

## Magnetic Properties and Molecular Structure of the $\mu$ -Oxo-bis{pentamminechromium(III)} Ion

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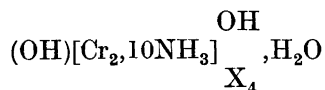
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Magnetically pure crystals of  $\mu$ -oxo-bis{pentamminechromium(III)} halides,  $[(\text{NH}_3)_5\text{Cr}-\text{O}-\text{Cr}(\text{NH}_3)_5]\text{X}_4 \cdot \text{H}_2\text{O}$ , have been obtained by a low temperature method. In contrast to all previous measurements the paramagnetic susceptibility could be fitted extremely accurately in the temperature range 50–300 K to an isotropic exchange model, coupling two spins with  $S = \frac{3}{2}$  and including the term  $J \cdot S_1 \cdot S_2$  in the Hamiltonian, with  $J = 450 \text{ cm}^{-1}$ . Coupling of two spins with  $S = \frac{1}{2}$  did not agree with the experimental data. Intermolecular interaction was found to be negligible. Samples prepared in the conventional way showed irreproducible magnetic behaviour due to the impurity  $[(\text{NH}_3)_5\text{Cr}-\text{OH}-\text{Cr}(\text{NH}_3)_4(\text{OH})]\text{X}_4$ . The susceptibility of these compounds fitted very accurately to the same model with  $J = 23 \text{ cm}^{-1}$ .

X-Ray analysis showed that the chloride and the bromide of the oxo-bridged complex belonged to the orthorhombic space group *Pbca* with the cell dimensions  $a$  11.97 Å,  $b$  11.62 Å,  $c$  13.64 Å, and  $a$  12.45 Å,  $b$  11.58 Å,  $c$  14.21 Å, respectively. Four formula units were found per unit cell. Therefore the symmetry of the space group requires the Cr–O–Cr bond to be linear.

The pure compounds were characterized by their infrared spectra and by visible-ultraviolet absorption spectra at  $-25^\circ\text{C}$ .

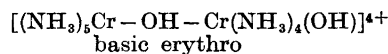
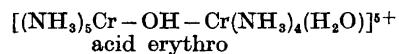
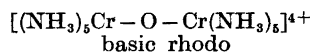
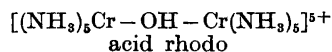
The origin of the indigo blue colour and the reason for the fast hydrolysis of the  $\mu$ -oxo-bis{pentamminechromium(III)} salts, first prepared by Jørgensen<sup>1</sup> and called "basic rhodo chromium" salts, have long been a challenge to chromium chemists. The compounds were originally formulated as



and were formed by the momentary reaction of red "acid rhodo chromium" salts,  $(\text{OH})[\text{Cr}_2, 10\text{NH}_3]\text{X}_5$ , in strongly basic solution. This reaction was reversible on immediate addition of acid. But after a few minutes in basic solution the basic rhodo salts were transformed to another red series, called "basic

erythro chromium" salts,<sup>2</sup> stable for several hours in solution. These latter compounds were transformed reversibly by the addition of acid to "acid erythro chromium" salts. Owing to inaccurate analytical results and an incorrectly interpreted experiment by Jørgensen purporting to show that acid erythro salts were completely retransformed to acid rhodo salts by heating the solid compounds at 100°C, it was believed for more than seventy years that the two series were simply isomers. Werner<sup>3</sup> assumed (by using the concept of "Nebenvalenz") that the rhodo and erythro salts were dimers with a hydroxo- and oxo-bridge, respectively. By arguments based on acid strengths of coordinated water and  $\mu$ -hydroxo groups Jensen<sup>4</sup> postulated the acid and basic rhodo compounds to have  $\mu$ -hydroxo and  $\mu$ -oxo groups, respectively, and the acid and basic erythro compounds both to have  $\mu$ -amine groups and a coordinated water and a hydroxo group, respectively. It was further claimed that the erythro and rhodo salts were isomorphous because of similar X-ray powder diagrams.

At this stage the problem was left until Wilmarth *et al.*<sup>5</sup> found the chromium to ammonia ratio to be 2 : 10 and 2 : 9 for the rhodo and erythro series, respectively. By cleaving experiments and determination of the p*K* values they proposed the following formulae:



Furthermore they showed the basic rhodo salts to have quite unique magnetic properties among all other known chromium(III) complexes in having a magnetic moment about one Bohr magneton per chromium atom at room temperature and decreasing moments at lower temperatures. The small room temperature moment was also mentioned independently by Bjerrum.<sup>6</sup> Wilmarth *et al.* related this behaviour to a linear Cr - O - Cr unit with considerable  $\pi$ -bonding and subsequent electron spin pairing according to the molecular orbital theory of Dunitz and Orgel<sup>7</sup> as applied to the diamagnetic complex  $[\text{Cl}_5\text{Ru} - \text{O} - \text{RuCl}_5]^{4-}$ , known to be linear.<sup>8</sup>

Schäffer<sup>9</sup> also measured the temperature dependence of the susceptibility of basic rhodo dithionate, but found it to be very irreproducible because of impurities. He further reported the reflectance spectrum to show quite unexpected maxima, especially some very narrow peaks in the range 24 - 30 kK.

The oxygen bridged structures proposed by Wilmarth *et al.* were further supported by the cleaving experiments, solubility measurements, p*K* determinations, and kinetic experiments by Linhard and Weigel<sup>10</sup> and by Schwarzenbach and Magyar.<sup>11</sup> Kinetic studies of the hydrolysis of basic rhodo chromium were also performed by Mori *et al.*<sup>12</sup> By these experiments and especially by the molecular weight determination of Schwarzenbach and Magyar<sup>11</sup> the dimeric structure was verified.

The magnetic properties were reinvestigated by various groups: Kobayashi *et al.*,<sup>13</sup> Earnshaw and Lewis,<sup>14</sup> and Jezowska-Trzebiatowska and Wojciechowski.<sup>15-19</sup> That the reported data are quite contradictory, may perhaps be attributed to the great preparative difficulties. The methods published all

result in microcrystalline powders contaminated with basic erythro salts. The same authors claim the chloride to be paramagnetic at room temperature, but the bromide to be diamagnetic. This cannot be explained by erythro impurities. The weak paramagnetism has been interpreted in terms of the Heisenberg-Dirac model with a term in the Hamiltonian of the form  $J \cdot S_1 \cdot S_2$ . All the previous experimental data published until now fit very poorly to this model (see Fig. 1), but nevertheless  $J$ -values above 150–200  $\text{cm}^{-1}$  have been estimated.<sup>9,13</sup>

It has been mentioned that EPR spectra are completely absent for the basic rhodo salts.<sup>15</sup> This was used to support the assumption of a singlet ground state and high lying states with higher multiplicity.

Quite recently the low temperature reflectance spectrum has been recorded.<sup>20</sup> Some of the narrow peaks showed a very pronounced temperature dependence of their intensities. These were interpreted as "hot" bands coming from a state about 400  $\text{cm}^{-1}$  above the ground state.

In the present paper we describe how the preparative difficulties have been circumvented by working with solutions in 12 M ammonia in the temperature range  $-10$  to  $-25^\circ\text{C}$ . In this way it has been possible to obtain single crystals of the chloride and the bromide sufficiently large for an X-ray structure determination to be performed. This is now in progress and is being carried out at this laboratory by E. Poulsen and E. Bang, who at an early stage of their work found the basic rhodo ions to have a center of symmetry at the position of the oxygen atom, confirming the postulate of a linear Cr–O–Cr bond. Susceptibility measurements in the range 50–300 K were independent of the anion type and agreed well with a Heisenberg-Dirac intramolecular spin-spin coupling between two spins with  $S = \frac{3}{2}$  and with a singlet triplet separation of 450  $\text{cm}^{-1}$ . It was further found that the earlier measurements of Earnshaw and Lewis<sup>14</sup> as well as new measurements on various samples prepared according to the old procedure<sup>1</sup> could be fitted nicely by assuming basic erythro salts to be the only other impurity. The main features of the EPR powder spectra at liquid nitrogen and room temperature were reasonable for a system with a singlet ground state and with a higher lying triplet with  $g = 1.98$ .

## EXPERIMENTAL

### Preparations

The initial material, acid rhodo chromium chloride, was prepared according to Linhard and Weigel<sup>10</sup> and recrystallized as the monohydrate.

*Large crystals of basic rhodo chromium chloride*,  $[(\text{NH}_3)_6\text{Cr}-\text{O}-\text{Cr}(\text{NH}_3)_6]\text{Cl}_4 \cdot \text{H}_2\text{O}$ . This preparation must be performed in the absence of daylight. 500 ml of 12 M ammonia was precooled to  $0^\circ\text{C}$  in ice. 200 g of crushed ice was added with stirring whereby the temperature fell to *ca.*  $-12^\circ\text{C}$ . 15 g of finely crystalline acid rhodo chloride monohydrate was added with vigorous magnetic stirring. After 1 min the deep blue solution was quickly filtered into a precooled suction flask through a 20 cm Büchner funnel with coarse filter paper. The filtrate was transferred to a precooled 1 l Dewar flask. This should not take more than one extra minute. A solution, prepared by dissolving 50 g of lithium chloride in 100 g of crushed ice and cooling to  $-5^\circ\text{C}$  was added dropwise without stirring. This addition should not take more than 15 min. In this way the size of the octahedral crystals obtained was about 0.15 mm. The dark blue crystalline product was quickly filtered and washed with 10 ml of ice-cold water and 96 % ethanol until all ammonia was removed.

The product was dried in air. The yield was not quite reproducible but varied between 2 and 5 g. The product was kept in a refrigerator at  $-20^{\circ}\text{C}$ . (Found: Cr 23.12;  $\text{NH}_3$  37.66; Cl 31.36. Calc. for  $[(\text{NH}_3)_5\text{Cr}-\text{O}-\text{Cr}(\text{NH}_3)_5]\text{Cl}_4 \cdot \text{H}_2\text{O}$ : Cr 23.12;  $\text{NH}_3$  37.81; Cl 31.50.) The experimental ammonia to chromium ratio was 4.98 : 1, a deviation from 5 : 1 which lies within the experimental accuracy of the ammonia determination.

*Magnetically pure basic rhodo chromium chloride* was obtained in the absence of daylight (electric light is almost harmless) by filtering the deep blue solution directly into a solution of 50 g of lithium chloride in 100 ml of water at  $-5^{\circ}\text{C}$ . The crystalline product was quickly filtered off and washed as before. By this procedure the average size of the crystals was about 0.02 mm.

*Basic rhodo chromium bromide*,  $[(\text{NH}_3)_5\text{Cr}-\text{O}-\text{Cr}(\text{NH}_3)_5]\text{Br}_4 \cdot \text{H}_2\text{O}$ . This salt was prepared in the same way as the chloride, except that a solution of 75 g of lithium bromide was used. Yield ca. 5 g. The products were always contaminated with a small amount of chloride. The best products contained 3 % of the halogen as chloride. The halogen was determined electrometrically in a medium of 0.01 M perchloric acid and 0.05 M aluminium perchlorate. The ammonia to chromium ratio was 5 : 1 within the experimental uncertainty.

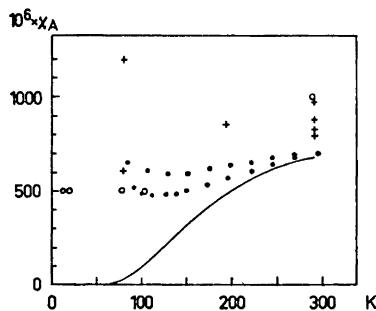


Fig. 1. Previously published magnetic susceptibilities of basic rhodo chromium salts. ● Earnshaw and Lewis,<sup>14</sup> + Schäfer,<sup>9</sup> ○ Kobayashi *et al.*<sup>13</sup> The solid curve is that calculated theoretically for an isotropic exchange model with  $J = 350 \text{ cm}^{-1}$ , coupling two spins with  $S = \frac{3}{2}$ .

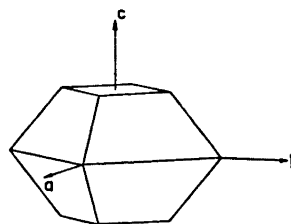


Fig. 2. Clinographic projection of the crystal shape of basic rhodo chromium chloride. The axes of the unit cell lie along the diagonals in the octahedron.

*Basic erythro chromium dithionate*,  $[(\text{NH}_3)_5\text{Cr}-\text{OH}-\text{Cr}(\text{NH}_3)_4(\text{OH})](\text{S}_2\text{O}_6)_2 \cdot 2.5\text{H}_2\text{O}$ . This salt was prepared according to Jørgensen<sup>1</sup> but found to crystallize with 2.5 mol of water instead of 3.0. (Found: Cr 15.82;  $\text{NH}_3$  23.31. Calc. for this composition: Cr 15.82;  $\text{NH}_3$  23.32.)

Attempts to determine the water content by thermogravimetry failed for all three compounds owing to accompanying loss of ammonia.

## X - R a y i n v e s t i g a t i o n

The external morphology of the crystals of the basic rhodo chromium chloride is shown in Fig. 2. Both the chloride and the bromide crystallize as beautiful dark blue octahedra, sometimes with Hopper development. Weissenberg diagrams of both salts showed diffraction symmetry  $mmm$ . The systematic absences of the reflections  $0kl$  for  $k = 2n$ ,  $h0l$  for  $l = 2n$ , and  $hk0$  for  $h = 2n$  indicated that the space group was  $Pbca$  (orthorhombic), assuming that these absences were not accidental. The cell dimensions were determined from Guinier powder diagrams using Cu-radiation and Si as internal standard.

For the chloride was found:  $a$  11.97 Å;  $b$  11.62 Å;  $c$  13.64 Å; and for the bromide:  $a$  12.45 Å;  $b$  11.58 Å;  $c$  14.21 Å. The densities are 1.56 and 2.0, respectively. For  $Z=4$  the calculated densities are 1.57 and 2.02, respectively. This result implies that the oxygen in the cations are placed at special positions in a center of inversion. Therefore the symmetry of the space group requires the Cr-O-Cr bond to be strictly linear.

### Absorption spectrum

At room temperature the half life of the basic rhodo chromium in solution is 44 sec. Therefore the spectrum can hardly be measured by conventional means. It has, however, been recorded by a flow technique by Schwarzenbach and Magyar.<sup>11</sup> But only few details are given. From the published activation energy of hydrolysis of 21 kcal/mol,<sup>12</sup>  $t_{1/2}$  at  $-25^\circ\text{C}$  is calculated to *ca.* 17 h. The spectrum of a  $1.5 \times 10^{-3}$  M solution in 12 M ammonia at this temperature is shown in Fig. 3. The measurements were performed with a Cary 14 spectrophotometer and a quartz Dewar-cuvette, cooled with solid carbon dioxide in acetone.

### Magnetic measurements

The average susceptibilities were measured by the Faraday method in the temperature range 50–300 K. All measurements were performed at *ca.* 5, 10, and 12 kOe field strengths, and the susceptibilities were field independent. The magnetic field was calibrated with  $\text{Hg}[\text{Co}(\text{NCS})_4]$  according to Figgis and Nyholm<sup>21</sup> and with a Hall probe Gauss-meter. These calibrations agreed within 0.5%. In order to obtain reasonable accuracy for these almost completely non-magnetic samples the susceptibility of the teflon sample container was carefully checked throughout the whole temperature range prior

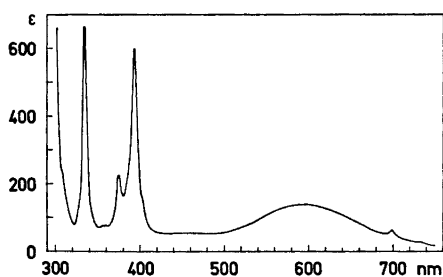


Fig. 3. Absorption spectrum of a  $1.5 \times 10^{-3}$  M solution of basic rhodo chromium chloride in 12 M aqueous ammonia at  $-25^\circ\text{C}$ . The extinction coefficient is calculated per mol.

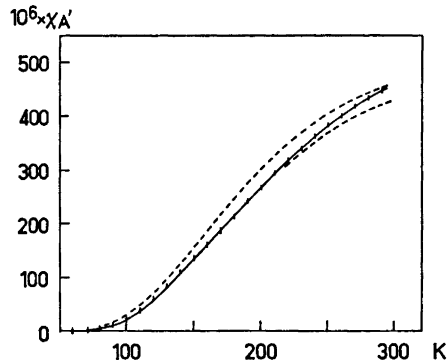


Fig. 4. Magnetic susceptibility of basic rhodo chromium chloride and bromide per chromium atom, corrected for diamagnetism and temperature independent paramagnetism. The vertical lines represent some of the experimental values and their estimated uncertainties. The solid curve is that calculated theoretically for an isotropic exchange model with  $J=450$   $\text{cm}^{-1}$ , coupling two spins with  $S=3/2$ . The upper and lower dashed curves are those calculated theoretically for two spins with  $S=1/2$  and with  $J=440$   $\text{cm}^{-1}$  and  $450$   $\text{cm}^{-1}$ , respectively.

to each measurement. The results of several measurements on different samples are shown in Fig. 4. The experimental deviations and estimated experimental uncertainties are shown by the vertical lines. All measurements started less than 1 h after the preparation of the sample. Corrections have been made for diamagnetism ( $-147 \times 10^{-6}$  cgs units) and temperature independent paramagnetism ( $+115 \times 10^{-6}$  cgs units). These estimates are further discussed later in this paper.

### I n s t r u m e n t a t i o n

A detailed description of the magnetic equipment will be published elsewhere shortly, but the construction is briefly mentioned here. The apparatus works according to the Faraday and Gouy methods quite automatically in the temperature range from liquid helium temperature to 400 K with simultaneous recording of the temperature and the force. The temperature may be changed throughout the whole range according to various programs by means of a servo mechanism. The force is measured with a Cahn RG microbalance. Force and temperature outputs are recorded on 0.2 % Varian recorders equipped with very accurate home made scale expanders covering 20 chart widths. During the temperature programming the magnetic field is automatically swept up and down as a square wave function with a period of 2 min. The sample container is maintained in very good thermal contact with the cryostat by performing the measurements in 0.5 atm. helium. A temperature program from 50–300 K used for the measurements discussed here normally lasts for about 24 h. In these cases solid nitrogen under vacuum was used as the coolant. That temperature equilibrium is obtained to a sufficient degree in this continuous method has been shown by reversal of the program giving the same results within the experimental reproducibility (0.02 % with maximum scale expansion). The temperature is measured with a nickel-chromium/nickel thermocouple relative to liquid nitrogen boiling at 760 torr. Below 78 K the thermocouple has been calibrated against the vapour pressure of nitrogen. The calibration throughout the entire range was found to agree within 0.2 K with the susceptibility of  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ . The magnet is of the type Bruker with a core diameter of 4'', equipped with specially designed pole caps giving rise to a constant force within a volume of  $1 \times 1 \times 2$  cm<sup>3</sup>, even though minimum pole gap is as high as 35 mm, necessary for the cryostat. The sample is placed in a small teflon container which can be closed tightly, avoiding loss during the measurements.

### D I S C U S S I O N

The nature of antiferromagnetic superexchange is very far from being known today. A fairly large amount of experimental data has, however, been collected and interpreted in terms of the Heisenberg-Dirac-Van Vleck model, more or less successfully. This model assumes that the coupling between two paramagnets can be expressed by the Hamiltonian

$$H = J \cdot S_1 \cdot S_2$$

Unfortunately there is hardly any theoretical justification for this assumption for the present case.

As a first step for a closer examination of this problem it was chosen to reinvestigate the magnetic susceptibility of the basic rhodo chromium ion because of its simplicity. The ground state of chromium is orbitally non-degenerate, the exchange interaction is expected to take place in one direction, preferably, between only two nearest neighbours, and the exchange is now from the X-ray analysis known to take place through a linear chromium-oxygen-chromium system. The only drawback of this system is the pronounced preparative difficulty. All the previous measurements have apparently been

performed on very impure products. This problem was solved by the procedure given here. But even though the advantage of the present low temperature method of preparation of such a labile complex is quite evident, we have not been able to solve the following dilemma. We could either obtain fairly large crystals of a magnetically impure product or small crystals of a pure product. This excluded an investigation of the magnetic susceptibility anisotropy of the complex. We plan shortly to investigate this problem further by studying the single crystal paramagnetic resonance spectra. We are firmly convinced that the measurement of the average magnetic susceptibility is not a very powerful method of testing models of magnetic coupling. The isotropic exchange Hamiltonian may completely fail to describe the principal magnetic susceptibilities.

The measurements of the chloride and the bromide showed the same temperature dependence of the susceptibilities, except for a constant difference ( $44 \times 10^{-6}$  cgs units) corresponding to the difference in diamagnetism. As the distance between adjacent dimers is larger in the bromide, especially in the direction of the *c*-axis, it is thus seen that the intermolecular exchange is of minor importance, especially in this direction.

The measurements were corrected for diamagnetism and temperature independent paramagnetism. Both of these quantities are fairly difficult to estimate. The diamagnetism was summed over the following contributions:  $\text{NH}_3$  - 17;  $\text{Cl}^-$  - 23; O 0;  $\text{H}_2\text{O}$  - 13;  $\text{Br}^-$  - 34; in  $10^{-6}$  cgs units. The temperature independent paramagnetism (T.I.P.) is perhaps even worse to estimate. Our calculation has been based on the assumption that the broad band at 595 nm and the band at 460 nm may be assigned as the two tetragonal components,  ${}^4E$  and  ${}^4B_2$ , respectively, of the octahedral  ${}^4T_{2g}$  function. The position of the  ${}^4B_2$  is the same as in the hexammine complex as expected. Neglecting an off-diagonal matrix element with the  ${}^4E$  ( ${}^4T_{1g}$ ) function the position of the band at 595 nm corresponds to a value of  $\Delta$  of about 2 kK for the oxygen ligator. This very low value may be attributed to a large value of  $\Delta_\pi$ , the  $\pi$ -bonding parameter, in the expression  $\Delta = \Delta_\sigma - \Delta_\pi$ . This interpretation of some of the bands in the absorption spectrum is hardly of much value as far as the spectrum itself is concerned, but for the calculation of the temperature independent paramagnetism the positions of these bands are not very critical, and the T.I.P. estimated here is close to estimated values for normal monomeric chromium complexes. The T.I.P. has been calculated in the conventional way<sup>22</sup> from

$$\chi_{\text{TIP}} = \sum_i \frac{8N\beta^2}{3\Delta_i} = 115 \times 10^{-6} \text{ cgs units}$$

where the summation runs over all the orbital components of the octahedral  ${}^4T_{2g}$  functions.

With these corrections we have obtained an extremely good and reproducible agreement between the average susceptibilities and an isotropic exchange interpretation of the coupling between two spins with  $S = \frac{3}{2}$  and with  $J = 450 \text{ cm}^{-1}$ . The temperature dependence of the susceptibility according to this model was calculated by the expression given by Earnshaw and Lewis:<sup>14</sup>

$$\chi_A' = \frac{Ng^2\beta^2}{kT} \left[ \frac{14 + 5 \exp(-3J/kT) + \exp(-5J/kT)}{7 + 5 \exp(-3J/kT) + 3 \exp(-5J/kT) + \exp(-6J/kT)} \right]$$

for  $g = 1.98$ .

The possibility of having low spin  $d^3$  systems under the influence of strong tetragonal distortions operating on the octahedral  $t_2^3$  configuration has been discussed by Ballhausen.<sup>23</sup> Using other parameters and some corrections of the conditions given in this paper, we find a doublet ground state provided

$$48B + 16C < \Delta_{\pi O} - \Delta_{\pi N}$$

where  $B$  and  $C$  are the Racah parameters, and  $\Delta_{\pi O}$  and  $\Delta_{\pi N}$  are the  $\pi$ -bonding parameters for the oxygen ligator and ammonia, respectively, in terms of the angular overlap model.<sup>24,25</sup>  $\Delta_{\pi N}$  may be assumed to be zero, and for  $C = 4B$  the condition for a low spin ground state is approximately

$$\Delta_{\pi O} > 112B \simeq 70 \text{ kK}$$

Such a high value of  $\Delta_{\pi O}$  is rather unexpected even though both  $\Delta_{\sigma O}$  and  $\Delta_{\pi O}$  are probably large.

A doublet ground state would be able to account for the room temperature susceptibility of the basic rhodo chromium ion, corresponding to about 1 Bohr magneton per chromium atom. In order to explain the magnetic behaviour at lower temperatures it must, however, be assumed that some coupling takes place between the two chromium atoms. An isotropic exchange model coupling two systems with  $S = \frac{1}{2}$  might account for the decreasing sus-

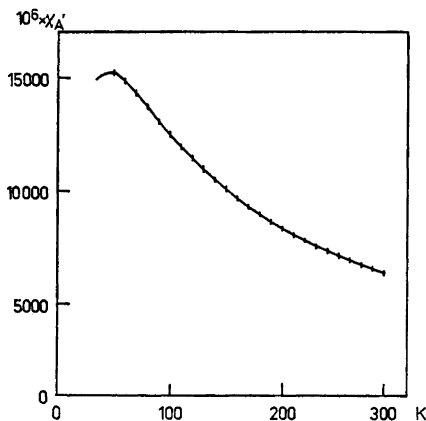


Fig. 5. Magnetic susceptibility of basic erythro chromium chloride, bromide and dithionate per chromium atom, corrected for diamagnetism and temperature independent paramagnetism. The vertical lines represent some of the experimental values and their estimated uncertainties. The solid curve is that calculated theoretically for an isotropic exchange model with  $J = 23 \text{ cm}^{-1}$ , coupling two spins with  $S = \frac{1}{2}$ .

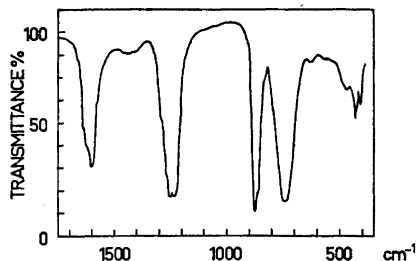


Fig. 6. Infrared spectrum of basic rhodo chromium chloride in a potassium bromide dish at room temperature. (This spectrum of the pure compound is rather similar to that of Dubicki and Martin.<sup>20</sup>)



ceptibility at lower temperatures. However, as seen from Fig. 4 such a model cannot explain the variation of the susceptibility in the entire range 50–300 K, in contrast to a model coupling two centers with  $S = \frac{3}{2}$ . The disagreement is pronounced at higher temperatures where the contributions from the quintet and septet states of the high spin model gain influence owing to increasing Boltzmann factors.

The infrared spectrum of basic rhodo chromium chloride (Fig. 6) shows some narrow peaks in the range 400–500  $\text{cm}^{-1}$ . Assignment of these has not been made. It is, however, tempting to say that the spin forbidden singlet-triplet transition is expected to lie in this range.

We have further been able to explain the irreproducible magnetic behaviour of the samples prepared by earlier workers. The conventional method of preparation gives various amounts of basic erythro chromium salts incorporated in the crystals of the rhodo salts. We have verified this by measuring the magnetic susceptibility of the pure basic erythro chromium chloride, bromide, and dithionate, and found that the results, corrected for diamagnetism, are almost completely independent of the anion (see Fig. 5). Also in this case excellent agreement was found with the isotropic exchange model with  $J = 23 \text{ cm}^{-1}$ . The measurements on the basic rhodo bromide by Earnshaw and Lewis<sup>14</sup> and on some of our own impure products can now be completely understood. The two samples of Earnshaw and Lewis fit accurately to the susceptibility calculated for 94.8 % and 95.5 % basic rhodo contaminated with 5.2 % and 4.5 % basic erythro, respectively. The amount of impurities estimated here is much greater than estimated by the authors themselves.

*Note added in proof.* After the completion of this manuscript two short communications concerning the crystal structure of basic rhodo chloride have appeared in the literature.<sup>26,27</sup> They confirm the preliminary crystallographic data given in this paper.

## REFERENCES

1. Jørgensen, S. M. *J. prakt. Chem.* [2] **25** (1882) 321.
2. Jørgensen, S. M. *J. prakt. Chem.* [2] **25** (1882) 398.
3. Werner, A. *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie*, 2. Aufl., 1909, p. 290.
4. Jensen, K. A. *Z. anorg. allgem. Chem.* **232** (1937) 257.
5. Wilmarth, W. K., Graff, H. and Gustin, S. T. *J. Am. Chem. Soc.* **78** (1956) 2683.
6. Bjerrum, J. *Reports to the Xth Solway Council*, Brussels, May 1956, p. 340.
7. Dunitz, J. D. and Orgel, L. E. *J. Chem. Soc.* **1953** 2594.
8. Mathieson, A. McL., Mellor, D. P. and Stephenson, N. C. *Acta Cryst.* **5** (1952) 185.
9. Schäffer, C. E. *J. Inorg. Nucl. Chem.* **8** (1958) 149.
10. Linhard, M. and Weigel, M. *Z. anorg. allgem. Chem.* **299** (1959) 15.
11. Schwarzenbach, G. and Magyar, B. *Helv. Chim. Acta* **45** (1962) 1425.
12. Mori, M., Ueshiba, S. and Yamatera, H. *Bull. Chem. Soc. Japan* **32** (1959) 88.
13. Kobayashi, H., Haseda, T., Kanda, E. and Mori, M. *J. Phys. Soc. Japan* **15** (1960) 1646.
14. Earnshaw, A. and Lewis, J. *J. Chem. Soc.* **1961** 396.
15. Jeżowska-Trzebiatowska, B. and Wojciechowski, W. *Theory and Structure of Complex Compounds*, Wrocław 1962, p. 375.
16. Jeżowska-Trzebiatowska, B. and Wojciechowski, W. *Proc. VIIth ICCG*, Uppsala 1962, p. 50.
17. Jeżowska-Trzebiatowska, B. and Wojciechowski, W. *J. Inorg. Nucl. Chem.* **25** (1963) 1477.

18. Jeżowska-Trzebiatowska, B. and Wojciechowski, W. *Bull. Acad. Polon. Sci. Ser. Sci. Chim.* **11** (1963) 79.
19. Jeżowska-Trzebiatowska, B. and Wojciechowski, W. *Zh. Strukt. Khim.* **4** (1963) 872.
20. Dubicki, L. and Martin, R. L. *Aust. J. Chem.* **23** (1970) 215.
21. Figgis, B. N. and Nyholm, R. S. *J. Chem. Soc.* **1958** 4190.
22. Penney, W. G. and Schlapp, R. *Phys. Rev.* **42** (1932) 666.
23. Ballhausen, C. J. *Introduction to Ligand Field Theory*, McGraw, New York 1962, p. 102.
24. Schäffer, C. E. *Struct. Bonding (Berlin)* **5** (1968) 68.
25. Glerup, J. and Schäffer, C. E. *Proc. XI ICCO, Progress in Coordination Chemistry*, Cais, M., Ed., Elsevier, Amsterdam - London - New York 1968, p. 500.
26. Yewitz, M. and Stanko, J. A. *J. Am. Chem. Soc.* **93** (1971) 1512.
27. Urushiyama, A., Nomura, T. and Nakahara, M. *Bull. Chem. Soc. Japan* **43** (1970) 3971.

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