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Magnetic Properties of Dimeric Cobalt(II) Carboxylates

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The magnetic susceptibilities of two dimeric Co(II) carboxylates were measured in the range 1.6 to 300 °K. The compounds studied have similar structures to copper acetate monohydrate. The experimental data are treated in terms of various theoretical models. The results obtained are discussed.

Introduction

The preparation of a wide variety of dimeric Co(II) biscarboxylates of the general formula $[LCo(OOCR)_2]_2$ was described in previous papers [1–3]. The compounds isolated contained various radicals R in the bridging carboxylate anions and various apical ligands L. Their magnetic properties in the temperature range 77 to 300 °K and IR spectra showed them to be structurally related to the quinoline adduct of cobalt benzoate, $[(quin)Co(OOCC_6H_5)_2]_2$. The structure of this compound is of the type of copper acetate monohydrate one. The present paper provides a detailed analysis of magnetic properties of some dimeric Co(II) biscarboxylates in terms of various possible models.

Experimental

Two cobalt complexes that can be prepared in the purest form with respect to monomer admixtures have been studied: the quinoline adducts of cobalt metafluorobenzoate, $[(C_9H_7N)Co(OOCC_6H_4F)_2]_2$, and furancarboxylate, $[(C_9H_7N)Co(OOCC_4H_3O)_2]_2$. The synthesis of these compounds is described in ref. [2].

Static magnetic susceptibilities were measured on a vibrating-type magnetomer in the temperature range 1.6 to 300 °K. The data were corrected for the diamagnetism of the ligands and temperature independent paramagnetism of Co^{2+}. The magnetic susceptibility and effective magnetic moment values are listed in Table I.

TABLE I. Magnetic Susceptibilities χ and Effective Magnetic Moments μ of Quinoline Adducts of Cobalt(II) Furancarboxylate (I) and Metafluorobenzoate (II).

I			II		
T,K	$\chi\cdot10^3$	μ	T,K	$\chi\cdot10^3$	μ
1.613	9.90	0.357	1.613	40.51	0.723
2.085	8.91	0.386	2.287	34.39	0.791
3.994	6.70	0.463	3.170	27.35	0.833
4.797	6.19	0.487	4.333	26.06	0.950
7.129	4.98	0.533	5.179	23.24	0.981
12.21	3.80	0.609	7.955	17.59	1.05
19.06	3.20	0.698	10.06	15.02	1.10
23.20	3.04	0.751	15.50	13.32	1.28
29.07	2.82	0.810	20.29	12.02	1.39
40.70	2.73	0.943	25.29	10.96	1.49
52.88	2.82	1.09	30.76	10.13	1.58
64.65	2.95	1.23	37.04	9.36	1.66
77.13	3.34	1.43	50.61	7.00	1.68
85.82	3.60	1.57	59.50	6.12	1.71
97.84	3.80	1.72	66.08	5.87	1.76
110.0	4.06	1.88	73.87	5.61	1.82
127.8	4.39	2.12	77.0	5.64	1.83
138.9	4.85	2.32	86.26	5.30	1.91
144.8	4.91	2.38	108.5	5.41	2.16
158.1	5.37	2.61	119.4	5.51	2.29
170.9	5.70	2.79	132.9	5.66	2.45
180.5	5.90	2.92	141.8	5.82	2.57
192.4	6.03	3.04	163.2	6.18	2.84
199.2	6.22	3.15	174.7	6.43	3.00
207.6	6.29	3.23	187.4	6.64	3.15
220.4	6.55	3.39	193.8	6.74	3.23
229.0	6.62	3.48	204.6	6.84	3.35
238.8	6.75	3.59	222.0	7.15	3.56
248.2	6.81	3.68	236.4	7.15	3.68
261.3	6.81	3.77	244.8	7.20	3.76
268.5	6.75	3.81	263.1	7.15	3.88
275.9	6.75	3.86	271.9	7.20	3.96

Theory

As is well known [5], the ground state of the free Co^{2+} ion is ^4F, which splits into terms $^4T_{2g}$, $^4A_{2g}$, and $^4T_{1g}$ in octahedral crystal field. Among the latter, the $^4T_{2g}$ orbital triplet has the lowest energy. As the energy difference between the ground and lowest excited states amounts to at least several thousand reciprocal centimeters, contributions from the excited states to magnetic properties of cobaltous compounds may be neglected to a first approximation. For our purposes, the analysis may be limited to the 12-fold degenerate $^4T_{1g}$ state with spin 3/2 and fictitious orbital moment $\tilde{L} = 1$. The matrix elements $\tilde{L}$ within $^4T_{1g}$ are equal to the orbital moment matrix elements between the p-functions multiplied by a factor of −3/2.

The simplest approximation that can be used at this stage is as follows. We assume that Co^{2+} ions have spin-only moments of 3/2 in the compounds under discussion, thus neglecting orbital degeneracy. This assumption is equivalent to the suggestion that the cobalt coordination polyhedron has symmetry considerably lowered from O_h, which causes strong splitting of the $^4T_{1g}$ term, and that the lowest energy state is a well isolated singlet. On this assumption the magnetic properties of dimeric cobalt carboxylates can be described in terms of the spin-Hamiltonian

$$\hat{H} = -2J\hat{S}_1\hat{S}_2 + g\beta H(\hat{S}_1 + \hat{S}_2) \qquad (1)$$

where $S_1 = S_2 = 3/2$, β is Bohr magneton, H is the external magnetic field strength, g is the effective g-factor.

The nearer the g-factor to the spin-only value, $g_e = 2$, the more reasonable the assumption of "quenching" of the orbital moment.

Other possible models take into account orbital degeneracy and spin–orbit coupling, but neglect symmetry lowering effects.

On the assumption of isotropic exchange coupling, the SH for dimeric species in external field (H || z) that includes the orbital moment has the form [6]

$$\hat{H} = -2J\hat{S}_1\hat{S}_2 + \Sigma_{i=1}^{2}\,[\beta H(2\hat{S}_{iz} - (3/2)\text{æ}\hat{L}_{iz})] \qquad (2)$$

where æ is the orbital reduction factor which reflects delocalization of unpaired electrons over the ligands.

Direct diagonalization of the operator matrix (2) is prohibitively difficult because, even if one restricts the analysis to the $^4T_{1g}$ terms, the matrix dimensions amount to $12^2 = 144$. Approximations to (2) should therefore be considered. For the cobalt clusters, in particular dimeric ones, the following approach can be suggested.

There are indications (see *e.g.* ref. [6]) that spin–orbit coupling splits the $^4T_{1g}$ term in such a way that the lowest energy component is a Kramers doublet separated by some 300 cm^{-1} from the higher energy levels.

To simplify the problem, one may neglect all the energy levels lying above this doublet. A comparison of the spin-matrix elements with the Pauli matrices shows immediately (see *e.g.* ref. [6]) that in this case Hamiltonian (2) can be replaced with an equivalent one:

$$\hat{H} = -50/9J\hat{S}_1\hat{S}_2 + g^*\beta H(\hat{S}_{1z} + \hat{S}_{2z}) \qquad (3)$$

where $S_1 = S_2 = 1/2$ are fictitious spins for the Kramers doublets, $g^* = 10/3 + \text{æ}$ is the effective g factor.

Although (3) is apparently a rather rough approximation, it can yield reasonable values for exchange parameters in the region of low temperatures ($kT < 300\ cm^{-1}$), if the possibility that the g factor may differ from the value $g^* = 10/3 + \text{æ} \approx 4.3$, because of contributions from the excited states, is taken into consideration.

An original technique for taking account of the upper levels that does not lead to significant mathematical complications was suggested by Lines [6]. The essence of the Lines approach is as follows. Magnetic properties of cobaltous octahedral exchange clusters are formally described by Hamiltonian (3) with temperature dependent g-factor, g(T). This g-factor represents a complex function of temperature, spin–orbit coupling constant, and orbital reduction factor. The analytical expression for g(T), though exceedingly cumbersome and for this reason not given here, is very convenient for computational treatment.

Neglecting the upper energy levels (lying above the lowest Kramers doublet), we have also attempted to describe the magnetic properties of dimeric cobaltous compounds in terms of the anisotropic Hamiltonian

$$\begin{aligned}\hat{H} = {} & 2J[\hat{S}_{1z}\hat{S}_{2z} + \gamma(\hat{S}_{1x}\hat{S}_{2x} + \hat{S}_{1y}\hat{S}_{2y})] + \\ & + \beta[g_\parallel H_\parallel(\hat{S}_{1z} + \hat{S}_{2z}) + g_\perp H_\perp(\hat{S}_{1x} + \hat{S}_{2x} + \hat{S}_{1y} + \hat{S}_{2y})],\end{aligned} \qquad (4)$$

where $0 \leqslant \gamma \leqslant 1$, $S_1 = S_2 = 1/2$, $H_\parallel$ and $H_\perp$ are the external magnetic field components parallel and perpendicular, respectively, to the four-fold axis of the dimer.

Some arguments for the applicability of SH (4) are presented in *e.g.* ref. [7].

Solution of this SH in the approximation $(\gamma - 1)J \gg \beta gH$ yields for magnetic susceptibilities

$$\chi_\parallel = \frac{g_\parallel^2\beta^2N}{kT} \cdot \frac{1}{2 + \exp[-J(1-\gamma)/kT] + \exp[-J(1+\gamma)/kT]} \qquad (5)$$

$$\chi_\perp = \frac{g_\perp^2\beta^2N}{kT} \cdot \frac{1 - \exp[-J(1-\gamma)/kT]}{2 + \exp[-J(1-\gamma)/kT] + \exp[-J(1+\gamma)/kT]} \qquad (6)$$

For powders, the mean χ value should be used:

$$\chi = 1/3(\chi_{\parallel} + 2\chi_{\perp}) \tag{7}$$

Thus, four models were tested in order to investigate their applicability to dimeric cobalt(II) complexes:

1. The isotropic model which neglects the orbital moving and the spin–orbit interactions (SH(1)).
2. The isotropic model neglecting all single-ion levels except the ground Kramers doublet (SH(2)).
3. The Lines model (SH(3)) with the temperature dependent g-factor.
4. The anisotropic exchange model (SH(4)).

Results and Discussion

We will now turn to interpretation of the experimental data. The first thing to be mentioned is that the effective magnetic moments do not approach zero even at very low temperatures, apparently due to small monomer admixtures. Rigorous accounting of the effects by monomer admixtures is hardly possible because the magnetic susceptibility of low symmetry cobalteous monomer compounds is a complex function of a large number of unknown parameters [8]. The following procedure was applied to estimate these effects. As the dimeric species under study feature rather strong antiferromagnetism, the susceptibility of dimers below 2 °K may be neglected. The observed magnetism at these temperatures should thus be attributed to monomer admixtures. Using the tables presented in the paper [8], we evaluated the monomer contents from the low temperature magnetic susceptibilities, which made it possible to introduce the corresponding corrections in the susceptibility data over the total temperature range.

As the precise values for the parameters determining the temperature dependence of the magnetic susceptibility of monomer admixtures are not known, the corrections thus introduced furnish only approximate estimate. The results obtained using this procedure can be relied upon so far as the corrections are small compared with the measured susceptibilities.

The admixture amounts estimated from the low temperature susceptibilities were below 1% for cobalt furancarboxylate and about 3% for cobalt metafluorobenzoate complexes. Such monomer concentrations give relatively small corrections at temperatures above 19 and 77 °K, respectively. We therefore restricted our analysis to the susceptibility values obtained above these temperatures. These were corrected for magnetism of monomer species as described above.

The corrected magnetic susceptibility *vs.* temperature dependences were subjected to the best fit treatment using the four models chosen. The best fit parameters were computed by minimizing the root mean square error

$$F = \left[\frac{1}{N}\sum_{i=1}^{N}\frac{(\chi_i - \chi_i^o)^2}{\chi_i^2}\right]^{1/2} \tag{8}$$

where χ_i and χ_i^o are the experimental and calculated magnetic susceptibilities, respectively, at the T_i temperature and N is the number of temperature points.

The data thus obtained are listed in Table II. Their analysis follows.

The Isotropic Exchange Model

The best fit parameters for both complexes fall close together; in particular, both complexes give a g of about 4. The large departure of g from the spin-only value (2.0023) is indicative of significance of the orbital effects neglected within the model under consideration.

The Isotropic Model Neglecting All except the Ground Kramers Doublet Single-ion States

Comparison of the data in Table II shows that the rms error increases significantly on going from the preceding model to this one. Furthermore, the calculated g value of 5.8 by far exceeds the theoretical one, 10/3 + x ≈ 4.3. A number of rough approximations implicit in this model are responsible for its inadequacy: the neglect of symmetry lowering, the unjustified use of isotropic exchange Hamiltonian, and the neglect of contributions from the excited states.

TABLE II. The Best Fit Parameters and Rms Values for $[(C_9H_7N)Co(OOCC_6H_4F)_2]_2$ (I) and $[(C_9H_7N)Co(OOCC_4H_3O)_2]_2$ (II).

No	Comp.	Model	$-J$ (cm^{-1})	$g_{\parallel}$	$g_{\perp}$	F (%)	Note
1	I	1	96	4.25	4.25	4	Isotropic g-factor
2		2	49	5.83	5.83	6.9	Isotropic g-factor
3		3	42	æ = 1; $\lambda = -250$ cm^{-1}		6.7	g = f(T)
4		1	31	6.23	1.92	3.5	Based on the data for T ⩽ 130 K
5		4	72	6.1	3.4	2.5	The same plus $\gamma = 0.2$
6	II	1	90	4.1	4.1	7.1	Based on the data obtained in the range 77 to 300 K
7		2	48	5.8	5.8	10.6	
8		3	41	æ = 1; $\lambda = -260$ cm^{-1}		10.0	

The Lines Model

The use of this model taking into account both ground and excited states leads to only insignificant decrease of F which has the smallest value at an apparently exaggerated spin–orbit coupling constant value of *ca.* -250 cm^{-1} (λ is about -180 cm^{-1} for the free ion). The results obtained for models 2 and 3 show that they are in principle inapplicable for the description of the magnetic behaviour of dimeric cobalt carboxylates in which cobalt local symmetry is considerably lowered from O_h. The discrepancies may also be due to the use of the isotropic exchange Hamiltonian.

The Anisotropic Exchange Model

The anisotropic exchange model neglecting all single-ion levels except the lowest Kramers doublet provides the best fit to the experimental data (Table II). The neglect of the excited levels may be justified at temperatures below 130 °K. Under this limitation, the temperature range for cobalt metafluorobenzoate (77 to 130 °K) becomes too narrow for the best fit procedure to be applied. For comparison, the data on cobalt furancarboxylate in the range 19 to 130 °K were also subjected to the best fit treatment in terms of the isotropic exchange model with anisotropic g-factor (see Table II).

The F value of 2.5% obtained for model 4 as applied to cobalt furancarboxylate may well be explained by experimental errors and low accuracy of corrections for monomer contributions to the observed susceptibility. The best fit g-factors agree well with the EPR values for cobaltous complexes with a strong axial component of the crystal field (*cf.*, *e.g.* [9]). The nonzero value for γ may be due to interactions with the excited states [7] and/or neglect of orbital moments in the interionic exchange Hamiltonian [10].

It should be pointed out that the good agreement of the data calculated using parametrization model (4) with the experimental susceptibilities merely demonstrates the general applicability of this SH; however, model 4, as opposed to models with isotropic exchange, gives J values that cannot be interpreted in a simple way [7].

Conclusions

The magnetic susceptibilities of dimeric Co(II) carboxylates having similar structures to copper acetate monohydrate are analyzed using various theoretical models. The model taking into account anisotropy of both exchange and Zeeman interactions provides the best agreement with the experimental results. It is noted that this model has the most general applicability; however, a number of parameters it involves (J, γ) have no clear-cut physical sense. It thus appears that further development of the microtheory describing exchange interactions in systems with orbital degeneracy is required.

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