769. *Magnetic Properties of Some Metal Carboxylates.*

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The paramagnetic susceptibilities of the anhydrous stearates and laurates of nickel, cobalt, and iron and of copper stearate are reported. Results are included for the hydrated forms of cobalt and nickel laurates. Measurements at five different temperatures in the range 105—333° K show that only the copper carboxylates fail to obey a Curie–Weiss law. The magnetic moments of the ferric compounds, however, are anomalously low, and the Weiss constant θ is very large.

In a previous paper [1] it was shown that copper laurate has unusual magnetic properties, the paramagnetic susceptibility decreasing sharply below room temperature. The present paper describes an investigation of the magnetic properties of the anhydrous stearates and laurates of nickel, cobalt, and iron. Magnetic measurements have also been made on copper stearate and the hydrated forms of the laurates of cobalt and nickel.

The metallic soaps have presented various features of interest to chemists for the past thirty years, in particular their behaviour in solution, both aqueous and organic, their polymorphic transitions, and their surface properties. In spite of this, and their economic importance,[2] the structure of these compounds has largely been ignored. The complexity of a single molecule, together with the non-crystallinity of the bulk compounds, has so far impeded complete structural analyses by *X*-ray methods of all but the alkali and alkaline-earth soaps. Also, the aggregation which occurs in common organic solvents [3] greatly reduces the significance of dipole-moment measurements in solution.[4]

Experimental

Preparation and Purification of Materials.—Stearic acid was purified by repeated crystallisation from aqueous ethanol. Lauric acid was similarly purified from " AnalaR " acetone. M. p.s were 69·2° and 43·9° respectively.

All the metal soaps were prepared by metathesis at 40° of the corresponding sodium soaps in aqueous ethanol.[5] The precipitated soaps were washed with distilled water till free from precipitant and then with cold aqueous ethanol to remove free acid, then dried by suction at a water pump and stored over calcium chloride. Prepared in this way nickel laurate and cobalt laurate were both obtained as the dihydrates,[6] which were readily dehydrated by boiling them in organic solvents. Ferric soaps made by precipitation from aqueous solutions have been

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[1] Gilmour and Pink, *J.*, 1953, 2198.

[2] " Encyclopædia of Chemical Technology," Interscience Publ. Inc., 1950, Vol. V, p. 203.

[3] Nelson and Pink, *J.*, 1952, 1744.

[4] Gilmour, Nelson, and Pink, *Nature*, 1953, **171**, 1075.

[5] Pink, *J.*, 1938, 1252.

[6] Cf. Oudemans, *J. prakt. Chem.*, 1863, **89**, 206.

described as basic compounds.[7] In these experiments, however, it was found that, provided the ferric soaps were dried without heating (*e.g.*, *in vacuo* over P_2O_5) the neutral soaps were obtained. The absence of hydroxyl groups in the products was confirmed by infrared absorption measurements on paraffin mulls (Perkin–Elmer Model 21 spectrometer). Nickel laurate dihydrate also decomposed when heated, losing lauric acid rapidly by volatilisation : a sample heated at 105° for 6 hr. lost 23·6% by weight. Part of the lauric acid volatilised was recovered and identified by a mixed m. p. determination. The water of hydration may be removed by desiccation *in vacuo* (P_2O_5 or H_2SO_4), the anhydrous soap being rehydrated rapidly in air. By means of a series of desiccation experiments with various strengths of sulphuric acid the dissociation pressure of the hydrate was estimated to be 12 mm. at 16° and 22 mm. at 45°, giving a value of 17·8 kcal. mole^{-1} for the heat of dissociation, comparable with that of crystalline hydrates. Dehydration is accompanied by a slight but distinct colour change from pale green to pale yellow. The colour change on hydration is more marked with the cobalt soaps, the dihydrates being rose-pink, the anhydrous compounds purple. Analytical data for the anhydrous compounds are shown in the Table : in all cases the compounds obtained were the neutral soaps.

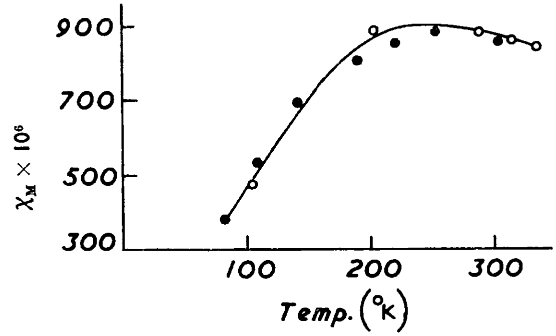

FIG. 1. *Effect of temperature on susceptibility of copper carboxylates*

○ *Cupric stearate.*
● *Cupric acetate monohydrate* (*plotted from Guha's data* [10]).

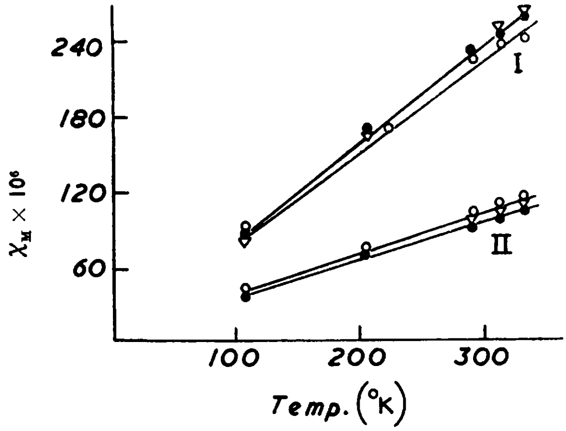

FIG. 2. *Effect of temperature on susceptibility of nickel and cobalt carboxylates.*

(i) *Nickel*, (ii) *cobalt compounds.*

● *Anhydrous laurates.*
○ *Anhydrous stearates.*
▽ *Hydrated laurates.*

	Laurates			Stearates			
	Ni	Co	Fe(ic)	Ni	Co	Fe(ic)	Cu
Metal, found (%) . . .	12·8	12·65	8·5	9·1	9·6	6·4	9·9
,, calc. (%) . . .	12·8	12·9	8·5	9·4	9·4	6·2	10·1

Magnetic Measurements.—Susceptibility measurements were made by the Gouy method on the finely powdered solids, by means of an apparatus described previously.[8] The solids were packed in the specimen tube at 10—12 mm. Hg. Temperatures were measured with a copper–constantan thermocouple, calibrated at low temperatures according to Scott's method.[9] All the magnetic measurements were made with the specimen tube in an atmosphere of oxygen-free (B.O.C. " white-spot ") nitrogen. The magnetic data are shown in Figs. 1—3 where χ_M is the

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[7] Soyenkoff, *J. Phys. Chem.*, 1930, **34**, 2519.
[8] McDonnell, Pink, and Ubbelohde, *Trans. Faraday Soc.*, 1950, **46**, 156.
[9] Scott, *J. Res. Nat. Bur. Stand.*, 1940, **25**, 459.

value of the molar susceptibility in c.g.s. units corrected for the diamagnetic contribution to the susceptibility from the organic part of the molecule. Standard Pascal corrections were employed throughout. In Fig. 1 the data for hydrated copper acetate obtained by Guha[10] are included for comparison. The effective magnetic moment, $\mu_{\text{eff.}}$, and the Weiss constant θ [derived from the relationship $\chi_M = C/(T - \theta)$ where C and θ are constants] for the nickel, cobalt, and iron soaps are shown in Table 1.

TABLE 1. *Magnetic constants of metal carboxylates.*

	$-\theta$ (°K)	$\mu_{\text{eff.}}$ (B.M.)		$-\theta$ (°K)	$\mu_{\text{eff.}}$ (B.M.)
Nickel stearate	18·1	3·35	Cobalt laurate	12·7	5·06
Nickel laurate	11·6	3·22	Cobalt laurate dihydrate	11·2	5·07
Nickel laurate dihydrate	0·0	3·18	Ferric stearate	377·9	5·04
Cobalt stearate	18·5	5·00	Ferric laurate	338·1	4·98

X-Ray Diffraction Measurements.—Attempts to produce single crystals of copper laurate, large enough for *X*-ray crystallographic examination, either from the melt or from solution in a variety of solvents, failed. Interplanar spacings obtained from powder photographs taken with a 3 cm. radius camera and filtered copper K_α radiation (exposure time 3 hr.) are shown in Table 2.

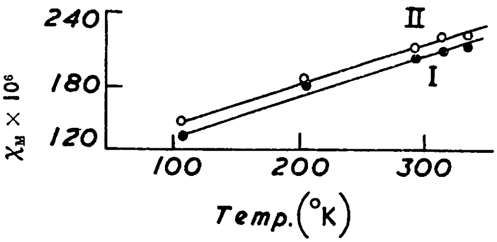


FIG. 3. *Effect of temperature on susceptibility of ferric carboxylates.*
(i) *Ferric laurate*; (ii) *ferric stearate.*

Both the accuracy of measurement and the small number of lines prevented any unique assignment of indices. The first four lines are, however, clearly orders of a long spacing (003, 004, 005, 006). Line 5 could be indexed as a further order of the long spacing (007), but because of its high intensity is attributed to a side spacing. The position and intensity of line 6 indicate that it also is due to a side spacing. By comparison with lauric acid these side spacings show that the hydrocarbon chains are close-packed in copper laurate. The calculated length of a copper laurate molecule is 35·3 Å. From the size of the long spacing (31·9 Å) it is clear that the chains must be inclined at an angle of 64·5° to the basal plane.

TABLE 2. *Interplanar spacings of copper laurate.*

Number	Spacing (Å)		Number	Spacing (Å)	
1	10·81	Strong, sharp	8	2·82	Very weak, sharp
2	7·92	Strong, broad	9	2·50	Medium, broad
3	6·35	Medium, sharp *	10	2·27	Medium, broad
4	5·31	Weak, sharp	11	2·04	Weak, diffuse
5	4·54	Strong, broad	12	1·83	Weak, diffuse
6	3·80	Strong, broad	13	1·62	Very weak, diffuse
7	3·29	Very weak, sharp	14	1·45	Very weak, diffuse

* Possible superposition of two rings, one sharp, one diffuse.

DISCUSSION

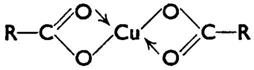
Copper Carboxylates.—Magnetic measurements on copper carboxylates have been reported by a number of workers.[11] In all these instances measurements were made at one temperature only. Measurements over a range of temperature have been reported by

[10] Guha, *Proc. Roy. Soc.*, 1951, *A*, **206**, 353.

[11] Bhatnagar, Singh, and Ghani, *Indian J. Phys.*, 1932, **7**, 323; Amiel, *Compt. rend.*, 1938, **207**, 1097; Ploquin and Vergneau, *ibid.*, 1951, **232**, 2439; Amiel, Ploquin, and Dixmier, *ibid.*, p. 2097; Vergneau, *ibid.*, 1951, **233**, 164; Ploquin, *Bull. Soc. chim. France*, 1951, **18**, 757.

Guha[10] (acetate) and Gilmour and Pink[1] (laurate). As for both copper laurate and copper acetate the susceptibility of copper stearate decreases sharply below room temperature. In view of the striking similarity of the magnetic behaviour of the long-chain compounds to that of copper acetate (Fig. 1) it seems probable that the explanation advanced by Bleaney[12] in connection with the acetate is generally applicable. According to Bleaney, isolated pairs of copper ions are coupled together strongly by exchange forces. The two electron spins interact to form a triplet state, in which the spins are parallel ($S = 1$) and a state with the spins antiparallel ($S = 0$). The former would be paramagnetic, the latter diamagnetic. If the former state lies higher in energy by about 450 $\boldsymbol{k}$ the drop in susceptibility at low temperatures can be accounted for by the pairs of ions draining out of the paramagnetic state into the diamagnetic state. Unequivocal support for this idea of interaction between pairs of copper atoms was provided by van Niekerk and Schoening's *X*-ray examination of copper acetate.[13] They showed that the molecule of copper acetate is binuclear with a Cu–Cu distance of only 2·64 Å (Fig. 4*a*). Each of the copper atoms is coplanar with four oxygen atoms arranged in a square. The magnetic evidence suggests strongly that this is also basically the structure of the laurate and stearate. In the light of this it is of interest to review previous ideas on the structure of the long-chain copper carboxylates. The earliest structure (I) was proposed in 1924 by French and Lowry[14] to account for the covalent nature of these compounds. Sidgwick[15] criticized this structure on the basis that the evidence did not necessarily indicate chelation and could be explained equally by the structure (II). Neither structure provides a means whereby exchange interaction may readily occur between the copper atoms, since their closest distance of approach will in either case be limited by the van der Waals radius[16] of the methylene group, to approximately 4 Å. In the van Niekerk and Schoening structure, on the other hand, the separation of the copper atoms is determined essentially by the oxygen–oxygen separation, which[17] is of the order of 2·2 Å.

(I)



R·CO·O·Cu·O·CO·R (II)

While the close similarity in magnetic properties between the acetate and the laurate suggests strongly that the latter also has a binuclear structure permitting close approach of the copper atoms it is clear that the structures of the acetate and the laurate are not identical. Cupric acetate exists only in the hydrated form and in the van Niekerk and Schoening structure (Fig. 4*a*) the water molecules complete the six-fold co-ordination of the copper. Copper laurate and copper stearate on the other hand are anhydrous. A possible structure for the long-chain compounds which retains the basic binuclear structure of the acetate is illustrated in Fig. 4*b*. This permits close packing of the hydrocarbon chains as required by the *X*-ray data but in contrast to the acetate contains five-co-ordinated copper. Structures containing five-co-ordinated metal atoms have recently been postulated for terpyridyl complexes of copper, zinc, and cadmium,[18] for the pent-ammino-type copper complex $[\mathrm{Cu\ en_2NH_3}]^{++}$ formed by the diethylenediaminecupric ion in strongly ammoniacal solution[19] and for a number of complexes of palladium and platinum.[20] Confirmation of the structure shown in Fig. 4*b* requires a full crystallographic examination.

Carboxylates of Nickel, Cobalt, and Iron.—Neither nickel nor cobalt long-chain carboxylates show deviations from a Curie–Weiss law in the range of temperature investigated (Fig. 2) and so, presumably, have conventional structures.

The bond character of the nickel compounds remains uncertain despite the assertion of Amiel, Ploquin, and Dixmier[11] that the magnetic results demonstrate the electrovalent

[12] Bleaney, *Rev. Mod. Phys.*, 1953, **25**, 161; Bleaney and Bowers, *Proc. Roy. Soc.*, 1952, *A*, **214**, 451.

[13] van Niekerk and Schoening, *Acta Cryst.*, 1953, **6**, 227.

[14] French and Lowry, *Proc. Roy. Soc.*, 1924, *A*, **106**, 489.

[15] Sidgwick, " Electronic Theory of Valency," Oxford Univ. Press, 1946, p. 254.

[16] Pauling, " Nature of the Chemical Bond," Oxford Univ. Press, 2nd edn., 1950, p. 190.

[17] Robertson and Woodward, *J.*, 1936, 1817.

[18] Corbridge and Cox, *J.*, 1956, 594.

[19] Bjerrum, *Acta Chem. Scand.*, 1948, **2**, 297.

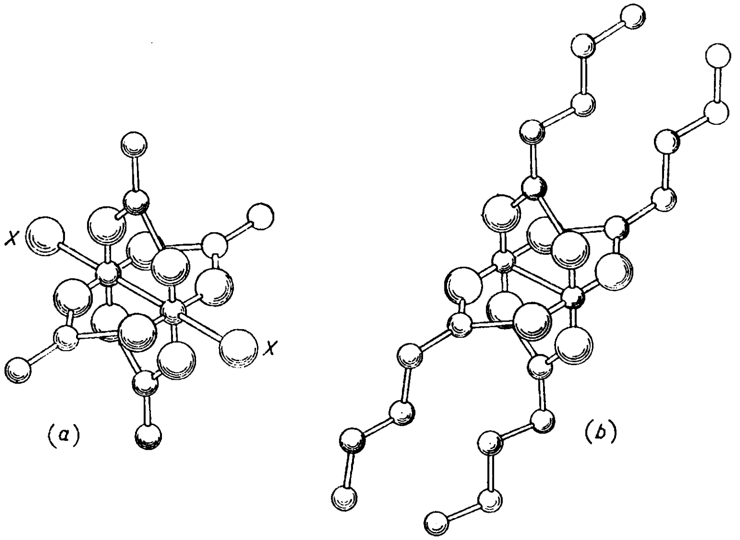
[20] Harris, Nyholm, and Stephenson, *Nature*, 1956, **177**, 1127.

character of these soaps. Magnetic results alone are unfortunately insufficient to distinguish between ionic nickel–oxygen bonds or covalent $4s4p^3$ bonds.[21] It should be noted, however, that irrespective of whether the metal–oxygen bonds are ionic or covalent the magnetic evidence indicates tetrahedral rather than coplanar co-ordination by the oxygen atoms.

Since the spin-only value of the magnetic moment of cobaltous compounds is 3·88 B.M. it is clear that in the laurate and stearate there is a substantial orbital contribution. While this is somewhat larger than that found in many quadrivalent cobalt complexes it cannot be regarded as incompatible with a tetrahedral configuration for the anhydrous compounds. The colours of the anhydrous and the dihydrated compounds are consistent with four and six co-ordinated cobalt respectively.

FIG. 4. (*a*) *The hydrated cupric acetate molecule. The two small central circles are copper atoms. The water molecules are labelled* (×). (*After van Niekerk and Schoening.*[13])

(*b*) *Proposed structure for copper laurate. The two small central circles are copper atoms. Only the first four carbon atoms of the hydrocarbon chains are shown.*



The magnetic behaviour of the ferric carboxylates, although conforming to a Curie–Weiss law in the range of temperature investigated (Fig. 3), is nevertheless unusual. The magnetic moment is much lower than that found in typical ferric compounds, while the magnetic field constant is exceptionally large (Table 1). Such characteristics recall the complex acetates, *e.g.*, $[Fe_3(CH_3{\cdot}CO_2)_6(OH)_2]NO_3,6H_2O$ studied by Welo[22] and later by Foex, Tsai, and Wucher.[23] As in the copper soaps, the decreased moment in ferric laurate may tentatively be attributed to exchange interaction between neighbouring iron atoms in the solid state. The calculated moment on the assumption of four unpaired electrons per iron atom is 4·90 B.M. (spin only) in fair agreement with the observed value for ferric stearate (4·84) and ferric laurate (5·13). Confirmation of this conclusion requires a full *X*-ray crystallographic examination. Attempts to obtain single crystals of ferric laurate suitable for such an examination have so far been unsuccessful.

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[21] Nyholm, *Quart. Rev.*, 1953, **7**, 377.
[22] Welo, *Phil. Mag.*, 1928, **6**, 481.
[23] Foex, Tsai, and Wucher, *Compt. rend.*, 1951, **233**, 1432.