

yielded positive values.<sup>7</sup> Initially, the small magnitudes of  $a$  for the chloro complexes led us to consider the possibility of negative contributions, but molecular orbital analyses of these systems<sup>17</sup> indicate that  $D$  is negative for  $[\text{FeCl}_2\text{H}_2\text{O}]^{2-}$ . The signs of  $a$  and  $D$  are opposite according to our experiments; thus no evidence of negative contributions to  $a$  has

been found. The magnitude of  $a$  does appear to depend strongly on the ligand, and further studies of the quartic parameters in molecular complexes are needed to clarify their origins.

Registry No.  $(\text{NH}_4)_2[\text{FeCl}_2\text{H}_2\text{O}]$ , 16774-56-4;  $(\text{NH}_4)_2[\text{InCl}_2\text{H}_2\text{O}]$ , 17949-59-6;  $\text{Fe}^{3+}$ , 20074-52-6.

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## Electron Resonance of Some Tetraamminechromium(III) Complexes

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Powder electron paramagnetic resonance (epr) spectra of  $\text{trans-}[\text{Cl}_2(\text{NH}_3)_4\text{Cr}]^+$  and  $\text{trans-}[\text{Cl}(\text{H}_2\text{O})(\text{NH}_3)_4\text{Cr}]^{2+}$  have been examined in a variety of host lattices. Even though the preparations of the chromium complexes yield mixtures of species and multiple spectra, a comparison of the data for different hosts allows an unequivocal assignment of the spectra. The spin-Hamiltonian parameters are shown to be molecular properties and are compared with the parameters of the pentaamminechromium analogs.

### Introduction

In a series of electron resonance (epr) studies of chromium(III) complexes we have been examining the effects of lattice perturbations and chemical substitution on the  $g$  shifts and the zero-field splittings.<sup>1-4</sup> Previous studies<sup>3</sup> of the chloro- and aquopentaamminechromium(III) complexes give an excellent basis for comparison with the trans disubstituted chloro- and aquotetraamminechromium(III) complexes. The disubstituted complexes are much less stable in solution precluding slow crystal growth; thus, epr studies of powder samples are necessary. The use of powder samples is convenient because this allows rapid evaluation of the effects of temperature and host lattice variations. In this study we have attempted to determine the intramolecular spin-Hamiltonian parameters for  $\text{trans-}[\text{Cl}_2(\text{NH}_3)_4\text{Cr}]^+$ ,  $\text{trans-}[\text{Cl}(\text{H}_2\text{O})(\text{NH}_3)_4\text{Cr}]^{2+}$ , and  $\text{trans-}[(\text{H}_2\text{O})_2(\text{NH}_3)_4\text{Cr}]^{3+}$ . Preparations of the latter complex did not yield interpretable spectra.

The theory of the spin-Hamiltonian parameters for trans disubstituted chromium(III) complexes is essentially the same as that for the monosubstituted complexes.<sup>1</sup> The  $g$  factors are determined by the orbital angular momentum admixture of excited states into the ground state. This means that for these tetragonal complexes  $g_z$  is determined by  $\sigma$ - $\pi$  mixing due to an effective rotation about the  $z$  axis and is thus a property of the bonding of the equatorial ligands alone. Similarly,  $g_{x,y}$  is determined by an admixture involving ligands of both axial and equatorial types. Thus, in a mixed ligand tetragonal complex the value of  $g_{x,y}$  is expected to lie in the range between the values of the  $g$  factors characteristic of the axial and equatorial ligands. These qualitative expectations were borne out with monosubsti-

tuted complexes,<sup>3</sup> and similar results are found for the disubstituted complexes.

The axial zero-field splitting parameter,  $D$ , measures the difference between the spin-orbit mixing about the  $z$  axis and that about an axis in the  $xy$  plane. Thus, if inductive effects are small, a disubstituted complex should have an axial splitting,  $D$ , of about twice the magnitude of the corresponding monosubstituted complex. The rhombic zero-field splitting parameter,  $E$ , measures differences in the spin-orbit mixing about the  $x$  and  $y$  directions. Thus,  $E$  should vanish for a tetragonal complex. The observed values of  $E$  reflect either lattice distortions of the complex or the effect of a low symmetry axial ligand such as water. No attempt will be made to examine the spin-Hamiltonian parameters with a detailed molecular orbital fitting as has been done in previous work.<sup>1,3</sup> Rather we content ourselves with a qualitative interpretation of the magnitudes and differences of the spin-Hamiltonian parameters.

### Experimental Section

Each of the guest and host compounds used in this study was first prepared and identified separately before magnetically dilute powder samples were made. Acid cleavage of the ion<sup>5</sup>  $[(\text{NH}_3)_5\text{CrOH}(\text{NH}_3)_4\text{Cl}]^{4+}$  provided entry into the series of trans disubstituted tetraamminechromium(III) complexes.<sup>6</sup> The  $\text{trans-}$ dichloro-tetraamminechromium(III) chloride ( $\text{trans-}[\text{Cl}_2(\text{NH}_3)_4\text{Cr}]\text{Cl}$ ) and  $\text{trans-}$ chloroaquatetraamminechromium(III) chloride ( $\text{trans-}[\text{Cl}(\text{H}_2\text{O})(\text{NH}_3)_4\text{Cr}]\text{Cl}_2$ ) were obtained directly upon cleavage of the binuclear complex and aqation of the latter salt yielded<sup>7</sup>  $\text{trans-}[(\text{H}_2\text{O})_2(\text{NH}_3)_4\text{Cr}](\text{ClO}_4)_3$ . Chloropentaamminechromium(III) chloride and the cobalt compounds  $\text{trans-}[\text{Cl}_2(\text{NH}_3)_4\text{Co}]\text{Cl}$ ,  $\text{trans-}[\text{Cl}(\text{H}_2\text{O})(\text{NH}_3)_4\text{Co}]\text{Cl}_2$ , and  $\text{trans-}[(\text{H}_2\text{O})_2(\text{NH}_3)_4\text{Co}]\text{Cl}_2$  were obtained by standard methods<sup>8</sup> as was the  $\text{trans-}[\text{Cl}_2(\text{NH}_3)_4\text{Rh}]\text{Cl}$ .<sup>9</sup> The  $[\text{Cl}(\text{NH}_3)_5\text{Co}]\text{Cl}_2$  was recrystallized from commercially available material.

Magnetically dilute samples of chromium(III) complexes were obtained as approximately 1% impurities in the cobalt or rhodium

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Table I. Spin-Hamiltonian Parameters for the Different Guest-Host Combinations<sup>a</sup>

Guest	Host	<i>D</i> , G	<i>E</i> , G	<i>g<sub>z</sub></i>	<i>g<sub>x,y</sub></i>
[Cl(NH <sub>3</sub> ) <sub>5</sub> Cr] <sup>2+</sup>	[ClH <sub>2</sub> O(NH <sub>3</sub> ) <sub>4</sub> Co]Cl <sub>2</sub>	1127.8	13.9	1.9860	1.9867
[ClH <sub>2</sub> O(NH <sub>3</sub> ) <sub>4</sub> Cr] <sup>2+</sup>		2088	129	1.9853	1.9845
[Cl(NH <sub>3</sub> ) <sub>5</sub> Cr] <sup>2+</sup>	[Cl(NH <sub>3</sub> ) <sub>5</sub> Co]Cl <sub>2</sub>	948.0	48.7	1.9858	1.9867
[ClH <sub>2</sub> O(NH <sub>3</sub> ) <sub>4</sub> Cr] <sup>2+</sup>		2096.3	141.1	1.9866	1.9844
[Cl <sub>2</sub> (NH <sub>3</sub> ) <sub>4</sub> Cr] <sup>+</sup>	[Cl <sub>2</sub> (NH <sub>3</sub> ) <sub>4</sub> Co]Br	1745.6	156.5	1.9860 <sup>b</sup>	1.9868 <sup>b</sup>
[ClH <sub>2</sub> O(NH <sub>3</sub> ) <sub>4</sub> Cr] <sup>2+</sup>		1977.5	199.1	1.986 <sup>b</sup>	1.985 <sup>b</sup>
[Cl <sub>2</sub> (NH <sub>3</sub> ) <sub>4</sub> Cr] <sup>+</sup>	[Cl <sub>2</sub> (NH <sub>3</sub> ) <sub>4</sub> Rh]Cl	1690.5	160.7	1.9862	1.9869
[ClH <sub>2</sub> O(NH <sub>3</sub> ) <sub>4</sub> Cr] <sup>2+</sup>		2003	165.9	1.9863	1.9868
[Cl <sub>2</sub> (NH <sub>3</sub> ) <sub>4</sub> Cr] <sup>+</sup>	[Cl <sub>2</sub> (NH <sub>3</sub> ) <sub>4</sub> Rh]Cl	1753.0	115.6	1.986 <sup>b</sup>	1.987 <sup>b</sup>
[ClH <sub>2</sub> O(NH <sub>3</sub> ) <sub>4</sub> Cr] <sup>2+</sup>	(77°K)	2137.9	118.5	1.986 <sup>b</sup>	1.987 <sup>b</sup>

<sup>a</sup> Two spectra are obtained with each host lattice. The first four lines correspond to spectra obtained from the chloroaquochromium(III) preparation. The latter spectra are all obtained from the dichlorotetraamminechromium(III) preparation. <sup>b</sup> These *g* values are uncertain because of possible frequency measurement error. This does not affect *D* and *E* nor the relative *g* values.

hosts. Due to the rapid aquation of both the chromium(III)<sup>7</sup> and cobalt(III)<sup>10</sup> acidotetraammines, the samples were recrystallized quickly. The saturated solution of the cobalt host with a 1% chromium(III) impurity was filtered into a saturated solution of ammonium halide. The resulting precipitate was ground to a fine powder and packed into a capillary. Good spectra reproducible in both line positions and relative intensities were obtained when the entire process (dissolution, filtration, reprecipitation) took less than 3 min. The samples were reasonably stable as dry powders. Previous work on chromium(III) ammine complexes<sup>9,11</sup> indicated that powder samples should be prepared by slow coprecipitation, but a sample of [Cl(NH<sub>3</sub>)<sub>5</sub>Cr]Cl<sub>2</sub> prepared as described above gave a spectrum like the slow grown sample as well as a minor spectrum with an 18% larger zero-field splitting (*D* = 1120 G). This minor spectrum is presumed to arise from misoriented guest ions in the host at lattice sites.

The spectra of both the dichlorotetraamminechromium and chloroaquochromium complexes in analogous cobalt hosts appeared as doubled spectra as shown in Figures 1 and 2, respectively. Various origins of the multiple spectra such as guest misorientation, cis-trans isomerism, and solvation of either the guest or the host were considered. Use of the much more stable dichlorotetraamminerhodium(III) salt as a host gave spectra with similar splittings and intensities which effectively eliminated any consideration of host lattice effects as the origin of the multiple spectra. The relative intensities of the spectra preclude guest misorientation as a cause of spectral doubling because misoriented guests would give very weak spectra. Cis-trans isomerization has not been observed for these complexes<sup>6,7</sup> and was not seriously considered. The sources of the second spectra in both cases were identified as impurities by comparison of the spectra in different host lattices. The impurity in the dichloro sample proved to be the aquochloro complex, and the impurity in the aquochloro complex proved to be chloropentaamminechromium(III). These identifications can be seen from comparisons of the data in Table I. The *D* values for the chloroaquo preparation are seen to be about 2000 G for the outside spectrum and near 1000 G for the inside spectrum. In the spectra obtained for the dichloro preparation the outside spectrum *D* is also around 2000 G, while the inside spectra have *D* close to 1700 G. The chloroaquo guest ion in chloropentaamminecobalt(III) chloride host has an interior spectrum which is identifiable as the chloropentaamminechromium(III) ion.<sup>3</sup> Similarly, a substitution of the dichlorotetraamminechromium(III) sample into chloropentaamminecobalt gave a messy spectrum from which one could identify the chloroaquo species in significant quantity. Thus, the spectra with *D* values near 1000, 1700, and 2000 G are attributable respectively to [Cl(NH<sub>3</sub>)<sub>5</sub>Cr]<sup>2+</sup>, [Cl<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>Cr]<sup>+</sup>, and [ClH<sub>2</sub>O(NH<sub>3</sub>)<sub>4</sub>Cr]<sup>2+</sup>. The impurities are as expected with the chloroaquo impurity in the dichloro sample being the result of rapid aquation during sample preparation. The chloropentaammine impurity in the aquochloro sample is also expected, as it is a by-product in the preparation of the chloroaquo complex.<sup>7</sup> The similarity of the charge distribution of the latter two complexes makes the separation of these species difficult.

All spectra were taken on a Varian E-12 spectrometer at 35 GHz. Line positions were reproducible within ±1 G which was the measurement accuracy with a Spectromagnetic Industries NME gauss meter Model 5200. Spectra were assigned according to the line shapes<sup>2</sup> and fitted by diagonalizing the spin Hamiltonian. The resonant fields

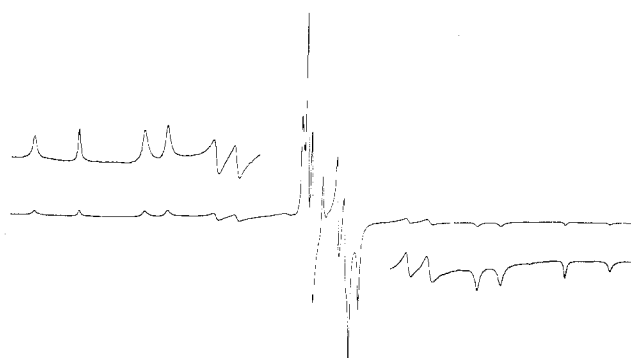


Figure 1. The powder epr spectrum of *trans*-[Cl<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>Cr]Br in *trans*-[Cl<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>Rh]Br at 35 GHz. The wing lines are also shown with a fivefold amplification for clarity.

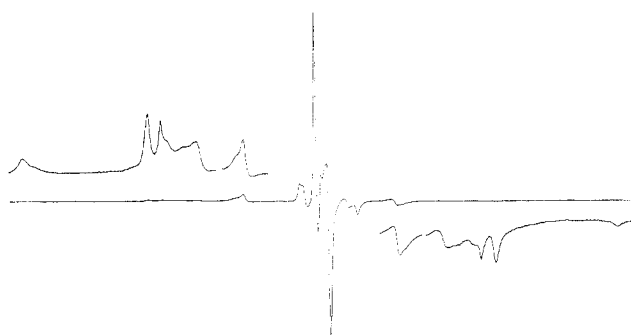


Figure 2. The powder epr spectrum of *trans*-[Cl(H<sub>2</sub>O)(NH<sub>3</sub>)<sub>4</sub>Cr]Cl<sub>2</sub> in *trans*-[Cl(H<sub>2</sub>O)(NH<sub>3</sub>)<sub>4</sub>Co]Cl<sub>2</sub> at 35 GHz. The extreme wings are also shown with ×40 amplification, and the separated interior wings have fivefold amplification.

corresponding to the spectra shown in Figures 1 and 2 are given in Table II.

## Discussion

Before we make detailed considerations of the spin-Hamiltonian parameters, we must establish the extent to which these parameters represent intramolecular effects and the magnitude of any lattice contributions to these parameters. Previous studies of acidopentaamminechromium(III) complexes have demonstrated the insensitivity of all of the spin-Hamiltonian parameters to variations in counterion charge and symmetry and established that for tetragonal ammine complexes  $g_z = 1.9860 \pm 0.0005$ .<sup>3</sup> The  $g_z$  values in Table I extend this observation and illustrate that the *g* factors of these systems have at most a very mild sensitivity to the environment. The larger *D* value in each of the five spectra reported in Table I has been assigned to the *trans*-[Cl(H<sub>2</sub>O)(NH<sub>3</sub>)<sub>4</sub>Cr]<sup>2+</sup>. This represents a wide range of host lattices with only a 7.5% variation in the value of *D*, which indicates that *D* is basically a molecular parameter

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**Table II.** Resonant Magnetic Fields (G) for the Spectra in Figures 1 and 2 Assigned as  $trans-[Cl_2(NH_3)_4Cr]^{2+} = A$ ,  $trans-[Cl(H_2O)(NH_3)_4Cr]^{2+} = B$ , and  $[Cl(NH_3)_5Cr]^{2+} = C$

Host			
$trans-[Cl_2(NH_3)_4Rh]Br$		$trans-[Cl(H_2O)(NH_3)_4Co]Cl_2$	
$\nu$ , GHz			
34.624		34.612	
Guest			
A	B	C	D
9,077	8,451	10,199	8,285
10,297	9,983	11,285	10,025
11,256	10,963	11,395	10,741
12,234	12,163	12,372	12,162
12,297	12,234	12,453	12,453
12,447	12,447	13,500	14,175
13,649	13,941	13,617	14,924
14,612	14,941	14,710	16,635
15,835	16,460		

with minor lattice contributions. A similar observation is applicable to the three spectra ( $D \sim 1700$  G) assigned to  $trans-[Cl_2(NH_3)_4Cr]^{2+}$ . The 20% increase of  $D$  for  $[Cl(NH_3)_5Cr]^{2+}$  when the ion is placed in  $trans-[Cl(H_2O)(NH_3)_4Co]^{2+}$  is probably attributable to either hydrogen-bonding effects or the differing steric requirements of the ammonia and water ligands. The rhombic zero-field splitting parameter  $E$  is clearly much more sensitive to the lattice than the other spin-Hamiltonian parameters, and each case will require specific comment.

The axial zero-field splitting parameters  $D$  for aquopentaamminechromium(III) and chloropentaamminechromium(III) complexes are 921 and 950 G, respectively.<sup>3</sup> Thus, additivity of axial zero-field splittings would give  $D \sim 1900$  G for trans disubstituted chloro- and aquotetraamminechromium(III) complexes. The observed values of 1700 and 2100 G indicate that there is such a gross additivity, but the deviation from additivity is much larger than the lattice effects. These deviations can be accounted for by an inductive effect between the trans positions. For like ligands in the trans positions there is a competition for the bonding capacity of the metal because the bonding demands of the two ligands are identical. Thus, similar ligands in the trans positions should yield a zero-field splitting somewhat less than twice the value for the monosubstituted complex. If the bonding demands of the trans ligands are dissimilar, then the disubstituted complex may have a zero-field splitting which is somewhat larger than the sum of the values of the monosubstituted complexes. This picture of the inductive contributions to the zero-field splitting is in accord with the data presented here, but there is not sufficient information available to determine whether the model is generally applicable. The gross additivity of  $D$  indicates that the sign of  $D$  is the same for  $trans-[Cl_2(NH_3)_4Cr]^{2+}$ ,  $[H_2O(NH_3)_5Cr]^{3+}$ ,  $[Cl(NH_3)_5Cr]^{2+}$ , and  $trans-[Cl(H_2O)(NH_3)_4Cr]^{2+}$ . It appears that a lattice compression tends to increase  $D$  in these com-

plexes. This effect is observed for both complexes in the dichlororhodium host at low temperature and in the observation of a large increase of the zero-field splitting for  $[Cl(NH_3)_5Cr]^{2+}$  when misoriented in the analogous cobalt host.

The first observation relative to the rhombic parameter  $E$  is that for  $[Cl(NH_3)_5Cr]^{2+}$   $E$  is an almost negligible 14 G in the  $trans-[Cl(H_2O)(NH_3)_4Co]Cl_2$  host as compared to about 50 G in the more natural  $[Cl(NH_3)_5Co]Cl_2$ . This indicates that the latter host incorporates a rhombic contribution and that the guest is essentially tetragonal which was not clear in previous studies.<sup>3</sup> The rhombic parameter  $E$  (129 G) for  $trans-[Cl(H_2O)(NH_3)_4Cr]^{2+}$  in the analogous cobalt host is almost identical with the 125-G value observed for the monosubstituted aquo complex.<sup>3</sup> And this value is observed in a host which, as we have seen above, does not possess a large rhombic lattice distortion. Thus, we believe that the rhombic splitting of the aquo complexes is intramolecular and arises from the  $\pi$ -bonding interaction with the water ligand.<sup>3,12,13</sup> The larger  $E$  values for the chloroaquo complexes in the other host lattices listed in Table I are the result of a superimposition of the rhombic contributions from the lattice onto the intramolecular rhombic term. The rhombic terms observed for  $trans-[Cl_2(NH_3)_4Cr]^{2+}$  must arise entirely from the lattice. This is supported by the large decrease in  $E$  for the rhodium host when the temperature is lowered to 77° K.

The values of  $g_z$  for all the complexes examined are near 1.9860 as they should be for chromium complexes with four ammine ligands in the equatorial plane. This extends to seven the number of complexes which agree with the correlation.<sup>3,4</sup> While the accuracy of the  $g$  factors does not allow detailed comparisons, it is clear from Table I that the  $g$  factors for  $trans-[Cl_2(NH_3)_4Cr]^{2+}$  are similar to those of  $[Cl(NH_3)_5Cr]^{2+}$  with  $g_{x,y} > g_z$ . The chloroaquo complex appears to have  $g_z \geq g_{x,y}$  indicating that both the chlorine and water ligands make contributions to the value of  $g_{x,y}$ .

In summary, the behavior of the spin-Hamiltonian parameters for the trans disubstituted tetraamminechromium(III) complexes are in accord with expectations based upon data for the monosubstituted complexes. In particular, the zero-field splittings are additive with possible inductive effects at the 10% level and with still smaller lattice effects. The  $g$  factors are also in accord with expectations. Before these conclusions can be considered final, it is desirable that several other disubstituted complexes including cis complexes be studied.

**Registry No.**  $[Cl(NH_3)_5Cr]^{2+}$ , 14482-76-9;  $trans-[ClH_2O(NH_3)_4Cr]^{2+}$ , 19052-43-8;  $trans-[Cl_2(NH_3)_4Cr]^{2+}$ , 22452-49-9;  $trans-[ClH_2O(NH_3)_4Co]Cl_2$ , 13820-61-6;  $[Cl(NH_3)_5Co]Cl_2$ , 13859-51-3;  $trans-[Cl_2(NH_3)_4Co]Br$ , 51472-28-7;  $trans-[Cl_2(NH_3)_4Rh]Cl$ , 37488-14-5;  $trans-[Cl_2(NH_3)_4Rh]Br$ , 51472-29-8.

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