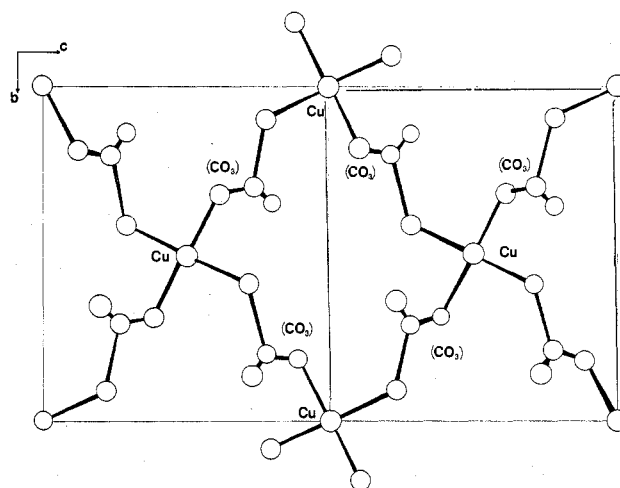
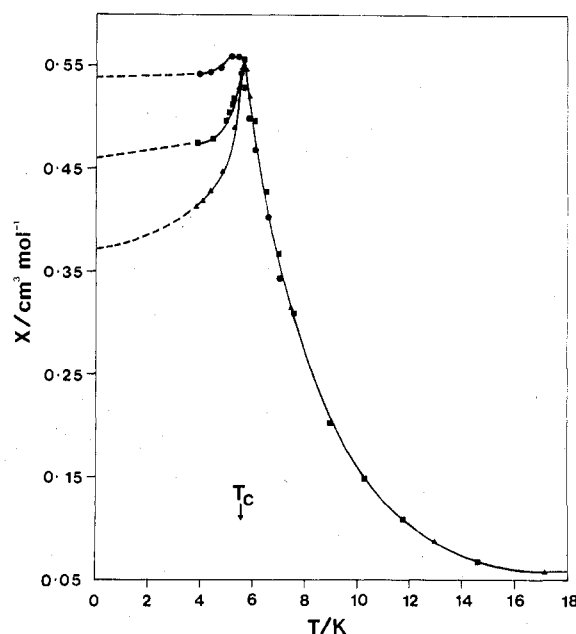


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Figure 1. Unit cell of $\text{Na}_2\text{Cu}(\text{CO}_3)_2$.Figure 2. Average susceptibility of a powdered sample of $\text{Na}_2\text{Cu}(\text{CO}_3)_2$ in various applied magnetic fields: \blacktriangle , 1.7 mT; \blacksquare , 28.7 mT; \bullet , 346.7 mT. Solid lines are a guide to the eye; dashed lines are extrapolations to $T = 0$ K.

structures and magnetic properties of $\text{Na}_2\text{Cu}(\text{CO}_3)_2 \cdot 3\text{H}_2\text{O}$ ^{6,7} and $\text{Cu}(\text{NH}_3)_2\text{CO}_3$.^{8,9}

Experimental Section

$\text{Na}_2\text{Cu}(\text{CO}_3)_2$ was prepared by previously published methods.⁵ The magnetization and susceptibility of a powdered sample were determined using the SQUID susceptometer described recently.¹⁰ No corrections for the diamagnetism of the substituent atoms have been made, the corrections below 70 K being negligible.

Results and Discussion

The average powder susceptibility of $\text{Na}_2\text{Cu}(\text{CO}_3)_2$ between 4 and 18 K is plotted in Figure 2. Above the transition temperature of 5.6 ± 0.2 K the susceptibility is characteristic of a ferromagnetic system. It increases more rapidly than expected for a simple paramagnetic ion although it is nearly field independent over the range of applied fields (1.7–350 mT) except near T_c where the maximum becomes less distinct and appears to move to lower temperatures in the highest field. The data between 15 and 70 K can be fitted by the Curie-Weiss expression $\bar{\chi} = C/(T - \Theta)$, where $C = Ng^2\beta^2/4k$, with

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Ferromagnetic Interactions in Sodium Bis(carbonato)cuprate(II)

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Simple compounds of copper are well suited to the study of magnetic interactions. None of the complications associated with $S > 1/2$ are present so factors involving cooperative phenomena are readily isolated and characterized. Materials of current interest are those with well-defined structural characteristics where comparisons between the dimensionality of the system and the details of the cooperative transition can be made. Particular systems relevant to the present study include K_2CuF_4 , which possesses two-dimensional ferromagnetic intralayer interactions as well as ferromagnetic interlayer coupling,² and layered $[\text{CuCl}_4]^{2-}$ derivatives^{3,4} where the copper atoms form a two-dimensional lattice of ferromagnetically coupled ions with each layer coupled antiferromagnetically. Below the transition temperature T_c these often unusually weak antiferromagnetic interactions can result in complex effects because the spin-flop field can be exceeded by rather smaller magnetic fields than is otherwise possible in normal three-dimensional antiferromagnets.³

Sodium bis(carbonato)cuprate(II) is best described⁵ (Figure 1) as a two-dimensional polymeric network of $[\text{Cu}(\text{CO}_3)_2]^{2-}$ with each copper in an approximately square-planar environment coordinated by the four symmetry-related binuclear bridging carbonate groups. Successive layers of $[\text{Cu}(\text{CO}_3)_2]^{2-}$ are bound ionically by the sodium ions. The two-dimensional structure of $\text{Na}_2\text{Cu}(\text{CO}_3)_2$ contrasts with the chain-like

Table I. Exchange Constants for Some Layered Copper Compounds

	T_c, K	J, K	$ J' / J $	kT_c/J	T_c/Θ	$d_1,^b$ Å
$\text{CuCl}_4^{2- a}$	8-15	18-22	10^{-3} - 10^{-5}	~ 0.6	0.2-0.3	~ 5.1
$\text{Na}_2\text{Cu}(\text{CO}_3)_2$	5.75	5.9	3.5×10^{-2}	1.25	0.625	4.89

^a Data for CuCl_4^{2-} are from ref 3. ^b d_1 is the intralayer Cu-Cu separation.

$\Theta = +9.2 \pm 0.2$ K and $g = 2.23 \pm 0.01$. The positive value of Θ confirms the presence of ferromagnetic interactions and from molecular field theory this corresponds to $J = k\Theta/2 = 3.2$ cm⁻¹ for the $S = 1/2$ layered lattice. When the data are fitted to Baker's¹¹ series expansion for the $S = 1/2$ layered lattice we find, in the temperature range $1.5J/k \leq T \leq 70$ K, that $J = 4.1 \pm 0.7$ cm⁻¹ and $g = 2.24 \pm 0.02$. This leads, via $H_e = 2zJS/g\beta$, to an intralayer exchange field of 15.97 T¹ [using $z = 4$, $J = 4.1$, and $S = 1/2$ and assuming an intralayer g value of 2.20].

Below 5.6 K the susceptibility is characteristic of an antiferromagnet, the susceptibility in the lowest field (1.7 mT) extrapolating to approximately $2/3\bar{\chi}_{\text{max}}(T_c)$ at $T = 0$ K, as expected from theory. However, in higher magnetic fields the measured susceptibility is strongly field dependent and is characteristic of the spin-flop phenomena observed in weakly coupled antiferromagnets.^{12,13} The interlayer exchange field can be calculated¹³ from $\bar{\chi}_{\text{max}}(T_c) = \chi_{\perp}(0) = Ng\beta S/2H_{\text{af}}$. With $\bar{\chi}(T_c) = 0.55$ cm³ mol⁻¹, $H_{\text{af}} = 0.54$ T which leads to an inter- to intralayer ratio $|J'|/|J|$ of ~ 0.035 . This is somewhat larger than for other compounds which behave in a similar manner (Table I) but still compatible with other types of systems.³ With this value of H_{af} the saturating field of $\sim 4z'|J'|S/g\beta \approx 2H_{\text{af}} \approx 1$ T is well outside our experimental range. It is almost impossible to obtain precise critical-field data from powder susceptibility measurements but qualitatively the critical field will be approached as soon as $\bar{\chi}(T = 0)$ increases from $2/3\bar{\chi}(T_c)$, and in $\text{Na}_2\text{Cu}(\text{CO}_3)_2$ this begins at ~ 10 mT.¹⁴

The closest approach of the intralayer copper atoms is 4.89 Å so no significant direct overlap of the metal ion d orbitals is expected. Superexchange via the intervening binuclear carbonate group must be responsible for the observed interaction and so appears to be the first well-documented case of ferromagnetic coupling through a bridging carbonate group. The exact mechanism for the observed interaction is difficult to isolate because the structure of the Cu-CO₃-Cu unit is far from ideal. However, there are two features of the $\text{Na}_2\text{Cu}(\text{CO}_3)_2$ structure which may influence the nature of the interaction. The first is the detailed geometry of adjacent copper ions and the second is the nonplanarity of the Cu-CO₃-Cu system. The Cu-O distances in the essentially square-planar chromophore are slightly different:^{5b} Cu-O(1)

$= 1.947$ (1) Å, Cu-O(2) = 1.934 (1) Å. If it is assumed that the σ framework of the Cu(1)-CO₃-Cu(2) unit forms a superexchange pathway, then antiferromagnetic coupling is expected if the Cu-O distances are all the same. However, in the distorted structure the orientation of the $d_{x^2-y^2}$ orbitals on adjacent copper ions (assumed to contain the unpaired electron) is such that they are orthogonal because the short and long Cu-O bonds are at right angles to each other on alternate copper ions. This orthogonal overlap between the copper ions via the carbonate group may lead, qualitatively at least, to the observed ferromagnetic interaction. Alternatively, deviations of the copper atoms from the carbonate plane allow increasing interaction of the $d_{x^2-y^2}$ orbital with the CO₃²⁻ π system which also leads to ferromagnetic coupling, provided both copper atoms deviate strongly from the plane. The magnitude of the interaction in $\text{Na}_2\text{Cu}(\text{CO}_3)_2$ is much less than in the $[\text{CuX}_4]^{2-}$ series (Table I) and might be expected because of the greater distance through which the exchange effects have to be transmitted in the carbonate group. This is notwithstanding a shorter direct Cu-Cu distance in $\text{Na}_2\text{Cu}(\text{CO}_3)_2$ and provides further implicit evidence for a superexchange mechanism.¹⁵

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Registry No. $\text{Na}_2\text{Cu}(\text{CO}_3)_2$, 37224-64-9.

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- (14) Below the spin-flop field and at T extrapolated to zero, the magnetization M_{\perp} is linear in H and so χ_{\perp} and hence the measured $\bar{\chi}$ will be independent of H . However, when the spin-flop field is reached, M_{\parallel} becomes nonzero and nonlinear in H giving rise to a strongly field-dependent average susceptibility.
- (15) We have succeeded in growing a suitable single crystal, and magnetic measurements confirm the antiferromagnetically ordered state below T_c . Other members of the series $\text{M}_2\text{Cu}(\text{CO}_3)_2$ ($M = \text{monovalent cation}$) have also been synthesized and will be reported upon in due course.