work is needed to prove or disprove this hypothesis for the binary carbonyl clusters.

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Average and Single-Crystal Magnetic Properties of Potassium Bis(carbonato)cuprate(II): A Three-Dimensional Ferromagnet

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Average and single-crystal magnetic measurements on the three-dimensional potassium bis(carbonato)cuprate(II) show that this material orders ferromagnetically at 6.6 K. Above 15 K the data are well represented by the $S = {}^1/_2$ series expansion for the three-dimensional fccub lattice with $g = 2.14$ and $J = 1.19\ \text{cm}^{-1}$. $K_2Cu(CO_3)_2$ appears to be the best example of a three-dimensional $S = {}^1/_2$ Heisenberg ferromagnet yet studied.

Introduction

Many different compounds can be isolated from aqueous solutions containing copper(II) and carbonate ions, depending on the conditions and the other cations present. For example, $Na_2Cu(CO_3)_2{\cdot}3H_2O$ has a discrete chainlike structure,[1-3] and $Cu(NH_3)_2CO_3$ possesses a complicated intertwinned structure[4] whereas $Na_2Cu(CO_3)_2$ has a two-dimensional network of $[Cu(CO_3)_2{}^{2-}]_\infty$, successive layers being bound by the sodium ions.[5] We have reported recently the magnetic properties of each of these materials. Susceptibility measurements on $Na_2Cu(CO_3)_2{\cdot}3H_2O$ provide evidence for ferromagnetic intrachain interactions.[6] We have also reanalyzed the magnetic susceptibility data on $Cu(NH_3)_2CO_3$ using a cluster approximation.[7] This material has an approximately two-dimensional structure with two different in-plane metal–metal interactions which are both antiferromagnetic in nature. Average[8] and single-crystal[9] magnetic measurements on $Na_2Cu(CO_3)_2$ show that this compound possesses ferromagnetic intralayer exchange interactions although it orders antiferromagnetically at 5.6 K. Spin–flop behavior was observed below 5.6 K.

We have also prepared and determined the crystal structure of another member of this system, namely, $K_2Cu(CO_3)_2$.[10] The basic crystallographic data are summarized in the Experimental Section. The structure is, suprisingly, somewhat different from $Na_2Cu(CO_3)_2$; the symmetry is higher, and although the structure comprises planar CuO_4 chomophores linked by bridging bidentate carbonate groups, with embedded potassium cations, it is more subtle and three dimensional in nature (Figure 1). The four oxygen atoms about each copper atom form a plane roughly parallel to the *ab* plane of the crystal. To this extent the structure is very similar to that of the sodium derivative. However, in the potassium derivative each bidentate carbonate group is oriented such that it coordinates to copper atoms 0.25 apart in *z*. Rather than propogating a planar structure, this has the effect of making a three-dimensional polymeric network of copper atoms connected by the bidentate carbonate groups. This subtle change in structure gives rise to different magnetic properties, which are reported herein.

Experimental Section

The preparation of $Na_2Cu(CO_3)_2$ proceeds via $Na_2Cu(CO_3)_2{\cdot}3H_2O$.[1,8,9] However, in the preparation of the potassium derivative we were unable to isolate the trihydrate so we proceeded directly with the preparation of anhydrous $K_2Cu(CO_3)_2$.[10] A nearly saturated solution of K_2CO_3 [K_2CO_3 (150 g) in boiling water (110 cm^3)] was cooled to slightly below 50 °C, and copper acetate monohydrate (20 g) was added with stirring. It is important that the temperature does not go above 50 °C because CuO will begin to form. The resulting solution was deep purplish blue, but on standing overnight, it turned into a thick pale blue gelatinous precipitate, which was difficult to characterize. Presumably this contains a hydrated form of $K_2Cu(CO_3)_2$. However, when the solution was allowed to stand for a week or more small, well-formed, very dark blue platelike crystals of anhydrous $K_2Cu(CO_3)_2$ formed, which were suitable for both crystallographic and magnetic work. The crystal structure of $K_2Cu(CO_3)_2$ has been determined[10] by single-crystal X-ray diffraction at 295 (1) K and refined by full-matrix least squares to a residual of 0.027 for 1441 "observed" reflections. Crystals are orthorhombic, of space group *Fdd*2, with $a = 11.425$ (3) Å, $b = 17.658$ (4) Å, $c = 6.154$ (2) Å, and $Z = 8$. The structure comprises potassium cations embedded in an infinite three-dimensional polymeric anionic array of square-planar coordinated copper atoms with bridging carbonate groups [Cu–O = 1.934 (2), 1.936 (2) Å]. Within the latter, the noncoordinating oxygen–carbon bond is shorter [1.259 (3) Å] than the other two [1.303 (3), 1.307 (2) Å] and the O–C–O angle opposite it is

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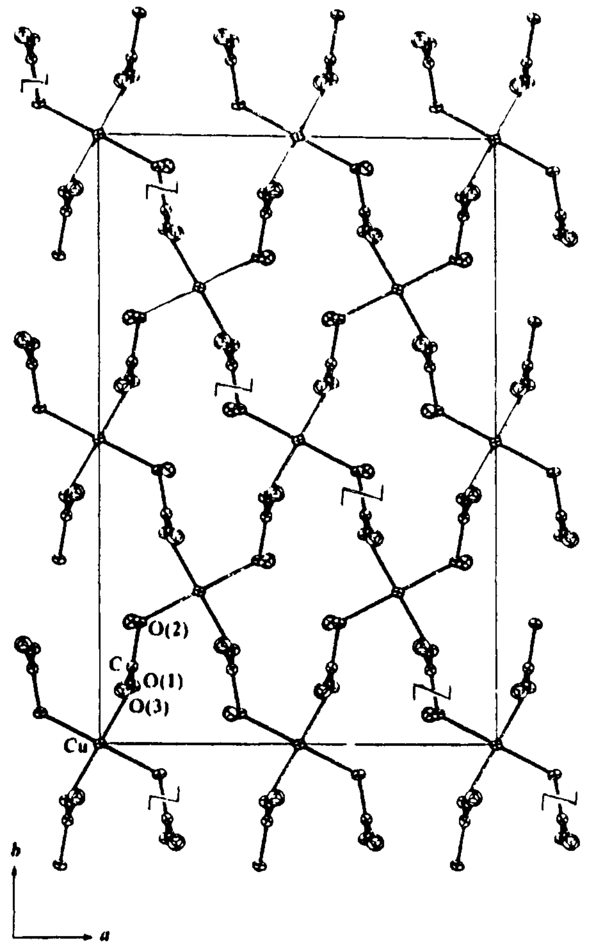

Figure 1. Unit cell contents of $K_2Cu(CO_3)_2$ projected down the *c* axis. Broken lines indicate contacts to the next upper or lower cell.

correspondingly reduced to 117.1 (2)°. The CO_3 plane lies at 83.9° to the CuO_4 plane.

The magnetization data were obtained on powder and single-crystal ($2 \times {}^1/_2 \times 2$ mm) samples with use of the SQUID susceptometer described recently.[11] For the crystal measurements the quartz sample tube used for powders was replaced with a quartz rod ground with vertical and horizontal faces, so allowing easy crystal alignment.[9] No corrections for demagnetizing effects were made as no quantitative information was derived from the measured susceptibility values below T_c. No corrections for the diamagnetism of the substituent atoms were made either; below 70 K they are negligible. Unfortunately our SQUID only operates to an applied magnetic field of ~0.35 T, so no high-field magnetization measurements could be performed.

The EPR spectra were obtained from a Varian E-3 X-band spectrometer. The free radical DPPH ($g = 2.0036$) was used as a field marker.

Results and Discussion

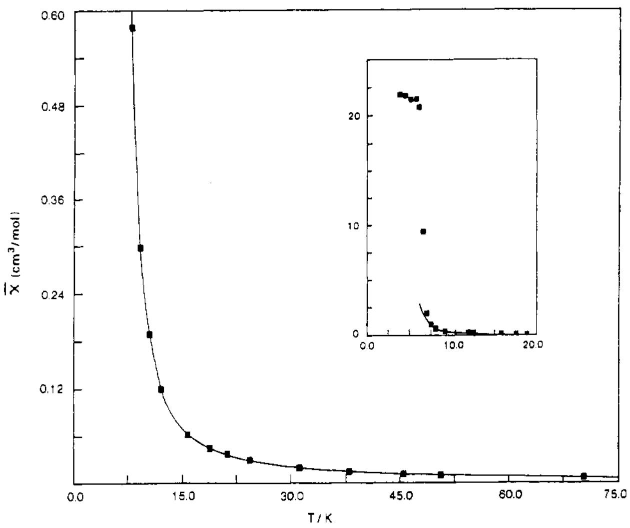

Figure 2. Average magnetic susceptibility for $K_2Cu(CO_3)_2$ in 2.23 mT. Solid line is the fit to the $S = {}^1/_2$ face-centered cubic lattice. Inset shows the region below 10 K.

Table I. Exchange Parameters for Some Copper Carbonate Compounds

	structure	Θ, K	J, cm^{-1}	T_c, K	ref
$K_2Cu(CO_3)_2$	3-D polymer	9.7	1.19	6.6	this work
$Na_2Cu(CO_3)_2$	layered	9.2	4.1	5.6	8, 9
$Na_2Cu(CO_3)_2 \cdot 3H_2O$	chainlike	1.8	0.59		6
$Cu(NH_3)_2CO_3$	interacting chains	−4.0	−5.2, −2.6		7

The average susceptibility of $K_2Cu(CO_3)_2$ in the temperature range 4–75 K is shown in Figure 2. The Curie–Weiss expression $\bar{\chi} = C/(T - \Theta)$, where $C = Ng^2\beta^2/4k$, with $g = 2.12$ and $\Theta = +9.3$ K represents the data above 15 K quite well. The positive value of Θ confirms the presence of ferromagnetic interactions. The very sharp rise in susceptibility at 6.6 K is indicative of a transition to a ferromagnetically ordered state. It is interesting to note that the limiting saturation value of the susceptibility (inset of Figure 2) depends on how tightly the powder is packed into the sample tube. The more tightly packed samples give smaller limiting values, and this is presumably because the applied magnetic field is not able to orient the anisotropic crystallites as well; anisotropy will be present in a ferromagnetic crystal with well-defined easy and hard directions. This then makes the quantitative analysis of these data below T_c very difficult and not very useful.

The structure of $K_2Cu(CO_3)_2$ consists of a three-dimensional polymeric network of copper ions coordinated by bidentate carbonate groups. With a space group of *Fdd*2 we might expect then that an appropriate magnetic model might be the $S = {}^1/_2$ Heisenberg expansion for the face-centered lattice. This has now been derived to nine terms:[12]

$$\chi = \frac{Ng^2\beta^2}{4kT}\left[1 + \frac{a_1}{\Theta} + \frac{a_2}{\Theta^2} + \frac{a_3}{\Theta^3} + \ldots + \frac{a_9}{\Theta^9}\right] \qquad (1)$$

where $\Theta = kT/J$ and $a_1 = 6.0$, $a_2 = 30.0$, $a_3 = 138.0$, $a_4 = 611.25$, $a_5 = 2658.55$, $a_6 = 11\,432.5125$, $a_7 = 48\,726.726\,19$, $a_8 = 206\,142.367\,41$, and $a_9 = 866\,895.506\,35$. The susceptibility data gathered in 2.23 mT and above 15 K are represented very well by eq 1 with $g = 2.14 \pm 0.02$ (very close to the experimental average value; see below) and $J = 1.19 \pm 0.02$ cm^{-1}.

It is most interesting to investigate the magnetic parameters of this material, particularly when it is known that very few insulating ferromagnets conform even closely to the ideal three-dimensional Heisenberg model. The only materials that even approach the ideal are the salts $CuM_2X_4 \cdot 2H_2O$ (M = NH_4, K, Rb, X = Cl; M = NH_4, Rb, X = Br), EuO, and EuS.[13] Simple tests of ideality are the values of T_c/Θ and J/kT_c, which are theoretically 0.67 and 0.249, respectively.[12] Our experimentally determined values (from the parameters listed in Table I) are 0.68 and 0.259, respectively, remarkably

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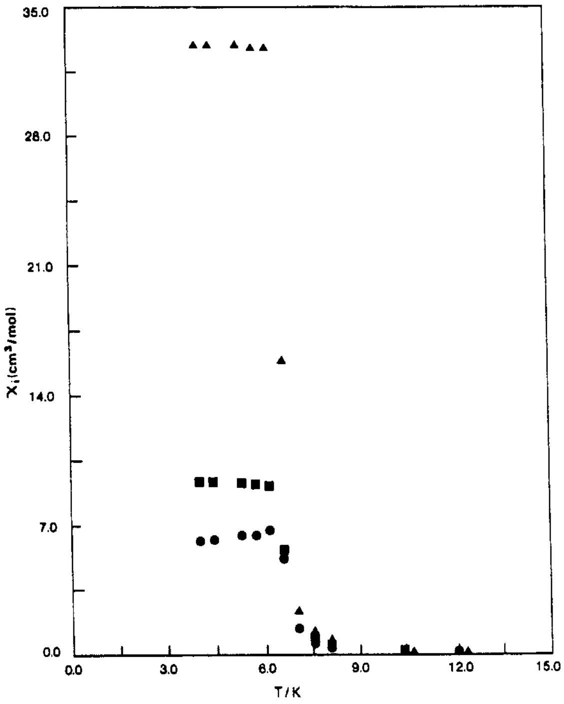

Figure 3. Crystalline magnetic susceptibilities of $K_2Cu(CO_3)_2$ in 2.23 mT: ●, *a* axis; ■, *b* axis; ▲, *c* axis.

close to the theoretical values derived for nearest-neighbor-only interactions for the fccub lattice. These are much closer to the ideal than those for $CuM_2X_4{\cdot}2H_2O$, EuO, and EuS.[13] This then suggests that $K_2Cu(CO_3)_2$ is the most ideal three-dimensional Heisenberg $S = {}^1/_2$ ferromagnet yet studied. This arises presumably because the structure has suprisingly high symmetry, and the rather large carbonate group guarantees that the only effective magnetic interactions are those between nearest neighbors.

Crystals of $K_2Cu(CO_3)_2$ grow as small platelets with a well-developed *ac* plane. When a crystal was mounted with the magnetic field contained in this plane, two *g* values were measured: $g_c = 2.25$ and $g_a = 2.04$. When it was rotated in a plane at right angles to this (*bc* plane) again $g_c = 2.25$ and $g_b = 2.04$. Within experimental error then the *ab* plane is magnetically isotropic with $g_a = g_b = 2.04$ and $g_c = 2.25$. It is known from the structure that the *ab* plane contains each of the planar CuO_4 chromophores and that those chromophores situated at *z* values of O or $^1/_2$ are oriented in the *ab* plane differently from those situated at $^1/_4$ or $^3/_4$. However, if it is assumed that each CuO_4 plane is magnetically isotropic, then g_a and g_b will be equal and equal to the molecular $g_\perp$. The molecular $g_\parallel$ will then correspond with g_c.

Susceptibility measurements on a crystal (Figure 3) confirm that $K_2Cu(CO_3)_2$ undergoes a transition to a ferromagnetically ordered state at 6.6 K. The *c* crystallographic axis (molecular symmetry axis) appears to be the easy axis. This is to be expected if the spin direction is determined by an anisotropy field dominated by the crystalline *g* values. The average value of the three crystalline susceptibilities below 6.6 K is smaller than the measured limiting average susceptibility, which indicates that partial orientation of even the tightly packed powder had taken place during these measurements.

This is now the third well-documented example of ferromagnetic nearest-neighbor interactions between copper atoms linked by the carbonate group (Table I). Copper(II) oxydiacetate is the only other material where superexchange via a similar bridging unit results in ferromagnetic intralayer interactions.[14] Diamminecopper(II) carbonate possesses antiferromagnetic interactions.[7] The local symmetry about each metal atom and the precise bridging configuration of the carbonate group then determine the sign of the nearest-neighbor superexchange interaction. In each of the ferromagnetic examples the carbonate group is bidentate and bridges two different copper atoms. In the one antiferromagnetic example the carbonate group coordinates in quite a different way: two oxygen atoms are bonded to one copper atom while it is the third oxygen atom that coordinates to a neighboring copper atom to propogate the lattice. The overall symmetry of the lattice determines whether magnetic order is sustained or not. No magnetic ordering is observed in $Na_2Cu(CO_3)_2{\cdot}3H_2O$ or $Cu(NH_3)_2CO_3$ because the interactions are, at best, only two-dimensional in nature. However, in $Na_2Cu(CO_3)_2$ and $K_2Cu(CO_3)_2$ the structures allow interactions in the third dimension. In the former these occur between layers whereas in the latter they form an integral component of the nearest-neighbor interactions. As a result $K_2Cu(CO_3)_2$ is probably the best example of a three-dimensional $S = {}^1/_2$ Heisenberg ferromagnet yet studied.

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