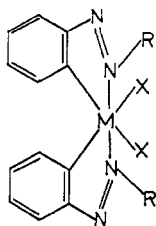
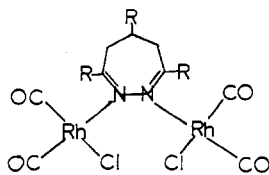
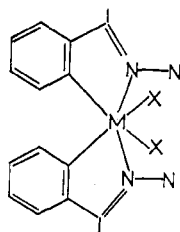
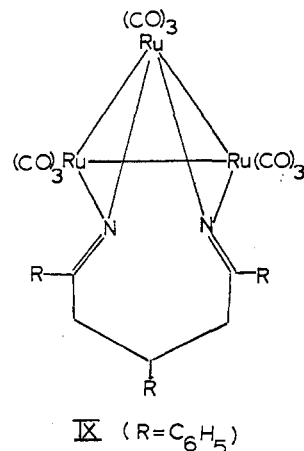
V (R=C<sub>6</sub>H<sub>5</sub>)VI (R=C<sub>6</sub>H<sub>5</sub>)VII (R=C<sub>6</sub>H<sub>5</sub>)

VIII

(CO)<sub>12</sub> in sufficient quantity for characterization. Infrared data (Table I) show nine  $\nu(\text{CO})$  bands and a ligand spectrum similar to that of the complex  $\text{Fe}_2(\text{CO})_8(\text{Diaz})$ . Complexes of similar composition have been reported as products from the reactions of azobenzenes

with  $\text{Fe}_3(\text{CO})_{12}$ .<sup>13</sup> A suggested structure analogous to that proposed by Pauson and coworkers<sup>13</sup> is shown as IX.

IX (R=C<sub>6</sub>H<sub>5</sub>)

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## Formal Potentials and Cyclic Voltammetry of Some Ruthenium–Ammine Complexes

By HONG SUP LIM, DONALD J. BARCLAY, AND FRED C. ANSON\*

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A number of formal redox potentials for  $\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{L} + e = \text{Ru}^{\text{II}}(\text{NH}_3)_5\text{L}$  and  $\text{Ru}^{\text{III}}(\text{NH}_3)_4\text{L}_2 + e = \text{Ru}^{\text{II}}(\text{NH}_3)_4\text{L}_2$  (where L represents a variety of ligands) have been measured by cyclic voltammetry, potentiometry, and polarography. The trends in the potentials are discussed in terms of ligand properties, such as  $\pi$ -accepting capability. For three complexes,  $\text{Ru}(\text{NH}_3)_5\text{Pz}^{2+}$  and *cis*- and *trans*- $\text{Ru}(\text{NH}_3)_4\text{Pz}_2^{2+}$ , where Pz  $\equiv$  pyrazine, the reduction of the coordinated ligand has been observed.

The solution chemistry of ruthenium–ammine complexes has received considerable attention<sup>1</sup> from a number of workers in recent years. The electrochemistry of these complexes, however, has been studied much less extensively. We report here on a number of aspects of the electrochemical behavior of some of the ruthenium–ammine complexes that we have been studying. One objective of the work was to compare the electrochemical behavior of reducible ligands coordinated to ruthenium(II) with their reduction when uncoordinated, in order to assess the extent to which metal-to-ligand back-bonding, a prominent feature in the coordination chemistry of ruthenium(II), influences the electrochemical reactivity of the ligands. Similar investigations, concentrating on the nitrosyl ligand, have been actively pursued by Masék and coworkers.<sup>2</sup>

### Experimental Section

**Reagents.**— $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  was prepared as described in the literature either from  $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ <sup>3</sup> (Matthey Bishop Inc.) or from  $\text{RuCl}_3$ <sup>4</sup> (Research Organic/Inorganic Chemical Corp.).  $[\text{Ru}(\text{NH}_3)_5\text{Br}]\text{Br}_2$  was prepared similarly by treating  $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$  with refluxing HBr. *cis*- and *trans*- $[\text{Ru}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  were prepared as described by Gleu and Breuel.<sup>5</sup>

$[\text{Ru}(\text{NH}_3)_5\text{NCS}](\text{ClO}_4)_2$  was prepared as follows. A 2 mM solution of  $\text{Ru}(\text{NH}_3)_5\text{Cl}^{2+}$  in 0.1 M  $\text{NaPF}_6$  was reduced at a mercury pool electrode ( $-700$  mV *vs.* sce) to yield  $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ . Excess sodium thiocyanate was added and the resulting orange-red solution was reoxidized at the electrode ( $-80$  mV *vs.* sce) to give a wine red solution from which solid  $[\text{Ru}(\text{NH}_3)_5\text{NCS}](\text{ClO}_4)_2$  was precipitated by addition of 5 F  $\text{NaClO}_4$ . The  $\text{Ru}(\text{NH}_3)_5\text{NCS}^{2+}$  ion had absorption maxima at 495 nm ( $\epsilon$  3500) and 327 nm ( $\epsilon$  520).

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[Ru(NH<sub>3</sub>)<sub>5</sub>py](ClO<sub>4</sub>)<sub>2</sub> (where py = pyridine) was prepared as described by Ford, *et al.*<sup>6</sup> [Ru(NH<sub>3</sub>)<sub>5</sub>Pz](ClO<sub>4</sub>)<sub>2</sub><sup>6</sup> and *cis*- and *trans*-[Ru(NH<sub>3</sub>)<sub>4</sub>Pz<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub><sup>7,8</sup> (Pz = pyrazine) were prepared as follows. One millimole of the corresponding chloropentaammine or dichlorotetraammine complex was converted to the trifluoroacetate salt with silver trifluoroacetate<sup>6</sup> (the volume of the solution was 5–10 ml). The pH was adjusted to about 3, and 1–1.5 g of pyrazine was added. The mixture was deaerated with argon, several pieces of amalgamated zinc were added, and the solution was stirred in the dark for a time (pentaammine, *ca.* 0.5 hr; others, *ca.* 2 hr). The solution was filtered from the zinc amalgam and 8 *F* sodium perchlorate solution was added dropwise to precipitate the complex. After cooling, the solid was collected by filtration, washed with ethanol and ether, and dried in a vacuum desiccator. The crude complex was dissolved in a minimum volume of hot (60–70°) water (for the pentaammine complex) or hot 1 *F* pyrazine solution (for tetraammine complexes). The solution was filtered and cooled slowly with addition of a few drops of 8 *F* NaClO<sub>4</sub> solution. The recrystallized solid was washed with ethanol and ether and dried in a vacuum desiccator. The solid [Ru(NH<sub>3</sub>)<sub>5</sub>Pz](ClO<sub>4</sub>)<sub>2</sub> gave a spectrum identical with that reported in ref 6 when it was dissolved in water. The dipyrazine complexes also gave spectral bands in the visible region matching those reported previously<sup>7,8</sup> (*cis* complex, λ<sub>max</sub> 398 and 472 nm; *trans* complex, λ<sub>max</sub> 487 nm). However, all of these complexes were contaminated to some extent by purple complexes which appeared to be the pyrazine-bridged diruthenium complexes. When aqueous solutions of the complexes were put onto a column of cation-exchange resin (Biorad, AG 50W-X4 100–200 mesh, sodium ion form) and eluted with 1 *F* NaCl solution, a deep purple band was left behind after the elution of the complexes. This band could not be totally eluted even with a saturated NaCl solution. The contaminant in the monopyrazine complex was present in such small quantities that it did not appear to affect the electrochemical behavior. With the dipyrazine complexes, however, the contamination was more serious so that the electrochemical studies with these complexes were conducted with solutions that had been eluted from the cation-exchange resin.

[(NH<sub>3</sub>)<sub>5</sub>RuPzRu(NH<sub>3</sub>)<sub>5</sub>](C<sub>2</sub>H<sub>7</sub>SO<sub>3</sub>)<sub>4</sub>·2H<sub>2</sub>O<sup>9</sup> was prepared by allowing stoichiometric quantities of [Ru(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub> and pyrazine to react in a manner similar to that for the preparation of [Ru(NH<sub>3</sub>)<sub>5</sub>Pz](ClO<sub>4</sub>)<sub>2</sub>. The uv-visible spectrum of the complex obtained matched that given by Creutz and Taube.<sup>9</sup> An ion-exchange experiment with this complex indicated that it was not contaminated by Ru(NH<sub>3</sub>)<sub>5</sub>Pz<sup>2+</sup>. For electrochemical studies, the tosylate anion in the complex was replaced with chloride ion by anion exchange (Amberlite IRA-400).

Ru(NH<sub>3</sub>)<sub>5</sub>H<sub>2</sub>O<sup>3+</sup> ion was prepared in solution as follows. A solution of 2 mM [Ru(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub> in 0.2 *M* CF<sub>3</sub>COONa was reduced at a mercury pool electrode at -700 mV *vs.* sce under an argon atmosphere. The resulting solution was transferred with a syringe to a solution containing silver trifluoroacetate in slight excess of the stoichiometric quantity needed to reoxidize the complex to ruthenium(III) and to precipitate the chloride. The solution was filtered from the precipitate of Ag and AgCl, and the excess Ag<sup>+</sup> ion was reduced to the metal at a mercury pool electrode (0 mV *vs.* sce). The Ru(NH<sub>3</sub>)<sub>5</sub>H<sub>2</sub>O<sup>3+</sup> was identified by its spectra.<sup>10</sup>

*cis*- and *trans*-Ru(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub><sup>2+</sup> ions were prepared by the reduction of the ruthenium(III) in the corresponding dichloro complexes to ruthenium(II) at a mercury pool electrode without removing the liberated chloride ion. Cyclic voltammetry indicated negligible complex formation between the ruthenium(II) and chloride in the resulting solution (concentrations of Cl<sup>-</sup> and Ru(II) in the millimolar range).

A stock solution of 8 *F* NaClO<sub>4</sub> was prepared from HClO<sub>4</sub> and Na<sub>2</sub>CO<sub>3</sub> as described previously.<sup>11</sup>

**Estimation of Formal Potentials. Potentiometric Measurements.**—A 2 mM solution of Ru(NH<sub>3</sub>)<sub>5</sub>H<sub>2</sub>O<sup>3+</sup> in 0.2 *F* CF<sub>3</sub>COONa was reduced at a mercury pool electrode until the concentrations of ruthenium(II) and ruthenium(III) were approximately

equal. The exact concentrations of the complexes in each oxidation state were determined polarographically. The equilibrium potential of a hanging mercury drop electrode in the resulting solutions was read with a digital pH meter. The process was repeated at various values of the solution pH. Formal potentials were calculated from these potential readings and the concentration data without attempting to correct for junction potentials.

**Cyclic Voltammetric Measurements.**—Cyclic voltammograms of those complexes which are substitution inert in both oxidation states (*e.g.*, Ru(NH<sub>3</sub>)<sub>5</sub>Pz) were recorded on an X-Y recorder at sweep rates of 50–400 mV/sec. Voltammograms of other complexes, such as Ru(NH<sub>3</sub>)<sub>5</sub>Cl<sup>2+</sup>, which aquate rapidly when reduced, were recorded on a storage oscilloscope at higher sweep rates (10–50 V/sec).

**Apparatus.**—The electronic apparatus employed for the cyclic voltammetry and conventional dme polarography has been described.<sup>12</sup> The electrodes used for cyclic voltammetry were either commercially available hanging mercury drop electrodes or a platinum ball attached to a fine platinum wire sealed in glass. The characteristics of the dme at open circuit in 1 *F* NaCl when *h* = 60 cm were the following: drop time, 4.85 sec; *m* = 0.954 mg/sec.

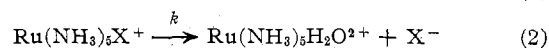
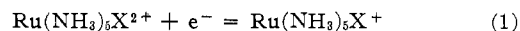
Potentials were measured with respect to a calomel electrode saturated with NaCl which had a potential 5 mV more negative than the sce but are reported with respect to the latter except in Table I where the formal potentials are converted to the nhe scale.

Spectra were recorded with a Cary recording spectrophotometer, Model 11M.

## Results and Discussion

### Formal Potentials of Ruthenium(III,II) Complexes.

Formal reduction potentials for a number of substituted ruthenium-amine complexes were evaluated by cyclic voltammetry, potentiometry, or standard dme polarography. In some cases the electrode reactions are followed by a fairly rapid further reaction of the initial electrode reaction product. In these cases, conventional polarography measurements could not be used to estimate the formal potentials because the polarographic half-wave potentials become functions of the rate of the succeeding chemical reaction. An example of this situation is Ru(NH<sub>3</sub>)<sub>5</sub>X<sup>2+</sup> (X = Cl, Br, and NCS) where the initial Ru(II) complex produced at the electrode undergoes aquation at an appreciable rate.



In cases such as this, the formal potential for the couple was evaluated from cyclic voltammetric curves recorded with potential sweep rates high enough to avoid the occurrence of the chemical reaction during the experiment.

The value of the rate constant for reaction 2 when X = Cl is reported to be 4.7 sec<sup>-1</sup>,<sup>13</sup> which corresponds to a half-life for the Ru(NH<sub>3</sub>)<sub>5</sub>Cl<sup>+</sup> complex of 0.15 sec. Reliable formal potentials for reaction 1 could therefore only be obtained if the 0.5-V excursion of the potential sweep was completed within times shorter than 0.1 sec. With most of the labile complexes studied, it proved possible to meet this criterion by using sweep rates of 20–30 V/sec. The continued Nernstian response of the electrode reactions at the highest sweep rates was confirmed by the peak potentials remaining independent of sweep rates and the potential separation between cathodic and anodic peaks remaining close to the theoretical value of 58 mV.

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TABLE I  
 FORMAL REDUCTION POTENTIALS OF RUTHENIUM COMPLEXES

Redox couples	$E^f$ , <sup>i</sup> mV vs. nhe	Supporting electrolytes
$\text{Ru}(\text{NH}_3)_5\text{OH}^{2+,+}$	-420 <sup>a,b</sup>	0.2-1 <i>F</i> NaOH
$\text{Ru}(\text{NH}_3)_5\text{Cl}^{2+,+}$	-42 <sup>b</sup>	0.2 <i>F</i> $\text{CF}_3\text{COONa}$ or $\text{NaClO}_4$
$\text{Ru}(\text{NH}_3)_5\text{Br}^{2+,+}$	-34 <sup>b</sup>	0.1 <i>F</i> $\text{NaClO}_4$
$\text{Ru}(\text{NH}_3)_6^{3+,2+}$	+51, <sup>b</sup> +88* <sup>f</sup>	0.1 <i>F</i> $\text{NaBF}_4$
$\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{3+,2+}$	+66, <sup>a-c</sup> +160* <sup>f</sup>	0.1 <i>F</i> $\text{CF}_3\text{COONa}$ and 0.1 <i>F</i> $\text{CF}_3\text{COOH}$
$\text{Ru}(\text{NH}_3)_5\text{NCS}^{2+,+}$	+133 <sup>b</sup>	0.9 <i>F</i> NaF
$\text{Ru}(\text{NH}_3)_5\text{py}^{3+,2+}$	+305, <sup>b</sup> +350* <sup>g</sup> +420* <sup>h</sup>	0.1 <i>F</i> $\text{CF}_3\text{COONa}$ and 0.1 <i>F</i> $\text{CF}_3\text{COOH}$
$\text{Ru}(\text{NH}_3)_5\text{NC}_5\text{H}_4\text{-4-CONH}_2^{3+,2+}$	+440* <sup>h</sup>	
$\text{Ru}(\text{NH}_3)_5\text{NC}_5\text{H}_4\text{-4-COOCH}_3^{3+,2+}$	+460* <sup>h</sup>	
$\text{Ru}(\text{NH}_3)_5\text{Pz}^{3+,2+}$	+490 <sup>b</sup>	1 <i>F</i> NaCl
$\text{Ru}(\text{NH}_3)_5\text{PzH}^{4+,3+}$	(+685) <sup>d</sup>	
$\text{Ru}(\text{NH}_3)_5\text{N}_2^{3+,2+}$	(+1120, 1050*) <sup>i,k</sup>	$\text{HClO}_4$
<i>cis</i> - $\text{Ru}(\text{NH}_3)_4\text{Cl}_2^{3+,2+}$	-100 <sup>b</sup>	0.2 <i>F</i> $\text{CF}_3\text{COONa}$
<i>cis</i> - $\text{Ru}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+,2+}$	+100 <sup>b</sup>	0.2 <i>F</i> $\text{CF}_3\text{COONa}$
<i>cis</i> - $\text{Ru}(\text{NH}_3)_4(\text{NC}_5\text{H}_4\text{-4-CONH}_2)_2^{3+,2+}$	+700* <sup>h</sup>	
<i>cis</i> - $\text{Ru}(\text{NH}_3)_4(\text{NC}_5\text{H}_4\text{-4-COOCH}_3)_2^{3+,2+}$	+740* <sup>h</sup>	
<i>cis</i> - $\text{Ru}(\text{NH}_3)_4\text{Pz}_2^{3+,2+}$	+860 <sup>b</sup>	1 <i>F</i> NaCl
<i>trans</i> - $\text{Ru}(\text{NH}_3)_4\text{Cl}_2^{3+,2+}$	(-180) <sup>b,e</sup>	0.2 <i>F</i> $\text{CF}_3\text{COONa}$
<i>trans</i> - $\text{Ru}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+,2+}$	(+20) <sup>b,e</sup>	0.2 <i>F</i> $\text{CF}_3\text{COONa}$
<i>trans</i> - $\text{Ru}(\text{NH}_3)_4\text{Pz}_2^{3+,2+}$	+780 <sup>b</sup>	1 <i>F</i> NaCl
$(\text{NH}_3)_5\text{RuPzRu}(\text{NH}_3)_5^{5+,4+}$	+350, <sup>b</sup> +400* <sup>i</sup>	1 <i>F</i> NaCl (weakly acidified)
$(\text{NH}_3)_5\text{RuPzRu}(\text{NH}_3)_5^{6+,5+}$	+740, <sup>b</sup> +760* <sup>i</sup>	1 <i>F</i> NaCl (weakly acidified)
$\text{Ru}(\text{NH}_3)_5\text{N}_2\text{Ru}(\text{NH}_3)_5^{4+,5+}$	+706* <sup>i</sup>	

<sup>a</sup> By potentiometry. <sup>b</sup> By cyclic voltammetry. The values reported are the arithmetic average of the cathodic and anodic peak potentials. These will differ from the actual formal potentials by  $30 \log (D_{\text{III}}/D_{\text{II}})$  mV, where  $D_{\text{III}}$  and  $D_{\text{II}}$  are the diffusion coefficients of the Ru(III) and Ru(II) complexes, respectively. <sup>c</sup> By polarography. <sup>d</sup> Calculated from  $\text{p}K_a$  values<sup>6</sup> for both oxidation states of the complex and the  $E^f$  value for the  $\text{Ru}(\text{NH}_3)_5\text{Pz}^{3+,2+}$  couple. <sup>e</sup> Approximate values at a sweep rate of 10 V/sec. <sup>f</sup> T. J. Meyer and H. Taube, *Inorg. Chem.*, **7**, 2369 (1968); potential quoted is the uncorrected value observed under similar, but not identical solution conditions. <sup>g</sup> Reference 7. <sup>h</sup> R. G. Gaunder and H. Taube, *Inorg. Chem.*, **9**, 2627 (1970). <sup>i</sup> Reference 9. <sup>j</sup> C. M. Elson, J. Gulens, I. J. Itzkovitch, and J. A. Page, *Chem. Commun.*, 875 (1970). <sup>k</sup> Values quoted are observed anodic peak potentials obtained by cyclic voltammetry in 0.1-1 *F*  $\text{HClO}_4$  or  $\text{H}_2\text{SO}_4$ . No corresponding cathodic peak is present. The actual value of  $E^f$  would be somewhat more positive than the anodic peak potential if the rate of oxidation of the Ru(II) in the complex is fast. <sup>l</sup> An asterisk denotes previously reported values.

Two complexes which displayed significant deviations from Nernstian behavior were *trans*- $\text{Ru}(\text{NH}_3)_4\text{Cl}_2^{3+,2+}$  and *trans*- $\text{Ru}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+,2+}$ . The rates of their reduction at the electrode are apparently appreciably lower than the other complexes investigated so that the values obtained for the formal potentials for these two complexes are only approximations.

The formal potentials evaluated in this study along with some values for related couples previously reported by others are collected together in Table I. In some cases rather substantial differences exist between previous values for the potentials and those obtained in the present study:  $\text{Ru}(\text{NH}_3)_6^{3+,2+}$ ,  $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{3+,2+}$ ,  $\text{Ru}(\text{NH}_3)_5\text{py}^{3+,2+}$ , and  $(\text{NH}_3)_5\text{RuPzRu}(\text{NH}_3)_5^{5+,4+}$ . Some of the disagreements may be attributable to differences in ionic strengths and junction potentials, but the discrepancies in the cases of  $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{3+,2+}$  and  $\text{Ru}(\text{NH}_3)_5\text{py}^{3+,2+}$  seem too large to be accounted for in this way. In these two cases we believe the present values are the more reliable.

There is good qualitative agreement between the trends evident in the  $E^f$  values in Table I and the  $\pi$ -accepting ability of the ligands. The formal potentials of Ru(III,II) complexes are expected to be sensitive to  $\pi$  back-bonding from metal to ligand because the electrons in the metal  $\pi$  orbitals are directly involved in the redox reaction. The  $\pi$  back-bonding tends to stabilize the metal  $\pi$  orbitals and to reduce interelectron repulsion in the metal ion. The greater the  $\pi$  back-bonding the more the lower oxidation state, Ru(II), is stabilized relative to Ru(III). Thus, in the series of pentaammine complexes studied, more positive values

of  $E^f$  are expected as the  $\pi$ -accepting capability of the sixth ligand increases. Zwickel and Creutz<sup>7</sup> have made the same point in noting a good correlation between polarographic half-wave potentials and the degree of  $\pi$  back-bonding calculated from spectral data in the cases where the sixth ligand is pyridine, isonicotinamide, or methyl isonicotinate. The relative tendency to act as  $\pi$  acceptors among the neutral ligands in Table I is therefore  $\text{N}_2 > \text{Pz} > \text{isonicotinamide} \sim \text{methyl isonicotinate} \gg \text{Pz}$  on the basis of the relative values of  $E^f$ .

In the complexes with ligands that are not  $\pi$  acceptors, those with anionic ligands ( $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ) have more negative  $E^f$  values than those with neutral ligands ( $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ). This is a result in accord with standard interpretations<sup>14</sup> which emphasize electrostatic interactions between the metal and the ligand. The added effects of repulsive  $\pi$  interactions between nonbonding electrons on the ligands and the metal d electrons act to produce the order of potentials shown in Table I. Kallen and Earley<sup>15</sup> have recently reported  $E^f$  values for  $\text{Ru}(\text{NH}_2\text{O})_5\text{L}^{2+,+}$  (where L = Cl, Br, and I) which follow this same order. The fact that thiocyanate anion produces a shift of  $E^f$  in the opposite direction from the other anions suggests that it functions as a weakly  $\pi$ -accepting ligand. This is consistent with thiocyanate being bonded to ruthenium *via* its nitrogen end as data to be presented later lead us to believe.

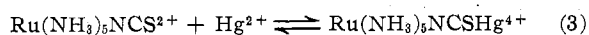
(14) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed., Wiley, New York, N. Y., 1967, p 76; D. D. Perrin, *Rev. Pure Appl. Chem.*, **9**, 157 (1959).

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When interchange between neutral, non- $\pi$ -bonding ligands is involved, the relative ligand field strengths of the ligands determines the order of the  $E^f$  values. Thus, in the series  $\text{Ru}(\text{NH}_3)_6^{3+,2+}$ ,  $\text{Ru}(\text{NH}_3)_5\text{OH}_2^{3+,2+}$ , *cis*- $\text{Ru}(\text{NH}_3)_4(\text{OH}_2)_2^{3+,2+}$ ,  $\text{Ru}(\text{H}_2\text{O})_6^{3+,2+}$ , the  $E^f$  values are 51, 66, 100, and 210 mV,<sup>15</sup> reflecting the greater stabilization of  $\text{Ru}^{3+}$  by the ligand ( $\text{NH}_3$ ) with the larger ligand field strength.

The effect on  $E^f$  of the substitution of a second ammonia by another ligand to give a *cis* tetraammine complex appears to be a simple cumulative one as is indicated qualitatively by the relative  $E^f$  values of the *cis* complexes in Table I. The reason for the observed trend in  $E^f$  values for the *trans* complexes is less clear.

**Bonding of  $\text{NCS}^-$  in  $\text{Ru}(\text{NH}_3)_5\text{NCS}^{2+,+}$ .**—When  $[\text{Ru}(\text{NH}_3)_5\text{NCS}](\text{ClO}_4)_2$  is dissolved in water a deep red-purple color results which is presumed to be that of the nitrogen-bonded thiocyanate isomer because addition of  $\text{Hg}^{2+}$  ions to the solution produces an immediate change in color (the solution becomes pale yellow). Addition of excess bromide ion to the resulting solution restores the original color and spectrum of the solution. This behavior is quite similar to that reported by Armor and Haim with the analogous thiocyanatopenta-aquochromium(III) complex<sup>18</sup> and appears to reflect the formation of the same kind of binuclear complex according to the reaction

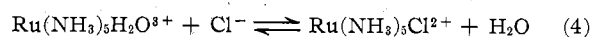


Additional evidence to support nitrogen bonding in the thiocyanate complexes is the fact that both  $\text{Ru}(\text{NH}_3)_5\text{NCS}^+$  and  $\text{Ru}(\text{NH}_3)_5\text{NCS}^{2+}$  spontaneously adsorb on the surface of mercury electrodes.<sup>17</sup> Both vanadium(III) and chromium(III) thiocyanate complexes display similar adsorption,<sup>18,19</sup> and they are known to be nitrogen-bonded complexes. (Thiocyanate is reported to be bonded *via* its nitrogen end in *trans*- $[\text{Ru}(\text{NH}_3)_4(\text{CO})\text{NCS}]\text{NCS}$ ,<sup>20</sup> but the carbonyl group would be expected to influence strongly the ligand *trans* to it so that the bonding in this complex is not a good model for the pentaammine complex.)

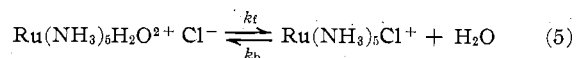
Very recently a synthesis appeared for what was claimed to be the S-bonded complex  $\text{Ru}(\text{NH}_3)_5\text{S-CN}^{2+}$ .<sup>21</sup> The reported visible and infrared spectra of this complex are essentially identical with those for the complex isolated from the electrochemical syntheses described in this work which we have assumed to be the N-bonded isomer for the reasons just given. To try to settle the question of the bonding in this complex, the relative integrated intensities of the infrared absorption bands corresponding to the C-N stretch were measured for samples of  $\text{NaNCS}$  and  $[\text{Ru}(\text{NH}_3)_5\text{NCS}](\text{ClO}_4)_2$  in KBr pellets. The band for the complex ( $\nu$  2060  $\text{cm}^{-1}$ ) yielded an integrated intensity about five times larger than that for the uncomplexed thiocyanate ( $\nu$  2080  $\text{cm}^{-1}$ ). This relative order of intensities strongly supports the assumption that the

complex is N bonded.<sup>22-24</sup> The spectral evidence and the fact that the reaction between the complex and mercuric ion is rapid and reversible persuade us that the complex we have prepared and studied is N bonded.

**Equilibrium Constants.**—It is possible to estimate some equilibrium constants of interest from the  $E^f$  values in Table I. The difference between the formal potential in Table I for aquopentaammine and hydroxopentaammine complexes combined with the known  $pK_a$  (4.2) of  $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ <sup>25</sup> leads to a value of 12.3 for the  $pK_a$  of  $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ . A value of 10.7 has been reported for this constant<sup>26</sup> from a direct pH titration, but it is difficult to obtain accurate  $pK_a$  values for such weak acids by means of acid-base titrations in aqueous media. The difference between the  $E^f$  values for the aquo- and chloropentaammine couples combined with an average of the reported values of the equilibrium constant for reaction 4<sup>25,26</sup> ( $K_4 = 105$



$M^{-1}$ ) leads to an estimated value of  $K_5 = 1.6 M^{-1}$  for the equilibrium constant for reaction 5. The back-



ward rate constant,  $k_b$ , for reaction 5 has been measured to be 4.7  $\text{sec}^{-1}$ .<sup>18</sup> The resulting value of  $K_1 (= K_5 k_b)$  is 7  $M^{-1} \text{sec}^{-1}$  which is about 100 times larger than typical constants for the same reaction with uncharged ligands.<sup>27</sup>

**Cyclic Voltammetry.**—The cyclic voltammograms for  $\text{Ru}(\text{NH}_3)_6^{3+}$ ,  $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ , and  $\text{Ru}(\text{NH}_3)_5\text{OH}^{2+}$  displayed highly reversible behavior at sweep rates up to 50 V/sec with no evidence of chemical reactions preceding or subsequent to the electrode reactions. Reversible voltammograms also resulted with  $\text{Ru}(\text{NH}_3)_5\text{Cl}^{2+}$ ,  $\text{Ru}(\text{NH}_3)_5\text{Br}^{2+}$ , and  $\text{Ru}(\text{NH}_3)_5\text{NCS}^{2+}$ , but, except at the highest sweep rates, the current-potential curves contained two peak currents during the anodic half of the first cycle and two corresponding peak currents on the subsequent cathodic half cycle. Figure 1 shows a typical example of the behavior observed. The pair of anodic-cathodic peaks centered at -176 mV *vs.* sce at the slower sweep rates clearly correspond to the  $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{3+,2+}$  couple formed by the aquation of the electrogenerated  $\text{Ru}(\text{II})$  form of the initial complex. By comparing the sweep rates which produced the same ratio of peak currents for the aquated and unreacted  $\text{Ru}(\text{II})$  complex during the anodic half cycles, it was possible to determine that the relative rates of aquation of the three complexes are  $\text{Ru}(\text{NH}_3)_5\text{Br}^+ > \text{Ru}(\text{NH}_3)_5\text{Cl}^+ > \text{Ru}(\text{NH}_3)_5\text{NCS}^+$ .

**Electrochemical Reduction of Pyrazine Coordinated to Ruthenium(II).**—Uncoordinated pyrazine in aqueous solution displays a reversible, pH-dependent, two-electron polarographic wave that splits into two one-electron waves at sufficiently low pH values.<sup>28</sup> The available evidence indicates that the electrode reaction

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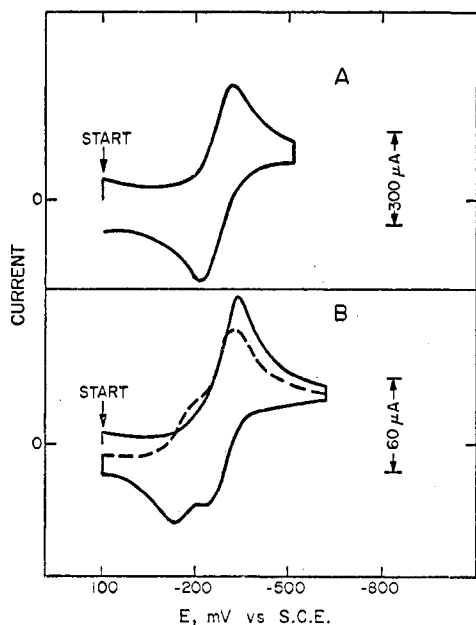
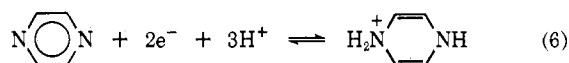


Figure 1.—Cyclic voltammograms of 3 mM  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ : (A) scan rate 47 V/sec; (B) scan rate 3.7 V/sec. Dotted curve is the second cathodic scan. Supporting electrolyte was 0.1 M  $\text{CF}_3\text{COOH} + 0.1 \text{ M } \text{CF}_3\text{COONa}$ ; pH 1.8. Electrode area was  $0.032 \text{ cm}^2$ .

proceeding under conditions where a single, two-electron wave appears is



As already noted, the coordination of pyrazine to  $\text{Ru}(\text{II})$  shifts the formal reduction potential of the  $\text{Ru}(\text{III})|\text{Ru}(\text{II})$  couple to more positive values because of the stabilization of the lower oxidation state of the ruthenium resulting from the strong metal-to-ligand  $\pi$  bonding. The same factor would be expected to shift the potential where coordinated pyrazine is reduced to more negative values. In fact, well-defined polarographic waves are obtained for  $\text{Ru}(\text{NH}_3)_5\text{Pz}^{2+}$  in neutral and alkaline solutions at potentials considerably more cathodic than those at which uncoordinated pyrazine is reduced at the same pH. (At pH values less than *ca.* 4 the pyrazine wave is masked by the current due to hydrogen evolution which is apparently strongly catalyzed by the pyrazine complex.) Unfortunately, no more quantitative conclusions about the relative reactivities toward reduction of bound and uncoordinated pyrazine could be pursued because the two processes display dissimilar pH dependences and lead to different products which could not be unambiguously characterized in the case of bound pyrazine.

The polarographic diffusion currents for  $\text{Ru}(\text{NH}_3)_5\text{Pz}^{2+}$  correspond to a two-electron reduction if the complex is assumed to have the same diffusion coefficient as  $\text{Ru}(\text{NH}_3)_5\text{Cl}^{2+}$ . Both polarographic half-wave potentials,  $E_{1/2}$ , and cyclic voltammetric peak potentials,  $E_p$ , are linearly dependent on pH between pH 7 and 13 (Figure 2). At higher pH values  $E_p$  attains a limiting value of *ca.*  $-1.44 \text{ V}$ .

The cathodic portions of the cyclic voltammograms indicate that the electrode process is complex: the peak current displays a nonlinear dependence on the

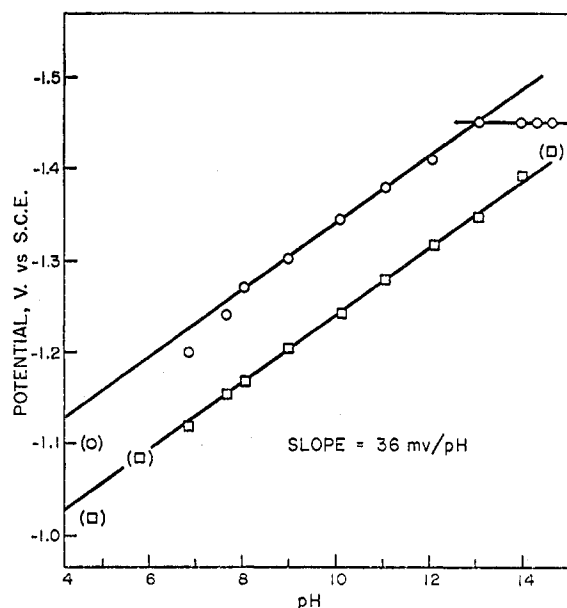


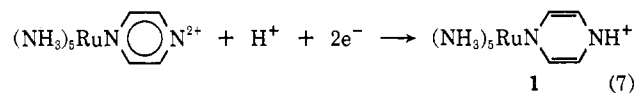
Figure 2.—pH dependence of polarographic half-wave potentials ( $\square$ ) and cathodic peak potentials ( $\circ$ ) for  $\text{Ru}(\text{NH}_3)_5\text{Pz}^{2+}$ . pH ranges and buffers were as follows: 4.82–7.69, phosphate; 8.07–10.13, borate; 11.11–12.15, phosphate;  $>13$ , NaOH. pH values  $\geq 14$  are calculated values based on the analytical concentration of NaOH. Except for pH values greater than 14, the solutions were maintained at unit ionic strength ( $0.9 \text{ M } \text{NaCl} + \text{buffer}$ ). The Ru complex was  $1.0 \text{ mM}$  and the temperature was  $25^\circ$ .

square root of sweep rate, increasing with sweep rate more rapidly than is expected for a simple diffusion-limited charge-transfer reaction; the peak potentials also become more cathodic with increasing sweep rates.

Typical cyclic voltammograms for the pyrazine complexes are shown in Figure 3. Except in very acidic solutions, a single anodic peak is coupled with the cathodic peak. Between pH 4 and 9 the potential of the anodic peak remains at about  $-0.4 \text{ V}$ . If the pH is increased beyond 9, this peak becomes broader and begins to shift to more negative values. At the highest pH values the shape of the anodic peak becomes normal again and in  $4 \text{ F } \text{NaOH}$  the cyclic voltammogram approaches that expected for a two-electron reversible couple: the cathodic and anodic peaks are separated by only 32 mV at a low sweep rate ( $0.1 \text{ V/sec}$ ) compared with 29 mV for a reversible couple. This separation increases to 50 mV at a sweep rate of  $8 \text{ V/sec}$ .

The split cathodic wave shown in Figure 3 is observed only in solutions having pH values less than 5. This splitting may reflect the one-electron reduction of the coordinated pyrazine to produce a complexed radical. Such radicals are known to be stabilized by the protonation of pyrazine,<sup>28</sup> but our data, while suggestive, are insufficient to prove that coordination with ruthenium(II) leads to a similar stabilization.

The  $\text{p}K_a$  of protonated pentaamminepyrazineruthenium(II) ion (2) is  $2.5^8$  so that in neutral and alkaline solutions the complex is unprotonated. The pH dependence of the reduction wave and its evident irreversibility (Figure 3) point to an overall electrode reaction of the form



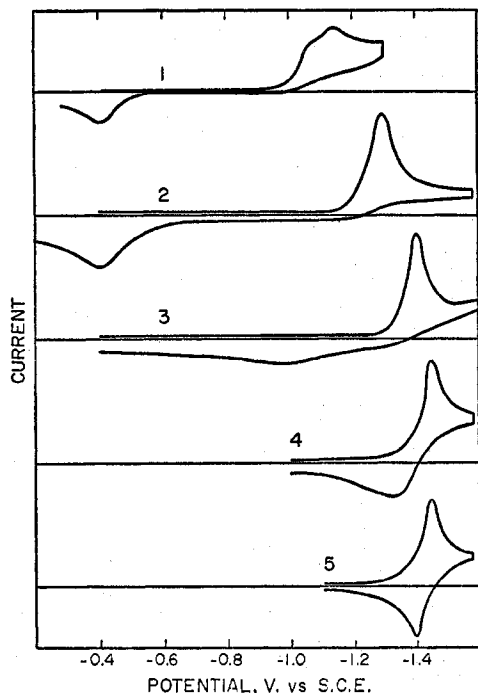
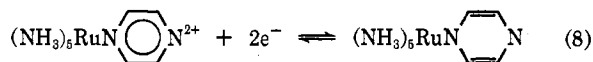


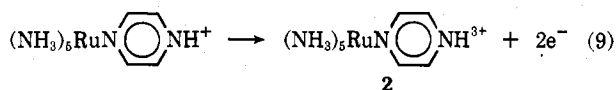
Figure 3.—Cyclic voltammograms of 1 mM  $\text{Ru}(\text{NH}_3)_6\text{Pz}_2^{2+}$ : (1) pH 4.8, phosphate buffer, scan rate 1.25 V/sec; (2) pH 8.3, phosphate buffer, scan rate 10 V/sec; (3) pH 12.5, phosphate buffer, scan rate 10 V/sec; (4) 1 F NaOH, scan rate 10 V/sec; (5) 4 F NaOH, scan rate 8 V/sec. The ionic strength was maintained at 1.0 with NaCl for 1, 2, and 3. The current scale for case 1 is smaller than for the other cases.

The fact that the peak potentials lose their pH dependence at about pH 13 (Figure 2) indicates that the  $\text{p}K_a$  for 1 is about 14–15. (Such a value seems reasonable inasmuch as  $\text{p}K_a = 15\text{--}16.5^{29}$  for the similar amine pyrrole.) The reversible-looking cyclic voltammogram obtained in 4 M NaOH (Figure 3, case 5) may result because the overall electrode process has become



with no protonation of reactant or product involved.

The rather large value of  $\text{p}K_a$  for 1 could well cause its net rate of deprotonation at lower pH values to become so slow that the anodic reaction becomes



followed by very rapid proton loss by the pyrazine complex. Since the proton loss follows the anodic electrode reaction, its potential will be independent of pH if the electrode reaction is rate limiting. The irreversible anodic peak at  $-0.4$  V (Figure 3) is independent of pH between pH 5 and 9 and may correspond to reaction 9. The gradual change in the shape of the anodic peak as the pH increases is understandable in terms of the growing importance of the reverse of reaction 8 as the pH increases. Under the conditions of case 3 of Figure 3, the anodic wave owes its appearance to sizable contributions from both reaction pathways with relative

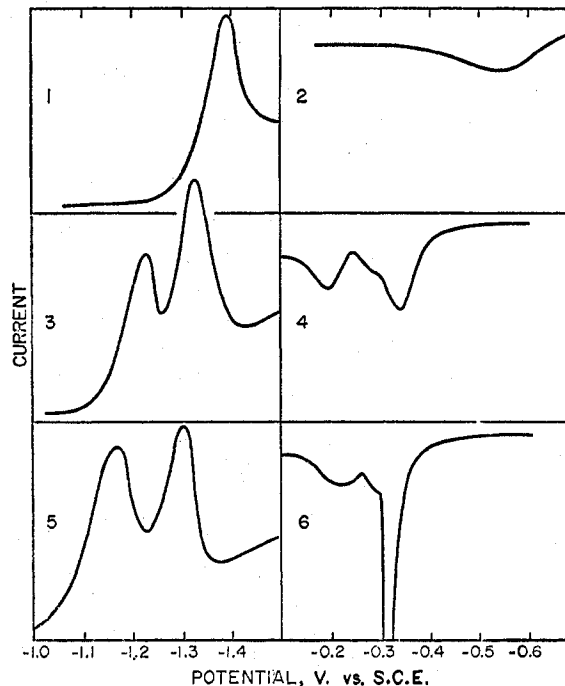
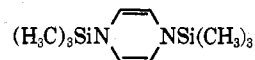


Figure 4.—Cyclic voltammograms of the mono- and dipyrazine complexes: 1 mM  $\text{Ru}(\text{NH}_3)_6\text{Pz}_2^{2+}$ , (1) cathodic scan, (2) anodic return; 0.3 mM *cis*- $\text{Ru}(\text{NH}_3)_4\text{Pz}_2^{2+}$ , (3) cathodic scan, (4) anodic return; 1 mM *trans*- $\text{Ru}(\text{NH}_3)_4\text{Pz}_2^{2+}$ , (5) cathodic scan, (6) anodic return. The supporting electrolyte was 1 M NaCl, unbuffered; scan rate 10 V/sec. The current scale was adjusted in each case to match the concentration of complex.

proportions governed by the kinetics of deprotonation of 1.

The electrode reaction product containing reduced pyrazine proved to be too unstable for isolation or reliable measurements of its spectrum. However, a compound containing reduced pyrazine



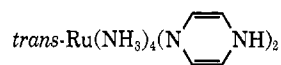
has been isolated recently.<sup>30</sup>

**Dipyrazine Complexes.**—*cis*- $\text{Ru}(\text{NH}_3)_4\text{Pz}_2^{2+}$  ion gives well-shaped polarographic and cyclic voltammetric waves at potentials slightly more anodic than  $\text{Ru}(\text{NH}_3)_6\text{Pz}_2^{2+}$ , and the polarographic diffusion currents correspond approximately to a four-electron reduction of the complex. The *trans* complex begins to reduce at a more positive potential than that of the *cis* complex at the dropping mercury electrode, but a well-shaped wave is not obtained. The cyclic voltammograms of the dipyrazine complexes are compared with that of the monopyrazine complex in Figure 4. Since four electrons appear to be involved in the electrode reactions of the dipyrazine complexes, reduction of both of the coordinated pyrazine ligands is indicated. The question as to whether the two discrete reduction steps displayed by the dipyrazine complexes in Figure 4 correspond to the intermediate formation of a complex which contains one pyrazine and one totally reduced pyrazine as ligands or if a complex containing two radical pyrazine ligands is formed could not be settled from the data available. The large anodic current obtained with the *trans* complex appears only if the cathodic

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sweep is allowed to traverse the range of potentials occupied by the second peak. It seems likely that the sharp anodic peak corresponds to oxidation of the uncharged complex



which is apparently adsorbed (or precipitated) at the electrode surface.

**Acknowledgment.**—We are grateful to Professor Peter Ford and Dr. Carol Creutz for helpful hints about the syntheses of several of the complexes studied. We are indebted to Dr. S. V. Srinivasan for performing the infrared absorption intensity measurements. This work was supported by the National Science Foundation. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
FLORIDA STATE UNIVERSITY, TALLAHASSEE, FLORIDA 32306

## Donor Properties of Positively Charged Ligands. Five-Coordinate, Trigonal-Bipyramidal Complexes of Manganese(II), Iron(II), Nickel(II), and Copper(II) with a Monoprotonated Ditertiary Amine

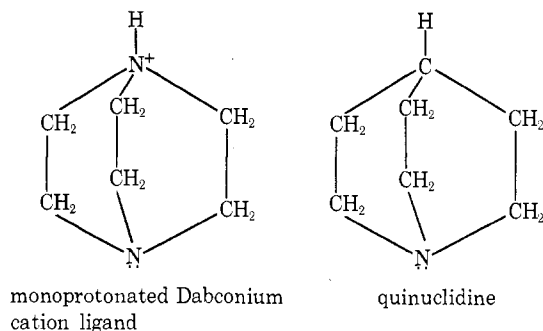
By L. M. VALLARINO,\* V. L. GOEDKEN, AND J. V. QUAGLIANO

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A series of complexes of formula  $[\text{MX}_3(\text{L}^+\text{H})_2]\text{X}$  was obtained, where M is Mn(II), Fe(II), Ni(II), and Cu(II); X is Cl and Br; and  $\text{L}^+\text{H}$  is the monoprotonated ditertiary amine 1,4-diazabicyclo[2.2.2]octane (Dabco). The five-coordinate complex cations  $[\text{MX}_3(\text{L}^+\text{H})_2]^+$  have a trigonal-bipyramidal configuration with  $D_{3h}$  symmetry and represent an unusual example of this stereochemistry for high-spin transition metal ions coordinated solely by monodentate ligands.

### Introduction

In preceding papers of this series<sup>1-3</sup> we pointed out that the positively charged ligands obtained by monoquaternization of the cage-like ditertiary amine 1,4-diazabicyclo[2.2.2]octane (Dabco) have unusual coordination properties which can logically be related to several cooperating factors. First, the presence of a positive charge on the ligand itself may be expected to give rise to strong electrostatic interactions even in complexes which do not carry net ionic charges, thus increasing their overall lattice energy and hence their solid-state stability. Also, the rigid cage-like structure of Dabco might be expected to minimize the steric requirements which ordinarily hinder coordination of tertiary aliphatic amines to metal ions. Finally, in the monoprotonated Dabconium ligand the availability of the lone pair on the N donor atom may be drastically reduced by direct electronic interaction with the positively charged, quaternized N atom, as reflected by the dramatic decrease in basicity compared to similar uncharged tertiary amines—for example, the  $\text{p}K_a$  of quinuclidine<sup>4</sup> is 10.65 vs. 2.97 for the monoprotonated Dabconium cation.<sup>5</sup> This change in the electronic requirements of the N donor atom of the Dabconium ligands may then result in the stabilization of metal complexes of unusual coordination numbers and geometries.



### Results and Discussion

The reaction between the chlorides and bromides of manganese(II), iron(II), nickel(II), and copper(II)—but not cobalt(II) and zinc(II)—and an excess of the corresponding halide of the monoprotonated Dabconium cation ligand ( $\text{L}^+\text{H}$ ) yields, as described in the Experimental Section, a series of compounds having the simple formula  $\text{MX}_2 \cdot 2(\text{L}^+\text{H})\text{X}$  ( $\text{M} = \text{Mn(II), Fe(II), Ni(II), Cu(II)}$ ;  $\text{X} = \text{Cl, Br}$ ). These compounds are crystalline solids, which dissolve with complete solvation in water and in other solvents of good donor properties (e.g., dimethyl sulfoxide) and are insoluble in nonpolar solvents or polar organic solvents such as alcohols and ketones. The structural elucidation of these compounds is based on the following experimental evidence.

The d-d electronic spectra of the Ni(II) compounds—the deep pink  $\text{NiCl}_2 \cdot 2(\text{L}^+\text{H})\text{Cl}$  and the pink-violet  $\text{NiBr}_2 \cdot 2(\text{L}^+\text{H})\text{Br}$  (Table II and Figure 1)—cannot be assigned to either a tetrahedral or an octahedral stereochemistry but rather strongly support a trigonal-bipyramidal coordination. In fact, the spectrum of

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