**495.** *Magnetic Studies with Copper(II) Salts. Part II.*[1] *Anomalous Paramagnetism and δ-Bonding in Anhydrous and Hydrated Copper(II) n-Alkanoates.*

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The temperature variation of the magnetic susceptibility, between 90° and 400° K, is reported for copper(II) propionate, butyrate, laurate (C$_{12}$), stearate (C$_{18}$), and behenate (C$_{22}$). The variation is anomalous in that antiferromagnetic rather than Curie-law characteristics are observed. For all the compounds, whether hydrated or anhydrous, the susceptibility at first increases with rising temperature, passes through a maximum in the range $278° \pm 28°$ K, and then decreases. This behaviour so closely resembles that of copper acetate (cf. Part I [1]) that it is concluded that all the salts have fundamentally identical molecular structures, consisting of binuclear inner complexes $[Cu_2(R \cdot CO_2)_4(H_2O)_{0 \text{ or } 2}]$ involving a very weak covalent δ bond between the copper atoms.

The anomalous magnetic behaviour can be interpreted by assuming that within each binuclear molecule the two copper atoms interact strongly through exchange forces, forming a lower singlet (diamagnetic) and an upper triplet (paramagnetic) state. The experimental results for all five compounds closely fit an expression containing J, the singlet–triplet separation, which also measures twice the exchange energy associated with the copper–copper δ bond. For the present compounds, values of J lie in the narrow range 309 ± 31 cm.$^{-1}$, *i.e.*, approximately 1 kcal. mole^{-1}.

IN Part I [1] the anomalous magnetic behaviour of copper(II) acetate was discussed in the light of a recent crystal-structure determination by Niekerk and Schoening.[2] The unusually low magnetic moment was shown to arise from exchange demagnetisation between copper atoms in each binuclear $[Cu_2(CH_3 \cdot CO_2)_4(H_2O)_2]$ molecule, the exchange resulting from an unusual type of overlap of atomic orbitals, namely, lateral overlap of two $3d_{x^2-y^2}$ orbitals so oriented that their lobar planes are parallel. Such overlap produces a covalent δ bond between copper atoms, copper acetate being the first compound in

(I)

(II)

R = *n*-alkyl
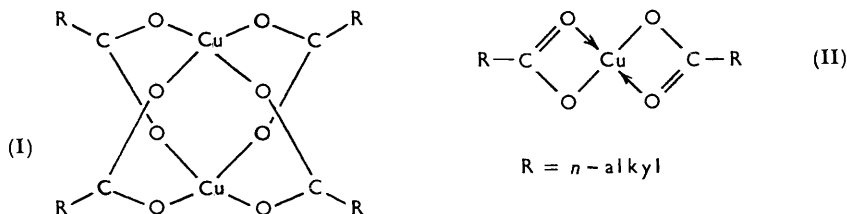
which this type of bond has been suggested as the sole covalent bond between two atoms.

It seemed probable that further examples of the binuclear configuration and δ-bonding would be found among the higher homologues of copper(II) alkanoates, since the dimensions of the potential bridging carboxylate group are not likely to depend significantly on the length of the attached alkyl chain. Furthermore, construction of Catalin molecular models clearly demonstrated that the *n*-alkyl chains can be easily accommodated around the periphery of the molecule without sterically hindering formation of the binuclear $[Cu_2(R \cdot CO_2)_4]$ molecule illustrated in structure (I).

Magnetic measurements, over a range of temperature, provide a particularly sensitive and convenient method for testing this hypothesis. If the salts adopt the proposed binuclear configuration their magnetic moments will fall to approximately the value

[1] Part I, Figgis and Martin, *J.*, 1956, 3837.
[2] Niekerk and Schoening, *Acta Cryst.*, 1953, **6**, 227.

observed for copper acetate. Further, the susceptibility–temperature curves will exhibit antiferromagnetic rather than Curie-law characteristics, closely matching the curve of the acetate. Accordingly, the magnetic susceptibilities of the copper(II) salts of propionic, butyric, lauric, stearic, and behenic acids have been measured between 90° and 400° K. The propionate and butyrate were examined both in anhydrous and hydrated forms, to established whether dehydration modifies the structure. The three higher homologues are anhydrous.

EXPERIMENTAL

Materials.—Copper(II) propionate and butyrate were prepared from excess of the diluted acid and E. Merck's " purissimus " grade copper carbonate. After effervescence had ceased the solutions were filtered and allowed to crystallize. Recrystallisation of the propionate from hot dilute propionic acid yielded dark green crystals of the monohydrate (Found : C, 31·6; H, 5·3; Cu, 27·7. Calc. for $CuC_6H_{10}O_4,H_2O$: C, 31·6; H, 5·3; Cu, 27·9%). Recrystallisation of the butyrate from 1 : 1 butyric acid–water yielded green crystals of the monohydrate (Found : C, 37·8; H, 6·2; Cu, 24·8. Calc. for $CuC_8H_{14}O_4,H_2O$: C, 37·6; H, 6·3; Cu, 24·8%). The anhydrous propionate and butyrate were prepared from the hydrated salts by dehydration at 100° c over phosphoric oxide in a vacuum pistol (Found : C, 34·2; H, 4·7; Cu, 30·3. Calc. for $CuC_6H_{10}O_4$: C, 34·4; H, 4·8; Cu, 30·3%. Found : C, 39·5; H, 5·8; Cu, 26·8. Calc. for $CuC_8H_{14}O_4$: C, 40·4; H, 5·95; Cu, 26·7%).

Copper(II) laurate, stearate, and behenate were prepared by metathesis of alcoholic copper(II) acetate with an alcoholic solution of the appropriate acid. The resulting precipitates were washed free from excess of acid and recrystallised from dioxan. Excess of solvent was removed at 100° over phosphoric oxide in a vacuum pistol, leaving as pale blue powders the laurate (Found : C, 62·0; H, 9·9; Cu, 13·8. Calc. for $CuC_{24}H_{46}O_4$: C, 62·4; H, 10·1; Cu, 13·8%), stearate (Found : C, 67·6; H, 11·1; Cu, 10·1. Calc. for $CuC_{36}H_{70}O_4$: C, 68·6; H, 11·2; Cu, 10·1%) and behenate (Found : C, 71·0; H, 11·6; Cu, 8·46. Calc. for $CuC_{44}H_{86}O_4$: C, 71·1; H, 11·7; Cu, 8·56%). Copper was determined by electrolytic deposition on a platinum electrode.

Magnetic Measurements.—The magnetic susceptibilities of the powdered copper alkanoates were determined at room temperature by the Gouy method with a field strength of *ca.* 5000 gauss. The gram susceptibility, χ_g, the molar susceptibility, χ_M (corrected for the underlying diamagnetism of all atoms, Δ), and the magnetic moment, μ, calculated from the expression $\mu = 2\cdot839[(\chi_M - N\alpha)T]^{0\cdot5}$, are listed in Table 1. The diamagnetic correction, Δ, was measured directly on samples of the free acids, and it includes the values -13×10^{-6} for water and -17×10^{-6} for copper. A value $N\alpha = 60 \times 10^{-6}$ has been used to correct for the temperature-independent paramagnetism of bivalent copper. Copper sulphate pentahydrate was used as a calibrant for these measurements. Room-temperature data for copper(II) formate, acetate, and valerate have also been included in Table 1 for comparison.

TABLE 1. *Room-temperature magnetic data for copper*(II) *n-alkanoates.*

Compound	Temp. (°c)	$10^6\chi_g$	$-10^6\Delta$	$10^6\chi_M$	μ (B.M.)
$CuSO_4,5H_2O$	20·0	5·90	122	1595	1·91
$Cu(H\cdot CO_2)_2$	16·2	7·33	48	1174	1·61
$Cu(H\cdot CO_2)_2,4H_2O$	15·5	4·95	100	1218	1·64
$Cu(CH_3\cdot CO_2)_2$	22·2	4·39	72	869	1·39
$Cu(CH_3\cdot CO_2)_2,H_2O$	21·0	4·03	85	889	1·40
$Cu(C_2H_5\cdot CO_2)_2$	15·7	3·61	96	854	1·36
$Cu(C_2H_5\cdot CO_2)_2,H_2O$	17·5	3·47	109	899	1·40
$Cu(C_3H_7\cdot CO_2)_2$	17·2	3·14	120	866	1·37
$Cu(C_3H_7\cdot CO_2)_2,H_2O$	23·7	2·67	133	816	1·35
$Cu(C_4H_9\cdot CO_2)_2$	19·8	2·84	144	899	1·41
$Cu(C_{11}H_{23}\cdot CO_2)_2$	20·4	1·32	280	890	1·40
$Cu(C_{17}H_{35}\cdot CO_2)_2$	17·2	0·842	315	846	1·36
$Cu(C_{21}H_{43}\cdot CO_2)_2$	17·5	0·708	376	900	1·40

The temperature variation of the magnetic susceptibility was determined between 90° and 400° K, as described in Part I, for the propionate, butyrate, laurate, stearate, and behenate. Each sample was studied at two different field strengths between 5000 and 8000 gauss, the

TABLE 2. *Experimental gram and molar susceptibilities (c.g.s., e.m.u.) and magnetic moments* (B.M.), *at various absolute temperatures.*

Anhydrous copper propionate

Temp. (K) ...	99·0°	111·2°	125·2°	149·5°	175·2°	209·8°	225·1°	248·9°	270·0°	274·5°	298·0°	326·0°	345·3°
$10^6\chi_g$	0·741	1·09	1·50	2·29	2·83	3·30	3·44	3·61	3·63	3·61	3·53	3·60	3·42
$10^6\chi_M$	251	324	411	576	690	788	817	853	857	853	836	850	813
μ (B.M.) ...	0·390	0·496	0·595	0·789	0·943	1·11	1·17	1·26	1·32	1·33	1·40	1·44	1·45

Copper propionate monohydrate

Temp. (K) ...	97·4°	109·7°	124·8°	150·0°	169·8°	206·5°	228·8°	254·0°	270·0°	292·1°	313·3°	351·8°	374·9°
$10^6\chi_g$	0·638	1·15	1·63	2·33	2·70	3·12	3·32	3·47	3·48	3·47	3·46	3·33	3·30
$10^6\chi_M$	254	371	480	640	724	819	865	899	901	899	897	867	860
μ (B.M.) ...	0·390	0·525	0·650	0·838	0·954	1·12	1·22	1·31	1·36	1·41	1·45	1·51	1·56

Anhydrous copper butyrate

Temp. (K) ...	101·2°	111·1°	125·3°	151·5°	179·8°	212·8°	225·2°	254·7°	274·8°	289·9°	308·6°	335·0°	386·2°
$10^6\chi_g$	0·447	0·774	1·16	1·84	2·41	2·84	2·94	3·10	3·14	3·14	3·12	3·12	2·92
$10^6\chi_M$	226	304	396	558	693	795	819	857	867	867	862	862	814
μ (B.M.) ...	0·368	0·468	0·583	0·780	0·958	1·12	1·17	1·29	1·34	1·37	1·41	1·47	1·53

Copper butyrate monohydrate

Temp. (K) ...	97·8°	121·3°	144·5°	171·2°	196·4°	220·8°	246·0°	276·5°	291·2°	298·0°	305·0°	319·2°	344·3°
$10^6\chi_g$	0·294	0·856	1·36	1·87	2·19	2·42	2·56	2·65	2·66	2·68	2·68	2·65	2·60
$10^6\chi_M$	208	352	481	611	693	751	788	811	813	819	819	811	798
μ (B.M.) ...	0·342	0·534	0·700	0·872	1·00	1·11	1·20	1·29	1·33	1·35	1·37	1·39	1·43

Copper laurate

Temp. (K) ...	97·1°	111·5°	122·9°	148·5°	173·0°	224·0°	245·4°	250·0°	275·3°	301·0°	351·2°
$10^6\chi_g$	0·228	0·483	0·668	0·985	1·12	1·33	1·36	1·36	1·33	1·28	1·22
$10^6\chi_M$	385	503	589	735	798	895	909	909	895	871	845
μ (B.M.) ...	0·504	0·631	0·724	0·899	1·02	1·23	1·30	1·31	1·36	1·40	1·49

Copper stearate

Temp. (K) ...	99·3°	111·2°	124·1°	144·3°	165·3°	203·8°	224·4°	249·4°	275·0°	299·7°	323·0°	352·2°
$10^6\chi_g$	0·163	0·329	0·484	0·585	0·690	0·833	0·863	0·877	0·867	0·821	0·786	0·738

structure should be associated with abnormally low susceptibilities. Obviously, chelation alone cannot quench the paramagnetism of these compounds.

Gilmour and Pink [5] have explained the anomalous temperature-dependence of the susceptibility which they observed for copper(II) laurate (cf. Fig. 1) in terms of Amiel's covalent chelate structure (II). They proposed a crystallographic stacking of these planar molecules to form planes of copper atoms separated by the fatty acid groups extending in both directions. Intermolecular exchange interactions of an antiferromagnetic nature could then take place between the copper atoms in any plane, and lead to both the diminished susceptibility and its anomalous temperature-dependence.

FIG. 1. *Experimental and calculated magnetic susceptibilities and moments of anhydrous cupric laurate.*
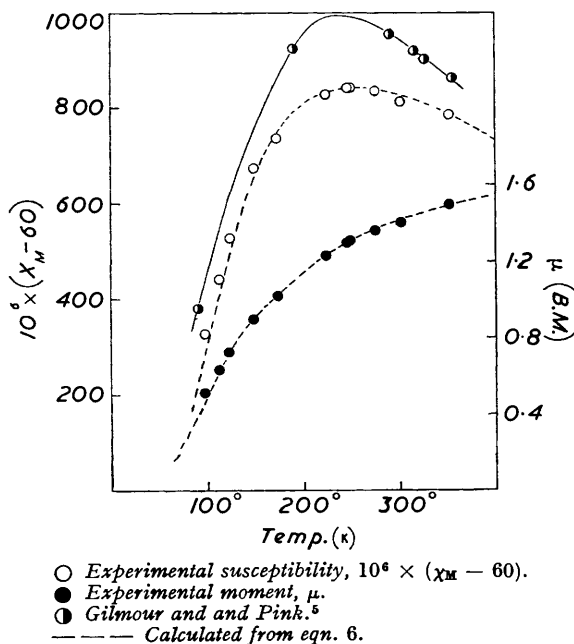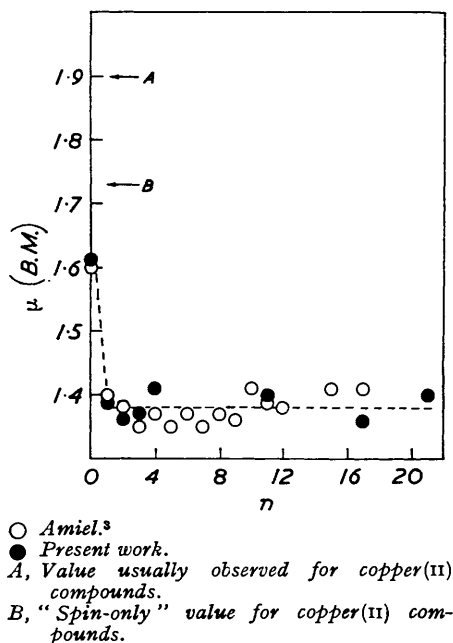
FIG. 2. *Experimental magnetic moments, μ, of anhydrous cupric n-alkanoates as a function of chain length $\{n$ in $Cu(H \cdot [CH_2]_n \cdot CO_2)_2\}$.*

O *Experimental susceptibility,* $10^6 \times (\chi_M - 60)$.
● *Experimental moment,* μ.
◑ *Gilmour and and Pink.*[5]
— — — *Calculated from eqn.* 6.

O *Amiel.*[3]
● *Present work.*
A, *Value usually observed for copper*(II) *compounds.*
B, *"Spin-only" value for copper*(II) *compounds.*

If this hypothesis is correct, the magnetic moments of copper(II) *n*-alkanoates should vary with increasing length of the *n*-alkyl chains, steric hindrance between adjacent chains leading to greater separation, and consequently to smaller intermolecular exchange interactions, between contiguous copper atoms. That this is not so can be seen from the variation of magnetic moment with chain length, illustrated in Fig. 2. A striking feature of the curve is the uniform quenching of magnetic moment, the values for all anhydrous alkanoates, with the exception of the formate, lying in the narrow region 1·38 ± 0·03 B.M.

(III)
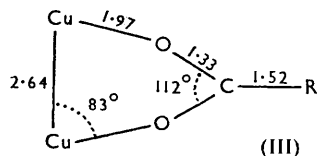
The marked independence of magnetic moment on length of the *n*-alkyl chain suggests that the magnetic anomaly has the same origin in all copper alkanoates between acetate and behenate, and this in turn implies that their molecular structures are closely similar. A binuclear structure has already been unambiguously established for copper acetate by Niekerk and Schoening,[2] and it is therefore suggested that all the higher homologues should be similarly formulated as the carboxylate-bridged binuclear inner complexes,

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

$[Cu_2(R \cdot CO_2)_4(H_2O)_{0 \text{ or } 2}]$, shown in (I). The five-membered Cu–O–C–O–Cu rings, illustrated with dimensions (Å) from ref. 2 for R = Me in (III), would be expected on steric grounds to be more stable than the four-membered Cu–O–C–O rings suggested by Amiel. Furthermore, since the dimensions of a carboxylate bridge are unlikely to be influenced by the length of the attached *n*-alkyl group, the copper–copper distance will be maintained close to the value 2·64 Å as in the acetate. It follows that the copper–copper intramolecular exchange interactions will also show little variation with chain length, and hence the magnetic properties of all homologues will be closely similar.

The susceptibility–temperature curves for these compounds are, in fact, remarkably similar. For each compound the susceptibility rises steeply from zero with increasing temperature, passes through a broad maximum in the region 278° ± 28° K, and then decreases with further increase in temperature (cf. Fig. 1). This characteristic shape of the χ–T curves reflects the thermal distribution of binuclear copper *n*-alkanoate molecules between a lower singlet (diamagnetic) and an upper triplet (paramagnetic) level as described in Part I. At 0° K, the binuclear molecules are in singlet states ($S = 0$), and make no contribution to the paramagnetic susceptibility. As the temperature is raised, the triplet level ($S = 1$) becomes increasingly populated at the expense of the singlet level and the susceptibility rapidly increases. In the region of 278° K Curie-law behaviour becomes dominant, the susceptibility passing through a maximum and then decreasing as the temperature is further raised.

This behaviour is remarkably well represented by the general expression * derived in Part I :

$$\chi_M = \frac{g^2 N \beta^2}{3kT} [1 + 1/3 \exp (J/kT)]^{-1} + N\alpha \quad . \quad . \quad . \quad . \quad (1)$$

where χ_M is the magnetic susceptibility per mole of copper atoms, g is the spectroscopic splitting factor, β is the Bohr magneton, J is the energy interval between the singlet and triplet levels, and $N\alpha$ is a small temperature-independent paramagnetic contribution to the susceptibility. If, to a first approximation, J is assumed to be temperature-independent, differentiation of eqn. (1) leads to the result $J = 1·6kT_c$, where T_c is the temperature at which the susceptibility attains its maximum value. For the present compounds, the splitting factor, g, has been estimated by substituting the experimental value of the susceptibility, at the arbitrary temperature T_c, into eqn. (1). The resulting susceptibility equations (curve in Fig. 1) are :

$$Cu(C_2H_5 \cdot CO_2)_2 : \qquad 10^6 \times \chi_M = (0·571/T)[1 + 1/3 \exp (432/T)]^{-1} + 60 \qquad (2)$$

$$Cu(C_2H_5 \cdot CO_2)_2,H_2O : \quad 10^6 \times \chi_M = (0·602/T)[1 + 1/3 \exp (432/T)]^{-1} + 60 \qquad (3)$$

$$Cu(C_3H_7 \cdot CO_2)_2 : \qquad 10^6 \times \chi_M = (0·621/T)[1 + 1/3 \exp (464/T)]^{-1} + 60 \qquad (4)$$

$$Cu(C_3H_7 \cdot CO_2)_2,H_2O : \quad 10^6 \times \chi_M = (0·614/T)[1 + 1/3 \exp (488/T)]^{-1} + 60 \qquad (5)$$

$$Cu(C_{11}H_{23} \cdot CO_2)_2 : \qquad 10^6 \times \chi_M = (0·563/T)[1 + 1/3 \exp (400/T)]^{-1} + 60 \qquad (6)$$

$$Cu(C_{17}H_{35} \cdot CO_2)_2 : \qquad 10^6 \times \chi_M = (0·536/T)[1 + 1/3 \exp (400/T)]^{-1} + 60 \qquad (7)$$

$$Cu(C_{21}H_{43} \cdot CO_2)_2 : \qquad 10^6 \times \chi_M = (0·605/T)[1 + 1/3 \exp (432/T)]^{-1} + 60 \qquad (8)$$

The agreement between the experimental results and these equations is unexpectedly good in view of the assumption of a temperature-independent value of J, and other assumptions made in the derivation of equation (1) (cf. Part I).

* In Part I, in equations (1) and (2), the symbol N should be replaced by $N/2$, *i.e.*, the number of very weak covalent copper–copper bonds formed by N copper atoms.

The close similarity in the magnetic properties of these compounds and those of binuclear copper acetate is further emphasised by the comparison of corresponding values for T_c, g, and J given in Table 3.

TABLE 3.   *Comparison of T_c, g, and J for copper(ii) n-alkanoates.*

Compound	$T_c°$, K	g	J cm.$^{-1}$	J kcal. mole^{-1}
$Cu(CH_3 \cdot CO_2)_2$	270	2·17	300	0·86
$Cu(CH_3 \cdot CO_2)_2, H_2O$	255	2·13	284	0·82
$Cu(C_2H_5 \cdot CO_2)_2$	270	2·14	300	0·86
$Cu(C_2H_5 \cdot CO_2)_2, H_2O$	270	2·20	300	0·86
$Cu(C_3H_7 \cdot CO_2)_2$	290	2·23	322	0·92
$Cu(C_3H_7 \cdot CO_2)_2, H_2O$	305	2·22	339	0·97
$Cu(C_{11}H_{23}CO_2)_2$	250	2·12	278	0·79
$Cu(C_{17}H_{35}CO_2)_2$	250	2·07	278	0·79
$Cu(C_{21}H_{43} \cdot CO_2)_2$	270	2·20	302	0·86

For all the compounds, including the acetate, these quantities lie in the following narrow ranges : $T_c = 278° \pm 28°$ K; $g = 2·15 \pm 0·08$; $J = 309 \pm 31$ cm.$^{-1}$ $= 0·88 \pm 0·09$ kcal. mole^{-1}. It must be stressed that these ranges include appreciable experimental scatter, first on account of the inherent difficulty in reproducing the packing of powdered samples in Gouy tubes, and secondly owing to the difficulty in selecting a value for T_c from such broad maxima as are exhibited by the χ–T curves. Even so, these results amply confirm that the length of the *n*-alkyl chain has no significant effect on the magnetic properties of these compounds. It is concluded that while only *X*-ray analysis can unequivocally establish the structure of these salts, the remarkable uniformity in their magnetic properties leaves little reason to doubt that their molecular structures are fundamentally identical and similar to that of copper acetate.

Although supporting crystallographic data are, at present, not available for alkanoates higher than the acetate, other evidence favouring a binuclear structure for these compounds has recently been published. For example, crystalline copper(ii) propionate displays anomalous paramagnetic absorption of microwaves identical with that of copper acetate.[6] Furthermore, the polarised absorption spectra of these two compounds, in the visible and near-ultraviolet regions, are closely similar, each exhibiting a new kind of absorption band at 3750 Å not previously observed in the spectra of copper(ii) compounds.[7] This band has been tentatively ascribed [7] to a direct linkage between copper atoms in these compounds, and in conjunction with the present data, indicates that the propionate, at least, adopts a binuclear configuration.

It was suggested in Part I that the small increase in J of 16 cm.$^{-1}$ observed on dehydration of copper acetate might be real, reflecting an increased $3d_\delta$–$3d_\delta$ overlap resulting from the removal of the two terminal water molecules. This possibility is not confirmed by the data for the propionate and butyrate in Table 3, the experimental scatter of J values over the range, 309 ± 31 cm.$^{-1}$, being too great to permit the detection of an effect of this small order of magnitude.

The magnetic properties of copper(ii) formate remain, at present, unexplained. The room-temperature moment of the powdered hydrated or anhydrous salt, $\mu \sim 1·6$ B.M., is intermediate between the value $\mu = 1·38$ B.M. consistently observed for its homologues and the value $\mu = 1·9$ B.M. observed for magnetically dilute copper(ii) compounds. This partial reduction in moment cannot be explained by intramolecular exchange forces of the present type, for a crystal-structure determination [8] of the tetrahydrate has shown that each copper atom is surrounded by four oxygen atoms from four different formate groups, in an approximately square configuration, and by two water molecules at a greater

[6] Abe, *Phys. Rev.*, 1953, **92**, 1572.
[7] Tsuchida and Yamada, *Nature*, 1955, **176**, 1171.
[8] Kiriyama, Ibamoto, and Matsuo, *Acta Cryst.*, 1954, **7**, 482.

distance to complete a distorted CuO_6 octahedron. In aqueous solution [9] the moment jumps from 1·6 to 1·9 B.M., which suggests that strong intermolecular exchange forces are present in the crystalline compound. This conclusion is supported by the paramagnetic resonance absorption of microwaves by the tetrahydrate [10] which, while displaying no marked anomalies, does indicate the presence of appreciable exchange interactions. Their existence is also reflected in a large value of the Weiss constant, $\theta = -150°$, for the tetrahydrate.[11] These results will be reported later.

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[9] Martin and Whitley, unpublished experiments.
[10] Lancaster and Gordy, *J. Chem. Phys.*, 1951, **19**, 1181.
[11] Martin and Waterman, unpublished experiments.