

Magnetic properties and molecular structure of cobalt(II) oxydiacetate trihydrate

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Abstract. The crystal and molecular structure of cobalt(II) oxydiacetate trihydrate, $\text{Co}(\text{C}_4\text{H}_4\text{O}_5)_2 \cdot 3\text{H}_2\text{O}$, has been determined from single-crystal, three-dimensional x-ray diffraction counter data. The compound crystallizes as dark red violet platelets in space group $P2_1/n$ of the monoclinic system with $Z = 4$ and having cell dimensions $a = 7.128(1)\text{Å}$, $b = 10.384(2)\text{Å}$, $c = 11.122(1)\text{Å}$, and $\beta = 91.51(1)^\circ$. The structure was refined to $R = 0.042$ and $R_w = 0.053$. The cobalt(II) ion has a distorted octahedral coordination in which the oxydiacetate acts as a tridentate chelate and the three remaining coordination sites are occupied by two water molecules and an oxygen atom from a carboxylate group of an adjacent oxydiacetate dianion. This latter linkage forms a chain structure. The chains are packed in layers and there is extensive hydrogen bonding between the layers. The magnetic susceptibility of cobalt(II) oxydiacetate trihydrate is dependent on the applied magnetic field. In an applied magnetic field of 1,000 Oe, the maximum susceptibility occurs at 2.51 K, and the inflection point below T_{max} lies at 2.40 K. (χ_{max} , T_{max}) at 100 Oe and 10,000 Oe are (0.257 emu/mole, 2.63 K) and (0.227, 1.76 K).

Keywords. Molecular structure; cobalt(II) oxydiacetate trihydrate; magnetic susceptibility; cobalt(II) chain compound; three-dimensional magnetic ordering.

1. Introduction

The study of low-dimensional magnetic materials continues to attract attention since these substances may provide real examples for the various theoretical models of magnetic behavior (de Jongh and Miedema 1974), or may be candidates for materials with prescribed properties. For example, there are few molecular based, chelated coordination compounds that exhibit cooperative ferromagnetic behavior. From previous work in our laboratory, the layered compound copper(II) oxydiacetate hemihydrate (Corvan *et al* 1980) was identified as being an insulating ferromagnet with $T_C = 3.3\text{ K}$, an intralayer exchange coupling constant of $+4.66\text{ cm}^{-1}$, and an out-of-plane anisotropy field of 250 Oe. The results of this work have stimulated the synthesis and characterization of other transition metal oxydiacetate salts. The molecular structure and magnetic properties of cobalt(II) oxydiacetate trihydrate are discussed in this article.

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2. Experimental

2.1 Synthesis

Samples of cobalt(II) oxydiacetate trihydrate were prepared by a modification of the procedure described earlier (Whitlow and Davey 1975). Excess oxydiacetic acid (diglycolic acid, obtained from the Aldrich Chemical Co.) was added to cobalt(II) carbonate, and the resultant deep red violet crystals were recrystallized from water to give irregular platelets. Analysis (Galbraith Laboratories, Inc., Knoxville, TN, USA). Calculated for $[\text{Co}\{\text{O}(\text{CH}_2\text{CO}_2)_2\}] \cdot 3\text{H}_2\text{O}$: C 19.61; H 4.11. Found: C 19.54; H 3.97.

2.2 Magnetic measurements

Magnetic susceptibility data were collected using a Princeton Applied Research Model 155 Foner-type (Foner 1959) vibrating sample magnetometer (VSM) using procedures that have been described earlier (Corvan *et al* 1980). The magnetometer was calibrated with $\text{HgCo}(\text{NCS})_4$ (Figgis and Nyholm 1958; Brown *et al* 1977). Samples of the standard and compounds under study were contained in precision milled Lucite sample holders. Approximately 150 mg of each were used. Diamagnetic corrections for the constituent atoms were made by using Pascal's constants, and corrections for temperature independent paramagnetism were estimated from tabulated data (Figgis *et al* 1960; König 1966; Weller *et al* 1979).

2.3 X-ray crystallography

Red violet colored crystals of the complex were grown by slow evaporation of a concentrated aqueous solution. All the larger crystals examined by Weissenberg and precession photographs turned out to be twinned. An untwinned monoclinic prism of dimensions $(0.30 \times 0.15 \times 0.10)$ mm was selected and used for data collection on an Enraf Nonius CAD4 diffractometer using a molybdenum tube and a graphite monochromator. The unit cell constants were obtained by a least-squares refinement of the setting angles of 25 reflections with $\theta \geq 30^\circ$. The intensity data were collected at $20 \pm 2^\circ\text{C}$ by the variable speed $\omega - 2\theta$ scan in the range $2^\circ \leq 2\theta \leq 55^\circ$. The scan range in ω for each peak was calculated from the formula $S = M_s + W_s \tan \theta$, where M_s is estimated from the mosaic spread of the crystal, and W_s allows for increasing peak width with θ due to wavelength dispersion. M_s and W_s were given values of 1.00 and 0.35, respectively. Scan ranges were extended by 25% on each side of a peak for the moving-background measurement. The total time spent on the two backgrounds was one-half of that spent on the peak. The intensities of three standard reflections monitored every three hours showed no significant variation thus assuring the stability of the crystal in the X-ray beam. The intensities were corrected for background and Lorentz and polarization factors with a locally written program based on a method described earlier (Corefield *et al* 1967), but the data were not corrected for absorption ($\mu = 21.0 \text{ cm}^{-1}$).

The structure was solved by the conventional heavy atom and difference Fourier techniques, and refined by the full-matrix least-squares method to the conventional residuals R and R_w of 0.042 and 0.053, respectively, where R and R_w are defined as

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|, \text{ and}$$

$$R_w = [\sum w(|F_o| - |F_c|)^2 / \sum |F_o|^2]^{1/2}.$$

The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$, and $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes. The anomalous dispersion factors, $\Delta f'$, and $\Delta f''$, for Co and Cl (International Tables for X-ray Crystallography 1974), were included in the calculations of F_c . The atomic scattering factors for hydrogen were taken from a standard source (Stewart *et al* 1965). All the non-hydrogen atoms were refined with anisotropic thermal vibration parameters and the hydrogen atoms with isotropic thermal vibration parameters. The two hydrogen atoms belonging to one of the water molecules could not be located from the difference Fourier. The largest peak in the final difference Fourier had a height of $0.4 e^-$. The crystal data are collected in table 1.

The positional parameters with their estimated standard deviations are given in table 2. Tables of structure amplitudes and thermal parameters are deposited as supplementary material.

Table 1. Crystal data.

Co(C ₄ H ₄ O ₅)·3H ₂ O	MW = 245.1
$a = 7.128(1)\text{\AA}$	$D_c = 1.98 \text{ g cm}^{-3}$
$b = 10.384(2)$	$Z = 4$
$c = 11.122(1)$	$\lambda(\text{Mo} - K_{\alpha 1}) = 0.70926 \text{ \AA}$
$\beta = 91.51(1)^\circ$	$\mu(\text{Mo} - K_{\alpha}) = 21.0 \text{ cm}^{-1}$
$U = 822.93 \text{ \AA}^3$	$\text{NO} = 1549 \geq 3\sigma(\text{I})$
Monoclinic, $P2_1/n$	$R = 0.042, R_w = 0.053$

Table 2. Positional parameters with their estimated standard deviations.

Atom	x/a	y/b	z/c
Co	0.0719 (1)	0.3927 (1)	0.3032 (1)
O (1)	0.2949 (5)	0.2822 (3)	0.2373 (3)
C (1)	0.2773 (7)	0.1618 (5)	0.2354 (4)
O (2)	0.4018 (5)	0.0872 (3)	0.1961 (3)
C (2)	0.0996 (8)	0.1005 (5)	0.2807 (6)
O (3)	-0.0179 (5)	0.2031 (3)	0.3165 (4)
C (3)	-0.1927 (7)	0.1734 (5)	0.3675 (6)
C (4)	-0.2737 (7)	0.2993 (5)	0.4148 (5)
O (4)	-0.4168 (5)	0.2921 (4)	0.4740 (3)
O (5)	-0.1880 (5)	0.4036 (3)	0.3883 (3)
OW (1)	0.2284 (6)	0.3881 (4)	0.4687 (4)
OW (2)	-0.0342 (5)	0.4045 (4)	0.1263 (3)
H1C (2)	0.138 (8)	0.042 (6)	0.353 (5)
H2C (2)	0.035 (9)	0.035 (7)	0.198 (6)
H1C (3)	-0.085 (8)	0.140 (5)	0.304 (5)
H2C (3)	-0.163 (9)	0.103 (7)	0.449 (6)
H1OW (1)	0.082 (12)	0.368 (8)	0.465 (7)
H2OW (1)	0.231 (10)	0.446 (7)	0.499 (6)
H1OW (3)	0.640 (9)	0.258 (7)	0.059 (6)
H2OW (3)	0.532 (11)	0.327 (9)	0.110 (9)

3. Results and Discussion

3.1 Molecular and crystal structure

The cobalt(II) ion has a distorted octahedral coordination in which the oxydiacetate anion acts as a tridentate chelate the three chelating atoms being the ether oxygen O(3) and an oxygen from each of the two carboxylate groups. The remaining three coordinating sites are occupied by two water molecules, and, as shown in the ORTEP (Johnson 1976) drawing of the structure, an oxygen atom from a carboxylate group of another oxydiacetate anion (figure 1). All Co–O bond distances (table 3) lie within a narrow range, the shortest being 2.028(3)Å and the longest 2.128(4)Å. Due to the constraints imposed by the oxydiacetate chelate the bond angles around the cobalt atom vary considerably from the ideal values of 90° or 180° expected for an octahedral coordination. Thus, the bond angles subtended at Co by the three pairs of *trans* oxygen atoms, i.e., the angles O(1)–Co–O(5), O(3)–Co–O(2'), and OW(1)–Co–OW(2) are 150.0°, 166.5°, and 169.4°, respectively, while the six O–Co–O bond angles subtended by the *cis* oxygen atoms range from a low of 75.3° to a high of 118.2° (table 3).

The oxydiacetate ligand is approximately planar with the cobalt atom lying approximately in the plane (table 4). It is apparent from the deviations of atoms from the mean plane that the two halves of the ligand are slightly folded about the

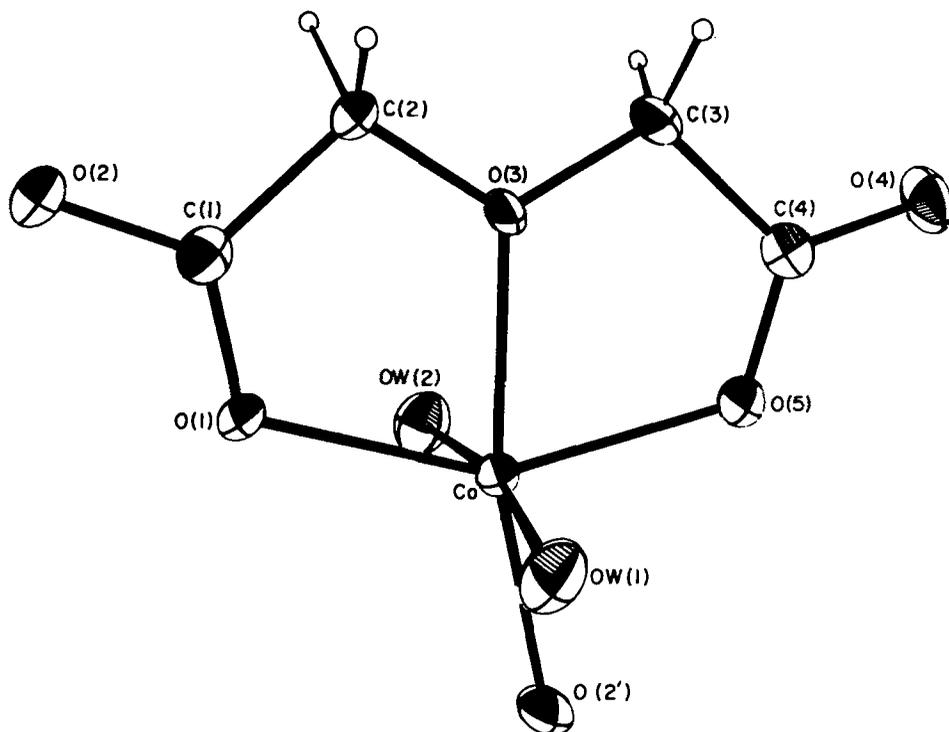


Figure 1. An ORTEP view of the complex with 40% probability of thermal ellipsoids for non-hydrogen atoms, and spheres of arbitrary size for hydrogen atoms. OW(1) and OW(2) are coordinated water molecules whose hydrogen atoms are not shown.

Table 3. Bond distances and bond angles with estimated standard deviations in parentheses.

<i>Bond distances</i> (Å)			
Co-O (1)	2.108 (3)	C(1)-O (2)	1.265 (6)
Co-O (3)	2.077 (4)	C(1)-C (2)	1.516 (7)
Co-O (5)	2.106 (3)	C(2)-O (3)	1.418 (6)
Co-O (2')	2.028 (3)	C(3)-O (3)	1.417 (6)
Co-OW (1)	2.128 (4)	C(3)-C (4)	1.528 (7)
Co-OW (2)	2.092 (4)	C(4)-O (4)	1.231 (6)
C(1)-O (1)	1.257 (6)	C(4)-O (5)	1.282 (6)
<i>Bond angles</i> (°)			
O(1)-Co-O (3)	75.3 (1)	OW(1)-Co-OW (2)	169.4 (2)
O(1)-Co-O (5)	150.0 (1)	Co-O(1)-C (1)	118.1 (4)
O(1)-Co-O (2')	118.2 (1)	O(1)-C(1)-C (2)	119.8 (5)
O(1)-Co-OW (1)	84.6 (2)	O(1)-C(1)-O (2)	123.5 (5)
O(1)-Co-OW (2)	87.8 (2)	O(2)-C(1)-C (2)	117.2 (5)
O(3)-Co-O (5)	75.1 (1)	C(2)-C(2)-O (3)	106.4 (4)
O(3)-Co-O (2')	166.5 (2)	C(2)-O(3)-C (3)	118.7 (4)
O(3)-Co-OW (1)	94.2 (2)	C(2)-O(3)-Co	120.5 (4)
O(3)-Co-OW (2)	91.0 (2)	C(3)-O(3)-Co	120.7 (4)
O(5)-Co-O (2')	91.5 (1)	O(3)-C(3)-C (4)	107.2 (4)
O(5)-Co-OW (1)	93.4 (2)	C(3)-C(4)-O (5)	117.2 (4)
O(5)-Co-OW (2)	96.8 (2)	C(3)-C(4)-O (4)	117.3 (5)
O(2')-Co-OW (1)	88.4 (2)	O(4)-C(4)-O (5)	125.5 (5)
O(2')-Co-OW (2)	88.6 (2)	C(4)-O(5)-Co	119.2 (4)

O(2') refers to atom O(2) in symmetry position ($\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$).

Table 4. Deviations in Å of atoms from the mean least-squares plane through designated atoms.

Co (06), O (1) (-0.03), C (1) (-0.04), C (2) (-0.01), O (3), O (3) (0.06) C (3) (0.05), C (4) (-0.09), O (5) (-0.01), O (2') (0.11),* O (2) (-0.07),* O (3) (-0.26),* OW (1) (-2.07),* OW (2) (2.14),* OW (3) (0.51)
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* Atoms not included in the mean plane calculation.

Co-O(3) bond. The bond distances and angles in the ligand are similar to those reported for the free ligand (Davy *et al* 1973) and for copper(II)-oxydiacetate hemihydrate (Whitlow *et al* 1975).

There are some noteworthy differences in the coordination geometry around the metal ion between the Co(II) complex reported here and copper(II)oxydiacetate hemihydrate. In the Co(II) complex the metal to ether oxygen distance is quite normal (2.077 Å) whereas in the Cu(II) complex it is quite long (2.488 Å). This has the effect of making the terminal chelating oxygens O(1) and O(5) *trans* to each other in the former and *cis* in the latter. Only one of the remaining two oxygen atoms of the ligand, i.e., O(2), is coordinated in the Co(II) complex whereas both O(2) and O(4) are coordinated in the Cu(II) complex.

The crystal structure consists of infinite chains of Co(II)oxydiacetate units covalently linked to each other through Co-O(2') bonds, where O(2') belongs to an adjacent ligand. The chain direction is delineated in figure 2 by showing the corresponding bonds as full dark lines. The chains are packed in layers. There is

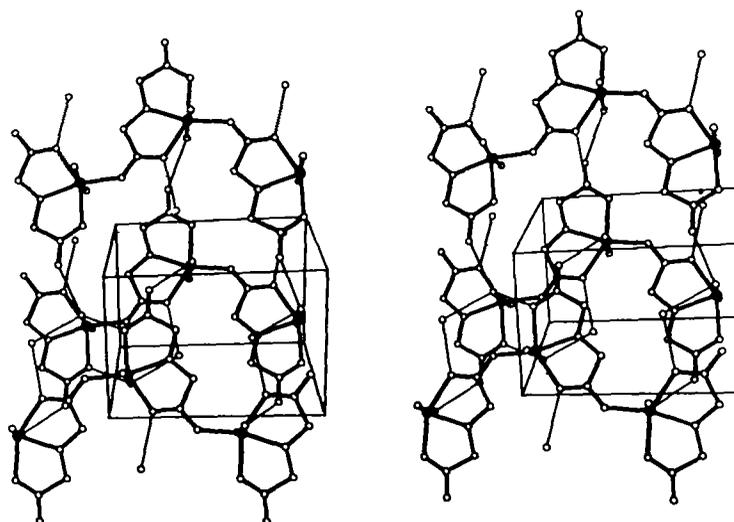


Figure 2. A stereoscopic view of the structure with the layers slightly tilted to show the *trans*-coordinated water molecules. Superexchange pathways are shown with full bonds and hydrogen bonds as thin lines.

intra- as well as interlayer interaction through hydrogen bond formation with the water molecules, with the three dimensional structure resulting from hydrogen bonding between the layers.

3.2 Magnetic properties

Magnetic studies of low-dimensional cobalt(II) compounds are of especial interest in view of the expected anisotropic nature of the exchange interactions as implied by the exchange Hamiltonian

$$H = -2J \sum_{i \leq j}^N \alpha S_i^z S_j^z + \beta S_i^x S_j^x + \gamma S_i^y S_j^y.$$

Diverse properties may be anticipated. Frequently, cobalt(II) chain compounds have Ising-like behavior ($\beta = \lambda = 0$), although XY behavior has been identified ($\alpha = 0$), and Heisenberg theory has been applied in certain cases. Both ferromagnetic ($+J$) and antiferromagnetic ($-J$) exchange coupling are known. Single ion anisotropy, g value anisotropy, and antisymmetric exchange interactions may result in spin canting, and metamagnetic materials are known (see Hatfield *et al* 1982).

The cobalt(II) single ion has an electronic configuration of d^7 , and the ground state is ${}^4T_{1g}$ in an octahedral environment. The degeneracy is lifted by low symmetry crystal field components and spin-orbit coupling (for the free ion $\lambda = -180 \text{ cm}^{-1}$) yielding six doublets. In some circumstances, such as those present in cobalt oxydiacetate trihydrate, the lowest lying doublet has $S' = 1/2$. In an octahedral environment, the g tensor is isotropic and has the value 4.33, but in lower symmetry environments the g tensor becomes very anisotropic. The three principal values sum to 13 in first order in the limit of a weak crystal field (Abragam *et al* 1951; Bleaney *et al* 1951), but experimentally observed g tensors

show a wide range of values (see Orton 1968). In addition to the orbital contributions, there are contributions to g from exchange interactions with the contributions being proportional to the sum of the exchange integrals from all of the neighbors (Hutchings *et al* 1963). For example, an excellent fit of the magnetic susceptibility data for $\text{Co}(\text{pyridine})_2\text{Cl}_2$, an Ising chain with ferromagnetic interactions, was obtained by using $g_{\parallel} = 7.0$ and $g_{\perp} = 5.0$ (Pires *et al* 1978).

The magnetic properties of cobalt oxydiacetate trihydrate are dependent on the applied magnetic field. Data collected in the temperature range 35 to 110 K in an applied magnetic field of 10,000 Oe may be fit by the Curie Weiss law by using a Simplex nonlinear least-squares fitting program (Spendley *et al* 1962; Nelder *et al* 1965; O'Neill 1971) with the parameters $C = 2.684$ and $\theta = -26.9^\circ$ while data collected in the same temperature range in an applied magnetic field of 1,000 Oe may be fit with the parameters $C = 2.806$ and $\theta = -24.1^\circ$. The data collected in an applied magnetic field of 1,000 Oe are displayed in figure 3 where it may be seen that the magnetic susceptibility reaches a maximum value at 2.5 K, and that there is an abrupt decrease at lower temperatures. The temperature at which an inflection occurs is at 2.40 K, and this may be tentatively identified as the critical temperature of a canted antiferromagnet, since the maximum value of the magnetic suscepti-

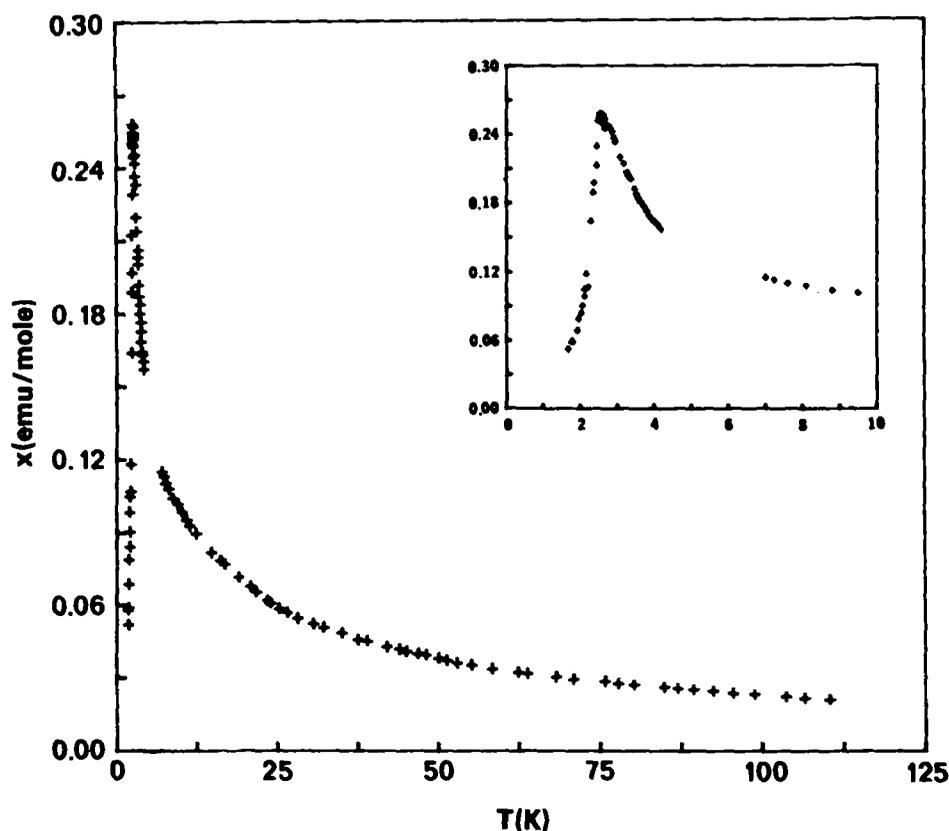


Figure 3. Magnetic susceptibility data for cobalt oxydiacetate collected in an applied field of 1,000 Oe. The low temperature data are shown in the inset with an expanded temperature scale.

bility is too low for ferromagnetic interactions. The transition seen in the 1,000 Oe magnetic data is suppressed at 10,000 Oe, and, thus, T_C must lie below the lowest temperature of the measurements, that being 1.8 K. Magnetic data were also collected in an applied magnetic field of 100 Oe in the temperature range 1.9–30 K. Owing to a poor signal to noise ratio, it was not possible to obtain magnetic susceptibility data above 30 K in the low applied magnetic field of 100 Oe by using the vibrating sample magnetometer, and, thus, data for a Curie-Weiss fit were not obtained. At 100 K, (χ_{\max} , T_{\max}) are (0.257 emu/mole, 2.63 K), and the inflection occurs at 2.47 K.

The parameters from the Curie-Weiss fits have limited meaning, but they do lead to the conclusion that the ground state is a doublet with the $|\pm 3/2\rangle$ state lying at much higher energies. With this fact in mind, the magnetic data were analyzed with Ising theory for $S = 1/2$ (Bonner *et al* 1964, Pires *et al* 1978). The appropriate equations are

$$\chi_{\perp} = [Ng_{\perp}^2 \mu_B^2/4|J|] [\tanh(\beta|J|/2) + (\beta|J|/2)\text{sech}^2(\beta|J|/2)]$$

$$\chi_{\parallel} = N\beta[g_{\parallel}^2 \mu_B^2/4] [\exp(\beta J)/\{1 + (\beta/\beta_C)\exp\{(\beta - \beta_C)J\}\}]$$

where $\beta = 1/kT$ and $\beta_C = 1/kT_C$. These equations were fitted to the experimental data collected with an applied field of 1000 Oe using a Simplex routine. The best-fit parameters are collected in table 5. The high temperature limit of the data used in the fitting calculations was taken to be 80 K in order to avoid population of the $|\pm 3/2\rangle$ state, and a low temperature limit of 3.8 K was selected in order to avoid pretransitional effects. However, the fit was not very good below 9–10 K. In the temperature range 3.8 to 9–10 K the calculated magnetic susceptibilities deviate as much as 10% from the observed data. As T_C is approached, the paramagnetic susceptibility rises more rapidly than predicted by the Ising chain model, and this may be a consequence of the onset of weak ferromagnetism. Such weak ferromagnetism could arise from antisymmetric exchange (Dzyaloshinsky 1958; Moriya 1963) of the form

$$D_{ij} \cdot [S_i \times S_j]$$

which results in a canting of the spins. It is apparent from figure 2 that adjacent cobalt(II) ions in the chain are not related by a center of symmetry, and, thus, antisymmetric exchange interactions are allowed.

The available magnetic data show that cobalt(II) oxydiacetate trihydrate is an excellent candidate for the study of changes to higher dimensionality in an anisotropic spin system. In view of the extensive hydrogen bonding network between chains and layers, it is anticipated that changes in the dimensionality will be reflected in the magnetic properties of single crystals. Unfortunately, all larger

Table 5. Magnetic data for cobalt oxydiacetate trihydrate.

Applied field (Oe)	T_{\max} (K)	T_c (K)	J (cm ⁻¹)	g_{\perp}	g_{\parallel}
10,000	1.7	< 1.7			
1,000	2.51	2.40	-4.0	8.27	2.93
100	2.63	2.47			

crystals examined to date have been twinned, and measurements on crystals in near-zero applied magnetic fields must await the growth of appropriate crystals for the measurements.

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