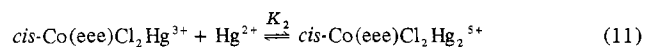


linearity at low Hg(II) concentrations. The nature of this deviation suggests a more complex rate equation that would be consistent with the formation of a second binuclear complex, i.e.



$$-d \ln [\text{Co(eee)Cl}_2^{+}] / dt = k_c [\text{Hg(II)}]^2 / 1 + KK_2 [\text{Hg(II)}]^2 \quad (12)$$

That the present data fit mechanism I so well can be attributed to the limiting form of eq 12 which obtains if most of the  $\text{Co(eee)Cl}_2^{+}$  is in the double-bridged complexed form  $\text{Co(eee)Cl}_2\text{Hg}^{3+}$  as dictated when  $K[\text{Hg(II)}] \gg 1$ . Similar conclusions exist for the reaction of Hg(II) with  $\text{cis-Co(en)}_2\text{Cl}_2^{+}$  and  $\text{cis-Cr(H}_2\text{O)}_4\text{Cl}_2^{+}$  ions: simply that the double-bridged configuration must be destroyed to accomplish the aquation reaction.<sup>30</sup>

Considering the affinity of mercury for sulfur, one must logically inquire as to the possible complexation or interaction of Hg(II) at the backside ligand thioether donor atoms, as opposed to positions adjacent to the leaving chloride groups. Evidence for such an interaction was expected to manifest itself in electronic absorption spectral changes for the free and complexed species. Using the technique of Armor and Haim,<sup>31</sup> the spectra of  $\text{Co(eee)C}_2\text{O}_4^{+}$ ,  $\text{Co(eee)(acac)}^{2+}$ , and  $\text{Co(eee)(H}_2\text{O)}_2^{3+}$  were examined as a function of Hg(II) concentration. No spectral evidence was found to support backside attack of Hg(II) on these complexes.

The Hg(II)-induced aquation of  $s\text{-cis-Co(eee)ClH}_2\text{O}^{2+}$  gave a second-order rate constant which did not exhibit a trend toward increased values at higher mercury(II) concentration. In addition, this second state of aquation was amenable to a temperature-dependence study. At 25° the observed second-order rate constant,  $5.36 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$ , indicates that this ion aquates 783 times slower than the corresponding  $\text{cis-Co(en)}_2\text{ClH}_2\text{O}^{2+}$  ion under similar conditions. As in the

first stage of aquation, spontaneous or induced, the presence of trans thioether donor atoms dramatically retards Co-Cl bond cleavage.

**Registry No.**  $s\text{-cis-Co(eee)Cl}_2^{+}$ , 32594-33-5;  $s\text{-cis-Co(eee)ClH}_2\text{O}^{2+}$ , 54983-97-0;  $s\text{-cis-Co(eee)(H}_2\text{O)}_2^{3+}$ , 54983-98-1; Hg(II), 14302-87-5.

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## Chemistry and Optical Properties of 4d and 5d Transition Metal Compounds. IV. Magnetic Circular Dichroism

### Characterization of the Low-Energy Charge-Transfer Bands of $[\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{L}]^{2+}$

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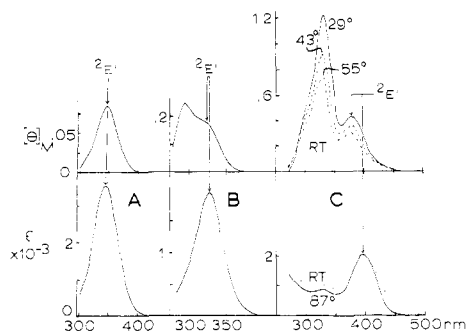
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The low-energy, intense electronic excitations of  $[\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{L}]^{2+}$  are assigned to the charge-transfer process  $e(\sim\pi\text{L}) \rightarrow t_2(\sim 4d \text{ Ru})$ , and the relevant spin-orbit states are  $\Gamma_7[{}^2\text{B} + {}^2\text{E}; {}^2\text{T}_{2g}(\text{t}_{2g}^5)] \rightarrow (\Gamma_6'[{}^2\text{E}'(\pi^3; \sim\text{L})] + \Gamma_7'[{}^2\text{E}'(\pi^3; \sim\text{L})])$ . It is found that the order is  $\Gamma_7' < \Gamma_6'$  for these two spin-orbit components of the excited state,  ${}^2\text{E}'(\pi^3; \sim\text{L})$ , with the hole localized on ligand L. The conclusions are based on (i) measurements of the temperature dependence of the electronic absorption and magnetic circular dichroism (MCD) intensities of the low-energy region of  $[\text{Ru}(\text{NH}_3)_5\text{Br}]_2\text{Br}_2$ , (ii) the sign of the net intensity of Faraday C parameters, (iii) the relative energies of bands for complexes with  $\text{L}^- = \text{NCO}^-$ ,  $\text{Cl}^-$ , and  $\text{Br}^-$ ; and (iv) the agreement of results of reliable computational models with the experimental data.  $\Gamma_6'$  of  $\Gamma_7 \rightarrow (\Gamma_6' + \Gamma_7')$  is experimentally found to have the dominating positive MCD activity as is predicted computationally with great reliance.

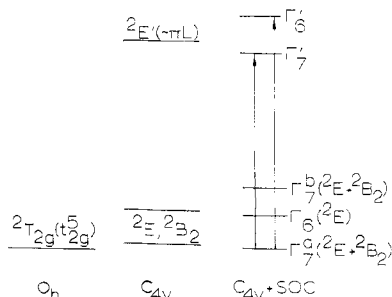
### Introduction

We have had occasion recently to report<sup>2</sup> the synthesis and optical spectra of several ruthenium(III)  $d^5$  molecule ions of  $C_{4v}$  symmetry having the formula  $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ , where  $\text{L}^-$  is  $\text{NCO}^-$ ,  $\text{OAc}^-$ ,  $\text{SCN}^-$ ,  $\text{SeCN}^-$ , or  $\text{Cl}^-$ . Optical spectra of the complex ions with  $\text{L}^-$  being  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  were also given by Hartmann and Buschbeck.<sup>3</sup> The interesting common feature about all of these spectra is the intense ( $\epsilon_{\text{max}} \geq 2000$ ;  $\geq 2 D^2$ ) optical band, the lowest energy band in each case as

shown in Figure 1 for  $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ , where  $\text{L}^-$  is  $\text{NCO}^-$ ,  $\text{Cl}^-$ , or  $\text{Br}^-$ , for example. It then seemed reasonable to suggest that these intense bands originate from the configuration change  $\sim\pi\text{L} \rightarrow t_2(\sim 4d \text{ Ru})$ , and in  $C_{4v}$  notation it was suggested<sup>2</sup> that it may be the ligand-to-metal transition  $e^4(\sim\pi\text{L}) \rightarrow e^3[(xz, yz)^3; \sim 4d \text{ Ru}]$  or  $\Gamma_7({}^2\text{E}) \rightarrow (\Gamma_6' + \Gamma_7')({}^2\text{E}')$  (Figure 2). We have now discovered that MCD confirms the suggestion that the excitation originates from  $\Gamma_7$ , and this Kramers ground state now has been found to be composed



**Figure 1.** Electronic and MCD spectra of  $[\text{Ru}(\text{NH}_3)_5\text{L}]_2^{2+}$ : (A)  $\text{L}^- = \text{NCO}^-$  and  $\text{A}^- = \text{Br}^-$ ; aqueous solution at room temperature; (B)  $\text{L}^- = \text{A}^- = \text{Cl}^-$ ; aqueous solution at room temperature; (C)  $\text{L}^- = \text{A}^- = \text{Br}^-$ ; poly(vinyl alcohol) film at the temperature given.



**Figure 2.** Energy levels of  $[\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{L}]_2^{2+}$  (see text).

unequally of single-group states,  ${}^2\text{E}'(xz, yz; \sim 4d \text{ Ru})$  and  ${}^2\text{B}_2'(xy; \sim 4d \text{ Ru})$ . These and related results and their analysis based on two independent and reliable computational models are being communicated here.

### Experimental Section

Electronic absorption spectra were obtained with a Cary 14 and the MCD spectra with a JASCO-UV/ORD/CD-5 (SS-20 modification). The temperature of  $[\text{Ru}(\text{NH}_3)_5\text{Br}]_2^{2+}$  was varied inside the liquid helium core of the superconducting magnet. Other details were previously described.<sup>4</sup>

### MCD Interpretation

The interesting nature of the excited-state assignment is that, while we are dealing with ligand-to-metal charge-transfer transitions from electronic ground to *excited* states, band assignments can be made by the careful combination of double-group theory and the explicit evaluation of the total angular momentum of the *ground* electronic state or one of its components.

Thus, the forecasting ability of the (first) computational model for assigning excited states by means of MCD rests largely on the capability of evaluating signs of components of the total angular momentum ( $L + 2S$ ) of the ground state after allowing for complete configuration interaction and first- and second-order spin-orbit coupling. This evaluation is accomplished with complete reliability by means of ligand field theory, since the open shell of the ground configuration is metal localized. Furthermore, only approximate ligand field parameters are required to evaluate the *sign* of  $\langle L + 2S \rangle$  with reliability.

Beginning with double-group theory one can write the MCD expressions

$$\frac{C}{D} [\Gamma_7 \rightarrow \Gamma_7'] = \frac{-1/2 \langle \Gamma_7^+ | \mu_z | \Gamma_7^+ \rangle}{1 + \frac{\langle z \rangle^2}{\langle x \rangle^2 + \langle y \rangle^2}}$$

$$\frac{C}{D} [\Gamma_7 \rightarrow \Gamma_6'] = \frac{1}{2} \langle \Gamma_7^+ | \hat{\mu}_z | \Gamma_7^+ \rangle$$

for the transitions to the two spin-orbit components of excited

state,  ${}^2\text{E}'(\pi^3; \sim L)$ .  $C$  is the Faraday parameter,<sup>5</sup> which for excitation  $\Gamma_7 \rightarrow J$  is  $(1/2) \sum [\langle \Gamma_7 | \hat{\mu} | \Gamma_7 \rangle \cdot \text{Im}(\langle \Gamma_7 | \hat{m} | J \rangle \times \langle J | \hat{m} | \Gamma_7 \rangle)]$ ;  $D$  is the electric dipole strength of the band;  $\Gamma_7$  is the spin-orbit ground state (mixture, as shown below, of  ${}^2\text{B}$  and  ${}^2\text{E}$  of  ${}^2\text{T}_{2g}(t_{2g}^5)$ );  $\Gamma_6'$  and  $\Gamma_7'$  are the two spin-orbit excited-state components (Figure 2) of  ${}^2\text{E}'(\pi^3; \sim L)$ ;  $\Gamma_7^+$  is one of the Kramers-doublet components of the ground state,  $|\Gamma_7^+\rangle = -i(|\Gamma_7x\rangle + i|\Gamma_7y\rangle)$ ;  $\langle q \rangle^2$  ( $q = x, y, \text{ or } z$ ) is equal to  $|\langle \Gamma_7 | \hat{m}_q | \Gamma_7' \rangle|^2$ ; and the basis is complex unless real components are indicated.

The two  $C/D$  expressions already as written demonstrate that  $\Gamma_6'$  and  $\Gamma_7'$  will have opposite MCD intensities at temperatures where the  $C$ -term mechanism will dominate, because the denominator of the expression for  $\Gamma_7 \rightarrow \Gamma_7'$  is positive. However, the angular momentum integral,  $\langle \Gamma_7^+ | \hat{\mu}_z | \Gamma_7^+ \rangle$ , must first be evaluated quantitatively over the *ground* state,  $\Gamma_7({}^2\text{B} + {}^2\text{E})$ , before the sign of any of the two  $C/D$  ratios can become known. This evaluation was carried out by constructing the  $d^5$  energy matrix (252  $\times$  252) of the total  $C_{4v}$  ligand field Hamiltonian  $H_T$ , or  $H_T = V_{e-e} + V_t + \zeta dJ$ . The tetragonal ligand field perturbation is

$$V_t = 14\pi^{1/2} \left\{ \left( -\frac{5^{1/2}}{5} Ds \right) Y_2^0 + (Dq - Dt) Y_4^0 + \left( \frac{5}{14} \right)^{1/2} Dq [Y_4^4 + Y_4^{-4}] \right\}$$

where  $Y_n$  is a spherical harmonic operator of degree  $n$ , which is appropriately written in equivalent unit tensor<sup>6</sup> form,  $U^n$ , before used, and

$$Dt = \frac{e}{21} \left[ \frac{Q_a r^4}{R_a^5} - \frac{Q_b r^4}{R_b^5} \right]$$

$$Ds = \frac{e}{7} \left[ \frac{Q_a r^2}{R_a^3} - \frac{Q_b r^2}{R_b^3} \right]$$

$$Dq = \frac{e}{6} \left[ \frac{Q_a r^4}{R_a^5} \right]$$

In a general vein the last three quantities,  $Ds$ ,  $Dt$ , and  $Dq$ , are used as parameters for these complex ions,  $[\text{Ru}^{\text{III}}(\text{X})_5\text{L}]_2^{2+}$ . The  $d^5$  electrostatic matrix elements of  $V_{e-e}$  were taken from Girffith's text,<sup>7</sup> and the spin-orbit coupling matrix,  $J$ , and elements of  $U^n$  were constructed by using the reduced-matrix elements of Koster.<sup>8</sup> Errors are avoided by generating only this one large single matrix in the  $SLJM_J$  basis via the  $3J-6J$  formalism. This procedure as used here accounts for complete configuration interaction and all first-order and second-order spin-orbit coupling effects. The eigenvectors of  $H_T$  are then employed to transform the independently constructed angular momentum,<sup>9</sup> or  $\mu_z$ , matrix (252  $\times$  252) of  $|\text{SLJM}_J\rangle$  into the tetragonal ligand field space.

The approximated ligand field parameters for carrying out the calculation for one member of this series,  $[\text{Ru}(\text{NH}_3)_5\text{Br}]_2^{2+}$ , were given the values  $B = 580 \text{ cm}^{-1}$ ,  $C = 4B = 2320 \text{ cm}^{-1}$ , and  $Dq = 3400 \text{ cm}^{-1}$ , as used for  $[\text{Ru}(\text{NH}_3)_6]^{3+}$ ;<sup>13</sup>  $Dt = (2/7)[Dq^{\text{NH}_3} - Dq^{\text{Br}^-}] = 430 \text{ cm}^{-1}$  on the basis of  $[\text{Rh}(\text{NH}_3)_6]^{3+}$  and  $[\text{RhBr}_6]^{3-}$  data;<sup>14</sup> and the Ru(III) free-ion value,<sup>10</sup> 1180  $\text{cm}^{-1}$ , was used for  $\zeta$ .  $Ds$  was given the value 490  $\text{cm}^{-1}$  for the following reason. On using his ESR  $g$  values for  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]_2$  and  $[\text{Ru}(\text{NH}_3)_5\text{I}]_2$ , Stanko<sup>10</sup> empirically derived 860 and 565  $\text{cm}^{-1}$  for the tetragonal splitting of  ${}^2\text{T}_2$ , or  ${}^2\text{B}_2 - 2\text{E}$ , of these chloro and iodo complexes, respectively. On using an intermediate value of 710  $\text{cm}^{-1}$  for  ${}^2\text{B}_2 - 2\text{E}$  of the bromo analog,  $[\text{Ru}(\text{NH}_3)_5\text{Br}]_2^{2+}$ , we derive  $Ds = 490 \text{ cm}^{-1}$ , since we find the splitting of the parent ground state,  ${}^2\text{T}_{2g}$ , is linearly proportional to  $Ds$ . Most important, however, the *sign* of  $\mu_z$  is determined primarily by the *sign* of  $Dt$ , and the latter is definitely known. The final result of

this analysis is that we obtain  $-1.6$  BM for  $\langle \Gamma_7^+ | \hat{\mu}_z | \Gamma_7^+ \rangle$  in the tetragonal basis.

There is available a second and independent analysis for the MCD intensity of the charge-transfer band,  $\Gamma_7(2B_2 + 2E; 2T_{2g}) \rightarrow 2E'(\sim \pi L)$ , of tetragonal complexes. The difference resides in the use of tetragonal state functions for (MA<sub>5</sub>L) which are linear combinations of octahedral functions. This approach<sup>11</sup> leads to the following expression for the *sum* of the band intensities,  $\Gamma_6'$  plus  $\Gamma_7'$

$$\frac{C}{D}(\Gamma_7 \rightarrow 2E) = -\frac{ACg_y}{2(A^2 + C^2)} \text{ BM}$$

Parameters  $A$  and  $C$  are uniquely defined, if ESR  $g_y$  and  $g_z$  values are available and if the orbital reduction factor,  $k$ , is set to unity; i.e.,  $g_y = 2[2ACk + C^2]$  BM and  $g_z = 2[2A^2(k + 1) - C^2]$  BM. The  $g$  values ( $g_z = 2.92$ ,  $g_y = 0.92$ ) are available<sup>10</sup> for the chloro analog,  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ , but not for the bromopentaammine. However, since the MCD structure is also reported here and found similar for the chloro complex, the prediction of the  $C/D$  expression can be used; there is also no reason to expect the sign of  $C/D$  for the bromopentaammine to be different.

### Results and Discussion

The focus of this analysis is on the lowest energy, intense electronic absorption band present in each of the complexes  $[\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{L}]^{2+}$ , where  $L = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NCO}^-$ ,  $\text{NCS}^-$ , etc. The electronic and MCD spectra of three of these complexes,  $L^- = \text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{NCO}^-$ , are shown in Figure 1, and the particular electronic bands in question are at 346 nm (28.9 kK), 328 nm (30.5 kK), and 397 nm (25.2 kK) for  $\text{NCO}^-$ ,  $\text{Cl}^-$ , and  $\text{Br}^-$ , respectively. There are several reasons for assigning each of these to be  $L \rightarrow \text{Ru}$  in nature,<sup>2,3</sup> i.e.,  $\sim \pi L \rightarrow t_2(\sim 4d \text{ Ru})$ . First, each such electronic absorption band is quite intense; e.g., for the three above examples  $\epsilon_{\text{max}} \sim 2000\text{--}3500$ . Second, we have established that the electronic intensity of the band of the bromo complex is independent of temperature between room temperature ( $\sim 300^\circ\text{K}$ ) and that of liquid nitrogen ( $\sim 87^\circ\text{K}$ ) (Figure 1). Third, in the halogen series  $[\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{X}]^{2+}$ , where  $X = \text{Cl}^-$ ,  $\text{Br}^-$ , or  $\text{I}^-$ , the intense band shifts increasingly toward the red,<sup>3,12</sup> i.e.,  $\text{Cl}^-$  at 328 nm (30.5 kK),  $\text{Br}^-$  at 397 nm (25.2 kK), and  $\text{I}^-$  at 543 nm (18.4 kK). This direction parallels the ease with which an electron is transferred from the halogen and is consistent with the suggested charge-transfer process  $L \rightarrow \text{Ru}$ . Since spin-orbit coupling is expected to be significant within the open shells of the ground configuration,  $e^3(\sim xz, yz \text{ Ru})$  or  $b_2^1(\sim xy \text{ Ru})$ , and of the excited configuration,  $e^3(\sim \pi L)$ , the band was previously<sup>2</sup> discussed in terms of its possible spin-orbit origin,  $\Gamma_7 \rightarrow \Gamma_6'(2E)$  and  $\Gamma_7 \rightarrow \Gamma_7'(2E)$ , of the excited state  $2E'(\sim \pi L)$ . However, the energy order of  $\Gamma_6'$  and  $\Gamma_7'$ , established here from MCD as  $\Gamma_7' < \Gamma_6'$ , remained to be determined (Figure 2).

The spin-doublet excited state derived from  $L \rightarrow \text{Ru}$  charge transfer involves most logically the motion of a  $\pi$  electron from  $L$ , so that the excited configuration  $[(\sim \pi L)^3(\sim xz, yz \text{ Ru})^4(\sim xy \text{ Ru})^2]$  results. This gives rise to excited state  $2E'$ , which upon spin-orbit coupling will split into  $\Gamma_6'$  and  $\Gamma_7'$ , with the magnitude of the splitting,  $\Delta E$ , approximately equal to the one-electron spin-orbit coupling constant of ( $\sim \pi L$ ). For the halopentaammines this ought to amount to an *upper* limit (at least for  $L = \text{Br}, \text{I}$ ) of the halogen atom's  $\zeta_{\text{mp}}$  value. Electronic spectra, however, reveal only a single band for  $\Gamma_7 \rightarrow 2E$ . As the first example, whether or not  $\Gamma_6'$  and  $\Gamma_7'$  have in reality equal intensities in  $[\text{Ru}(\text{NH}_3)_5\text{NCO}]^{2+}$  (Figure 1A) a single band is expected to be observed in the electronic absorption or MCD spectra, since  $\zeta$  of ( $\sim \pi \text{NCO}$ ) is expected to be very small. Figure 1A shows, in fact, that this is observed experimentally; i.e., MCD and electronic maxima coincide (346 nm or 28.9 kK) and there is no splitting of either one.

The corresponding spectrum of  $[\text{Ru}(\text{NH}_3)_5\text{Br}]^{2+}$ , which is the other extreme of these three complexes of Figure 1, since  $\zeta$  of ( $\sim \pi \text{Br}$ ) is much larger ( $\zeta_{\text{Br}} = 2460 \text{ cm}^{-1}$ ), demonstrates that  $\Gamma_6'$  and  $\Gamma_7'$  components (analysis given below) are separated much farther ( $1200 \text{ cm}^{-1}$ ) (see Figure 1C). On the other hand,  $\zeta_{\text{Cl}}$  is significantly smaller ( $590 \text{ cm}^{-1}$ ) than  $\zeta_{\text{Br}}$ , and indeed we find that while  $\Gamma_6'$  and  $\Gamma_7'$  of the chloropentaammine are separated, the apparent separation ( $400 \text{ cm}^{-1}$ ) is less than for the bromo complex (Figure 1). The energy order of  $\Gamma_6'$  and  $\Gamma_7'$  can be established on the basis of the sign of the Faraday  $C$  term of  $\Gamma_7 \rightarrow \Gamma_6'(2E')$  and the net sign of  $2E'$  as follows.

It was shown above that

$$\frac{C}{D}[\Gamma_7 \rightarrow \Gamma_6'] = \frac{1}{2} \langle \Gamma_7^+ | \hat{\mu}_z | \Gamma_7^+ \rangle$$

and our computation yields the value  $-1.6$  BM for the integral. Therefore,  $\Gamma_7 \rightarrow \Gamma_6'$  will have *positive* MCD intensity,  $\theta$ , due to this  $C$  term since

$$[\theta]_{\text{M}} = (-)\gamma \left[ \frac{C(\Gamma_7 \rightarrow \Gamma_6') f_s}{kT} \right]$$

where  $\gamma$  is a constant number and  $f_s$  is a band-shape function. Indeed, the *higher* energy  $2E'$  component of  $[\text{Ru}(\text{NH}_3)_5\text{Br}]^{2+}$  (Figure 1C) is shown to have the appropriate temperature dependence and sign which allow one to assign it to  $\Gamma_6'$ . Furthermore, the net experimental MCD intensity is positive, which is entirely consistent with our predictions, viz.,  $(C/D)[\Gamma_7 \rightarrow \Gamma_6']$  (negative value and positive intensity) is much larger than  $(C/D)[\Gamma_7 \rightarrow \Gamma_7']$  (positive value and negative intensity), because the denominator of the latter expression (vide supra), or  $(1 + \langle z \rangle^2 / (\langle x \rangle^2 + \langle y \rangle^2))$ , is expected to be much larger than unity. The last conclusion derives from the fact that the  $\Gamma_7 \rightarrow \Gamma_7'$  electronic absorption band of the analogous iodo complex has a  $\pi:\sigma$  polarization ratio<sup>10</sup> of approximately 18. This ratio is expected to be even larger for the bromopentaammine, since the  $\sigma$  polarization is a second-order effect whose presence depends on the magnitude of spin-orbit coupling. Additionally, on using our experimentally derived net  $C$  parameter for  $2E'$ , the dipole strength, and the polarization ratio of 18 for  $\Gamma_7 \rightarrow \Gamma_7'$ , etc., we derive a net  $C$  parameter of  $-0.03 \text{ D}^2 \text{ BM}$ , which is in excellent agreement with the experiment value,  $-0.026 \text{ D}^2 \text{ BM}$ .

We add here that the above conclusions are also consistent with the prediction of the net MCD activity for  $\Gamma_7 \rightarrow 2E'(\Gamma_6' + \Gamma_7')$  when the perturbation formula (vide supra)

$$\frac{C}{D}(\Gamma_7 \rightarrow 2E) = -\frac{ACg_y}{2(A^2 + C^2)} \text{ BM}$$

is used. On employing the  $g$  values of the chloropentaammine (vide supra),  $\zeta_{4d} = 1180 \text{ cm}^{-1}$ , and orbital reduction factor  $k = 1$  and solving the secular equation of the tetragonal components of the  $2T_{2g}(t_{2g}^5)$  ground state, we obtain  $C/D = -0.18 \text{ BM}$ . This agrees with the sign prediction made with our more complete  $C_{4v}$  model ( $\sim -0.8 \text{ BM}$ ), so that the sign predicted by this second model is also consistent with our experimentally determined sign. We are also led to the conclusion that the room-temperature MCD activity ( $(B + C/kT)$  is  $-6.3 \times 10^{-4} \text{ D}^2 \text{ BM cm}$ ) of  $2E'$  is largely  $B$  term in nature (experimental  $C/kT$  is  $-1.3 \times 10^{-4} \text{ D}^2 \text{ BM cm}$  at  $295^\circ\text{K}$ ). The close proximity of  $\Gamma_6$ ,  $\Gamma_7^b$ , and  $\Gamma_7^a$  of  $2T_{2g}(t_{2g}^5)$  may in large part account for this.

A final point of interest is that the solution of the secular equation predicts  $\Gamma_7^a(0) < \Gamma_6(1463 \text{ cm}^{-1}) < \Gamma_7^b(2746 \text{ cm}^{-1})$ . While  $\Gamma_7$  was expected to be the ground state, it was found with interest that  $\Gamma_7^a$  of the chloropentaammine contains an unequal mixture of the parent tetragonal components,  $2B_2$

(~10%) and  ${}^2E$  (90%), of  ${}^2T_{2g}$ . This leads us to point out that, even when large spin-orbit interaction is present, arguments about the energy order of  ${}^2T_{2g}$  descendants, i.e., whether  ${}^2E[(xz, yz)^3(xy)^2]$  is higher or lower in energy than  ${}^2B_2[(xy)^1(xz, yz)^4]$ , are still applicable, and in this case are as predicted,  ${}^2E < {}^2B_2$  (vide supra).

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## Studies of Ammineaquocobalt(III) Chemistry. Kinetics and Mechanisms of Formation and Dissociation of Monochlorodiammineaquocobalt(III) Complexes and of the Reduction of *cis*-Diammineaquocobalt(III) Species by Br<sup>-</sup> in Acid Perchlorate Solution<sup>1</sup>

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The synthesis and characterization of nitrate and perchlorate salts of *cis*-Co(NH<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub><sup>3+</sup> and *fac*-Co(NH<sub>3</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub><sup>3+</sup> is described. Reactivity studies indicate that diammineaquo species are moderately strong oxidizing agents in acid solution but are much more inert to substitution than is Co<sup>3+</sup><sub>aq</sub>. The rate law for the approach to equilibrium in the reaction between *cis*-Co(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup><sub>aq</sub> and Cl<sup>-</sup> in the concentration ranges [H<sup>+</sup>] = 0.10–1.20 *M* and [Cl<sup>-</sup>] = 0.10–1.60 *M* at ionic strength 2.0 *M* (NaClO<sub>4</sub>, HClO<sub>4</sub>) over the temperature range 28.0–47.6° is given by  $d \ln [\text{Co}(\text{NH}_3)_2\text{Cl}^{2+}_{\text{aq}}] / dt = A'[\text{Cl}^-] / [\text{H}^+] + B' / [\text{H}^+]$ , where  $A' = (1.50 \pm 0.03) \times 10^{-4} \text{ sec}^{-1}$  and  $B' = (2.7 \pm 0.2) \times 10^{-5} \text{ sec}^{-1}$  at 28.0°. The inverse acidity dependence of the rate law is ascribed to the involvement of hydroxodiammineaquocobalt(III) species in the formation and dissociation of the monochlorodiammineaquocobalt(III) complex. The rate law for the *cis*-Co(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup><sub>aq</sub> oxidation of Br<sup>-</sup> to Br<sub>2</sub> under similar experimental conditions follows the rate law  $-d[\text{Co}^{\text{III}}] / dt = 2d[\text{Br}_2] / dt = (C + D / [\text{H}^+])[\text{Co}^{\text{III}}][\text{Br}^-]$ , where  $C = (6.0 \pm 0.2) \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$  and  $D = (1.7 \pm 0.2) \times 10^{-4} \text{ sec}^{-1}$  at 28.0°. Consideration of the rate laws and kinetic parameters obtained in these two reactions suggests that the rate-determining process in the oxidation of Br<sup>-</sup> by Co(NH<sub>3</sub>)<sub>2</sub>OH<sup>2+</sup><sub>aq</sub> is substitution of the reductant at the metal center. The possible stereochemical directing influence of inner-sphere hydroxide ion is discussed; it appears that a trans-directing influence predominates in these aquo complexes.

## Introduction

The Co<sup>3+</sup><sub>aq</sub> ion is much more labile to substitution than are typical ammineaquocobalt(III) complexes.<sup>3</sup> This unusual property has prompted speculation concerning the decreasing availability of labile, high-spin electronic states of cobalt(III) in the series Co(NH<sub>3</sub>)<sub>*n*</sub>(H<sub>2</sub>O)<sub>6-*n*</sub><sup>3+</sup><sub>aq</sub> as *n* increases from 0 to 5.<sup>4,5</sup>

Although a wealth of data has been accumulated concerning the kinetic properties of ammineaquocobalt(III) complexes with *n* ≥ 4,<sup>6</sup> comparatively little is known about aquocobalt(III) species which carry fewer ammonia molecules.<sup>7-9</sup>

This paper describes the synthesis and characterization of solid *cis*-diammineaquocobalt(III) and *fac*-triammineaquocobalt(III) nitrates and perchlorates, together with studies of the spectral, substitutional, and redox properties of diammineaquo species in acid perchlorate media. Kinetic and spectral data obtained from a detailed investigation of the kinetics of the base-catalyzed reactions of the diammineaquocobalt(III) species with chloride and bromide ions are reported.

## Experimental Section

**Reagents and Analytical Procedures.** The water used throughout this work was doubly distilled from an all-glass apparatus. Sodium perchlorate stock solutions were prepared by neutralization of perchloric acid with sodium carbonate and contained no detectable chloride ion impurities. These solutions were standardized gravimetrically. Reagent grade sodium chloride and sodium bromide were dried at 110° for 8 hr prior to making up stock solutions. All other chemicals were of reagent grade and were used without further purification.

Concentrations of cobalt(II) were determined spectrophotometrically as the thiocyanato complex in 50% v/v aqueous acetone ( $\epsilon_{623} = 1842 \text{ M}^{-1} \text{ cm}^{-1}$ ).<sup>10</sup> Cobalt(III) was determined by treatment of an aliquot with a measured excess of acidic iron(II) solution;<sup>7</sup> the remaining iron(II) was titrated with standardized chromium(VI) using diphenylamine as the indicator. The stoichiometric cobalt concentrations of reagent solutions were conveniently and accurately measured by treatment of aliquots with 50% w/v aqueous NaOH to pH 13 and dropwise addition of concentrated HCl to bring the pH to 5. This treatment resulted in quantitative reduction to cobalt(II), which was analyzed by the thiocyanate-acetone procedure.<sup>11</sup>

The stoichiometric ammonia content of reagent solutions was