Magnetic Susceptibility of Trinuclear Chromium(III) and Iron(III) Monochloroacetates in the Temperature Range 1.6 to 300 °K

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The temperature dependence of magnetic susceptibility has been studied from 1.6 to 300 °K for four trinuclear cluster compounds of the composition $[M_3O(CH_2ClCOO)_6(H_2O)_3]NO_3$ where M_3 stands for Cr_3, Cr_2Fe, $CrFe_2$, or Fe_3.

The experimental dependences $\chi(T)$ are analyzed in terms of two most probable models: (i) the Heisenberg–Dirac–Van Vleck (HDVV) model accounting for possible lowering of cluster symmetry from D_{3h}: (ii) the D_{3h} model accounting for contributions from non-Heisenberg exchange mechanisms.

Model (i) is shown to provide a better agreement with the experimental data. The results obtained are discussed with reference to the literature data.

Introduction

Despite considerable efforts directed towards elucidation of exchange mechanisms operating in chromium(III) and iron(III) trinuclear carboxylates, many details of importance remain unclarified. The principal results obtained until now are as follows.

The first experimental data on magnetic susceptibility of triads in the temperature range 200 to 300 °K [1] were analyzed by Kambe [2] in terms of equivalent isotropic exchange model with the spin-Hamiltonian (SH) of the form

$$\hat{H} = -2J(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3 + \hat{S}_3\hat{S}_1) \tag{1}$$

Insufficiency of this model, however, was soon recognized. It was shown that the thermomagnetic data [3, 4] as well as the data on specific heats of triads [5] over a wider temperature range could only be explained in terms of the HDVV model on the assumption of considerable lowering of triad symmetry from D_{3h}. Further investigations showed that this assumption was incompatible with the X-ray structure data on metal acetato complexes obtained at ambient temperatures (see, *e.g.* refs. [6, 7]). More recently, trinuclear chromium acetate was shown to undergo a phase transition at 215 °K with possible change of molecular structure [8]. This finding seemed to remove the discrepancy. In fact, the earlier X-ray studies were carried out at temperatures above the transition point, while magnetic susceptibility and specific heat data indicative of symmetry lowering were obtained at low temperatures, T ~ J/K = 15–50 °K. The EPR studies [9–11], however, showed that for a number of homonuclear chromium and iron clusters, the EPR line shapes measured at as low as helium temperatures fitted well undistorted structures, but indicated a small (*ca.* 0.1 cm^{-1}) antisymmetric exchange contribution. In order to bring all the data available into conformity, it was suggested [11] that magnetic properties of triads should be interpreted in terms of a high symmetry model accounting for non-Heisenberg biquadratic and antisymmetric exchange mechanisms.

Partly, our aim was to test this suggestion. For this purpose, we compared the distorted symmetry model and the model accounting for non-Heisenberg exchange as applied to analysis of the experimental data on magnetic susceptibilities of chromium(III) and iron(III) monochloroacetato complexes obtained in this work.

Experimental

Samples were prepared by reacting the anhydride of monochloroacetic acid with chromium(III) and iron(III) nitrates as described elsewhere [12]. The products recrystallized from water contained six H_2O molecules three of which cleaved off on drying the substance under vacuum at 56 °C. The elemental analysis data fitted well the general formula $[M_3O(CH_2ClCOO)_6(H_2O)_3]NO_3$ ($M_3 = Cr_3$, Cr_2Fe, $CrFe_2$, or Fe_3).

Susceptibilities of polycrystalline compounds were measured by the Faraday method from 1.6 to 300 °K. Effective magnetic moments were calculated for each

temperature point from the expression $\mu_{eff} = 2.839$ $(\chi'_M \cdot T)^{1/2}$ where χ'_M is the molar susceptibility, that is susceptibility per mol of metal ions. Corrections for diamagnetism were introduced as recommended in [13].

All the calculation results were obtained on a BESM-6 computer.

Theory

The applicability of two models will be considered: (i) The model accounting for biquadratic exchange in a trinuclear cluster with D_{3h} symmetry.

The corresponding SH for homonuclear species has the form [9]

$$
\begin{aligned}
\hat{H} = &-2J(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3 + \hat{S}_3\hat{S}_1) \\
&- 2J'[(\hat{S}_1\hat{S}_2)(\hat{S}_2\hat{S}_3) + (\hat{S}_2\hat{S}_3)(\hat{S}_3\hat{S}_1) + \\
&+ (\hat{S}_3\hat{S}_1)(\hat{S}_1\hat{S}_2) + (\hat{S}_2\hat{S}_3)(\hat{S}_1\hat{S}_2) + (\hat{S}_3\hat{S}_1)(\hat{S}_2\hat{S}_3) + \\
&+ (\hat{S}_1\hat{S}_2)(\hat{S}_3\hat{S}_1)] - \\
&- 2J''[(\hat{S}_1\hat{S}_2)^2 + (\hat{S}_2\hat{S}_3)^2 + (\hat{S}_3\hat{S}_1)^2] \qquad (2)
\end{aligned}
$$

In the case of heteronuclear clusters containing two sorts of ions, SH including biquadratic terms is given by

$$
\begin{aligned}
\hat{H} = &-2J_{MM}(\hat{S}_1\hat{S}_2) - 2J_{MM'}(\hat{S}_2\hat{S}_3 + \hat{S}_3\hat{S}_1) - \\
&- 2J_{MM}[(\hat{S}_2\hat{S}_3)(\hat{S}_3\hat{S}_1) + (\hat{S}_3\hat{S}_1)(\hat{S}_2\hat{S}_3)] - \\
&- 2J'_{MM'}[(\hat{S}_1\hat{S}_2)(\hat{S}_2\hat{S}_3) + (\hat{S}_2\hat{S}_3)(\hat{S}_1\hat{S}_2) + \\
&(\hat{S}_3\hat{S}_1)(\hat{S}_1\hat{S}_2) + (\hat{S}_1\hat{S}_2)(\hat{S}_3\hat{S}_1)] - \\
&- 2J''_{MM}[(\hat{S}_1\hat{S}_2)^2] - 2J''_{MM'}[(\hat{S}_2\hat{S}_3)^2 + (\hat{S}_3\hat{S}_1)^2] \\
& \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (3)
\end{aligned}
$$

Spins of two identical ions are labelled by subscripts 1 and 2. Solutions of (2,3) are too cumbersome to be given here. (ii) The second model stresses the significance of symmetry lowering but neglects contributions from biquadratic exchange.

The D_{3h} symmetry of the M_3 triangle can be lowered to C_{2v} or C_s.

In the first case, SH of exchange interactions can be written in the form

$$
\hat{H} = -2J_1\hat{S}_1\hat{S}_2 - 2J_2(\hat{S}_2\hat{S}_3 + \hat{S}_3\hat{S}_1) \qquad (4)
$$

On the assumption of isotropic g-factor, Zeeman interaction for the C_{2v} model is given by

$$
\hat{H}_z = g\beta H(\hat{S}_{1z} + \hat{S}_{2z} + \hat{S}_{3z}) \qquad (5)
$$

for homonuclear compounds and by

$$
\hat{H}_z = g\beta H(\hat{S}_{1z} + \hat{S}_{2z}) + g_3\beta H\hat{S}_{3z} \qquad (6)
$$

for heteronuclear ones.

In the case of three different exchange integrals and three different ions (the C_s model), SH has the form

$$
\begin{aligned}
\hat{H} = &-2J_{12}\hat{S}_1\hat{S}_2 - 2J_{23}\hat{S}_2\hat{S}_3 - 2J_{31}\hat{S}_3\hat{S}_1 + \\
&+ \beta H(g_1\hat{S}_{1z} + g_2\hat{S}_{2z} + g_3\hat{S}_{3z}) \qquad (7)
\end{aligned}
$$

Solutions of equations (4)–(7) are given in [9, 12] (the C_{2v} model) and [14] (the C_s one).

Calculations of theoretical magnetic susceptibilities were made according to the well known Van Vleck equation [15]. The Zeeman interaction terms were calculated on the assumption of isotropic g-factors of 1.98 for chromium and 2.0 for iron ions.

The exchange integral values were determined from the best fit procedure minimizing the error functional

$$
R = \left[\frac{1}{L}\sum_{i=1}^{L}(\chi_i - \chi_i^0)^2 \chi_i^{-2}\right]^{1/2} \qquad (8)
$$

where χ_i and χ_i^0 are theoretical and experimental susceptibilities at the T_i temperature, respectively, and L is the number of points. Minimization was carried out by varying exchange parameters corresponding to the alternative models.

Results and Discussion

A detailed analysis of the experimental data in terms of the two theoretical models described in the preceding section is given below.

$[Cr_3O(CH_2ClCOO)_6(H_2O)_3]NO_3$

The top part of Fig. 1 shows the experimental $\chi'_M(T)$ values and the best fit curves calculated for the model involving biquadratic exchange and for the model with symmetry lowered to C_{2v}. In the first case (SH (2) + (5)) the minimum value of root mean square deviation (R = 2.7%) occurs at J = −10 cm^{-1}, J' = 0.1 cm^{-1}, and J'' = 0.3 cm^{-1}. In the case of the C_{2v} model (SH (4) + (5)) the minimum r.m.s. value (R = 2.5%) corresponds to J_1 = −9.6 cm^{-1} and J_2 = −11 cm^{-1}.

Evidently, both models agree reasonably well with the experimental data, so that no choice between them can be made on the basis of magnetic
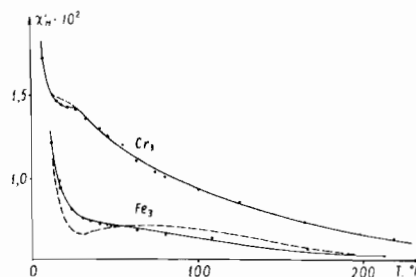

Figure 1. Experimental values of $\chi'_M(T)$ (.....) and theoretical best fit curves for biquadratic exchange (-----) and C_{2v} symmetry (———) models. I: $M_3 = Cr_3$; II: $M_3 = Fe_3$.
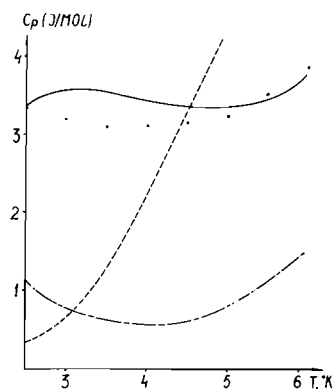
Figure 2. Specific heats of chromium acetate (.....) and theoretical best fit curves for biquadratic exchange (-----) and C_{2v} symmetry (——) models. The theoretical curve for the D_{3h} model with antisymmetric exchange (—·—) corresponds to J of -10 cm^{-1} and D of 0.1 cm^{-1}.

Figure 3. Theoretical curves for undistorted triiron clusters obtained using various biquadratic exchange parameters:

	J	J'	J''	(cm^{-1})
1.	-30	0	0	
2.	-30	-0.3	0	
3.	-30	0	-0.3	
4.	-30	0	0.3	
5.	-30	0.3	0	

susceptibility measurements for chromium mono-chloroacetate.

An additional evidence has been derived from measurements of magnetic specific heat for chromium acetate reported in [5]. It should be noted that magnetic susceptibility of chromium acetate [4] is nearly the same as that of chromium monochloro-acetate at all temperatures. One may also suggest close similarity of their magnetic specific heats which, like susceptibilities, depend on spin–spin interactions.

Figure 2 shows the experimental specific heats of chromium acetate against the best fit curves for the model including biquadratic exchange (J = -11 cm^{-1}, J' = 0, J'' = 0.5 cm^{-1}, R = 50%) and for the C_{2v} model (J$_1$ = -9.4 cm^{-1}, J$_2$ = -10.6 cm^{-1}, R = 10%). These results strongly argue against the former one.

An attempt has been made to improve the model neglecting symmetry lowering by accounting for anti-symmetric exchange. The most significant contribution to this mechanism arises from the Dzyaloshinksky–Moria antisymmetric exchange

$$\hat{H}_{as} = -2\vec{D}\,[(\hat{S}_1 \times \hat{S}_2) + (\hat{S}_2 \times \hat{S}_3) + (\hat{S}_3 \times \hat{S}_1)] \quad (8)$$

As the removal of four-fold degeneracy from the ground state of triads is only due to the z- component of the antisymmetric exchange operator [11], we assume D = D$_z$ thus excluding all the other terms of SH (8) from consideration.

Addition of (8) to (1) leads to the SH, the application of which yields heat capacity values shown in Fig. 2 alongside of those predicted by theoretical models discussed above. The corresponding curve was obtained with D set at 0.1 cm^{-1}, according to the estimate given in [11]. It is easy to see that the latter model provides a far poorer agreement with the experimental data than that accounting for symmetry lowering.
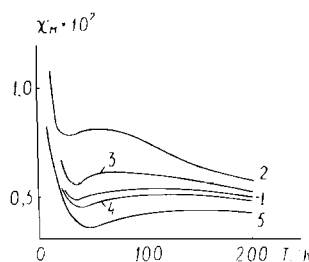
$[Fe_3O(CH_2ClCOO)_6(H_2O)_3]NO_3$

The observed susceptibilities of the three-iron cluster and calculation results obtained by adjusting different models to the experimental data are shown in Fig. 1 (the bottom part). The biquadratic exchange model gives the best fit (R = 7.2%) at J -33 cm^{-1}, J' 0.17 cm^{-1}, and J'' 0.3 cm^{-1}. The symmetry lowering model yields R of 3.6% at J$_1$ -24.5 cm^{-1} and J$_2$ -30.5 cm^{-1}. Again, the latter model provides better results than the former one.

Inapplicability of the biquadratic exchange model is most evident from the data shown in Fig. 3 where theoretical magnetic susceptibility curves for iron complexes are depicted which correspond to various contributions from biquadratic exchange. All the curves feature a characteristic minimum not present in the experimental curve.

Analysis of magnetic behaviour of mixed iron/-chromium clusters in terms of the biquadratic exchange model has led us to similar conclusions. For this reason, further discussion is limited to the results obtained using models with various degrees of symmetry lowering.

It is quite clear that mixed complexes cannot have symmetry higher than C_{2v}. This limits our analysis to consideration of SH including two ((4) + (6)) or three (7) different exchange integrals. The results obtained for the heteronuclear clusters are shown in Fig. 4.

$[Fe_2CrO(CH_2ClCOO)_6(H_2O)_3]NO_3$

With two different exchange integral values, the best fit procedure yields R of 6.6% for J$_1$ = -35 cm^{-1} and J$_2$ = -24 cm^{-1}. The fully non-equivalent exchange model leads to a somewhat improved root mean square deviation value (R = 4.2%) and exchange integrals J_{Fe-Fe}, J_{Fe-Cr}, and J_{Fe-Cr} of -31, -30, and -24.5 cm^{-1}, respectively.
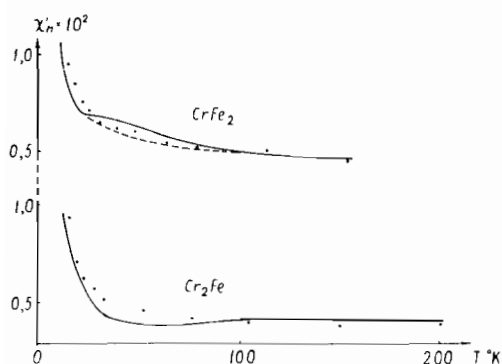
Figure 4. Experimental magnetic susceptibilities (.....) and theoretical best fit curves for models including two (———) and three (-----) exchange integrals. I: $M_3 = Cr_2Fe$; II: $M_3 = CrFe_2$.

$[FeCr_2O(CH_2ClCOO)_6(H_2O)_3]NO_3$

In this case, the C_{2v} model agrees rather poorly with the experimental data ($R = 11.6\%$, $J_1 = -10$ cm^{-1}, $J_2 = -27$ cm^{-1}); the application of the C_s model with exchange integral values varied within reasonable limits leads to only insignificant improvement.

We conclude that the spin Hamiltonian including biquadratic and antisymmetric terms does not give an adequate description of magnetic behaviour of the trimeric compounds studied if the D_{3h} symmetry is assumed. In the case of homonuclear complexes, a considerable improvement between theoretical and experimental susceptibilities can be achieved by assuming a certain lowering of cluster symmetry. As for the heteronuclear compounds, even the C_s model proves insufficient in this case.

We suggest the following explanation of the results obtained.

Suppose that two types of trimeric molecules occur in the carboxylate structures at low temperatures. Some arguments in favour of this suggestion are given in e.g. [8, 16]. Suppose, then, that a good many of these molecules are undistorted or slightly distorted species. Such species may be responsible for the broad bands with complex structures observed in the EPR spectra [9–11]. It seems reasonable to suggest that these bands will obscure the signals from distorted species which should give relatively narrow singlet lines (cf. the spectra of heteronuclear complexes [17]). The overall spectrum of such systems is difficult to distinguish from the spectrum of systems where all molecules are undistorted.

On the other hand, it is clear that magnetic behaviour of such systems can be described by the model involving some effective symmetry lowering. Statistical distribution of metal ions over non-equivalent positions may occur in heteronuclear compounds, which further complicates the situation. Perhaps, this is the reason why our attempts to account for magnetic behaviour of these compounds were a failure.

Possible theoretical models involve so many parameters that their treatment in the absence of additional experimental data can hardly be justified. The number of these parameters can be reduced by detailed analysis of the EPR spectra and/or by low-temperature X-ray studies. These investigations are now under way.

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