454. *Magnetic Properties and Structure of Copper Laurate.*

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Copper laurate has a maximum magnetic susceptibility at approximately 230° K, the experimental data indicating that at 35° K, the paramagnetic contribution to the susceptibility would be zero. This is explained by assuming the existence of strong quantum-mechanical exchange forces between the copper atoms. A covalent chelate structure for copper laurate is suggested, based on magnetic and chemical evidence provided by measurements on copper laurate and its co-ordination compounds with ammonia and pyridine.

ALTHOUGH early measurements of the magnetic susceptibility of copper soaps revealed no abnormal behaviour (Bhatnagar, Singh, and Ghani, *Indian J. Phys.*, 1932, **7**, 323), subsequent measurements have indicated that the magnetic moment of the copper in these compounds is anomalously low. Thus, Amiel (*Compt. rend.*, 1938, **207**, 1097), found for the molar susceptibility of copper in copper laurate at 20° a value of only $0{\cdot}875 \times 10^{-3}$ c.g.s.u. in contrast to the value of $1{\cdot}700 \times 10^{-3}$ c.g.s.u. in hydrated copper sulphate. In view of the difficulty of obtaining pure metal soaps (cf. Elliott, " The Alkaline Earth and Heavy Metal Soaps," Reinhold Publishing Corp., New York, 1946) information on the purity of the materials used in these investigations is unfortunately not available.

The present measurements confirm the anomalously low value reported by Amiel and show further that copper laurate becomes anti-ferromagnetic at low temperatures. Susceptibility data for complexes of copper laurate with ammonia and pyridine are also reported.

These measurements throw some light on the nature of the bonding in the copper soaps which is in accord with other evidence.

EXPERIMENTAL

Preparation and Analysis of Materials.—The lauric acid was a pre-war " purissimus grade " sample from Schering-Kahlbaum (m. p. 44·1°). Copper laurate was prepared by metathesis of sodium laurate in 60% ethanol with an aqueous solution of copper sulphate at 40°. The precipitated soap was set aside overnight and then washed repeatedly on a sintered-glass filter with aqueous ethanol to remove excess of precipitant and free fatty acid. After drying in an air oven at 80° for 2 hr. the product was recrystallised from warm carbon tetrachloride and finally dried *in vacuo*. It was stored over phosphoric oxide (Found : Cu, 13·5, 13·6. Calc. for $C_{24}H_{46}O_4Cu$: Cu, 13·8%). Preparation of copper laurate was also attempted by Amiel's method (*loc. cit.*) in which the fatty acid is added to a cuprammonium solution containing potassium hydroxide. The violet precipitate obtained in this way, proved to be the diammine (Found : NH_3, 6·9. Calc. for $C_{24}H_{46}O_4Cu,2NH_3$: NH_3, 6·85%). This complex lost ammonia readily when warmed, yielding a product identical with that obtained by direct metathesis. The diammine was also obtained by passing ammonia into a solution of copper laurate in chloroform. A bright green monopyridine complex of copper laurate (Found : C_5H_5N, 14·6. Calc. for $C_{24}H_{46}O_4Cu,C_5H_5N$: C_5H_5N, 14·6%) was similarly obtained by adding pyridine to a chloroform solution of the soap. Although pyridine solutions of copper laurate are blue, attempts to isolate a stable dipyridine complex were not successful. A solution of copper laurate in dry pyridine yielded a very small quantity of violet-blue platelets after 48 hr. at 0° but this product rapidly lost pyridine, yielding the green monopyridine complex. No magnetic measurements were made with the violet-blue product.

For analysis, copper laurate was hydrolysed with 2N-sulphuric acid, and the copper in the hydrolysate estimated gravimetrically as dipyridinecopper dithiocyanate, after the free fatty acid had been removed by filtration. Ammonia and pyridine in the complexes were estimated by determining the loss in weight after heating them at 80° to constant weight.

Magnetic Measurements.—Susceptibility measurements were made by the Gouy method with an apparatus described previously (McDonnell, Pink, and Ubbelohde, *Trans. Faraday Soc.*, 1950, **46**, 156). The only modification was the provision of a heater winding on the brass jacket so that measurements could be made above room temperature. The current for the heater was supplied by an electronically stabilised power unit which permitted temperature control of the Gouy tube to ±0·2°. The measurements at 90° K and 190° K were made in an atmosphere of nitrogen. At least three completely separate measurements were made with each sample. With the powdered specimens the accuracy, which was limited by the reproducibility of packing, was estimated to be ±1%. The magnetic data are summarised in the Table, which gives the molar susceptibility of copper at 291° K (χ_{Cu}) in each of the compounds studied.

	$10^3\chi_{Cu}$, c.g.s.u.		$10^3\chi_{Cu}$, c.g.s.u.
Copper sulphate pentahydrate	1·700	Copper laurate monopyridine complex	0·928
Copper laurate	0·954	Copper laurate in pyridine solution ...	1·648
Diamminocopper laurate	1·761		

The values shown have been corrected for the diamagnetic contribution to the susceptibility from the organic part of the molecule. Standard Pascal corrections were employed throughout. The value for solid copper sulphate pentahydrate, which has been shown to obey the Curie–Weiss law almost perfectly down to 14° K, is included in the Table for comparison. The variation of χ_{Cu} in copper laurate with temperature is shown in Fig. 1.

Volatility of Copper Laurate.—When copper laurate was heated in a molecular still at pressures $<10^{-4}$ mm. small quantities of a blue product, which appeared to be identical with copper laurate, were obtained (Found : Cu, 13·6, 12·4, 14·5%). Approximately 10 mg. were obtained after 5 hours' distillation at 200—210° with a still path of 1 cm. At higher temperatures considerable darkening occurred and a paler material was obtained which appeared to contain a proportion of copper-free products.

DISCUSSION

The most important observation is the rapid fall in the paramagnetic susceptibility of copper laurate below 230° K. Extrapolation of the experimental data indicates that, at 35° K, the paramagnetic contribution to the measured susceptibility would be zero (Fig. 1). In copper compounds which obey the Curie–Weiss law, like copper sulphate pentahydrate, the measured susceptibility can be accounted for on the basis of a contribution to the magnetic moment from the spin only, the orbital moment being effectively quenched by the interatomic forces (Van Vleck, " Theory of Electric and Magnetic Susceptibilities," Clarendon Press, Oxford, 1932). In copper laurate below room temperature a mechanism for quenching the spin must also be found. While internal magnetic coupling between the spin and orbit provides a possible mechanism (Van Vleck, *loc. cit.*), it seems more likely that quenching occurs through the existence of sufficiently strong exchange forces between the copper atoms to aline the spins into an antiparallel and therefore diamagnetic state. At higher temperatures, states with higher energies will be favoured and a proportion of the spins will remain uncoupled. These uncoupled spins will contribute to the paramagnetic susceptibility and give rise to the normal negative temperature coefficient of susceptibility observed above 230° K. A similar explanation has been advanced recently by Bleaney and Bowers (*Proc. Roy. Soc.*, 1952, *A*, **214**, 451), to account for the anomalous susceptibility and paramagnetic resonance spectrum of hydrated copper acetate. Although detailed *X*-ray data for copper laurate are not available, Vold and Hattiangdi (*Ind. Eng. Chem.*, 1949, **41**, 2311), have shown that the crystal structure in a large number of heavy-metal soaps has the characteristic features illustrated in Fig. 2. The metal ions are arranged in planes, between which the fatty acid radicals extend in both directions, with their axes slightly inclined to the planes containing the metal-carboxylate groups. The feature of this structure which is of importance, in the present connection, is the very high localised concentration of metal atoms along the planes *XX'*, *YY'*. In copper acetate, Bleaney and Bowers (*loc. cit.*) postulated exchange forces between isolated pairs of copper ions. In copper laurate, on the other hand, the markedly anisotropic character of such a lattice might permit co-operative effects along the planes *XX'*, *YY'*, which extend throughout the crystal. In this sense the phenomenon may properly be referred to as anti-ferromagnetism.

FIG. 1. *Effect of temperature on the magnetic susceptibility of copper* (χ_{Cu}) *in copper laurate.*

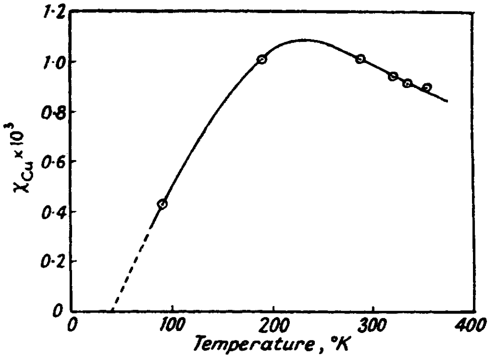
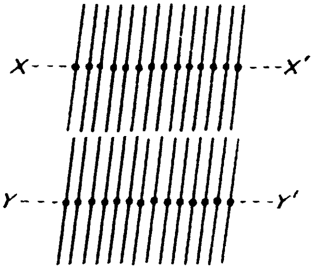
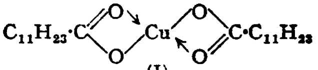
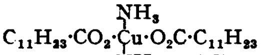


FIG. 2. *Metal soap lattice.*

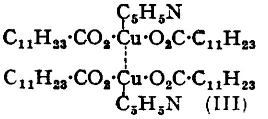


The chemical evidence is also in favour of an explanation based on strong interatomic exchange forces. In the neutral copper atom the lowest level of the spectrum is a ^2S term and the Cu^+ ion is therefore diamagnetic. Formation of a Cu^{++} ion involves excitation of the copper atom to the ^2D level, the relative ease of obtaining the cupric ion in solution being attributed to the heat of hydration, which supplies the necessary energy for the excitation process. Also, Joos (*Ann. Physik*, 1926, **81**, 1076; 1928, **85**, 641) has emphasised that the colour of solutions containing elements of the iron group must be associated with transitions between different energy levels of complexes, as the metal ions have no normal absorption lines softer than 1300 Å. Since cupric laurate is not hydrated, but is strongly coloured, it seems probable that the necessary energy required to stabilise the copper in the cupric state is provided by internal co-ordination of the type shown in (I). In this chelate structure the covalent bonding would permit the close approach of the metal atoms necessary for the full development of the exchange forces. In most salts of the transition-group elements, these forces are of subordinate importance because of the distance between the paramagnetic centres which results from the high dilution with diamagnetic atoms or ions. Niekerk and Schoennig (*Nature*, **1953**, **171**, 37) have reported that the Cu–Cu distance in hydrated copper acetate is 2·64 Å which is only slightly greater


(I)


(II)

$$C_{11}H_{23}\cdot CO_2\cdot \overset{NH_3}{\underset{NH_3}{Cu}}\cdot O_2C\cdot C_{11}H_{23}$$


(III)

$$\begin{array}{c} C_{11}H_{23}\cdot CO_2\cdot \overset{C_5H_5N}{Cu}\cdot O_2C\cdot C_{11}H_{23} \\ \vdots \\ C_{11}H_{23}\cdot CO_2\cdot \underset{C_5H_5N}{Cu}\cdot O_2C\cdot C_{11}H_{23} \end{array}$$

than the value 2·56 Å found in metallic copper. The fact that the susceptibility of copper acetate is closely similar to that of copper laurate (Amiel, *loc. cit.*) supports the suggestion that the copper atoms in copper laurate are sufficiently close for the exchange forces to play an important part in the susceptibility. It should be noted that chelation alone does not account for the anomalously low susceptibility of copper laurate below 230° K. The electronic configuration of cupric copper either in the ionic state or in the covalent planar (dsp^2) or tetrahedral (sp^3) states, involves one unpaired electron. Co-ordinated cupric copper is therefore paramagnetic unless other forces intervene to quench the spin component.

The ready solubility of copper laurate in a number of organic solvents and the relative ease with which copper laurate can be volatilised, *in vacuo*, provide additional evidence for the chelate structure (I). Magnetic data for the ammonia and pyridine complexes are also consistent with this hypothesis. In the blue diammine, $Cu(C_{11}H_{23}\cdot CO_2)_2,2NH_3$ (II), close approach of the copper carboxylate groups will be prevented by the co-ordinated ammonia molecules and the copper should exert its normal spin moment. In the green monopyridine complex, on the other hand, the low susceptibility indicates that close approach of pairs of copper atoms is possible as in copper acetate. A structural unit consisting of two molecules of the monopyridine complex is therefore likely (III), but has not been confirmed. Since pyridine solutions of copper laurate are blue and since, in these solutions, the soap is known to be dispersed as single molecules (Nelson and Pink, *J.*, 1952, 1744) the susceptibility derived from measurements with pyridine solutions might be expected to approach the normal spin-only value. The data in the Table fully confirm these expectations and provide supporting evidence both for the chelate structure (I) and for the proposed mechanism for the quenching of the spin moment in copper laurate at low temperatures.

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