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Reactions of Coordination Compounds in the Solid State. 1. Behavior of Cobalt(III) Bis(ethylenediamine) Diammine Salts

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The behavior of solid, crystalline *cis*-diamminebis(ethylenediamine)cobalt(III) salts, *cis*-$[Co(en)_2(NH_3)_2]^{3+}$, upon heating, has been studied. Both the chloride and the hexafluorophosphate contain lattice water, which is readily lost upon heating. The hexafluorophosphate also loses PF_5, forming *cis*-$[Co(en)_2(NH_3)_2]F(PF_6)_2$ and then *cis*-$[Co(en)_2(NH_3)F](PF_6)_2$. The salts tend to lose ammonia upon heating, but at moderate temperatures (e.g., 100 °C), the optically active salts racemize without such loss, retaining the cis configuration completely. The changes have been followed by polarimetry, TGA, and proton NMR spectroscopy.

Introduction

There have been many studies of the reactions of coordination compounds in solution[1] but relatively few such studies of these compounds in the solid state. The behavior of solids is, however, of considerable interest, for aside from the light it may shed on the nature of the bonding and the mechanism of reactions, it has a bearing on preparative procedures and catalysis. We have therefore undertaken a study of such reactions.

There are several types of reactions that solid complexes may undergo, some of which are as follows:

A. Dissociation (loss of a volatile ligand and its replacement by a counter ion),[2] e.g.

$$[M(edta)(H_2O)]^- \rightarrow [M(edta)]^- + H_2O \quad (M = Co(III), Cr(III))$$

$$[Cr(en)_3]Cl_3 \rightarrow \textit{cis}\text{-}[Cr(en)_2Cl_2]Cl + en \quad (en = \text{ethylenediamine})$$

B. Penetration (substitution of a negative ligand by a neutral one),[3] e.g.

$$[Co(en)_2Cl_2]Cl + NH_3 \rightarrow [Co(en)_2(NH_3)Cl]Cl_2 \rightarrow [Co(en)_2(NH_3)_2]Cl_3$$

C. Polymerization,[4] e.g.

$$[NiBr_2\{P(CH_2CH_2CN)_3\}_2] \rightarrow \text{polymer}$$

D. Migration of ligands,[5] e.g.

$$[Cr(NH_3)_6][Al(C_2O_4)_3] \rightarrow Al[Cr(C_2O_4)_3] + 6NH_3$$

E. Formation of chelate rings,[6] e.g.

$$Na[CoX(Hedta)] \rightarrow Na[Co(edta)] + HX \quad (X = Cl^- \text{ or } Br^-)$$

F. Geometrical isomerization,[7] e.g.

$$\textit{trans}\text{-}[Co(NH_3)_4Cl_2]IO_3{\cdot}2H_2O \rightarrow \textit{cis}\text{-}[Co(NH_3)_4Cl_2]IO_3 + 2H_2O$$

G. Racemization,[8,9] e.g.

$$d\text{-}[Fe(phen)_3]X_2 \rightarrow \textit{rac}\text{-}[Fe(phen)_3]X_2$$

$$d\text{-}[Co(en)_3]I_3{\cdot}H_2O \rightarrow \textit{rac}\text{-}[Co(en)_3]I_3 + H_2O$$

We are particularly interested in the last two types—that is, cis–trans isomerizations and racemizations within the coordination sphere. In this paper, we describe the behavior of optically active *cis*-$[Co(en)_2(NH_3)_2]X_3$ when it is heated in the solid, crystalline state.

Experimental Section

(1) Preparation of Compounds. (i) *cis*-$[Co(en)_2(NH_3)_2]Cl_3{\cdot}H_2O$ was prepared from *cis*-$[Co(en)_2Cl_2]Cl$ with gaseous ammonia as described in the literature.[10] A slow stream of dry ammonia gas was passed over 10.0 g (0.035 mol) of the finely powdered dichloro salt that was heated on the steam bath at about 100 °C. The reaction was completed in 5 days, as indicated by the change in color of the complex from violet to yellow. The cis-diammine salt was recrystallized from a little water by adding ethanol; yield 9.6 g.

(ii) The same method was tried for the trans isomer, but it changed almost entirely to the cis form by the reaction *trans*-$[Co(en)_2Cl_2]Cl$ + $2NH_3 \rightarrow$ *cis*-$[Co(en)_2(NH_3)_2]Cl_3$. *trans*-$[Co(en)_2(NH_3)_2]Cl_3$ was prepared from *trans*-$[Co(NCS)_2(en)_2]Cl{\cdot}H_2O$[11] by the known procedure.[12]

(2) Optical Resolution of Compounds. The *cis*-diammine compound was resolved by the use of silver *d*-α-bromocamphor-π-sulfonate (BCS). The diastereoisomers *d*- and *l*-$[Co(en)_2(NH_3)_2](BCS)_3$ were prepared by analogy to its chloroammine analogue[13] and then converted to the chloride by using concentrated HCl according to the method of Werner and Shibata.[14] The active salt was recrystallized from a little water by adding a small amount of HCl and an excess of ethanol: $\alpha_D = +0.374 \pm 0.003°$ (19.98 mg in 5 mL of water with a 2-dm cell); $[\alpha]_D = +46.8°$ (literature value +50°).[14] The optically active salt *cis-l*-$[Co(en)_2(NH_3)_2](PF_6)_3$ was prepared by crystallizing the cis-l-chloride from a little water containing concentrated HPF_6 and washing with alcohol. The product was recrystallized by dissolution in a minimum volume of water and subsequent concentration in a stream of air at room temperature: $\alpha_D = -0.157 \pm 0.004°$ (18.00 mg in 5 mL of water with a 2-dm cell); $[\alpha]_D = -21.8°$.

(3) Analysis. Calcd for *cis-d*-$[Co(en)_2(NH_3)_2]Cl_3{\cdot}H_2O$: C, 14.23; H, 7.17; N, 24.90. Found: C, 14.52; H, 7.02; N, 24.82. Calcd for *cis-l*-$[Co(en)_2(NH_3)_2](PF_6)_3{\cdot}1.5H_2O$: C, 7.12; H, 3.73; N, 12.45. Found: C, 7.13; H, 3.52; N, 12.37.

(4) NMR Measurements. The NMR spectra were recorded on a Varian XL-200 200-MHz FT-NMR spectrometer fitted with a computer at the normal temperature of the probe (ca. 20 °C); 32 transients (scanning times) were employed. Sodium 2,2-dimethyl-2-silylpentane-5-sulfonate (DSS) was used as a reference standard. All spectra were run in acidic D_2O solutions.

(5) TGA Measurements. Thermogravimetric analysis (TGA) was carried out with a Perkin-Elmer TGA7 thermogravimetric analyzer. Samples ranged from 4 to 5 mg in mass. A heating rate of 10°/min and a flow of He (ca. 20 mL/min) were employed in all runs.

(6) Rate Studies. Kinetic runs were conducted by heating solid samples of the powdered complex compounds. Each sample (19–21 mg) was mounted in an aluminum boat (ca. 10 mm in length, ca. 7 mm in width). A densely packed, shallow bed of sample was used, so that all samples

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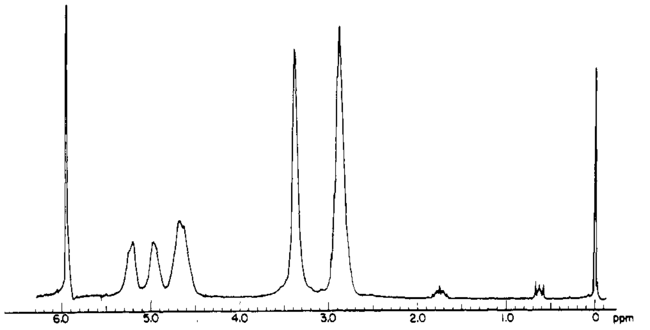

Figure 1. Proton NMR spectrum of *cis*-$[Co(en)_2(NH_3)_2](PF_6)_3$ in 1.9 M D_2SO_4.

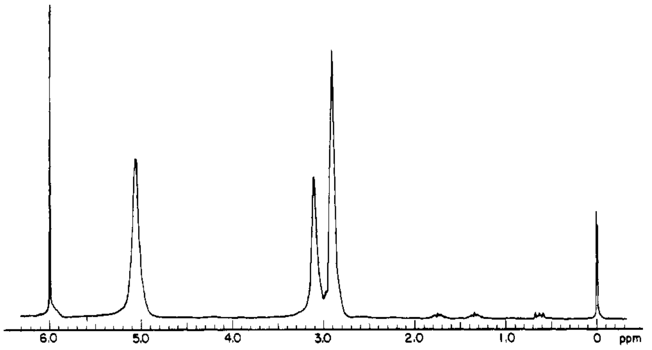

Figure 2. Proton NMR spectrum of *trans*-$[Co(en)_2(NH_3)_2]Cl_3$ in 1.9 M D_2SO_4.

might have the same packing characteristics (the sample thickness being less than 0.5 mm). Temperature control during the course of the kinetic runs was maintained by placing the sample boats in the drying chamber by an Abderhalden drying apparatus and a liquid of appropriate boiling point in the boiler. Water (bp 100 °C), *n*-butyl alcohol (bp 118 °C), cyclopentanone (bp 130 °C), propionic acid (bp 140 °C), and *N,N*-dimethylformamide (bp 152 °C) were employed. The heating apparatus was wrapped with glass wool in order to maintain an exact temperature. In this way the temperature could be controlled within less than ±0.5 °C.

Two sample boats were heated simultaneously during a single experiment. These were removed from the heating apparatus at fixed times and cooled quickly to room temperature after which the racemization proceeded at a negligible rate. Mass loss accompanying the heating was measured.

Each sample of the complex was weighed into a 1-mL vial and dissolved in D_2O–D_2SO_4 (about 1.8 M D^+) by vigorous shaking. The NMR spectrum of the solution was scanned as soon as possible after dissolution. In order to get an exact concentration for the polarimetric measurement, the solution was weighed into a 5-mL volumetric flask and diluted to volume. The optical activity of this solution was measured with an automatic polarimeter using a 2-dm cell and sodium lamp.

Results

The spectrum of *cis*-$[Co(en)_2(NH_3)_2]^{3+}$ is similar to that reported.[15] The cis complex has three NH bands at 4.70, 5.01, and 5.23 ppm from DSS with intensity ratio 4:2:2; coordinated ammonia absorbs at 3.39 ppm (6 protons), and the CH absorption appears at 2.87 ppm (8 protons) (Figure 1).

For the trans complex, the appearance of only two absorptions has been reported:[15] one of them was attributed to the symmetrical NH_2 groups and another to both NH_3 and CH_2 protons, assuming that the NH_3 absorption coincides with the methylene peak. However, we found that the trans complex has two clearly separated NH and CH bands (Figure 2). These are assigned to the NH_3 groups at 3.10 ppm and to the CH_2 groups at 2.91 ppm, respectively, with the intensity ratio 6:8. These are distinct from the symmetrical NH_2 absorptions at 5.06 ppm (8 protons). The racemic cis complex prepared here shows an NH_3 absorption at 3.10 ppm with a small intensity, indicating the presence of about 15% of the trans isomer.[16] On the other hand, the absorption in the resolved cis isomer and its PF_6 salt is negligible (Figure 1).

Table I. Rates of Racemization and Deammination

fixed temp, °C	time of heating, h	% loss of optical activity	% loss of cis isomer	% loss of wt
	cis-d-$[Co(en)_2(NH_3)_2]Cl_3 \cdot H_2O$			
100	91.3	1.6	1.1	2.6
	244.2	3.5	3.2	1.2
118	26.4	3.5	2.8	2.0
140	1.70	2.0	1.7	
	3.58	5.2	4.5	4.5
	cis-l-$[Co(en)_2(NH_3)_2](PF_6)_3 \cdot 1.5H_2O$			
118	21.2	6.6	0.0	22.4
	28.2	8.4	0.0	25.6
130	5.5	5.7	1.6	17.8
	26.5	14.1	2.6	29.2
140	5.8	11.0	3.6	25.4
	21.8	26.4	9.4	27.2
152	1.2	7.9	4.7	23.2
	3.3	18.9	7.8	24.8

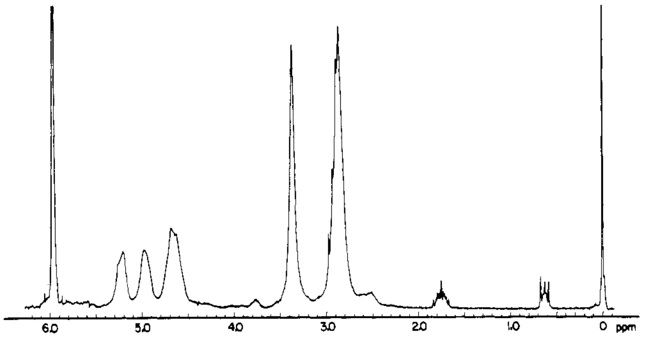

Figure 3. Proton NMR spectrum of a sample of *cis*-$[Co(en)_2(NH_3)_2](PF_6)_3$ after heating at 140 °C for 21.8 h (sample 26.4% racemized in Table I).

The H_2O peak of the solvent appears at lowest field (ca. 6 ppm) and moves upfield with a decrease of the acid concentration. In the CH region, DSS shows one CH_2 absorption; it overlaps with that of the complex.

TGA runs on the hydrated salts of the *cis-rac*-, *cis-d*-, and *trans*-$[Co(en)_2(NH_3)_2]Cl_3$ complexes show that dehydration occurs soon after heating is begun (at about 30–35 °C). Anhydrous weight levels are attained at 120–130 °C for the cis isomers and at 165–175 °C for the trans isomer. As the temperature is raised further, there is a slow loss of weight resulting from the decomposition of the complexes. The TGA curve for $[Co(en)_2(NH_3)_2](PF_6)_3$ shows that it also begins to lose water soon after the heating is begun. The loss does not cease when the anhydrous weight level is reached at 80–85 °C but continues until there is a sudden loss in weight at 210–215 °C, when the compound decomposes, with loss of PF_5.

When loss of the NH_3 molecule in the diammine complex occurs, NMR measurements show that the intensity of the NH_3 signal decreases compared to that due to the NH_2 groups, which remains unaltered. Thus, the bands assigned to the NH_3, NH_2, and CH_2 groups of the *cis*-$[Co(en)_2(NH_3)X]^{2+}$ complex[17] that is formed by anation appear, overlapping the spectrum of the diammine complex; however, the chloride in the byproduct gives

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(16) It is difficult to determine the amount of the trans isomer in a sample mixed with the cis isomer spectrophotometrically because the trans isomer shows almost the same visible absorption maxima as the cis isomer; the data are available from: Jørgensen, C. K. *Absorption Spectra and Chemical Bonding in Complexes*; Pergamon: London, 1962; p 293.

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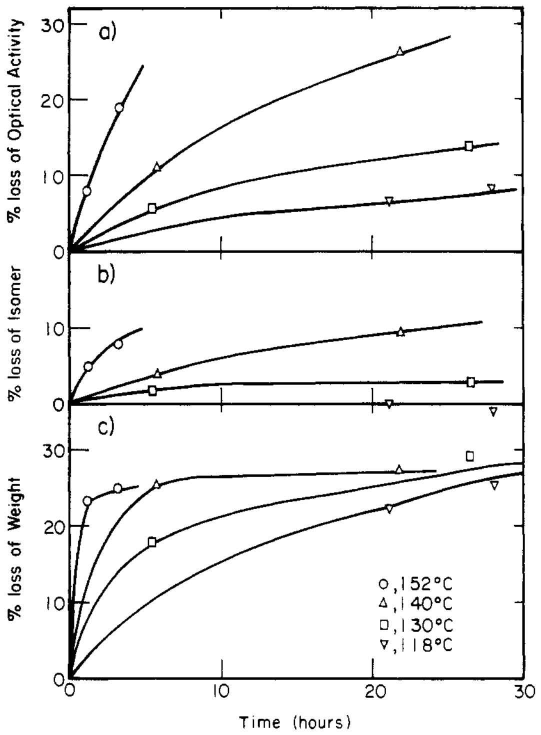

Figure 4. Racemization and deammination of *cis-l*-$[Co(en)_2(NH_3)_2](PF_6)_3$.

an NH band at 4.34 ppm; for the hexafluorophosphate this appears at 3.75 ppm.

The relative amounts of cis and trans isomers of the diammine and of the byproduct were calculated from the peak areas (or intensity ratios) of the NH protons. Table I compares the loss of the cis isomer on heating the diammine salts with the loss of optical activity and the mass loss. No trans isomer was found in any of the samples heated (for example, Figure 3).

In addition, no anation or isomerization of the trans diammine chloride complex occurs upon heating it at 130 °C for 53.3 h or at 152 °C for 25.5 h, indicating that the thermal stability of the trans isomer is greater than that of the cis isomer, in agreement with the result of TGA measurements.

When *l-cis*-$[Co(en)_2(NH_3)_2](PF_6)_3 \cdot 1.5H_2O$ is put in the heater (Figure 4, Table I), the water (amounting to about 4% of the total weight) is lost first, followed by a loss of PF_5 (about 19%), leaving $[Co(en)_2(NH_3)_2]F(PF_6)_2$, and then by a slow loss of ammonia (about 2.5%), leaving $[Co(en)_2(NH_3)F](PF_6)_2$. This may be followed by other reactions.

Discussion

Several different mechanisms have been proposed for isomerizations and racemizations of octahedral complexes: the tetragonal (Rây–Dutt) twist,[18] the trigonal (Bailar) twist,[19] the rhombic (Springer–Sievers) twist,[20] and dissociation.[21] We are led to the conclusion that all of these, and perhaps others, are operative, for no one mechanism seems to explain all cases. Indeed, at this time we have no clear explanation of some of the results reported in this paper and are performing further experiments that, it is hoped, will clarify the situation. To date, we have studied *d*- and *l*-*cis*-$[M(en)_2Cl_2]Cl$ (M = Co(III), Cr(III))[22] and *d*- and *l*-*cis*-$[Co(en)_2(NH_3)_2]X_3$. The striking feature of these is that the solid dichloro Co(III) and Cr(III) complexes, upon being heated to 160 °C, lose their optical activity but retain the cis configuration, although it has been indicated recently from thermodynamic data that the trans dichloro cobalt isomer possesses a greater thermal stability than the cis isomer.[23]

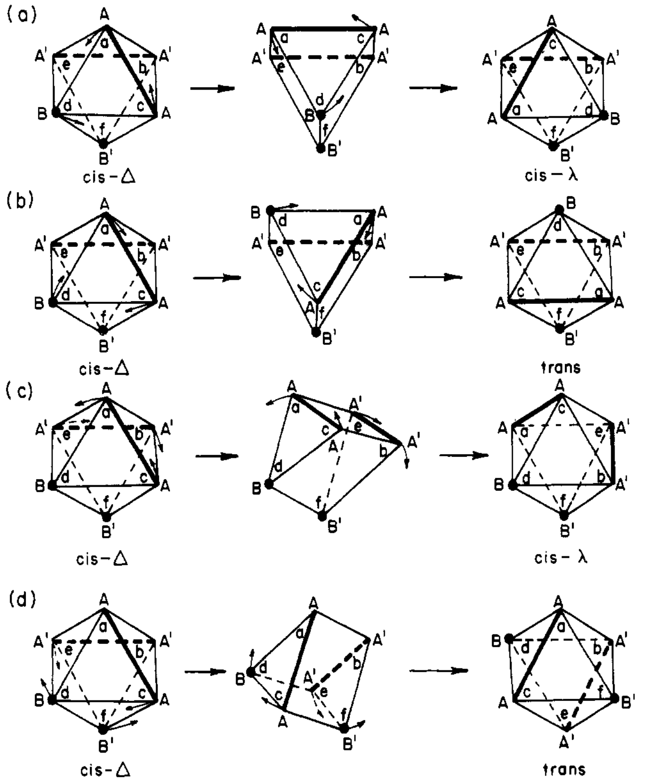

Figure 5. Rearrangement of compounds of the type $[M(AA)_2B_2]^{n\pm}$: (a) racemization (inversion) and (b) isomerization by the trigonal twist; (c) racemization (inversion) by the tetragonal twist extended in ref 24; (d) isomerization by the twist proposed here.

The diammine complex, heated at various temperatures (100–152 °C) isothermally, behaves in the same way, although, again, the trans isomer is more stable thermally than the cis isomer.

The trigonal-twist mechanism explains this result if it is assumed that only certain faces of the octahedron can undergo the twist and that the twist is in a certain direction (for example, clockwise rotation of the face *acd* in Figure 5a). On the other hand, counterclockwise rotation of face *acd* gives the trans isomer (Figure 5b).

Rây and Dutt discussed the mechanism of racemization of a tris(chelate) complex but not the reactions of complexes containing unidentate groups. Their theory can be extended to the racemization of compounds of the type *cis*-$[M(AA)_2B_2]^{n\pm}$[24] if it is assumed that only the bidentate groups move and the unidentate groups remain fixed (for example, the fixed atoms, B and B′, in Figure 5c) or that the unidentate groups move as a unit. However, there is no experimental justification for such an assumption. The same situation is encountered in the rhombic twist. Brady[25] and Serpone and Bickley[26] have concluded that the three twist mechanisms are basically the same, the intermediate being a trigonal prism with the only difference being in the interatomic angles in it. Cis-to-trans isomerization of such compounds can be also explained by a different twist motion if it is assumed that the unidentate groups move away from each other with twisting of the two faces (for example, *acd* and *bef*, in Figure 5d). This does not seem to happen, for the cis compounds $[M(en)_2X_2]^{n+}$ do not change to the trans configuration upon heating.

An aquation–anation pathway has been proposed for the racemization of *l-cis*-$[Cr(en)_2Cl_2]Cl \cdot H_2O$.[22] Although the racemization of its cobalt analogue has not been studied in detail, it has been found from radiochloride-exchange studies of the chloro

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chloride and bromo bromide complexes that halide exchange occurs when the compound is heated;[27] the racemization of the complex by the same intermolecular (dissociation) process seems likely. However, virtually identical rates and activation energies exhibited by all the complexes studied indicate that bond making or breaking is not rate-determining. This still does not explain why no trans isomer is formed. If the diammine compound racemizes by a dissociation mechanism, anation would be expected. This result is observed in the case of *cis-d*-$[Co(en)_2(NH_3)_2]Cl_3$. The percent loss of the optical activity is almost equal to that of the cis diammine complex when heated (Table I), and a reddish color of the product is observed, indicating that *cis*-$[Co(en)_2(NH_3)Cl]Cl_2$ is present in the product.

On the other hand, *cis-l*-$[Co(en)_2(NH_3)_2](PF_6)_3$ is found to racemize, in part, without anation. When heated at 140 °C for 21.8 hr, for example, the complex undergoes 26.4% loss of the optical activity and gives 17.0% racemic cis isomer with some reddish byproduct (9.4%), probably *cis*-$[Co(en)_2(NH_3)F](PF_6)_2$. When heated at 118 °C for 28.2 h, large mass loss is observed despite of no loss of ammonia. This result indicates the formation of what is probably *cis*-$[Co(en)_2(NH_3)_2](PF_6)_2{\cdot}F$ (loss of PF_5 and lattice water only). However, the reaction is accompanied by 8.4% loss of optical activity (Table I). These results could be interpreted as evidence for a twist process. When the complex is heated at a higher temperature, the dissociation process seems to be more prominent, for a large amount of *cis*-$[Co(en)_2(NH_3)F](PF_6)_2$ is formed. The difference in the kinetic behavior between the chloride and the PF_6^- salts can be explained by different chemical properties between the anions: the anion PF_6^- has negligible ability to hydrogen bond with the protons on the nitrogen atoms of the ligand and negligible donor ability in attack on the metal, compared with the case of the anion Cl^- (or F^-). Thus, such properties of anions may be important in determining the solid-state reaction mechanisms of coordination compounds as discussed previously.[8,9,28] To determine this, we are examining the behavior of nonionic, optically active, octahedral complexes.

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Stabilization of Transition-Metal Complexes in High Oxidation States by Macrocyclic Tertiary Amines. Electrochemical Generation and Spectroscopic Properties of Novel Dihalogeno and Pseudohalogeno Tetraamine Complexes of Ruthenium(IV)

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1,4,8,12-Tetramethyl-1,4,8,12-tetraazacyclopentadecane (15-TMC) was synthesized by the reaction of 1,4,8,12-tetraazacyclopentadecane with formaldehyde. Reactions of $K_2[RuCl_5H_2O]$ with 15-TMC and 16-TMC (16-TMC = 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane) in ethanol yielded *trans*-$[RuLCl_2]Cl$ (L = 15-TMC and 16-TMC, respectively) in high yields. The syntheses of *trans*-$[RuLBr_2]ClO_4$ [L = $(TMEA)_2$ (TMEA = *N,N,N′,N′*-tetramethyl-1,2-ethanediamine), 14-TMC (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane), and 15-TMC], *trans*-$[Ru(TMEA)_2(NCS)_2]NCS$, and *trans*-$[Ru(14\text{-}TMC)(CH_3CN)_2][ClO_4]_2$ are also described. The electrochemistry of *trans*-$[RuLX_2]^+$ [L = $(TMEA)_2$, 14-TMC, 15-TMC, and 16-TMC; X = Cl, Br, and NCO] in acetonitrile were examined. The $E_f°$ values of *trans*-$[RuLCl_2]Cl$ in 2 M HCl have been found to decrease with L in the order 14-TMC > 15-TMC > 16-TMC. Reversible/quasi-reversible Ru(IV)/Ru(III) couples in acetonitrile with $E_f°$ values ranging from 1.05 to 1.27 V vs. the ferrocene couple were observed. Controlled-potential electrolyses of *trans*-$[RuLX_2]^+$ at 1.30 V vs. the ferrocene couple generated some novel *trans*-$[Ru^{IV}LX_2]^{2+}$ complexes. The ligand-to-metal charge-transfer transitions in the UV-vis spectra of *trans*-$[Ru^{IV}(TMEA)_2X_2]^{2+}$ have been identified at 410 (X = Cl) and 570 nm (X = Br), which are considerably red-shifted with respect to their Ru(III) counterparts.

Introduction

High-valent ruthenium amine complexes having oxidation states greater than +3 are currently receiving our close attention in view of their potential usefulness as oxidative catalysts. In fact, most of the known mononuclear Ru(IV) and Ru(VI) complexes are largely confined to oxo species although complexes like $Ru(C_5Me_4Et)(CO)Br_3$, $[Ru(Me_2dtc)_3(PPh_3)]BF_4$ (Me_2dtc = dimethyldithiocarbamate), and $Ru(bpy)_3^{4+}$ (bpy = 2,2′-bipyridine) have also been reported.[1-3] We have recently reported the synthesis of some stable monooxo $Ru^{IV}{=}O$[3] and dioxo $O{=}Ru^{VI}{=}O$ complexes of 14-TMC (1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane), 15-TMC (1,4,8,12-tetramethyl-1,4,8,12-tetraazacyclopentadecane), 16-TMC (1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane), and TMEA (*N,N,N′,N′*-tetramethyl-1,2-ethanediamine)[5,6] (Figure 1). These tertiary amine ligands, being resistant to oxidation upon coordination to a metal ion, are capable of stabilizing high-valent ruthenium complexes because of their *strong σ-donor properties*. As part of our program to investigate the chemistry of high-valent ruthenium and osmium amine complexes, we describe here the electrochemical generation of some novel Ru(IV) complexes of the type *trans*-$[RuLX_2]^{2+}$ [L = 14-TMC, 15-TMC, 16-TMC, and

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