

- (34) J. S. Miller and K. G. Caulton, *J. Am. Chem. Soc.*, **97**, 1067 (1975).
 (35) J. D. Drulliner, A. D. English, J. P. Jesson, P. Meakin, and C. A. Tolman, *J. Am. Chem. Soc.*, **98**, 2156 (1976).
 (36) J. P. Jesson and P. Meakin, *J. Am. Chem. Soc.*, **96**, 5760 (1974); **95**, 7272 (1973).
 (37) M. J. Hynes and P. F. Brannick, *J. Chem. Soc., Chem. Commun.*, 942 (1977).
 (38) C. A. Tolman, *Chem. Soc. Rev.*, **1**, 337 (1972).
 (39) P. F. Meier, A. E. Merbach, M. Dartiguenave, and Y. Dartiguenave, to be submitted for publication.

Contribution from the Department of Chemistry,
 The University of North Carolina, Chapel Hill, North Carolina 27514

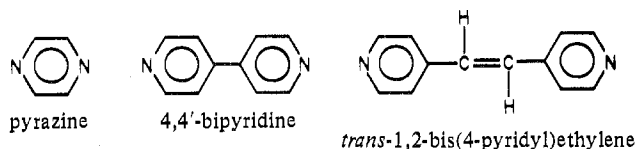
Ligand-Bridged Complexes of Ruthenium(III). Magnetic Properties of Ligand-Bridged, Dimeric and Pyrazine-Bridged, Polymeric Complexes

EUGENE C. JOHNSON, ROBERT W. CALLAHAN, RICHARD P. ECKBERG, WILLIAM E. HATFIELD,* and THOMAS J. MEYER*

Received March 17, 1978

A series of ligand-bridged complexes of ruthenium(III) have been prepared utilizing pyrazine, 4,4'-bipyridine, and 1,2-bis(4-pyridyl)ethane as the bridging ligands. The preparations involve the use of Ce(IV) to oxidize complexes of ruthenium(II) whose preparations were described previously. Dimeric complexes of the three bridging ligands, as well as trimeric and tetrameric pyrazine-bridged complexes, were prepared. The electronic spectra and magnetic properties of these formally low-spin d^5 metal complexes were studied, the latter down to liquid-helium temperatures. The flexibility in the synthetic chemistry allowed, in principle, for a systematic study of the magnetic effects of different metal-metal interactions arising from changes in the bridging ligand and in polymer chain length. However, the magnetic results indicate little, if any, interactions in any of the complexes including the polymeric cases where the possibility of extended metal-metal interactions exists.

In past work we have developed a synthetic chemistry which has led to the preparation of a series of ligand-bridged dimeric and oligomeric complexes of ruthenium.¹ Dimeric complexes have been prepared using a series of N-heterocyclic ligands, $(bpy)_2ClRu(L)RuCl(bpy)_2^{2+}$ (bpy is 2,2'-bipyridine; L is pyrazine (pyz), 4,4'-bipyridine (4,4'- bpy), or *trans*-1,2-bis(4-pyridyl)ethylene (BPE)), and pyrazine-bridged oligomeric



complexes have been prepared with controlled chain lengths, $[(bpy)_2ClRu(pyrazine)[Ru(bpy)_2(pyrazine)]_nRuCl(bpy)_2]^{(2n+2)+}$ ($n = 0-4$). The preparative chemistry involved uses the reactivity properties of the bound nitrosyl and nitro groups in a series of stepwise reactions.² From the known stereochemistry of bis(2,2'-bipyridine) complexes, the coordination geometry at each ruthenium site in the oligomeric chains is most likely *cis*.³

Questions of fundamental interest in ligand-bridged metal complexes are the nature and extent of metal-metal interactions across the bridging ligands and the effects of the interactions on the chemical and physical properties of the system. The role of metal-metal interactions has been studied extensively in dimeric ruthenium complexes especially in mixed-valence systems.^{4,5} From these studies it has been shown that the extent of electronic interaction can vary from interactions which are sufficiently strong to modify the chemical and physical properties of the system in a significant way⁶⁻⁸ to weak interactions where the separate redox sites are only slightly perturbed compared to isolated monomeric sites.^{4,5,9-11} The differences in properties observed appear to be understandable based on the properties of a series of closely related dimeric compounds.^{4b,11}

Localized valences are favored for cases where significant vibrational trapping energies exist for the excess electron. The trapping energy arises because a change in oxidation state at

the metal leads to differences in the inner- and the outer-coordination spheres at the two redox sites. Orbital overlap leads to electronic delocalization and reduces the vibrational trapping energy by making the two sites more nearly equivalent. In one limit, the electronic resonance energy arising from the overlap is sufficient to overcome the trapping energy, and the vibrational structures at the two sites become identical. Delocalization is favored by strong metal-metal overlap, and in ligand-bridged systems, the distance for significant overlap can be extended by mixing metal orbitals with orbitals on the bridging ligand.

Ruthenium(III) is a readily accessible oxidation state in dimeric 2,2'-bipyridine complexes of ruthenium as shown by electrochemical studies on ions like $[(bpy)_2ClRu(pyrazine)RuCl(bpy)_2]^{12+}$.^{9,10} Complexes of ruthenium(III) have been found to be spin-paired d^5 cases with one unpaired electron¹²⁻¹⁴ which means that in dimeric ions like the 4+ ion, $[(bpy)_2ClRu(pyrazine)RuCl(bpy)_2]^{4+}$ magnetic techniques provide a sensitive probe for detecting Ru(III)-Ru(III) electronic interactions. Magnetic measurements on ligand-bridged, oligomeric complexes containing ruthenium in the 3+ oxidation state could reveal extended magnetic interactions involving more than two metal sites. It is conceivable that cooperative interactions within such polymeric chains could lead to materials having chemical and electronic properties intermediate between the properties of simple dimers and the properties of extensively linked, solid-state materials.

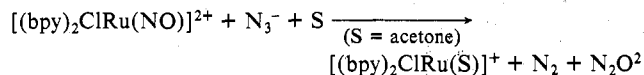
Experimental Section¹⁵

Measurements. Infrared spectra were recorded on a Perkin-Elmer 421 spectrophotometer in KBr pellets at room temperature. Ultraviolet-visible spectra were recorded on Cary Model 14, Cary Model 17, or Unicam Model SP800B spectrophotometers in 1-cm silica cells using MCB Spectrograde acetonitrile at room temperature. ESCA measurements were obtained on a Du Pont Instruments 650 electron spectrometer equipped with a Du Pont Instruments multichannel analyzer. Samples were prepared by grinding the solid complex into the surface of a gold sample probe using a clean glass rod. Magnetic susceptibility measurements from 1.7 to 77 K were conducted on powdered samples of the complexes using a PAR Foner-type vibrating

sample magnetometer. $\text{Hg}[\text{Co}(\text{SCN})_4]$ was used as the calibrant. The field strength was 10 000 G in all cases. The temperature was determined by means of a calibrated gallium arsenide diode. The susceptibilities were corrected for diamagnetism of constituent atoms using Pascal's constants.

Materials. Acetonitrile (MCB, Spectrograde) was used without further purification for all spectroscopic studies. Water was deionized and redistilled from alkaline potassium permanganate. Pyrazine, 2,2'-bipyridine, and 1,2-bis(4-bipyridyl)ethane were obtained commercially and used without further purification. The ligand 4,4'-bipyridine was prepared by the method of Smith¹⁶ as the dihydrochloride salt and converted to the free base by neutralization with sodium hydroxide in water. All other solvents (Reagent Grade) were purchased commercially and used without further purification. Cerium(IV) was purchased from G. F. Smith as stock Ce(IV) solutions (~0.5 M) in 6 M HClO_4 . Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Preparations. Ligand-Bridged Ruthenium(III) Complexes. The ligand-bridged ruthenium(II) complexes, whose preparations were described earlier,¹ along with the complexes $[(\text{bpy})_2\text{ClRu}(\text{BPA})\text{RuCl}(\text{bpy})_2](\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}$ and $[(\text{bpy})_2\text{ClRu}(\text{py})](\text{PF}_6)_2$, were converted to ruthenium(III) using Ce(IV) as the oxidant. In all cases the same basic procedure was used. In a typical experiment, 0.327 g (2.5×10^{-4} mol) of $[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{RuCl}(\text{bpy})_2](\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}$ was placed in a mortar and pestle in the dark, ~5.0 mL of 0.5 M HCl was added, and the suspension was ground for 1 min. To the suspension was slowly added 1.7 mL (5.74×10^{-4} mol, 10% excess) of a stock Ce(IV) solution 0.338 M in Ce(IV), as determined spectrally by the method of Braddock,¹⁷ in 6 M HClO_4 , dropwise with grinding. The total volume of solution was brought to 10 mL with 0.5 M HCl and the suspension ground for ~10 min. During this time the red-brown suspension became greenish brown. The perchlorate concentration of the suspension was brought to ~3.0 M by the addition of 2.8 g (2.28×10^{-2} mol) of sodium perchlorate. The resulting mixture was ground for about 1 min and filtered and the solid washed twice with cold 0.5 M HClO_4 and allowed to air-dry. The solid samples were stored in a desiccator in the dark; yield 91% (0.320 g, 2.27×10^{-4} mol). The same basic technique was used for each of the ruthenium(II) salts: $[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{RuCl}(\text{bpy})_2](\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}$, $[(\text{bpy})_2\text{ClRu}(4,4'\text{-bpy})\text{RuCl}(\text{bpy})_2](\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}$, $[(\text{bpy})_2\text{ClRu}(\text{BPA})\text{RuCl}(\text{bpy})_2](\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}$, $[(\text{bpy})_2\text{ClRu}(\text{py})](\text{PF}_6)_2 \cdot \text{H}_2\text{O}$, $[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{Ru}(\text{bpy})_2](\text{PF}_6)_2 \cdot 3\text{H}_2\text{O}$, and $[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{Ru}(\text{bpy})_2(\text{pyz})\text{Ru}(\text{bpy})_2(\text{pyz})\text{RuCl}(\text{bpy})_2](\text{PF}_6)_4 \cdot 4\text{H}_2\text{O}$. The ruthenium(II) complexes were prepared as described previously.¹ In the oxidations a 10% stoichiometric excess of Ce(IV) was used for each mole of Ru(II) in the complexes. The results of the elemental analyses for these complexes are given below. The salts reported all are shown by infrared and elemental analysis to contain waters of crystallization which are held tenaciously. Strong association of molecules of water with other α, α -diimine complexes has been previously noted.¹⁸⁻²¹ Anal. Calcd for $[(\text{bpy})_2\text{ClRu}(\text{py})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$: C, 41.29; N, 9.64; H, 2.89. Found: C, 41.09; N, 9.59; H, 2.98. Calcd for $[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{RuCl}(\text{bpy})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$: C, 36.44; N, 9.70; H, 3.04; Cl, 14.9. Found: C, 36.13; N, 9.71; H, 2.96; Cl, 12.1. Calcd for $[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{Ru}(\text{bpy})_2(\text{pyz})\text{RuCl}(\text{bpy})_2](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$: C, 36.75; N, 10.09; H, 2.79. Found: C, 36.51; N, 10.04; H, 2.77. Calcd for $[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{Ru}(\text{bpy})_2(\text{pyz})\text{Ru}(\text{bpy})_2(\text{pyz})\text{RuCl}(\text{bpy})_2](\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$: C, 36.44; N, 10.17; H, 2.77. Found: C, 36.52; N, 10.09; H, 2.85. Calcd for $[(\text{bpy})_2\text{ClRu}(4,4'\text{-bpy})\text{RuCl}(\text{bpy})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$: C, 40.35; N, 9.41; H, 2.96. Found: C, 38.88; N, 9.09; H, 2.67. Calcd for $[(\text{bpy})_2\text{ClRu}(\text{BPA})\text{RuCl}(\text{bpy})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$: C, 41.18; N, 9.24; H, 3.16. Found: C, 38.78; N, 8.74; H, 2.98. $[(\text{bpy})_2\text{ClRu}(\text{py})](\text{PF}_6)_2 \cdot \text{H}_2\text{O}$. The coordinated nitrosyl group in $[(\text{bpy})_2\text{ClRu}(\text{NO})](\text{PF}_6)_2 \cdot \text{H}_2\text{O}$ was displaced by a solvent molecule using the reaction



In the preparation of the solvent-bound complex, to 0.532 g (7.85×10^{-4} mol) of $[(\text{bpy})_2\text{ClRu}(\text{NO})](\text{PF}_6)_2 \cdot \text{H}_2\text{O}$ in 15 mL of acetone was added dropwise 0.0637 g (7.85×10^{-4} mol) of KN_3 in 5 mL of methanol and the solution was stirred at 35–40 °C for 30 min. The resulting solution was added dropwise to a solution containing 2 mL of pyridine (2.4×10^{-2} mol, 30-fold excess) in 5 mL of acetone and after stirring of the mixture at 35–40 °C for 1 h, a red-brown solid

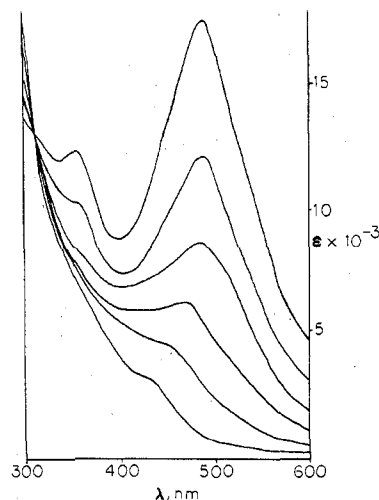


Figure 1. Spectrophotometric titration of $[(\text{bpy})_2\text{ClRu}(\text{py})\text{RuCl}(\text{bpy})_2]^{2+}$ with Ce(IV) in 1.0 M H_2SO_4 .

Table I. Results of Titration of the Ru(II) Complexes with Ce(IV)

complex	mol of Ce(IV) consumed	equiv of Ce(II)/equiv of Ru(II)
$[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{RuCl}(\text{bpy})_2]^{2+}$	1.98	0.99
$[(\text{bpy})_2\text{ClRu}(4,4'\text{-bpy})\text{RuCl}(\text{bpy})_2]^{2+}$	2.03	1.01
$[(\text{bpy})_2\text{ClRu}(\text{BPA})\text{RuCl}(\text{bpy})_2]^{2+}$	2.09	1.04
$[(\text{bpy})_2\text{ClRu}(\text{pyz})\{\text{Ru}(\text{bpy})_2(\text{pyz})\}_n\text{RuCl}(\text{bpy})_2]^{(2n+2)+}$		
$n = 1$	2.91	0.97
$n = 2$	4.15	1.04

was precipitated by adding the solution to 300 mL of anhydrous ether. The solid was collected on a frit and purified by reprecipitation from dichloromethane (25 mL) and ether (250 mL). Yield was 0.379 g (70% based on $[(\text{bpy})_2\text{ClRu}(\text{NO})](\text{PF}_6)_2 \cdot \text{H}_2\text{O}$). Anal. Calcd for $[(\text{bpy})_2\text{ClRu}(\text{py})](\text{PF}_6)_2 \cdot \text{H}_2\text{O}$: C, 43.4; H, 3.33; N, 10.12. Found: C, 43.23; H, 3.14; N, 10.01.

$[(\text{bpy})_2\text{ClRu}(\text{BPA})\text{RuCl}(\text{bpy})_2](\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}$. This complex was prepared in the same manner as reported previously for the compounds $[(\text{bpy})_2\text{ClRu}(\text{L})\text{RuCl}(\text{bpy})_2](\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}$, L = pyrazine, 4,4'-bipyridine, and *trans*-1,2-bis(4-pyridyl)ethylene;¹² yield 70–75%. Anal. Calcd for $[(\text{bpy})_2\text{ClRu}(\text{BPA})\text{RuCl}(\text{bpy})_2](\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}$: C, 44.35; H, 3.41; N, 9.95. Found: C, 43.05; H, 3.53; N, 9.99.

Results

Spectrophotometric Titrations. The reduction potentials of bis(2,2'-bipyridine)ruthenium(III)/-(II) couples measured in acetonitrile show that the ruthenium(III) complexes are usually relatively strong oxidants.¹ In aqueous acidic solution, the Ru(II) forms of the redox couples require a strong oxidant such as Ce(IV) for conversion to Ru(III).^{22,25} Spectrophotometric titrations were used to determine the stoichiometries of the reactions between $[(\text{bpy})_2\text{ClRu}(\text{py})](\text{PF}_6)_2$, $[(\text{bpy})_2\text{ClRu}(\text{L})\text{RuCl}(\text{bpy})_2](\text{PF}_6)_2$ (L = pyrazine, 4,4'-bipyridine, 1,2-bis(4-pyridyl)ethane), and $[(\text{bpy})_2\text{ClRu}(\text{pyz})\{\text{Ru}(\text{bpy})_2(\text{pyz})\}_n\text{RuCl}(\text{bpy})_2](\text{PF}_6)_{2n+2}$ ($n = 1, 2$), and cerium(IV) in 1.0 M H_2SO_4 . Aliquots of the salts were titrated in 1.0 M H_2SO_4 with varying concentrations of cerium(IV) and the visible spectra of the solutions were monitored in the range 650–330 nm. The results of a typical titration are shown in Figure 1 for $[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{RuCl}(\text{bpy})_2](\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}$. Table I shows the results of the titrations for the salts mentioned above. Plots of moles of Ce(IV) consumed per moles of Ru(II) in solution were made at fixed wavelengths. There was no spectral evidence for intermediate absorbing

Table II. Ultraviolet-Visible Data for the Ruthenium(III) Complexes in Acetonitrile

complex	λ_{max} , nm (ϵ , L mol ⁻¹ cm ⁻¹)
[(bpy) ₂ Ru(py)Cl](ClO ₄) ₂ ·2H ₂ O	410 (1900)
	303 (24 000)
	290 (22 000)
	237 (24 000)
[(bpy) ₂ ClRu(py)RuCl-(bpy) ₂](ClO ₄) ₄ ·2H ₂ O	420 (3900)
	312 (42 000)
	300 (42 000)
	245 (38 000)
	245 (38 000)
[(bpy) ₂ ClRu(py)z][(bpy) ₂ Ru(py)z]RuCl-(bpy) ₂](ClO ₄) ₇ ·3H ₂ O	428 (5900)(8500)
	312 (61 300)(69 400)
	300 (60 500)(75 800)
	246 (56 000)(74 900)
	246 (56 000)(74 900)
[(bpy) ₂ ClRu(py)z][(bpy) ₂ Ru(py)z] ₂ RuCl-(bpy) ₂](ClO ₄) ₁₀ ·4H ₂ O	428 (11 500)
	312 (94 000)
	300 (106 400)
	245 (101 500)
[(bpy) ₂ ClRu(4,4'-bpy)RuCl-(bpy) ₂](ClO ₄) ₄ ·2H ₂ O	415 (3950)
	312 (45 000)
	278 (45 000)
	245 (46 000)
[(bpy) ₂ ClRu(BPA)RuCl-(bpy) ₂](ClO ₄) ₄ ·2H ₂ O	420 (4200)
	312 (38 000)
	300 (39 400)
	245 (38 200)
	415 (5900)
	480 (5200)

species in the titrations involving dimers and polymers.

The addition of 1 drop of an approximately 5% aqueous-hydrazine solution to the completely oxidized complexes in acetonitrile gave back the spectra of the starting Ru(II) complexes ($\pm 8\%$).

Ultraviolet-Visible Spectra. The ultraviolet-visible spectra of the Ru(III) complexes in acetonitrile from 600 to 200 nm are all similar. In the spectra there is a band at 410–420 nm in the visible with a molar extinction coefficient per ruthenium of approximately 2000 in all cases. The ultraviolet spectra contain bands at 245, 300, and 310 nm, with ϵ/Ru of ~ 20000 . Similar bands have been found in related Ru(III) complexes.²³

Bryant and Fergusson have assigned the 410–420-nm band in related chlororuthenium(III) complexes as a $t_2(\text{Ru}) \leftarrow p(\text{Cl}^-)$ charge-transfer transition.²³ In the complexes studied here, a better assignment may be $t_2 \leftarrow \pi(\text{bpy})$ since the ϵ values per Ru(III) have no direct correlation to the number of Cl groups in the complexes. The bands at 310, 300, and 245 nm have been assigned to $\pi^* \leftarrow \pi$ bipyridine intraligand transitions. The spectra of the ligand-bridged complexes show no indication of new or unexpected transitions nor of intensity enhancements of any of the bands. In short, there is no spectral evidence which indicates significant Ru(III)–Ru(III) interactions in ground or excited states for the bridged complexes. Table II summarizes the UV-visible spectral results.

ESCA. Ru(3d_{5/2}) binding energies for the complexes [(bpy)₂ClRu(py)z]RuCl(bpy)₂^{2+/3+/4+} have been obtained by ESCA.¹⁹ The Ru(III) complexes reported here all have the Ru(3d_{5/2}) peak appearing as a prominent shoulder on the low-energy side of the C 1s peak with a binding energy of ~ 282.6 eV relative to C 1s at 284.4 eV. In addition, the Ru(3d_{3/2}) band, which should appear with a binding energy of approximately 287.1 eV, can often be seen as a shoulder on the high-energy side of the C 1s peak. The ESCA data are important since they show that the complexes contain only Ru(III). Related Ru(II) complexes have Ru(3d_{5/2}) binding energies at ~ 280 eV.⁶

Magnetic Susceptibilities. The magnetic susceptibility data for the six compounds are presented graphically in Figures 2–4. In the range 1.4–10 K, the precision of the temperature

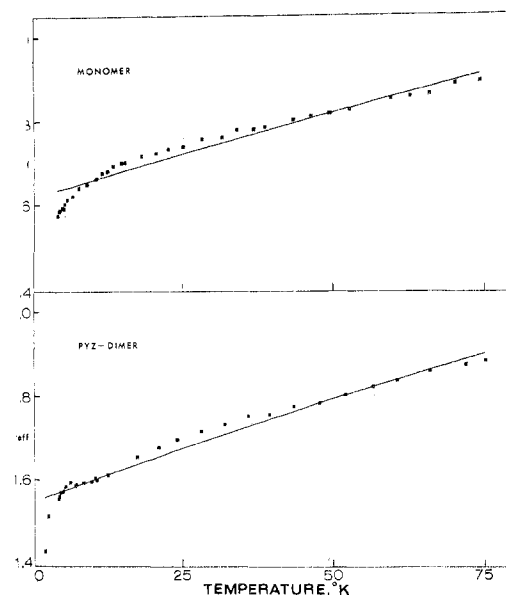


Figure 2. Temperature dependence of experimental effective moment, per mole of Ru(III) ion, of the monomeric and pyrazine-bridged dimeric complexes. Experimental data are shown as solid squares. The best fits to the experimental moments are depicted as full lines. The full lines were calculated using the values of k , Δ , and λ in Table III.

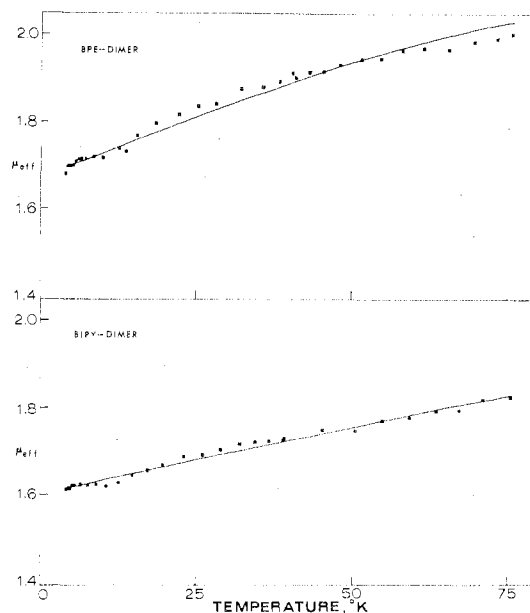


Figure 3. Temperature dependence of experimental effective moment, per mole of Ru(III) ion, of the BPE and 4,4'-bpy dimers. Experimental data are shown as solid squares, while the best fit results to the experimental moments are depicted as full lines (parameters in Table III).

measurements was ± 0.01 K, while above 10 K the precision was ± 0.03 K. The magnetic data are of somewhat lower accuracy than we normally report because of the small volume susceptibilities of these high molecular weight compounds. The precision of the moments at the high-end of the temperature region studied here (where the volume susceptibilities are low) are estimated to be $\pm 0.05 \mu_B$. This estimate arose from a consideration of the magnitude of the magnetometer output, the magnitude of the diamagnetic corrections for the sample holders, and the reproducibility from sample to sample of duplicate runs. The precision of the measurements is much better at the low end of the temperature region, where the uncertainty range is $\pm 0.02 \mu_B$. It may be seen from the data

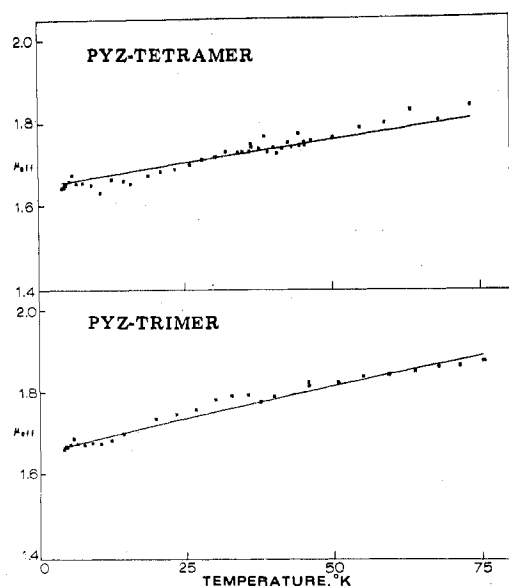
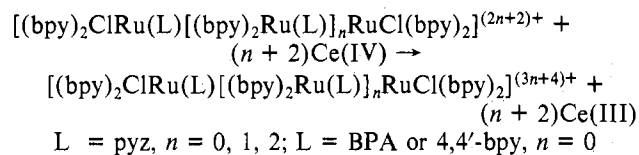


Figure 4. Temperature dependence of experimental effective moment, per mole Ru(III) ion, of the pyrazine-bridged trimeric and tetrameric complexes. Experimental data are shown as solid squares, while the best fit results to the experimental moments are depicted as full lines (parameters in Table III).

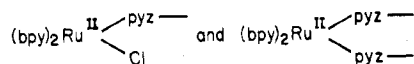
illustrated in Figures 2–4 that the data for all compounds deviate markedly from Curie–Weiss behavior, although no maxima in susceptibility were observed. Furthermore, the susceptibilities were field independent in the region studied, 10 000 G.

Discussion

From the results of spectrophotometric titrations and chemical isolation studies, it is clear that the ligand-bridged dimeric and pyrazine-bridged polymeric complexes remain intact in solution and in the solid state with the component ruthenium ions in either the 2+ or 3+ oxidation states. The results of spectrophotometric titrations with Ce(IV) in acidic aqueous solution clearly show that each of the ruthenium(II) sites is oxidized to ruthenium(III) by 1 equiv of Ce(IV).



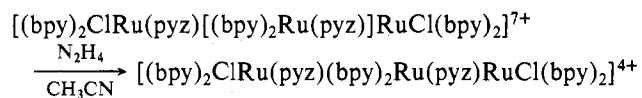
For the trimeric and tetrameric complexes, $[(bpy)_2ClRu(pyz)[(bpy)_2Ru(pyz)]_nRuCl(bpy)_2]^{(2n+2)+}$ ($n = 1, 2$), the Ce(IV) titrations failed to show distinct breaks indicative of the two different chemical sites



even though the related monomeric couples, $Ru(bpy)_2(pyz)_2^{3+/2+}$ and $Ru(bpy)_2(pyz)Cl^{2+/+}$, have different reduction potentials.²⁴ However, electrochemical experiments in acetonitrile have shown that multiple voltammetric waves, which may be characteristic of different ruthenium ion sites, do exist, but that the half-wave potentials are not well separated.²⁵ Presumably, if different chemical sites in the polymeric chains have different reduction potentials, the differences in potential values are insufficient for the titrations to distinguish between them. Alternatively, the spectral differences among the various one-electron oxidation products, e.g., $[(bpy)_2ClRu(pyz)Ru(bpy)_2(pyz)RuCl(bpy)_2]^{6+/5+}$, may be insufficient to define sharp end points in the titrations. Partial oxidation of the

ligand-bridged polymers gives a series of mixed-valence ions, e.g., the 5+ and 6+ trimeric ions mentioned above, which contain both ruthenium(II) and ruthenium(III) sites. The properties of several mixed-valence dimers have been reported and the electronic spectra are close to those calculated assuming localized Ru(II) and Ru(III), weakly interacting sites.

The fully oxidized complexes, which contain only ruthenium(III), can be reduced chemically to ruthenium(II), e.g.,



From the results of the spectrophotometric titrations, the various ruthenium sites in the polymeric complexes appear to behave as simple Ru(III)–Ru(II) redox sites and in their electron transfer behavior are probably similar to related monomeric Ru(III)–Ru(II) couples.

The Ru(III) complexes were prepared with the idea of investigating magnetic interactions across the aromatic N-heterocyclic ligands. For example, magnetic interactions across pyrazine have been found in the linear chain polymer $[Cu(pyz)(NO_3)_2]_n$.²⁹ Because of the complicated nature of the magnetism of $^2T_{2g}$ states, and in an attempt to separate intermolecular interactions from intramolecular interactions, the magnetism of two reference compounds was also determined. The first compound was the monomer $[Ru(bpy)_2(py)Cl](ClO_4)_2 \cdot 2H_2O$, and the second, the 1,2-bis(4-pyridyl)ethane-bridged dimer $[(bpy)_2ClRu(BPA)RuCl(bpy)_2](ClO_4)_4 \cdot 2H_2O$ where there is saturation in the chemical bridge between Ru(III) sites.

Susceptibility studies of magnetically dilute ruthenium(III) and low-spin iron(III) complexes have been published previously.^{12–14,30,31} Our data closely resembled that reported in the literature, so that the same kind of analysis of the magnetically dilute Ru(III) systems utilized by Figgis and others^{13,14} seemed applicable here.

The model of Kamimura,³² expanded and corrected by Gerloch³³ and Nassif^{34,35} to include the entire basis set of the free-ion metal d wave functions, was used for describing the magnetic properties of the mono- and polynuclear ruthenium complexes studied. Because the two 2,2'-bipyridyl ligands attached to ruthenium(III) ions in these complexes are cis to each other, the local geometry about the metal ions undergoes a trigonal distortion away from octahedral symmetry. Therefore, the five-parameter model for the magnetism of trigonally distorted $^2T_{2g}$ ions was chosen to describe the experimental results. These five parameters are the following: Dq , one-tenth the value of the splitting of the $^2T_{2g}$ and 2E_g levels caused by the cubic crystal field; Δ' , the splitting of the 2E_g state caused by axial distortion from cubic symmetry; Δ , the axial splitting of the $^2T_{2g}$ state; λ , the spin-orbit coupling constant; k , the orbital reduction factor first introduced by Stevens.³⁶ Because intense, charge-transfer bands masked the d–d transitions of the visible spectra of these compounds, Dq was simply assigned a value of 2600 cm^{-1} (the probable lowest limit of one-tenth the 2E_g – $^2T_{2g}$ splitting of octahedral ruthenium(III)³⁷). This value was held constant in all calculations, and since the splitting in the 2E_g levels has little effect on the magnetism, Δ' was set equal to zero in all cases. Therefore, only the three parameters λ , Δ , and k were treated as variables. A computer program³⁴ was used to fit experimental results to the moments generated by the theoretical model for the magnetism using various values of the three fitting parameters. The final parameters obtained from the best fits of experimental data to theoretical susceptibilities are presented in Table III. The sign of Δ is defined as negative for trigonal distortion,³² and values of λ , the spin-orbit coupling constant, are much reduced in absolute magnitude from the

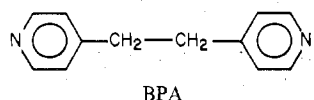
Table III. Best-Fit Parameters for the Series of Ruthenium(III) Complexes

compound	Δ , cm ⁻¹	λ , cm ⁻¹	k	Δ/λ
[(bpy) ₂ (py)ClRu](ClO ₄) ₂ ·H ₂ O	-204	-364	0.867	0.56
[(bpy) ₂ ClRu(L)RuCl(bpy) ₂]- (ClO ₄) ₄ ·2H ₂ O				
L = pyrazine	-210	-276	0.683	0.76
L = 4,4'-bipyridine	-384	-455	0.820	0.84
L = <i>trans</i> -1,2-bis(4-pyridyl)ethylene ^a	-596	-170	0.730	3.51
L = 1,2-bis(4-pyridyl)ethane ^b	-376	-204	0.800	1.43
[(bpy) ₂ ClRu(py ₂)(bpy) ₂ Ru(py ₂) _n - RuCl(bpy) ₂](ClO ₄) _{3n+4} ·(n+2)H ₂ O				
n = 1	-434	-403	0.841	1.08
n = 2	-787	-552	0.800	1.84

^a All three parameters varied. ^b Only Δ and λ varied.

free-ion value, λ_0 , of -1180 cm⁻¹.³⁸

These results are not in good agreement with parameters calculated by Figgis¹² for ruthenium(III) complexes. Although it is possible that the use of the larger basis set in these calculations may have led to better results than those of Figgis, the discrepancy between the two sets of calculated parameters is probably due to the insensitivity of the powder susceptibilities (particularly at temperatures >80 K) to large changes in the fitting parameters. Figgis attributes this insensitivity to the large absolute value of λ for ruthenium(III), which greatly restricts the claimed accuracy of his estimations of Δ , to ± 500 cm⁻¹. Gregson and Mitra's study³⁹ confirmed that the fit of the anisotropic (single crystal) data for Ru(acac)₃ (where acac = acetylacetonate) in the temperature range 80–300 K is strongly affected by large changes in the parameter Δ , but the average moment ($\bar{\mu}$) varies only some 3% at room temperature as Δ is varied from -500 to -5000 cm⁻¹ (using $\lambda = -1000$ cm⁻¹). The best fits of theoretical results to experimental data noting the parameters in Table III are plotted in Figures 2, 3, and 4. The decrease in moment recorded at lowest experimental temperatures for the pyrazine-bridged dimer could be taken as evidence for an exchange interaction across the pyrazine bridge, except that a similar effect was also observed for the monomeric ion [Ru(bpy)₂(py)Cl](ClO₄)₂·H₂O, where no exchange is expected. With the exception of the BPA



dimer, the computed "best fit" values of k and λ of all the complexes studied are in essential agreement with the limits of accuracy imposed by the measurements.

The best fit calculated for the BPA dimer yielded parameters which differed considerably from those of the other five compounds. Since there are no major chemical or structural differences and since the experimental magnetic results parallel those of the other compounds, the value of k was fixed at 0.8 (a value in line with those obtained for the rest of the compounds).

It should also be remembered that there are chemically different ruthenium sites in the trimer and tetramer, these being (bpy)₂ClRu^{III}(pyz) and (bpy)₂(pyz)₂Ru^{III}. The different ruthenium sites have different redox potentials, slightly different optical spectra, and presumably, slightly different single-ion magnetic susceptibilities. Of course, the susceptibilities of the different sites cannot be separated from the average data, and the parameters reported here should be taken as an average for the cases where there are different sites.

The important conclusion to be derived from the analysis given here is that no metal-metal interaction need be invoked to explain the temperature variation of the magnetic susceptibility. The same conclusions have been reached for salts

of the pyrazine-bridged dimer [(NH₃)₅Ru(py₂)Ru(NH₃)₅]⁶⁺ based on the results of susceptibility measurements.⁴⁰ While the experiment was not sensitive enough to detect very small interactions (less than 2 cm⁻¹), whether they be ferromagnetic or antiferromagnetic in nature, it is clear that significant magnetic interactions between the Ru(III) sites do not occur. Since the average electronic environment at each of the Ru sites is probably nearly the same in each complex, it is not surprising that the calculated orbital reduction factors are fairly constant.

Considerable quenching of spin-orbit coupling is observed for all the complexes studied; $\lambda/\lambda_0 < 0.5$ in all cases. Such a result is not unexpected in view of the comparatively large variations in ($\bar{\mu}$) over the temperature ranges studied. About the only evidence of a trend in the results (ignoring the parameters for the BPA dimer) is the steady increase in the parameter Δ/λ as the number of ruthenium sites per complex unit increases. The observed trend suggests that there is an increasing degree of splitting in the ²T_{2g} state in the order monomer < trimer < tetramer. The ligand bridging systems in all cases are constrained to be *cis*, and the data may suggest that the average magnetic microsymmetries at the metal sites are increasingly distorted as the chain length increases.

Our study is the first reported investigation of the temperature-dependent magnetic moments of magnetically dilute ruthenium(III) complexes in the liquid-helium temperature range. Although the ambiguities associated with the interpretation of powder susceptibilities of low-spin d⁵ systems are not eliminated by cryogenic measurements, the results demonstrate that the magnetic properties of the Ru(III) ions in the polymeric complexes investigated here are largely determined by the local electronic environment and local symmetry about each metal ion and not by magnetic exchange interactions between ruthenium(III) ions across the bridging ligands.

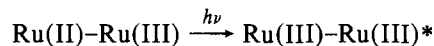
The failure to observe significant Ru-Ru interactions is a surprising result, and one which has important implications. The lack of metal-metal interactions across the N-heterocyclic bridging ligands is not a general result since significant metal-metal interactions have been found in related mixed-valence systems.^{4,5,9-11}

When compared to the properties of related ruthenium systems, it seems apparent that the extent of delocalization between Ru sites in ligand-bridged systems is critically dependent on oxidation state at the metal, on the bridging ligand, and, also, on nonbridging ligand effects.^{4,5,11} In mixed-valence Ru(II)-Ru(III) complexes, metal-metal electronic interactions occur by overlap between d π (Ru) orbitals at the two sites. The effects of metal-metal overlap can be profound as shown by mixed-valence ions like [(NH₃)₅Ru(NCCN)Ru(NH₃)₅]⁵⁺⁴¹ and [(bpy)₂ClRuORuCl(bpy)₂]³⁺⁶ where the additional electron appears to be delocalized between both metal sites on the infrared time scale. In these ions, the electronic resonance energy arising from orbital overlap must be sufficient to overcome the differences in inner- and outer-coordination sphere vibrational trapping energies. The differences in vibrational energies arise because of the changes in inner- and outer-coordination spheres which occur with changes in oxidation state at the metal. They would trap the additional electron on the Ru(II) site in the absence of significant electronic overlap.

Because of large Ru-Ru distances where a group like pyrazine is the bridging ligand (6.9 Å) metal-metal overlap must occur by metal-ligand mixing, e.g., d π (Ru(II))- π^* (pyr), which essentially carries Ru(II) character across the ligand bridge to Ru(III). For ligands like pyrazine, both filled π and empty π^* levels are available for mixing with d orbitals. For the Ru(III)-Ru(III) dimers and higher oligomers: (1) the

absence of low-energy metal to ligand CT bands argues that $d\pi-\pi^*(\text{pyr})$ mixing is not important and (2) the absence of significant magnetic interactions argues that $d\pi-\pi(\text{pyr})-d\pi$ mixing is also of negligible importance.

In contrast to the Ru(III)-Ru(III) systems, in the mixed-valence dimer $(\text{bpy})_2\text{ClRu}(\text{pyz})\text{RuCl}(\text{bpy})_2^{3+10}$ there is clear evidence for an observable metal-metal interaction as seen by the appearance of a low-energy intervalence transfer



absorption band. The difference between the Ru(II)-Ru(III) and Ru(III)-Ru(III) cases suggests that the orbital mechanism for interaction in the mixed-valence ion is by $d\pi(\text{Ru(II)})-\pi^*(\text{pyr})$ mixing since oxidation leads to orbital contraction of the $d\pi$ orbitals and to their stabilization relative to $\pi^*(\text{pyr})$.

Acknowledgment. We wish to thank the National Science Foundation for support of this research through Grant No. CHE77-09913, the Materials Research Center of The University of North Carolina under Grant No. DAHC15-73-G9 with the National Science Foundation, and the Army Research Office—Durham under Grant No. DAAG29-76-G-0135.

Registry No. $[(\text{bpy})_2\text{Ru}(\text{py})\text{Cl}](\text{ClO}_4)_2$, 62387-79-5; $[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{RuCl}(\text{bpy})_2](\text{ClO}_4)_4$, 36673-48-0; $[(\text{bpy})_2\text{ClRu}(\text{pyz})(\text{bpy})_2\text{Ru}(\text{pyz})\text{RuCl}(\text{bpy})_2](\text{ClO}_4)_7$, 68438-48-2; $[(\text{bpy})_2\text{ClRu}(\text{pyz})[(\text{bpy})_2\text{Ru}(\text{pyz})]_2\text{RuCl}(\text{bpy})_2](\text{ClO}_4)_{10}$, 68438-50-6; $[(\text{bpy})_2\text{ClRu}(4,4'\text{-bpy})\text{RuCl}(\text{bpy})_2](\text{ClO}_4)_4$, 68438-52-8; $[(\text{bpy})_2\text{ClRu}(\text{BPA})\text{RuCl}(\text{bpy})_2](\text{ClO}_4)_4$, 68438-54-0; $[(\text{bpy})_2\text{ClRu}(\text{py})](\text{PF}_6)_3$, 36413-31-7; $[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{RuCl}(\text{bpy})_2](\text{PF}_6)_2$, 36554-31-1; $[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{Ru}(\text{bpy})_2(\text{pyz})\text{RuCl}(\text{bpy})_2](\text{PF}_6)_4$, 36643-58-0; $[(\text{bpy})_2\text{ClRu}(\text{pyz})\text{Ru}(\text{bpy})_2(\text{pyz})\text{Ru}(\text{bpy})_2(\text{pyz})\text{RuCl}(\text{bpy})_2](\text{PF}_6)_6$, 12771-98-1; $[(\text{bpy})_2\text{ClRu}(4,4'\text{-bpy})\text{RuCl}(\text{bpy})_2](\text{PF}_6)_2$, 49734-40-9; $[(\text{bpy})_2\text{ClRu}(\text{BPA})\text{RuCl}(\text{bpy})_2](\text{PF}_6)_2$, 68438-56-2; $[(\text{bpy})_2\text{ClRu}(\text{NO})](\text{PF}_6)_2$, 29102-12-3; $[(\text{bpy})_2\text{ClRu}(\text{BPE})\text{RuCl}(\text{bpy})_2](\text{ClO}_4)_4$, 68438-58-4; Ce(IV), 16065-90-0.

References and Notes

- (1) (a) S. A. Adeyemi, J. N. Braddock, G. M. Brown, J. A. Fergusson, F. J. Miller, and T. J. Meyer, *J. Am. Chem. Soc.*, **94**, 300 (1972); (b) S. A. Adeyemi, E. C. Johnson, F. J. Miller, and T. J. Meyer, *Inorg. Chem.*, **12**, 2371 (1973); (c) M. J. Powers, R. W. Callahan, D. J. Salmon, and T. J. Meyer, *ibid.*, **15**, 894 (1976); (d) R. W. Callahan, G. M. Brown, and T. J. Meyer, *J. Am. Chem. Soc.*, **96**, 7829 (1974); (e) R. W. Callahan, E. C. Johnson, G. M. Brown, T. R. Weaver, and T. J. Meyer, *ACS Symp. Ser.*, No. 5, 66 (1975); (f) R. W. Callahan, G. M. Brown, and T. J. Meyer, *Inorg. Chem.*, **14**, 1443 (1975).
- (2) J. B. Godwin and T. J. Meyer, *Inorg. Chem.*, **10**, 2150 (1971); F. J. Miller and T. J. Meyer, *J. Am. Chem. Soc.*, **93**, 1294 (1971).
- (3) F. P. Dwyer, H. A. Goodwin, and E. C. Gyrfas, *Aust. J. Chem.*, **16**, 42, 544 (1963); J. G. Gibson, R. Laird, and E. D. McKenzie, *J. Chem. Soc. A*, 2089 (1969); B. P. Sullivan, J. A. Baumann, D. J. Salmon, H.

- Lehmann, A. Ludi, and T. J. Meyer, *J. Am. Chem. Soc.*, **99**, 7368 (1977).
- (4) (a) T. J. Meyer, *Adv. Chem. Ser. No. 150*, Chapter 7 (1976); (b) T. J. Meyer, *Ann. N.Y. Acad. Sci.*, **313**, 481 (1978).
- (5) H. Taube, *Ann. N.Y. Acad. Sci.*, **313**, 496 (1978).
- (6) T. R. Weaver, T. J. Meyer, S. A. Adeyemi, G. M. Brown, R. P. Eckberg, W. E. Hatfield, E. C. Johnson, R. W. Murray, and D. Untereker, *J. Am. Chem. Soc.*, **97**, 3039 (1975).
- (7) G. M. Tom and H. Taube, *J. Am. Chem. Soc.*, **97**, 5310 (1975).
- (8) H. Krentzien and H. Taube, *J. Am. Chem. Soc.*, **98**, 6379 (1976).
- (9) (a) M. J. Powers, R. W. Callahan, D. J. Salmon, and T. J. Meyer, *Inorg. Chem.*, **15**, 894 (1976); (b) M. J. Powers and T. J. Meyer, *ibid.*, **17**, 1785 (1978).
- (10) (a) R. W. Callahan and T. J. Meyer, *Chem. Phys. Lett.*, **39**, 82 (1976); (b) R. W. Callahan, F. R. Keene, D. J. Salmon, and T. J. Meyer, *J. Am. Chem. Soc.*, **99**, 1064 (1977); (c) M. J. Powers, D. J. Salmon, R. W. Callahan, and T. J. Meyer, *ibid.*, **98**, 6731 (1976).
- (11) T. J. Meyer, *Acc. Chem. Res.*, **11**, 94 (1978).
- (12) B. N. Figgis, J. Lewis, F. E. Mabbs, and G. A. Webb, *J. Chem. Soc. A*, 422 (1966).
- (13) B. N. Figgis, J. Lewis, and F. E. Mabbs, *J. Chem. Soc.*, 2473 (1963).
- (14) B. N. Figgis, J. Lewis, and F. E. Mabbs, *J. Chem. Soc.*, 2480 (1960).
- (15) Abbreviations used here include bpy for 2,2'-bipyridine, 4,4'-bpy for 4,4'-bipyridine, BPE for *trans*-1,2-bis(4-pyridyl)ethylene, BPA for 1,2-bis(4-pyridyl)ethane, pyz for pyrazine, and py for pyridine.
- (16) C. R. Smith, *J. Am. Chem. Soc.*, **46**, 414 (1924).
- (17) J. N. Braddock, Ph.D. Dissertation, The University of North Carolina, Chapel Hill, 1973.
- (18) R. W. Callahan, G. M. Brown, and T. J. Meyer, *J. Am. Chem. Soc.*, **96**, 7829 (1974).
- (19) E. C. Johnson, Ph.D. Dissertation, The University of North Carolina, Chapel Hill, 1974.
- (20) S. Burchett and C. E. Meloan, *J. Inorg. Nucl. Chem.*, **34**, 1207 (1972).
- (21) G. N. LaMar and G. R. Van Hecke, *Inorg. Chem.*, **12**, 1767 (1973).
- (22) J. N. Braddock and T. J. Meyer, *J. Am. Chem. Soc.*, **95**, 3158 (1973).
- (23) G. M. Bryant and J. E. Fergusson, *Aust. J. Chem.*, **24**, 275 (1971).
- (24) D. J. Salmon, Ph.D. Dissertation, The University of North Carolina, Chapel Hill, 1976.
- (25) G. M. Brown, Ph.D. Dissertation, The University of North Carolina, Chapel Hill, 1974.
- (26) J. N. Braddock and T. J. Meyer, *Inorg. Chem.*, **12**, 723 (1973).
- (27) J. N. Braddock, J. L. Cramer, and T. J. Meyer, *J. Am. Chem. Soc.*, **97**, 1972 (1975).
- (28) J. D. Miller and R. H. Prince, *J. Chem. Soc. A*, 1048 (1966).
- (29) J. F. Villa and W. E. Hatfield, *J. Am. Chem. Soc.*, **93**, 4081 (1971).
- (30) H. Hartmann and C. Buschbeck, *Z. Phys. Chem. (Frankfurt am Main)*, **11** (2), 130 (1957).
- (31) T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **28**, 2285 (1966).
- (32) H. Kamimura, *J. Phys. Soc. Jpn.*, **11**, 1171 (1956).
- (33) M. Gerloch, *J. Chem. Soc. A*, 2023 (1968).
- (34) P. J. Nassif, Ph.D. Dissertation, The University of North Carolina, Chapel Hill, 1969.
- (35) P. J. Nassif, T. W. Couch, W. E. Hatfield, and J. F. Villa, *Inorg. Chem.*, **10**, 368 (1971).
- (36) K. W. H. Stevens, *Proc. R. Soc. London, Ser. A*, **219**, 542 (1953).
- (37) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 2nd ed., Interscience, New York, 1966, Chapter 26.
- (38) B. N. Figgis and J. Lewis, *Prog. Inorg. Chem.*, **6**, 37 (1965).
- (39) A. K. Gregson and S. Mitra, *Chem. Phys. Lett.*, **3**, 392 (1969).
- (40) I. Treitel, Ph.D. Dissertation, California Institute of Technology, 1970; B. C. Bunker, R. S. Drago, D. N. Hendrickson, R. M. Richman, and S. L. Kessel, *J. Am. Chem. Soc.*, **100**, 3805 (1978).
- (41) G. M. Tom and H. Taube, *J. Am. Chem. Soc.*, **97**, 5310 (1975).