Magnetic Susceptibility and EPR Spectra of (*μ*-Hydroxo)bis[pentaamminechromium(III)] Chloride Monohydrate

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From magnetic susceptibility measurements the *J*-value of (*μ*-hydroxo)bis[pentaamminechromium(III)] chloride hydrate was found to be 32.3 cm^{-1}. The EPR spectra of the complex diluted in the analogous cobalt(III) complex have been recorded down to 4 K. The spectrum from the quintet state has been identified by the temperature variation of the intensity. Below 200 K the quintet spectra consist of two spectra originating from two different sites in the crystal. Both spectra have been computer simulated, and the following two parameter sets were obtained for the two different ions in the crystal: $D_e = -0.0512(1)$ cm^{-1}, $E_e = -0.0263(1)$ cm^{-1}; $D_e = -0.0498$ cm^{-1}, $E_e = -0.0263$ cm^{-1}.

Introduction

The cation "acid rhodo" (*μ*-hydroxo)bis[pentaamminechromium(III)] (5+) was first prepared by Jørgensen[2] in 1882, and since that time, it has been subject to considerable interest. Two modifications of the chloride salts are known, mono- and dihydrates, both of which have been examined by X-ray crystallography.[3,4]

In a recent paper Güdel[5] has shown by single-crystal spectroscopy that the acid rhodo monohydrate $[(NH_3)_5CrOHCr(NH_3)_5]Cl_5\cdot H_2O$ contains two inequivalent sets of complexes in the unit cell which contradicts the crystal structure determination.[3] In recent work[6−8] we have simulated EPR spectra of antiferromagnetically coupled dinuclear chromium(III) complexes, and with this technique at our disposal we will show that the EPR spectra of the acid rhodo mono hydrate diluted in the analagous cobalt(III) complex definitely confirm that the crystals contain two different sites. Furthermore we will show that the usual spin Hamiltonian operator (eqs 4−6; *vide supra*) is not sufficient simultaniously to simulate the EPR spectra from the triplet, quintet, and septet states which emerge as a result of the antiferromagnetic coupling between the two chromium(III) ions.

Experimental Section

Magnetic Measurement. The magnetic susceptibility was measured on a Faraday balance which has been described elsewhere.[9]

EPR Spectra. The EPR spectra have been recorded with a Bruker ESP 300 spectrometer equipped with an Oxford ESR-900 continous-flow cryostat. The spectra were recorded at 9.38 GHz, 20 mW microwave power, and with modulation frequency 100 kHz and modulation amplitude of 5 G.

Synthesis. $[(NH_3)_5CrOHCr(NH_3)_5]Cl_5\cdot H_2O$ was prepared according to Linhard et al.,[10] and $[(NH_3)_5CoOHCo(NH_3)_5]Cl_5\cdot H_2O$ was prepared according to Siebert et al.[11] A mixture of the chromium complex (1%) and the cobalt complex was recrystallized[10] from 10^{-2} M acetic acid.

X-Ray Powder Diagrams. These were measured on a Guinier−Hägg camera using Cu Kα radiation. The data from the Guinier film was fitted by a least-squares program to a tetragonal cell. For the cobalt and chromium complexes the following cell constants were obtained: Co, $a = 15.980(5)$ Å, $c = 7.330(3)$ Å, Cr, $a = 16.269(4)$ Å, $c = 7.393(3)$ Å. The X-ray data[3] for the chromium complex were solved in the centrosymmetric space group $P4_2/mnm$ with the cell constants $a = 16.259(7)$ Å and $c = 7.411(7)$ Å. We conclude that the Cr- and Co-containing crystals are isomorphous.

Computer Simulation. The simulation of the EPR spectrum was performed by generating the energy matrix for each orientation of the molecule relative to the magnetic field. The resonance condition for each transition was then found by successive diagonalizations and iterations of the energy matrix, and the relative intensities were calculated from the eigenvectors multiplied by the appropriate Boltzmann factor at the actual temperature. Summation of all the transitions over the whole space, where each transition is represented by a differentiated Lorentzian curve, gives the simulated spectrum. A more detailed description of the numerical method will be given elsewhere.

Results and Discussion

Magnetic Susceptibility. The temperature dependence of the magnetic susceptibility of $[(NH_3)_5CrOHCr(NH_3)_5]Cl_5\cdot H_2O$ was measured in the temperature range 4−300 K. As seen in Figure 1, the susceptibility curve has a maximum at approximately 70 K and the effective magnetic moment declines from 5.0 μ_B at room temperature to almost zero at 4 K. This is the expected behavior characteristic for an antiferromagnetically coupled dimeric chromium(III) complex. The susceptibility data was analyzed by fitting to the following expression:

$$\chi'_{\rm mol} = -\frac{N}{H}\frac{\sum_i \frac{\partial E_i}{\partial H}\exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)} + K + C/T \qquad (1)$$

Here E_i are the energies of the 16 components of the ground-state manifold. The energies of the different components were

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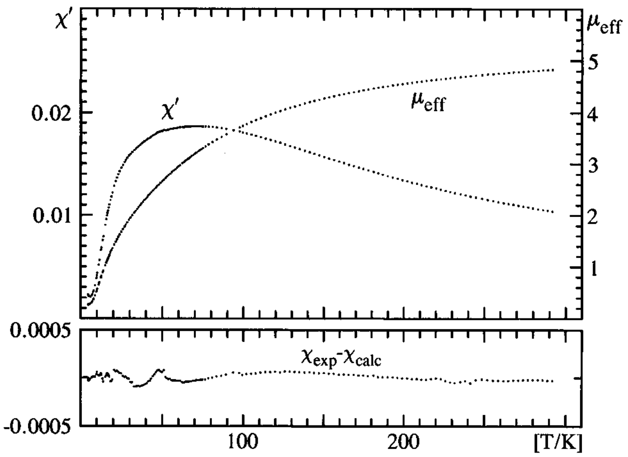

Figure 1. Magnetic susceptibility (cgs units) and the effective magnetic moment of $[(NH_3)_5CrOHCr(NH_3)_5]Cl_5\cdot H_2O$ as a function of temperature. The lower graph gives the difference between the measured and the calculated susceptibility.

obtained by means of the isotropic spin Hamilton operator

$$\hat{\mathbf{H}} = g_a\mu_B\hat{S}_a\cdot\hat{H} + g_b\mu_B\hat{S}_b\cdot\hat{H} + J\hat{S}_a\cdot\hat{S}_b \qquad (2)$$

where we have choosen $g_a = g_b$. This is justified because the crystal structure[3] shows that the two chromium atoms are connected by a 2-fold axis.

The following parameters were obtained: $g = 1.985(3)$ and $J = 32.3(1)$ cm^{-1}. The compound contained 0.56% monomeric impurity. The lower curve in Figure 1 shows the difference between the measured and the calculated susceptibility. This curve has an irregularity in the temperature interval 30−50 K. This is due to the condensation of a slight amount of oxygen on the sample container and later the evaporation of the oxygen as the temperature is increased. The found J-value is in accordance with the previously reported[3] one: 31.5 cm^{-1}. By spectroscopic methods Güdel[4] finds the triplet−singlet separations for the two sites to be 32.4 and 32.1 cm^{-1}, respectively.

EPR Spectra. The X-band EPR spectra of the acid rhodo were measured at temperatures down to 4 K on a frozen glass of the complex dissolved in a mixture of water and glycerol (50/50 v/v) as well as a on crystal powder of the complex diluted in the analagous cobalt(III) complex. The main features of the two sets of spectra are identical. The upper curve in Figure 2 shows the powder spectrum at 292 K, the middle curve that at 42 K, and the lower curve that at 4 K. The energy of the state causing the spectrum at 42 K was calculated by fitting the temperature dependence of the line intensities to the following expression:

$$I \propto \frac{1}{T}\frac{\exp(-E/kT)}{\sum_i \exp(-E_i/kT)} \qquad (3)$$

This gives $E = 102(10)$ cm^{-1}. This energy corresponds to the quintet state and gives $J = 34(3)$ cm^{-1} in excellent agreement with the susceptibility data. The spectrum at 292 K is dominated by the spectrum from the septet state; the spectrum at 42 K is almost solely from the quintet state, while the spectrum at 4 K is from the triplet state together with some monomeric impurities, *e.g.* chromium(III) and cobalt(II). The broad line centered at 1300 G in the 4 K spectrum must be an impurity, presumably monomeric chromium(III) in low symmetry,[12,13] and the line centered at 6115 G is also an impurity because this line is not present in all the crystals measured; furthermore, we were unable to simulate the line as originating from the dinuclear complex. The signal observed at 3322 G in the 42 K spectrum is an impurity in the cavity of our EPR spectrometer.

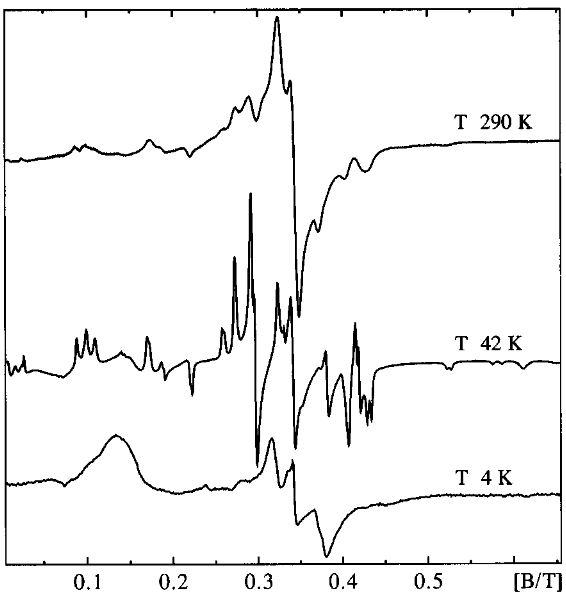

Figure 2. Powder EPR spectrum of $[(NH_3)_5CrOHCr(NH_3)_5]Cl_5\cdot H_2O$ diluted in the analogous cobalt(III) complex measured at 290, 42, and 4 K. The relative intensities are arbitrary.

Interpretation of EPR Spectra. The EPR spectra were simulated by means of the following spin Hamiltonian operator:

$$\hat{\mathbf{H}} = \hat{\mathbf{H}}_a + \hat{\mathbf{H}}_b + \hat{\mathbf{H}}_{ex} \qquad (4)$$

Here

$$\hat{\mathbf{H}}_{ex} = J\hat{S}_a\cdot\hat{S}_b + D_e(2\,\hat{S}_{az}\hat{S}_{bz} - \hat{S}_{ax}\hat{S}_{bx} - \hat{S}_{ay}\hat{S}_{by}) + E_e(\hat{S}_{ax}\hat{S}_{bx} - \hat{S}_{ay}\hat{S}_{by}) \qquad (5)$$

and

$$\hat{\mathbf{H}}_a = g\mu_B\hat{S}_a\cdot\hat{H} + D_a[\hat{S}_{az}^{\,2} - {}^1\!/_3S_a(S_a + 1)] + E_a(\hat{S}_{ax}^{\,2} - \hat{S}_{ay}^{\,2}) \qquad (6)$$

and with a similar Hamiltonian operator for atom b. Again it has been assumed that the g values for the two chromium atoms are identical, *i.e.*, the two chromium atoms can be interchanged. In the incorrect crystal structure the molecule contains a 2-fold axis.[3]

As previously shown[6] the calculations can be simplified if the molecule contains either a 2-fold axis, an inversion center, or a mirror plane, because the 16 × 16 complex energy matrix can then be reduced to a 6 × 6 matrix containing the even S values and a 10 × 10 matrix containing the uneven S values.

The spectrum from the quintet state is easy to simulate, because at 42 K the spectrum from the septet state has disappeared and the two parameters which matter for the quintet state are D_e and E_e which can be determined from the two lines at highest fields. By the method of trial and error the D_e value is determined so that the simulated line at highest field fits the observed line at the highest field, and similarly the E_e parameters are fitted to the line at the next highest field.

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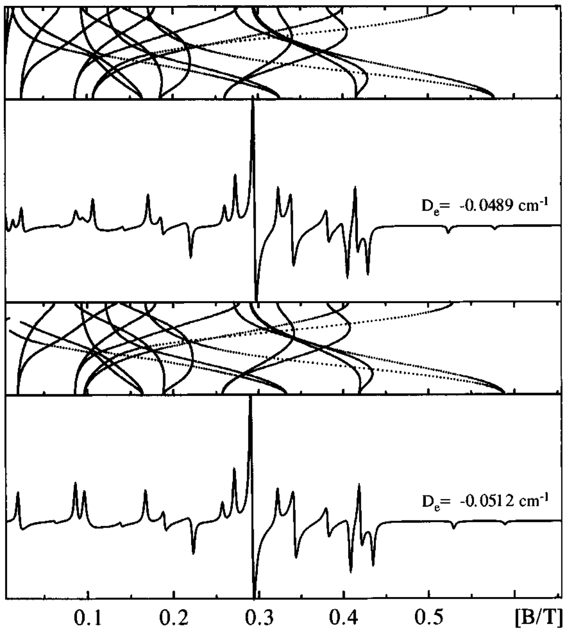

Figure 3. Simulated EPR spectra from the quintet states of the two sites in the crystal $[(NH_3)_5CrOHCr(NH_3)_5]Cl_5{\cdot}H_2O$, where the parameters in the upper spectrum are $g = 1.985$, $J = 32.3$ cm^{-1}, $D_e = -0.0489$ cm^{-1}, and $E_e = -0.0263$ cm^{-1} and the parameters in the lower spectrum are $g = 1.985$, $J = 32.3$ cm^{-1}, $D_e = -0.0512$ cm^{-1}, and $E_e = -0.0263$ cm^{-1}. The diagrams above the two simulated spectra give the angular dependence of the resonance condition within the quintet state as function of the orientation of the magnetic field relative to the molecular *z*-axis.

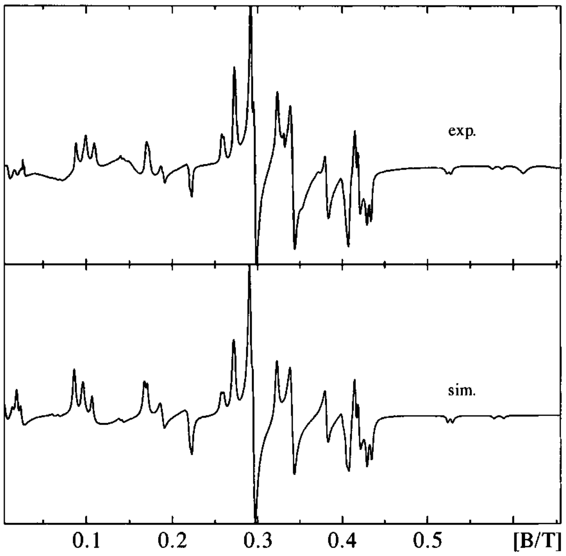

Figure 4. Experimental spectrum at 42 K and the sum of the two simulated quintet spectra from Figure 3.

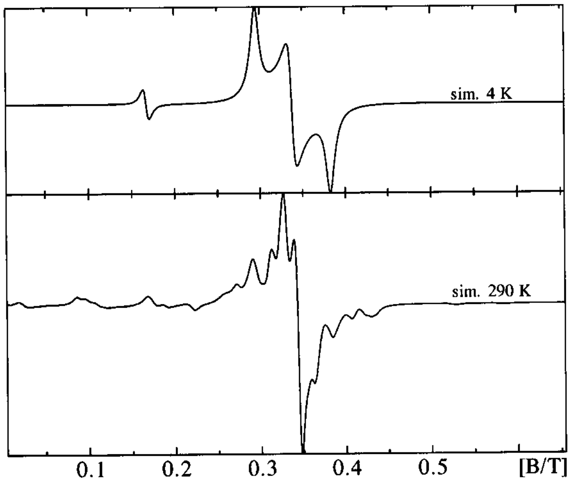

Figure 5. Triplet spectrum simulated at 4 K with the parameters $D = -0.1255$ cm^{-1} and $E = -0.0242$ cm^{-1} and with the same parameters for D_e and E_e as in Figure 3. The sum of the septet and quintet spectra is weighted with the appropriate Boltzmann factors at 290 K. The parameters are $D = 0.076$ cm^{-1} and $E = 0.020$ cm^{-1} and with D_e and E_e as before for the two sites.

The middle spectrum in Figure 2 has a set of double lines around 5250 G and around 5800 G, and the doubling of lines is not observed in the spectra measured on frozen glases. This is an unusual feature, and the most tempting explanation is that there are two different sites in the crystal. If it is assumed that the lines at 5278 G and at 5865 G belong to one site and the lines at 5208 G and at 5753 G belongs to the other site, two quintet spectra can be simulated. All other combinations of the four lines and two sites do not fit with the experimental spectra. The spectra in Figure 3 were simulated with the bandwidth 35 G and the following parameters: $g = 1.985$, $J = 32.3$ cm^{-1}; with $D_e = -0.0489$ cm^{-1} and $E_e = -0.0263$ cm^{-1} for the one site and $D_e = -0.0512$ cm^{-1} and $E_e = -0.0263$ cm^{-1} for the other site. We have here assumed D_e negative because this parameter can be written as a sum of a dipolar and a pseudodipolar term[14] and with a bond distance[3] of 3.852(9) Å the dipolar term is calculated to be -0.0303 cm^{-1}. The two simulated quintet spectra for the two sites do not match the experimental spectrum especially around 1000 G and around 4200 G, where in both cases three lines are observed; however, the sum of the two spectra weighted 1:1 fits extremely well with the experimental spectrum as seen in Figure 4. This weighting factor means that the two sites are equally represented in the crystal. From these simulations we have proved that the acid rhodo monohydrate contains two inequivalent sites in the crystal.

The simulation of the spectrum from the septet state is more difficult. In this case the lines at the highest fields cannot be identified because the septet spectrum is superimposed on the top of the quintet spectrum. The quintet spectrum is rather insensitive to the single atom zero-field splitting (zfs) parameters *D* and *E* because these parameters appear only in the matrix as nondiagonal elements between the quintet and the singlet states. These parameters then have to be determined from the septet spectrum, by the method of trial and error. The septet spectrum was then added to the quintet spectrum weighted with the appropriate Boltzmann factor. The results in Figure 5 were simulated with the parameters for the quintet spectrum and zfs parameters $D = 0.076$ cm^{-1} and $E = 0.020$ cm^{-1}. The bandwidth for the quintet spectrum was increased from 35 to 100 G, while the bandwidth for the septet spectrum is 120 G. With the parameters thus obtained the triplet spectrum was simulated, but the result was useless. If the quintet and the triplet spectra are simulated simultaneously, the zfs parameters for the triplet state became $D = -0.1255$ cm^{-1} and $E = -0.0242$ cm^{-1}. From this we must conclude that the spin Hamiltonian in the eqs 4−6 are not sufficient to simulate all the three states. The same conclusion can be obtained from Kremer's[15] single-crystal EPR spectra of the cation $[L_3Cr(OH)_3CrL_3]^{3+}$, where L_3 is 1,3,5-trimethyl-1,3,5-triazacyclononane. In this paper he has determined three zfs parameters, one for each spin state,[14] and then unsuccessfully tried to translate these parameters by means of Judd's formulas[14] to the

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parameters used here. These formulas are based on the approximation that the nondiagonal elements between the different spin states can be neglected.

An estimate of the size of D can be made from the visible absorption spectra provided that the two split components of the first spin allowed transition are observed, however, this is not the case. By means of the angular overlap model[16] the energies of the two split components $^4B_2$ and ^4E can be calculated from the octahedral ligand field parameters of the ligands ammonia and hydroxide. The exact value for the bridging hydroxide ligand is not known, but it cannot be far from the value for water. With[16] $\Delta_N = 21.600\ \text{cm}^{-1}$ and $\Delta_{OH} = 17.400\ \text{cm}^{-1}$ and for the spin−orbit constant $\zeta = 273\ \text{cm}^{-1}$ one obtains[7]

$$D = {}^1/_2[E(\pm{}^3/_2) - E(\pm{}^1/_2)] = \frac{4}{9}\cdot\frac{\zeta^2(^4B_2 - {}^4E)}{\Delta_{av}{}^2} \approx \frac{4}{9}\,\frac{\zeta^2[\Delta_N - {}^1/_4(3\Delta_N + \Delta_{OH})]}{\Delta_{av}{}^2} \approx 0.08\ \text{cm}^{-1} \quad (7)$$

This value is in fair agreement with the value found from the septet spectrum but far from the value from the triplet spectrum.

The single ion operator (eq 6) is well established for monomeric $S = {}^3/_2$ systems, while the magnetic interaction operator (eq 5) besides the isotropic interaction term and the dipolar term must be expected to contain further terms. A way to construct a better operator is to consider how the antiferromagnetic interaction separates the different spin states. This splitting is due to the mixing of charge-transfer states into the ground states,[17−19] where the charge-transfer states are those where one electron is moved from one metal to the other and *vice versa*. If these charge-transfer states possess a zfs, then this zfs will be mixed into the ground levels with the result that the septet state will not receive any contribution, while it can be shown that the triplet state will receive a contribution which is minus five times the contribution the quintet state will receive. Qualitatively this model can explain why the septet spectrum is less split than the quintet spectrum.[7] By further work on these guidelines we hope to construct a spin Hamiltonian which can describe the energies of all the levels in the spin multiplets.

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