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Electron Paramagnetic Resonance and Line Width Behavior of *trans*-Bis(oxalato)chromium(III) Complexes in Frozen Solutions

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Electron paramagnetic resonance spectra and parameters are reported for the following trans-substituted $[Cr(ox)_2X_2]^{n-}$ anions, in which X = H_2O, OH^-, NH_3, pyridine, or aniline. For all complexes the zero-field splittings (D) have values of about 1 cm^{-1}, while the rhombic distortions (E) are about 0.2 cm^{-1}. For all complexes hyperfine structure is observed in the frozen-solution spectra, from which the anisotropic hyperfine parameters A and B are determined. The dependence of the line width on the composition of the solvent is investigated. From the variation in line width with magnetic field strength it is concluded that the main contribution to line width is due to deviations in the rhombic parameter E.

Introduction

In the recording of electron paramagnetic resonance (epr) spectra of a series of corresponding paramagnetic compounds it is often difficult to find suitable diamagnetic lattices. However, from frozen-solution spectra all parameters can be obtained. It was the purpose of the present investigation to study the effect of trans substitution on the epr parameters of a series of trans-substituted $[Cr(ox)_2X_2]^{n-}$ complexes, as has been done lately[1] for *trans*-$[Cr(en)_2X_2]^{n+}$ complexes and very recently[2] for *trans*-$[Cr(NH_3)_4XY]^{n+}$ and *trans*-$[Cr(pyr)_4XY]^{n+}$ compounds. Often, the line widths of frozen solutions are too broad to give well-resolved spectra. In order to increase resolution of the peaks the influence of the composition of the frozen solution was investigated.

Table I. Epr Parameters for *trans*-$Cr(ox)_2X_2$ Complexes[a]

X	g_x[b]	g_y	g_z	D,[b] cm^{-1}	E, cm^{-1}	Δ_{av},[c] cm^{-1}
H_2O	1.98	1.99	1.98	1.08	0.293	18,000
H_2O-OH	1.97	1.97	1.98	1.07	0.294	*d*
NH_3	1.98	1.97	1.98	1.03	0.294	18,650
Aniline	1.99	1.98	1.98	1.15	0.336	18,000
Pyridine	1.97	1.97	1.98	0.98	0.288	19,000

[a] The calculated parameters are based on data from X-band spectra. [b] The accuracy of the parameters is estimated to be within 1%. [c] The average energy of the $^4T_{2g}$ band. [d] Owing to the very rapid isomerization to the cis complex no reliable value could be determined.

Experimental Section

Epr spectra were recorded at approximately −160° on X band and Q band on a Varian Model 4052 spectrometer. The magnetic field strengths were measured with an AEG gaussmeter. The microwave frequency was measured with a Takeda Riken 5502A counter equipped with a 5023 frequency converter.

The compounds were prepared by established methods.[3] Depending on the solubility of the compounds, epr spectra were recorded of frozen solutions of water–methanol–dimethylformamide (WMD) of varying composition. In all cases the solutions were frozen rapidly to prevent decomposition or in the case of H_2O–OH complexes to prevent trans to cis isomerization.[4] In doing experiments at Q band the sample was frozen immediately in liquid nitrogen, because the freezing rate of the sample in the cavity was too low.

Open thin-walled quartz tubes were used for recording spectra which showed the dependence of the line widths on the composition of the solvent. These tubes could be sealed with silicon grease.

Calculations

The spin Hamiltonian for the Cr(III) system is[5]

$$\mathcal{H}_S = \beta H\cdot\mathbf{g}\cdot S + S\cdot\mathbf{D}\cdot S + S\cdot\mathbf{A}\cdot I \qquad (1)$$

In which the first term is the Zeeman interaction, the second the zero-field splitting, and the third the hyperfine interaction. **g**, **D**, and **A** are tensors. The features of powder spectra have been described in detail.[6,7] Frozen-solution spectra can be analyzed in the same manner as powder spectra.[1] With an automatic fitting procedure[8] the parameters g_x, g_y, g_z, D, and E were calculated.

Hyperfine Splitting

By means of first-order perturbation theory the values of the hyperfine interaction constants A and B can be obtained.[9] In the spectrum only the hyperfine transitions of the $M_I = \pm{}^3/_2$ components are observed. The distance of this hyperfine line to the middle of the central line is given by

$$\Delta H = [(\alpha_m{}^2 + 3\beta_m{}^2)^{1/2} - (\alpha_{m'}{}^2 + 3\beta_{m'}{}^2)^{1/2}]/ [\mathrm{d}\epsilon_m/\mathrm{d}H - \mathrm{d}\epsilon_{m'}/\mathrm{d}H] \qquad (2)$$

$$\alpha_m = {}^3/_4 A N_m{}^{-2}(3 + |a_m|^2 - |b_m|^2 - 3|c_m|^2)$$

$$\beta_m = {}^1/_2 B N_m{}^{-2}(3a_m + 2\sqrt{3}a_m{}^*b_m + 3b_m{}^*c_m)$$

a_m, b_m, and c_m are the coefficients of the spin function m. These can be obtained by solving the 4 × 4 secular determinant from eq 1 minus the hyperfine interaction term. $\mathrm{d}\epsilon_m/\mathrm{d}H$ is the derivative of the energy belonging to spin function m with respect to the magnetic field strength. In a simple strong-field model for Cr^{3+} in D_{2h} symmetry of these complexes, the determinant wave function must be constructed out of the following 3d orbitals:[10] $b_{2g} = d_{yz}$, $b_{3g} = d_{xz}$, and $a_g = a d_{x^2-y^2} + b d_{z^2}$. In octahedral symmetry $a = 1$ and $b = 0$. The hyperfine interaction of d electrons is given by[11]

$$H_M = P(L\cdot I - KS\cdot I + {}^1/_7\Sigma a_k\cdot I)$$

$$a_k = 4s_k - (l_k\cdot s_k)l_k - l_k(l_k\cdot s_k)$$

K is the isotropic contact term and $P = 2\gamma\beta\beta_N\langle r^{-3}\rangle = -40 \times 10^{-4}$ cm^{-1} (for Cr^{3+}). From first-order perturbation theory it follows that

$$\begin{aligned} A &= P[{}^4/_{21}(1 - 2a^2 + b^2) - K] \\ B &= P[-{}^2/_{21}(1 - 2a^2 + b^2) - K] \end{aligned} \qquad (3)$$

It is assumed that A and B have the same sign because K is the largest term in the expressions.

Results

Frozen-solution spectra in different WMD mixtures were recorded for several $Cr(ox)_2X_2$ complexes in which X = H_2O, OH^-, NH_3, pyridine, or aniline. All epr spectra were very similar. As an example the frozen-solution spectrum of $[Cr(ox)_2(H_2O)_2]^-$ at X as well as at Q band is represented in Figure 1. Analysis of the spectra with an automatic fitting procedure gave the values for the magnetic parameters reported in Table I.

In Table II the measured and calculated field extremes are reported for the Q-band spectra. In general for Q-band spectra other WMD mixtures with a high water content were used to increase the solubility of the paramagnetic compounds.

Natural Cr contains 9.54% ^{53}Cr isotope with nuclear spin $I = {}^3/_2$. For all the complexes the hyperfine interaction could be observed for the first two extremes as a result of the small

Table II. Experimental and Calculated Q-Band Field Extremes

X	$H_{z\alpha}$[a]	$H_{y\beta}$	$H_{x\beta}$[c]	$H_{x\alpha}$	ν, GHz
H_2O	4544 (4540)	4852 (4825)	11,190 (11,190)	14,320 (14,200)	35.00
H_2O-OH[b]	4545 (4544)	4867 (4887)	(11,300)	(14,290)	35.04
NH_3[b]	4568 (4565)	4807 (4838)	(11,550)	(13,810)	35.00
Aniline[b]	4568 (4579)	4799 (4786)	(11,620)	(13,670)	35.04
Pyridine	4588 (4591)	4800 (4840)	11,850 (11,790)	13,590 (13,650)	35.04

[a] The values in parentheses are calculated with the parameters of Table I. Magnetic field in gauss. H_i ($i = x, y, z$) is the extreme resonance value if the corresponding principal axis is parallel to the direction of the static magnetic field. See also ref 6. [b] As a result of the weakness of the signal, only the z and y extremes could be observed. [c] For the distinction between $H_{x\beta}$ and $H_{x\alpha}$ see the caption of Figure 1.

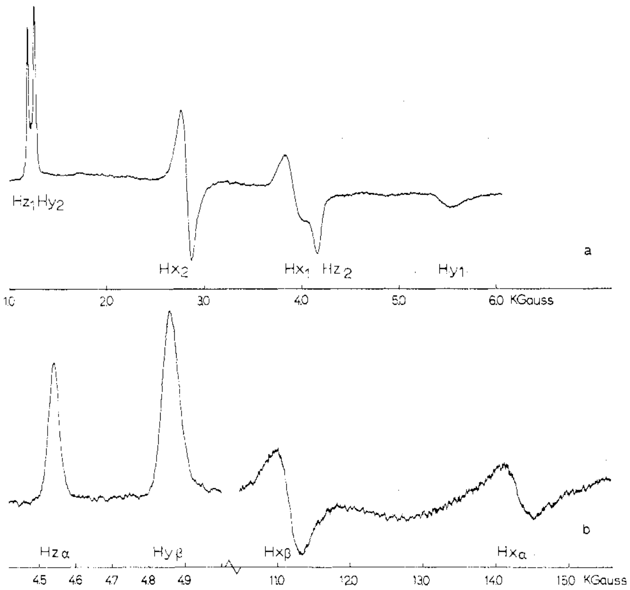

Figure 1. Frozen-solution spectra of *trans*-K[Cr(ox)$_2$(H$_2$O)$_2$]·2H$_2$O: (a) X-band spectrum in 1:8:1 WMD; H_{z1}, H_{y1}, and H_{x1} belong to the $\Delta M_S(^1/_2 \rightarrow {^3/_2})$ transition, while H_{z2}, H_{y2}, and H_{x2} are the extremes of the $\Delta M_S(-^3/_2 \rightarrow -^1/_2)$ transition; (b) Q-band spectrum in 3:4:3 WMD; $H_{z\alpha}$ and $H_{x\alpha}$ are due to $\Delta M_S(^1/_2 \rightarrow {^3/_2})$ and $H_{y\beta}$ and $H_{x\beta}$ to $\Delta M_S(-^3/_2 \rightarrow -^1/_2)$.

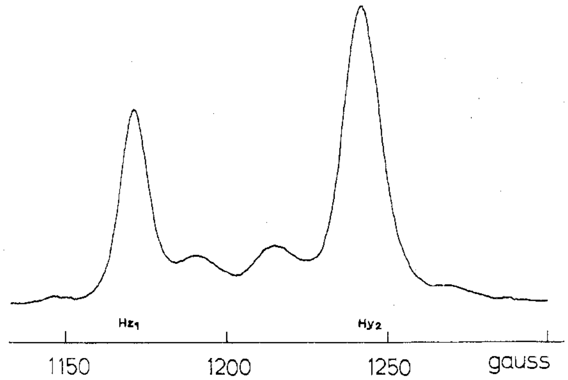

Figure 2. Hyperfine interaction of *trans*-[Cr(ox)$_2$(H$_2$O)$_2$]$^-$; X-band spectrum, ν = 9088 MHz. The hyperfine peaks outside the central lines H_{z1} and H_{y2} arise from the $M_I = \pm^3/_2$ levels.

line widths of these two peaks. As an example the hyperfine pattern of *trans*-[Cr(ox)$_2$(H$_2$O)$_2$]$^-$ is represented in Figure 2. The last term of formula 1 can be written as $AS_zI_z + {^1/_2}\cdot B(S_+I_- + S_-I_+)$, in which A and B are the anisotropic hyperfine constants. From the observed distance of the hyperfine line to the middle of the central line the hyperfine constants can be calculated with eq 2. The calculated values are reported in Table III. It is assumed that in first order the hyperfine interaction has axial symmetry.

In order to get good resolution of the peaks it is extremely important to have solvents which give as narrow lines as possible. Therefore the line width of the first peak in the frozen-solution spectrum of *trans*-K[Cr(ox)$_2$(H$_2$O)$_2$] was measured as a function of the composition of the solvent. For the ternary system of water, methanol, and dimethylformamide this behavior is represented in Figure 3. From this diagram it is evident that mixtures with not too high water contents gave narrow lines. As best mixture WMD in a ratio of 1:8:1 was taken. If the complexes were less soluble, a mixture of 3:4:3 was used.

Table III. Hyperfine Constants for *trans*-Cr(ox)$_2$X$_2$ Complexes

X	H_z[d]	H_y[d]	A[e]	B[e]	a^2[f]	KP
H_2O	24	27	14.7	16.7	0.61	16.0
H_2O-OH	22	29	13.6	17.8	0.54	16.4
NH_3[a]	25	30	15.4	18.4	0.58	17.4
Aniline[b]	25	28	15.4	17.2	0.61	16.6
Pyridine[c]	26	24	16.0	14.7	0.70	15.1

[a] The two inner hyperfine peaks were superposed. The outer H_{y2} hyperfine line was not well resolved, so that the accuracy of this splitting is not high. [b] The two inner hyperfine peaks could not be observed. [c] The two inner hyperfine peaks were superposed. [d] Observed splittings in gauss. [e] Values in 10^{-4} cm^{-1}. [f] a^2 is the square of the coefficient of $d_{x^2-y^2}$ in the determinant wave function.

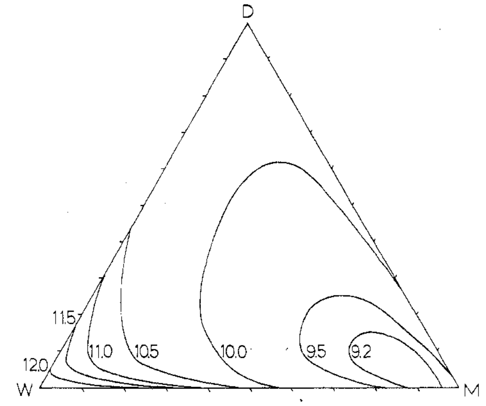

Figure 3. Line width of the first peak of *trans*-K[Cr(ox)$_2$(H$_2$O)$_2$]·2H$_2$O as function of the composition of the solvent; W = water, M = methanol, and D = dimethylformamide. Note: All measurements were carried out at the same freezing rate and with the same quartz tube. The concentration of the sample was always 10 mg in 10 ml of mixture. The composition of the mixtures was varied by steps of 10%.

Discussion

All measured *trans*-Cr(ox)$_2$X$_2$ complexes exhibit a large axial zero-field parameter D and a very large rhombic parameter E. The origin of the magnitude of these parameters is yet not clearly understood, but the deviation from octahedral symmetry can play an important part in it. For *trans*-K-[Cr(ox)$_2$(H$_2$O)$_2$]·2H$_2$O the molecular structure has been determined.[12] From this it follows that the O–Cr–O angle in the oxalate ligand is only 83° and the Cr–O(H$_2$) distance is 2.02 Å, while the Cr–O(X) distance is 1.92 Å. The Cr–O(H$_2$) distance is elongated considerably with respect to several hexahydrates, for which the Cr–O distance is about 1.92 Å. The calculated value of a^2 is in accordance with the deviation of octahedral symmetry of the complex.

In the case of the pyridine complex it is assumed that also the π system plays an important part in the bonding, so the bonding is more covalent than in other complexes, which is in accordance with the low value[13] of KP (Table III). Therefore the simple crystal field model is less appropriate in this compound.

If in the first instance it is supposed that the trans complex has tetragonal symmetry, then from second-order perturbation theory on a simple crystal field model the following expression for the zero-field splitting D can be derived[5]

$$2D = \frac{-8\lambda^2}{\Delta_0} + \frac{8\lambda^2}{\Delta_1}$$

where λ is the spin–orbit coupling constant, Δ_0 is the energy difference between the $^4A_{2g}$ ground state and the $^4T_{2g}(\zeta)$ level, and Δ_1 is the energy difference with $^4T_{2g}(\xi,\eta)$. The preceding expression can be simplified to

$$|D| = \frac{4\lambda^2}{\Delta_{av}^2}|\delta| \tag{4}$$

where $\delta = \Delta_0 - \Delta_1$ is the energy splitting of the $^4T_{2g}$ level and Δ_{av} is the average energy of the $^4T_{2g}$ band.

From formula 4 it can be seen that the zero-field splitting (zfs) depends on the value of Δ_{av} and on the splitting δ of the $^4T_{2g}$ level. Inspection of Table I shows that for the H_2O, NH_3, and pyridine complexes the zfs decreases with increasing Δ_{av}. This can lead to the conclusion that the influence of Δ_{av} is dominant compared to that of δ, although it may be expected that the latter parameter increases with increasing ligand field strength of the trans substituents. From visible spectra there are no estimations of δ, but the half-bandwidths of the various complexes do not differ much, so the splittings of the $^4T_{2g}$ levels are of the same order and this can explain the dependence of zfs on Δ_{av}. The aniline complex forms an exception, first to the unexpected value of 18,000 cm^{-1} for Δ_{av} and second to a much higher rhombic distortion of 0.336 cm^{-1}. With respect to above-mentioned explanations it must be kept in mind that formula 4 has been derived for a pure tetragonal case in the crystal field model, while for the investigated *trans*-$Cr(ox)_2X_2$ series the rhombic deviation is large and also overlap with the ligand molecules cannot be excluded entirely.

There is a great difference in the variation of the zfs of these series of *trans*-$Cr(ox)_2$ complexes and in those of the series of *trans*-$Cr(NH_3)_4$ and *trans*-$Cr(pyr)_4$ complexes.[2] In the latter two series the zfs depends mainly on the variation of the splitting of the $^4T_{2g}$ level. Also in the series of the *trans*-$Cr(en)_2$ complexes,[1] the zfs increases somewhat with increasing ligand field strength of the trans substituent. A reason for this difference may be the deviation from tetragonal symmetry and the fact that NH_3, pyridine, and ethylenediamine are all relatively strong ligands, while the oxalate ion is a weak one. Thus in the oxalate series the trans-substituted ligands are all stronger.

From investigations on the behavior of the line width, it followed that the line width of frozen-solution spectra is very dependent on the freezing rate and on the composition of the solvent. Reduction of the freezing rate increased the line width considerably. At low freezing rate segregation takes place in the solution. Domains of high concentration of paramagnetic molecules arise. Through magnetic dipolar interaction the lines are broadened.[14] In Figure 3 the influence of the composition of the solvent is represented. It is evident from Figure 3 that a high water content of the solvent also gives rise to considerable line broadening, probably because of segregation. No displacements of the peaks were observed with different WMD mixtures. Up to a concentration of 40 mg of $K[Cr(ox)_2(H_2O)_2]\cdot 2H_2O$ in 10 ml of WMD mixture no effect could be observed on the peak widths.

From Figure 1 it can be seen that in the X-band as well as in the Q-band spectrum the line widths of the peaks increase with increasing magnetic field, with exception of the fifth peak in the X-band spectrum. As a result of this proportionality it is best to take mixtures with a high methanol content, in order to get the greatest resolution of the peaks in the epr spectrum. In Table IV the line widths of the peaks of the frozen-solution spectrum of $K[Cr(ox)_2(H_2O)_2]\cdot 2H_2O$ in 3:4:3 WMD are reported.

Table IV. Line Widths of the Epr Peaks in the Frozen-solution X-Band Spectrum of *trans*-$K[Cr(ox)_2(H_2O)_2]\cdot 2H_2O$ in 3:4:3 WMD

	H_{z_1}[a]	H_{y_2}	H_{x_2}[b]	H_{x_1}[b]	H_{z_2}	H_{y_1}
Line width, G	11	14	156	208	103	320
$\lvert\delta H/\delta D\rvert$, G cm[c]	128	191	1703	3153	1953	4187
$\lvert\delta H/\delta E\rvert$, G cm[c]	469	711	6205	11,400	6473	20,077

[a] The numbering of the peaks corresponds to that of Figure 1. [b] The shape of all peaks is almost gaussian. As a measure for the peak width the half-width $\Delta H_{1/2}$ is taken. The typical first-derivative shapes of the two x peaks are reduced to $\Delta H_{1/2}$ with the formula $\Delta H_{1/2} = 1.777\Delta H_{pp}$, in which ΔH_{pp} is the peak-to-peak line width. [c] Calculated for this complex with the parameters of Table I.

There are several mechanisms such as spin–spin,[14] spin–lattice interaction, and zero-field modulation[15] which can contribute to the line width. It is believed that these interactions give no important contribution to the line width under the applied experimental conditions. Another origin of the increasing line width with increasing magnetic field can be the variation in resonance field as a function of the angle near the extremes. To verify this effect the peak widths of the frozen-solution spectrum were calculated with a semiempirical method.[16] An individual line width of 30 G, which could account for the peak half-widths of H_{z1} and H_{y2}, for H_{x2} gave a width of about 50 G, which is much smaller than the observed value of 208 G. Also the calculated values of the other peaks were much smaller than the experimental ones. In this case it is probable that the main contribution to the line width in frozen solutions comes from variations in the zero-field parameters, either by different surroundings of the solvent molecules (dislocations in the frozen-solution matrix) or by distortions of the dissolved paramagnetic molecules themselves. Thus the line widths must be proportional to $|\delta H/\delta D|$ and/or $|\delta H/\delta E|$. From Table IV it can be seen that the line width follows the trend in both, but no conclusions about the contributions of each to the line width can be made. The reason for this is that the reported line widths in Table IV are also dependent on the transition probability and on the rotation distribution of the resonance field in the neighborhood of one of the extremes. From other observations[8,17] it followed that D is less sensitive to other symmetries of the surroundings than E. From calculations it follows that a mean departure of a few per cent from the value of E can account for the trend in the observed line width.

From an investigation on powder spectra of isomorphic mixed crystals of Cr and Co complexes it followed that the peak widths increased with increasing magnetic field, but to a lesser extent than in the case of frozen solutions. Of great influence on the observed line widths is the carefulness with which the crystals are grown.[18] Also in this case distortion of symmetry plays an important part, because misalignment of the molecules[19] in the lattice does not broaden very much the peaks of the extremes in powder spectrum.

Cis Spectra. For the H_2O–H_2O and H_2O–OH complexes the epr spectra of the cis isomers were recorded too. The spectra did not resemble the corresponding trans spectra. In the *cis*-H_2O–H_2O spectrum only two peaks were observed on X band and an intense one was observed on Q band. From this it is concluded that the value of E/D is close to $^1/_3$ and the value of D is somewhat more than 0.5 cm^{-1}. The spectra of the *cis*-H_2O–OH complex were very similar to those of the H_2O–H_2O complex. From this followed a value of E/D somewhat lower than $^1/_3$ and a value of D about 0.45 cm^{-1}. Both cis spectra were contaminated with the trans spectra as a result of cis–trans isomerization.[4] In the case of cis–trans octahedral isomers it can be derived that the tetragonal splitting of the trans configuration is twice the rhombic splitting[20] of the cis isomer. So from formula 4 it follows that the zero-field splitting of a cis complex is only half of that of the corresponding trans complex, if Δ_{av} for both isomers does not differ much. It was observed indeed that for the H_2O–H_2O and H_2O–OH complexes the D parameters of the cis complexes are about half of those of the trans complexes. In both cases the values of Δ_{av} of the cis and trans complexes do not differ much.

Conclusion

The paramagnetic values of the reported trans complexes do not differ much with the trans substituent, so the main features are determined by the $Cr(ox)_2$ skeleton. Under special conditions, such as small line width and not too low $D/h\nu$ values, epr spectra of frozen solutions can be used to distinguish isomers, for instance in the case of cis–trans isomers. In this investigation it became evident that the pink pyridine, the lilac aniline, and the NH_3 compounds have the trans configuration.

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Registry No. *trans*-$[Cr(ox)_2(H_2O)_2]^-$, 18954-99-9; *trans*-$[Cr(ox)_2(H_2O)(OH)]^{2-}$, 36444-11-8; *trans*-$[Cr(ox)_2(NH_3)_2]^-$, 54053-39-3; *trans*-$[Cr(ox)_2(\text{aniline})_2]^-$, 53992-87-3; *trans*-$[Cr(ox)_2(\text{pyridine})_2]^-$, 36444-16-3; *cis*-$[Cr(ox)_2(H_2O)_2]^-$, 15489-30-2; *cis*-$[Cr(ox)_2(H_2O)(OH)]^{2-}$, 53992-86-2.

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