

Powder Electron Paramagnetic Resonance Studies of Some Pentaamminechromium(III) Complexes

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Electron paramagnetic resonance spectra of magnetically dilute powder samples have been used to study bonding effects in $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$, $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$, and $[\text{Cr}(\text{NH}_3)_5\text{Br}]^{2+}$. The influence of the lattice has been shown to be negligible for the former two complexes which demonstrates the intramolecular origin of the spin-Hamiltonian parameters. Bonding of the equatorial ammine ligands was shown to be invariant to the axial ligand changes. The zero-field splitting parameters, appear to be sensitive to π -bonding effects with significant π bonding being indicated for the water ligand in the aquo complex.

Introduction

Ideas concerning the origins of the spin-Hamiltonian parameters obtained from electron paramagnetic resonance (epr) have evolved from the early crystal field model¹⁻³ through simple molecular orbital extensions⁴⁻⁶ to the inclusion of charge-transfer state admixture,⁷ spin-orbit effects on the ligands,⁷⁻⁹ and metal spin-orbit reduction effects.^{10,11} The formulation of an essentially complete theory for d^3 ions¹¹ together with methods for evaluating all of the necessary parameters¹² allows detailed comparisons of metal-ligand bonding in a variety of complexes provided that the effects of the lattice are small. The advent of powder epr spectra techniques for high-spin systems¹³ has eliminated the necessity of performing detailed angular dependence studies in order to determine the spin-Hamiltonian parameters and allows rapid experimental evaluation of lattice effects by the simple expedient of varying the host compound.

In this study we have determined the spin-Hamiltonian parameters g_{\parallel} , g_{\perp} , D , and E for a series of tetragonal chromium(III) complexes $[\text{Cr}(\text{NH}_3)_5\text{X}]$ with $\text{X} = \text{H}_2\text{O}$, Cl^- , and Br^- . We also examined the lattice (counterion) dependence of these parameters for $\text{X} = \text{H}_2\text{O}$ and Cl^- .

Qualitative and later quantitative considerations about the bonding implications of the spin-Hamiltonian parameters are facilitated by examining the molecular orbital expressions for the g shifts, Δ_{\parallel} and Δ_{\perp} , and for the axial zero-field splitting parameter, D , for a d^3 ion in C_{4v} symmetry. The following equations correct some misprints in a previous paper¹¹

$$\Delta_{\parallel} = 2 \left(\frac{(2\beta\beta_1\lambda_M - \beta'\beta'_1\lambda_L)(2\beta\beta_1 - 2\beta_1\beta'_1S_{b_2} - 2\beta\beta'_1S_{b_1} - \beta'\beta'_1)}{\Delta E(^4B_2)} - \frac{(2\beta\beta_{1b}\lambda_M + \beta'\beta'_{1b}\lambda_L)(2\beta\beta_{1b} - 2\beta'\beta'_{1b}S_{b_2} + 2\beta\beta'_{1b}S_{b_1} + \beta'\beta'_{1b})}{\Delta E(^4B_2^c)} \right) \quad (1)$$

$$\Delta_{\perp} = \frac{1}{2} \left(\frac{[\epsilon(\beta_1 + 3\alpha)\lambda_M - (\epsilon'\beta'_1/\sqrt{2})\lambda_L][\epsilon(\beta_1 + 3\alpha) - \epsilon'(\beta_1 + 3\alpha)S_e - \epsilon(\beta'_1S_{b_1} + 3\alpha'S_a) - (\epsilon'\beta'_1/\sqrt{2})]}{\Delta E(^4E)} - \frac{[\epsilon(\beta_{1b} + 3\alpha_b)\lambda_M + (\epsilon'\beta'_{1b}/\sqrt{2})\lambda_L][\epsilon(\beta_{1b} + 3\alpha_b) - \epsilon'(\beta_{1b} + 3\alpha_b)S_e + \epsilon(\beta'_{1b}S_{b_1} + 3\alpha'_bS_a) + (\epsilon'\beta'_{1b}/\sqrt{2})]}{\Delta E(^4E^c)} \right) \quad (2)$$

$$D = \frac{(2\beta\beta_1\lambda_M - \beta'\beta'_1\lambda_L)^2}{\Delta E(^4B_2)} - \frac{1/4[\epsilon(\beta_1 + 3\alpha)\lambda_M - (\epsilon'\beta'_1/\sqrt{2})\lambda_L]^2}{\Delta E(^4E)} + \frac{(2\beta\beta_{1b}\lambda_M + \beta'\beta'_{1b}\lambda_L)^2}{\Delta E(^4B_2^c)} - \frac{1/4[\epsilon(\beta_{1b} + 3\alpha_b)\lambda_M + (\epsilon'\beta'_{1b}/\sqrt{2})\lambda_L]^2}{E(^4E^c)} \quad (3)$$

The notation is that of ref 11. Briefly, α , β , β_1 , and ϵ are one-electron molecular orbital coefficients for orbitals of symmetry a_1 , b_2 , b_1 , and e , respectively, with primes indicating ligand coefficients and subscript b implying bonding orbitals. The spin-orbit coupling constants λ_M and λ_L are for the metal and ligand centers. Group overlap integrals are symbolized S with symmetry subscripts. The energy difference denominators are labeled by the excited-state symmetry with a superscript c for charge-transfer states. The latter terms in these equations which represent the charge-transfer state contributions to the ground-state splittings are recognizable by the appearance of bonding orbital coefficients.

Experimental Section

Suitable samples for epr powder spectra require some care in preparation. Both guest and host compounds were first prepared by standard methods.¹⁴⁻²¹ A saturated solution of the host compound

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containing about 1 mol % guest ion at room temperature was prepared, cooled in an ice bath to retard decomposition, and subjected to a gentle stream of dry air to encourage evaporation. Crystalline precipitates with distinguishable microcrystals (not powders) were necessary to obtain good epr spectra. Even crystalline samples which were grown too rapidly showed evidence of guest ion clustering and random lattice distortions. Guest ion clustering is indicated by the presence of a very broad line (~ 1000 G) near $g = 2$, whereas lattice distortions are characterized by excessive line broadening for lines well removed from the center of the spectrum.

Powder epr spectra were obtained for samples containing $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$, $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$, and $[\text{Cr}(\text{NH}_3)_5\text{Br}]^{2+}$ in cobalt hosts. Many and varied attempts to prepare the fluoro and iodo analogs were unsuccessful. In order to determine the influence of the host lattice on the spin-Hamiltonian parameters, spectra of the aquo and chloro complexes were compared in different host lattices. $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$ in $[\text{Co}(\text{NH}_3)_5\text{Cl}]_2$, $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$, and $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ gave identical spectra as did $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]$ in $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Z}_3$ with $Z = \text{ClO}_4^-$, NO_3^- , and Cl^- . Similar comparisons with $[\text{Cr}(\text{NH}_3)_6]^{3+}$ in $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$ and $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ in $[\text{Co}(\text{NH}_3)_6](\text{ClO}_4)_3$ gave recognizably different spectra. These results suggest that changes of the metal ion or counterion of the host has little effect if a substitutional site of proper symmetry exists. It is also apparent that the spin-Hamiltonian parameters obtained in this study are molecular parameters of the chromium complexes alone. This insensitivity to the host lattice is not expected to be general but must be demonstrated for each system before molecular interpretations are attempted. Other symmetries and different electron configurations may be much more sensitive to the lattice than the systems studied here.

A large number of attempts were made to prepare random orientation samples of the chromium complexes in glassy matrices composed of the following solvents and mixtures thereof: water, glycerine, alcohols, halogen acids, dimethyl sulfoxide, dimethylformamide, ethylene carbonate, and numerous others. Attempts were also made under a variety of conditions with ion-exchange resins. These attempts with resins and glasses were consistent failures yielding at best very broad, ill-resolved spectra.

Earlier epr spectra were obtained on a Varian Model 4500 spectrometer with later work done on a Varian E12 spectrometer. Data were taken both at 9.5 and 35 GHz with line positions determined to within 1 G. The powder spectra were assigned and fitted to the spin Hamiltonian, as described previously,¹³ to yield the parameters given in Table I. The well-resolved rhombic spectrum of $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$ shown in Figure 1 and the nearly axial spectrum of $[\text{Cr}(\text{NH}_3)_5\text{Br}]^{2+}$ shown in Figure 2 illustrate the features of two extreme types of d^3 epr powder spectra.

Discussion

The most important result of this study has been the experimental demonstration that the spin-Hamiltonian parameters are properties of the chromium complex if the guest site in the host lattice has the proper symmetry and is matched in charge distribution. While all of the host lattice structures are not known, it is clear that sulfate and chloride ions could not form the same structure with $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$. The freedom to substitute rhodium for cobalt in this host is less surprising but even this difference should cause sufficient dimensional change to alter the magnitude of the crystalline potential at the guest site.

The lattice variations used in the case of $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ were designed to alter the hydrogen bond potentialities within the lattice. Tetrahedral perchlorate, planar nitrate, and monatomic chloride ions should offer a sufficient range of hydrogen-bonding possibilities both in strength and in geometric requirements that one could eliminate hydrogen

Table I. Spin-Hamiltonian Parameters of Some Pentaamminechromium(III) Complexes

	Aquo	Chloro	Bromo
$ D ,^a$ G	921.1	950.4	2208
$ E $, G	125.0	45.3	13
g_{\parallel}	1.9860	1.9861	1.9853
g_{\perp}	1.9841	1.9868	1.9917

^a The same sign is expected for D in each case because H_2O , Cl , and Br are lower in the spectrochemical series than NH_3 .

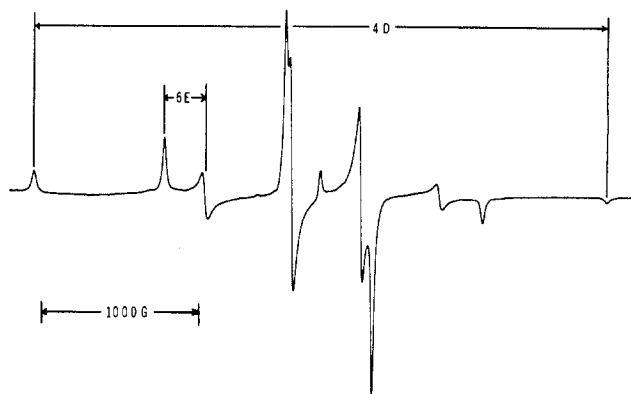


Figure 1. The epr powder spectrum of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2\text{-Cr}$ at 9.5 GHz with approximate splittings.

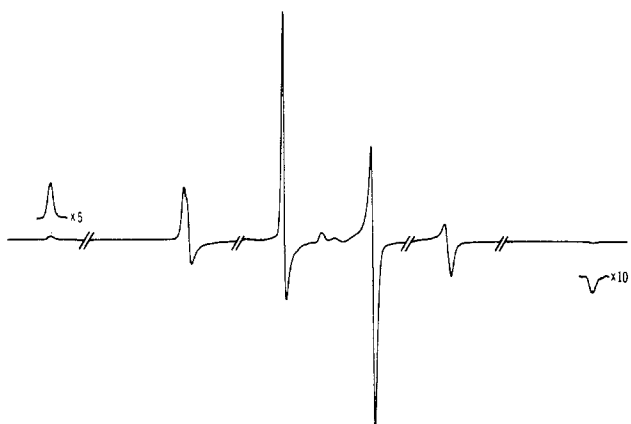


Figure 2. The epr powder spectrum of $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2\text{-Cr}$ at 35 GHz. The small rhombic splitting can be seen in the second line from the left but not in the corresponding high-field line under these conditions. The breaks in the spectrum are 1000-G gaps and the extremal lines are 8800 G apart.

bonding as a possible source of the rhombic distortion found for $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$. The only intramolecular interaction which could account for the large E to D ratio (0.13) in the aquo complex is asymmetric π bonding by the water ligand. This, however, raises the question of the origin of the similar, but much smaller, asymmetry ($E/D = 0.047$) for the chloride complex. A threefold smaller E has been observed for $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$ in $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$ in other work.²² The still smaller ratio ($E/D = 0.006$) for the bromide complex suggests that rhombic contributions do not arise from a mechanism involving the ammine ligands. We conclude that the large rhombic distortion in the aquo complex must arise primarily from water π bonding with perhaps some lattice contribution.

The axial zero-field splitting parameter, D , measures the difference in the amount of unquenched orbital angular momentum about the z axis and the average value of this quantity in the xy plane. This parameter has been shown to

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depend on (a) radial expansion of the d orbitals, (b) electron delocalization onto the ligands, (c) spin-orbit interaction on the ligands, and (d) charge-transfer state admixture.¹¹ Thus, it is not surprising that D follows no simple trend with respect to the properties of the X ligand in the series $[\text{Cr}(\text{NH}_3)_5\text{X}]$. Such correlations might be expected for the nephelauxetic series ($\text{Br} > \text{Cl} > \text{H}_2\text{O}$), the spectrochemical series as reflected in the splitting of the ${}^4\text{E}(\text{T}_2)$ and ${}^4\text{B}_2(\text{T}_2)$ levels in these complexes,²³ or the g -factor anisotropy, $g_{\parallel} - g_{\perp}$. The similarity of the D 's for the aquo and chloro complexes (921 and 950 G, respectively) compared with the much larger value for the bromo complex ($D = 2208$ G) is surprising even when one considers the multifaceted origins of D . The chloro and bromo complexes should be much more nearly alike than the chloro and aquo complexes. The zero-field parameter alone is not useful for direct bonding comparisons.

The g factors obtained in this study are somewhat more informative than the zero-field splittings. The molecular information is actually contained in the g shift, $\Delta = g_e - g$, which measures the deviation of the g factor from the free-electron g factor ($g_e = 2.0023$). The g shifts for the complexes examined in this study are reported in Table II along with similar data for several other chromium(III) species. The parallel g shift as described by eq 1 depends on interactions involving the bonding in the xy plane, specifically, the $b_1(x^2 - y^2)$ and $b_2(xy)$ orbitals. It can be seen in Table II that for the hexaammine- and the three pentaamminechromium(III) complexes $\Delta_{\parallel} = 0.0166 \pm 0.0004$. This observation indicates that the equatorial bonding in the pentaammine series is essentially independent of the sixth ligand. That the invariance of Δ_{\parallel} is significant can be seen from the widely ranging values of the other g shifts in Table II.

The perpendicular g shifts of the tetragonal complexes in Table II show the effects of the odd ligand by deviating from Δ_{\parallel} toward a Δ value characteristic of a complex containing only the odd ligand. For example $\Delta[\text{Cr}(\text{H}_2\text{O})_6] = 0.0254 > \Delta_{\perp} = 0.0182 > \Delta_{\parallel} = 0.0163$ for $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]$. (Note that $\Delta_{\parallel} = 0.0152$ for $[\text{CrCl}_5\text{H}_2\text{O}]$ is now assumed to be characteristic of six chlorine ligands by virtue of the arguments in the preceding paragraph.) These deviations of Δ_{\perp} and Δ_{\parallel} are not weighted averages of the Δ values characteristic of the two types of ligand. Indeed, no such averaging is expected because of the complicated dependence of Δ_{\perp} (eq 2) on the ligand spin-orbit interaction and on the molecular orbital coefficients in both bonding and antibonding orbitals of symmetry: $e(xz, yz)$, $b_1(x^2 - y^2)$, and $a_1(z^2)$.

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Table II. g Shifts of Some Chromium(III) Complexes: $\Delta = 2.0023 - g$

Ion	Δ_{\parallel}	Δ_{\perp}
$[\text{Cr}(\text{NH}_3)_6]^{3+}$ ^{a,b}	0.0166	
$[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ ^b	0.0163	0.0182
$[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$ ^b	0.0162	0.0155
$[\text{Cr}(\text{NH}_3)_5\text{Br}]^{2+}$ ^b	0.0170	0.0106
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ^c	0.0254	
$[\text{CrF}_6]^{3-}$ ^d	0.0303	
$[\text{Cr}(\text{CN})_6]^{3-}$ ^e	0.0103	
$[\text{CrO}_6]^{4-}$ ^f	0.0223	
$[\text{CrCl}_5\text{H}_2\text{O}]^{2+}$ ^g	0.0152	0.0187

^a K. Okumura, *J. Phys. Soc. Jap.*, **17**, 1341 (1962). ^b This work.

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^g Reference 11.

Equations 1-3 can be used to compare the various molecular orbital coefficients if one assumes that there is no equatorial π bonding in pentaammine complexes, *i.e.*, the xy orbital is nonbonding, and if one makes appropriate estimates of the other parameters as was done previously for $[\text{CrCl}_5\text{H}_2\text{O}]$.¹¹ These calculations were performed for the three pentaammine complexes in this study,²⁴ but only the significant qualitative features of the results will be presented. Notice that eq 1-3 assume C_{4v} symmetry which means that the results for the rhombic aquo complex are qualitative at best. As mentioned above, the equatorial σ bondings are necessarily identical in the three systems. The fittings require a significant amount of π bonding from each of the ligands Cl, Br, and H_2O . The water result is in accord with the interpretation of the large rhombic zero-field splitting of $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]$. Bromine and chlorine appear to behave similarly in their σ bonding with bromine being a somewhat better π bonder. This result is in accord with the position of chlorine above bromine in the spectrochemical series because π bonding tends to attenuate Dq . The magnitude of the axial zero-field splitting parameter, D , is very sensitive to all of the MO coefficients but appears to correlate well with axial π bonding in this series.

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Registry No. $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$, 15975-47-0; $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$, 14482-76-9; $[\text{Cr}(\text{NH}_3)_5\text{Br}]^{2+}$, 22289-65-2.