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Magnetochemical Properties of Tetranuclear Rhodoso and Pfeiffer Chromium(III) Complexes in a Series of Compounds

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Seven salts of the structurally related tetranuclear rhodoso and Pfeiffer chromium(III) complexes were prepared. Magnetic susceptibilities were measured and the energy splittings of the electronic ground state caused by exchange interactions were determined. There are marked differences in the low-temperature magnetic properties. Crystal packing and hydrogen bonding effects are the most likely causes for the differences in the exchange-splitting pattern.

1. Introduction

Di-μ-hydroxotetrakis-μ-hydroxobis-(tetraamminechromium(III)-bis-(diamminechromium(III)) (rhodoso complex) and di-μ-hydroxotetrakis-μ-hydroxobis-(diethylenediamminechromium(III)) bis (ethylenediamminechromium(III)) (Pfeiffer complex) are chemically and structurally related tetranuclear complexes. They were first synthesized a long time ago (*1*, *2*). But it is only in the past 15 years that their interesting and unusual physical properties have been systematically investigated (*3*–*7*). Exchange interactions between the four paramagnetic chromium(III) centers are responsible for a number of extraordinary magnetic and spectroscopic features in these compounds.

Recently we have studied in detail the electronic groundstate properties of deuterated rhodoso chloride, $[Cr_4(OD)_6(ND_3)_{12}]Cl_6 \cdot 4D_2O$. Using inelastic neutron scattering in addition to magnetic susceptibility measurements it was possible to unravel the complex exchange splitting pattern in the electronic ground state (*7*). The splitting was described in terms of five empirical exchange parameters.

In the course of a systematic investigation of the exchange coupling of tetranuclear chromium(III) complexes a number of rhodoso $[Cr_4(OH)_6(NH_3)_{12}]^{6+}$ and Pfeiffer $[Cr_4(OH)_6(en)_6]^{6+}$ compounds were prepared. Quite distinct differences in the low-temperature magnetochemical behavior were found to occur not only between the rhodoso and Pfeiffer series but also within the same series. We therefore decided to investigate the properties of the various compounds in more detail. For economical reasons a study of all compounds by neutron inelastic scattering was out of the question. In the present paper the results of our magnetochemical experiments are reported.

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2. Experimental

2.1. Preparations

Rhodoso chloride (RC), $[Cr_4(OH)_6(NH_3)_{12}]Cl_6 \cdot 4H_2O$. RC was prepared as described by Bang (*3*). The compound crystallizes in two different modifications. The modification used for our experiments was found from its powder X-ray pattern to be identical to that used by Bang for the crystal structure determination (*3*). It is obtained on slow crystallization in the form of dark red crystals.

Deuterated rhodoso chloride (DRC), $[Cr_4(OD)_6ND_3)_{12}]Cl_6 \cdot 4D_2O$. DRC was obtained from RC by a procedure described elsewhere (*7*). The degree of deuteration of the product used for the magnetochemical measurements was estimated from the infrared spectrum to be 90%. RCA and DRC have the same X-ray powder pattern.

Rhodoso bromide (RB), $[Cr_4(OH)_6(NH_3)_{12}]Br_6 \cdot 2H_2O$. RB was prepared by dissolving RC in water containing a few drops of 2 *M* HCl, precipitating with NH_4Br, and washing with 2 *M* HBr and ethanol. The identity of the crystals was checked by single crystal X-ray techniques. The unit cell was found to be identical to that determined previously (*8*).

Rhodoso azide (RA), $[Cr_4(OH)_6(NH_3)_{12}](N_3)_6 \cdot 4H_2O$. A few drops of 2 *M* HCl were added to a saturated solution of RC. The azide was then precipitated by adding solid NaN_3. The polycrystalline material was filtered off, and washed with a small amount of ice cold water and ethanol. It crystallizes in long prisms. Analysis: H_2O 8.60% exp/8.59% calc; Cr 24.63% exp/24.80% calc; H 6.25% exp/6.01% calc; N 49.81% exp/50.11% calc.

Pfeiffer chloride (PC), $[Cr_4(OH)_6(en)_6]Cl_6 \cdot 6H_2O$. The procedure given by Pfeiffer (*2*) was followed for the preparation. A small modification was found necessary in the second step. For the transformation of the sulfate to the chloride 8 ml of 2 *M* HCl was added drop by drop to 2 g of the sulfate. Analysis: H_2O 10.99% exp/10.90% calc; Cr 20.34% exp/20.98% calc; C 14.49% exp/14.54% calc; H 6.62% exp/6.71% calc; N 16.75% exp/16.96% calc; Cl 21.29% exp/21.46% calc.

Pfeiffer bromide (PB), $[Cr_4(OH)_6(en)_6]Br_6 \cdot 4H_2O$. PB was prepared by dissolving PC in water, precipitating with solid NH_4Br, and washing with 2 *M* HBr and ethanol. Analysis: H_2O 5.70% exp/5.90% calc; Cr 17.34% exp/17.02% calc; C 11.79% exp/11.79% calc; H 5.16% exp/5.11% calc; N 13.44% exp/13.75% calc; Br 38.79% exp/39.23% calc.

Pfeiffer azide (PA), $[Cr_4(OH)_6(en)_6](N_3)_6 \cdot 4H_2O$. PA was obtained from a saturated aqueous solution of PC by adding solid NaN_3.

The product was identified by single crystal X-ray techniques. The unit cell was found to be identical to that reported earlier (*4*).

2.2. Magnetic Susceptibilities

All the susceptibility measurements were done on powders using a moving sample technique described before (*9*). Great care was taken to measure well-defined products. For that purpose crystals, wherever available, were ground to a fine powder immediately before the measurements. Magnetization curves were measured at 4.2 K. They showed no deviations from linearity up to 2–3 *T*. All the susceptibility measurements were carried out with a field of 1 *T*. A diamagnetic correction was applied to the data in order to obtain the molar susceptibilities χ'_M (*10*).

For the fitting of theoretical models to the experimental μ^2_{eff} data ($\mu^2_{\text{eff}} = 8\chi'_M T$) a nonlinear regression program was used (*11*). Standard deviations of the data points were estimated and used in the statistical weighting function.

The reliability factor R and the correlation coefficient C were used as a measure of the quality of the fits. They are defined as follows:

$$R = \left(\frac{\sum_{i}^{N} w_i F^2(i)}{\sum_{i}^{N} w_i \, (\mu_{\mathrm{eff}}^2 \text{ obs } (i))^2} \right)^{1/2} \tag{1}$$

$$C = \frac{\sum_{i=2}^{N} (w_i \cdot w_{i-1})^{1/2} F(i) \cdot F(i-1)}{\left[\sum_{i=2}^{N} w_i \, (\mu_{\mathrm{eff}}^2 \text{ obs } (i))^2 \cdot \sum_{i=1}^{N-1} w_i \, (\mu_{\mathrm{eff}}^2 \text{ obs } (i))^2 \right]^{1/2}}$$

where $F(i) = \mu_{\mathrm{eff}}^2 \text{ obs } (i) - \mu_{\mathrm{eff}}^2 \text{ calc } (i)$.

3. Theory

3.1. Exchange Coupling

The crystal structures of RC, RB, and PA have been determined (*3, 4, 8*). It was found that the rhodoso and Pfeiffer complexes are structurally very closely related. In all the three compounds the complex has an exact center of inversion. The Cr^{3+} ions occupy the corners of a regular rhombus in RC. In RB and PA small deviations from this idealized D_{2h} symmetry were found. In the following it is assumed that the magnetochemical properties of all the compounds investigated can be treated in the idealized D_{2h} symmetry; i.e. the exchange parameters along the edges of the rhombus are taken to be identical.

We can express the exchange interactions in this tetranuclear complex in terms of an empirical Heisenberg Hamiltonian of the form

$$\begin{aligned} \hat{H}_{\mathrm{ex}} &= J(\mathbf{S}_1 \cdot \mathbf{S}_3 + \mathbf{S}_1 \cdot \mathbf{S}_4 + \mathbf{S}_2 \cdot \mathbf{S}_3 + \mathbf{S}_2 \cdot \mathbf{S}_4) \\ &\quad + J'\mathbf{S}_1 \cdot \mathbf{S}_2 + J''\mathbf{S}_3 \cdot \mathbf{S}_4 - j\{(\mathbf{S}_1 \cdot \mathbf{S}_3)^2 \\ &\quad + (\mathbf{S}_1 \cdot \mathbf{S}_4)^2 + (\mathbf{S}_2 \cdot \mathbf{S}_3)^2 + (\mathbf{S}_2 \cdot \mathbf{S}_4)^2\} \\ &\quad - j'(\mathbf{S}_1 \cdot \mathbf{S}_2)^2 - j''(\mathbf{S}_3 \cdot \mathbf{S}_4)^2. \end{aligned} \tag{2}$$

The exchange parameters are defined in Fig. 1.

It is most convenient to use the following exchange coupling scheme:

$$\begin{aligned} \mathbf{S}_{12} &= \mathbf{S}_1 + \mathbf{S}_2 \\ \mathbf{S}_{34} &= \mathbf{S}_3 + \mathbf{S}_4 \\ \mathbf{S} &= \mathbf{S}_{12} + \mathbf{S}_{34}. \end{aligned} \tag{3}$$

The wave functions of the coupled system are of the form

$$|(S_1, S_2)S_{12}(S_3, S_4)S_{34}SM\rangle \tag{4}$$

or simply

$$|S_{12}S_{34}SM\rangle$$

The matrix elements of the operator (2) with the set of basis functions (4) are most conveniently evaluated using tensor operator techniques. Details of the calculation as well as the matrix elements have been published (*7*). It was found that off-diagonal matrix elements depend only on j. They can to a very good approximation be neglected. They are neglected in the present study. Under the action of the operator (2) the

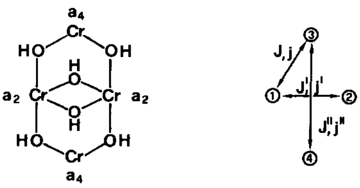


FIG. 1. Schematic structure of rhodoso and Pfeiffer complexes. a = NH_3 for rhodoso and a_2 = en for Pfeiffer. Empirical exchange parameters are defined on the right-hand side.

electronic ground state is split into 44 $|S_{12}S_{34}S>$ levels.

3.2. *Magnetic Susceptibilities*

According to van Vleck (*12*) the molar magnetic susceptibility is given by

$$\chi'_M = \frac{N}{H} \frac{\sum_i [-W_i^{(1)} - 2W_i^{(2)}H] \exp\{-W_i/kT\}}{\sum_i \exp\{-W_i/kT\}} \qquad (5)$$

where

$$W_i = W_i^0 + W_i^{(1)}H + W_i^{(2)}H^2. \qquad (6)$$

$W_i^{(1)}$ and $W_i^{(2)}$ are first- and second-order Zeeman coefficients, respectively. In (5) effects from zero-field splittings and temperature-independent paramagnetism, which are expected to be small, are neglected. Formula (5) can be simplified if

$$W_i^{(1)}H \ll kT \quad \text{and} \quad W_i^{(2)}H^2 \ll kT \qquad (7)$$

Neglecting second-order Zeeman effects and assuming that we are dealing with a pure spin system with isotropic g values we obtain (*13*):

$$\chi'_M = \frac{N\beta^2g^2}{3kT} \frac{\sum_{S_{12}S_{34}S} S(S+1)(2S+1)\exp\{-E(S_{12}S_{34}S)/kT\}}{\sum_{S_{12}S_{34}S} (2S+1)\exp\{-E(S_{12}S_{34}S)/kT\}}. \qquad (8)$$

At very low temperatures we expect formula (8) to fail because conditions (7) are no longer strictly met. We found, however, only negligibly small differences using formulas (8) and (5) in a least-squares fit of the DRC data. This is due to the fact that the magnetic field chosen for our susceptibility measurements was small. For subsequent calculations formula (8) was used.

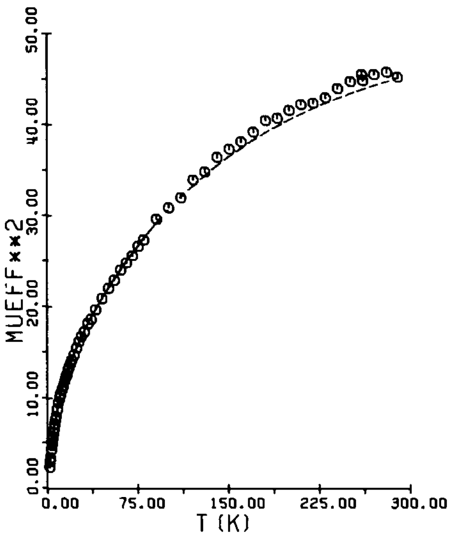


FIG. 2. Temperature dependence of μ^2_{eff} of deuterated rhodoso chloride (DRC). The solid curve was obtained from a least-squares fit to the data using a model with the four parameters J, j, J', j' (cf. Table I for parameter values). Only data points for $T \leq 100$ K were considered in the fit. The broken curve is an extrapolation of the susceptibility computed with the low-temperature parameter values.

4. Results and Analysis

For an analysis of the results it is most convenient to express the magnetochemical data in terms of μ^2_{eff} of the tetranuclear complexes where $\mu^2_{\text{eff}} = 8\chi'_M T$. This is justified since we are dealing with homonuclear complexes and the constituting Cr^{3+} centers are all orbitally nondegenerate with angular momentum distributions very close to spherically symmetrical.

The squares of effective magnetic moment of seven rhodoso and Pfeiffer compounds are presented in Figs. 2 to 8. The

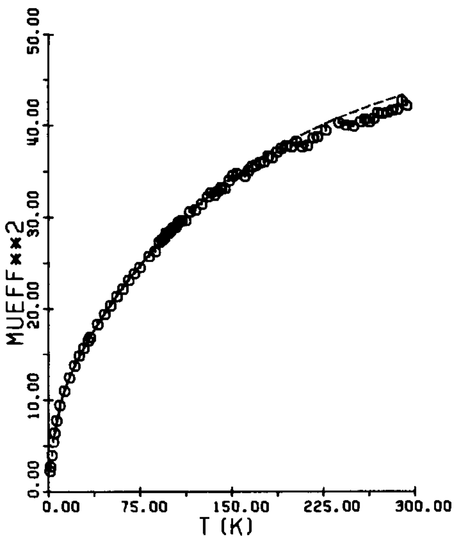


FIG. 3. As for Fig. 2, but for rhodoso chloride (RC).

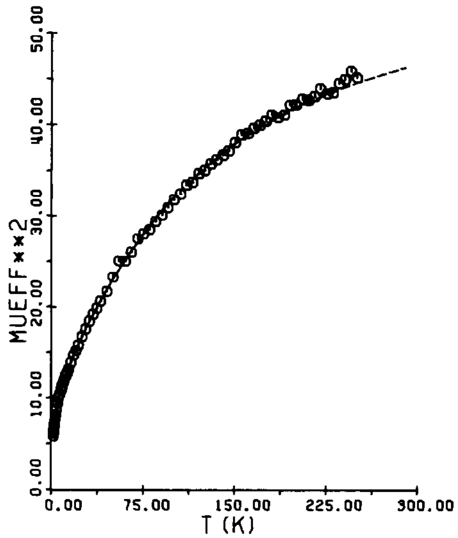


FIG. 4. As for Fig. 2, but for rhodoso bromide (RB).

temperature range of the measurements is 1.5 K to 270 K. There are distinct differences between the experimental curves, particularly at temperatures below 40 K. These differences reflect changes in the ordering and splitting of the lowest spin levels of the ground state of the complex in the various crystal environments. It is possible to derive some important features of the groundstate coupling from a qualitative discussion of the low-temperature data in Figs. 2 to 8. In a later step quantitative information will be obtained from least-squares fits using theoretical models.

μ_{eff}^2 of rhodoso and Pfeiffer chlorides and bromides converges to zero as the temperature approaches 0 K. This immediately shows that in all these compounds the lowest level of the ground-state multiplet must be a spin singlet. For spin triplets and quintets μ_{eff}^2 values of 8 and 24, respectively, are expected from the spin-only formula. Comparison of Figs. 2 and 3 demonstrates that the effect of deuteration on the magnetic properties up to 40 K is small. The splitting pattern of the complex in the deuterated salt is known very accurately from inelastic neutron scattering experiments, which allow the direct observation of spectroscopic transitions between the split levels of the ground state. Part of the energy level scheme is shown in Fig. 9. Quite clearly the magnetic susceptibility at temperatures below 10 K is largely deter-

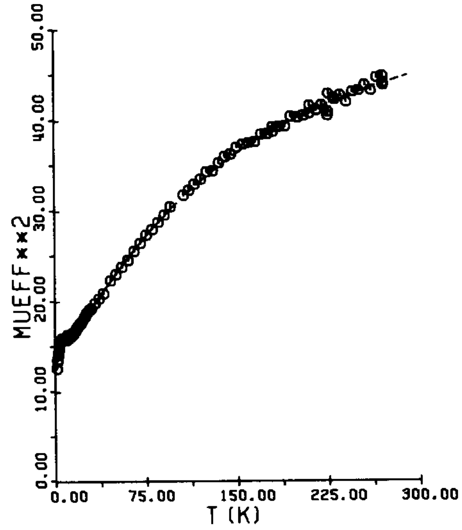


FIG. 5. As for Fig. 2, but for rhodoso azide (RA).

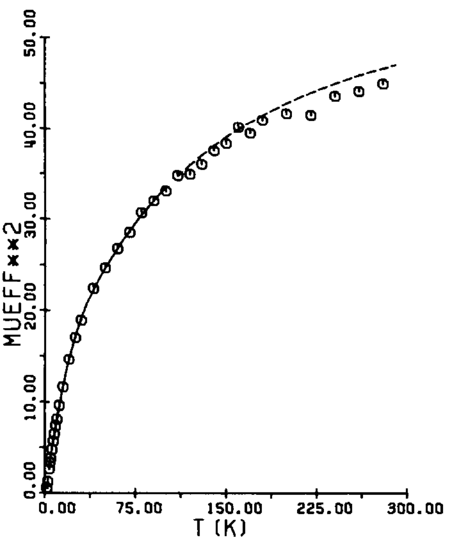


FIG. 6. As for Fig. 2, but for Pfeiffer chloride (PC).

mined by the two levels |330> and |231>. The $\mu_{\rm eff}^2$ curve of PB is quite similar to the curves of RC and DRC. A singlet (|330>)–triplet (|231>) separation of 2–4 $\rm cm^{-1}$ is expected. In PC the drop of $\mu_{\rm eff}^2$ below 20 K is not as steep as in RC and PB indicating a somewhat larger singlet–triplet separation. In RB, on the other hand, the drop of $\mu_{\rm eff}^2$ with temperature is very sharp, reaching a value of 5.6 at 1.7 K. This behavior is compatible with a |330> ground level but |231> lying within 1 $\rm cm^{-1}$.

The behavior of both RA and PA is qualitatively different from the others. They both exhibit a bump in the $\mu_{\rm eff}^2$ curve. This structure is more pronounced in the rhodoso compound. $\mu_{\rm eff}^2$ does not drop below 12.6 and 8.9, respectively at 1.6 K. This indicates that in both compounds the |330> level no longer plays the dominant role at the lowest temperatures. Instead some $S = 2$ level must contribute to the susceptibility below 10 K. For a qualitative interpretation of the RA data below 10 K one has to place a spin triplet and a spin quintet very close together with the triplet lying lower. The situation is not as clear cut in PA. From the shape of the curve below 30 K the lowest level can neither be a spin singlet nor a spin quintet. It is a spin triplet with both a spin quintet and a singlet lying quite close.

In DRC, where the exchange splittings are known very accurately (7), it was found that an empirical Heisenberg Hamiltonian of the form (2) used on the set of basis functions (4) very well accounted for the observed energy separations. Biquadratic exchange parameters were found to be necessary for an adequate description. Inclusion of three- and four-body interaction terms, on the other hand, was not necessary. It was also found that great care had to be taken in any attempt to determine three and more exchange parameters from a set of magnetic susceptibility data. In order to reduce and partly avoid the risks inherent in the least-squares fitting procedure we used the known set of exchange parameters of DRC as a point of reference for the present work. The $\mu_{\rm eff}^2$ data of DRC were fitted with models containing two (J and J'), three (J, J', and J''), four (J, j, J', j') and five (J, j, J', j', J'') parameters, respectively. The four and five parameter

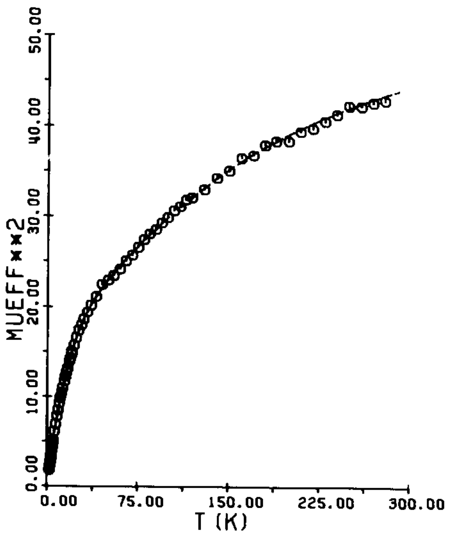


FIG. 7. As for Fig. 2, but for Pfeiffer bromide (PB).

fits did not lead to one unique solution. Of the various parameter sets obtained only one was close to the "true" set, while the other ones, which produced equally good fits, could be rejected as physically unreasonable. The same procedure was then used for the whole series of compounds. And it was found that, whenever multiple solutions were obtained, only one of the parameter sets was close enough to the DRC set to be considered physically meaningful. We must emphasize here that the magnetochemical fitting procedure employed here crucially depends on the availability of some additional independent information. In our case it is the spectroscopically determined splitting pattern of DRC. Because of the differences in the exchange parameters of the various compounds there remains a weak point in our procedure. And we certainly do not wish to put too much physical significance into those numbers. We feel, however, confident that the parameters properly reflect the trends in the rhodoso and Pfeiffer series. The main reason for this lies in the fact that the exchange splittings of the lowest groundstate levels (Fig. 9), as calculated from the parameters in Table I, are in good agreement with the qualitative level ordering discussed in the previous paragraphs. The level ordering is a very sensitive indicator of changes of exchange parameters. And it is nicely reflected in different shapes of the susceptibility curves below 30 K.

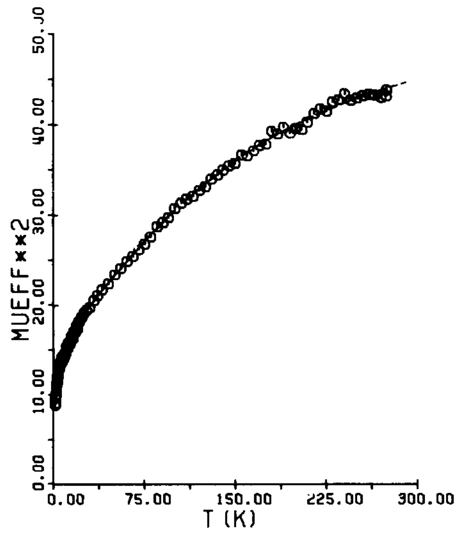


FIG. 8. As for Fig. 2, but for Pfeiffer azide (PA).

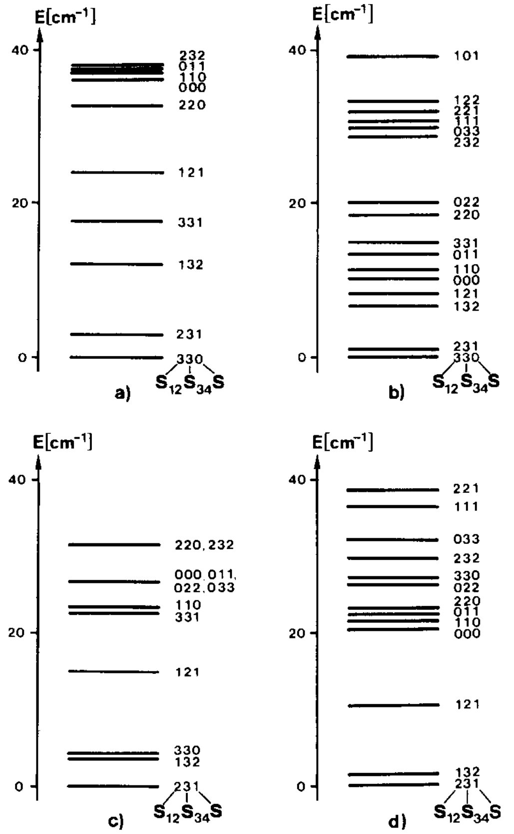


FIG. 9. Low part of energy level diagram of tetranuclear rhodoso and Pfeiffer complexes in four selected compounds: (a) DRC, (b) RB, (c) PA, (d) RA. The DRC diagram corresponds to the first line in Table I.

The standard deviations of the exchange parameters obtained in the least-squares fitting process (Table I) cannot be considered physically meaningful from a comparison with the well-known DRC parameters. They are too small by up to an order of magnitude. For all the fits only data points

TABLE I

Exchange Parameters[a] Obtained in the Least-Squares Fits of Figs. 2 to 8[b]

	J	j	J'	j'	J''	R	C
DRC (exact)	17.4 ± 0.3	0.1 ± 0.1	25.1 ± 0.6	1.60 ± 0.2	1.7 ± 0.5		
DRC	16.6 ± 0.1	−0.22 ± 0.04	22.4 ± 0.2	1.64 ± 0.02	—	0.005	0.10
RC	19.6 ± 0.1	−0.64 ± 0.06	25.0 ± 0.3	2.12 ± 0.03	—	0.005	0.23
RB	13.5 ± 0.2	0.35 ± 0.09	21.6 ± 0.4	1.17 ± 0.06	3.3 ± 0.3	0.011	0.31
RA	15.0 ± 0.1	—	29.2 ± 0.1	—	2.0 ± 0.1	0.006	0.06
PC	14.0 ± 0.3	0.67 ± 0.07	21.9 ± 0.8	0.77 ± 0.05	−5.8 ± 1.4	0.008	0.13
PB	17.7 ± 0.2	1.13 ± 0.04	30.5 ± 0.5	1.25 ± 0.03	−5.7 ± 0.5	0.007	0.44
PA	15.5 ± 0.1	0.77 ± 0.04	28.1 ± 0.4	1.25 ± 0.10	—	0.009	−0.13

[a] In cm^{-1}.

[b] Hamiltons significance criterion was used to decide on the number of parameters (Ref. *14*). j'' was always set to zero. Only data points at $T \leq 100$ K were considered in the fit. $g = 1.98$ was chosen for all the computations. The "exact" values on the first line were determined by inelastic neutron scattering (Ref. *7*).

for $T \leq 100$ K were considered. No attempts were made to include data of the full temperature range because of the possibility of a temperature dependence of the exchange parameters. In a dinuclear chromium(III) complex exchange splittings have recently been found to vary by 5–10% between 4.2 and 300 K (*15*). Temperature variations of 5–10% of the principal exchange parameters J and J' in our tetranuclear complexes would affect the susceptibility curve as much as the inclusion of the small parameters. With our choice of the temperature range considered for the fit we are, of course, assuming that the main part of the possible temperature dependence of exchange occurs above 100 K along with a slight expansion of interatomic distances.

5. Discussion

In all the seven compounds the two dominant interactions J and J' are antiferromagnetic. Except for RA inclusion of biquadratic terms, in particular the j' term, greatly improved the fits. The j' parameters obtained are positive and of the order of 5–10% of the corresponding bilinear parameter J'. This is a clear indication for exchange striction effects (*16*). True biquadratic exchange is not expected to be larger than approximately 1% of the corresponding bilinear term (*17*). It can have either sign. True biquadratic exchange is thus the most likely explanation for the j values obtained for most of the compounds.

J'' is of the order of 10% of J. It can be taken as a measure of the importance of next-nearest-neighbor interactions in magnetically ordered materials as compared to nearest-neighbor interactions. A value of $\frac{1}{10}$ is reasonable for the $J(n \cdot n \cdot n)/J(n \cdot n)$ ratio (*18*).

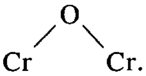
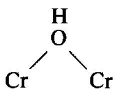
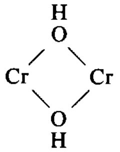
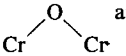
From Fig. 9, but even from a purely qualitative consideration of the data in Figs. 2 to 8, it is obvious that there are differences in the magnitude and ordering of the splitting of the lowest levels of the electronic ground state between the various compounds. These differences are somewhat surprising, since one tends to consider the exchange coupling and the corresponding energy splitting pattern as a property of a given complex. Equally interesting is the fact that there appears to be more similarity between rhodoso and Pfeiffer salts of the same anion than within the two series. This is rather unexpected at first sight, because corresponding rhodoso and Pfeiffer salts are not isostructural. Crystal packing effects and the resulting distortions of the tetranuclear skeleton, therefore, could only account for the different exchange splittings within the rhodoso and Pfeiffer series. The similarities in the magnetochemical behavior of rhodoso and Pfeiffer salts with the same anion, however, cannot be explained this way. And they indicate that crystal packing may not be the main cause for the observed differences. This is underlined by the fact that interatomic Cr–O distances and Cr–O–Cr angles are rather similar in the crystal structures that have been determined so far (RC, RB, PA) (*3*, *8*, *4*). In all those crystal structures there is strong evidence that some of the hydroxo bridging groups of the tetranuclear complex are involved in hydrogen bonds with the anions or with water molecules. Hydrogen positions were determined only in the PA structure (*4*). But distances oxygen–anion or oxygen–oxygen (H_2O) suitable for hydrogen bonding were found in all the three compounds. Relevant distances and angles are collected in Table II. There are significant differences in the O–H · · · X distances for the three different anions. This is of course not unexpected. It reflects different ionic radii and different strengths of the bonds. All are close to "normal" O–H · · · X distance (*19*). We can therefore safely assume that hydrogen bonds in corresponding rhodoso and Pfeiffer salts are similar even though the crystals are not isostructural. The involvement of the hydroxo bridging ligands in hydrogen bonds is most likely to affect the superexchange if the hydrogen bonds do not lie in the plane defined by  Table II shows that deviations of up to 25° do occur. We conclude that hydrogen bonding of the hydroxo bridging groups is a likely reason for the different magnetochemical behavior at low temperatures. Similar conclusions have been drawn for a number of dinuclear chromium(III) complexes (*20*).

TABLE II

DISTANCES O–H · · · X (Å) AND ANGLES α (DEGREES) OF HYDROGEN BONDS IN RC, RB, AND PA[a]

				
	O–H · · · X	α	O–H · · · X	α
RC	2.79 (H_2O)	0.8	3.15 (Cl)	16.1
	3.08 (Cl)	21.5		
RB	3.22 (Br)	1.5	3.26 (Br)	1.0
	3.36 (Br)	25.4		
PA	2.82 (N_3)	16.4	2.86 (N_3)	3.8

[a] α is the angle between the plane defined by  and the straight line O · · · X.

Acknowledgments

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