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Heat Capacity and Magnetic Susceptibility of Copper(II) Tetrammine Sulfate Monohydrate from 1.3 to 24°K.

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The heat capacity and magnetic susceptibility of copper tetrammine sulfate have been investigated between 1.3 and 29°K. The results indicate strong interactions between copper ions, leading to a transition, of order higher than the second, with a maximum in the heat capacity of 0.75 cal. mole^{-1} deg.$^{-1}$ at 3.0°K. The magnetic susceptibility is nearly constant between 1 and 4°K., and thereafter falls gradually; the maximum value of the molar susceptibility is 0.04. It is believed that the interaction is directly related to the coördination with ammonia.

Introduction

The magnetic behavior of crystalline salts of cupric ion varies considerably from salt to salt. The Tutton salt, $CuSO_4 \cdot K_2SO_4 \cdot 6H_2O$, is one of the most ideal of all paramagnetic salts, and has been used in the attainment of temperatures far below 1°K.^{1} The ordinary hydrated sulfate, $CuSO_4 \cdot 5H_2O$, has a magnetic transition^2 in the vicinity of 1°K., the exact nature of which is not clear. The hydrated chloride, $CuCl_2 \cdot 2H_2O$, has a lambda-type transition at about 4.2°K. below which the salt becomes anti-ferromagnetic.^{3} The acetate, $Cu(C_2H_3O_2)_2 \cdot H_2O$, becomes diamagnetic at about 50°K.^{4}

With the exception of the acetate, the properties of all the salts described above may be explained in terms of the effect of crystalline environment on a substantially free copper ion. The ground state of free cupric ion is $^2D_{5/2}$. At temperatures above the magnetic transitions, the typical copper salts behave almost as ^2S states; their magnetic susceptibilities are but slightly higher than the "spin-only" values.

Copper tetrammine sulfate differs formally from $CuSO_4 \cdot 5H_2O$ only in the replacement of four of the water molecules by ammonia molecules. In the crystal the basic unit is $Cu(NH_3)_4^{++}$, rather than $Cu(H_2O)_4^{++}$; due to differences in crystal structure, the less near neighbors of the copper ion are different in the two salts. At the outset of this research, it was expected that the ammine salt would behave in the same general fashion as the hydrate, so that comparison of the two would show the effect of the ammonia and in addition shed further light on the behavior of the ordinary hydrate.

Experimental

The experimental procedures were substantially the same as those employed by Fritz and Pinch in the investigation of vanadium ammonium alum,^{5} and will not be described in detail. The ellipsoidal sample container had an internal volume of 31.13 cm.^{3}, and contained 32.64 g. of the salt. The weight of the container was 19.56 g. The carbon thermometer had a resistance at room temperature of about 6000 ohms. At low temperatures its sensitivity was decidedly higher than that of the thermometer previously described,^{5} but it was also considerably less stable.

The specimen used in the investigation was prepared by addition of C.P. ammonium hydroxide to a solution of C.P. copper sulfate according to the method of Walton.^{6} The crystalline salt was obtained by cooling of the resulting hot solution. The crystals used were ground to a powder; the portion selected for use passed through a 20-mesh screen, but failed to pass through a 100-mesh screen. The irregular particles were stored for a time under a saturated solution of the salt and then dried manually.

A sample for analysis was withdrawn during the filling of the sample tube. Its copper content was determined electrolytically to be 25.92% (theoretical 25.87%); the ammonia–copper ratio was determined by titration to be 3.92 to 1.

Measurements of heat capacity and magnetic susceptibility were made in the manner previously described.^{5} For the low temperature susceptibility measurements, the coil constants were obtained with the specimen near 70°K., after the coils had been cooled by liquid helium or hydrogen. The effect of the sample at 70°K., upon the coils was determined in a separate experiment in which the specimen was cooled from room temperature to 70°K. The susceptibilities were thus based upon the room temperature susceptibility of the salt. The molar susceptibility at 290°K. is 1.40×10^{-3}, according to Bhatnage, Lessheim and Khanna.^{7} An independent check on our specimen by the Gouy method gave a result of 1.35×10^{-3}. (For the purpose of the correction this susceptibility is required only to about 20%.)

Results

The heat capacity of the salt was measured between 1.3 and 24°K. The observed measurements were corrected for the heat capacity of 19.56 g. of Pyrex as previously described.^{5} At the highest temperatures, this represented $^1/_4$ of the observed heat capacity. In view of the unusual behavior of the heat capacity between 12 and 20°K., this region was investigated in three separate sets of experiments; the results of the several sets were consistent. The heat capacity measurements are given

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(1) J. Ashmead, *Nature*, **143**, 853 (1939).

(2) T. H. Geballe and W. F. Giauque, THIS JOURNAL, **74**, 3515 (1952).

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(4) B. C. Guha, *Proc. Roy. Soc. (London)*, **A206**, 353 (1951).

(5) J. J. Fritz and H. L. Pinch, THIS JOURNAL, **78**, 6223 (1956).

(6) H. F. Walton, "Inorganic Preparations," Prentice-Hall, New York, N. Y., 1948, p. 79.

(7) S. S. Bhatnage, H. Lessheim and M. L. Khanna, *J. Ind. Chem. Soc.*, 445 (1937).

in Table I. The accuracy of the heat capacity measurements below 20°K. is estimated as 1%; above 20°K., the errors are probably 2–3%, due to uncertainty in thermometer calibration.

TABLE I

MOLAR HEAT CAPACITY OF COPPER TETRAMMINE SULFATE MONOHYDRATE

Temp., °K.	Heat capacity, cal. deg.$^{-1}$ mole^{-1}	Temp., °K.	Heat capacity cal. deg.$^{-1}$ mole^{-1}
1.355	0.405	8.99	0.662
1.417	.418	10.01	.797
1.530	.432	10.77	.934
1.662	.491	13.17	1.56
2.323	.701	14.44	1.96
2.638	.721	14.89	2.05
2.910	.732	15.35	2.16
3.223	.732	15.72	2.16
3.579	.714	16.36	2.43
3.950	.685	16.42	2.51
4.336	.661	17.30	2.67
4.792	.614	17.72	2.74
5.325	.579	18.88	3.32
5.86	.566	19.09	3.26
6.44	.558	20.61	3.79
6.99	.551	22.06	3.90
7.58	.576	23.68	4.49
8.23	.585		

The magnetic susceptibility was measured between 1.2 and 20.2°K. The results are shown in Fig. 1, where the molar susceptibility is plotted against the temperature. Because of the small magnitude of the susceptibility, the error is estimated as 5%, although (as will be seen from Fig. 1) the internal consistency of the measurements was better than this. The results indicate a slight maximum near 4°K., but the diminution below 4° is within the accuracy claimed; accordingly the curve is drawn with the maximum at the lowest temperature. The results between 11 and 20°K. are represented by the formula

$$\chi_M = 0.53/(T + 5.3)$$

Upon adiabatic magnetization of the salt at 1.4°K., the temperature remained constant within 0.002°K.

Discussion

The nature of the heat capacity of the salt was unexpected and remarkable. There is a maximum at 3.0°K. which evidently is due to a magnetic transition. The height of the maximum is very nearly half that required for a transition from a single lower state to a doubly degenerate upper state. (In this connection, it is interesting to note that for $CuSO_4 \cdot 5H_2O$ Giauque and Geballe[2] obtained a maximum which was half that required for a transition between two singly degenerate states.) Moreover, the heat capacity between 1 and 6°K., after correction for the small lattice heat capacity, may be represented within several per cent. by a function

$$C/R = 0.975(\delta/kT)^2 e^{-\delta/kT}(1 - 2e^{-\delta/kT})^{-2}$$

with $\delta/k = 7.9$°K. (The lattice heat capacity may be estimated as about 0.006 cal. mole^{-1} deg.$^{-1}$ at 2.5°K. and about 0.08 cal. mole^{-1} deg.$^{-1}$ at 6°K.)

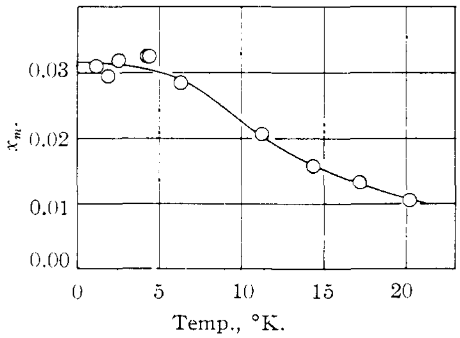

Fig. 1.—Magnetic susceptibility of copper tetrammine sulfate monohydrate.

In view of the fit of the Schottky function given above, it is tempting to view the basic unit in the salt (at low temperatures) as a pair of ions with their spins coupled. In this view, the state observed is the "triplet" state of the pairs, with total spin of unity. Such a state would have three magnetic energy levels, just as in vanadium alum,[5] and would give rise to the observed heat capacity below 6°K. There are two serious arguments against such specific "pairing" of ions. First, if the ions are paired, there should be both the "triplet" state and a "singlet" state, the latter with total spin of zero. This state of affairs has been observed with copper acetate[8]; both states are observed, with the singlet having the lower energy. In the present case, there is no evidence for a low-lying singlet level; on the other hand, it would be surprising to find it at an energy well above the ground state. Second, the crystal structure of copper tetrammine sulfate at room temperature[9] gives no evidence of pairing of copper ions. On the other hand, in copper acetate the crystal structure[10] indicates clearly the grouping of copper ions by pairs. A change in structure so as to bring copper ions together by pairs would require a substantial change in crystal structure below room temperature.

Actually it is not necessary to assume a coupling mechanism as specific as pair-formation to explain the observed results. The crystal structure of the tetrammine salt indicates that the copper ions are arranged in zig-zag chains parallel to the 100 planes of the crystal, with the units linked together by coordination with water molecules. Strong exchange interactions (with energy of the order of that given above as δ) along the chains will give rise to the same general behavior as the pairing considered above.[11] In chemical terms this mechanism corresponds to a weak bonding along the chains $Cu(NH_3)_4$–H_2O–$Cu(NH_3)_4$–H_2O—. The microwave results at room temperature[12] show the single transition typical of single electron spins, but the line is abnormally narrow; this narrowing previously has been attributed to strong exchange coupling between copper ions.

Either of the coupling (exchange) mechanisms suggested will give rise to the sort of behavior ob-

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[8] B. Bleaney and K. D. Bowers, *Proc. Roy. Soc.* (*London*), **A214**, 451 (1952).

[9] F. Mazzi, *Acta Cryst.*, **8**, 137 (1955).

[10] J. F. Niekirk and F. R. L. Schoening, *ibid.*, **6**, 227 (1953).

[11] We thank Dr. Julian Eisenstein for suggesting this possibility.

[12] T. Okamura and M. Date, *Phys. Rev.*, **94**, 314 (1954).

served for the magnetic susceptibility. Detailed theoretical treatment should aid in a more exact description.

Above 10°K. the low lying magnetic "transition" contributes only a small fraction of the total heat capacity. The heat capacity between 10 and 20°K. does not show the steep rise characteristic of heat capacity due to lattice vibrations. (For example, see ref. 5.) Instead, it is a nearly linear function of the temperature between 12 and 24°K. Moreover, the values of the molal heat capacity are considerably higher than those given by Duyckaerts[13] for the analogous salt, $CuSO_4 \cdot 5H_2O$. Comparison of the data for the two salts shows that the difference between the heat capacities reaches a maximum near 20°K. and diminishes at higher temperatures. Any other reasonable assignment for the lattice heat capacity gives a similar broad maximum in the heat capacity due to other causes. It is possible that the excess heat capacity is due to a second magnetic "transition." There is no evidence of a sharp rise in the heat capacity such as might be associated with a coöperative transition. Complete examination of this "transition" will require additional measurements above 20°K.

Magnetic Behavior of Copper Tetrammine Sulfate.—The unquestionably large coupling between copper ions in the tetrammine sulfate was surprising, particularly in view of the observed crystal structure. It is possible that this coupling is an accident of the structure, but we think this quite unlikely in view of the rather large distance between copper ions. In the tetrammine, the smallest distance between copper ions is 5.3 Å. compared with 5.7 Å. in $CuSO_4 \cdot 5H_2O$, 3.5 Å. in $CuCl_2 \cdot 2H_2O$, and 2.6 Å. in $Cu(C_2H_3O_2)_2 \cdot H_2O$. The chloride displays large exchange interactions, leading to the previously cited transition to antiferromagnetism at 4.2°K. However, the minimum Cu–Cu distance is much smaller than in the tetrammine, and there are in fact two other pairs of copper ions within only 5.5 Å. of each ion. The exchange interactions in the tetrammine are much larger than would be expected by comparison.

We believe that the (comparatively) large exchange interactions are no accident, but are probably enhanced greatly by the presence of the ammonia molecules. Ammonia is well known to coördinate with copper (and some other iron group ions) much more strongly than does water or the sulfate ion. (Copper acetate is a special case, in that in crystalline copper acetate adjacent copper ions in a pair are at a distance almost equal to the Cu–Cu separation in metallic copper.[16] Thus it is almost certain that the very strong exchange interactions in the acetate occur because of directly coupling between adjacent copper ions.[8]) To our knowledge, the present case is the first where extensive low temperature investigation has been made of a cupric salt in which the copper was coördinated with species other than water, halide ions or oxygenated anions. The latter species are notoriously poor coördinating agents for copper ion, and it is not surprising that the introduction of stronger coördinating agents might enhance interactions between the cupric ions.

Conclusions

The heat capacity and magnetic susceptibility of copper tetrammine sulfate below 20°K. indicate that there is strong interaction between cupric ions. This coupling may be simply of the exchange variety, or may occur as a result of a low temperature crystal transition. It will be highly desirable to carry out both X-ray and microwave investigations on this salt below 90°K. There is evidence of a transition (not first order) in the salt starting about 10°K. We propose to investigate this transition further by other means, and plan for the future a complete Third Law study of the salt. In addition we strongly recommend investigations of copper salts containing strong coördinating and chelating agents. One such investigation is already in progress.

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[13] G. Duyckaerts, *Soc. Roy. Sci. Liege*, **14**, 284 (1941).