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Magnetic and Thermodynamic Properties of Copper(II) Acetonylacetone

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The magnetic and thermodynamic properties of the copper(II) chelate of acetonylacetone have been measured from 1.0 to 20°K. There is a small but sharp maximum in the zero-field heat capacity at about 1.25°K., below which the specimen absorbs energy from an alternating magnetic field. The total magnetic entropy removed down to 1.0°K. is only about 10% of the $R \ln 2$ expected at high temperatures. Above 2°K., the magnetic susceptibility follows a Curie–Weiss law.

Introduction

The present research is a continuation of studies of the magnetic and thermodynamic properties of copper(II) compounds. In previous investigations we have reported a thermodynamic and magnetic study of copper tetrammine sulfate,[1] and the magnetic susceptibility for bis-(ethylenediamine) copper sulfate both as an anhydrous material and the tetrahydrate.[2] In these and previous investigations by others, two features are especially notable. First, the behavior of each compound is highly individual; second, all but the most dilute copper salts are greatly subject to coöperative "exchange" interactions, which are frequently quite complex. The chelate studied in the present research is no exception.

The chelate compound offered *a priori* an interesting object of study. The copper atom is surrounded by four oxygens, as in the sulfate and double sulfates. However, it is covalently bonded to the oxygens of two acetonylacetone molecules, and has an average charge of zero, in contradistinction to ordinary salts and "ionic" coördination compounds in which the copper retains its formal charge of plus 2. The double ring structure, with the copper at its center, offers many interesting possibilities for resonance, including perhaps even delocalization of the unpaired electron of the copper. To our knowledge the only previous examples of low temperature work on chelates of acetonylacetone were demagnetization studies made (in another connection) by Daunt on the acetonylacetone chelates of iron(III) and chromium(III).[3]

Experimental

The low temperature apparatus used in these measurements has been described previously in the investigation of vanadium ammonium alum.[4] Certain additional techniques required are discussed below. In the handling necessary for emptying and refilling the ellipsoidal specimen container, the resistance of the carbon thermometer increased by about 4%, but was thereafter nearly as stable as before.

The magnetic fields in this investigation (up to 7200 oersteds) were provided by an iron-free solenoid magnet 6.5 in. i.d., 22 in. o.d., and 30 in. long. The magnet windings are of 0.200″ × 0.400″ copper (two 0.200 in. square conductors laid side by side) with bakelite separators to hold the wires in position. The inner 18 layers were wound continuously over the length of the magnet. The outer three layers consist of two coils, each 8 inches long, spaced 8 inches above and below the center of the magnet. These "compensating" coils, in series with the main coil, smooth out the central field so as to give an axial field uniform to within 0.1% for 5 cm. on either side of the center of the magnet. (The ellipsoidal sample 12 cm. long was placed with its center at the center of the magnet.) Power for the magnet was supplied by a 100 kw. shunt-wound d.c. motor generator. The voltages required for various magnetic fields were obtained and regulated by manual control of the field rheostats of the generator. The heat dissipated in the windings was removed by circulation of a light transformer oil (Westinghouse Electric Corp., Wemco C) which was in turn cooled by water in an external heat exchanger.

Magnetic susceptibilities in the absence of a magnetic field were measured with the "internal" flux-meter, as before.[4] Magnetic susceptibilities at fields other than zero (and some at zero field) were measured in terms of the inductance of the pair of coils about the specimen, by use of the modified General Radio Inductance Bridge described elsewhere.[2] For measurements in magnetic fields the coils were connected in series, opposed so as to minimize the effect of transitory variations in the magnetic field. In this arrangement the pair of coils had a self-inductance of about 0.24 henrys. All bridge measurements reported in this paper were made at 400 cycles. The inductance of the coils in the absence of the specimen and the proportionality constant connecting the charge of inductance with the susceptibility were evaluated by comparison with the fluxmeter measurements. The precision and consistency of measurement was about 1 micro-henry, corresponding to about 0.002 in the molar susceptibility. The estimated limits of error are greater than this because of effects discussed immediately below.

Measurements made with the bridge had to be corrected for two disturbances. First, the observed geometrical inductance drifted slightly with time, the maximum shift being about 0.01% (the specified accuracy of the bridge) in the course of a day. At all but the lowest temperatures the "zero" of the inductance could be obtained directly by comparison, in the absence of a magnetic field, with the flux meter. At the lowest temperatures, the specimen absorbed energy from the 400 cycle field; for these measurements the "zero" had to be obtained by interpolation (in time). Second, the observed inductance of the coil was affected by the external magnetic field in addition to the effect of the specimen. The magnitude of this effect varied approximately as the square of the magnetic field, and was at most about 0.02%; it probably was due to mutual inductance coupling with the magnet coils. It was evaluated as a function of external field at 77 and 20°K., where the susceptibility of the specimen could be assumed independent of field; the corrections were nearly the same in each case, and these obtained at 20° were used. The results on intensity of magnetization indicated that this procedure slightly over-corrected the results below 4°.

The specimen of copper acetonylacetone was supplied by Prof. W. C. Fernelius. It was in the form of needle-like crystals averaging 2–3 mm. long and about 0.5 mm. across. These were packed into the ellipsoidal sample tube of volume 37.5 cm.^{3} as tightly as possible, and showed no evidence of preferred orientation. The sample used weighed 16.677 g.; the weight of the glass, thermometer, etc., in thermal contact with the specimen was 34.08 g. The specimen was analyzed electrolytically for copper content; the average result was 24.39% copper (theoretical 24.27%). The

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(1) J. J. Fritz and H. L. Pinch, THIS JOURNAL, 79, 3644 (1957).

(2) J. J. Fritz, R. V. G. Rao and S. Seki, *J. Phys. Chem.*, 62, 703 (1958).

(3) W. L. Pellinger, J. W. Snider and J. G. Daunt, "Some Magnetic Properties of Ferric and Chromic Acetylacetonates at Very Low Temperatures," N.S.F. Conference on Low Temperature Physics and Chemistry, Baton Rouge, La., 1955. ADDED IN PROOF, 7-14-58.—Since the submission of this paper, magnetization curves of the iron and chromium chelates have been reported by W. E. Henry, "Proceedings of the Kamerlingh Onnes Conference on Low Temperature Physics," 1958, to be published.

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

ellipsoid contained 0.0637 gram atom of copper. For measurement of susceptibility, it was assumed, by analogy with other copper–ketone chelates, that the Curie constant was 0.40 at 300°K., and the geometrical turn area of the coils was obtained by correction of the observed turn area for the very small effect of the specimen (at room temperature) on the coils cooled in the refrigerant bath.

As before, the accuracy of heat capacity measurements is estimated at 1%, and that of zero field susceptibilities as about 0.002 in the molar susceptibility.

Results

The heat capacity was measured from 1.10 to 21°K. in several series of measurements. The results are given in Table I. The data below 5°K. are plotted in Fig. 1. The solid line is drawn through the experimental points. Deviations from the line indicate the reproducibility of the data. There is a peak at about 1.25°K., with a maximum value of about 0.50 cal. mole^{-1} deg.$^{-1}$. The broken line of positive slope is the lattice heat capacity, and the second broken line the "magnetic" heat capacity. In the region between 1.7 and 2.6°K., the magnetic contribution to the heat capacity could be represented accurately by the equation $C_{\text{mag}} = 0.356/T^2$, and this equation was used for extrapolation of the magnetic heat capacity above 2.6°K. The lattice heat capacity was obtained by subtraction of the (generally small) magnetic contribution from the observed heat capacity. It was extrapolated by use of the function $C_{\text{lattice}} = 1.13 \times 10^{-3}\, T^3$, which fitted the data between 2.6 and 8°K. It will be observed from Table I that the data scatter by several per cent. above 15°K. The corresponding total heat capacities (substance plus calorimeter) were consistent to about a per cent., but the correction for the glass present was quite large (as much as 50%) and greatly enhanced the variations.

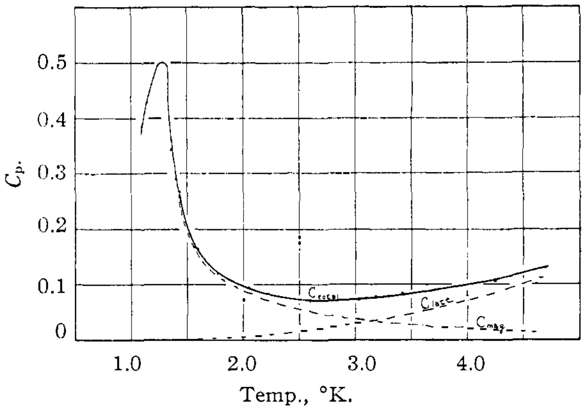

Fig. 1.—Heat capacity of copper acetonylacetone below 5°K.

TABLE I

HEAT CAPACITY OF COPPER ACETONYLACETONE

Temp., °K.	C_P, cal. mole^{-1} deg.$^{-1}$	Temp., °K.	C_P, cal. mole^{-1} deg.$^{-1}$
1.099	0.380	6.16	0.280
1.143	.427	6.56	.324
1.220	.488	7.08	.420
1.345	.324	7.74	.521
1.356	.341	8.31	.650
1.387	.284	9.18	.850
1.42	.250	9.84	1.110
1.43	.264	10.44	1.225
1.57	.168	10.55	1.33
1.59	.164	11.50	1.65
1.69	.138	11.76	1.66
1.76	.120	12.82	2.14
2.00	.096	13.20	2.11
2.08	.094	14.35	2.62
2.24	.084	14.92	2.69
2.59	.071	15.97	2.91
3.05	.072	16.77	2.91
3.16	.081	17.66	2.97
3.42	.088	18.54	3.30
3.88	.095	19.42	3.74
4.25	.106	21.28	4.85
4.69	.128		

The molar magnetic susceptibility in zero magnetic field, as measured by use of the fluxmeter, is given in Table II. The magnetic susceptibility and the product $\chi_m T$ are shown in Fig. 2. The plot for $\chi_m T$ has been smoothed; only two points were outside the estimated error in χ_m. The magnetic susceptibility appears to reach a maximum at about 1.03°K. The product $\chi_m T$ begins to bend down steeply in the vicinity of the heat capacity anomaly. Between 1.2 and 10°K. the data can be fitted, with an average deviation of 1.5%, by the equation $\chi_m = 0.386/(T \times 0.22)$ (the estimated accuracy is 1%

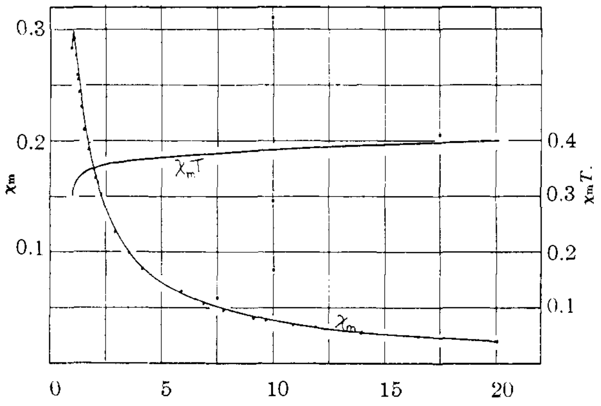

Fig. 2.—Magnetic susceptibility of copper acetonylacetone.

TABLE II

MOLAR MAGNETIC SUSCEPTIBILITY OF COPPER ACETONYLACETONE

1.015	0.284	0.289	2.95	0.119	0.351
1.035	.295	.305	3.15	.110	.347
1.050	.293	.308	3.59	.100	.359
1.097	.291	.319	4.20	.085	.357
1.188	.277	.329	5.93	.065	.386
1.280	.255	.326	6.90	.0545	.376
1.280	.254	.325	7.80	.0478	.373
1.294	.259	.336	9.20	.0408	.375
1.35	.244	.329	9.77	.0392	.383
1.47	.232	.340	10.98	.0353	.388
1.58	.210	.334	11.96	.0325	.389
1.76	.192	.337	14.00	.0283	.396
2.11	.168	.355	16.52	.0240	.396
2.14	.165	.351	20.25	.0198	.401
2.32	.152	.353			

at 1.2° and 8% at 10°K.) with no systematic deviation. Between 10 and 20°K. there were positive deviations of 2 to 5% from the equation, and the points in this region were fitted by an equation $\chi_m = 0.411/(T+0.53)$. The equation used for the region above 10°K. is more consistent with the observed susceptibilities of copper chelates at ordinary temperatures; in view of the estimated accuracy in this region the fit obtained probably indicates mainly the consistency of the data.

Nine separate adiabatic magnetizations were made at starting temperatures from 1.02 to 3.25°, during the course of which temperatures were measured with the carbon thermometer and magnetic susceptibilities at (400 cps.) with the bridge. Seven of these, all starting above 1.18°K., were used in calculating the intensity of magnetization, by use of the equation

$$I = \int_0^H (\partial I/\partial H)_S \mathrm{d}H$$

as a function of magnetic field and temperature. The remaining two could not be used for this purpose, since at the lower temperatures there was noticeable absorption of energy from the a.c. field. The intensities of magnetization above 1.18°K. fell on a single curve when plotted against (H/T) and could be represented by the function $I = 0.337\,H/T - 9.5 \times 10^{-6}\,(H/T)^2$. The "intensities of magnetization" calculated from the data in the region of absorption lay uniformly below this curve, as might be expected.

The temperature changes during adiabatic magnetization are plotted in Fig. 3. These have been corrected, where necessary, for energy absorption, although the corrections would be barely visible on the graph. The relatively small changes in temperature at the lower temperatures are indicative of the high heat capacity and low susceptibility below 1.5°K., particularly in high external magnetic fields. As a check on the thermodynamic consistency of the measurements, several of the observed curves were compared with isentropes calculated from the observed zero-field heat capacities and the equation for I given above, using the relationship

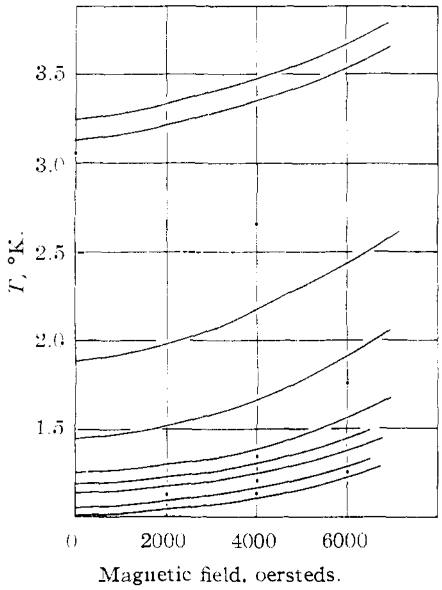

Fig. 3.—Effect of magnetic field on temperature.

$$S_H - S_0 = \int_0^H (\partial S/\partial H)_T \partial H = \int_0^H (\partial I/\partial T)_H \mathrm{d}H$$

The agreement in each case was quite satisfactory, in view of the uncertainties involved.

The lowest bath temperature used was 1.26°K. and all starting temperatures below this were obtained by adiabatic demagnetization from fields of about 7200 oersteds. The temperatures below 1.26°K. were evaluated by extrapolation of the resistance of the carbon thermometer using a function of the form $R = A - B \log T + C (\log T)^2$, which fitted the calibration between 1.26 and 2.0°K. within 0.002°K. In view of the uncertainty about the values of I below 1.16°K., calculation of the thermodynamic temperatures was not considered reliable. However, a calculation of the thermodynamic temperature, using the equation for I given above, gave a temperature of 1.12 ± 0.03° corresponding to the thermometer temperature of 1.105°K. For temperatures in the magnetic field, the resistance of the thermometer was corrected by amounts interpolated from a separate calibration of the effect of magnetic field on the thermometer. The maximum correction was 0.3% in the resistance, corresponding to 0.02°K.

Discussion

The most interesting feature of the measurements was the small but relatively sharp anomaly in the heat capacity at about 1.25°K. The entropy above 1.05°K. associated with this (magnetic) anomaly was calculated to be 0.21 cal. mole^{-1} deg.$^{-1}$ (including 0.01 unit above 4°K., evaluated by use of the equation $C_H = 0.356/T^2$). The magnetic susceptibility above 4°K. is sufficiently like that of other copper salts to indicate that the substance must have a magnetic entropy of $R \ln 2$ (1.38 e.u.) at high temperatures. The remaining entropy (1.17 e.u.) cannot be removed by any reasonable and simple extrapolation of 0°K., and it appears likely that there are additional peaks in the heat capacity below 1°K.

The heat capacity maximum in the present case is in some ways similar to that observed by Geballe and Giauque[5] for a single crystal of copper sulfate pentahydrate. They observed a maximum of about 0.45 cal. mole^{-1} deg.$^{-1}$ at 1.37°K. and one of 0.3 cal. mole^{-1} deg^{-1} at about 0.75°K. The envelope of these maxima corresponded to a magnetic entropy of 0.64 e.u. (approximately 1/2 $R \ln 2$). By demagnetization from 8500 oersteds, 0.85°K., they were able to reach 0.22°K., at which point there was evidence for a heat capacity peak below 0.2°K.

There are several significant differences between the effects observed here and those observed by Geballe and Giauque. In the first place, our maximum is much sharper; on the high temperature side the heat capacity falls to 0.1 at 2.0°K., whereas with copper sulfate the corresponding

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(5) T. H. Geballe and W. F. Giauque, THIS JOURNAL, **74**, 3513 (1952).

decrease reaches only 0.3. It is for this reason that the entropy removed above 1.05° is only 0.21 e.u. in the present case. In the second place, Geballe and Giauque made very careful tests for energy absorption in a 60-cycle field, and found none at temperatures as low as 0.24°K. This is in contrast to the absorption of energy from a 400 cycle field by the present substance below 1.18°K. Finally, the decrease in $\chi_m T$ with decreasing temperature is much less rapid above 2°K. and much more rapid below 2° than was observed with the sulfate. The resemblance between the two substances in position and magnitude of the heat capacity peak above 1°K. appears to be more coincidence than any fundamental phenomenological resemblance.

The energy absorption in the 400 cycle field was obviously due to a relaxation effect with a relaxation time near 1°K. of the order of a millisecond. It was accompanied by a corresponding decrease in the zero-field dynamic susceptibility (χ') at 400 cycles below the static susceptibility (χ_0) measured by the fluxmeter. This decrease was about 5% at 1.03°K. Using a Debye-type relation between the real component of the susceptibility (χ') and the imaginary part (χ''),[6] one obtains an estimate of χ'' as about $0.20\chi_0$ under these conditions. Estimates of the average value of χ'' from the energy absorption during the two magnetizations which started near 1°K. also gives $\chi'' \approx 0.20\chi_0$. This agreement may be fortuitous but is not surprising since the specimen was at or near zero field and the lowest temperature during most of the time the 400 cycle field was on.

On the basis of present evidence, we can do little more than speculate on the causes of the observed behavior. The sharpness of the observed heat capacity maximum makes it likely that the effect is coöperative in nature; the relatively low maximum would argue for a highly degenerate (or nearly degenerate) lower state (or states). The relaxation observed below 1.18°K. is reminiscent of the effects observed in the free radical triphenylmethyl[7] and is quite different from the highly reversible behavior of copper salts such as $CuSO_4 \cdot 5H_2O$.[5] It is possible that the "transition" at 1.25°K. marks the attainment of energies low enough to permit delocalization of the unpaired electron or coöperative pairing of d-electrons between molecules leading to a highly degenerate ground state. It is our belief that at very low temperatures large groups of molecules act coöperatively, tied together by exchange forces between their electrons.

It is evident that this substance will provide fruitful material for additional measurements, and different types of measurement, at temperatures below those which are reported here.

The lattice heat capacity shows the sort of behavior observed with previous substances.[1,4] The "constant" in the expression $C_{\text{lattice}} = aT^3$ is 5×10^{-4} at 18-20°K., rises gradually to 11×10^{-4} at 10°K. and remains constant at lower temperatures. A rather similar behavior was observed with copper tetrammine sulfate,[1] but in that case the lower end of the lattice heat capacity curve was obscured by a much higher magnetic heat capacity above 3°K.

Acknowledgments.—We wish to thank Mr. L. F. Shultz for production of the refrigerants used and Dr. R. V. G. Rao and Mr. L. Gregor for help in the measurements and calculations. We thank Prof. J. G. Aston for suggesting investigation of this compound and for helpful discussions. We gratefully acknowledge funds provided by the Research Corporation and the Westinghouse Electric Corporation for contribution of the iron-free solenoid magnet. The research described herein was partially supported by funds from the National Science Foundation.

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[6] See C. J. Gorter, "Paramagnetic Relaxation," Elsevier Press, New York, N. Y., 1947, p. 24.

[7] S. I. Weissman, THIS JOURNAL, **79**, 5584 (1957).

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Chemical Effects of Atomic Hydrogen in Aqueous Solutions[1]

BY THOMAS W. DAVIS, SHEFFIELD GORDON AND EDWIN J. HART

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Evidence has been obtained for the oxidation of ferrous ions in sulfuric acid solution by hydrogen atoms. The hydrogen atoms were produced externally and circulated through the cell containing the ferrous ions. On the basis of these results and the non-chain character of the γ-ray induced water–deuterium reaction, the authors conclude that oxidation is not through H_2^+. Two mechanisms proposed are: $H + H^+ + Fe^{++} = H_2 + Fe^{+++}$ and $H + Fe^{++}\cdot(H_2O)_n = H_2 + Fe^{+++}\cdot(H_2O)_{n-1} + OH^-$.

As late as 1950, the basic free radical reactions of the radiation promoted oxidation of acidic air-free ferrous sulfate solutions were uncertain. The stoichiometry of this reaction is closely approximated by equation 1[2]

$$2Fe^{++} + 2H^+ = 2Fe^{3+} + H_2 \qquad (1)$$

Hydrogen formation is equivalent to ferric ion formation.

Weiss[3] suggests participation of a hypothetical hydrated hydrogen molecule ion formed from a hydrogen atom and a hydrogen ion in the oxidation step as

$$Fe^{++} + H_2^+\cdot aq. = Fe^{3+} + H_2 \qquad (2)$$

Reaction 2 followed by 3 therefore accounts for the stoichiometry observed in 1

$$Fe^{++} + OH = Fe^{3+} + OH^- \qquad (3)$$

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] H. Fricke and E. J. Hart, *J. Chem. Phys.*, **3**, 60 (1935).

[3] J. Weiss, *Nature*, **165**, 728 (1950).