reported in ref 29 with use of the same data set.

the photoanation quantum yield and probably explains the greater photoactivity of Ru(bpz)₃²⁺ relative to that of [Ru(bpz)₂(CH₃CN)Cl]⁺.

Photoanation of Ru(bpz)₃²⁺ has also been observed in methanol, ethanol, and DMF, and so care must be taken to exclude potential anion ligands from these solvents when Ru(bpz)₃²⁺ is used as a photosensitizer. Nevertheless, photoanation appears to be a successful source route into the preparation of ruthenium(II) bis(bipyrazyl) complexes.

¹H NMR Spectra of the Ruthenium(II) Complexes. The proton NMR spectrum of free 2,2'-bipyrazine in Me₂SO-*d*₆ is shown in Figure 3a. The simplicity of the spectrum suggests both pyrazine moieties are equivalent. The exact conformation of free bipyrazine in solution is not known. The *cis* conformation (see Figure 3a) is expected to be the least stable due to steric repulsion of H3 protons. 2,2'-bipyridine is known to be in the *trans* conformation in the solid.^{21,22} Measurements of the electric dipole moment,²³ and ¹H NMR²⁴ as well as of ultraviolet spectroscopy²⁵ data are also consistent with a *trans*-planar conformation in solution. Nevertheless, the H3 protons of bipyrazine in solution are expected to be deshielded by either the nonbonding electrons of nitrogen in the *trans* conformation and/or the diamagnetic anisotropy of the opposing pyrazine ring. Thus, proton H3 is assigned to the singlet resonance at 9.53 ppm and protons H5 and H6 are assigned to the singlet peak at 8.84 ppm.

A detailed ¹H NMR examination of ruthenium(II) bipyrazyl complexes (see Figure 3 and Table II) reveals unusual chemical shifts and simple splitting patterns that prove useful in determining the exact three-dimensional structure and purity of the complexes. When bonded to ruthenium(II), bipyrazine is forced into a *cis* conformation and the protons of each pyrazine moiety form an ABX system. $J_{5,6}$ and $J_{3,6}$ coupling is observed but not $J_{3,5}$ coupling, and so H5 protons can be distinguished readily from H6 protons. The ring protons of bipyrazine experience three additional effects when bipyrazine bonds to ruthenium(II). First, when bipyrazine is in the *cis* conformation, the H3 protons are forced together, giving rise to a van der Waals deshielding interaction. Second, the in-

ductive effect of ruthenium(II) deshields ring protons. Finally, the diamagnetic anisotropic effect of the aromatic ring of the adjacent ligand shields ring protons, particularly H6 protons. These effects have been discussed in detail in explaining the observed proton chemical shifts for Ru(bpy)₃²⁺,²⁶ Ru(bpy)₂en²⁺,²⁶ (en = ethylenediamine), and Ru(DMBP)₃²⁺²⁷ (DMBP = 4,4'-dimethyl-2,2'-bipyridyl) ¹H NMR spectra, and so the arguments for the proton assignments given in Table II will not be repeated in this analysis.

Figure 3 clearly demonstrates how decreasing symmetry increases the complexity of a ¹H NMR spectrum. The ¹H NMR spectrum of Ru(bpz)₃²⁺ (Figure 3b) is made up of a single ABX pattern since all pyrazine moieties in the complex are equivalent as expected for a complex with *D*₃ symmetry. The ¹H NMR spectra of Ru(bpz)₂Cl₂ and [Ru(bpz)₂(CH₃CN)Cl]⁺ are only consistent with a *cis* stereochemistry. *cis*-Ru(bpz)₂Cl₂ has *C*₂ symmetry with two inequivalent pyrazine moieties producing two ABX patterns in the ¹H NMR spectrum. This is confirmed nicely by experiment (see Figure 3c). *cis*-[Ru(bpz)₂(CH₃CN)(Cl)]⁺ has no symmetry, and so we expect to see four ABX patterns in the ¹H NMR spectrum from four inequivalent pyrazine moieties. Four ABX patterns (see Figure 3d) can indeed be distinguished, although two of them (H3', H5', and H6' protons) are nearly equivalent.

A *trans*-ruthenium(II) bis(bipyrazyl) complex has not yet been synthesized. However, its ¹H NMR spectrum is expected to resemble the spectrum of Ru(bpz)₃²⁺ except that H5 will be shifted upfield relative to H6. The ¹H NMR spectra of M(CO)₄bpz (M = Mo or W) (see Figure 4 and Table II) are similar to that expected for a *trans*-ruthenium(II) bis(bipyrazyl) complex.

Mo(CO)₄bpz (IV) and W(CO)₄bpz (V). The carbonyl compounds IV and V were prepared from reaction of bipyrazine with the corresponding hexacarbonyls to provide a further comparison with the bipyridyl analogues.⁴ The bipyridyl and bipyrazyl complexes have similar carbonyl stretching frequencies in the infrared (Table III) but the latter are shifted to higher energies. The spectra were assigned and force constants calculated with the methods of Cotton and Kraihanzel^{28,29} (Table III). We turn to their significance

- (21) Bertinotti, F.; Liguori, A. M.; Parisi, R. *Gazz. Chim. Ital.* **1956**, *86*, 893.
 (22) Merritt, L. L., Jr.; Schroeder, E. D. *Acta Crystallogr.* **1956**, *9*, 801.
 (23) Cureton, P. H.; LeFevre, C. G.; LeFevre, R. J. W. *J. Chem. Soc.* **1963**, 1736.
 (24) Castellano, S.; Gunther, H.; Ebersole, S. *J. Phys. Chem.* **1965**, *69*, 4166.
 (25) Nakamoto, K. *J. Phys. Chem.* **1960**, *64*, 1420.

- (26) Lytle, F. E.; Petrosky, L. M.; Carlson, L. R. *Anal. Chim. Acta* **1971**, *57*, 239.
 (27) Bryant, G. M.; Fergusson, J. E. *Aust. J. Chem.* **1971**, *24*, 441.
 (28) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432.

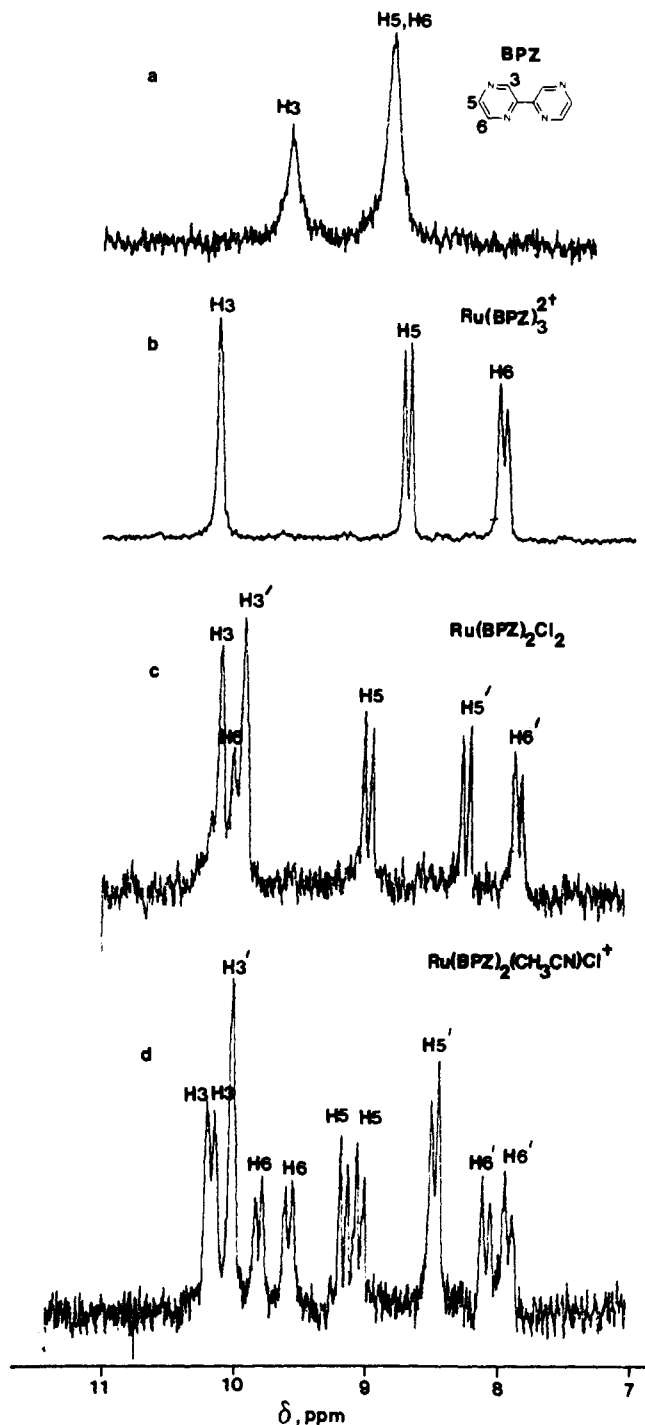


Figure 3. ^1H NMR spectra of (a) bpz, saturated at $\sim 2 \times 10^{-2}$ M, (b) $\text{Ru}(\text{bpz})_3(\text{PF}_6)_2$, 3.6×10^{-2} M, (c) *cis*- $\text{Ru}(\text{bpz})_2\text{Cl}_2$, saturated at $\sim 2 \times 10^{-2}$ M, and (d) *cis*- $[\text{Ru}(\text{bpz})_2(\text{CH}_3\text{CN})(\text{Cl})]^+[\text{PF}_6]^-$, 2.5×10^{-2} M, in $\text{Me}_2\text{SO}-d_6$.

below, after discussion of the electronic and electrochemical data.

Electronic Spectra. Clear comparisons can be made between the electronic spectra of the bipyrazyl complexes and those of their bipyridyl analogues. Low-energy bands in the visible region are clearly ascribed to $\text{Ru}(\text{II})$, $\text{Mo}(\text{0})$, or $\text{W}(\text{0})$ to bipyrazine charge transfer. Higher energy bands are $\pi-\pi^*$ transitions within the bipyrazine rings, $\text{M}-\text{CO}$ charge transfer and additional MLCT (to bipyrazine) as discussed for individual compounds as follows. The electronic absorption spectra of $\text{Ru}(\text{bpz})_3^{2+}$, $[\text{Ru}(\text{bpz})_2(\text{CH}_3\text{CN})\text{Cl}]^+$, and $\text{Ru}(\text{bpz})_2\text{Cl}_2$ are

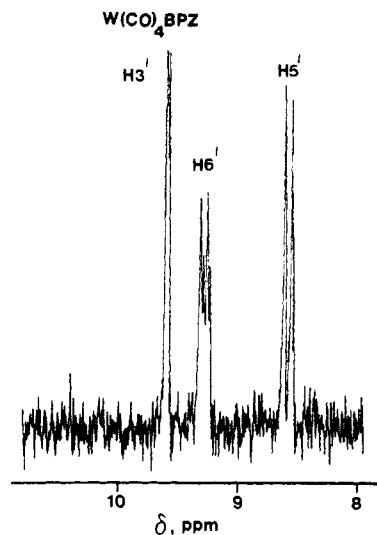


Figure 4. ^1H NMR spectrum of $\text{W}(\text{CO})_4\text{bpz}$, saturated solution in CDCl_3 .

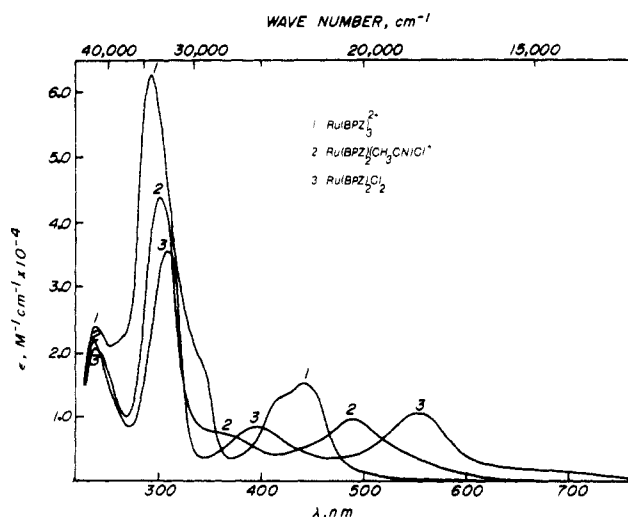


Figure 5. UV-vis spectra of (1) $\text{Ru}(\text{bpz})_3(\text{PF}_6)_2$, (2) $[\text{Ru}(\text{bpz})_2(\text{CH}_3\text{CN})(\text{Cl})]^+[\text{PF}_6]^-$, and (3) $\text{Ru}(\text{bpz})_2\text{Cl}_2$. All are 3.20×10^{-5} M in acetonitrile.

compared in Figure 5 and Table IV. There is a very close similarity between the visible spectra of these complexes and those of their bipyridyl analogues.^{11,30} The band at $22\,575\text{ cm}^{-1}$ in the spectrum of $\text{Ru}(\text{bpz})_3^{2+}$ is a $d\pi-\pi^*$ MLCT transition as extensively studied in its bipyridyl analogue.³¹ Corresponding low-energy visible-region bands in the spectra of the other complexes are also MLCT in origin.¹¹ The two major peaks in the ultraviolet spectra are essentially independent of the detailed nature of the complex and must be assigned as $\pi-\pi^*$ transitions within the bipyrazine rings. A composite band near $40\,000\text{ cm}^{-1}$ has, in the spectrum of $\text{Ru}(\text{bpy})_3^{2+}$, been assigned as a higher energy MLCT transition rather than $\pi-\pi^*$.³² Such an assignment here appears untenable in view of a study of bipyridine $\pi-\pi^*$ transitions by Nakamoto²⁵ and the constancy of the energy in compounds I-III while the visible MLCT transitions shift so much. Moreover there is a weaker absorption near $37\,455\text{ cm}^{-1}$ in $\text{Ru}(\text{bpz})_3^{2+}$ that may correspond to this higher energy MLCT band. It shifts out of this region, presumably to lower energy, in concert with the shift in visible-region MLCT transitions from compounds I-III. The major shoulder near $29\,155\text{ cm}^{-1}$

(30) Klaasen, A. M.; Crosby, G. A. *J. Chem. Phys.* **1968**, *48*, 1853.

(31) Crosby, G. A. *Acc. Chem. Res.* **1975**, *8*, 231.

(32) Lytle, F. E.; Hercules, D. M. *J. Am. Chem. Soc.* **1969**, *91*, 253.

Table IV. Electronic Spectroscopic Data for Ruthenium(II), Molybdenum(0), and Tungsten(0) Bipyrazyl and Bipyridyl Complexes^a

species	MLCT ^b	$\pi-\pi^*$
bpz ^c		34 720 (4.29), 44 055 (4.02)
bpy ^{c,d}		35 335 (4.01), 42 195 (3.87)
Ru(bpz) ₃ ²⁺	22 575 (4.18), 29 155 (4.27), 37 455 (4.34)	33 900 (4.79), 41 495 (4.37)
Ru(bpy) ₃ ²⁺ e	22 125 (4.16), 28 985 (3.81), 30 960 (3.81)	35 090 (4.94), 40 000 (4.40), 42 015 (4.47)
Ru(bpz) ₂ (CH ₃ CN)Cl ⁺	20 365 (4.00), 26 955 (3.89)	32 785 (4.63), 41 665 (4.33)
Ru(bpy) ₂ (CH ₃ CN)Cl ⁺	20 790 (3.94), 28 985 (3.90)	34 245 (4.73), 41 665 (4.36)
Ru(bpz) ₂ Cl ₂	18 020 (4.03), 25 315 (3.94)	32 050 (4.54), 41 325 (4.31)
Ru(bpy) ₂ Cl ₂	18 280 (3.95), 26 595 (3.94)	33 555 (4.70), 41 495 (4.33)
Mo(bpz) ₄ (CO) ₄ ^c	18 280 (3.84), 26 525 (3.76), 31 645 (4.31)	32 680 (4.35), 39 060 (4.48), 45 250 (4.40)
Mo(bpy) ₄ (CO) ₄ ^c	21 185 (3.66), 25 775 (3.53), 28 900 (3.59)	33 670 (4.46), 38 910 (4.44)
W(bpz) ₄ (CO) ₄ ^c	17 920 (3.88), 26 315 (3.74), 31 350 (4.22)	32 575 (4.23), 39 685 (4.56), 45 870 (4.40)
W(bpy) ₄ (CO) ₄ ^c	20 620 (3.64), 24 270 (3.40), 28 410 (3.54)	33 445 (4.40), 39 215 (4.45), 45 660 (4.34)

^a All data were recorded in acetonitrile solution, except where indicated, and are in cm⁻¹ (log ϵ in parentheses). ^b In the ruthenium complexes, the MLCT transitions are Ru–diimine. The higher energy transitions in the carbonyl derivatives will also contain MLCT to CO transitions. ^c Recorded in EtOH. ^d Reference 25. ^e Recorded in H₂O.

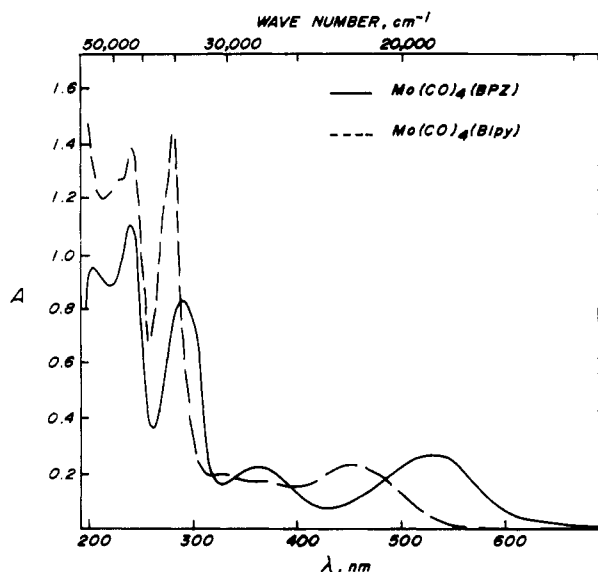


Figure 6. UV-vis spectra of Mo(CO)₄bpz (—), 3.7×10^{-5} M, and Mo(CO)₄(bpy) (---), 5.0×10^{-5} M, in ethanol.

in the spectrum of Ru(bpz)₃²⁺ could be an enhanced-intensity d–d band or a second MLCT transition. To be consistent, we favor the latter assignment since the energy separation between the two MLCT transitions is then approximately equal to the energy separation between the two assigned $\pi-\pi^*$ transitions. In these ruthenium derivatives the successive substitution of halogen results in a red shift in the MLCT to bipyrazine transitions as the metal atom becomes more readily oxidizable (see the discussion on electrochemistry below).

The visible-region bands in the tungsten and molybdenum complexes (IV and V) are also clearly identifiable as MLCT to bipyrazine³³ (Figure 6). The four bands in the ultraviolet region must be ascribed to a mixture of bipyrazine $\pi-\pi^*$, MLCT to bipyrazine, and MLCT to CO. The significance of these various electronic spectroscopic data is assessed below.

Electrochemical Data. The results of cyclic voltammetry experiments on ruthenium(II) bipyrazyl complexes in acetonitrile with 0.1 M TEAH as supporting electrolyte are compared with those of their bipyridyl analogues in Table V. $E_{1/2}$ values were calculated from the average of the anodic and cathodic peak potentials ($E_{1/2} = (E_{pa} + E_{pc})/2$) at a scan rate of 100 mV s⁻¹. The difference in potential between anodic and cathodic peak currents varied from 60 to 75 mV largely independent of scan rate. Both Ru(bpz)₃²⁺ and [Ru(bpz)₂(CH₃CN)Cl]⁺ undergo reversible one-electron oxidations and

Table V. Electrochemistry Data

complex	$E_{1/2}$, V			
	oxidn	redn		
Ru(bpz) ₃ (PF ₆) ₂ ^a	1.86	-0.80	-0.98	-1.24
Ru(bpy) ₃ (PF ₆) ₂ ^b	1.354	-1.332	-1.517	-1.764
Ru(bpz) ₂ (CH ₃ CN)(Cl)PF ₆ ^a	1.32	-0.99	-1.25	
Ru(bpy) ₂ (CH ₃ CN)(Cl)PF ₆ ^c	0.84			
Ru(bpz) ₂ Cl ₂ ^a	0.80	-1.04 ^e	-1.27 ^e	
Ru(bpy) ₂ Cl ₂ ^d	0.31			
bpz ^a		-1.76		
bpy ^f		-2.21	-2.46	
Ni(bpz) ₃ (PF ₆) ₂ ^a		g	-0.71 ⁱ	
Ni(bpy) ₃ (ClO ₄) ₂ ^h	1.66	-1.31		
Mo(CO) ₄ bpz ^{a,j}	1.73 ⁱ	0.65 ⁱ	-1.17	-1.77 ^e
Mo(CO) ₄ bpy ^{a,j}	1.08 ⁱ	0.52 ⁱ	-1.68	
W(CO) ₄ bpz ^{a,j}		0.68 ⁱ	-1.08	-1.69 ^e
W(CO) ₄ bpy ^{a,j}	1.02 ⁱ	0.53 ⁱ	-1.58	

^a 0.1 M TEAH in CH₃CN vs. SCE; potential range +2.0 to -2.0 V. ^b 0.1 M tetrabutylammonium tetrafluoroborate vs. SCE:

Tokel-Takvoryan, N. E.; Hemingway, R. E.; Bard, A. J. *J. Am. Chem. Soc.* 1973, 95, 6582. ^c 0.1 M tetrabutylammonium hexafluorophosphate vs. SSCE: Johnson, E. C.; Sullivan, B. P.; Salmon, D. J.; Adeyemi, S. A.; Meyer, T. J. *Inorg. Chem.* 1978, 17, 2211. ^d 0.1 M tetraethylammonium perchlorate vs. SSCE.¹⁷

^e Partially reversible. ^f 0.1 M tetraethylammonium perchlorate vs. SCE: Weiner, M. A.; Basu, A. *Inorg. Chem.* 1980, 19, 2797.

^g No oxidation wave observed up to +2.3 V. ^h 0.1 M tetraethylammonium perchlorate in CH₃CN vs. SCE. ⁱ Irreversible. ^j Scan rate 500 mV s⁻¹.

reductions in acetonitrile. Ru(bpz)₂Cl₂ undergoes reversible one-electron oxidation, but only partially reversible reduction in acetonitrile. Apparently, once the reduction product of Ru(bpz)₂Cl₂ is formed, it deposits on the working platinum electrode. Data for the pair of nickel(II) complexes and for the carbonyl derivatives (IV and V) are also reported in Table V. By analogy with the ruthenium electrochemical data, the assignment of these one-electron couples is straightforward.³⁴

All of the cited oxidation waves refer to oxidation of the metal (Ru(III)/Ru(II), Ni(III)/Ni(II), and M(I)/M(0), M = Mo, W), since oxidation of bipyrazine occurs at very positive potentials and is expected to shift positively when bipyrazine is coordinated to a metal atom. The negative shift in Ru(III)/Ru(II) potentials with successive substitution of chloride ion reflects increasing oxidizability of the metal with substitution of the more σ -donor chloride ion. Bipyrazine itself is reduced at -1.76 V (Table V). This wave is expected to shift positively when bipyrazine is coordinated to a metal. Thus all reduction waves observed in the metal complexes, and listed in Table V, are attributed to bipyrazyl reduction and not metal reduction.³⁴⁻³⁶

(33) Balk, R. W.; Snoeck, T.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* 1980, 19, 3015.

(34) ESR studies are in progress to confirm these assignments.

The most striking observation is the almost precise 0.5-V positive shift in passing from bipyrazyl to the analogous bipyridyl complex seen for all oxidation and reduction couples except for oxidation of the metal carbonyl derivatives.

Significance of the Spectroscopic and Electrochemical Data.

Despite their overt similarity, there are at least two important distinctions between bipyridine and bipyrazine. On the basis of the pK_a of pyridine (5.25) and pyrazine (0.65), it is clear that bipyrazine is a very much weaker base than bipyridine.

Secondly, the shift of 0.5 V in the reduction potential of bipyrazyl and its derivatives vs. bipyridyl requires that the LUMO π^* orbital in bipyrazyl is stabilized by about 0.5 V vs. that of bipyridyl.

This latter situation ought to ensure that bipyrazyl is a much better π acceptor toward π -donor metal ions than is bipyridyl. The charge-transfer data (MLCT transitions) do not, however, provide convincing support for such an argument.

Comparison of the ruthenium data shown here (Table IV) and MLCT data for bipyridyl and bipyrazyl complexes of nickel and iron in the literature^{6,37} reveals that the MLCT transition energies in these complexes are essentially the same and are independent of the diimine ligand. There is a small but not remarkable shift to the blue in the MLCT transitions of the bipyridyl analogues of complexes IV and V. Given that the π^* orbital of bipyrazyl has been stabilized by 0.5 V, the most simple conclusion to draw would be that the donor metal orbital has also been stabilized by 0.5 V, resulting in no change in MLCT transition energy between the two diimines. Indeed, the electrochemical data show that this has occurred, since, with the exception of the carbonyl derivatives IV and V, oxidation of the metal has shifted 0.5 V positively from bipyridyl to bipyrazyl. An initial response to this observation might be that the increased 0.5-V stabilization of the metal $d\pi$ orbital reflects increased back-donation to the bipyrazyl ligand. For ruthenium(II) this could be possible. However, it is an unacceptable conclusion for the pair of nickel(II) complexes. The MLCT energies are almost identical ($Ni(bpy)_3^{2+}$ 26 000 cm^{-1} , $Ni(bpz)_3^{2+}$ 27 600 cm^{-1}),^{6,37,38} but nickel(II) has essentially no π -back-donation capability.³⁹

A more convincing explanation is that the much weaker σ -donor strength of bipyrazyl causes the metal ion to have a significantly higher effective nuclear charge relative to that

of bipyridyl analogues, and it is this effect that causes, primarily at least, the stabilization of the metal d orbitals. That the degree of stabilization is the same as that for the π^* orbital of bipyrazyl vs. bipyridyl may then be fortuitous. Support for this argument arises through consideration of the carbonyl data. With a zerovalent metal the difference in σ -donor strength of bipyrazyl vs. bipyridyl is much less relevant than it is for the 2+ metal ions. Therefore, the relative stabilization of the metal orbitals is very much less (0.13–0.15 V), and the MLCT transitions differ rather more. The higher C–O stretching force constants seen in compounds IV and V relative to those of their bipyridyl analogues (Table III) are then ascribed to a more positive effective nuclear charge on the metals impeding back-donation to the carbonyl groups.

For the ruthenium complexes, the difference between metal oxidation and ligand reduction is the same for both bipyridyl and bipyrazyl. Thus, the essential identity in charge-transfer transitions is consistent.

For the metal carbonyl derivatives (IV and V), this difference is some 0.35 V less for bipyrazyl relative to that for bipyridyl. In agreement, the bipyrazyl charge-transfer bands are red shifted by approximately the same amount. The validity of using electrochemical data to calculate charge-transfer energies has recently been discussed in more depth in an analysis of the charge-transfer spectra and redox chemistry of transition-metal phthalocyanines.⁴⁰

In conclusion, despite stabilization of the π^* orbital, bipyrazyl is not a very much better π acceptor than bipyridyl. With bipyridyl the strong σ -donor strength can cause a synergistic enhancement of π back-donation with π -donor metals; this is largely absent for bipyrazyl and serves, thereby, to diminish its π -acceptor capability.⁴¹

Acknowledgment. The authors are indebted to Imperial Esso and the Natural Sciences and Engineering Research Council (Ottawa) for financial support. This is part of a joint project with Professor A. J. Bard (The University of Texas at Austin) supported by the Office of Naval Research (Washington, D.C.) to whom we are also indebted.

Registry No. I-Cl₂, 80925-50-4; I-2PF₆, 80907-56-8; II, 80907-58-0; III, 80907-59-1; IV, 80907-60-4; V, 80925-51-5; 2,2'-bipyrazine, 10199-00-5; Ru(Me₂SO)₄Cl₂, 11070-19-2; Mo(CO)₆, 13939-06-5; W(CO)₆, 14040-11-0; bis(2-pyrazinecarboxylato)copper(II), 80907-61-5; [Ru(bpy)₂(CH₃CN)Cl]PF₆, 38123-76-1; Mo(bpy)(CO)₄, 15668-64-1; Ru(bpy)₂Cl₂, 19542-80-4; W(bpy)(CO)₄, 15668-66-3; Ni(bpz)₃(PF₆)₂, 80907-63-7; Ni(bpy)₃(ClO₄)₂, 16166-37-3.

(35) Motten, A. G.; Hanck, K.; DeArmond, M. K. *Chem. Phys. Lett.* **1981**, *79*, 541.

(36) Heath, G. A.; Yellowlees, L. J.; Braterman, P. S. *J. Chem. Soc., Chem. Commun.* **1981**, 287.

(37) Jørgensen, C. K. *Adv. Chem. Phys.* **1963**, *5*, 33.

(38) Byers, W.; Chou, B. F. C.; Lever, A. B. P.; Parish, R. V. *J. Am. Chem. Soc.* **1969**, *91*, 1329.

(39) Lever, A. B. P.; London, G.; McCarthy, P. J. *Can. J. Chem.* **1977**, *55*, 3172.

(40) Lever, A. B. P.; Licocchia, S.; Minor, P. C.; Ramaswamy, B. S.; Pickens, S. R.; Magnell, K. *J. Am. Chem. Soc.* **1981**, *103*, 6800.

(41) Balk, R. W.; Stufkens, D. J.; Crutchley, R. J.; Lever, A. B. P. *Inorg. Chim. Acta* **1981**, *64*, L49.