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Effects of Weak Metal–Metal Interactions in Ligand-Bridged Complexes of Ruthenium. Dimeric Complexes Containing Ruthenium Ions in Different Coordination Environments[1]

ROBERT W. CALLAHAN, GILBERT M. BROWN, and THOMAS J. MEYER*

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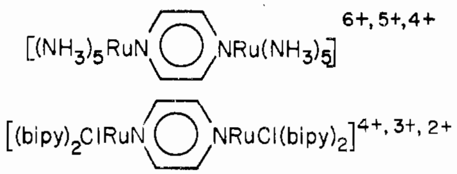
The preparation and characterization of the salts $[(NH_3)_5Ru(L)RuCl(bipy)_2](PF_6)_3$ (L = pyrazine (pyz), 4,4'-bipyridine (4,4'-bipy), *trans*-1,2-bis(4-pyridyl)ethylene (BPE), and 1,2-bis(4-pyridyl)ethane (BPA)) are described. The 3+ dimeric ions undergo a reversible one-electron oxidation either chemically or electrochemically in acetonitrile giving the mixed-valence (Ru(III)–Ru(II)) ions, $[(NH_3)_5Ru(L)RuCl(bipy)_2]^{4+}$. In the mixed-valence ions, the site of oxidation is largely localized on the $(NH_3)_5Ru-$ group. The twice-oxidized 5+ ions have also been shown to exist in solution using electrochemical methods. For the ions where the bridging ligand has an intact π system (pyz, 4,4'-bipy, or BPE), the effects of weak metal–metal interactions are observed in spectral and reduction potential data and in the appearance of intervalence transfer bands for the mixed-valence ions. With BPA as the bridging ligand, the N-heterocyclic π systems are separated by the saturated $-CH_2-CH_2-$ linkage, and no evidence for metal–metal electronic interactions has been obtained. From the properties of the intervalence transfer band for the mixed-valence pyrazine-bridged dimer, it can be estimated that electronic interactions in the ground state are lower by a factor of 3 than for the Creutz and Taube ion, $[(NH_3)_5Ru(pyz)Ru(NH_3)_5]^{5+}$.

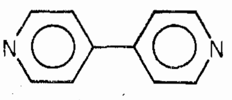
In recent papers, synthetic routes have been described for the preparation of complexes in which ruthenium ions are linked by dibasic, N-heterocyclic ligands[1,2,3a,8,9] such as pyrazine,[1,2,8,9] as for example, in the complexes

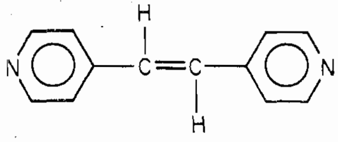


(bipy is 2,2'-bipyridine). From the spectral and redox properties of the dimeric complexes, it is apparent that metal–metal interactions can occur, apparently through the π systems of the bridging ligands, even over considerable distances. The mixed-valence forms of ligand-bridged ions, such as $[(NH_3)_5Ru(pyz)Ru(NH_3)_5]^{5+}$ (pyz is pyrazine), are of particular interest.[4–7] For mixed-valence ions, intervalence transfer (IT) bands are often observed.[10–12] From the properties of IT bands, it is possible to estimate both the extent of metal–metal interaction in the ground state and the rate of thermal electron transfer between the metal centers.[11]

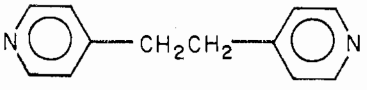
The properties of the ligand-bridged complexes and the extent of metal–metal interactions are expected to be controlled by both the bridging ligand and the nonbridging ligands which surround the ruthenium ions. Changes in bridging and nonbridging ligands should be reflected in the properties of IT bands. Bands which have been assigned to intervalence transfer have been found for $[(NH_3)_5Ru(pyz)Ru(NH_3)_5]^{5+}$ [1,2] and related ions and for the ion $[(bipy)_2ClRu(pyz)RuCl(bipy)_2]^{3+}$.[8,9] A recent ESCA study has shown clearly that both mixed-valence ions contain discrete Ru(II) and Ru(III) sites,[7] but in the pentaammine system the bandwidth and solvent dependence of the IT band are not in agreement with predictions made by Hush.[11]

We have prepared the series of unsymmetrical ligand-bridged complexes, $[(NH_3)_5Ru(L)RuCl(bipy)_2]^{3+}$ (L is pyrazine (pyz), 4,4'-bipyridine (4,4'-bipy), *trans*-1,2-bis(4-pyridyl)ethylene (BPE), and 1,2-bis(4-pyridyl)ethane (BPA))


4,4'-bipyridine



trans-1,2-bis(4-pyridyl)ethylene



1,2-bis(4-pyridyl)ethane

and have investigated the spectral and redox properties of the 3+ and mixed-valence 4+ ions. The work was undertaken in order to understand the differences between the pentaammine and bis(2,2'-bipyridine)ruthenium systems and to investigate the effects of the metal–metal interactions in this interesting series of complexes.

Experimental Section

Measurements. Infrared spectra were recorded on a Perkin-Elmer 421 spectrophotometer in KBr pellets at room temperature. Ultraviolet–visible spectra were obtained using Cary Model 14, Cary Model 17, and Unicam Model SP 800 B spectrophotometers at room temperature. All electrochemical measurements were vs. the saturated sodium chloride calomel electrode (SSCE) at 25 ± 2° and are uncorrected for junction potentials. In all electrochemical experiments, standard three-electrode operational amplifier circuitry was used as previously described.[13] All voltammetric measurements were carried out at platinum electrodes in solutions deaerated by a stream of dry argon or nitrogen.

Materials. Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was prepared by standard techniques,[14] recrystallized three times from hot ethanol–water mixtures, and vacuum-dried at 70° for 10 hr.

Acetonitrile (MCB Spectrograde) was dried over Davison 4-Å molecular sieves for electrochemical measurements and used without drying for spectral measurements. Water was deionized and then distilled from alkaline permanganate. All other solvents (reagent grade) were used without further purification. The ligands pyrazine, 4,4'-bipyridine, *trans*-1,2-bis(4-pyridyl)ethylene, and 1,2-bis(4-pyridyl)ethane were obtained commercially and used without further purification. Argon was scrubbed by passing it through a solution ~0.1 *M* in chromium chloride and ~0.1 *M* in acid over zinc–mercury amalgam. Solutions of Ce(IV) in acetonitrile were prepared using ceric ammonium nitrate. Aqueous solutions of Ce(IV) were prepared from G. F. Smith reagent grade solutions (~0.5 *M* Ce(IV) in 6 *M* $HClO_4$). Elemental analyses were carried out by Galbraith Laboratories, Knoxville, Tenn.

Preparations. The preparations of the salts $[Ru(bipy)_2LCl](PF_6)$, where L = pyz, 4,4'-bipy, or BPE, have been described previously.[8,9] The same procedure was used for the preparation of $[Ru(bipy)_2(BPA)Cl](PF_6)\cdot H_2O$. Anal. Calcd for $[Ru(bipy)_2(BPA)Cl](PF_6)\cdot H_2O$: C, 48.28; H, 3.80; N, 10.56; Cl, 4.45. Found: C, 47.56; H, 3.75; N, 11.07; Cl, 5.22.

$[Ru(NH_3)_5Cl](Cl)_2$. The salt was prepared according to the procedure of Vogt et al.[15] and recrystallized from hot (ca. 80–90°) 0.1 *M* hydrochloric acid.

$[Ru(NH_3)_5H_2O](PF_6)_2\cdot H_2O$. The $[Ru(NH_3)_5H_2O]^{2+}$ ion was generated essentially as described by Harrison et al.[16] In a typical preparation, about 20 ml of ~0.1 *M* sulfuric acid or preferably 0.01–0.001 *M* hexafluorophosphoric acid was placed in a one-necked 100-ml round-bottom flask containing several pieces of zinc–mercury amalgam. A serum cap was placed over the flask opening and the solution was deaerated with argon for 15–20 min. $[Ru(NH_3)_5Cl](Cl)_2$ (286 mg, 0.978 mmol) was added to the solution. Argon bubbling was continued. With time, the solid $[Ru(NH_3)_5Cl](Cl)_2$ reacted and dissolved giving a yellow-orange solution of $[Ru(NH_3)_5H_2O]^{2+}$. After ca. 1 hr, the solution was transferred using syringe techniques to a 200-ml, one-necked argon-deaerated round-bottom flask. A saturated, deaerated aqueous solution of NH_4PF_6 (5 ml) was added giving a yellow precipitate. The solution was cooled to ca. 3–4° and then filtered. The yellow solid was collected and washed with cold (ca. 3–4°), deaerated water (5–10 ml) and and finally with 30–60 ml of anhydrous ether in small portions. The salt, $[Ru(NH_3)_5H_2O](PF_6)_2$, was dried in a vacuum desiccator and stored in a desiccator at 3–4°; yield 394 mg (77%). The complex is stable up to periods of 1 month or longer if stored in a vacuum desiccator at 3–4°. Exposure of the dry salt to air for short periods (0.5–1 hr) led to no noticeable decomposition. However, over longer periods (3–4 days), slow air oxidation does occur. Anal. Calcd for $[Ru(NH_3)_5H_2O](PF_6)_2\cdot H_2O$: N, 13.67; H, 3.73; P, 12.09; F, 44.51. Found: N, 12.96; H, 3.54; P, 12.22; F, 44.89.

$[Ru(NH_3)_5L](PF_6)_2$ (L = Pyridine, Pyrazine, 4,4'-Bipyridine, *trans*-1,2-Bis(4-pyridyl)ethylene, 1,2-Bis(4-pyridyl)ethane). $[Ru(NH_3)_5(py)](PF_6)_2$ was prepared by the method of Ford et al.[17] except that NH_4PF_6 instead of $NaClO_4$ was used to precipitate the complex from aqueous solution. The pyrazine,[17,18] 4,4'-bipyridine,[3a,18] and *trans*-1,2-bis(4-pyridyl)ethylene[3a] complexes have been reported previously, but we have developed a modified procedure which uses $[Ru(NH_3)_5H_2O](PF_6)_2\cdot H_2O$ in acetone. In a typical preparation, $[Ru(NH_3)_5H_2O](PF_6)_2\cdot H_2O$ (120 mg, 0.234 mmol) was placed in a 50-ml erlenmeyer flask which had been fitted with a serum cap. The flask was deaerated with argon for 10–15 min. A second flask containing pyrazine (585 mg, 7.30 mmol) was also deaerated. Deaerated acetone (~5 ml) was added to both flasks, and the acetone solution of $[Ru(NH_3)_5H_2O]^{2+}$ was added slowly to the stirred pyrazine solution using a syringe. The solution, protected from light, was allowed to stir for 10–15 min and was then added slowly to a flask containing anhydrous ether (~100 ml). The orange-red precipitate which immediately formed was filtered onto a frit and washed twice with ~30 ml ether; yield 117 mg (90%). An analogous procedure was used for the 4,4'-bipyridine and *trans*-1,2-bis(4-pyridyl)ethylene complexes. The purity of the pyridine, pyrazine, 4,4'-bipyridine, and *trans*-1,2-bis(4-pyridyl)ethylene complexes was determined by comparison with published molar extinction coefficient data.[3a,17,18] The 1,2-bis(4-pyridyl)ethane (BPA) complex, $[Ru(NH_3)_5BPA](PF_6)_2\cdot H_2O$, was prepared by an analogous procedure, except that the complex was precipitated by addition to chloroform. The yellow solid was washed several times with ether and reprecipitated from acetone–ether; yield 90%. Anal. Calcd for $[Ru(NH_3)_5BPA](PF_6)_2\cdot H_2O$: C, 21.24; H, 4.31; N, 14.45. Found: C, 21.10; H, 4.16; N, 14.37.

$[(NH_3)_5Ru(L)RuCl(bipy)_2](PF_6)_3$ (L = Pyrazine, 4,4'-Bipyridine, *trans*-1,2-Bis(4-pyridyl)ethylene, 1,2-Bis(4-pyridyl)ethane). In a typical experiment, $[Ru(bipy)_2(BPA)Cl](PF_6)\cdot H_2O$ (549.8 mg, 0.707 mmol) and $[Ru(NH_3)_5H_2O](PF_6)_2\cdot H_2O$ (349.2 mg, 0.707 mmol) were placed in a 50-ml erlenmeyer flask which was wrapped with aluminum foil for protection from light. A serum cap was placed on the flask, and the flask was deaerated by flushing with argon for 20–30 min. Deaerated acetone (~20 ml) was added by a syringe to the flask which contained the two complexes. After 10 min with stirring, the color of the solution had changed from the original orange-red to red-purple when L was pyrazine, 4,4'-bipyridine, or *trans*-1,2-bis(4-pyridyl)ethylene. For L = 1,2-bis(4-pyridyl)ethane, no significant color change was observed. The reaction mixture was stirred for 1 hr. A constant stream of argon was blown over the solution. After 1 hr, the serum cap was removed, and the solution was added to a flask containing ether or preferably dichloromethane (100 ml) with stirring. Care was taken in all procedures to minimize the exposure of either solutions or solid samples to the light. The orange (red-purple in the case of L = pyrazine, 4,4'-bipyridine, or *trans*-1,2-bis(4-pyridyl)ethylene) precipitate which formed immediately was collected on a glass frit and washed with dichloromethane (~30 ml). The product was purified by reprecipitation from acetone–ether in the absence of light; yield 720 mg (81%). Comparable yields were obtained when the complexes with L = pyrazine, 4,4'-bipyridine, and *trans*-1,2-bis(4-pyridyl)ethylene were prepared. The solid samples were stored in glass vials protected from light over argon at 3–4°. Anal. Calcd for $[(NH_3)_5Ru(pyz)RuCl(bipy)_2](PF_6)_3$: C, 25.06; H, 3.07; N, 13.40; Cl, 3.08; F, 29.70. Found: C, 25.14; H, 2.96; N, 13.32; Cl, 2.96; F, 29.73. Calcd for $[(NH_3)_5Ru(4,4'\text{-bipy})RuCl(bipy)_2](PF_6)_3\cdot 2H_2O$: C, 28.54; H, 3.43; N, 12.21; Cl, 2.81; F, 27.09. Found: C, 28.66; H, 3.36; N, 11.85; Cl, 2.55; F, 26.00. Calcd for $[(NH_3)_5Ru(BPE)RuCl(bipy)_2](PF_6)_3\cdot 2H_2O$: C, 29.83; H, 3.52; N, 11.96; Cl, 2.75; F, 26.55. Found: C, 29.03; H, 3.53; N, 11.91; Cl, 2.62; F, 27.53. Calcd for $[(NH_3)_5Ru(BPA)RuCl(bipy)_2](PF_6)_3$: C, 30.64; H, 3.46; N, 12.28; Cl, 2.83; F, 27.27. Found: C, 30.78; H, 3.56; N, 12.09; Cl, 2.95; F, 27.49.

$[(NH_3)_5Ru(pyz)RuCl(bipy)_2](PF_6)_4$. The preparation was carried out in the absence of light. $[(NH_3)_5Ru(pyz)RuCl(bipy)_2](PF_6)_3$ (150 mg, 0.131 mmol) was dissolved in deaerated acetonitrile (~5 ml). A deaerated acetonitrile solution (~5 ml) which had been saturated with tetra-*n*-butylammonium hexafluorophosphate was then added to the stirred solution. A solution of bromine in acetonitrile (5.2 ml, 1.26×10^{-2} *M*, 0.065 mmol) was added to the stirred solution. After 10 min, the resulting red solution was added slowly, dropwise to stirred anhydrous ether (~100 ml) giving a red precipitate. The product was collected on a frit and washed several times with dichloromethane in order to remove excess tetra-*n*-butylammonium hexafluorophosphate and tetra-*n*-butylammonium bromide; yield 153 mg (90%). The product was placed in a glass vial under argon, protected from light, and stored at 3–4°. Anal. Calcd for $[(NH_3)_5Ru(pyz)RuCl(bipy)_2](PF_6)_4$: C, 22.26; H, 2.72; N, 11.90. Found: C, 22.61; H, 2.75; N, 12.01.

$[(NH_3)_5Ru(pyz)Ru(NO_2)(bipy)_2](PF_6)_3$. The preparation of this orange-red salt was identical with that described above for the related dinuclear complexes except that the monomeric complex $[Ru(bipy)_2(pyz)(NO_2)](PF_6)\cdot H_2O$[9] was used instead of $[(bipy)_2Ru(pyz)Cl](PF_6)$. Anal. Calcd for $[(NH_3)_5Ru(pyz)Ru(NO_2)(bipy)_2](PF_6)_3$: C, 24.84; H, 3.04. Found: C, 25.46; H, 2.97.

$[(NH_3)_5Ru(pyz)Ru(NO)(bipy)_2](PF_6)_5$. Coordinated nitrite ion in the dimeric complex described above was converted into coordinated nitrosyl by reaction with acid.[9,19,20] $[(NH_3)_5Ru(pyz)Ru(NO_2)(bipy)_2](PF_6)_3$ was suspended in methanol (~15 ml) in the absence of light. HPF_6 (65%, 0.5–1 ml) was added. The slurry was stirred for ca. 0.5 hr. The orange-red product was collected and purified by reprecipitation from acetone–ether.

$[(NH_3)_5Ru(pyz)Ru(CH_3CN)(bipy)_2]^{4+}$ in Acetonitrile. The coordinated nitrosyl group in the dimer described above was replaced by acetonitrile by the reaction between the nitrosyl group and azide ion in acetonitrile.[9,21]

$$[(NH_3)_5Ru(pyz)Ru(NO)(bipy)_2]^{5+} + N_3^- + CH_3CN \rightarrow$$
$$[(NH_3)_5Ru(pyz)Ru(CH_3CN)(bipy)_2]^{4+} + N_2 + N_2O$$

A stock solution of $[(NH_3)_5Ru(pyz)Ru(NO)(bipy)_2]^{5+}$ was prepared by dissolving the hexafluorophosphate salt (31.44 mg) in acetonitrile (50 ml) giving a solution 4.4 × 10^{-4} *M* in the nitrosyl ion. To the stock solution was added an equimolar amount of potassium azide (1.78 mg). An immediate reaction occurred giving an orange-red solution of the ion $[(NH_3)_5Ru(pyz)Ru(CH_3CN)(bipy)_2]^{4+}$. All procedures were carried out in the dark.

Spectrophotometric Titrations. Solutions of bromine in acetonitrile were standardized as described below.

A solution of bromine in acetonitrile (~0.1 *N*) was prepared by adding 0.68 ml of Br_2 to 250 ml of deaerated acetonitrile. The bromine–acetonitrile solution was standardized by titration using the standardized thiosulfate solution.[22] New solutions of Br_2 in CH_3CN were then prepared by diluting the standardized solution. From measurements of absorption spectra in the concentration range (2.50–1.0) × 10^{-3} *M*, it was found that Beer's law is obeyed at the absorption maximum at 392 nm. The molar extinction coefficient at 392 nm is ϵ 183 ± 4 M^{-1} cm^{-1}. Later solutions of Br_2 in CH_3CN were standardized spectrally using ϵ 183 M^{-1} cm^{-1} at 392 nm. Solutions of Br_2 in CH_3CN are remarkably stable, showing little change in concentration over periods of months when protected from light.

Solutions of Ce(IV) in acetonitrile were standardized in a similar manner. A stock solution of ceric ammonium nitrate in CH_3CN was prepared and standardized using a procedure described previously.[23] From uv–visible spectral measurements, Beer's law is obeyed at the absorption maximum at 326 nm (ϵ (6.98 ± 0.07) × 10^3 M^{-1} cm^{-1}) over the concentration range (1.01–2.01) × 10^{-4} *M*. Later solutions were standardized spectrophotometrically using ϵ 6.98 × 10^3 M^{-1} cm^{-1} at 326 nm. Ce(IV) solutions in acetonitrile are not stable. The addition of 1–2 drops of concentrated H_2SO_4/100 ml of solution stabilized dilute solutions (10^{-4}–10^{-5} *M*) for ~$^1/_2$ day and more concentrated solutions (10^{-1}–10^{-2} *M*) for 3–4 days. Acidic solutions of Ce(IV) were standardized spectrophotometrically as described previously.[24]

All spectrophotometric titrations were carried out in the absence of light using deaerated solvents. Titrations were carried out by adding aliquots of oxidant to solutions of the complex and monitoring the changes in absorbance. To establish the reaction stoichiometry, Job plots were made of absorbance at a particular wavelength (normally at an absorption maximum) vs. the moles of oxidant added per mole of complex. In titrations with Br_2, solutions of the oxidized complexes could be reduced essentially quantitatively to give a spectrum identical with the initial, unoxidized complex. Reductants used included $SnCl_2{\cdot}2H_2O$ and dilute solutions of hydrazine in CH_3CN (1–2 drops of 64% N_2H_4 in H_2O to ~25 ml of CH_3CN).

Results[25]

Preparations. The majority of preparations described in the Experimental Section utilize as a synthetic intermediate $[Ru(NH_3)_5(H_2O)](PF_6)_2{\cdot}H_2O$ dissolved in acetone. The state of "$Ru(NH_3)_5H_2O^{2+}$" in acetone is unclear. Either an acetone or a water molecule may occupy the sixth coordination site. In any case, the reactions in acetone, $[Ru(NH_3)_5S]^{2+} + L \rightarrow [Ru(NH_3)_5L]^{2+} + S$ (S = acetone or water) are rapid, apparently quantitative, and are useful for cases where the entering ligand is insoluble in water. In the preparation of the ligand-bridged dimeric complexes, the reactivity of the bis(2,2'-bipyridine) complexes $[Ru(bipy)_2LCl]^+$ as ligands was utilized, e.g.

$$[Ru(NH_3)_5S]^{2+} + [Ru(bipy)_2(pyz)Cl]^+ \rightarrow [(NH_3)_5Ru(pyz)RuCl(bipy)_2]^{3+} + S$$

The reactions can also be carried out in the reverse sense

$$[Ru(NH_3)_5pyz]^{2+} + [Ru(bipy)_2SCl]^+ \rightarrow [(NH_3)_5Ru(pyz)RuCl(bipy)_2]^{3+} + S$$

S = acetone or methanol

since the solvent-coordinated bis(2,2'-bipyridine)ruthenium intermediate can be generated by the reaction[9,21]

$$[Ru(bipy)_2(NO)Cl]^{2+} + N_3^- + S \rightarrow [Ru(bipy)_2SCl]^+ + N_2 + N_2O$$

However, reaction in the reverse sense is noticeably slower and less useful synthetically.

For all of the complexes reported here, the configuration of the 2,2'-bipyridine ligands around the ruthenium ion is apparently cis.[26,27]

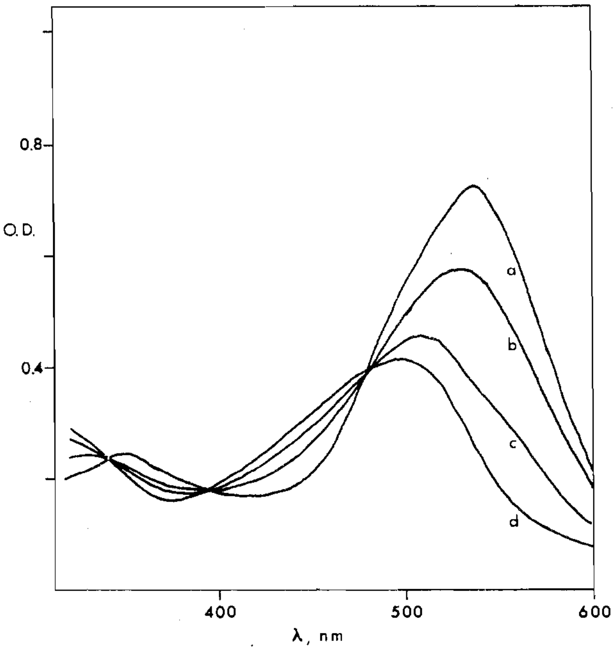


Figure 1. Spectrophotometric titration of $[(NH_3)_5Ru(pyz)RuCl(bipy)_2]^{3+}$ (4 × 10^{-5} *M*) with bromine in acetonitrile (1-cm pathlength): (a) initial spectrum; (b) 0.17 mol of Br_2/mol of dimer; (c) 0.33 mol of Br_2/mol of dimer; (d) 0.50 mol of Br_2/mol of dimer.

As shown by infrared and elemental analysis, some of the salts reported contain waters of crystallization which are held tenaciously. Strong association of molecules of water with other α,α-diimine complexes has been noted previously.[28–30]

Spectrophotometric Titrations. The stoichiometries of the reactions between the dimeric complexes $[(NH_3)_5Ru(L)RuCl(bipy)_2]^{3+}$ (L is pyrazine, 4,4'-bipyridine, *trans*-1,2-bis(4-pyridyl)ethylene, and 1,2-bis(4-pyridyl)ethane) and bromine in acetonitrile were determined by spectrophotometric titrations. The titrations were carried out as described in the Experimental Section. The results of a typical experiment are shown in Figure 1 for the ion $[(NH_3)_5Ru(pyz)RuCl(bipy)_2]^{3+}$. From the titrations, the ratio of moles of Br_2 consumed per mole of dimer was determined. The results were 0.45 for $[(NH_3)_5Ru(pyz)RuCl(bipy)_2]^{3+}$, 0.51 for $[(NH_3)_5Ru(4,4'\text{-}bipy)RuCl(bipy)_2]^{3+}$, 0.48 for $[(NH_3)_5Ru(BPE)RuCl(bipy)_2]^{3+}$, and 0.48 for $[(NH_3)_5Ru(BPA)RuCl(bipy)_2]^{3+}$. The ratios indicate the stoichiometry

$$[(NH_3)_5Ru(L)RuCl(bipy)_2]^{3+} + {}^1/_2Br_2 \rightarrow [(NH_3)_5Ru(L)RuCl(bipy)_2]^{4+} + Br^- \quad (1)$$

The result was expected since initial experiments had shown that Br_2 in CH_3CN rapidly oxidizes monomeric pentaammineruthenium(II) complexes, e.g., $[Ru(NH_3)_5py]^{2+}$, but does not oxidize chlorobis(2,2'-bipyridine)ruthenium(II) complexes like $[Ru(bipy)_2(py)Cl]^+$. Given the differences in reduction potentials for the couples $[Ru(NH_3)_5L]^{3+,2+}$ and $[Ru(bipy)_2LCl]^{2+,+}$ (Table III below), the results of the titrations indicate that the one-electron oxidation of the Ru(II)–Ru(II) dimeric ions gives the mixed-valence ions $[(NH_3)_5Ru^{III}(L)Ru^{II}Cl(bipy)_2]^{4+}$, in which the oxidation is localized largely on the pentaammine end.

The reactions with Br_2 involve simple electron transfer. The oxidized 4+ ions are rapidly reduced to the starting 3+ ions by both hydrazine and stannous chloride

$$[(NH_3)_5Ru(L)RuCl(bipy)_2]^{4+} \xrightarrow{SnCl_2\cdot 2H_2O \text{ or } N_2H_4} [(NH_3)_5Ru(L)RuCl(bipy)_2]^{3+}$$

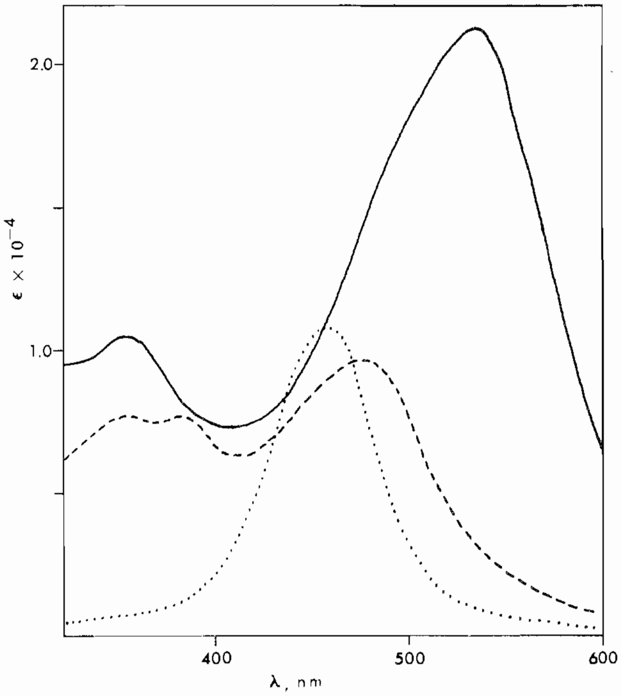


Figure 2. Spectra of (——) $[(NH_3)_5Ru(pyz)RuCl(bipy)_2]^{3+}$, (· · ·) $[(NH_3)_5Ru(pyz)]^{2+}$, and (- - -) $[(bipy)_2ClRu(pyz)]^+$ in acetonitrile.

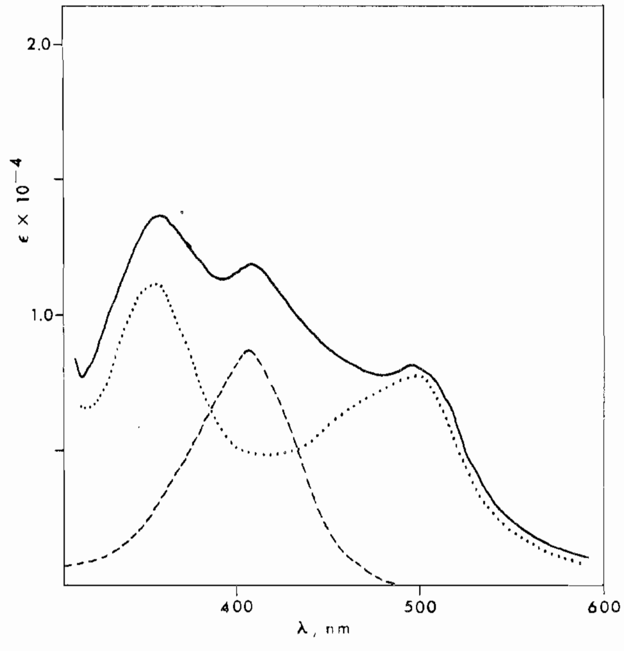


Figure 3. Spectra of (——) $[(NH_3)_5Ru(BPA)RuCl(bipy)_2]^{3+}$, (- - -) $[(NH_3)_5Ru(BPA)]^{2+}$, and (· · ·) $[(bipy)_2ClRu(BPA)]^+$ in acetonitrile.

The reactions are quantitative as shown by spectral measurements. On a preparative scale, reaction 1 provides a useful synthetic route to salts of the mixed-valence 4+ ions. The preparation of $[(NH_3)_5Ru(pyz)RuCl(bipy)_2](PF_6)_4$ was described in the Experimental Section.

Spectrophotometric titrations of the ion $[(NH_3)_5Ru(pyz)RuCl(bipy)_2]^{3+}$ by Ce(IV) were carried out in 1.0 *M* $HClO_4$, 1.0 *M* H_2SO_4, and acetonitrile. In all cases the addition of 1.0 mol of Ce(IV)/mol of dimer gave the 4+ ion quantitatively

$$[(NH_3)_5Ru(pyz)RuCl(bipy)_2]^{3+} + Ce(IV) \rightarrow [(NH_3)_5Ru(pyz)RuCl(bipy)_2]^{4+} + Ce(III)$$

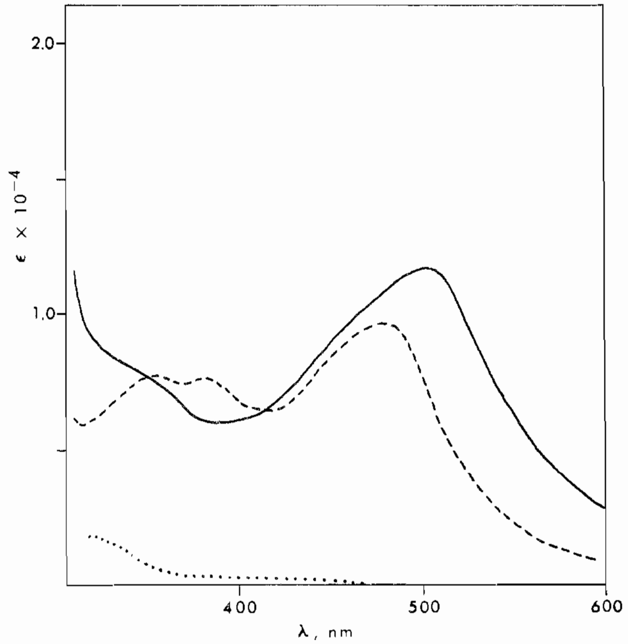


Figure 4. Spectra of (——) $[(NH_3)_5Ru(pyz)RuCl(bipy)_2]^{4+}$, (· · ·) $[(NH_3)_5Ru(pyz)]^{3+}$, and (- - -) $[(bipy)_2ClRu(pyz)]^+$ in acetonitrile.

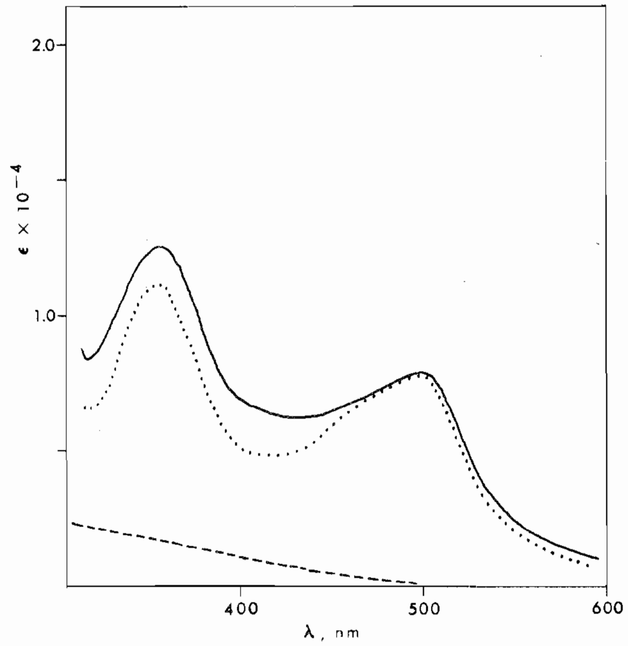


Figure 5. Spectra of (——) $[(NH_3)_5Ru(BPA)RuCl(bipy)_2]^{4+}$, (- - -) $[(NH_3)_5Ru(BPA)]^{3+}$, and (· · ·) $[(bipy)_2ClRu(BPA)]^+$ in acetonitrile.

Addition of further aliquots of Ce(IV) gave limiting spectra, indicating complete oxidation only after ~4.0 additional mol of Ce(IV)/mol of dimer was added. Preliminary experiments indicate that with excess Ce(IV), net conversion of coordinated NH_3 to nitrosyl occurs as evidenced by the appearance of a strong ν_{NO} band at ~1930 cm^{-1}. Similar reactions have been reported in related systems.[31]

Ultraviolet–Visible Spectra. The ultraviolet–visible spectra of the dimers $[(NH_3)_5Ru(pyz)RuCl(bipy)_2]^{3+}$ and $[(NH_3)_5Ru(BPA)RuCl(bipy)_2]^{3+}$ and of related, model, monomeric complexes are shown in Figures 2 and 3. The spectra of the corresponding mixed-valence 4+ ions are shown in Figures 4 and 5. In Table I are given in summary form the important features of the spectra of the 3+ and mixed-valence 4+ dimeric ions and of some related monomeric complexes. The probable assignments for the absorption bands

Table I. Spectral Data for Ru(II) and Ru(III) Monomeric and Dimeric Complexes in Acetonitrile[a]

Complex	λ_{max}, nm[b]	$10^{-4}\epsilon_{max}$, M^{-1} cm^{-1} [c]
$[Ru(NH_3)_5pyz]^{2+}$	455	
	253	
$[Ru(NH_3)_5(4,4'\text{-bipy})]^{2+}$	470	
	242	
$[Ru(NH_3)_5BPE]^{2+}$	500	
$[Ru(NH_3)_5BPA]^{2+}$	404	0.844
	244	0.526
$[Ru(NH_3)_5BPA]^{3+}$ [d]	320 sh	
	249	
$[(bipy)_2RuCl(pyz)]^+$	480	0.807
	450 sh	
	385	0.636
	355	0.622
	290	
	243	
$[(bipy)_2RuCl(4,4'\text{-bipy})]^+$	487	1.07
	461 sh	
	375	1.11
	293	5.37
	243	3.51
$[(bipy)_2RuCl(BPE)]^+$	485 sh	
	467	1.37
	401	1.35
	293	8.60
	254 sh	
	243	2.35
$[(bipy)_2RuCl(BPA)]^+$	496	0.765
	465 sh	
	350	1.10
	292	5.0
	243	2.32
$[(NH_3)_5Ru(pyz)RuCl(bipy)_2]^{3+}$	534	2.11
	495 sh	
	354	1.08
	292	5.4
	254 sh	
	242	3.0
$[(NH_3)_5Ru(pyz)RuCl(bipy)_2]^{4+}$ [d]	498	1.14
	450 sh	
	350 sh	
	291	3.4
	257 sh	
	245	2.0
$[(NH_3)_5Ru(pyz)Ru(NO_2)(bipy)_2]^{3+}$	495	
	440	
	294	
	253	
$[(NH_3)_5Ru(pyz)Ru(NO_2)(bipy)_2]^{4+}$ [d]	434	
	294	
	252	
$[(NH_3)_5Ru(pyz)Ru(CH_3CN)(bipy)_2]^{4+}$ [e]	470 sh	
	430	
$[(NH_3)_5Ru(pyz)Ru(CH_3CN)(bipy)_2]^{5+}$ [d]	500 sh	
	430	
$[(NH_3)_5Ru(4,4'\text{-bipy})RuCl(bipy)_2]^{3+}$	503	2.4
	405 sh	
	370	0.93
	350 sh	
	292	5.0
	285 sh	
	243	3.4
$[(NH_3)_5Ru(4,4'\text{-bipy})RuCl(bipy)_2]^{4+}$ [d]	486	1.5
	465 sh	
	418 sh	
	343	0.90
	288	5.3
	239	3.7
$[(NH_3)_5Ru(BPE)RuCl(bipy)_2]^{3+}$	507	2.21
	425 sh	
	344	0.94
	293	6.9
	255 sh	
	242	2.1
$[(NH_3)_5Ru(BPE)RuCl(bipy)_2]^{4+}$ [d]	480	
	470 sh	
	435 sh	
	330 sh	
$[(NH_3)_5Ru(BPA)RuCl(bipy)_2]^{3+}$	495	0.806
	405	1.19
	356	1.35
	292	5.2
	285 sh	
	242	2.6
	238 sh	
$[(NH_3)_5Ru(BPA)RuCl(bipy)_2]^{4+}$ [d]	496	0.785
	480 sh	
	350	1.26
	292	5.3
	286 sh	
	243	2.8
	238 sh	

[a] Spectra were recorded on solutions at room temperature which had been deaerated and protected from the light. [b] Deviations ±1 nm. [c] Values reported to three places are estimated to be good to ±5%; values reported to two places are estimated to be good to ±10%. [d] Species generated in solution by the addition of a stoichiometric amount of Br_2 in CH_3CN to the corresponding monomeric or dimeric complex. [e] Species generated in solution by the addition of a stoichiometric amount of N_3^- to $[(NH_3)_5Ru(pyz)Ru(NO)(bipy)_2]^{5+}$.

Table II. Near-Infrared, Low-Energy Visible Bands for the Mixed-Valence Ions $[(NH_3)_5Ru^{III}(L)Ru^{II}Cl(bipy)_2]^{4+}$

Ion	Band, kK	λ_{max},[a] nm	ϵ
$[(NH_3)_5Ru(pyz)RuCl(bipy)_2]^{4+}$	10.4	960	530
$[(NH_3)_5Ru(pyz)Ru(NO_2)(bipy)_2]^{4+}$	12.7	790	
$[(NH_3)_5Ru(pyz)Ru(CH_3CN)(bipy)_2]^{5+}$	13.3 sh	750 sh	
$[(NH_3)_5Ru(4,4'\text{-bipy})RuCl(bipy)_2]^{4+}$	14.4 sh	695 sh	<300
$[(NH_3)_5Ru(BPE)RuCl(bipy)_2]^{4+}$	14.7 sh	680 sh	<300
$[(NH_3)_5Ru(BPA)RuCl(bipy)_2]^{4+}$	*b*	*b*	*b*

[a] In dearated acetonitrile; ±3 nm. [b] No band observed.

based on previous work[17,32,33] will be discussed in a later section.

Near-Infrared Spectral. In Table II are given bands found in the near-infrared, low-energy visible region of the spectrum for the unsymmetrical, mixed-valence ions. The bands are not present in the spectra of the 3+ Ru(II)–Ru(II) ions. The band at λ_{max} 10.4 kK for the $[(NH_3)_5Ru(pyz)RuCl(bipy)_2]^{4+}$ ion was found to shift to 11.2 kK in $\sim 10^{-2}$ *M* aqueous $HClO_4$ and to 8.33 kK in nitrobenzene. As discussed in a later section the bands can be assigned to intervalence transfer transitions.

Infrared Spectra. Strong, characteristic bipyridine bands[34,35] are found at 3120, 3080, 1599, 1460, and 1420 cm^{-1} (KBr pellets) in the dinuclear complex $[(NH_3)_5Ru(pyz)RuCl(bipy)_2](PF_6)_3$. Characteristic ammine bands[36] are also found at 3350 cm^{-1} ($\nu(NH_3)$), 1620 cm^{-1} ($\delta(NH_3)$(degen)), and 1292 cm^{-1} ($\delta(NH_3)$(sym)). Bipyridine and PF_6^- bands at 700–900 cm^{-1} make the observation of the expected ammine rocking band ($\rho(NH_3)$) difficult. Similar bipyridine and ammine bands are found in the other dinuclear complexes. The infrared spectrum of the oxidized complex $[(NH_3)_5Ru(pyz)RuCl(bipy)_2](PF_6)_4$ shows that the bipyridine bands—3120, 3080, 1605, 1465, and 1424 cm^{-1}—are all only slightly shifted. However, the ammine bands—3330, 1630, and 1310 cm^{-1}—are more significantly shifted.

Electrochemistry. Voltammetric half-wave potentials vs. the saturated sodium chloride calomel electrode are given in

Table III. Voltammetric Data for Bis(2,2′-bipyridine) and Pentaammine Complexes of Ruthenium in Acetonitrile

Couple	$E_{1/2}$,[a] V
$[Ru(NH_3)_5py]^{3+,2+}$	0.38
$[Ru(bipy)_2(py)Cl]^{2+,+}$	0.79
$[Ru(NH_3)_5BPA]^{3+,2+}$	~0.35[b,c]
$[(NH_3)_5Ru(BPA)RuCl(bipy)_2]^{4+,3+}$	0.37 $E_{1/2}(1)$
$[Ru(bipy)_2(BPA)Cl]^{2+,+}$	0.77
$[(NH_3)_5Ru(BPA)RuCl(bipy)_2]^{5+,4+}$	0.79 $E_{1/2}(2)$
$[Ru(NH_3)_5(4,4'\text{-bipy})]^{3+,2+}$	0.43
$[(NH_3)_5Ru(4,4'\text{-bipy})RuCl(bipy)_2]^{4+,3+}$	0.43 $E_{1/2}(1)$
$[Ru(bipy)_2(4,4'\text{-bipy})Cl]^{2+,+}$	0.79
$[(NH_3)_5Ru(4,4'\text{-bipy})RuCl(bipy)_2]^{5+,4+}$	0.83 $E_{1/2}(2)$
$[Ru(NH_3)_5BPE]^{3+,2+}$	0.37
$[(NH_3)_5Ru(BPE)RuCl(bipy)_2]^{4+,3+}$	0.41 $E_{1/2}(1)$
$[Ru(bipy)_2(BPE)Cl]^{2+,+}$	0.78
$[(NH_3)_5Ru(BPE)RuCl(bipy)_2]^{5+,4+}$	0.81 $E_{1/2}(2)$
$[Ru(NH_3)_5pyz]^{3+,2+}$	0.55
$[(NH_3)_5Ru(pyz)RuCl(bipy)_2]^{4+,3+}$	0.61 $E_{1/2}(1)$
$[Ru(bipy)_2(pyz)Cl]^{2+,+}$	0.88
$[(NH_3)_5Ru(pyz)RuCl(bipy)_2]^{5+,4+}$	1.03 $E_{1/2}(2)$

[a] Potential measurements were at a Pt electrode and are referred to the saturated sodium chloride calomel electrode in 0.1 *M* TBAH–CH_3CN at 25 ± 2°. The estimated error in the potential measurements is ±0.01 V. [b] Estimated from cyclic voltammetry at a 200-mV/sec scan rate. [c] Oxidation is quasireversible in the cyclic voltammetry experiment ($\Delta E_p = E_{pa} - E_{pc}$ is a function of sweep rate).

Table III for the monomeric and dimeric complexes studied. The potentials are formally reduction potentials, except for a usually small correction term for differences in diffusion coefficients,[37] and refer to the reactions

$$[Ru(bipy)_2LCl]^{2+} + e \rightarrow [Ru(bipy)_2LCl]^{+}$$

$$[Ru(NH_3)_5L]^{3+} + e \rightarrow [Ru(NH_3)_5L]^{2+}$$

$$[(NH_3)_5Ru(L)RuCl(bipy)_2]^{4+} + e \rightarrow [(NH_3)_5Ru(L)RuCl(bipy)_2]^{3+} \quad E_{1/2}(1)$$

$$[(NH_3)_5Ru(L)RuCl(bipy)_2]^{5+} + e \rightarrow [(NH_3)_5Ru(L)RuCl(bipy)_2]^{4+} \quad E_{1/2}(2)$$

Voltammograms for the dimeric complexes $[(NH_3)_5Ru(L)RuCl(bipy)_2]^{3+}$ gave two anodic waves in the potential region 0–1.5 V. The voltammetric waves arise from the one-electron oxidation of the 3+ ions to $[(NH_3)_5Ru(L)RuCl(bipy)_2]^{4+}$ followed at higher potentials by a second one-electron oxidation giving $[(NH_3)_5Ru(L)RuCl(bipy)_2]^{5+}$. The two waves are labeled $E_{1/2}(1)$ and $E_{1/2}(2)$ in Table III according to their order of appearance in the voltammograms in sweeping from 0. to 1.5 V. The $E_{1/2}$ values were measured in 0.1 *M* tetra-*n*-butylammonium hexafluorophosphate–acetonitrile solution at 25 ± 2°.

The electrode reactions were all essentially electrochemically reversible. The reversibility was shown by plots of E vs. log $[i/(i_l - i)]$ for voltammetry experiments and by differences in anodic and cathodic peak potentials from cyclic voltammetry experiments (ΔE_p = 60–75 mV). The only exception was the couple $[Ru(NH_3)_5BPA]^{3+} + e \rightarrow [Ru(NH_3)_5BPA]^{2+}$ which was shown to be quasireversible by cyclic voltammetry (ΔE_p = 95 mV at 0.20-V/sec sweep rate).

For the monomeric complexes of ruthenium(II), $[Ru(NH_3)_5L]^{2+}$ and $[Ru(bipy)_2LCl]^{+}$, a single voltammetric oxidation wave is observed giving ruthenium(III).

In all cases, the electrochemical oxidation of complexes containing ruthenium ammines was sensitive to the history of the platinum electrode.[38] It appears that with partial oxidation of the platinum surface adsorption may become a problem.

Stability of the Complexes. In the absence of light in deaerated solvents such as acetonitrile, acetone, or water, $[(NH_3)_5Ru(pyz)RuCl(bipy)_2]^{3+}$ is stable for at least 2–3 days. The complex undergoes relatively efficient light-catalyzed decomposition reactions. When exposed to normal room lighting, the absorbance at λ_{max} 534 nm decreases ~10% in 20 min. After 5–6 hr, the decomposition is complete. From the absorption spectra of acetonitrile solutions after prolonged exposure to light, the decomposition reactions (in the absence of oxygen) apparently involve a series of net photosolvation steps giving $[Ru(NH_3)_5(CH_3CN)]^{2+}$ and $[Ru(bipy)_2(CH_3CN)Cl]^{+}$.[39] The mixed-valence ion $[(NH_3)_5Ru(pyz)RuCl(bipy)_2]^{4+}$ is reasonably stable in deaerated acetonitrile solution in the absence of light. Only slight changes (~10% decrease in absorption at λ_{max} 498 nm) were observed in the absorption spectrum after 2.5 hr.

Certain of the complexes are unstable in the solid state as PF_6^- salts even when stored under argon in the dark. For example, $[(NH_3)_5Ru(BPA)RuCl(bipy)_2](PF_6)_3$ was found to decompose ~15% after 1.5 months.

Discussion

Site of Oxidation in the Unsymmetrical Dimeric Complexes. The sites of oxidation in the unsymmetrical dimers appear to be largely localized giving in the first oxidation step $(NH_3)_5Ru^{III}(L)$–

$$[(NH_3)_5Ru^{II}(L)Ru^{II}Cl(bipy)_2]^{3+} \xrightarrow{-e^-} [(NH_3)_5Ru^{III}(L)Ru^{II}Cl(bipy)_2]^{4+}$$

and in the second –$(L)Ru^{III}Cl(bipy)_2$

$$[(NH_3)_5Ru^{III}(L)Ru^{II}Cl(bipy)_2]^{4+} \xrightarrow{-e^-} [(NH_3)_5Ru^{III}(L)Ru^{III}Cl(bipy)_2]^{5+}$$

The oxidations occur at well-separated potentials. Reduction potentials for the first redox process fall in the same range as potentials for the related $[Ru(NH_3)_5L]^{3+,2+}$ couples (Table III), and potentials for the second process are in the same range as for the related $[Ru(bipy)_2LCl]^{2+,+}$ couples (Table III).

That the sites of oxidation are localized is also indicated by the electronic spectra of the 3+ and 4+ ions. As shown in Figure 3, the near-ultraviolet–visible spectrum of the 1,2-bis(4-pyridyl)ethane dimer, $[(NH_3)_5Ru(BPA)RuCl(bipy)_2]^{3+}$, is essentially the sum of the spectra of the monomeric ions $[Ru(NH_3)_5BPA]^{2+}$ (λ_{max} 404 nm) and $[Ru(bipy)_2(BPA)Cl]^{+}$ (λ_{max} 496 and 350 nm). This is the expected result since the two π systems of the bridging ligand are separated by a saturated $-CH_2-CH_2-$ linkage. Because of the absence of an extended π system between the ruthenium ions, the two separated ruthenium groups behave as noninteracting chromophores. Upon oxidation of the 3+ to the 4+ ion (Figure 5), the only change in the spectrum is the disappearance of the band at 405 nm. The band at 405 nm can be assigned to the d → π^* (BPA) transition of the $(NH_3)_5Ru^{II}(BPA)$ group.[17] The loss of absorbance at 405 nm is expected if the oxidation occurs at the pentaammine end of the dimer since $Ru^{III}(NH_3)_5py$– type complexes are essentially transparent in the visible region of the spectrum (Figure 5 and ref 17). The spectrum of the oxidized ion is essentially identical with that of $[Ru^{II}(bipy)_2(BPA)Cl]^{+}$ with a small amount of residual absorbance by the $(NH_3)_5Ru^{III}(BPA)$ group. From the spectral data for the 1,2-bis(4-pyridyl)ethane dimer, the conclusions to be drawn are that the site of oxidation is localized on the pentaammine group and that the two ruthenium ions are isolated electronically.

Essentially the same conclusion is reached about the site of oxidation in the mixed-valence pyrazine-bridged dimer $[(NH_3)_5Ru(pyz)RuCl(bipy)_2]^{3+}$. The lower energy portion of a broad band at λ_{max} 534 nm (Figure 2) can be assigned to the d → π^*(pyz) transition of the $(NH_3)_5Ru^{II}(pyz)$ group.[17,32] The spectra of the dimeric complexes are discussed in detail in a later section. Upon oxidation to the 4+ ion, the low-energy portion of the 534-nm band disappears giving a spectrum similar to but not identical with that of [Ru-

$(bipy)_2(pyz)Cl]^+$ (Figure 4). For the dimeric complexes where the bridging ligand includes an unbroken π system—pyrazine, 4,4'-bipyridine, and *trans*-1,2-bis(4-pyridyl)ethylene—the site of oxidation appears to be localized. However, the spectra are not simply the sum of the spectra of the monomeric ions. The spectral differences arise apparently because of weak interactions between the metal centers as discussed in a later section.

Reduction Potentials. The most useful comparisons involving the $E_{1/2}$ data (Table III) come from differences in values between the dimeric complexes and the monomeric complexes, $[Ru(NH_3)_5L]^{3+,2+}$ and $[Ru(bipy)_2LCl]^{2+,+}$. In principle, such comparisons can give information about the extent and nature of interactions between the metal centers since the sites of oxidation in the dimeric complexes for the two oxidation steps are largely localized. Differences between $E_{1/2}(1)$ and $E_{1/2}$ for the reaction $[Ru(NH_3)_5L]^{3+} + e \rightarrow [Ru(NH_3)_5L]^{2+}$ arise because of the presence of the second, ligand-bridged ruthenium group at a relatively remote site.

The most clear-cut conclusions can be reached for the 1,2-bis(4-pyridyl)ethane-bridged dimer. From the electronic spectra of the ions $[(NH_3)_5Ru^{II}(BPA)Ru^{II}Cl(bipy)_2]^{3+}$ and $[(NH_3)_5Ru^{III}(BPA)Ru^{II}Cl(bipy)_2]^{4+}$, the two ruthenium groups in both the 3+ and 4+ ions do not interact electronically because of the saturated $-CH_2-CH_2-$ linkage. In comparing reduction potentials for the dimer with potentials for related monomeric complexes, the presence of the second metal ion will still be felt because of electrostatic effects. The comparisons involve couples of different charge types

$$[Ru^{III}(NH_3)_5BPA]^{3+} + e \rightarrow [Ru^{II}(NH_3)_5BPA]^{2+}: \quad E_{1/2} = 0.35 \text{ V}$$

$$[(NH_3)_5Ru^{III}(BPA)Ru^{II}Cl(bipy)_2]^{4+} + e \rightarrow [(NH_3)_5Ru^{II}(BPA)Ru^{II}Cl(bipy)_2]^{3+}: \quad E_{1/2}(1) = 0.37 \text{ V}$$

$$[Ru^{III}(bipy)_2(BPA)Cl]^{2+} + e \rightarrow [Ru^{II}(bipy)_2(BPA)Cl]^{+}: \quad E_{1/2} = 0.77 \text{ V}$$

$$[(NH_3)_5Ru^{III}(BPA)Ru^{III}Cl(bipy)_2]^{5+} + e \rightarrow [(NH_3)_5Ru^{III}(BPA)Ru^{II}Cl(bipy)_2]^{4+}: \quad E_{1/2}(2) = 0.79 \text{ V}$$

Both potentials for the dimeric complexes are expected to be higher than potentials for the related monomeric couples since the charges on the dimeric complexes are higher. Electrostatic effects vary as the charges on the ions squared. The extent of the increase in potentials because of electrostatic effects will depend on the ionic charges involved, on the distance between the metal centers, and on the dielectric properties of the material between the metal centers. For the BPA-bridged dimer, the increase in $E_{1/2}$ values is small (0.02 V) and nearly within the experimental error (±0.01 V). The slight increase in $E_{1/2}$ values indicates that when the metal ion centers are well separated, electrostatic effects are small.

The interpretation of the reduction potential data for the remaining dimeric complexes is more involved. In comparing reduction potentials for the reactions

$$[(NH_3)_5Ru^{III}(pyz)Ru^{III}(NH_3)_5]^{6+} + e \rightarrow [(NH_3)_5Ru^{II}(pyz)Ru^{III}(NH_3)_5]^{5+}$$

$$[(NH_3)_5Ru^{III}(pyz)Rh^{III}(NH_3)_5]^{6+} + e \rightarrow [(NH_3)_5Ru^{II}(pyz)Rh^{III}(NH_3)_5]^{5+}$$

with the potential for the $[Ru(NH_3)_5pyz]^{3+,2+}$ couple,[40] Creutz[2] found that the dimeric values were at higher potentials by 0.270 V for the Ru(III)–Ru(III) dimer and by 0.220 V for the Ru(III)–Rh(III) dimer. The pentaammine groups of neither Rh(III) nor Ru(III) are known to back-bond significantly to pyrazine. Electrostatic effects must play a role and perhaps a more significant role than for the 1,2-bis(4-pyridyl)ethane (BPA) dimer, since the distance between the metal ions is considerably less. In addition, Creutz[18] has suggested that the Rh(III) and Ru(III) ions function as "acidic" centers of positive charge. The role of the Rh(III) and Ru(III) ions is seen as stabilizing the $Ru^{II}(NH_3)_5pyz$ group by removing negative charge density from the bridging pyrazine ligand; negative charge density builds up because of back-bonding from the $(NH_3)_5Ru^{II}$ group. d(Ru)–π^*(pyz) back-donation is known to be important in complexes like $[Ru(NH_3)_5pyz]^{2+}$. For example, stabilization of the Ru(II) state by back-bonding is thought to play a large role in explaining the increase in reduction potential for couples such as $[Ru(NH_3)_5py]^{3+,2+}$ when compared to the $[Ru(NH_3)_6]^{3+,2+}$ couple.[41]

For the reaction

$$[(NH_3)_5Ru^{III}(pyz)Ru^{II}(NH_3)_5]^{5+} + e \rightarrow [(NH_3)_5Ru^{II}(pyz)Ru^{II}(NH_3)_5]^{4+}$$

the reduction potential is *lowered* by 0.120 V when compared to the $[Ru(NH_3)_5pyz]^{3+,2+}$ couple.[2] The decrease in potential can be explained in terms of decreased d(Ru)–π^*(pyz) back-bonding for each of the separate ruthenium ions in the dimer making them more like $[Ru(NH_3)_6]^{2+}$.[18] The decrease in back-bonding for a given ruthenium ion is expected since the two ions must share the π^* system of the pyrazine.

For the unsymmetrical pyrazine-bridged dimer, $E_{1/2}(1)$ for the reaction

$$[(NH_3)_5Ru^{III}(pyz)Ru^{II}Cl(bipy)_2]^{4+} + e \rightarrow [(NH_3)_5Ru^{II}(pyz)Ru^{II}Cl(bipy)_2]^{3+}$$

is *raised* by 0.06 V when compared to the $[Ru(NH_3)_5pyz]^{3+,2+}$ couple. As for the symmetrical Ru(III)–Ru(III) dimer and for the Ru(III)–Rh(III) dimer, the reduction potential is expected to increase on electrostatic grounds and also by the stabilizing effect of having a remote positive charge. However, the increase is considerably smaller for the $[(NH_3)_5Ru(pyz)RuCl(bipy)_2]^{4+,3+}$ couple.

Intense bands appear in the electronic spectra of compounds such as $[Ru(bipy)_2(pyz)Cl]^+$ which can be assigned to d → π^*(pyz) transitions. The appearance of such intense bands and the dependence of $(bipy)_2Ru^{III}$–$(bipy)_2Ru^{II}$ potentials on the presence of additional back-bonding ligands[42] imply that ground-state d(Ru)–π^*(pyz) back-bonding does exist. The extent of back-bonding to pyrazine is expected to be less in bis(2,2'-bipyridine) complexes of ruthenium(II) than for pentaammine complexes. In $[Ru(bipy)_2(pyz)Cl]^+$, strong back-bonding occurs between ruthenium orbitals and 2,2'-bipyridine π^* orbitals leaving the d electrons less available for back-donation to pyrazine.

The observed slight increase in reduction potential for the $[(NH_3)_5Ru(pyz)RuCl(bipy)_2]^{4+,3+}$ couple when compared to that of the $[Ru(NH_3)_5pyz]^{3+,2+}$ couple apparently arises from charge effects which are partly counterbalanced by decreased $(NH_3)_5Ru \rightarrow pyz$ back-bonding. The decrease in back-bonding is expected since the π^* system of the pyrazine is shared, if somewhat unequally, with the $Ru^{II}Cl(bipy)_2$ group.

$E_{1/2}(2)$ for the reaction

$$[(NH_3)_5Ru^{III}(pyz)Ru^{III}Cl(bipy)_2]^{5+} + e \rightarrow [(NH_3)_5Ru^{III}(pyz)Ru^{II}Cl(bipy)_2]^{4+}$$

is higher by 0.15 V than $E_{1/2}$ for the $[Ru(bipy)_2(pyz)Cl]^{2+,+}$ couple. The origin of the increase in potential for the dimer containing a remote $(NH_3)_5Ru^{III}$ group is presumably the same as in the $[(NH_3)_5Ru(pyz)Ru(NH_3)_5]^{6+,5+}$ couple. The remote $(NH_3)_5Ru^{III}$ group should increase the reduction potential both by electrostatic effects and by the effect of its charge in compensating for d(Ru)–π^*(pyz) back-donation. The effect of charge compensation should be of less importance in the unsymmetrical dimer if $(bipy)_2ClRu^{II} \rightarrow pyz$ back-bonding is less.

The remaining dimeric systems have 4,4'-bipyridine and *trans*-1,2-bis(4-pyridyl)ethylene as the bridging ligands. In these dimers, the bridged ligands are considerably longer than pyrazine, and yet the π systems linking the metal ions are uninterrupted,[43] in contrast to BPA. Changes in $E_{1/2}(1)$ values (+0.04 V for BPE and 0.00 V for 4,4'-bipy) and in $E_{1/2}(2)$ values (+0.03 V for BPE and +0.05 V for 4,4'-bipy) when compared to the monomers are sufficiently small that meaningful conclusions cannot be drawn.

In summary, the reduction potential data are consistent with a model for the dimeric complexes in which the oxidation state sites are localized and in which interactions between the ruthenium ions are relatively weak. Where meaningful interactions do occur, they appear to arise largely from electrostatic effects or from the effect of a remote ruthenium ion acting as an "acidic" center of positive charge. Electronic interactions may occur between the ruthenium ions, but such interactions are weak and not chemically significant, at least, as measured by reduction potential values.

Ultraviolet–Visible Spectra. The ultraviolet–visible spectra of the ligand-bridged complexes are dominated by a series of intense absorption bands (Table I). The bands in the ultraviolet spectra for $[Ru^{II}(NH_3)_5py]^{2+}$ type complexes have been assigned to ligand-localized $\pi \rightarrow \pi^*$ transitions involving the aromatic systems of the N-heterocyclic ligands.[17] For complexes of the type $[Ru^{II}(bipy)_2(py)Cl]^+$, very intense uv bands characteristically occur at ~290 and ~240 nm which have been assigned to $\pi \rightarrow \pi^*$ transitions of the 2,2'-bipyridine ligands.[33] The $\pi \rightarrow \pi^*$(bipy) transitions are sufficiently intense that they apparently mask the expected $\pi \rightarrow \pi^*$ transitions of the remaining N-heterocyclic group (e.g., $\pi \rightarrow \pi^*$(py) in $[Ru(bipy)_2(py)Cl]^+$).[44]

The intense bands in the visible spectra for complexes like $[Ru^{II}(NH_3)_5py]^{2+}$ have been assigned to Ru → py charge transfer (CT) transitions (e.g., d → π^*(py) in $[Ru(NH_3)_5py]^{2+}$ [17,32]). For the bis(2,2'-bipyridine) complexes, there are also intense bands in the visible spectra which have been assigned to d → π^*(bipy) CT transitions.[33]

The spectral properties of the ligand-bridged dimeric complexes are of interest in that they should reflect the effects of interactions between the ruthenium ions. If electronic interactions between ruthenium ions are weak, certain of the transitions are expected to be essentially localized on one of the two metal ions in the dimers. Transitions in the 3+ and 4+ dimeric complexes for which absorption bands might be expected include

$$\begin{array}{l} [(NH_3)_5Ru^{II}\text{–}L\text{–}Ru^{II}Cl(bipy)_2]^{3+} \\ d_A \rightarrow \pi^*(L)\ \ \pi \rightarrow \pi^*(L)\ \ d_B \rightarrow \pi^*(bipy) \\ \qquad\qquad\qquad\qquad\qquad d_B \rightarrow \pi^*(L) \\ \qquad\qquad\qquad\qquad\qquad \pi \rightarrow \pi^*(bipy) \end{array} \tag{A}$$

$$\begin{array}{l} [(NH_3)_5Ru^{III}\text{–}L\text{–}Ru^{II}Cl(bipy)_2]^{4+} \\ \qquad\qquad \pi \rightarrow \pi^*(L)\ \ d_B \rightarrow \pi^*(bipy) \\ \qquad\qquad\qquad\qquad\qquad d_B \rightarrow \pi^*(L) \\ \qquad\qquad\qquad\qquad\qquad \pi \rightarrow \pi^*(bipy) \end{array} \tag{B}$$

Here d_A refers to the pentaammineruthenium d orbitals of π symmetry (t_{2g} orbitals in O_h symmetry) and d_B the similar set of d orbitals for the bis(2,2'-bipyridine)ruthenium group.

A detailed interpretation of the visible spectra of the dimeric complexes is complicated by the nature of the absorption bands. The bands are broad since they consist of a composite of CT transitions. In some cases distinct shoulders appear in the spectra. This is especially the case in the $d_B \rightarrow \pi^*$(bipy) region, where a series of symmetry-allowed $d_B \rightarrow \pi^*$(bipy) transitions are expected.[33] However, where band assignments are possible, some useful qualitative conclusions can be reached.

From the data in Table I, the $\pi \rightarrow \pi^*$(bipy) transitions at ~290 and ~240 nm and the $d_B \rightarrow \pi^*$(bipy) transitions at ~480 nm are essentially unchanged in comparing spectra of the $[Ru(bipy)_2LCl]^+$ ions with the spectra of the $[(NH_3)_5Ru^{II}(L)Ru^{II}Cl(bipy)_2]^{3+}$ and $[(NH_3)_5Ru^{III}(L)Ru^{II}Cl(bipy)_2]^{4+}$ ions. Both the $\pi \rightarrow \pi^*$(bipy) and $d_B \rightarrow \pi^*$(bipy) transitions are apparently localized on the $-(L)Ru^{II}Cl(bipy)_2$ group as expected if interactions between the metal ions are weak. An exception occurs in the $d_B \rightarrow \pi^*$(bipy) transition for the pyrazine-bridged system (at 495 nm for the 4+ ion) where metal–metal interactions are greatest from electrochemical and IT spectral data (see below). For the other systems, the $\pi \rightarrow \pi^*$(bipy) and $d_B \rightarrow \pi^*$(bipy) transitions are unaffected by the presence of a remote ruthenium(II) or -(III) ion.

It is expected that $\pi \rightarrow \pi^*$(L) transitions of the bridging ligand might be strongly affected in comparing dimer and monomer spectra. Unfortunately, the $\pi \rightarrow \pi^*$(L) bands are hidden under the very intense $\pi \rightarrow \pi^*$(bipy) bands, and no conclusions can be reached.

Clearly, the $d_A \rightarrow \pi^*$(L) and $d_B \rightarrow \pi^*$(L) transitions should be affected most strongly by a remote metal ion since the transitions are directed into the bridging ligand, along the metal–metal axis. The $d_A \rightarrow \pi^*$(L) bands can be assigned for the 3+ ions $[(NH_3)_5Ru^{II}(L)Ru^{II}Cl(bipy)_2]^{3+}$, since one-electron oxidation gives the 4+ ions $[(NH_3)_5Ru^{III}(L)Ru^{II}Cl(bipy)_2]^{4+}$ in which the Ru(II) $d_A \rightarrow \pi^*$(L) transition is not present. On this basis the lowest energy bands in Table I for the 3+ dimers can be assigned to the $d_A \rightarrow \pi^*$(L) transition. The exception is the BPA dimer for which the $d_A \rightarrow \pi^*$(L) transition occurs at 405 nm.

For $[Ru(bipy)_2(pyz)Cl]^+$, a band appears at 385 nm in acetonitrile which on the basis of chemical studies (photosolvation, protonation of the coordinated pyz group) can be assigned to the d → pyz(π^*) transition.[44] Similar bands apparently exist in the same region for the remaining $[Ru(bipy)_2LCl]^+$ complexes, but their exact positions are masked by intense d → π^*(bipy) bands at ~350 and ~480 nm. We have been unable to assign $d_B \rightarrow \pi^*$(L) bands for any of the dimeric ions, apparently because of interfering absorption by other bands.

The $d_A \rightarrow \pi^*$(L) transition is strongly affected in the pentaamminepyrazineruthenium(II) system by the presence of remote acidic groups. For example, in the ions $[(NH_3)_5Ru(pyz)M]^{n+}$ (M = H, n = 3; M = $Rh^{III}(NH_3)_5$, n = 5), λ_{max} for the $d_A \rightarrow \pi^*$(pyz) bands is shifted to significantly lower energy when compared to the $d_A \rightarrow \pi^*$(pyz) transition for $[Ru(NH_3)_5pyz]^{2+}$.[2,3a,17,18] Defining Δ_{CT} to be the difference in energy (in kK) between the λ_{max} values for the ligand-bridged dimeric complexes and for the related monomeric complexes

$$\Delta_{CT} = \bar{\nu}_{max}(\text{dimer}) - \bar{\nu}_{max}(\text{monomer})$$

gives $\Delta_{CT} \approx -2.3$ kK for the pyrazine-bridged systems (M = H^+ or $Rh(NH_3)_5{}^{3+}$). The red shifts for the dimeric complexes have been explained by the effect of the remote positive charge in stabilizing the CT(Ru→L) excited state.[2,18] The magnitude of the effect is essentially independent of the remote acidic group where M is H^+ or $Rh(NH_3)_5{}^{3+}$.

In the pentaammineruthenium(II) series, the magnitude of Δ_{CT} is also independent of the nature of the bridging ligand, at least where M is H^+. For the protonated complexes $[Ru(NH_3)_5LH]^{3+}$ (L is 4,4'-bipy or BPE), Δ_{CT} is −2.4 kK.[3a]

For the Ru(II)–Ru(II) unsymmetrical dimers (Table IV), the situation is quite different. The shifts in λ_{max}, $|\Delta_{CT}|$, increase in the series L = BPA < BPE < 4,4'-bipy < pyz. For pyrazine as the bridging ligand, the shifts in λ_{max} are affected by the nonbridging cis ligand X. $|\Delta_{CT}|$ increases in the order X = Cl^- < NO_2^- < CH_3CN, which from electrochemical and spectral studies is also the order of increasing π-back-bonding ability of X.[45] Apparently, the nature and/or extent of the metal–metal interaction, as observed spectrally in the Δ_{CT} values, can be varied by varying either the bridging ligand or

Table IV. Band Positions (kK) for the $d[(NH_3)_5Ru^{II}L-] \rightarrow \pi^*(L)$ Charge-Transfer Bands[a]

L	X	$[(NH_3)_5Ru^{II}L]^{2+}$	$[(NH_3)_5Ru^{II}(L)Ru^{II}(X)(bipy)_2]^{3+}$	Δ_{CT}[c]
pyz	Cl	22.0	18.7	−3.3
pyz	NO_2	22.0	20.2	−1.8
pyz	CH_3CN[b]	22.0	21.3	−0.7
4,4′-bipy	Cl	21.3	19.9	−1.4
BPE	Cl	20.0	19.7	−0.3
BPA	Cl	24.8	24.7	−0.1

[a] In acetonitrile; λ_{max} values are known to ±1 nm. [b] Where $X = CH_3CN$, the ion has a 4+ charge. [c] $\Delta_{CT} = \bar{\nu}_{max}(\text{dimer}) - \bar{\nu}_{max}(\text{monomer})$.

the X ligand in the remote $RuX(bipy)_2$ group.

Infrared Spectra. It has been noted previously that $\delta(NH_3)(sym)$ usually occurs at a lower frequency for ruthenium(II) ammines than for ruthenium(III) ammines.[36] Of specific interest here is that Creutz and Taube found $\delta(NH_3)(sym)$ occurred at 1280 cm^{-1} for $[(NH_3)_5Ru(pyz)Ru(NH_3)_5]Br_4$, but at 1345 cm^{-1} for the fully oxidized salt $[(NH_3)_5Ru(pyz)Ru(NH_3)_5](ClO_4)_6$. However, the infrared spectrum of the mixed-valence salt $[(NH_3)_5Ru(pyz)Ru(NH_3)_5]Br_5$ showed that $\delta(NH_3)(sym)$ was intermediate (1295 cm^{-1}) between that expected for either a ruthenium(II) or a ruthenium(III) ammine complex.[2,18] The intermediacy of $\delta(NH_3)(sym)$ appears to support a delocalized description ($Ru^{2.5+}-Ru^{2.5+}$) for the mixed-valence ion $[(NH_3)_5Ru(pyz)Ru(NH_3)_5]^{5+}$, in which the separate ruthenium ions are equivalent. However, other physical and chemical evidence indicates that a localized valence description (Ru(II)–Ru(III)) is correct.[1,2,5,6,7]

Our infrared results relate to this problem in an interesting way. In comparing the infrared spectrum of the salt $[(NH_3)_5Ru^{II}(pyz)Ru^{II}Cl(bipy)_2](PF_6)_3$ ($\delta(NH_3)(sym)$ 1292 cm^{-1}), with the spectrum of the mixed-valence salt $[(NH_3)_5Ru^{III}(pyz)Ru^{II}Cl(bipy)_2](PF_6)_4$ ($\delta(NH_3)(sym)$ 1310 cm^{-1}), $\delta(NH_3)(sym)$ is found to shift only 18 cm^{-1} even though the site of oxidation is localized on the pentaammine end

$$(NH_3)_5Ru^{II}- \xrightarrow{-e^-} (NH_3)_5Ru^{III}-$$

from previous work, shifts of 40–100 cm^{-1} are expected.[2,36] It thus appears that solid-state infrared results can be inconclusive in deciding between localized and delocalized descriptions for ammine complexes of ruthenium.

Intervalence Transfer (IT) Bands. Mixed-valence compounds often have relatively intense bands in the visible and near-infrared regions of their spectra which are present only for the mixed-valence materials. The bands have been described as intervalence transfer (IT) bands in which light-induced electron transfer occurs between the metal centers.[10–12] For the mixed-valence ion $[(NH_3)_5Ru^{II}(pyz)Ru^{III}(NH_3)_5]^{5+}$, an intense band at ~1570 nm has been assigned to the IT absorption

$$[(NH_3)_5Ru^{II}(pyz)Ru^{III}(NH_3)_5]^{5+} \xrightarrow{h\nu} [(NH_3)_5Ru^{III}(pyz)Ru^{II}(NH_3)_5]^{5+*}$$

The immediate product of the light-induced electron-transfer reaction contains Ru(II) with a coordination sphere appropriate to Ru(III) and vice versa.[1,2]

Hush has used configurational–coordinate energy diagrams in describing IT transitions.[11] In Figure 6 are shown configurational coordinate energy diagrams for the symmetrical ion $[(NH_3)_5Ru^{II}(pyz)Ru^{III}(NH_3)_5]^{5+}$ and for the unsymmetrical ion $[(NH_3)_5Ru^{III}(pyz)Ru^{II}Cl(bipy)_2]^{4+}$.

As described by Hush, the energy of the IT transition (E_{op}) for the unsymmetrical ion will equal the sum of the Franck–Condon energy (E_{FC}) and E_0

$$E_{op} = E_{FC} + E_0 \qquad (2)$$

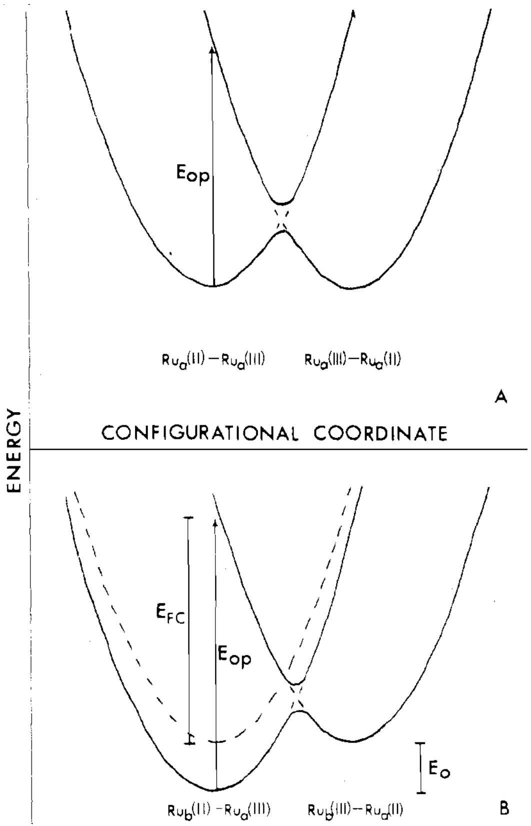


Figure 6. Energy–configurational coordinate diagram for (A) the $[(NH_3)_5Ru^{II}(pyz)Ru^{III}(NH_3)_5]^{5+}$ ion and (B) the $[(NH_3)_5Ru^{III}(pyz)Ru^{II}Cl(bipy)_2]^{4+}$ ion.

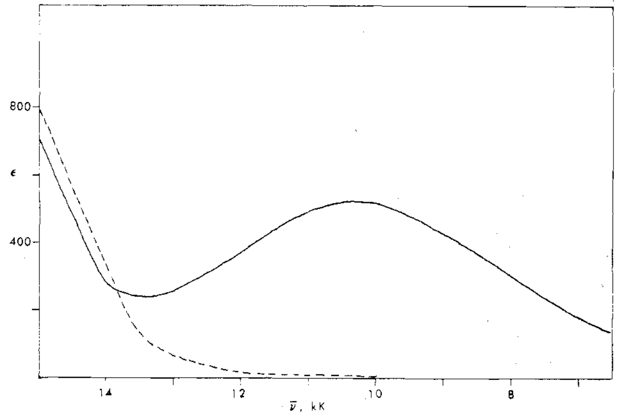


Figure 7. Near-infrared spectra of (- - -) $[(NH_3)_5Ru(pyz)RuCl(bipy)_2]^{3+}$ and (——) $[(NH_3)_5Ru(pyz)RuCl(bipy)_2]^{4+}$ in acetonitrile.

This relationship is shown diagrammatically in Figure 6. E_0 is the difference in internal energy between the thermally equilibrated ion $[(NH_3)_5Ru^{III}(pyz)Ru^{II}Cl(bipy)_2]^{4+}$ and its oxidation-state isomer $[(NH_3)_5Ru^{II}(pyz)Ru^{III}Cl(bipy)_2]^{4+}$. The high-energy oxidation-state isomer $[(NH_3)_5Ru^{II}(pyz)Ru^{III}Cl(bipy)_2]^{4+}$, in which the oxidation-state configuration is reversed from the configuration of the ground-state ion, is the product of light-induced electron transfer (IT absorption) which has undergone vibrational and rotational relaxation.

From eq 2 and Figure 6 it can be predicted that IT absorption for $[(NH_3)_5Ru^{III}(pyz)Ru^{II}Cl(bipy)_2]^{4+}$ will occur at a higher energy than in $[(NH_3)_5Ru^{III}(pyz)Ru^{II}(NH_3)_5]^{5+}$. This will be the case if the difference in the Franck–Condon energies for the two systems is small compared to E_0; E_0 can be estimated to be ~0.3 V for this case.[46] An IT band is found for the pyrazine-bridged dimer at 10.4 kK (Table II and Figure 7) which is at a higher energy than the IT band for $[(NH_3)_5Ru(pyz)Ru(NH_3)_5]^{5+}$ as predicted.

A variety of results support the assignment of the band at 10.4 kK to an IT transition.

1. As seen in Table II, by replacing Cl^- by NO_2^- or CH_3CN in the dimers $[(NH_3)_5Ru^{III}(pyz)Ru^{II}X(bipy)_2]^{3+}$, the IT band maximum shifts to higher energies (12.7 and 13.3 kK, respectively). The shifts are expected. In the series, E_0 is expected to increase because of stabilization of the Ru(II) in the $-Ru^{II}(L)(bipy)_2$ end by the back-bonding ligands NO_2^- and CH_3CN. The stabilization of Ru(II) by good back-bonding ligands has been noted in a related series of monomeric complexes.[32,40,45] The same effect was reported earlier for the IT bands of substitution products of the $[(NH_3)_5Ru^{III}(pyz)Ru^{II}(NH_3)_5]^{5+}$ ion.[1,2,18]

2. IT bands are usually broad having half-widths on the order of 4–8 kK.[11,12] A half-bandwidth of 5.8 kK ($\Delta\bar{\nu}_{1/2}$(obsd)) is found for the band at 10.4 kK. Using the approximation that $E_0 \approx 2.4$ kK (0.3 V), a calculated half-width of ~4.3 kK ($\Delta\bar{\nu}_{1/2}$(calcd)) is obtained using the formula given by Hush, $\bar{\nu}_{op} - \bar{\nu}_0 = (\Delta\bar{\nu}_{1/2})^2/2.31$ ($\bar{\nu}$ in kK).[11] The agreement between $\Delta\bar{\nu}_{1/2}$(obsd) and $\Delta\bar{\nu}_{1/2}$(calcd) ($\Delta\bar{\nu}_{1/2}$(obsd) $\simeq 1.3\Delta\bar{\nu}_{1/2}$(calcd)) is considerably better than that found for $[(NH_3)_5Ru(pyz)Ru(NH_3)_5]^{5+}$ where $\Delta\bar{\nu}_{1/2}$(obsd) $\simeq 0.4\Delta\bar{\nu}_{1/2}$(calcd).[2,18]

3. Hush has suggested that IT bands should show a solvent dependence proportional to $(1/n^2 - 1/D)$, where n is the index of refraction and D the static dielectric constant of a particular solvent.[11] Such a dependence is found for the 10.4-kK band. The predicted solvent dependence has not been found for the ion $[(NH_3)_5Ru^{III}(pyz)Ru^{II}(NH_3)_5]^{5+}$. For the 5+ symmetrical dimer, solvent shifts are small (0.14 kK, maximum).[2,18] The lack of solvent dependence for the IT band of the symmetrical dimer has led Creutz and Taube to suggest that the contribution to the Franck–Condon energy from outer-sphere distortions is small.[2] Since the unsymmetrical dimers show the expected solvent dependence, outer-sphere distortions are important for them. We have not attempted to use eq 2 to make a quantitative prediction for the position of the IT band maximum for $[(NH_3)_5Ru^{III}(pyz)Ru^{II}Cl(bipy)_2]^{4+}$ relative to the IT band for $[(NH_3)_5Ru^{III}(pyz)Ru^{II}(NH_3)_5]^{5+}$ because of the differences in solvent dependence for the two IT bands and possible differences in E_{FC} for the symmetrical and unsymmetrical dimers.

4. The extent of the electronic interaction in the ground state of a mixed-valence ion can be estimated from α^2 which is a measure of the extent of electron delocalization from Ru(II) to Ru(III). α^2 can be estimated from the oscillator strengths and energies of IT bands and the distances separating the metal centers using an equation derived by Hush.[11] Using the value 7 Å estimated by Creutz[18] as the distance separating the metal centers and the equation derived by Hush, it can be calculated that α^2 is ~0.003 for $[(NH_3)_5Ru^{III}(pyz)Ru^{II}Cl(bipy)_2]^{4+}$. Creutz has calculated $\alpha^2 \approx 0.009$[18] for the ion, $[(NH_3)_5Ru^{III}(pyz)Ru^{II}(NH_3)_5]^{5+}$. From the α^2 values, both of the ions are class II ions in the Robin and Day classification[6,10] indicating that metal–metal interactions are relatively weak. However, from the α^2 values, ground-state electronic interactions are greater by a factor of 3 in the Creutz and Taube ion. Less interaction is expected for the unsymmetrical dimers since the metal ions are in significantly different cocoordination environments.[10] In addition, the delocalization of d electrons from the $-Ru^{II}Cl(bipy)_2$ group is expected to be less than for the $-Ru^{II}(NH_3)_5$ group because of extensive π bonding with the 2,2'-bipyridine ligands.

The shoulders at 14.4 and 14.7 kK in $[(NH_3)_5Ru^{III}(4,4'\text{-}bipy)Ru^{II}Cl(bipy)_2]^{4+}$ and $[(NH_3)_5Ru^{III}(BPE)Ru^{II}Cl(bipy)_2]^{4+}$, respectively, are probably also due to intervalence transfer. They have the correct solvent dependence. The shift of the IT band to higher energies, relative to those of $[(NH_3)_5Ru^{III}(pyz)Ru^{II}Cl(bipy)_2]^{4+}$, may result from the greater distance separating the metal centers. The intersection region between the Ru(II)–Ru(III) and Ru(III)–Ru(II) surfaces (Figure 6) and therefore the energy of the IT band are dependent upon the distance separating the metal ions.[11]

No IT band is observed for the $[(NH_3)_5Ru^{III}(BPA)Ru^{II}Cl(bipy)_2]^{4+}$ ion. The result was expected since the bridging ligand (BPA) does not have an uninterrupted π system. No orbital pathway is available for metal–metal interactions and the ion is an example of a class I case in the Robin and Day scheme.[6,10]

Conclusions

From our observations, it appears that cooperative electronic interactions between metal centers in ligand-bridged complexes can be varied by a series of relatively simple chemical modifications. Even though metal–metal interactions are weak, they influence the properties of the complexes in detectable ways. Band maxima shift for the Ru(II)–Ru(II) 3+ ions, but only for certain electronic transitions. Intervalence transfer transitions appear in the visible or near-infrared spectra of the mixed-valence 4+ ions. The redox properties of the complexes, as measured by reduction potentials, are also affected, if only slightly. Perhaps the most important point to be made here is that the properties of the ligand-bridged ions can be modified in a controlled and systematic way by chemical synthesis.

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Registry No. $[Ru(NH_3)_5H_2O](PF_6)_2$, 34843-18-0; $[Ru(bipy)_2(BPA)Cl](PF_6)$, 54713-80-3; $[(NH_3)_5Ru(pyz)RuCl(bipy)_2](PF_6)_3$, 54713-82-5; $[(NH_3)_5Ru(4,4'\text{-}bipy)RuCl(bipy)_2](PF_6)_3$, 54713-84-7; $[(NH_3)_5Ru(BPE)RuCl(bipy)_2](PF_6)_3$, 54713-86-9; $[(NH_3)_5Ru(BPA)RuCl(bipy)_2](PF_6)_3$, 54713-88-1; $[(NH_3)_5Ru(pyz)RuCl(bipy)_2](PF_6)_4$, 54750-85-5; $[(NH_3)_5Ru(pyz)Ru(NO_2)(bipy)_2](PF_6)_3$, 54713-90-5; $[(NH_3)_5Ru(pyz)Ru(NO)(bipy)_2](PF_6)_5$, 54713-92-7; $[Ru(NH_3)_5BPA](PF_6)_2$, 54713-94-9; $[Ru(NH_3)_5pyz]^{2+}$, 19471-65-9; $[Ru(NH_3)_5(4,4'\text{-}bipy)]^{2+}$, 54714-01-1; $[Ru(NH_3)_5BPE]^{2+}$, 54750-49-1; $[Ru(NH_3)_5BPA]^{3+}$, 54714-02-2; $[(bipy)_2RuCl(pyz)]^+$, 47690-99-3; $[(bipy)_2RuCl(4,4'\text{-}bipy)]^+$, 47794-83-2; $[(bipy)_2RuCl(BPE)]^+$, 48236-77-7; $[(NH_3)_5Ru(pyz)Ru(NO_2)(bipy)_2]^{4+}$, 54065-83-7; $[(NH_3)_5Ru(pyz)Ru(CH_3CN)(bipy)_2]^{4+}$, 54750-91-3; $[(NH_3)_5Ru(pyz)Ru(CH_3CN)(bipy)_2]^{5+}$, 54065-97-3; $[(NH_3)_5Ru(4,4'\text{-}bipy)RuCl(bipy)_2]^{4+}$, 54065-98-4; $[(NH_3)_5Ru(BPE)RuCl(bipy)_2]^{4+}$, 54065-99-5; $[(NH_3)_5Ru(BPA)RuCl(bipy)_2]^{4+}$, 54066-00-1; $[Ru(NH_3)_5py]^{3+}$, 33291-25-7; $[Ru(bipy)_2(py)Cl]^{2+}$, 54714-08-8; $[Ru(bipy)_2(BPA)Cl]^{2+}$, 54714-09-9; $[(NH_3)_5Ru(BPA)RuCl(bipy)_2]^{5+}$, 54750-50-4; $[Ru(NH_3)_5(4,4'\text{-}bipy)]^{3+}$, 54714-03-3; $[Ru(bipy)_2(4,4'\text{-}bipy)Cl]^{2+}$, 54714-07-7; $[(NH_3)_5Ru(4,4'\text{-}bipy)RuCl(bipy)_2]^{5+}$, 54750-51-5; $[Ru(NH_3)_5BPE]^{3+}$, 54750-52-6; $[Ru(bipy)_2(BPE)Cl]^{2+}$, 54714-04-4; $[(NH_3)_5Ru(BPE)RuCl(bipy)_2]^{5+}$, 54750-53-7; $[Ru(NH_3)_5pyz]^{3+}$, 38139-16-1; $[Ru(bipy)_2(pyz)Cl]^{2+}$, 54714-06-6; $[(NH_3)_5Ru(pyz)RuCl(bipy)_2]^{5+}$, 54750-54-8; $[(NH_3)_5Ru(pyz)Ru(NH_3)_5]^{5+}$, 35599-57-6.

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(46) E_0 is the internal energy change for the reaction $[(NH_3)_5Ru^{III}(pyz)Ru^{II}Cl(bipy)_2]^{4+} \rightarrow [(NH_3)_5Ru^{II}(pyz)Ru^{III}Cl(bipy)_2]^{4+}$. If for the reaction, $\Delta S \approx 0$, E_0 is approximately the free energy difference between the two oxidation-state isomers, ΔG. ΔG can be calculated from the difference in reduction potentials between the couples $[(NH_3)_5Ru^{II}(pyz)Ru^{III}Cl(bipy)_2]^{4+}$–$[(NH_3)_5Ru^{II}(pyz)Ru^{II}Cl(bipy)_2]^{3+}$ (E_1) and $[(NH_3)_5Ru^{III}(pyz)Ru^{II}Cl(bipy)_2]^{4+}$–$[(NH_3)_5Ru^{II}(pyz)Ru^{II}Cl(bipy)_2]^{3+}$ ($E_2 = 0.61$ V; Table II): $\Delta G\ (V) = E_1 - E_2$. E_1 can be estimated from the potentials for related redox couples. The potentials for the couples $[(NH_3)_5Ru^{III}(pyz)Ru^{III}Cl(bipy)_2]^{5+}$–$[(NH_3)_5Ru^{III}(pyz)Ru^{II}Cl(bipy)_2]^{4+}$ (1.03 V; Table II) and $[(bipy)_2ClRu^{II}(pyz)Ru^{III}Cl(bipy)_2]^{3+}$–$[(bipy)_2ClRu^{II}(pyz)Ru^{II}Cl(bipy)_2]^{2+}$ (0.89 V; ref 8) are similar, indicating little dependence of the $Ru^{III}Cl(bipy)_2$–$Ru^{II}Cl(bipy)_2$ potential on the remote group. Choosing the potential of the $[(bipy)_2ClRu(pyz)RuCl(bipy)_2]^{3+,2+}$ couple for E_1, since it is a case where the remote group is Ru(II), gives $E_0 \approx \Delta G = 0.3$ V.

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Synthesis and Properties of Cobalt(I) Compounds. II.
An Ortho-Metalated (Triphenyl phosphite)cobalt(I) Complex

L. W. GOSSER

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The preparation and properties of the ortho-metalated compound $[(C_6H_5O)_3P]_3(C_6H_5O)_2\overline{POC_6H_4Co}$ are described. This compound was prepared by reaction of triphenyl phosphite with $Co(C_8H_{12})(C_8H_{13})$ as well as by heating solutions of $CoH[(C_6H_5O)_3P]_4$. The ortho-metalated compound catalyzed the hydrogenation of 1-butene and exchanged ligand hydrogens with D_2 under mild conditions.

There has been increasing interest in ortho-metalation reactions of triaryl phosphite complexes of transition metals. A number of ortho-metalation products of triphenyl phosphite complexes of the later transition metals have been isolated.[1] The ortho-metalation compounds derived from triaryl phosphite complexes of the first-row transition elements have, however, been elusive. An ortho-metalated triphenyl phosphite complex of manganese has recently been reported.[2a] A coordinatively unsaturated ortho-metalation product was proposed as an intermediate in the ortho deuteration of hydridotetrakis(triphenyl phosphite)cobalt,[1a] and ortho metalation is said to be the reason for the formation of complex products in the reaction of (triaryl phosphito)cobalt hydrides with potassium hydride,[2b] but the ortho-metalated compounds have not previously been isolated. Because of the potential for interesting catalytic properties, a method for the preparation of an ortho-metalated triphenyl phosphite complex of cobalt was sought.

Preparation and Properties

The ortho-metalated compound $[(C_6H_5O)_3P]_3(C_6H_5O)_2\overline{POC_6H_4Co}$ (I) has now been prepared by two different methods. In the first method mixtures of I and the corresponding hydride, $CoH[P(OC_6H_5)_3]_4$, were prepared by heating solutions of the hydride (in accord with the earlier proposal that ortho-metalated intermediates participated in the ortho deuteration of the hydride[1a]). Compound I and the hydride had similar solubility properties, and since I was available by another procedure, the fractionation of the mixtures was not pursued. In the second method I was prepared by the reaction of $Co(C_8H_{12})(C_8H_{13})$[3] with triphenyl phosphite at room temperature. An earlier report[4] of the