only is there a conversion to low-spin Fe^{III}, but there appears high-spin Fe^{2+}. The process was reversible with a decrease in applied pressure. However, when water is removed by vacuum pyrolysis, we find that the conversion is reasonably stable.

The pyrolysis does not completely destroy the well-ordered structure of Prussian Blue. The X-ray diffraction patterns indicate the ferrous ferricyanide is also crystalline, different from Prussian Blue. The major peaks in ferrous ferricyanide have moved to larger diffraction angles which is consistent with considerable shrinkage in the lattice. A slow conversion occurs in humid air, ferrous ferricyanide to Prussian Blue. X-Ray diffraction patterns of reconstituted ferric ferrocyanide by acid treatment are identical with those of Prussian Blue. The X-ray spectrum of ferrous ferricyanide has not been satisfactorily interpreted. Attempts to index all lines to a cubic lattice have failed. Hence, either the lattice is noncubic or there are more than one lattice present. We expect that the structure of ferrous ferricyanide will be found to be very close to that of Prussian Blue, except that the lattice spacing will be less as a result of water loss and, of course, the valences of the iron ions differ.

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Binuclear Complexes of Ruthenium Ammines

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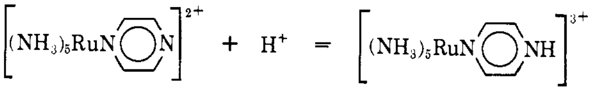
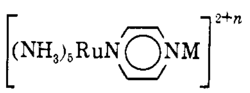
Abstract: The preparation of the species $[(NH_3)_5Ru]_2pyr^{4+,5+,or 6+}$ in solution is described, as is that of solid phases containing each of the three cations. The species of intermediate oxidation state with the ion bearing a charge of 5+ is shown to be stable in solution with respect to disproportionation to the 4+ and 6+ states. In addition to a band at 565 nm (ϵ 2.1 × 10^4), where the 4+ (but not the 6+ ion) also shows strong absorption, it shows absorption at 1560 nm. Neither the 4+ nor 6+ species shows absorption in this region of the spectrum. Following Hush, this absorption is assigned as an intervalence transition. The validity of this interpretation of the spectrum depends on the ion in the ground state conforming to the oxidation state description [2+, 3+] rather than to $[2^1/_2, 2^1/_2]$. The evidence in support of the "deeply trapped" description is reviewed. When the ruthenium atoms are made substitutionally nonequivalent, the near-ir absorption always shifts to shorter wavelengths, the shift corresponding in energy to the stabilization of one oxidation state relative to the other brought about by the substitutional changes. When the solvent is changed, only slight shifts in the ir absorption maximum are recorded (to 1580 in ethanol (D = 24), 1595 in formamide (D = 109)).

Physical properties of a number of ruthenium(II) pentaammine complexes with π-acceptor ligands (aromatic heterocycles,[1,2] organonitriles,[3] carbon monoxide,[4] and dinitrogen[5]) have been reported. The studies of Ford, *et al.*,[1] on the equilibrium



demonstrating the enhanced basicity of pyrazine when complexed to Ru(II), suggested to us the possibility of replacing the proton with another metal ion M^{n+} to give binuclear complex $[(NH_3)_5Ru(pyr)M]^{2+n}$ (pyr = pyrazine)



Such binuclear complexes are of interest in the further study of the Ru(II)–ligand backbonding interaction[1,6] and in studies of metal–metal interaction mediated by bridging ligands.

In the course of our experiments, we prepared a series of mixed-valence Ru(II)–Ru(III) complexes. The physical properties of these ions are of interest in the growing field of mixed valence compound studies.[7,8] In addition, the interpretation of their electronic spectra may lead to greater understanding of the energetic requirements of electron transfer processes.[9,10] Spectral and other physical properties of $[(NH_3)_5Ru]_2pyr^{n+}$ (n = 4, 5, 6) and related compounds are reported and discussed here.

Experimental Section

Spectra. Ultraviolet–visible range spectra were measured on a Cary 14 or Cary 15 recording spectrophotometer at room temperature. Extinction coefficients of binuclear Ru(II) complexes in the ultraviolet–visible region were measured as follows. An exactly weighed *ca.* 3-mg sample of the solid salt weighed into a weighing

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[1] P. C. Ford, D. F. P. Rudd, R. G. Gaunder, and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1187 (1968).

[2] R. G. Gaunder and H. Taube, *Inorg. Chem.*, **9**, 2627 (1970).

[3] R. E. Clarke and P. C. Ford, *ibid.*, **9**, 495 (1970).

[4] C. H. Campbell, A. R. Dias, M. Green, T. Saito, and M. Swanwich, *J. Organometal. Chem.*, **14**, 349 (1970).

[5] D. E. Harrison, E. Weissberger, and H. Taube, *Science*, **159**, 320 (1968).

[6] A. M. Zwickel and C. Creutz, *Inorg. Chem.*, **10**, 2395 (1971).

[7] N. S. Hush, *Progr. Inorg. Chem.*, **8**, 357 (1967).

[8] (a) M. B. Robin and P. Day, *Advan. Inorg. Chem. Radiochem.*, **10**, 247 (1967). (b) E. B. Fleischer and D. K. Lavallee, *J. Amer. Chem. Soc.*, **94**, 2599 (1972).

[9] C. Creutz and H. Taube, *ibid.*, **91**, 3988 (1969).

[10] N. S. Hush, *Progr. Inorg. Chem.*, **8**, 391 (1967).

boat was added to 50.0 or 100 ml of redistilled, deoxygenated water under a positive argon pressure. A 3-ml portion of this solution was removed with a syringe and transferred to an air-purged 10.0-mm quartz cell capped with a rubber septum cap. The spectrum of the solution was recorded immediately. To minimize disproportionation, extinction coefficients of salts containing Ru(III) only were measured in acid solutions (0.1 *N* $HClO_4$). The extinction coefficient of $[(NH_3)_5Ru(pyr)]^{2+}$ was determined by forming the ion directly in solution as follows. Three milliliters of a solution 0.3 *M* in pyrazine and 1.00×10^{-4} *M* in $(NH_3)_5RuCl^{2+}$ in a 10.0-mm quartz cell was purged of O_2 by bubbling 0.5 hr with argon. Afterwards 10.0 μl of 0.02 *M* chromium(II) perchlorate solution was added to the cell by syringe. The maximum absorbance attained at 472 nm (found within 10 min of Cr(II) addition) was used in calculating the value $13.7 \pm 0.2 \times 10^3\ M^{-1}\,cm^{-1}$.

Measurements of the absorption spectrum in the near-infrared region were made on the Cary 14 at room temperature. Most scans were done using 10.0-mm quartz cells and solutions 10^{-4} to 10^{-3} *M* in Ru, with D_2O as solvent. Solution spectra were run against complete solvent blanks. In studies of solvent effects in the near-infrared region, solutions *ca.* 10^{-3} *M* in Ru contained in 1.00-mm cells were run against matched cells containing solvent only. Infrared spectra were recorded on either a Perkin-Elmer 237B, 421, or 457.

Reduction Potentials.[11] Reduction potentials were found by potentiometric titration of either the reduced Ru complex with cerium(IV) perchlorate or of the oxidized Ru complex with chromium(II) perchlorate or vanadium(II) sulfate. Titrant (0.01 *N*) was added by syringe to 35 ml of a solution 10^{-5} *M* in Ru complex, 0.10 *M* in potassium chloride, and 0.001 *N* in hydrochloric acid. The titration was carried out under an argon atmosphere using a cell such as that described by Gaunder[2] and a silver–silver chloride (0.10 *M* potassium chloride) reference electrode. The formal electrode potential for each couple studied was calculated from the halfway potential in the titration. The behavior of all couples reported here followed the Nernst equation.

Reagents. Except for the following, chemicals used were reagent grade: silver(I) *p*-toluenesulfonate, *p*-toluenesulfonic acid, and vanadyl sulfate (Fisher Certified); sodium *p*-toluenesulfonate (Eastman Organic); trifluoroacetic acid (Matheson Coleman and Bell (boiling range 71–73°); 2,2′-bipyridine, pyrazine (Purissima grade) (Aldrich). Isonicotinamide (Aldrich) was recrystallized from water before use. For use as a precipitant, a saturated solution of sodium tetrafluoroborate (Alfa) was prepared freshly and filtered from an insoluble grayish residue. Cerium(IV) perchlorate solutions were made by diluting G. F. Smith reagent grade solution (0.5 *M* Ce(IV), 6 *N* $HClO_4$) standardized by titrating primary standard sodium oxalate in hot sulfuric acid. Chromium(II) perchlorate solutions were generated using amalgamated zinc to reduce acidic chromium(III) perchlorate solutions which had been prepared by reducing primary standard potassium dichromate with acidic hydrogen peroxide. Vanadium(II) sulfate solutions were prepared by reducing acidic vanadyl sulfate stock solution with zinc amalgam.

Deionized, distilled water was redistilled before use from a solution 0.04% in potassium hydroxide and 0.2% in potassium permanganate. Bio-Rad 99.8% enriched deuterium oxide was distilled before use from a solution 0.04% in sodium deuterioxide and 0.2% in potassium permanganate. Sodium deuterioxide was generated by sodium metal acting on deuterium oxide.

Argon, prepurified grade, was scrubbed by passing it through a solution 0.1 *M* in chromium(II) perchlorate and through water.

Microanalyses were carried out by the Stanford Microanalytical Laboratory, Stanford, Calif.

Syntheses: Chloropentaammineruthenium(III) chloride was prepared from Johnson and Matthey hexaammineruthenium(III) chloride according to the procedure of Vogt, *et al.*,[12] and recrystallized from hot (*ca.* 80°) 0.1 *N* hydrochloric acid.

***cis*-Dichlorotetraammineruthenium(III) chloride** was made from aquopentaammineruthenium(III) by the method of Gleu and Breuel.[13]

Trichlorotriammineruthenium(III). *cis*-Dichlorotetraammineruthenium(III) chloride (0.15 g) was dissolved in 30 ml of 6 *N* hydrochloric acid. The solution was boiled several hours until formation of orange triammine crystals ceased. The product crystals were collected by filtration and washed with 6 *N* hydrochloric acid and ethanol. *Anal.* Calcd for $(NH_3)_3RuCl_3$: Ru, 39.1; N, 16.3; H, 3.49; Cl, 41.1. Found: Ru, 39.0; N, 16.2; H, 3.45; Cl, 40.8.

Aquopentaamminerhodium(III) Perchlorate. Chloropentaamminerhodium(III) chloride (Alfa Inorganics) (1.00 g) was mixed with 1.19 g of silver(I) oxide which had been dissolved in 40 ml of water containing a slight excess of perchloric acid. The mixture was heated at 50 to 60° for about 12 hr, cooled, then filtered from the silver chloride which had formed. About 10 ml of 60% perchloric acid was added to the filtrate and the solution was chilled. The pale yellow crystals of aquopentaamminerhodium(III) perchlorate which formed were collected on a glass filter and washed with 30% perchloric acid.

Pyrazinepentaamminerhodium(III) Perchlorate. Aquopentaamminerhodium(III) perchlorate (0.313 g) was dissolved along with 0.6 g of pyrazine in 5 ml of dimethylformamide and heated at 90 to 100° for 28 hr. Dimethylformamide was stripped from the product solution on a rotary evaporator. The viscous, pale-yellow oil resulting was treated with ethanol and ether alternately and the container was scratched with a glass rod until crystal formation was induced. The solid which formed consisted of fine white crystals; it was purified by recrystallization from hot water. *Anal.* Calcd for $[(NH_3)_5Rh(pyr)](ClO_4)_3$: C, 8.5; N, 17.3; H, 3.36; Cl, 18.6. Found: C, 8.7; N, 17.3; H, 3.39; Cl, 18.7.

Pyrazinepentaammineruthenium(II)[14] Perchlorate. To 0.100 g of chloropentaammineruthenium(III) chloride covered with about 3 ml of water was added a solution of silver(I) made by dissolving 0.079 g of silver(I) oxide in 2 ml of water by the dropwise addition of trifluoroacetic acid. The mixture of dissolved Ru and solid silver chloride resulting was digested at 80° on a hot plate until the silver chloride had coagulated. After cooling, the silver chloride was removed by filtration and the pH of the filtrate was adjusted to 3–5 by adding solid sodium bicarbonate. Several pieces of freshly prepared amalgamated zinc and 0.3 g of pyrazine were added to the solution, and the mixture was left in the dark for 0.5 hr with occasional stirring. The orange-red solution of pyrazine complex was filtered from the remaining zinc amalgam and mixed with 2 ml of saturated sodium perchlorate solution. The beaker was scratched to induce crystallization and the solution was cooled at 4° until no additional solid formed. The crude product was collected by filtration and recrystallized from hot water. To prepare iodide and tetrafluoroborate salts, an analogous procedure was followed, making the obvious modifications. *Anal.* Calcd for $[(NH_3)_5Ru(pyr)](ClO_4)_2$: C, 10.3; N, 21.2; H, 4.12; Cl, 15.2. Found: C, 10.4; N, 21.2; H, 4.02; Cl, 15.0. The purity of the fluoroborate salt was ascertained by comparing its extinction coefficient ($13.3 \times 10^3\ M^{-1}\,cm^{-1}$) to that found when the pyrazine complex was generated in solution ($13.7 \times 10^3\ M^{-1}\,cm^{-1}$).

Pyrazinepentaammineruthenium(III) *p*-Toluenesulfonate. Pyrazine pentaammineruthenium(II) perchlorate was oxidized in 2 *N* sulfuric acid with a suspension of lead(IV) oxide in excess. Following reaction, the solids were removed by filtration. Addition of 60% perchloric acid to the filtrate yielded a yellow, impure, perchlorate[14] salt whose purity (judged by results of microanalysis) was not improved by recrystallization from dilute perchloric acid. The impure perchlorate salt was dissolved in the minimum volume of warm (40°) 1 *N* sulfuric acid and solid *p*-toluenesulfonic acid was added to the solution until yellow solid began to form. A little warm water was added to redissolve this solid. The warm, saturated solution was filtered and chilled to yield light-yellow crystals of the ruthenium(III) *p*-toluenesulfonate salt. *Anal.* Calcd for $[(NH_3)_5Ru(pyr)](C_7H_7SO_3)_3 \cdot 3H_2O$: C, 36.0; N, 11.8; H, 5.52; S, 11.5. Found: C, 36.1; N, 12.0; H, 5.53; S, 11.6.

(*N*-Methylpyrazinium)pentaammineruthenium(II) Perchlorate.[14] A solution of $(NH_3)_5RuCl^{2+}$ was prepared as for preparation of $(NH_3)_5Ru(pyr)^{2+}$. After filtration from silver chloride (the pH of the solution was *not* adjusted), zinc amalgam and *N*-methylpyrazinium *p*-toluenesulfonate were added to the filtrate. The preparation was completed as described for $(NH_3)_5Ru(pyr)^{2+}$ above. *N*-Methylpyrazinium *p*-toluenesulfonate was made by treating *N*-methylpyrazinium iodide provided by Dr. J. Malin with an equimolar amount of silver *p*-toluenesulfonate. The silver iodide formed was removed by filtration and the filtrate was evaporated to dryness. The residue was dissolved in methanol and mixed with ether to induce crystallization.

(*N*-Methylpyrazinium)pentaammineruthenium(III) perchlorate[14] was prepared by adding 0.5 *M* Ce(IV) in 6 *N* perchloric acid drop-

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[11] We wish to acknowledge the assistance of J. R. Kuempel with these studies.

[12] L. H. Vogt, Jr., J. L. Katz, and S. E. Wiberley, *Inorg. Chem.*, **4**, 1157 (1965).

[13] K. Gleu and K. Breuel, *Z. Anorg. Allg. Chem.*, **127**, 335 (1938).

[14] Caution: ruthenium perchlorates are potentially explosive and should be handled with care and only in milligram quantities.

wise to solid Ru(II) complex until all traces of purple color in the solution disappeared. Addition of saturated sodium perchlorate to the yellow Ru(III) solution yielded solid Ru(III) perchlorate salt. This salt was found to be very unstable to light and traces of reducing agents.

μ-Pyrazined-ecaamminediruthenium(II)*p*-Toluenesulfonate(I). To 1.00 g (3.44 mmol) of chloropentaammineruthenium(III) chloride covered with 3 ml of water was added 6.46 mmol of silver(I) trifluoroacetate (from neutralization of silver(I) oxide with trifluoroacetic acid). The mixture was digested on a hot plate at 80° until the silver chloride had coagulated. It was then cooled and filtered. The pH of the filtrate was adjusted to between 2 and 3 by adding solid sodium bicarbonate. After adding several pieces of freshly prepared amalgamated zinc and 0.137 g of pyrazine (1.72 mmol) to the solution (*ca.* 10 ml total volume), argon was bubbled for 0.5 hr through the solution which was contained in a rubber-capped 25-ml erlenmeyer flask. The deoxygenated solution was stored overnight in the dark with occasional agitation. The next day the purple solution was filtered from the remaining zinc under argon in a glove bag. Sodium *p*-toluenesulfonate (3 g) was added to the filtrate and the solution was cooled under argon to yield a purple deposit. The solid was collected by filtration in an argon-filled glove bag, washed with 1 *M* sodium *p*-toluenesulfonate and ethanol, then stored at 0° under argon. To recrystallize, the solid was transferred to a 50-ml erlenmeyer flask. The flask was sealed with a rubber serum cap and purged with argon. Boiling water was then added to the flask by syringe until the solid dissolved. The hot solution was allowed to cool slowly, yielding purple needles. These were collected by filtration under argon and washed with ethanol. The recrystallized material was dried over night under vacuum and then stored over calcium chloride at 0°. *Anal.* Calcd for $[(NH_3)_5Ru]_2pyr(C_7H_7SO_3)_4 \cdot H_2O$: C, 32.8; N, 14.3; H, 5.63; S, 10.9. Found: C, 33.0; N, 14.1; H, 5.68; S, 11.4.

μ-Pyrazine-decaamminediruthenium(5+) *p*-Toluenesulfonate (II). Crude I was dissolved in the minimum volume of water and treated with an equimolar quantity of silver(I) *p*-toluenesulfonate. More water was added as required to dissolve the rather insoluble II which formed. The dark purple solution of II resulting was filtered from the silver metal produced and solid sodium *p*-toluenesulfonate was added to the filtrate until the residual solution was only faintly purple. The crude solid was collected by filtration and recrystallized from 60 to 70° water. The purple needles resulting were washed with ethanol, dried overnight at room temperature under vacuum, then stored at 0° over calcium chloride. *Anal.* Calcd for $[(NH_3)_5Ru]_2pyr(C_7H_7SO_3)_5 \cdot 3H_2O$: Ru, 14.4; C, 34.4; N, 12.3; H, 5.51; S, 11.7. Found: Ru, 14.8; C, 34.3; N, 12.4; H, 5.44; S, 11.8.

μ-Pyrazine-decaamminediruthenium(III) Perchlorate (III).[14] Solid I or II was covered with a small volume of water. Cerium(IV) perchlorate solution (0.5 *M* in 6 *N* $HClO_4$) was added dropwise to the mixture with stirring until an orange-red solution resulted. Orange crystals of ruthenium(III) perchlorate resulting after solid sodium perchlorate was added were collected by filtration, washed with ethanol, dried under vacuum at room temperature overnight, and stored over calcium chloride at 0°. *Anal.* Calcd for $[(NH_3)_5Ru]_2pyr(ClO_4)_6$: C, 4.56; N, 16.0; H, 3.24; Cl, 20.0. Found: C, 4.75; N, 15.9; H, 3.32; Cl, 19.8.

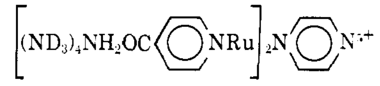
Stability of I, II, and III. At room temperature and in the absence of air and light, dilute (10^{-5} to 10^{-4} *M*) solutions of I and II undergo little (<10%) decomposition for periods up to 1 or 2 months (as determined by periodic scans of the uv–visible spectra of the solutions). I is oxidized by air only slowly (*i.e.*, overnight) in neutral solution but the rate of its oxidation to II is markedly increased (to the time scale of minutes) in acidic solution. II was not observed to undergo air oxidation.

No long-term studies of the resistance of III to hydrolysis were undertaken, but we have found that the spectrum of *ca.* 10^{-4} *M* III in 0.1 *N* $HClO_4$ is unchanged if the solution is stored at 4° in the dark overnight. On the other hand, III is subject to rapid decomposition at pH 4 or greater. One of the decomposition products is II. As up to $^2/_3$ mol of II was found to be formed for each mole of III initially present in the solution,[15a] this decomposition process is probably a disproportionation of the $(Ru(III))_2$ cation[15b] leading to production of the mixed-valence ion and Ru(IV). The Ru(IV) product was not detected, however. II was not found to undergo such a disproportionation reaction in the range studied (up to pH 10).

μ-Pyrazine-decaamminerhodium(III)ruthenium(II) Perchlorate.[14] Pyrazinepentaamminerhodium(III) perchlorate (0.128 g, 0.23 mmol) was dissolved in *ca.* 4 ml of water and the solution was passed through a column of Bio-Rad Analytical Grade Anion Exchange Resin AG3-X4 (100–200 mesh) in the chloride form so as to replace perchlorate by chloride ion. Chloropentaammineruthenium(III) chloride (0.080 g, 0.27 mmol) was dissolved in 7 ml of 0.1 *N* sulfuric acid and reduced over amalgamated zinc under argon for *ca.* 0.5 hr. The reduced Ru solution was transferred by syringe to the deoxygenated solution of the complex rhodium(III) chloride. Shortly after mixing, the very pale-yellow solution became intensely pink, with a new absorption band appearing in the solution spectrum at 528 nm. The reactant solution was stored under argon in the dark overnight. The next day the solution was opened to the air and mixed with 2 ml of saturated sodium perchlorate solution. The perchlorate salt of the Rh–Ru complex which formed was collected on a filter and washed with ethanol. A small amount of purer (97%) material was obtained by dissolving the crude solid in methanol, filtering the solution and adding benzene to give a purple powder. *Anal.* Calcd for $[(NH_3)_5Rh(pyr)Ru(NH_3)_5][ClO_4]_5$: C, 5.06; N, 17.7; H, 3.59; Cl, 18.4. Found: C, 5.06; N, 17.1; H, 3.37; Cl, 18.4. The Rh(III)–Ru(III) complex was not isolated as a solid. Spectra of the ion were observed by dissolving the Rh(III)–Ru(II) complex in 0.1 *N* perchloric acid and oxidizing the solution with Ce(IV).

In the following experiments, argon used as blanket gas was scrubbed through a deuterium oxide solution of Cr^{2+}.

μ-Pyrazine-*cis*-isonicotinamideoctaammineruthenium(II)ruthenium(III) Ion. A mixture was prepared containing 0.189 mmol of *cis*-dichlorotetraammineruthenium(III) chloride, and 0.084 mmol of pyrazine, 2.0 ml of redistilled deuterium oxide, and 0.05 ml of 12 *N* hydrochloric acid. The resulting solution was deoxygenated by purging for 0.5 hr with argon. To the oxygen-free solution was added 0.3 ml of 0.8 *M* vanadium(II) sulfate solution 0.1 *N* in deuteriosulfuric acid. The resulting Ru(II) solution was left 1 hr in the dark under argon to allow time for substantial formation of the binuclear ion *cis*-$[(ND_3)_4OD_2Ru_2]pyr^{4+}$ (IV). Preliminary experiments had shown that pyrazine reacts about 100 times more rapidly with *cis*-$(NH_3)_4Ru(OH_2)_2{}^{2+}$ than with $(NH_3)_4Ru(OH_2)pyr^{2+}$. The experimental conditions used here were chosen in the hope of favoring formation of the binuclear ion at the expense of $(NH_3)_4Ru(pyr)_2{}^{2+}$. That this end was achieved was indicated by the product spectrum in this experiment. The ion $(NH_3)_4Ru(pyr)_2{}^{2+}$ had an absorption maximum at 470 nm while the spectrum of the product solution contained a single maximum at 538 nm. After an hour's wait the absorbance of the tetraammine solution was found to increase negligibly at 538 nm, and the formation of the binuclear ion III was judged to be essentially complete. At that time isonicotinamide (3.4 mmol) was added to the solution of IV as a solution in deuterium oxide adjusted to pD 5 by adding deuteriochloric acid. This mixture was left under argon, in the dark overnight. The half-oxidized ion



was prepared by adding to the solution above dropwise a D_2O solution 0.01 *M* in potassium persulfate until absorbance of the solution in the near-infrared region attained its maximum value.

μ-Pyrazine-*cis*-(2,2′-bipyridine)hexaammineruthenium(II)ruthenium(III). Trichlorotriammineruthenium(III) (0.2 mmol) was treated with 0.6 mmol of silver(I) trifluoroacetate in acidic deuterium oxide (2 to 3 ml) and heated to accelerate removal of bound chloride and to coagulate the silver chloride formed. The $(ND_3)_3Ru(OD_2)_3{}^{3+}$ solution was filtered from the silver chloride, mixed with 0.08 mmol of pyrazine, and transferred to a 5-ml flask closed with a serum cap. The Ru(III) solution was bubbled with argon 0.5 hr whereupon 0.3 ml of 0.8 *M* vanadium(II) sulfate solution 0.1 *N* in deuteriosulfuric acid was added by syringe. The reduced solution was kept in the dark under argon until the absorbance at 526 nm (an absorption maximum for $[(ND_3)_3(OD_2)_2Ru]_2pyr^{4+}$) had attained its maximum value. After 5 hr, 2,2′-bipyridinebipyridinium deuteriochloride solution at pH 5 was added to bring the solution of binuclear ion to 0.5 in total bipyridine. After 3 hr potassium peroxydisulfate solution was added dropwise to the product solution contained in a 10.0-mm spectrophotometer cell until the maximum absorbance in the near-infrared region was obtained for the solution.

***cis*-$(ND_3)_4LRu(pyr)Ru(ND_3)_5{}^{n+}$ (L = D_2O, Cl^-, pyrazine, pyridine, etc.).** *cis*-$(ND_3)_4D_2ORu(pyr)Ru(ND_3)_5{}^{5+}$. A solution 0.03 *M* in

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[15] (a) C. Creutz, Ph.D. Thesis, Stanford University, 1971; (b) D. F. P. Rudd and H. Taube, *Inorg. Chem.*, **10**, 1543 (1971).

cis-$(ND_3)_4D_2ORu(pyr)Ru(ND_3)_5^{4+}$ (solution A) was prepared by mixing 0.050 mmol of $[(NH_3)_5Ru(pyr)][BF_4]_2$, 0.12 mmol of cis-$(NH_3)_4RuCl_3$, and 1.5 ml of 0.02 M D_2SO_4 solution. This solution was purged of oxygen by bubbling 0.5 hr with argon and mixed with 0.13 ml of 1 M vanadium(II) sulfate solution 0.1 N in D_2SO_4. The mixture was left under argon in the dark for 5 hr. After that time no further change in the ultraviolet–visible region spectrum was observed and so formation of the diruthenium ion was judged to be complete. A solution of potassium peroxydisulfate was added dropwise to the diruthenium(II) ion solution until the maximum absorbance in the near-infrared region was obtained for the solution (to be denoted as B). The spectrum of the 5+ ion was measured for a solution made by diluting 0.25 ml of solution B with 7.0 ml of deuterium oxide.

cis-$[(ND_3)_4ClRu(pyr)Ru(ND_3)_5]^{4+}$. Solution B (0.25 ml) was added to 7.0 ml of 2.1 M NaCl in deuterium oxide 0.02 N in D_2SO_4. An initial scan of the near-infrared spectrum gave the same spectrum as observed for the diluted solution B above, but the position of the near-infrared hand shifted gradually from 1530 to 1420 nm, implying slow replacement of D_2O by Cl^- in the complex coordination sphere, the reaction being complete after about an hour.

cis-$(NH_3)_4LRu(pyr)Ru(ND_3)_5^{5+}$ (L = Pyridine, Pyrazine, Isonicotinamide). Solution A (0.5 ml) was added by syringe to 7.0 ml of deoxygenated 1.0 M amine in deuterium oxide. For pyridine and isonicotinamide as ligand, the pD of the solutions was adjusted to 5 using dilute D_2SO_4 before adding the Ru(II) solution. After 12 to 16 hr, potassium persulfate (0.008 mmol) was added to the mixture to produce the 5+ ion of interest. The spectrum of the resulting solution was run directly in a 10.0-mm cell against a complete reagent blank.

Results

Composition of the Dinuclear Ions. Job's Plot[16] for the System $(NH_3)_5RuOH_2^{2+}$ + Pyrazine. Aqueous mixtures in which the total concentration of reactants, $[(NH_3)_5RuOH_2^{2+}]$ + [pyr], was 0.10 M, but the fractions of the two components varied, were left to react several days in the absence of air and light. Spectra of portions of these solutions diluted with water by 10^4 were scanned from time to time. Limiting values of the absorbances at 530 nm were plotted as a function of F (F = initial [Ru(II)/(initial [Ru(II)] + initial [pyr]), Ru(II) here denoting $(NH_3)_5RuOH_2^{2+}$). The plot displayed a sharp maximum at $F = 0.67$. From the plot it can be concluded that the species absorbing at 530 nm contained Ru(II) and pyrazine in a 2:1 mole ratio. The formula $[(NH_3)_5Ru(pyr)Ru(NH_3)_5]^{4+}$ is consistent with this composition and with the results of microanalyses of the p-toluenesulfonate salt isolated from solutions in which Ru(II) and pyrazine in a 2:1 mole ratio were allowed to react completely.

Oxidation of I. Oxidation of I (the p-toluenesulfonate salt of the diruthenium complex) by Ag(I), followed by addition of sodium p-toluenesulfonate yields a solid which has a composition consistent with the formula $([(NH_3)_5Ru]_2pyr)(C_7H_7SO_3)_5 \cdot 3H_2O$ (II). Oxidation of either I or II with 2 or 1 equiv of Ce(IV) per mole of complex, respectively, yields, on treatment with excess sodium perchlorate, a salt having a composition consistent with the formula $([(NH_3)_5Ru]_2pyr)(ClO_4)_6$ (III). Thus analytical results for the solids I, II, and III indicate the existence of three distinct oxidation states of the $(NH_3)_5Ru(pyr)Ru(NH_3)_5^{n+}$ (V) moiety in the solid state. Results of potentiometric and spectrophotometric experiments bear on the question of the oxidation of V in aqueous solution.

Potentiometric Studies of V.[11] A solution 10^{-5} M in I was titrated with ceric perchlorate, and the potential of this solution with respect to a Ag|AgCl (0.10 M KCl, 10^{-3} M HCl) electrode was monitored. A plot of potential $vs.$ the number of equivalents of Ce(IV) added gave two steep inflections corresponding to the addition of 1 and 2 equiv of oxidant per mole of I initially present. The potentials half-way to the two inflections were found to be −0.09 and −0.47 V (relative to the silver electrode), respectively. Subsequently this oxidized solution was titrated with Cr_{aq}^{2+} and the potential was monitored as before. The plot of potential observed $vs.$ the number of equivalents of Cr(II) added showed two steep inflections as well. The potentials half-way to these two inflections (at 1 and 2 equiv Cr(II) per mole of I initially) were −0.47 and −0.09 V, respectively.

The results of these experiments constitute evidence for the existence of three distinct oxidation states of V in aqueous solution. If V ($n = 6$) were the sole oxidation product of V ($n = 4$) in solution, one inflection, not two, should be observed in the potential plot. In addition, these experiments show that oxidation–reduction reactions of the three oxidation states of IV are reversible, the same half-way potentials being found in both the oxidation and reduction titrations. Furthermore as pointed out earlier, the measured potentials follow behavior predicted by the Nernst equation.

Spectrophotometric Titration of V. A solution $ca.$ 10^{-5} M in I was titrated with Ce(IV) and visible–ultraviolet spectra of the solutions were scanned after the addition of each aliquot of Ce(IV). The spectrum of the starting solution (pure I) showed the 547-nm band characteristic of the cation of I. Addition of oxidant caused this visible band to shift to a somewhat longer wavelength and to diminish in intensity. After the addition of 1 equiv of Ce(IV) per mole of I, the band was centered at 565 nm. Adding more Ce(IV) lowered the intensity of the 565-nm absorption, but caused no further shift in its position. In addition new bands were found to appear at 350, 289, and 254 nm as Ce(IV) was added after the first equivalence point. Spectra taken for the solutions containing up to 1 equiv of Ce(IV) have an isosbestic point at 478 nm; those taken for solutions containing between 1 and 2 equiv of Ce(IV) have an isosbestic point at 420 nm.

Spectra of the fully reduced and fully oxidized solutions correspond to those of I and III as observed for solutions prepared from the solids; the spectrum of the half-oxidized solution is the same as that found for a solution of II. The existence of the three ions of V (n = 4, 5, and 6) is required to explain the spectral behavior reported above. Direct conversion of V ($n = 4$) to V ($n = 6$) could not lead to the complex behavior found. Thus the independent existence of the intermediate oxidation state ion in aqueous solution is demonstrated by these experiments as by the potentiometric studies.

Reduction Potentials. In Table I are summarized the results of potential measurements for a number of Ru(III)–Ru(II) couples. Those measured by us were referred to the potential of a solution equimolar in the Ru(III) and Ru(II) complexes in question in a medium 0.10 M in KCl and 10^{-3} M in HCl at 25°.[17] The tabulated values are formal potentials for the 0.1 M Cl^- medium, relative to the standard hydrogen electrode.

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(16) M. M. Jones, "Elementary Coordination Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1964, p 282.

(17) T. J. Meyer and H. Taube, *Inorg. Chem.*, 7, 2369 (1968).

Table I. Reduction Potentials

$(NH_3)_5Ru(pyr)^{3+} + e = (NH_3)_5Ru(pyr)^{2+}$	0.490 ± 0.005 V[a]
$(NH_3)_5Ru(pyr)H^{4+} + e = (NH_3)_5Ru(pyr)H^{3+}$	0.685 ± 0.015 V[a]
$(NH_3)_5Ru(pyr)CH_3{}^{4+} + e = (NH_3)_5Ru(pyr)CH_3{}^{3+}$	0.87 ± 0.02 V[b]
$[(NH_3)_5Ru]_2pyr^{6+} + e = [(NH_3)_5Ru]_2pyr^{5+}$	0.76 ± 0.02 V[b]
$[(NH_3)_5Ru]_2pyr^{5+} + e = [(NH_3)_5Ru]_2pyr^{4+}$	0.37 ± 0.02 V[b]
$(NH_3)_5Ru(pyr)Rh(NH_3)_5{}^{6+} + e = (NH_3)_5Ru(pyr)Rh(NH_3)_5{}^{5+}$	0.71 ± 0.02 V[b]

[a] For 1 *M* ClO_4^- medium: H. S. Lim, D. J. Barclay, and F. C. Anson, *Inorg. Chem.*, **11**, 1460 (1972). [b] This work, for 0.1 *M* Cl^- medium.

Ultraviolet–Visible Spectra of Pyrazine Complexes. The properties of the uv–visible spectra of the Ru(II), Ru(III), and Rh(III) complexes with pyrazine (measured in 10^{-5} to 10^{-4} *M* aqueous solutions at 25°) are summarized in Table II.

Table II. Band Maxima and Extinction Coefficients of Pyrazine Complexes

Complex	λ_{max}, nm	ϵ_{max}, M^{-1} cm^{-1}
$[(NH_3)_5Ru(pyr)](BF_4)_2$	472	1.33×10^4
	263	
$[(NH_3)_5Ru(pyr)](C_7H_7SO_3)_3$	330 (sh)	
	270	0.6×10^4
	230	0.3×10^4
$[(NH_3)_5Rh(pyr)](ClO_4)_3$	262	0.596×10^4
$[(NH_3)_5Ru(pyr)CH_3](ClO_4)_3$	538	1.3×10^4
	269	0.6×10^4
	228	0.3×10^4
$[(NH_3)_5Ru(pyr)CH_3](ClO_4)_4$	385	
	290	
	252	
	238	
$[(NH_3)_5Ru(pyr)Ru(NH_3)_5]^{n+}$		
$n = 4$, $(C_7H_7SO_3)^-$ salt	547	3.0×10^4
	254	0.27×10^4
$n = 5$, $(C_7H_7SO_3)^-$ salt	565	2.1×10^4
	270 (sh)	
	252	0.56×10^4
$n = 6$, $(ClO_4)^-$ salt	352	0.61×10^4
	288	0.56×10^4
	245	0.44×10^4
$[(NH_3)_5Ru(pyr)Rh(NH_3)_5](ClO_4)_n$		
$n = 5$	528	1.8×10^4
	263	0.65×10^4
$n = 6$	350, 310, 275, 268	
cis-$[(NH_3)_4LRu]_2pyr^{4+}$		
L = pyrazine[a]	568, 450, 413	
L = H_2O[a]	538	
$[(NH_3)_3(OH_2)_2Ru]_2pyr^{4+}$ [a]	526	
$[(NH_3)_3(2,2'\text{-bipy})Ru]_2pyr^{n+}$		
$n = 4$[a]	555, 480 (sh) 360	
$n = 5$[a]	565, 380 (sh)	

[a] Species not isolated as solids; see Experimental Section for composition of solution.

The intense lower energy bands found in the spectra of Ru(II)–aromatic N-heterocycle complexes have been assigned to d → π* charge transfer absorption. These have been discussed in detail elsewhere.[1,6] The bands at *ca.* 250 nm observed in the spectra of these and the corresponding Ru(III) complexes have been ascribed to a ligand-centered, π → π* transition. In some of the Ru(III) spectra reported here (*i.e.*, for the pyrazine and methylpyrazinium complexes of Ru(III)) an additional band appears at somewhat lower energy (330–400 nm). Spectra of I, II, and III are discussed in greater detail below.

Near-Infrared Spectra of Mixed-Valence (Ru(II)–Ru(III)) Complexes. The spectrum of II in both the solid (potassium bromide pellet) and aqueous solution differs dramatically from those of I and III in showing an additional intense (ϵ 5000) band at 1570 nm. Such a band was also found for the binuclear, pyrazine-bridged Ru(II)–Ru(III) complexes in which one or more of the NH_3 groups in II had been replaced by other ligands. The spectra of the fully reduced and oxidized forms of all these ions lacked this additional band. Below are summarized the effects of asymmetric NH_3 replacement in II (Table III), symmetric NH_3 replacement in II (Table IV), and the results of solvent effect studies on II (Table V). In addition a weak shoulder was observed in the spectrum of II at ~850 nm (see Figure in ref 9).

Table III. Near-Infrared Band Maxima for *cis*-$[(NH_3)_4LRu(pyr)Ru(NH_3)_5]^{n+}$ in D_2O at 25°

L	*n*	λ_{max}, nm
NH_3	5	1570
D_2O	5	1530
Cl^-	4	1420
Isonicotinamide	5	1330
Pyrazine	5	1130
Pyrazine H^+	6	1030
Pyridine	5	1380

Table IV. Near-Infrared Band Maxima for Symmetrically Substituted Mixed-Valence Complexes[a]

Complex	λ_{max}, nm
$[(NH_3)_5Ru(pyr)Ru(NH_3)_5]^{5+}$	1570
$[(NH_3)_4(isn)Ru]_2pyr^{5+}$	1650
$[(NH_3)_4(pyr)Ru]_2pyr^{5+}$	1650
$[(NH_3)_3(2,2'\text{-bipy})Ru]_2pyr^{5+}$	1720

[a] pyr = pyrazine; py = pyridine; isn = isonicotinamide.

Table V. Near-Infrared Band Maximum for $[(NH_3)_5Ru]_2(pyr)^{5+}$ as a Function of Solvent

Solvent	λ_{max}	*D*[a]	n^2 [b]
Deuterium oxide	1570	78	1.70
Water	1560	78	1.76
Ethanol	1580	24	1.85
Formamide	1595	109	2.09
Dimethyl formamide	1580	47	2.14
Dimethyl sulfoxide	1580	47	2.19
1,1-Tetrahydrothiophene dioxide	1580	44	2.2

[a] Static dielectric constant; E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1966, p 269. [b] (Index of refraction),^{2} R. C. Weast, Ed., "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1969, p 154.

Infrared Spectra.[18] The infrared spectra of several

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[18] We are grateful to M. Abe for assistance in making band assignments.

Table VI. Vibrational Frequencies[c] (cm^{-1}) and Assignments for Ruthenium(II) and (III) Ammines

Complex	$\nu(NH_3)$	δ (NH_3), deg	δ (NH_3) sym	ρ (NH_3)	Ref
$[(NH_3)_6Ru]Cl_2$[a]	3300, 3195 s	1610 m	1220 s	769 s	*e*
$[(NH_3)_5RuN_2](X)_2$ (range for several salts X^-)	3100–3350	1605–1634	1266–1298	769–798	*f*
$[(NH_3)_5Ru(pyr)]I_2$[b]	3280, 3180	1620, 1580	1260	750	This work
$[(NH_3)_6Ru]Cl_3$[a]		1612	1362 m	788	*g*
			1338 s		
			1316 vs		
$[(NH_3)_5Ru(py)](ClO_4)_3$[a,i]		1625	1345	780	*h*
$[(NH_3)_5Ru(isn)(ClO_4)_3$[a,j]		1672	1340	785	*h*
		1598	1375 w		
$([(NH_3)_5Ru]_2pyr)Br_4$[b]	3200–3300[d]	1625	1280 s	750	This work
$([(NH_3)_5Ru]_2pyr)Br_5$[b]	3220	1580	1295 m	790	This work
	3120	1630	1330 w		
	3080		1230 w		
$([(NH_3)_5Ru]_2pyr)(ClO_4)_6$[b]	3100–3200[d]	1620	1345 s	820	This work
			1310 w	760	
			1360 w		

[a] Nujol mull. [b] KBr pellet. [c] s, strong; m, medium; w, weak. [d] Region of broad absorption. [e] M. B. Fairey and R. J. Irving, *Spectrochim. Acta*, **22**, 359 (1966). [f] A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Amer. Chem. Soc.*, **89**, 5595 (1967). [g] A. D. Allen and C. V. Senoff, *Can. J. Chem.*, **45**, 1337 (1967). [h] M. Abe, unpublished results. [i] py = pyridine. [j] isn = isonicotinamide.

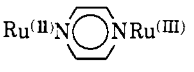
Ru(II) and Ru(III) ammines were investigated. For $[(NH_3)_5Ru(pyr)]I_2$ and the *cis*- and *trans*-$[(NH_3)_4Ru(pyr)_2]I_2$ complexes δ (NH_3) (sym) was found to lie between 1260 and 1290 cm^{-1}, while ρ (NH_3) appeared between 740 and 760 cm^{-1}. For the Ru(III) complexes, $[(NH_3)_5RuL](ClO_4)_3$, L = pyridine and isonicotinamide, δ (NH_3) (sym) was observed in the range 1330–1360 cm^{-1}. For these ρ (NH_3) lies in the range 790 to 810 cm^{-1}.

For the binuclear complexes $[(NH_3)_5Ru]_2pyr^{4+,5+,6+}$ the spectra of the 4+ and 6+ ions are similar to those of the mononuclear Ru(II) and Ru(III) complexes described above: for the 4+ ion, δ (NH_3) (sym) 1280 cm^{-1}; ρ (NH_3) 750 cm^{-1}. For the 6+ ion, these frequencies are respectively 1345 cm^{-1}. The infrared spectrum of the 5+ ion in this region is however rather intermediate between those of 4+ and 6+; δ (NH_3) (sym) 1295 cm^{-1}, ρ (NH_3) 790 cm^{-1}.

These results and the spectral features of other Ru(II) and (III) ammines are summarized in Table VI.

Discussion

Electronic Structure of $[(NH_3)_5Ru]_2pyr^{5+}$. Recently, Mayoh and Day[19] have pointed out that the *a priori* calculation of the class of a mixed valence compound is possible and by making use of spectral data[9] concluded that the 5+ ion is of class II. Earlier,[9] on the basis of its electronic spectrum, we assigned to this ion the class II electronic structure[8]



this notation implying that the two ruthenium sites are different. Electron exchange between the two is in all likelihood very rapid and the sites will appear to be different only in the limit of very short times. Since that report, additional physical measurements bearing on the electronic structure of the ion have been made; these will now be summarized and discussed.

Creutz, Good, and Chandra have reported the Mössbauer spectra of compounds I, II, and III.[20] They conclude that equal concentrations of Ru(II) and Ru(III) exist in crystals of the mixed valence 5+ ion at 4°K. This finding implies that electron exchange between the two sites is slower than 10^9/sec (the lifetime of the Mössbauer excited state is 10^{-9} sec) in the solid at 4°K. At the present time, the Mössbauer data may well be the least ambiguous of those which bear on the electronic structure of the ion, but, as nearly all other studies of this mixed valence species have been made at *ca.* 25° for solutions, the problem of extrapolating the Mössbauer data to these conditions arises. Spectra (KBr pellets and nujol mulls) of the mixed valence compound in the visible and near-infrared regions determined at and between room temperature and 77°K[21] are essentially indistinguishable from those obtained for dilute aqueous solutions of the salt at 25°.[15] Thus there is no indication of a fundamental change in electronic state on passing from solution to crystal or on cooling the crystal for this range of temperature. The effect of cooling the crystals from 77 to 4°K is, however, unknown and so we shall review the results of other measurements made at room temperature in an effort to learn if the electronic structure of the ion is the same under these conditions.

Strekas and Spiro[22] have investigated the Raman spectra of the binuclear ions, using various laser exciting lines from 647.1 to 488.0 nm. The 6+ ion gives normal Raman scattering, but both the 4+ and 5+ complexes show strong resonance enhancement, associated with the 550-nm metal-to-pyrazine charge transfer excitation. Various modes of the Ru–pyrazine system can be identified in the enhanced spectra. They occur at *identical* frequencies for the 4+ and 5+ ions, whereas corresponding frequencies in the 6+ spectrum are shifted significantly. The interpretation is that the $Ru^{II}pyrRu^{III}$ ion gives a resonance enhanced spectrum characteristic of Ru(II). The normal scattering expected from the Ru(III) portion could be too weak to be observed under the required experimental conditions. The identical frequencies found for the 4+ and 5+

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(19) B. Mayoh and P. Day, *J. Amer. Chem. Soc.*, **94**, 2885 (1972).

(20) C. Creutz, M. Good, and S. Chandra, *Inorg. Nucl. Chem. Lett.*, submitted for publication.

(21) I. M. Treitel, Ph.D. Thesis, California Institute of Technology, 1970.

(22) T. Strekas and T. Spiro, Princeton University, in preparation for publication.

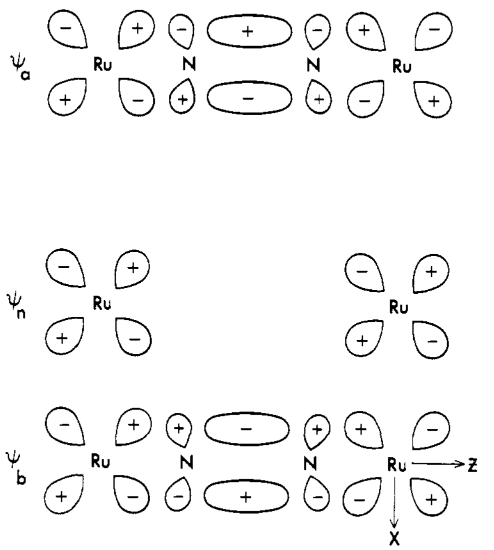

Figure 1. Symmetry properties of the orbitals resulting from πd–π^*–πd interaction.

ions are consistent with the view that the mixed valence ion is unsymmetrical.

The most persuasive evidence for the conclusion that the valences of the metal ions are moderately trapped (that is, that electron transfer is not so rapid as to contribute significantly to the energy of interaction between the two sites, and thus to a substantial modification of their properties) may well be the following, which is purely chemical in nature. The rate at which the first isonicotinamide substitutes into *cis*-[$(H_2O)(NH_3)_4Ru(pyr)Ru(NH_3)_4(OH_2)$]$^{5+}$ is observed[23] to be the same (within a factor of 2) as that for substitution into *cis*-[$(H_2O)(NH_3)_4Ru(pyr)Rh(NH_3)_5$]$^{5+}$. In the latter species, there is no electron hole which might introduce ambiguity into the interpretation of electronic structure, and the ruthenium atom is expected to exhibit the characteristics of Ru(II) with an unsaturated ligand attached. The agreement of rates of substitution shows that Ru(III) compared with Rh(III) at the remote end of the pyrazine does not markedly alter the properties of the ruthenium ion at the other end. It needs to be added that substitution on Ru(III) under the same conditions would involve periods of time on the order of days, if, in fact, substitution were even thermodynamically favored. To the extent that the Ru(II) center is modified by acquiring Ru(III) character, the rate would be severely and adversely affected.

Elias and Drago have carried out proton nmr studies of the 5+ ion at room temperature and found evidence for only two types of ammine proton (cis and trans to the pyrazine).[24] Since on the time scale of the specific rate estimated for internal electron transfer, the proton signals are expected to be averaged, the nmr result neither provides support for nor disproves the interpretation advanced earlier.[9] Our infrared results (Table VI) are consistent with either the delocalized Ru(II$^1/_2$)–Ru(II$^1/_2$) or valence trapped (Ru(II)–Ru(III)) description of the 5+ ion. In principle, the metal–ligand stretch region in the infrared should be the most useful for distinguishing between the two alternatives. Studies of this region for various salts of the 5+ ion and other complexes are currently in progress.

The most straightforward interpretation of the visible spectrum of the ion is that the Ru(II)–ligand (πd–π^*) transition is retained in the ion of mixed oxidation state, admitting that it is somewhat altered by having Ru(III) at the remote end of the pyrazine and admitting as well that Ru(III) (and Ru(II) for that matter) exerts a somewhat greater effect than does Rh(III)[25] (Table II). It has also been suggested[21,24] that a delocalized molecular orbital description of the 5+ ion is consistent with its electronic spectrum. Below we argue that a delocalized description is appropriate, if at all, only for the 4+ ion.

In any MO description of the unit $(NH_3)_5Ru(pyr)Ru(NH_3)_5{}^{n+}$ wherein Ru(II) or Ru(II$^1/_2$) is present, the primary delocalization mechanism considered must be that resulting from π interaction of filled Ru 4d and vacant π^* pyrazine orbitals. Zwickel and Creutz[6] had considerable success in explaining and predicting the numbers and positions of Ru(II)-to-ligand charge transfer bands in Ru(II) ammines containing aromatic N-heterocycles by considering only the interaction of the lowest lying ligand π^* orbital with the 4d orbital oriented so as to overlap effectively the π orbital. In discussing the properties of the binuclear ions assuming delocalization we shall also use this model since it has so far proved to be useful in understanding the Ru–heterocyclic interaction. For the RupyrRu unit then the lowest pyrazine π^* orbital is mixed with one 4d orbital from each Ru (see Figure 1). Three molecular orbitals result: ψ_b, a bonding orbital predominantly metal in character; ψ_n, a nonbonding metal orbital; and ψ^*, an antibonding molecular orbital mostly ligand in character.

For the 4+ ion the set of three molecular orbitals will contain four electrons, two each in the bonding and nonbonding levels. Only one of the symmetry allowed transitions, ψ_n to ψ^* is possible. A satisfying feature of this description is that it offers a ready explanation for the fact that the charge transfer band for [$(NH_3)_5Ru$]$_2$pyr^{4+} is found at lower energy than that for the mononuclear ion $(NH_3)_5Ru(pyr)^{2+}$. In the former the transition is from a nonbonding orbital to the antibonding molecular orbital, whereas in the latter the observed charge transfer band derives from promotion of a bonding electron to the antibonding orbital. The two bands should and do differ by an energy roughly equal to the backbonding stabilization energy calculated for the mononuclear complex (2.1 kK compared with 2.3 kK). This argument is pursued at a more quantitative level elsewhere.[15a]

In the case of the 6+ cation, on the other hand, there seems no particular reason to invoke metal–ligand–metal π interaction of this type. The Mössbauer isomer shifts indicate Ru(III) in this ion to be essentially identical with that in $(NH_3)_6Ru^{3+}$.[20] Treitel's magnetic studies give a normal magnetic moment per Ru(III) in the 6+ ion down to 77°K.[21] Undetectably weak metal–ligand–metal interaction in 6+ is not surprising for several reasons. The spatial overlap of the ligand π^* and Ru(III) 4d orbitals is expected to be poor; in addition the energy separation between d and π^* orbitals must be much greater for Ru(III) than for Ru(II).

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(23) S. Isied and H. Taube, in preparation for publication.

(24) J. H. Elias and R. Drago, *Inorg. Chem.*, **11**, 415 (1972).

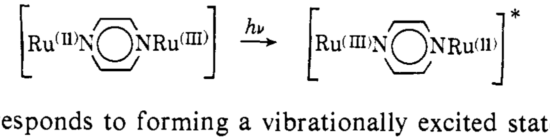
(25) P. Ford, *ibid.*, 10, 2153 (1971).

In contrast to the case of Ru(II), there is no evidence that backbonding makes a significant contribution to the interaction of Ru(III) with π acid ligands.

For the 5+ ion in the $\mathrm{Ru}^{2\frac{1}{2}}\mathrm{pyrRu}^{2\frac{1}{2}}$ description, using the MO scheme above, the electron population would be $(\psi_b)^2(\psi_n)^1$. Both allowed transitions, $\psi_b \rightarrow \psi_n$ and $\psi_n \rightarrow \psi^*$ are possible in this case. In the spectrum of the 5+ ion these would of necessity correspond to the 1570- and 565-nm bands, respectively. Ascribing the 565-nm band to the $\psi_n \rightarrow \psi^*$ transition presents no particular difficulty. Comparing the 4+ and 5+ ions one might expect that since ψ_n is more binding for the latter, the charge transfer band for 5+ should be found at higher energy than that for the 4+. The opposite ordering is found. This is not a serious defect because the energy differences are small but we believe that ascribing the agreement of the absorption maxima for the 4+ and 5+ ions to coincidence is a defect of this interpretation. A serious problem arises in assigning the 1570-nm band to the ψ_b to ψ_n transition. The band energy (6.4 kK) must then correspond to the stabilization energy resulting from electron delocalization in the $\mathrm{Ru(pyr)Ru}^{5+}$ unit. The value 6.4 kK is two to three times larger than that found in any of the Ru(II) complexes studied by Zwickel and Creutz[6] (for Ru(III) the stabilization energy is presumably zero). This result is in conflict with chemical intuition. The degree of delocalization must be determined by two factors: spatial overlap of the interacting 4d and π^* orbitals and the energy separation between these levels. By the same arguments used above for Ru(III) it is impossible to understand how $\mathrm{Ru}(2^1/_2)$ can be two to three times stronger in its backbonding interaction to pyrazine than is Ru(II).

If however, the electronic structure of the 5+ ion corresponds to a valence trapped case, its visible-near infrared spectrum is readily explained; the 565-nm band is assigned to Ru(II)-to-pyrazine π^* charge transfer and the 1570-nm band to Ru(II)-to-Ru(III) charge transfer.[9] The latter process has been denoted intervalence charge transfer absorption[10] (IT). The shift in in Ru(II)-to-pyrazine π^* charge transfer band energy in 5+ relative to that for $(\mathrm{NH_3})_5\mathrm{Ru(pyr)}^{2+}$ ($\lambda_{\max}$ 472 nm) is in line with the trend observed for the series $(\mathrm{NH_3})_5\mathrm{Ru^{II}pyr\text{-}X}$ (X = $\mathrm{H^+}$, $\mathrm{CH_3}^+$, $\mathrm{Rh(NH_3)_5}^{3+}$) (Table II) if it is recalled that in addition to stabilizing the charge-transfer excited state by virtue of its 3+ charge, Ru(III) also has π-acceptor properties[24] which the other listed X groups lack. Arguments in favor of assigning the 1570-nm band to an IT process have already been given.[9]

Intervalence Charge-Transfer Band. The assignment just made of the 1570-nm band in the spectrum of the mixed-valence ion rests on the electronic structure ascribed to this ion. The energy of the transition



corresponds to forming a vibrationally excited state of the ion; as nuclear motion is much slower than electron motion, the immediate product of the light-induced electron exchange contains Ru(II) with a first coordination sphere and solvation sphere appropriate to Ru(III), and *vice versa*. In theory, the energy required to form this excited state is at most four times[26] that needed to form the symmetrical transition state for the thermal electron exchange reaction.[9,10] As a consequence of this relationship, understanding contributions to IT band energies may be of great value in elucidating the detailed energetics of electron transfer reactions between metal ions in general. Hush has proposed a model correlating rates of electron exchange and IT band energies.[10] We shall discuss some of our results in terms of this model.

Altering the first coordination sphere of the mixed valence ion by replacing one $\mathrm{NH_3}$ group by another ligand L (Table III) shifts the IT band energy to a shorter wavelength. For small changes in E_0 (the equilibrium barrier to electron transfer), a plot of the reduction potential for the pentaammine Ru(III)–Ru(II) couple containing L *vs.* the energy of the near-infrared band of the asymmetric complex is linear with a slope of 1, as predicted by Hush.[10]

As the IT band energy is determined in part by the extent to which Ru(II) and -(III) sites in the mixed valence ion differ in metal–ligand bond lengths and solvation, we expect that modifications of the 5+ ion which diminish these differences would shift the IT band to lower energies. This expectation is documented in Table IV wherein data are shown for complexes in which ammine groups are symmetrically replaced by ligands capable of backbonding to Ru(II). Recently Adeyemi, *et al.*,[27] reported that for the ion $[(\mathrm{bipy})_2\mathrm{ClRu}]_2\mathrm{pyr}^{3+}$, no band identifiable with IT is observed. It may be that this ion represents the limiting case for the series of Table IV, the coordination sphere of Ru(II) so closely resembling Ru(III) that the Franck–Condon barrier to electron transfer is so small as to lie outside the near-infrared region. Alternatively, and perhaps more reasonably, it may be that the intensity of this transition is so low due to delocalization of the Ru(II) electrons over the ligands that the band cannot be seen.

At room temperature, the integrated intensity of the band at 1570 nm corresponds to an oscillator strength of 0.03 for the transition.[10,15a] For the $\mathrm{Ru^{II}pyrRu^{III}}$ description this implies that, in the ground state, the Ru(II) electron spends 99% of its time on the Ru(II) site and 1% of its time on the Ru(III) site. This is consistent with the valence-trapped description of the ground state of the ion.

The results above are in accord with the predictions of the Hush model and with qualitative expectations based on results of electron-transfer reaction-rate studies. At a quantitative level we note, however, several difficulties encountered in attempting to fit our results to the Hush model. The Hush model is derived for the high temperature limit, the criterion for that limit being that $2RT > h\nu$, where $h\nu$ is the energy associated with a metal–ligand vibrational transition. For either a Ru(II)- or Ru(III)–$\mathrm{NH_3}$ vibration in the 5+ ion, $h\nu \simeq 2RT$, *i.e.*, at room temperature we are not at high temperature limit for this ion. Possibly as a consequence of this fact, Hush's correlation of band energy with band width (at room temperature, $\bar{\nu}_{\max}$ =

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(26) Owing to the splitting of the energy surfaces at the crossover point, the specific rate of the spontaneous internal electron transfer calculated from the energy of the IT transition is a lower limit.

(27) S. A. Adeyemi, J. N. Braddock, G. M. Brown, J. A. Ferguson, F. J. Miller, and T. J. Meyer, *J. Amer. Chem. Soc.*, **94**, 300 (1972).

$(\bar{\nu}_{1/2})^2/2310)$ fails; the band is about six times *narrower* than predicted by this formula.

The most serious conflict between model and experiment is found in attempting to break down the observed band energy into contributions deriving separately from inner coordination sphere and solvation sphere distortions. For the inner sphere contribution theory predicts an energetic contribution of $^1/_2k(\Delta X)^2$ for each metal–ligand band. Here k is the force constant for the Ru–ligand vibration and ΔX is the distortion introduced by the electron transfer. To arrive at a rough estimate of E_{inner}, we approximate the Ru–pyrazine bands to Ru–NH_3 bands and assume, for simplicity, that the force constants for Ru(II)–NH_3 and Ru(III)–NH_3 bonds are the same. Then the total inner sphere contribution is $6k(\Delta X)^2$. Using the Ru–NH_3 bonds in $(NH_3)_6Ru^{2+}$ and $(NH_3)_6Ru^{3+}$ as models (ΔX = 0.04 A[28] and $k = 1.4 \times 10^3$ g sec^{-2}, calculated from the reported hexaammine spectra[29]) we find E_{inner} to be about 1000 cm^{-1}, about $^1/_6$ the total IT band energy. For solvation sphere distortions, using a continuous dielectric medium as model, Hush calculates that

$$E_{\text{outer}} = (1/d)(1/n^2 - 1/D)e^2$$

where d is the distance between the Ru(II) and -(III) nuclei in 5+ and n^2 and D are the values for the optical and static dielectric constants of the solvent, respectively. Using this formula and the tabulated bulk dielectric constant values in Table V, the contribution for E_{outer} is found to be 8700 cm^{-1} for water and 7900 cm^{-1} for ethanol.[20] The calculated solvation sphere contributions for E_{outer} for all solvents studied are considerably greater than the total band energies found (for D_2O, 6370 cm^{-1}). In addition, the IT band position does not exhibit the solvent effect behavior expected from the formula; although the shifts observed are in the right direction, their magnitude is only one-tenth that predicted. Both these observations could be a consequence of dielectric saturation in the solvent region surrounding the 5+ ion. If saturation occurs, the value of the bulk static dielectric constant appropriate in these calculations would be smaller, leading to a smaller calculated value for E_{outer}. On the other hand, these observations may only reflect the limitations of the simple Hush model.

The conclusion that the species $[(NH_3)_5Ru^{II}pyrRu^{III}NH_3]^{5+}$ contains ruthenium in distinct oxidation states of 2+ and 3+ seems at present on rather firm grounds. The interpretation we have advanced for the transition giving rise to the band in the near-infrared region is supported by the effects on the band position of substitution on the ruthenium centers. The fact that the solvent effects do not conform quantitatively to the predictions of Hush theory, in view of the approximate nature of the model on which the theory is based, cannot be construed as weakening seriously the case for the band assignment we have made.

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

[29] Table VI, footnotes *e* and *g*.