establishes the nonzero values of these parameters. Instead of the good agreement with experiment shown in Table I, we obtain the following results with variation of the $e_{\pi\sigma}$(O):

(i) with $e_{\pi\sigma}$(ax) = 0 (other parameters as in Table VII)

principal *g* value	orientation (deg) ref to		
	a	*b*	*c′*
1.89	12	79	84
3.50	93	109	19
5.72	79	157	108

(ii) with $e_{\pi\sigma}$(eq) = 0 (other parameters as in Table VII)

principal *g* value	orientation (deg) ref to		
	a	*b*	*c′*
1.87	16	74	89
3.26	93	76	166
5.87	74	159	104

Variations in either $e_{\pi\sigma}$ value by these magnitudes, but in combination, give results essentially as might be guessed from these individual responses. Altogether, neglect of $e_{\pi\sigma}$(eq) is again not recompensed by variation of the remaining parameters. Many calculations of this nature have led to the error estimates in Table VII.

Appendix II

Fenske–Hall calculations[17] were carried out on both pyridine *N*-oxide and picoline *N*-oxide. Molecular geometries were taken from reported X-ray structural analysis[18,19] except for C–H distances in the pyridine oxide ligand, which were idealized to lie at 0.98 Å from appropriate carbon atoms. Basis functions were chosen as single Slater orbitals for the 1s and 2s functions of N, C, and O, in which exponents were obtained by curve-fitting the double-ζ functions of Clementi[20] but with retention of orthogonality. The 2p basis was represented by the double-ζ functions directly. For hydrogen, an exponent of 1.16 was used. Calculated molecular orbital energies are illustrated in Figure 4, from which the near identity of HOMOs and LUMOs in the two amine oxides is apparent. For each molecule, the HOMO and sub-HOMO are nearly degenerate. The characters of these two orbitals, in each system, are shown numerically in Table VIII with respect to valence atomic functions. The HOMOs are essentially pure atomic O $2p_{\perp}$ functions, and the sub-HOMOs are ca. 75% O $2p_{\parallel}$ with significant contributions from the framework of each heterocycle. Atom numbering is given in Figure 5, and ∥ and ⊥ relate to the planes of the heterocycles.

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Canted Antiferromagnetism in Single-Crystal Cobalt(II) Oxydiacetate Trihydrate

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A single-crystal magnetic study of cobalt(II) oxydiacetate trihydrate is presented. The extended structure of $Co(C_4H_4O_5)\cdot 3H_2O$ consists of carboxylate-bridged cobalt(II) chains. The highly anisotropic principle magnetic susceptibilities display parallel and perpendicular Ising behavior in the *b* and *a′* directions. The susceptibilities are fit with the appropriate models where $J_{a'} = -8.84$ cm^{-1}, $g_{a'} = 2.193$ and $J_b = -6.44$ cm^{-1}, $g_b = 6.888$. A small *xy* contribution leads to a larger exchange coupling constant in the perpendicular (*a′*) direction. Canting of the antiferromagnetically coupled moments along the cobalt chain (*b*) direction leads to weak ferromagnetism in the *c′* direction, and the various canting mechanisms are discussed in relation to $Co(C_4H_4O_5)\cdot 3H_2O$. The canting angle and interchain coupling are estimated from the magnetization and the critical field to be $\phi \approx 8.7°$ and $J_{c'} \approx -0.028$ cm^{-1}.

Previous work in our laboratory has shown that the layered compound copper(II) oxydiacetate hemihydrate[2] is an insulating ferromagnet. Since there are few molecular based, chelated coordination compounds that exhibit cooperative ferromagnetic behavior, the synthesis and characterization of other transition-metal oxydiacetate salts were undertaken. One of these, cobalt(II) oxydiacetate trihydrate, also exhibits cooperative magnetic behavior.[3] $Co(ODA)\cdot 3H_2O$ has the molecular structure shown in Figure 1. The coordination about the Co(II) ion consists of three oxygens from the tridentate oxydiacetate ligand (O1, O3, O5), two water molecules (OW1, OW2), and an oxygen from an adjacent oxydiacetate ligand (O2′). The distortion from an octahedral coordination geometry is significant. The ligand is nonplanar with the dihedral angle between the planes formed by O1–Co–O3 and O3–Co–O5 being 49.5°. A complete description of the crystal structure may be found in ref 3.

The linkage of the Co(II) ions to adjacent molecules via O2′ leads to carboxylate-bridged cobalt chains that lie along the *b* direction. The chains, in turn, are bound together through weak hydrogen bonding to form sheets. From these structural considerations, one may expect primarily one-dimensional behavior with a small degree of higher dimensionality in the physical properties.[4] The powder magnetic susceptibility exhibits a sharp maximum below 3 K. The position of this peak is field dependent with an increase in the applied magnetic field leading to a decrease in $T(\chi_{max})$. This behavior is indicative of canted antiferromagnetism[5] and arises when the components of the moment vectors are not colinear. Measurements on single crystals were undertaken to determine the nature of the cooperative behavior.

Experimental Section

Synthesis. Cobalt(II) chloride (0.0025 mol) was dissolved in 200 mL of distilled water and oxydiacetic acid (0.0025 mol) was added with stirring. The solution was titrated with concentrated KOH solution until the cobalt solution turned cloudy (formation of $Co(OH)_2$). The solution was then back-titrated with 10 M HCl until the solution was clear again, and ~1 mL of excess 10 M HCl was added. This treatment removes the acidic protons on the oxydiacetic acid but keeps the solution acidic enough so that $Co(OH)_2$ does not form when the solution is concentrated. The solution was filtered and the filtrate then concentrated slowly by

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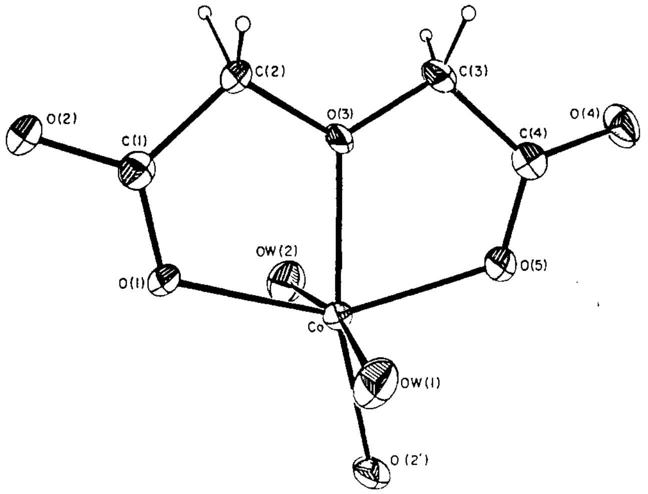

Figure 1. Molecular structure of cobalt(II) oxydiacetate trihydrate.

solvent evaporation. Crystals were collected after 3 days. Large single crystals (~0.5–1 cm) were obtained by repetitively concentrating a saturated aqueous solution that contained single-crystal seeds.

Magnetic Measurements. Low-temperature (1.8–100 K) magnetic susceptibility data were collected by using a Princeton Applied Research Model 155 vibrating-sample magnetometer. The Magnion H-96 electromagnet was operated at fields from 0 to 1.5 T by using a Magnion HSR-1365 power supply with a Magnion FFC-4 and a Rawson-Lush Model 920 MCM rotating-coil gaussmeter field control system. The field was calibrated with $HgCo(NCS)_4$.[6] Diamagnetic corrections for the compounds were estimated from Pascal's constants.[7]

Symmetry principles require that one of the principle magnetic axes in a monoclinic system be coincident with the crystallographic *b* axis, while the other two mutually perpendicular magnetic axes will by necessity lie in the *a*,*c* plane although not necessarily coincident with either axis. A single crystal of $Co(C_4H_4O_5)\cdot 3H_2O$ with dimensions 3.4 mm × 2.97 mm × 1.5 mm was used. The crystallographic axes were related to the crystal morphology by X-ray diffraction measurements. All single crystals had well-formed faces (001), (101), (011), and $(01\bar{1})$, and the edges formed by the intersections of the (001) and (101) planes and the (011) and $(01\bar{1})$ planes were used to align the crystal on the VSM single-crystal mount. From goniometer measurements, the principle magnetic axis *c′* was determined to lie along the crystallographic *c* axis, and the magnetic axis *a′* was found to be 1.5° away from the *a* axis. Measurements were accurate to within 0.5°.

The best fit parameters from theoretical models were obtained by using a Simplex[8] nonlinear fit to the experimental data, and the function minimized was the sum of the squares of the residuals.

Results

Magnetic susceptibility data were collected in the *a′*, *b*, and *c′* directions at an applied field of 1000 Oe. The data with the applied field along *a′* show an increase to a rounded maximum ($T(\chi_{max}$ = 0.0444 emu/mol), followed by a gradual decrease in the magnetic susceptiblity toward some finite value at the low-temperature limit of the instrument. Data in the *b* direction exhibit a broad maximum ($T(\chi_{max}) = 8.49$ K, $\chi_{max} = 0.1776$ emu/mol) with a decrease toward $\chi = 0$ at low temperature. In the *c′* direction, χ increases to a sharp maximum ($T(\chi_{max}) = 2.96$ K, $\chi_{max} = 1.664$ emu/mol) and drops off rapidly toward zero at low temperatures.

In cobalt oxydiacetate trihydrate there are four magnetic sublattices, and from symmetry arguments and experimental evidence, it is possible to predict the moment structure.[9] The moments along the chain (*b*) axis are coupled antiferromagnetically via ligand carboxylate bridges. In the absence of an applied field, for a given chain there is no net moment in the *b* direction. As a consequence of mechanisms to be discussed later, the moments on adjacent cobalt centers are canted with respect to one another. Therefore, for an individual chain, a weak ferromagnetic moment exists in the *c′* direction perpendicular to the chain axis. Because of the crystal symmetry, weak ferromagnetic moments associated with adjacent chains are aligned antiparallel to one another. This type of moment structure is termed hidden canting.

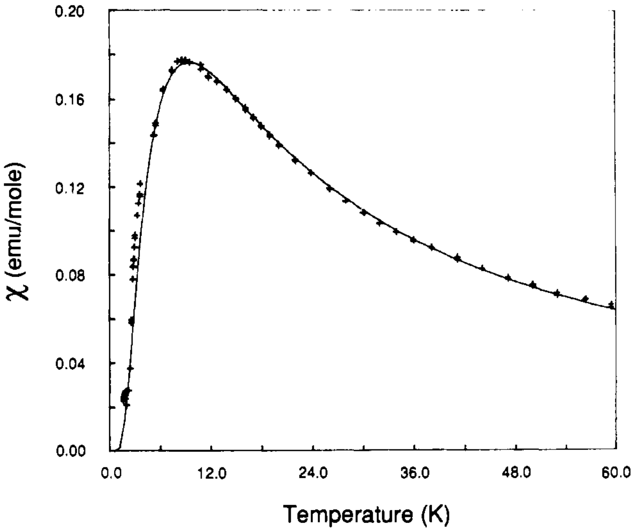

Figure 2. Magnetic susceptibility of cobalt(II) oxydiacetate trihydrate in the *b* direction fit with a parallel Ising chain model. $J = -6.44$ cm^{-1}, $g = 6.888$.

Magnetic Models. Cobalt(II) has a d^7 electronic configuration with a ^4F ground-state free-ion term. Under a cubic field, the degeneracy of the ^4F term is lifted, leaving a $^4T_1$ state lying lowest.[5] Spin–orbit coupling splits the $^4T_1$ state into six Kramer's doublets, with a single doublet lying $(^9/_4)$ $|\lambda|$ below the next highest levels. The low-symmetry axial and rhombic distortions produce anisotropic *g* values. A typical value for the spin–orbit coupling constant λ is ~−180 cm^{-1} for Co^{2+}, so the splitting between the ground-state doublet and the next highest levels is on the order of 400 cm^{-1} or 580 K. Since the excited states are so high, the magnetic properties at lower temperatures are entirely determined by the ground doublet. Therefore, a fictitious spin of $S = {}^1/_2$ may be used to describe the magnetism.

Cobalt(II) is typically Ising in nature, and the exchange and Zeeman parts of the Hamiltonian are[10]

$$H = -2J\sum_{i\leq j}^{N}[\alpha S_i^z\cdot S_j^z + \beta S_i^x\cdot S_j^x + \gamma S_i^y\cdot S_j^y] + g\mu_B\sum_{i=1}^{N}S_i\cdot H$$

where, for pure Ising interaction, $\alpha = 1$, and $\beta = \gamma = 0$. The parallel and perpendicular magnetic susceptibility expressions are

$$\chi_{\parallel} = \frac{Ng^2\mu_B{}^2}{4kT}\exp\left(\frac{J}{kT}\right)$$

$$\chi_{\perp} = \frac{Ng^2\mu_B{}^2}{4|J|}\left[\tanh\left(\frac{|J|}{2kT}\right) + \frac{|J|}{2kT}\operatorname{sech}^2\left(\frac{|J|}{2kT}\right)\right]$$

The best fit of the $\chi_{\parallel}$ expression to the magnetic susceptibility data in the *b* direction yielded parameters $J = -6.44$ (1) cm^{-1} and $g = 6.888$ (5) (Figure 2). The maximum in the susceptibility at 8.5 K is indicative of the small antiferromagnetic coupling constant, while the large *g* value is proof that the easy magnetic axis direction is parallel to the chain.

A best fit to the susceptibility data from the *a′* direction using the $\chi_{\perp}$ model was obtained with parameters $J = -8.84$ (1) cm^{-1}

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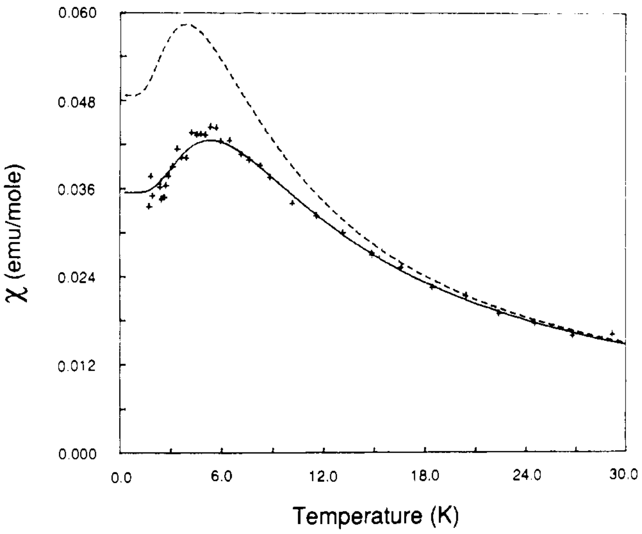

Figure 3. Magnetic susceptibility of cobalt(II) oxydiacetate trihydrate in the *a′* direction fit with a perpendicular Ising chain model: (solid line) $J = -8.84\ \text{cm}^{-1}$, $g = 2.193$; (dashed line) $J = -6.44\ \text{cm}^{-1}$, $g = 2.193$.

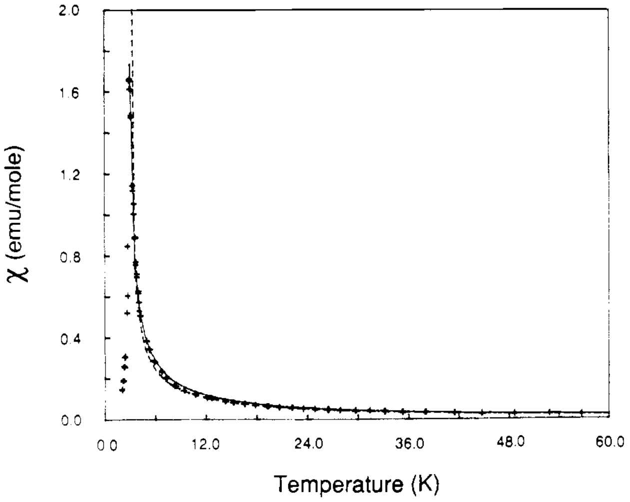

Figure 4. Magnetic susceptibility of cobalt(II) oxydiacetate trihydrate in the *c′* direction fit with a single-ion anisotropy model (solid line) and Moriya's canted antiferromagnet model (dashed line) with parameters as described in the text.

and $g = 2.193$ (5). This J value warrants comment. Two perpendicular Ising chain curves are plotted in Figure 3, one with the best fit J value from the parallel chain fit, $-6.44\ \text{cm}^{-1}$, and the other obtained from the best fit to the perpendicular Ising model, $-8.84\ \text{cm}^{-1}$. The most plausible explanation for the discrepancy in the exchange coupling constant between the parallel and perpendicular models is that the system is not of pure Ising character; there is a small contribution from xy character in the exchange, which can significantly lower $\chi_{\max}$.[11]

A description of the susceptibility in the *c′* direction (Figure 4) must involve an understanding of the canting mechanism. The origin of weak ferromagnetism due to canting of moments arises from anisotropic spin couplings. There are two components of the spin Hamiltonian responsible for this anisotropy, single-ion anisotropy and anisotropic spin–spin coupling.

Single-Ion Anisotropy. The single-ion anisotropy energy[12] involves those terms of the Hamiltonian that are expressed in terms of single-ion spin operators and, if dipolar and pseudodipolar terms are neglected, are given by

$$\sum_i [DS_{iz}^2 + E(S_{ix}^2 - S_{iy}^2)]$$

where D and E are the axial and rhombic distortion parameters. These terms can be derived from the fine-structure energy of an ion under the influence of the crystalline electric field, in which spin–orbit coupling plays the major role.

An expression has been derived for the susceptibility of an exchange-coupled system perpendicular to the canting axis by means of a molecular field approximation.[13] The magnetic susceptibility is given by

$$\chi_\perp = \frac{(g_1^2 + g_2^2)\mu_B^2 S(S+1)}{3k(T+\Theta)}\left(1 + \frac{T_N - T_0}{T - T_N}\right)$$

where

$$T_N - T_0 = \frac{1}{k}\left(\frac{3E^2}{16\Gamma} + \frac{E^2}{|\lambda|}\right)$$

$$T_N = \frac{2\Gamma}{3k}\left(1 + \frac{D}{4\Gamma} - \frac{6D^2 + 21E^2}{32\Gamma^2}\right)$$

and where

$$\Gamma_i = -2\sum_j J_{ij}$$

It was found that D and E are insensitive to the fitting procedure, so the susceptibility was fit by using the parameters g, T_N, and T_0, and D and E were calculated from these values. The best fit by using Simplex yielded the parameters $g = 3.672$ (5), $T_N = 2.6237$ K, and $T_0 = 1.4486$ K. During the fitting procedure, Θ was held at -3.778×10^{-3} K, the Curie–Weiss value. With insertion of the values from Simplex, $\lambda = -180\ \text{cm}^{-1}$ and $J = -6.44\ \text{cm}^{-1}$ (from Ising chain fit) yielded $E = 6.39$ (10) cm^{-1} and $D = 33.63$ or -16.46 (25) cm^{-1}. The model, of course, cannot distinguish the sign of D. The magnitude of these values are in agreement with the high degree of distortion away from octahedral coordination environment about Co^{2+}. The fit is shown in Figure 4 (solid line).

g-value anisotropy has been proposed as being responsible for the canting.[5] It is intimately related to the single-ion anisotropy with the difference being reflected in where the anisotropy is assumed to occur. In the former approach, since the spin–orbit coupling is large for Co^{2+}, one chooses as a basis spin–orbit functions that diagonalize $\lambda\mathbf{L}{\cdot}\mathbf{S}$. This leaves a Kramer's doublet lowest with the next levels being $(^9/_4)|\lambda|$ higher. Perturbation theory may be used to treat the effects of axial and rhombic distortion.[14] If a true spin Hamiltonian is assumed, there are no real single-ion anisotropy effects since all squares of the fictitious spin $^1/_2$ matrices are multiples of the unit matrix and therefore cannot have any anisotropy effects.[5] However, the anisotropy can be reflected in the $\mathbf{g}$ tensor.

The g factors, accurate to first order, can be written in terms of their spin and orbit components as $g_i = (g_s)_i + k(g_L^0)_i$, where k is the reduction of the matrix elements or orbital angular momentum by charge transfer and i is the coordinate system in which the $\mathbf{g}$ tensor is diagonal. For Co^{2+}, the following expressions have been derived:[14]

$$g_x = (^{10}/_3 - {^8/_3}a) + k(1 - 2a)$$

$$g_y = (^{10}/_3 + {^4/_3}a + {^4/_3}r) + k(1 + a + r)$$

$$g_z = (^{10}/_3 + {^4/_3}a - {^4/_3}r) + k(1 + a - r)$$

where "a" and "r" represent the axial and rhombic distortions and can be expressed in terms of crystal field parameters. The total g value is $g_x + g_y + g_z = 10 + 3k$, where typically $k \approx 0.9$ for Co^{2+}. From the g values determined from the various fit models ($g_a = 2.193$, $g_b = 6.888$, $g_c = 3.672$), values for k, a, and r may be calculated: $k = 0.917$, $a = 0.46$, $r = 0.71$. These values are only estimates because the $\mathbf{g}$ tensor is probably not diagonal along

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[11] See, for example, Figure 2 in ref 10.

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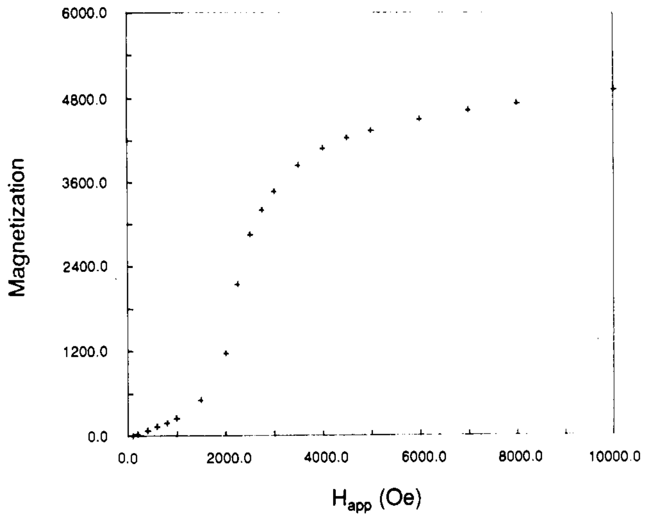

Figure 5. Magnetization of cobalt(II) oxydiacetate trihydrate in the c' direction at 2.24 K.

these directions, but nevertheless, the values are another indication of the large amount of distortion around the metal ion.

Anisotropic Spin–Spin Coupling. Anisotropic spin–spin interaction arises from a combination of effects due to spin–orbit coupling and the superexchange interaction. It has terms of the form[15]

$$\mathbf{d}_{ij}\cdot[\mathbf{S}_i\mathbf{S}_j]$$

The energy is minimized when $\mathbf{S}_i$ and $\mathbf{S}_j$ are perpendicular to one another, and so the coupling tends to cant $\mathbf{S}_i$ and $\mathbf{S}_j$.

By using a molecular field approximation, Moriya[15] derived the following expression for the magnetic susceptibility in the direction of the weak ferromagnetism.

$$\chi_\perp = \frac{Ng^2\mu_B^2S(S+1)}{3k(T+T_N)}\left(\frac{T-T_0}{T-T_N}\right)$$

where

$$T_N = T_0\left[1 + \left(\frac{\mathbf{d}}{-2J}\right)^2\right]^{1/2}$$

and

$$T_0 = \frac{-2zJS(S+1)}{3k}$$

At high temperatures, the magnetic susceptibility essentially follows Curie–Weiss behavior, while at low temperatures, the susceptibility increases rapidly as T approaches T_N. The larger the value for **d**, the higher the transition temperature T_N. The best fit parameters from Simplex with J obtained from T_0 are $g = 3.67$ (1), $T_N = 2.85$ K, and $\mathbf{d} = 3.84$ (5) cm^{-1}. The fit is shown in Figure 4 (dashed line). The small value for **d** is a reflection of the low transition temperature.

The antiferromagnetic exchange interaction along the chain ($J_1 = -6.44$ cm^{-1}) occurs via the ligand carboxylate bridges. There is no such pathway for superexchange to occur between the cobalt chains except perhaps through hydrogen bonding. If a weak antiferromagnetic coupling (J_2) does exist between the chains, when a field is applied perpendicular to the chain axis in the c' direction, behavior similar to that of a metamagnet should be seen. At low fields, the magnetization should be very small until, at some critical field, the antiferromagnetic alignment is broken, the moments flip, and a first-order transition to a ferromagnetic state begins. The magnetization vs field plot in Figure 5 taken in the c' direction at 2.24 K shows just such a transition.

An estimation of the canting angle can be made from the magnetization versus field data. The angle between the moment direction and the chain (b) axis is defined as ϕ_M. This angle can be related to the weak ferromagnetic moment obtained from the magnetization when the moments flip over (~2900 Oe·emu/mol) and the saturation magnetization M_S:

$$\phi_M = \arcsin\left(\frac{\Delta M}{M_S}\right)$$

where

$$M_S = N\mu_B g_{\phi_M} S$$

and where g is the **g** tensor component along the moment vector **M**. If g is approximated as the g component along the b direction ($g_b = 6.888$), then the canting angle $\phi_M \approx 8.7°$.

From the magnetization curve the interchain coupling J_2 may be determined by equating the energies of the spin system before and after spin reversal.[16] Assuming only nearest-neighbor chains interact and that the coupling in the a' direction is much smaller than that in the c' direction, the exchange energy for one spin in zero field is

$$E_1 = -2z^bJ^b\mathbf{S}_1\cdot\mathbf{S}_2 - 2z^{c'}J^{c'}\mathbf{S}_1\cdot\mathbf{S}_2$$

At $T = 0$ K, after a field was applied in the c' direction, the energy after spin reversal of the sum of the exchange and Zeeman energies is

$$E_2 = -2z^bJ^b\mathbf{S}_1\cdot\mathbf{S}_2 + 2z^{c'}J^{c'}\mathbf{S}_1\cdot\mathbf{S}_2 - \mu_B\mathbf{S}\cdot\overleftrightarrow{\mathbf{g}}\cdot\mathbf{H}$$

where the sign of $J^{c'}$ has changed. Since **H** is applied in the c' direction, the Zeeman term becomes

$$-\mu_B g_{\phi_M} SH \sin\phi_M$$

At the critical field H_c, the energies E_1 and E_2 are equal, and, assuming J_2 is isotropic and antiferromagnetic

$$J_2 = \frac{-\mu_B g_{\phi_M} H_c \sin\phi_M}{4z^{c'}S}$$

Finally, if the assumption is made that H_c ($T = 0$ K) $\approx H_c$ ($T = 2.24$ K) = 2275 Oe and the calculation made that $g_{\phi_M} = 6.843$, an estimate for the interchain coupling can be obtained as $J_2 \approx -0.028$ cm^{-1}.

Conclusion

Cobalt(II) oxydiacetate trihydrate represents the first carboxylate-bridged cobalt chain to exhibit canted antiferromagnetic behavior. From the above arguments, a good picture of the magnetic structure emerges. In addition, the magnetic properties are well correlated with the molecular and crystal structure. The primary superexchange interaction occurs via the carboxylate bridges between cobalt ions along the chain (b) axis. This interaction is Ising-like and $J^b = -6.44$ cm^{-1}. The interchain interaction is much weaker and, assuming the coupling to be isotropic, the magnetization results yield $J^{c'} \approx -0.028$ cm^{-1}.

The magnetic unit cell is that of a hidden canted antiferromagnet. This can be predicted from the crystal symmetry and was confirmed experimentally.

This result is true regardless of the canting mechanism. If anisotropic spin–spin coupling indeed has some influence on the spins, the effect is small as evidenced by the low value for **d** (~3.8 cm^{-1}). As Moriya has pointed out,[15] the single-ion anisotropy energy does not depend upon the superexchange and therefore is more important in compounds with low Néel temperatures, whereas the anisotropic spin–spin-coupling mechanism is important for substances with high Néel temperatures. Since in cobalt oxydiacetate the superexchange is small, the anisotropic coupling is also small, and effects due to single-ion anisotropy are probably of greater significance.

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Registry No. Co($C_4H_4O_5$)·3H_2O, 109955-15-9.

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