TABLE I

EXPERIMENTAL RATE CONSTANTS FOR THE DEUTEROLYSIS OF 0.048 F $Na_2PO_3F^a$

	15°		25°		40°	
$[D^+]$, M	10^3k_{obsd}, min^{-1}	10^2k	10^3k_{obsd}, min^{-1}	10^2k	10^3k_{obsd}, min^{-1}	10^2k
0.200	0.974	2.66	2.70	7.38	10.21	27.93
0.400	4.24	2.84	11.44	7.68	42.68	28.66
0.670	9.76	2.79	24.28	6.92	99.49	28.34
		Av 2.76		Av 7.33		Av 28.31

[a] $k = (k_{obsd})([D^+] + k_1)/[D^+]^2$.

mined to be stable toward deuterolysis in neutral D_2O solutions. Typically, 10 ml of the Na_2PO_3F solution, 0.096 M, was added to 10 ml of thermostated DCl solution in a plastic bottle with a screw-cap top. At intervals during the reaction, 2 ml of this solution was withdrawn and discharged into a plastic dish containing 10 ml of a buffer solution. The buffer solution was composed of 3.78 M ammonium chloride and sufficient ammonium hydroxide to give a total ammonium ion concentration of *ca.* 4 M. Each sample collected was analyzed for fluoride by reading the emf *vs.* sce with the Orion Model 94-09 fluoride electrode. Emf measurements were made with a Beckman Research Model pH meter. A calibration curve was prepared by reading potentials developed from standard solutions containing sodium fluoride, Na_2PO_3F, and DCl. These materials were added to an ammonium chloride–ammonium hydroxide buffer solution so as to give solutions which would be similar to those analyzed from the kinetic studies. The sampling technique and analyses were checked by determining a k_{obsd} for the hydrolysis of Na_2PO_3F in water at 40°. In H_2O k_{obsd} (this work) was determined to be 69.3×10^{-3} min^{-1} *vs.* $k_{calcd} = 66.8 \times 10^{-3}$ min^{-1} obtained from ref 1.

Results and Discussion

The observed rate constants for the $D_2O-D^+-PO_3F^{2-}$ system are reported in Table I. Kinetic runs were made in which the fluoride was monitored to 70–80% of the deuterolysis of PO_3F^{2-}. Rate constants (k_{obsd}) were calculated from the linear plots of log $([F^-]_\infty - [F^-]_t)$ *vs.* time. The k_{obsd} values were calculated from least-squares slopes all of which involved more than 15 data points and are based on reaction times corresponding to 40–50% reaction. The rate data were treated as before[1] by assuming that $[D^+]$ is equal to the difference between the deuteriochloric acid concentration and the monofluorophosphate ion concentration. The primary ionization constant for H_2PO_3F, K_1, had been assumed to be equal to 0.8 by Devonshire and Rowley[1] for a satisfactory treatment of their kinetic data while Clark and Jones[2] used $K_1 = 0.3$, the reported value of K_1,[3] for the treatment of their kinetic data. In order to achieve the greatest constancy for k (in the D_2O system), a value of K for D_2PO_3F was determined to be 0.48. From a plot of log k *vs.* $1000/T$(°K), the apparent Arrhenius energy of activation for the deuterolysis of PO_3F^{2-} is estimated to be 16.7 ± 0.3 kcal/mol as compared with 16.9 ± 0.8 kcal/mol reported[2] for the hydrolysis reaction. At 25° with similar concentrations of acid and PO_3F^{2-}, the observed rate constant ratio k_{obsd}(in H_2O)/k_{obsd}(in D_2O) is found to be equal to 2.1. This observation is consistent with the proposed mechanism for the hydrolysis reaction in which a proton transfer occurs in the rate-determining step. A mechanism for the deuterolysis reaction is thus postulated to be

$$D_2PO_3F + D^+ \rightleftharpoons D_3PO_3F^+$$

$$D_3PO_3F^+ + D_2O \longrightarrow D_3PO_4 + DF + D^+$$

which is consistent with the observed kinetics.

Acknowledgment.—The authors are indebted to the Office of Research and Projects, Southern Illinois University, Edwardswille, Ill., for support of this work.

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Antiferromagnetic Interactions in Diamminecopper(II) Carbonate

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From an X-ray diffraction study, Hanic[2,3] determined that the structure of the complex $Cu(NH_3)_2CO_3$ consisted of chains of copper(II) ions. As shown in Figure 1, two ammine groups and two oxygen atoms from the bidentate carbonate ion define a plane which contains the copper ion, and the third oxygen from a carbonate ligand of an adjacent unit occupies the fifth coordination position of a tetragonal pyramid at a distance of 2.55 Å. Tomlinson and Hathaway[4] have concluded from the results of an electron paramagnetic resonance investigation on this compound that the presence of exchange coupling between nonequivalent copper(II) ions is likely. In order to document the magnetic properties of $Cu(NH_3)_2CO_3$, we have measured the magnetic susceptibility of a powdered sample over the temperature range 4.2–295°K. Here we report the results of our study.

Experimental Section

Preparation of the Complex.—Diamminecopper(II) carbonate was prepared in the manner suggested by Tomlinson and Hathaway.[4] Basic copper carbonate was dissolved in ammonium hydroxide and undissolved residue was filtered away. To the dark blue solution was added several milliliters of 95% ethanol. The resulting greenish blue precipitate which formed was filtered off, and the remaining blue solution was allowed to stand until very dark blue crystals formed. These were collected and washed with ethanol. *Anal.* Calcd for $Cu(NH_3)_2CO_3$: C, 7.62; H, 3.84; N, 17.78. Found: C, 7.58; H, 3.90; N, 17.61.

Magnetic Measurements.—At 77, 195, and 295°K, the magnetic susceptibility of a powdered sample was determined using the Faraday technique.[5] Measurements in the temperature range 4.2–60.7°K were made using a Foner-type vibrating-sample magnetometer,[6] which was operated at field strengths of 10.0,

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[3] F. Hanic, *Chem. Zvesti*, **17**, 365 (1963).

[4] A. A. G. Tomlinson and B. J. Hathaway, *J. Chem. Soc. A*, 2578 (1968).

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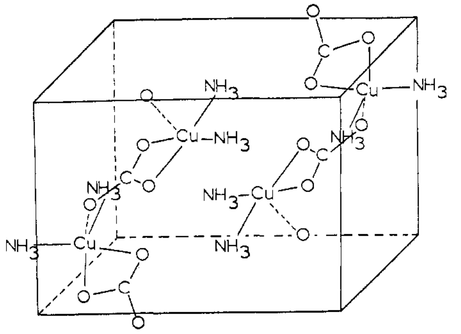

Figure 1.—The structure of $Cu(NH_3)_2CO_3$.

12.5, and 15.0 kOe. Mercury tetrathiocyanatocobaltate(II) was used as a magnetic susceptibility standard,[7] and a correction for the diamagnetism of the substituent atoms was made using Pascal's constants.[8]

Results and Discussion

Antiferromagnetic exchange between interacting copper(II) ions in $Cu(NH_3)_2CO_3$ is apparent from the temperature variation of the inverse susceptibility. Down to approximately 20°K, the magnetism obeys the Curie–Weiss law, $\chi = C/(T + \Theta)$, with $C = 0.44$, $\Theta = 4°$, and $\mu_{\text{eff}} = 1.88$ BM. At temperatures below this, however, the susceptibility deviates from the Curie–Weiss law and reaches a maximum value at approximately 11°K. Such a deviation is usually characteristic of antiferromagnetic interactions.

Among the possibilities for the spin–spin coupling interaction, the two most likely mechanisms include superexchange through the bridging carbonate ligands or incipient bond formation between pairs of copper ions in adjacent chains. It is also possible that spin–spin coupling includes contributions from both mechanisms. A schematic representation of a unit cell which shows the relative orientations of the copper(II) ions is shown in Figure 1. The copper(II) ions are bridged along the chains by nearly planar carbonate ions, where the copper–carbonate–copper angle is 119°. It should be noted that this avenue is fairly long for an exchange interaction. Also, as shown in the figure, the basal planes of adjacent tetragonal-pyramidal units in neighboring chains are nearly eclipsed and parallel to one another, and the copper–copper internuclear separation is approximately 3.5 Å. There is a strong resemblance in this latter arrangement to structural features present in dimeric copper(II) acetate monohydrate,[9] except there are no ligands bridging these planar units.

If the spin–spin interaction is operating through the bridging carbonate groups, it would be expected that the magnetism could be explained in terms of the anisotropic Ising model for chain antiferromagnetism. Fisher[10] has shown that the exact closed-form expressions for the anisotropic susceptibility of infinite chains of $S = {}^1/_2$ ions are

$$\chi_{\perp} = \frac{Ng^2\beta^2}{8J}\left[\tanh\left(\frac{J}{kT}\right) + \left(\frac{J}{kT}\right)\operatorname{sech}^2\left(\frac{J}{kT}\right)\right]$$

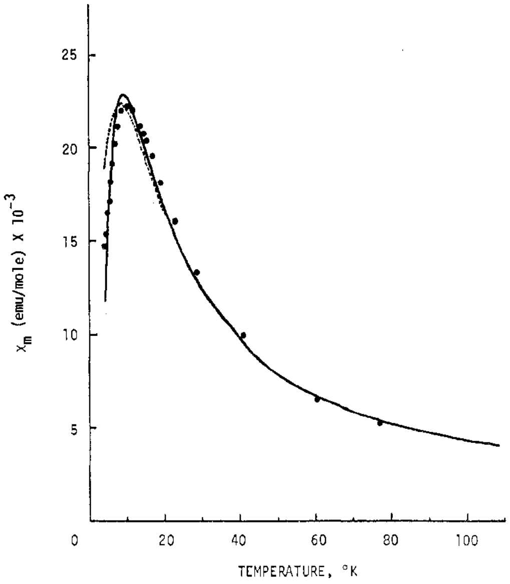

Figure 2.—The temperature variation of the experimental susceptibility (●) and the best fits using the Ising (broken line) and modified dimer (solid line) models.

and

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

where J is the exchange energy, g the Landé factor, and N, β, k, and T have their usual meanings. The total susceptibility is given by

$$\chi = \frac{1}{3}\chi_{\parallel} + \frac{2}{3}\chi_{\perp}$$

It can be seen in Figure 2 that the best least-squares fit of the susceptibility data ot these equations gives a rather poor approximation of the observed results. The parameters giving the best fit are $g = 2.20$ and $J = -6.2$ cm^{-1} with the sum of the squares of the deviations between the experimental and calculated $\chi_i T_i$ being 6.4×10^{-3}.

The second possibility mentioned above is that pairs of copper ions in neighboring chains interact and give rise to singlet and triplet states only. The experimental data were fit to this model using the appropriate equation[11] with the modification used by Kubo, *et al.*,[12] in which the molar susceptibility is given by

$$\chi_m = \frac{Ng^2\beta^2}{3k(T - \Theta)}\left[1 + \frac{1}{3}\exp\left(\frac{-2J}{kT}\right)\right]^{-1}$$

In this instance $2J$ is the energy separation between the singlet and triplet spin states and Θ allows for additional lattice interactions. The treatment gave a somewhat better fit, as can be seen in Figure 2, with $J = -4.5$ cm^{-1} and $g = 2.19$ which compares well with the average g value of 2.18 which may be calculated from the electron paramagnetic resonance data of Tomlinson and Hathaway.[4] The value of Θ is $-1.9°$, and $\Sigma_i \Delta\chi_i T_i$ was 2.8×10^{-3}.

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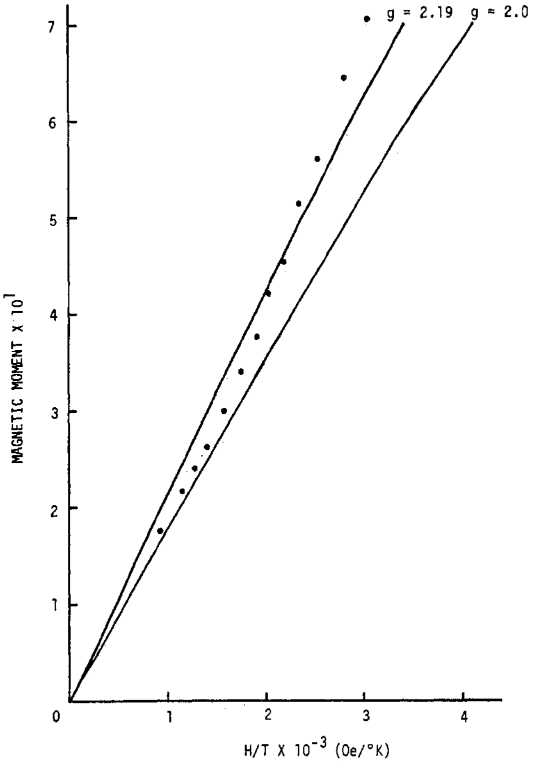

Figure 3. The variation of the experimental magnetic moment $\langle\mu\rangle$ (●) *vs.* H/T for an effective spin equal to 1 (solid lines) system.

A magnetization study was also undertaken in an attempt to understand more clearly the cooperative magnetic phenomenon. The results of the magnetization experiment are shown in Figure 3. Susceptibility measurements were made at multiple temperatures at three different magnetic field strengths. In this antiferromagnetic system it is certain that the excited paramagnetic states are only partially occupied. The susceptibility measured, however, arises from the molecules which populate these states. Thus, using the value of $2J$ found in the dimer fit and Boltzmann's expression for population distributions we are able to normalize approximately the experimental susceptibilities to values that would be expected if all the molecules were in a triplet state. These values can then be compared to the result calculated for a $S = 1$ system by making use of the Brillouin functions.[13] The Brillouin function can be written as

$$B_S(x) = \frac{2S' + 1}{2S'} \coth\left(\frac{2S' + 1}{2S'}\, x\right) - \frac{1}{2S'} \coth \frac{x}{2S'}$$

where $x = 2S'\beta H/kT$ and S' is the effective spin for the system. The relationship

$$\langle\mu\rangle = \frac{\chi H}{N\beta} = gS'B_S(x)$$

then allows us to calculate the expected magnetic moment for a triplet state. The plot of magnetic moment *vs.* H/T is presented in Figure 3. The solid lines are the moments that would be expected for a system with $S = 1$ having the g values indicated on the plots. It is seen in this plot that the compound is apparently more easily magnetized than would be expected for triplet states alone. Consequently, it appears that the antiferromagnetic interaction may contain contributions from both inter- and intrachain effects, although there is no compelling reason to include interchain effects other than the observation that the Ising model does not provide a satisfying account of the experimental data. The alternate Heisenberg model for intrachain interactions or one of intermediate anisotropy may be more appropriate since the magnetic susceptibilities predicted by such models exhibit more rounded cusps when plotted as a function of temperature.

There are similarities in the behavior observed here and that described by Flippen and Friedberg[14] for $Cu(HCO_2)_2 \cdot 4H_2O$. They pointed out that the anisotropic exchange term $D \cdot S_1 \times S_2$ described by Moriya[15] can lead to weak ferromagnetism. A weak ferromagnet is an antiferromagnet whose sublattice magnetizations are slightly canted.[16] Pairs of copper ions in the chains in $Cu(NH_3)_2CO_3$ are not related by a center of symmetry as required for the Moriya anisotropic exchange, while the pairs of copper ions at 3.5 Å are related by a center of symmetry. Thus, the data are consistent with a model which involves a superexchange interaction along the chains which leads to a short-range antiferromagnetism and weak ferromagnetism. The superexchange mechanism in this model may be more important than the through-space mechanism which has been termed incipient bond formation. The d orbitals of the copper ions are expected to overlap only slightly at 3.5 Å, while the magnetic wave functions may be coupled through the bridging carbonate group by covalent bond formation.

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The Preparation and Characterization of Methylchlorofluorophosphine, CH_3PFCl, and Methylbromofluorophosphine, CH_3PFBr

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The P–N bond in aminodifluorophosphines is subject to facile cleavage by hydrogen halides to give cleanly the appropriate halodifluorophosphine and the amine