

direct influence of this ligand on the electronic state used for electron transfer. A comparison of data¹⁷ for electron-transfer reactions between $\text{Cr}_{\text{aq}}^{2+}$ and *cis*- and *trans*- $\text{Cr}(\text{en})_2(\text{OH}_2)\text{Cl}^{2+}$ (*en* = ethylenediamine) with the plots in Figure 2 gives good agreement for the *cis*-chloroaquo complex; however, the *trans* complex results are significantly different from that expected, suggesting that chelation brings in still another factor which must be considered in a calculation of E_{e} . Al-

though isotopic fractionation studies^{4,26} suggest that ligand motion on the oxidant is more important for Cr(III) than for Co(III) in the formation of the activated complex, the range of calculated E_{io}^{\ddagger} values (0–3.3 kcal mol⁻¹) indicates that this term makes a small but sometimes significant contribution to the overall activation energy for Cr(II)–Cr(III) electron-transfer reactions.

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Electron Paramagnetic Resonance of *trans*-Disubstituted Bis(ethylenediamine)chromium(III) Complexes in Frozen Solutions^{1a}

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Received March 19, 1970

Electron paramagnetic resonance (epr) spectra are reported for low-temperature glassy solutions of the *trans*-dichloro-, -diaquo-, -dihydroxo-, and -dithiocyanatobis(ethylenediamine)chromium(III) complexes. Spin-Hamiltonian parameters are determined from the spectra by a method applicable to other transition metal ion systems with zero-field splittings large in comparison to $h\nu$. It is shown that the absolute magnitude of the experimentally determined spin-Hamiltonian parameter E for these *trans*- $\text{Cr}(\text{en})_2\text{A}_2^{n+}$ complexes is proportional to the ligand field strength of the A ligands as deduced from the visible absorption spectra of the corresponding $\text{CrA}_6^{3\pm}$ complexes.

Introduction

The *trans*- $\text{Cr}(\text{en})_2\text{A}_2^{n+}$ complexes make up a well-characterized series and have been the subjects of a number of visible absorption spectral investigations.^{2–4} A single-crystal epr study has been carried out only for the dichloro complex,⁵ at least partially because of the difficulty involved in growing suitable single crystals. However, even when magnetically dilute single crystals cannot be prepared, all magnetic resonance information except the orientation of the symmetry axes can be obtained from epr spectra of low-temperature glassy solutions. Spectra and spin-Hamiltonian parameters for the quartet ground-state *trans*- $\text{Cr}(\text{en})_2\text{A}_2^{n+}$ complexes with A = SCN^- , Cl^- , H_2O , and OH^- are reported in this paper.

The method used to analyze the epr spectra of these quartet ground-state ions involves techniques which are similar to those recently described by Dowsing and coworkers in the interpretation of epr spectra of randomly oriented sextet ground-state ions.^{6–10} Relevant

discussions of techniques are given by Dowsing and Gibson⁹ and by Aasa, Falk, and Reyes.¹¹ Because of the greater simplicity of the experimental systems, analysis of these quartet ground-state spectra can be carried further than was possible for the sextet ground-state spectra. The analyses are more quantitative than those previously reported for chromium(III) systems in glasses^{12–16} with results comparable to those for magnetically dilute powders.^{11,17–19}

Experimental Procedures

Epr spectra of frozen solutions were recorded at approximately -120° on a Varian X-band spectrometer, Model 4502. Field strengths were obtained using the Fieldial. The compounds were prepared by established procedures as indicated and their visible absorption spectra in solution agree with those of Baker and Phillips^{2a} and of Woldbye.²⁰

(1) (a) Work supported by National Science Foundation Grant GP-6323 and in part by the Robert A. Welch Foundation, Houston, Texas. (b) The University of Texas at Austin. (c) Los Alamos Scientific Laboratory; under the auspices of the U. S. Atomic Energy Commission.

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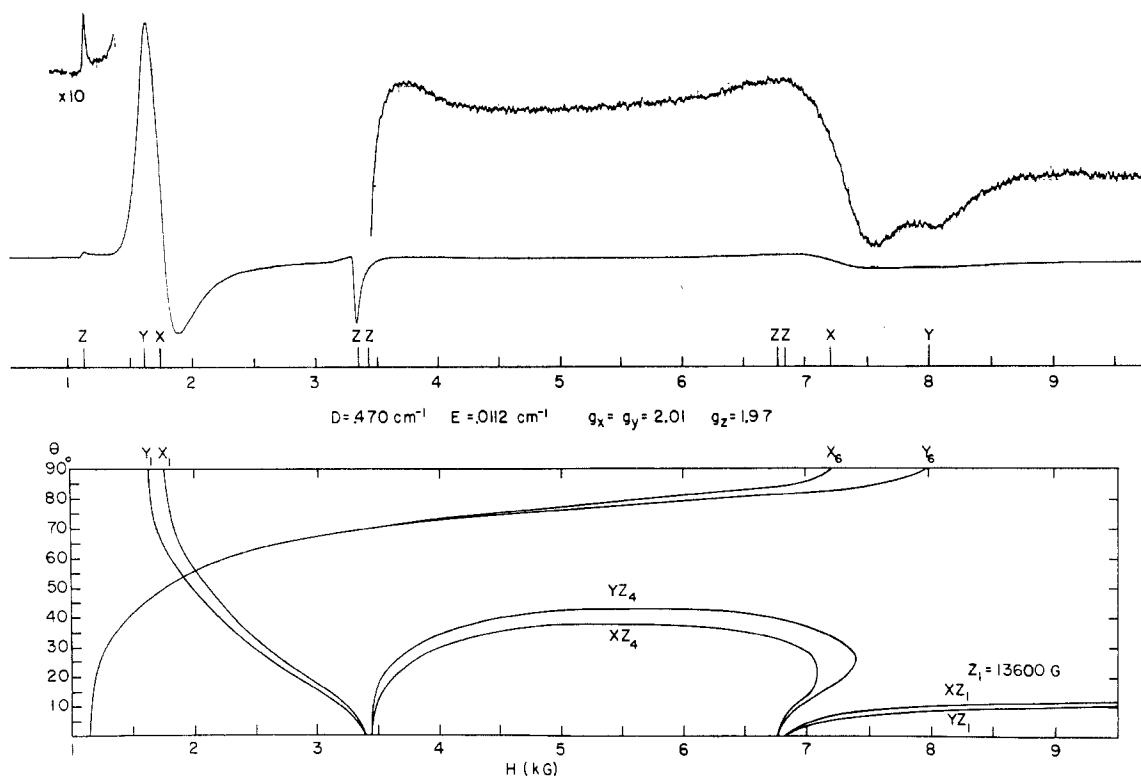


Figure 1.—Top: X-band epr spectrum at -120° of $\text{trans-}[\text{Cr}(\text{en})_2(\text{SCN})_2]\text{Cl}$ in 1:1:2 water-DMF-methanol. Bottom: Resonance positions as a function of magnetic field orientation in the xz and yz planes. Spin-Hamiltonian parameters minimize the function F , eq 4, given assignments in Table I. Subscripts refer to transitions: 1, between two lowest energy levels; 4, between levels 2 and 3; 6, between levels 3 and 4.

trans-Dichlorobis(ethylenediamine)chromium(III) Chloride.²¹—Epr spectra were obtained for a 1:1:2 water-dimethylformamide (DMF)-methanol solution (by volume).

trans-Dithiocyanatobis(ethylenediamine)chromium(III) Chloride.—This compound was precipitated with concentrated hydrochloric acid from a solution of *trans*-dithiocyanatobis(ethylenediamine)chromium(III) thiocyanate²² in DMF. Epr spectra were obtained for a 1:1:2 water-DMF-methanol solution.

trans-Aquo-hydroxobis(ethylenediamine)chromium(III) Bromide.²⁰—As reported by Woldbye,²⁰ this compound gives rise to $\text{trans-Cr}(\text{en})_2(\text{H}_2\text{O})_2^{3+}$ in acidic solution and to $\text{trans-Cr}(\text{en})_2(\text{OH})_2^+$ in basic solution. Spectra of the diaquo species were obtained for a 1:1 0.1 *M* perchloric acid-glycerol solution. Spectra of the dihydroxo species were obtained for a 1:1 ethylenediamine-glycerol solution.

Spectra were obtained for the designated chromium(III) complexes in a variety of media and with different counterions. Epr parameters were found to be insensitive to changes in both medium and counterion, although variations in apparent line width were observed. One example for each complex is presented here.

Results and Discussion

Epr spectra of low-temperature glasses containing $\text{trans-Cr}(\text{en})_2\text{A}_2^{n+}$, $\text{A} = \text{SCN}^-$, Cl^- , H_2O , and OH^- , are given in Figures 1-4. They are similar to previously reported glassy spectra of transition metal complexes with large zero-field splittings in that they are broad and are not centered at $g = 2^6, 15, 23$ and are

unique in that all have a number of well-defined features at low field.²⁴

Theory.—A satisfactory spin-Hamiltonian, excluding hyperfine interactions, for chromium(III) and other systems with a quartet ground state is²⁵

$$H = \beta\vec{H} \cdot g \cdot \vec{S} + D[S_z^2 - 5/4] + E[S_x^2 - S_y^2] \quad (1)$$

At zero magnetic field the quartet ground state is split into doublets separated by $2[D^2 + 3E^2]^{1/2}$ in energy. The low-field features of the chromium(III) spectra considered may be described by the effective g' tensor for an $S' = 1/2$ system

$$H' = \beta\vec{H} \cdot g' \cdot \vec{S}' \quad (2)$$

which indicates that transitions are confined to zero-field doublets at low fields.^{11, 25b}

Typical absorption curves for randomly oriented $S' = 1/2$ systems are shown in Figure 5.^{26, 27} Features of the experimental spectra at low field are assigned on the basis of these models as

$$H_k^{ij} = h\nu/\beta g_k' \quad (3)$$

where k indexes the x , y , or z symmetry axis of the chromium(III) complex; $i, j = 1, 2$ refer to the energy levels arising from the lower zero-field doublet and i, j

(24) One powder spectrum of this type has been reported previously by Aasa and coworkers¹¹ for the compound $\text{NH}_4\text{CrY} \cdot 4\text{H}_2\text{O}$ where $\text{H}_4\text{Y} = \text{ethylenediaminetetraacetic acid}$, and similar glassy spectra of chromium(III) transferrin complexes have been observed.¹⁸

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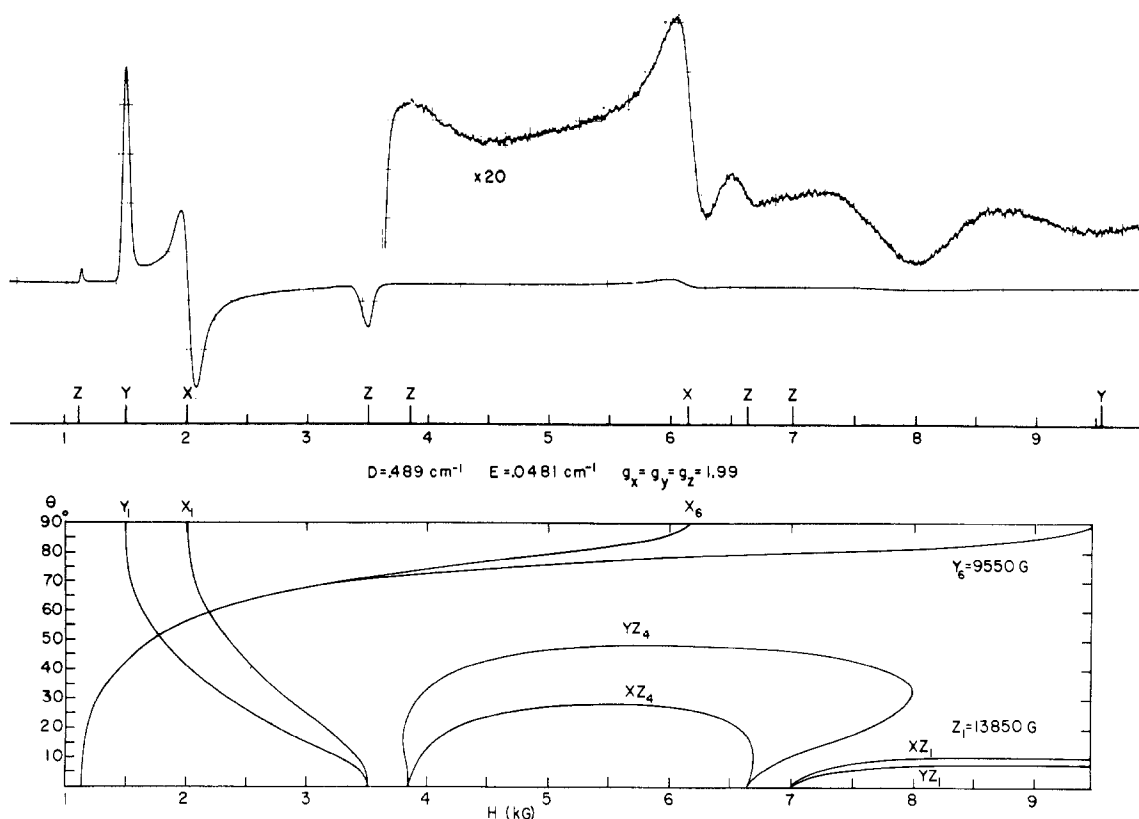


Figure 2.—Top: X-band epr spectrum at -120° of $\text{trans-}[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ in 1:1:2 water-DMF-methanol. Bottom: Resonance positions as a function of magnetic field orientation in the xz and yz planes. Spin-Hamiltonian parameters minimize the function F , eq 4, given assignments in Table I. Subscripts refer to transitions: 1, between two lowest energy levels; 4, between levels 2 and 3; 6, between levels 3 and 4.

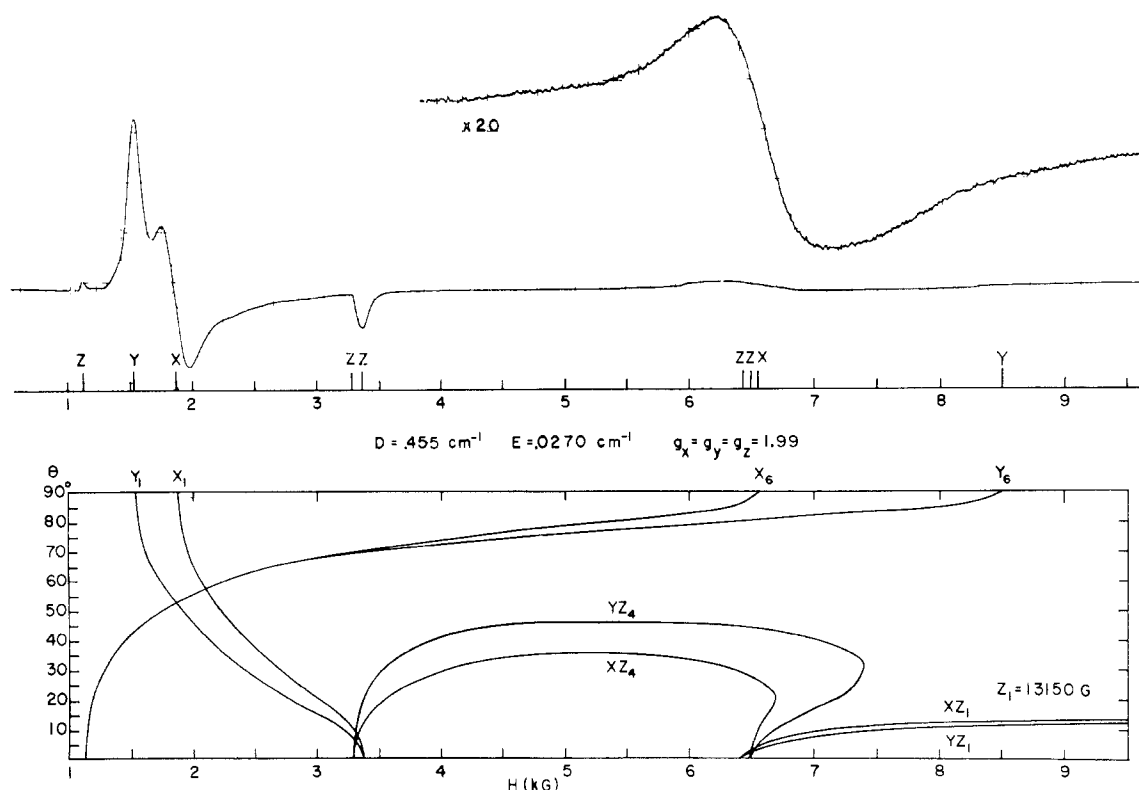


Figure 3.—Top: X-band epr spectrum at -120° of $\text{trans-Cr}(\text{en})_2(\text{H}_2\text{O})_2^{3+}$ in 1:1 0.1 M perchloric acid-glycerol. Bottom: Resonance positions as a function of magnetic field orientation in the xz and yz planes. Spin-Hamiltonian parameters minimize the function F , eq 4, given assignments in Table I. Subscripts refer to transitions: 1, between two lowest energy levels; 4, between levels 2 and 3; 6, between levels 3 and 4.

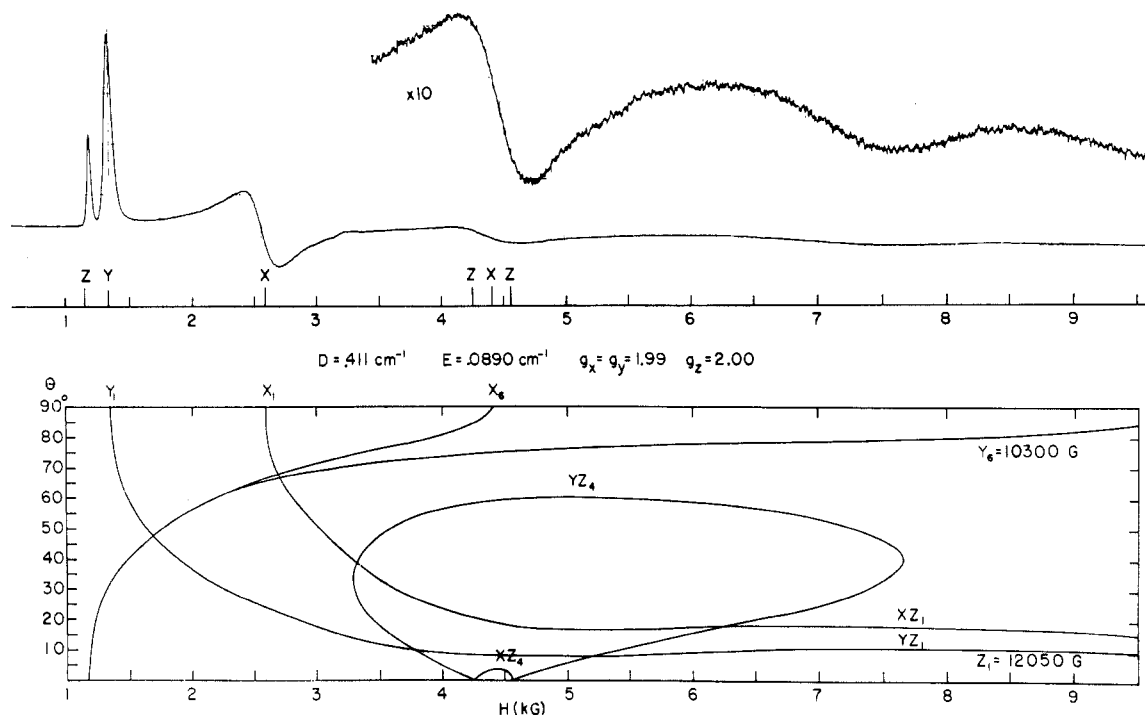


Figure 4.—Top: X-band epr spectrum at -120° of $trans\text{-Cr(en)}_2(\text{OH})_2^+$ in 1:1 ethylenediamine-glycerol. Bottom: resonance positions as a function of magnetic field orientation in the xz and yz planes. Spin-Hamiltonian parameters minimize the function F , eq 4, given assignments in Table I. Subscripts refer to transitions: 1, between two lowest energy levels; 4, between levels 2 and 3; 6 between levels 3 and 4.

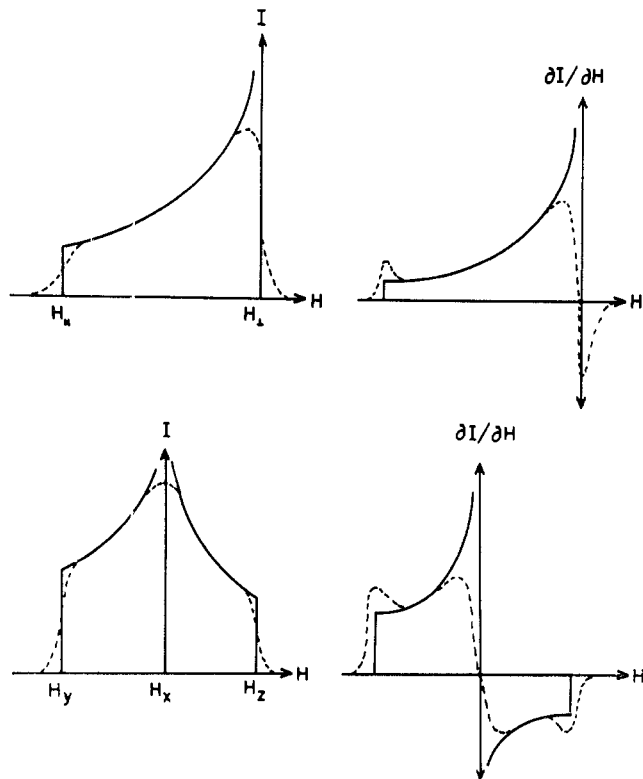


Figure 5.—Theoretical curves for randomly oriented $S' = 1/2$ systems. See ref 26 and 27.

= 3, 4 refer to those from the higher zero-field doublet as calculated with the Hamiltonian of eq 1 and the basis $\{|SM\rangle; S = 3/2\}$ (Appendix).²⁸ Transitions are

(28) Closed-form expressions for the energy levels when the magnetic field is along one of the molecular symmetry axes are given in ref 25b.

assigned according to the convention that spin-Hamiltonian parameters be defined in a coordinate system that makes the ratio E/D positive and equal to or less than $1/3$.²⁹ D is assumed to be positive in all calculations.³⁰

Spin-Hamiltonian parameters are fitted by a minimization of the function¹¹

$$F = \sum_i \sum_j \sum_k [|E_k^i - E_k^j| - h\nu]^2 \quad (4)$$

E_k^i and E_k^j are the energies of levels i and j when the magnetic field is along the k axis.²⁸ Summations include only assigned transitions. Four assignments are possible in the low-field range for each of the $trans\text{-Cr(en)}_2\text{A}_2^{n+}$ systems considered (Table I). Because

TABLE I
LOW-FIELD H_k^{ij} FOR $trans\text{-Cr(en)}_2\text{A}_2^{n+}$

ij	k	A							
		SCN ⁻		H ₂ O		Cl ⁻		OH ⁻	
		H_k^{ij} , G	g'	H_k^{ij} , G	g'	H_k^{ij} , G	g'	H_k^{ij} , G	g'
34	z	1122	5.92	1112	5.97	1122	5.92	1160	5.72
12	y	1622	4.00	1560	4.25	1480	4.48	1325	5.01
12	x	1748	3.80	1878	3.53	2011	3.30	2590	2.56
12	z	3378	1.96	3394	1.95	3500	1.89
34	x	4400	1.50

it is possible to fit four unknowns given solutions to only four equations, we set g_x equal to g_y and fit D , E , $g_x = g_y$, and g_z for each system. This choice is experimentally reasonable since the g tensor is often isotropic for chromium(III) in an octahedral field with large rhombic

(29) vanReijen¹⁸ has shown that such a solution is always possible.

(30) For a method of determining the absolute sign of D , see, for example, A. W. Hornig and J. S. Hyde, *Mol. Phys.*, **6**, 33 (1963).

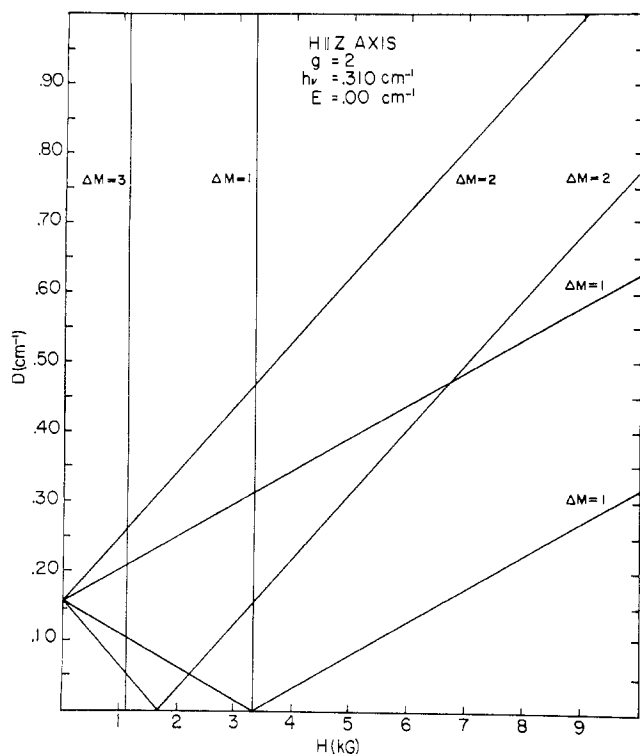


Figure 6.—Resonance positions plotted as a function of D for the magnetic field parallel to the z molecular axis, $E = 0$, $g = 2.0$, and $h\nu = 0.310 \text{ cm}^{-1}$.

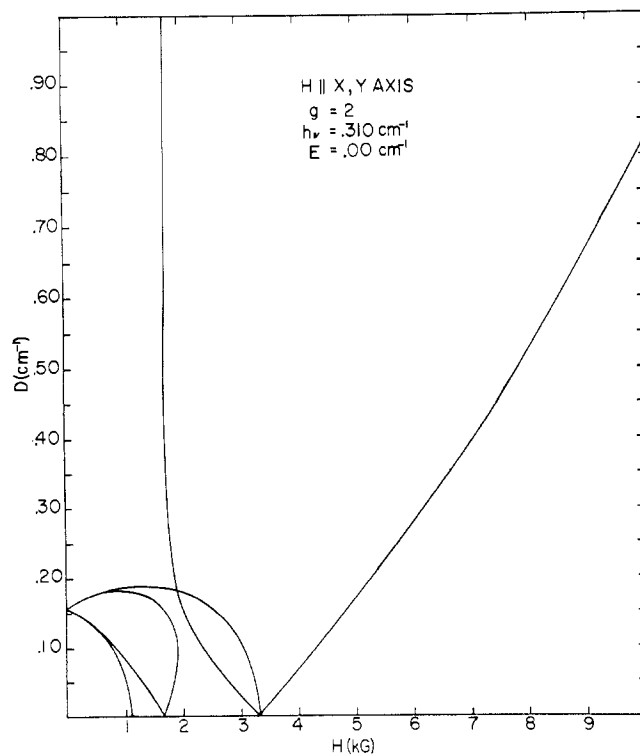


Figure 7.—Resonance positions plotted as a function of D for the magnetic field parallel to the x or y molecular axis, $E = 0$, $g = 2.0$, and $h\nu = 0.310 \text{ cm}^{-1}$.

distortion, and, in cases where g is not isotropic, g_x often equals or nearly equals g_y .^{25b}

Calculations.—The function F was minimized by a combined gradient and direct search routine for the minimization of a continuous function of several

variables.³¹ As successful minimizations require good initial parameter choices,³² preliminary calculations were done to provide a basis for the initial choice of spin-Hamiltonian parameters for quartet ground-state systems. Results of those calculations were summarized as plots of magnetic field positions at which a transition is possible between the four energy levels of an $S = 3/2$ system *vs.* the spin-Hamiltonian parameter D . In each graph E , g , and $h\nu$ are constant and the magnetic field is along the x , y , or z symmetry axis.³³ The parameter g equals 2.0 and $h\nu$ equals 0.310 cm^{-1} , the experimental value, in all graphs. Examples are given in Figures 6–10. Figure 6 shows all possible resonance positions when the magnetic field is parallel to the z or symmetry axis of the molecular system, $E = 0$, and D is allowed to vary from 0.0 to 1.0 cm^{-1} . For this special case the representation of the spin-Hamiltonian, eq 1, on the $\{|SM\rangle; S = 3/2\}$ basis is diagonal (Appendix) and transitions can be labeled by ΔM values with transitions for $\Delta M > 1$ strictly forbidden.³⁴ When the magnetic field is in any other direction with respect to the symmetry axes, or when $E \neq 0$, the representation is not diagonal and transitions cannot be labeled by a ΔM value.

Because the ratio E/D characteristically varies from system to system,^{25b} constant E graphs which incorporate results for a wide range of E/D values are especially useful in the interpretation of experimental spectra. Comparisons of the $E = 0$ graphs, Figures 6 and 7, with graphs for $E = 0.04 \text{ cm}^{-1}$, given in Figures 8–10, illustrate the very regular trends observed for x , y , and z transitions as E is varied. Working graphs were also constructed for $E = 0.02, 0.06, 0.08$, and 0.10 cm^{-1} . The graphs included in this paper may be interpolated to estimate the effects of variation in E . Results of similar preliminary calculations plotted with E/D held constant have been reported by Dowsing and coworkers,^{7–9} by Griscom and Griscom,^{25b} and by Aasa^{25c} for sextet ground-state ions and by vanReijen¹⁸ for various transitions of quartet ground-state ions. However, the regularity in the behavior of the x , y , and z transitions of quartet ground-state ions, which is apparent from constant E graphs, is not obvious from constant E/D graphs.

Choice of Parameters.—Many initial parameter sets were considered in the minimization procedure for each chromium(III) system. Results indicate that the function³¹ used to minimize F is well behaved, that the preliminary graphs are accurate, and that the low-field features in the spectra which are described by the $S' = 1/2$ spin-Hamiltonian are more sensitive to the ratio E/D than to the magnitudes of E and D .³⁵ It was

(31) The University of Texas Computation Center Library Function C3 UTEX MIN.

(32) For a discussion of fitting procedures see, for example, J. R. Kittrell, R. Mezaki, and C. C. Watson, *Ind. Eng. Chem.*, **57**, 19 (1965).

(33) Resonance positions were determined by a computer calculate and search routine. Energy level separations were calculated and compared to $h\nu$ at 100-G intervals in the 0–10,000-G range for each D value.

(34) See, for example, A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967, p 21.

(35) This result is also evident from a comparison of two or more constant E/D graphs. See the preceding section and ref 9.

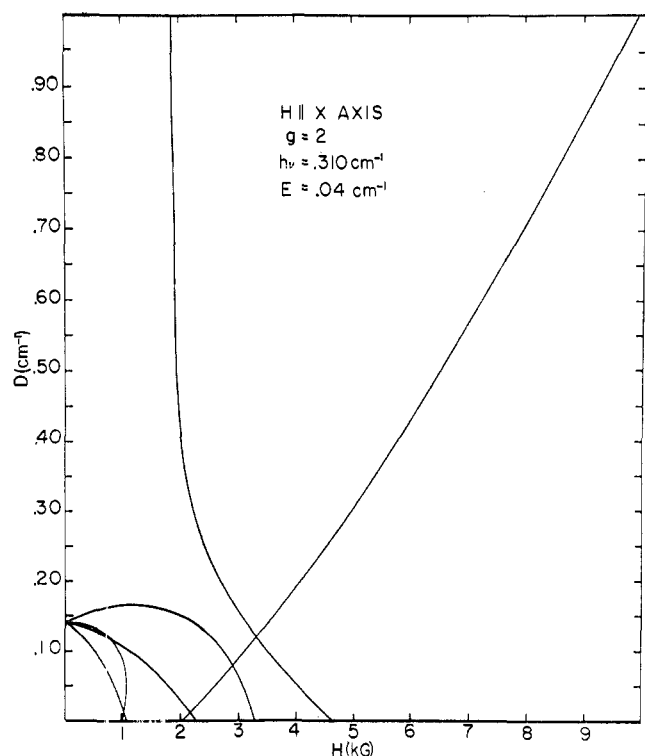


Figure 8.—Resonance positions plotted as a function of D for the magnetic field parallel to the x molecular axis, $E = 0.04 \text{ cm}^{-1}$, $g = 2.0$, and $h\nu = 0.310 \text{ cm}^{-1}$.

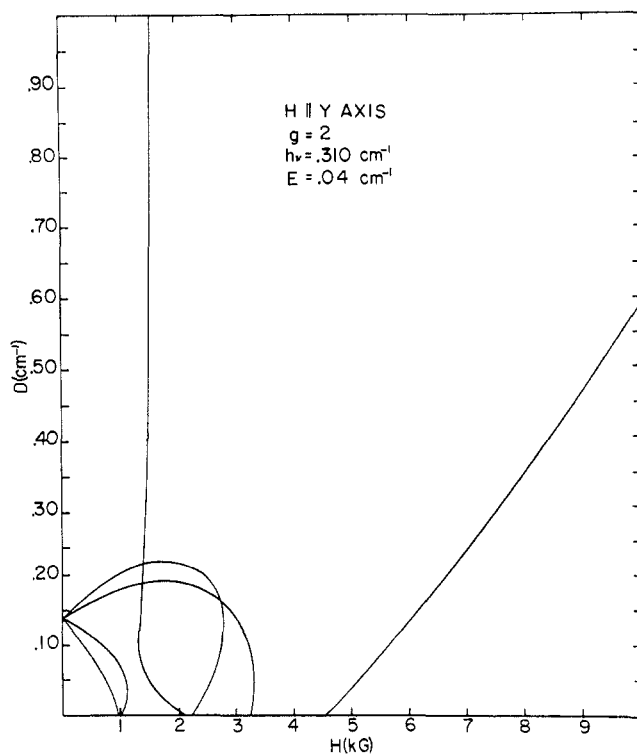


Figure 9.—Resonance positions plotted as a function of D for the magnetic field parallel to the y molecular axis, $E = 0.04 \text{ cm}^{-1}$, $g = 2.0$, and $h\nu = 0.310 \text{ cm}^{-1}$.

found that one E/D value is characteristic of each compound in its experimental environment, although a large number of parameter sets corresponding to that ratio minimize the function F with summations restricted to the low-field $S' = 1/2$ features. High-field features are very sensitive to the magnitudes of D and E , so that comparison of predicted high-field transitions with experimentally observed spectral features eliminates all but a few of the minimized parameter sets from consideration.

A single set of values can be obtained if one of the high-field transitions is assigned and included in the fitting procedure. However, assignment of magnetic field positions of the very broad high-field transitions involves more uncertainty than does assignment of the much sharper features at low field. Therefore, whenever possible spin-Hamiltonian parameters are fitted using low-field assignments and the set of parameters which best predict high-field transitions is chosen to describe the system. Parameters chosen in this fashion are entered in Table II for the *trans*- $\text{Cr}(\text{en})_2\text{A}_2^{n+}$ systems of interest. Single-crystal results are included for the dichloro complex.⁵

A significant difference between single-crystal and polycrystalline materials on one hand and glassy solutions on the other lies in the spatial relationship of counterions to the paramagnetic complex. In the former cases, systematic orientation may result in a significant secondary field which contributes to the total symmetry of the field about the paramagnetic ion. In the latter case, such an ordered relationship of the counterions may not occur. Rather, interactions with

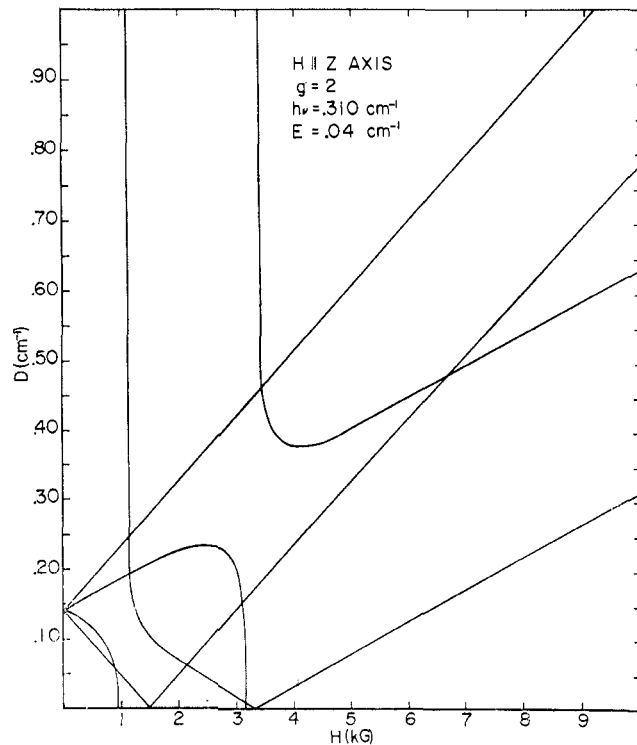


Figure 10.—Resonance positions plotted as a function of D for the magnetic field parallel to the z molecular axis, $E = 0.04 \text{ cm}^{-1}$, $g = 2.0$, and $h\nu = 0.310 \text{ cm}^{-1}$.

randomly oriented counterions and solvent molecules contribute to the widths of absorption lines. For these reasons, epr parameters for transition metal complexes in solution can be expected to reflect the intrinsic symmetry of the complexes involved.

TABLE II
 SPIN-HAMILTONIAN PARAMETERS FOR *trans*-Cr(en)₂A₂ⁿ⁺

	A				
	OH ⁻ , glass ^a	Cl ⁻ , glass ^a	Cl ⁻ , single crystal ^b	H ₂ O, glass ^a	SCN ⁻ , glass ^a
<i>D</i> , cm ⁻¹	0.411	0.489	0.504 ±0.001	0.455	0.470
<i>E</i> , cm ⁻¹	0.089	0.048	0.036 ±0.001	0.027	0.011
<i>g</i>	1.99	1.99	1.9765 ±0.0005	1.99	1.99

^a The estimated uncertainty for these parameters is ±2%, corresponding to an uncertainty of between 50 and 100 G in the assignment of one or more low-field resonance positions. ^b *trans*-[Cr(en)₂Cl₂]Cl·HCl·2H₂O; see ref 5.

Test of Parameter Choices.—The interpretation of spectra for randomly oriented species is complicated by the fact that features in addition to those at resonance positions for the magnetic field along a symmetry axis of the system can be expected in certain situations.¹⁸ These include transitions for which the maximum or minimum effective *g* value, a *g'* value, does not correspond to the *x*, *y*, or *z* resonance position.¹⁰ A maximum *g'* value, in addition to the *x*, *y*, and *z* values, has been observed for the $\Delta M = 2$ transition of triplet states.³⁶ It is also possible that transitions which cannot occur for a specific value of $h\nu$ when the magnetic field is along one or more symmetry axes do occur for intermediate orientations of the magnetic field with respect to the symmetry axes. Transitions of this kind occur for all sets of parameters reported in Table II.³⁷ A plot of resonance positions predicted with the spin-Hamiltonian parameters deduced for each *trans*-Cr(en)₂A₂ⁿ⁺ complex *vs.* the angle θ is compared with the corresponding experimental spectrum in Figures 1–4.

Resonance positions are included in the graphs for all transitions possible between the four energy levels of an $S = 3/2$ system when the magnetic field is in the *xz* or *yz* plane of the molecule-fixed coordinate system. Resonance positions when the magnetic field is parallel to the *z* axis ($\theta = 0^\circ$) and the *x* and *y* axes ($\theta = 90^\circ$) are also indicated on the magnetic field axis of the experimental spectrum. Energy levels were calculated by a diagonalization of the representation of the spin-Hamiltonian (Appendix), with resonance positions determined by a computer calculate and search routine. Energy levels were ordered according to increasing energy at each search step and the transitions were labeled. Transition 1 is between levels 1 and 2, transition 4 between levels 2 and 3, and transition 6 between levels 3 and 4. Comparison of experimental spectra with plots of predicted resonance positions indicates that a minimum corresponding to the high-field extremum of transition 4, a feature which does not correspond to an *x*, *y*, or *z*, transition, appears in each of the experimental spectra (Figures 1–4). As expected, *x*, *y*, and *z* transitions correspond to maxima, minima, or inflection points. Note that features corresponding to

z transitions are characteristically less intense than the associated *x* and *y* transitions.

For these calculations, which assume *D* positive,^{30,38} the low-field transition designated as 1 contributes more intense features to the spectrum than do transitions 4 and 6.¹⁹ Intensities of spectral features are functions of (1) how the absorption lines for each paramagnetic complex in the randomly oriented array superimpose^{26,27} and (2) the relative transition probability for each transition and orientation involved.^{10,35,39}

Correlation of Data.—McGarvey's analysis⁵ of the magnetically dilute *trans*-[Cr(en)₂Cl₂]Cl·HCl·2H₂O single-crystal epr spectra indicates that the principal spin-spin interaction axis lies in the plane of the ethylenediamine nitrogen atoms and bisects the open angles in that plane. Results of crystal structure investigation⁴⁰ of the complex suggest an N–Cr–N bond angle in the chelate ring of $85 \pm 5^\circ$, and MO calculations⁵ based on the epr results are most consistent with that angle choice. The complex species considered in this work are all expected to be similar to the dichloro complex and, as a first approximation, may be considered to have similar spin interaction coordinate systems. On the basis of McGarvey's results,⁵ the *z* and *y* symmetry axes of the complexes are assumed to lie in the plane of the ligand N atoms and the *x* axis is assumed to lie along the axis of the "trans" substituents. In that case the experimental values of *D* should not vary greatly and *E*, as a measure of rhombic character of the complexes, should reflect changes in the "trans" substituents. As that appears to be true (Table II), an investigation of the relationship of epr results with other observed properties of the metal-ligand bonds is in order.

An experimental correlation can be drawn between the absolute magnitudes of the spin-Hamiltonian parameter *E* for the *trans*-Cr(en)₂A₂ⁿ⁺ complexes studied and the ligand field strength of the A ligands as determined from the visible absorption spectra of the corresponding CrA₆^{3±} complexes. The spin-Hamiltonian parameters *D* and *E* are defined^{25b} in terms of the components of a traceless, diagonal spin-spin interaction tensor

$$\begin{aligned}
 D &\equiv \frac{3}{2}D_{zz} \\
 &= -\frac{3}{2}[D_{xx} + D_{yy}] \\
 E &\equiv \frac{1}{2}[D_{xx} - D_{yy}]
 \end{aligned}
 \quad (5)$$

The assumption is made that components of a diagonal spin-spin interaction tensor, *D'*, are proportional to the ligand field strengths along the *x*, *y*, and *z* axes of the appropriate coordinate system and that

$$D_{ii} = D'_{ii} - \frac{1}{3}\text{Tr}(D') \quad (6)$$

where

$$\text{Tr}(D') = D'_{xx} + D'_{yy} + D'_{zz} \quad (7)$$

(38) For the same *E/D* value and *D* negative, energy levels are inverted but otherwise unchanged in character.

(39) M. Kopp and J. H. Mackey, *J. Comput. Phys.*, **3**, 539 (1969).

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(36) P. Kottis and R. Lefebvre, *J. Chem. Phys.*, **39**, 393 (1963).

(37) Transitions of this type are also observed to occur in sextet ground-state systems; see ref 23c.

For the *trans*-Cr(en)₂A₂ⁿ⁺ complexes of interest, D'_{xx} is proportional to the ligand field strength of the A groups and D'_{yy} and D'_{zz} are proportional to the ligand field strength of ethylenediamine.⁴¹ Substituting eq 6 into eq 5

$$E = \frac{1}{2}[D'_{xx} - D'_{yy}] \quad (8)$$

$$= aR(A) - \frac{1}{2}D'_{yy}$$

where

$$R(A) \equiv \nu(^4T_2)/\nu(^2E)$$

$$\cong 10Dq/21B$$

The experimentally determined parameter $R(A)$ is essentially a measure of the ligand field strength of the CrA₆^{3±} complex in units of the Racah parameter B . The energy of the transition from the ⁴A₂ ground state to the ⁴T₂ excited state, $\nu(^4T_2)$, equals $10Dq$ while $\nu(^2E)$ is approximately $21B$.⁴² $R(A)$ has been shown to correlate with the luminescence spectra⁴³ as well as the absorption spectra⁴⁴ of CrA₆^{3±} complexes.

If the *trans*-Cr(en)₂A₂ⁿ⁺ complexes are isomorphic, eq 8 implies that a plot of E vs. $R(A)$ will be a straight line with intercept at the $R(\text{en})$ value. A plot of experimental E values vs. experimental $R(A)$ values for A = SCN⁻, Cl⁻, and H₂O does yield a straight line with very nearly the predicted intercept and is given in Figure 11. Predicted E and $R(A)$ values are indicated

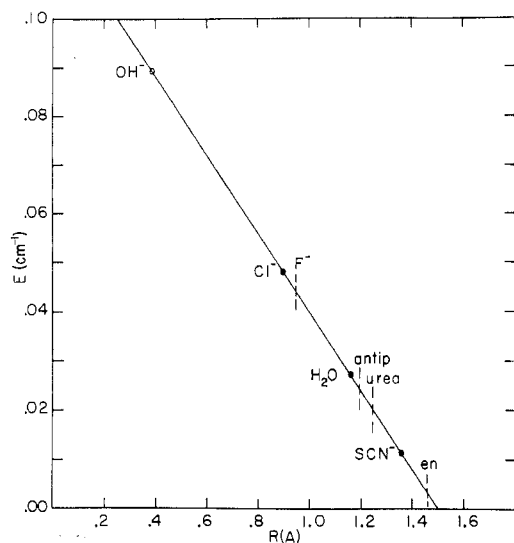


Figure 11.—A plot of the spin-Hamiltonian parameter E vs. $R(A)$ for a number of *trans*-Cr(en)₂A₂ⁿ⁺ complexes. Experimental E values are indicated by circles. See Table III.

in Figure 11 and included in Table III. It should be emphasized that predictions of this kind imply that the symmetry and conformation of the complexes are unchanged upon substitution of the A ligands.

(41) This follows from an additivity argument like that used by Ballhausen in his explanation of the tetragonal splitting of *cis* and *trans* complexes: C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962.

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TABLE III

E AND R(A) VALUES ^a FOR <i>trans</i> -Cr(en) ₂ A ₂ ⁿ⁺ COMPLEXES					
A ^b	R(A) ^c	E, cm ⁻¹	A ^b	R(A) ^c	E, cm ⁻¹
OH ⁻	(0.39)	0.089	H ₂ O	1.16	0.027
Cl ⁻	0.90	0.048	SCN ⁻	1.36	0.011
F ⁻	0.94	(0.044)	NH ₃	1.40	(0.007)
antip	1.12	(0.030)	en ^d	1.46	(0.003)
Urea	1.12	(0.030)	CN ⁻	2.14	(-0.052)

^a Values predicted assuming all structures to be isomorphic are enclosed in parentheses. ^b antip, antipyrene; en, ethylenediamine. ^c Tabulated in ref 43 and calculated from references therein. ^d Hypothetical complex.

Orientation of Molecular Symmetry Axes.—The relation illustrated in Figure 11 and the experimentally determined E value for *trans*-Cr(en)₂(OH)₂⁺ suggest that $R(\text{OH}^-) \cong \frac{1}{3}R(\text{H}_2\text{O})$. It is perhaps more reasonable to assume⁴⁵ that $R(\text{OH}^-) \cong R(\text{H}_2\text{O})$ which implies that the *trans*-Cr(en)₂A₂ⁿ⁺ complex with A = OH⁻ behaves differently than do the complexes with A = SCN⁻, Cl⁻, and H₂O. In terms of eq 8, this difference could be due to a variation in the proportionality factor a , to a variation in D'_{yy} , or to both. Thus, the results of this work imply that, while the symmetries of the complexes with A = SCN⁻, Cl⁻, and H₂O are essentially isomorphic, the symmetry of the A = OH⁻ complex may be significantly different. Further, the similarity of the spin-Hamiltonian parameters for the dichloro complex in the low-temperature glass and in the single crystal (Table I) suggests that the orientation of the symmetry axes is unchanged by medium and that the orientation of the symmetry axes for the complexes with A = SCN⁻, Cl⁻, and H₂O is essentially the same as that found for the dichloro single crystal.⁵ Preliminary epr results for the mixed-ligand complex *trans*-Cr(en)₂(OH)(H₂O)₂⁺ indicate that the parameters D and E for the complex are averages of the corresponding parameters for the *trans*-Cr(en)₂(OH)₂⁺ and *trans*-Cr(en)₂(H₂O)₂³⁺ complexes. This suggests that the relation illustrated in Figure 11 is an experimentally useful correlation for all four A ligands considered when the predicted $R(\text{OH}^-)$, regardless of its true meaning, is retained.

Summary

Epr parameters are derived from the spectra of a series of *trans*-Cr(en)₂A₂ⁿ⁺ complexes in low-temperature solutions. The experimental correlation of epr parameters with visible absorption spectral parameters suggests that epr spectral studies of complexes in low-temperature solutions are interesting not only as a substitute for single-crystal studies but as a probe of the intrinsic symmetry of transition metal ions in solution.

Acknowledgments.—We wish to acknowledge helpful discussions of some aspects of this problem with Professors B. B. Garrett and F. A. Matsen.

Appendix

Calculation of Energy Levels.—Euler angles Θ , Φ , and Ψ relate a laboratory-fixed coordinate system with the z axis along the external magnetic field direction to a

(45) The complex Cr(OH)₃³⁻ has not been observed experimentally.

molecule-fixed coordinate system with the z axis along the symmetry axis of the molecule. Components of the magnetic field \vec{H} in the molecular coordinate system are⁴⁶

$$\begin{aligned} H_x &= |H| \sin \Theta \cos \Phi \\ H_y &= |H| \sin \Theta \sin \Phi \\ H_z &= |H| \cos \Theta \end{aligned} \quad (9)$$

Equations 9 are substituted in the general spin-Hamiltonian given in eq 1. Exact eigenvalues and

(46) This Euler angle convention is the same as that established by Kottis and Lefebvre.³⁸

eigenvectors for a given set of parameters arise from a diagonalization of the representation of the spin-Hamiltonian on the basis $\{|SM\rangle; S = 3/2\}$, which is defined with respect to the molecule-fixed coordinate system. Eigenvalues, ordered according to increasing energy, are denoted

$$E^i(H, \Theta, \Phi); \quad i = 1, 2, 3, 4 \quad (10)$$

and the corresponding eigenvectors are denoted

$$|i\rangle = \sum_M c_M^i(H, \Theta, \Phi) |^3/2M\rangle; \quad i = 1, 2, 3, 4 \quad (11)$$

for a given D , E , g_x , g_y , and g_z value.

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The Chromium(II) Reduction of Maleatopentaamminecobalt(III)¹

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Received April 1, 1970

An extensive study of the stoichiometry, kinetics, and mechanism of the Cr(II) reduction of maleatopentaamminecobalt(III) is reported. The inner-sphere reaction gives an initial 80:20 ratio of chelated to monodentate maleate complexes of Cr(III). Cr(II) catalyzes the equilibration of the two Cr(III) complexes on a time scale comparable to that of the initial Cr(II)-Co(III) reaction. A comparison of the rates of these two maleate-bridged redox processes suggests that electron transfer to the ligand is a reasonable description of the slow step. Stoichiometric studies show that no isomerization, hydration, or net reduction of the maleate bridging group attends any of the electron-transfer reactions. The methylmaleatopentaamminecobalt(III) complex is reduced by Cr(II) at nearly the same rate as is the maleato complex (150 vs. 200 $M^{-1} \text{sec}^{-1}$, 25.0°, $\mu = 1.00 M$).

Introduction

Since the first report² in 1953 of a demonstrably inner-sphere electron-transfer reaction, systems featuring this kind of mechanism have received wide study. The class of inner-sphere reactions in which the bridging ligand is an organic molecule has itself developed into a major field. A recent review by Gould and Taube³ indicates the scope of work in this area.

A system often touched on in earlier work is the Cr(II) reduction of maleatopentaamminecobalt(III) and the related ester complex methylmaleatopentaamminecobalt(III). Taube⁴ first called attention to the rapid rate of reduction of the maleato complex compared to analogous reactions involving simple carboxylate bridging ligands. There followed reports on the stoichiometry of the chromium(II)-maleatopentaamminecobalt(III)^{5,6} and the chromium(II)-methylmaleatopentaamminecobalt(III)⁵⁻⁷ reactions by Fraser and Taube. These stoichiometric studies indicated substantial *cis-trans* isomerization of the ligand in conjunc-

tion with both electron-transfer reactions and quantitative ester hydrolysis in the latter case.

More recently Schwarz⁸ has reported that he was unable to reproduce Fraser and Taube's observation^{5,6} of *cis-trans* isomerization in the vanadium(II)-maleatopentaamminecobalt(III) reaction, and other reports^{9,10} as well have cast doubt on various aspects of the earlier work. We have undertaken a detailed reinvestigation of the stoichiometry of the chromium(II)-maleatopentaamminecobalt(III) and chromium(II)-methylmaleatopentaamminecobalt(III) reactions. Besides dealing with issues raised previously, we report some novel effects which are not touched upon in the earlier work.

Fraser¹¹ has published rate data for the chromium(II)-maleatopentaamminecobalt(III) reaction, but Gould's¹² later study is in disagreement with the earlier rate law. Kinetic studies described here support Gould's results. Recent experiments by Hurst and Taube,⁹ Nordmeyer and Taube,¹³ and Diaz and Taube¹⁴ as well as rate

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