269. *Magnetic Studies with Copper*(II) *Salts. Part IV.*[1] *Remarkable Magnetic Behaviour of Copper*(II) *Formate and its Hydrates.*

By R. L. MARTIN and HANNEKE WATERMAN.

Four crystalline derivatives of copper(II) formate have been isolated from aqueous formic acid solutions. They are the known tetrahydrate, the known dihydrate, a royal-blue anhydrous compound, and a tetra-formic acid analogue of the tetrahydrate. Dehydration of the di- and the tetra-hydrate yields two further forms of the anhydrous compound. These modifications have been characterised by *X*-ray diffraction and room-temperature magnetic measurements on powders. Spectrophotometry indicates the ephemeral existence of a blue-green binuclear derivative, $[Cu_2(H{\cdot}CO_2)_4]$, in formic acid solution, which however could not be isolated.

The temperature variation of the magnetic susceptibility has been determined between 80° and 360° K for each of the stable compounds. The dihydrate and the royal-blue anhydrous formate obey simple Curie laws, and have normal moments (*ca.* 1·9 B.M.) which are nearly independent of temperature. The remaining compounds have sub-normal moments which decrease with decreasing temperature. However, their susceptibilities can be fitted to Curie–Weiss laws with large negative values of the Weiss constant ($\theta \simeq -175°$). The most highly hydrated formate, $Cu(H{\cdot}CO_2)_2,4H_2O$ is magnetically concentrated, in marked contrast to the magnetically dilute dihydrate and royal-blue anhydrous formate. The origin of this anomalous magnetic behaviour is sought in terms of its known crystal structure, and a consideration of the potential bonding modes of the formate ion. It is suggested that antiferromagnetic exchange demagnetisation takes place *via* a superexchange mechanism which is novel in that formate ion is functioning as a polyatomic counterpart of monatomic anions, such as fluoride and oxide ions, customarily associated with antiferromagnetism.

Our failure to isolate copper formate in the binuclear form is discussed, with reference to possible factors which may influence the adoption of this particular structure by copper *n*-alkanoates.

BINUCLEAR copper *n*-alkanoates are a unique group of compounds which retain much of their spin paramagnetism in the presence of a direct copper–copper bond,[2] which most probably arises from a lateral overlap of $3d_\delta$-orbitals centred on each copper atom.[3] This

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[1] Part III, Martin and Whitley, *J.*, 1958, 1394.
[2] Martin and Waterman, *J.*, 1957, 2545.
[3] Figgis and Martin, *J.*, 1956, 3837.

situation offers an unusual opportunity for direct experimental measurement of the exchange energy associated with a single covalent bond, and values of the order of 1 kcal. mole^{-1} have been obtained.[2,4] In the homologous series of *n*-alkanoic acids, the first member, formic acid, is characterised by unconformable behaviour, so it is of interest to ascertain whether its cupric derivative will inherit the nature of the parent acid.

The literature contains only limited information on cupric formate, but it is well established that it crystallises as a tetrahydrate from aqueous solution, and that a dihydrate can be prepared.

Early attempts (1931) to examine the crystal structures of the two hydrates by *X*-ray methods were made by Kabraji [5] and by Prasad and Mapara.[6] More recently Kiriyama, Ibamoto, and Matsuo published a complete structure for the tetrahydrate on the basis of a single-crystal *X*-ray analysis.[7] This reveals a layer-type structure with two non-co-ordinated water molecules per copper atom hydrogen-bonded between adjacent layers. The basic structural unit (I) is an elongated CuO_6 octahedron, each copper atom being surrounded by four oxygen atoms from four different formate groups in an approximately square configuration (Cu–O = 2·00 and 2·01 Å), and two *trans*-co-ordinated water molecules at a greater distance (2·36 Å) to complete a tetragonally distorted octahedron. Obviously the acetate type binuclear structure is not favoured.

Some ambiguity exists as to the exact value of the room-temperature magnetic moment of copper formate. Bhatnagar *et al.* report [8] the value * $\mu = 1{\cdot}77$ B.M. at 290° K for the anhydrous salt, whereas Amiel [9] quotes $\mu = 1{\cdot}67$ B.M. for the tetrahydrate and $\mu = 1{\cdot}59$ B.M. for the anhydrous compound at comparable temperatures. Our own results [2] substantiate Amiel's observations.

A variety of absorption spectra for copper(II) formate indicate that the binuclear acetate-type structure is not naturally adopted by the formate, either in anhydrous or hydrated forms. Thus paramagnetic absorption of microwaves by both forms produces spectra quite different from those characterising the heavier homologues.[10-13] Similarly, all copper(II) alkanoates except the formate show only one absorption band (at about 1600 cm.$^{-1}$) in the infrared region [14] between 1500 and 2000 cm.$^{-1}$. Again the visible and ultraviolet spectra of the binuclear homologues are characterised by absorption at 3750 Å, which is absent from the spectra of both the aqueous [1] and the crystalline [15] tetrahydrate. Clearly, those factors which favour the binuclear structure for the heavier copper alkanoates are not effective in causing its adoption by copper formate.

The present work was undertaken to elucidate the nature of these factors. First, we attempted the preparation of binuclear copper(II) formate in the hope of comparing its properties with those of the higher homologues. Secondly, we wished to measure the temperature dependence of the susceptibility for the different modifications of copper formate, and to ascertain the origin of the sub-normal room temperature magnetic moment of the tetrahydrate.

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* These values are recalculated to match our own data, by including a temperature-independent paramagnetic correction for Cu^{2+} equal to 60×10^{-6} c.g.s., e.m.u. The magnetic moment is then $\mu = 2{\cdot}839[(\chi_M - 60)T]^{\frac{1}{2}}$.

[4] Bleaney and Bowers, *Proc. Roy. Soc.*, 1952, *A*, **214**, 451.
[5] Kabraji, *Ind. J. Phys.*, 1931, **6**, 81, 115.
[6] Prasad and Mapara, *idem*, 1931, **6**, 41.
[7] Kiriyama, Ibamoto, and Matsuo, *Acta Cryst.*, 1954, **7**, 482.
[8] Bhatnagar, Lessheim, and Khanna, *J. Ind. Chem. Soc.*, 1937, **14**, 445.
[9] Amiel, *Compt. rend.*, 1938, **207**, 1097.
[10] Lancaster and Gordy, *J. Chem. Phys.*, 1951, **19**, 1181.
[11] Abe, *Phys. Rev.*, 1953, **92**, 1572.
[12] Uebersfeld, *Compt. rend.*, 1953, **236**, 1645.
[13] Sundaramma, *Proc. Ind. Acad. Sci.*, 1955, *A*, **42**, 292.
[14] Tsuchida, Yamada, and Nakamura, *Nature*, 1956, **178**, 1192.
[15] Tsuchida and Yamada, *Nature*, 1955, **176** 1171.

EXPERIMENTAL

Materials.—(a) *Solutions of copper carbonate in formic acid.* If copper carbonate is treated slowly without agitation with a large excess of 90% formic acid, a blue-green solution is obtained, the colour being like that of copper(II) acetate. After a few minutes, the solution becomes blue and crystals separate which vitiate magnetic measurements.

The visible and ultraviolet spectrum of the blue-green solution, recorded between 3250 and 8000 Å with a Cary recording spectrophotometer (Model 11 MS–50), is in Fig. 1 (curve *A*) together with that of copper formate in 35% formic acid–acetone (curve *B*). All attempts to crystallise or precipitate the blue-green compound failed.

(b) *Copper formate tetrahydrate.* The preparation of this compound has been described.[1] It crystallises from dilute aqueous solutions of formic acid in large, light-blue prisms which show excellent cleavage.

FIG. 1. *Visible spectra of copper formate: A, in 90% formic acid–water; B, in 35% formic acid–acetone.*

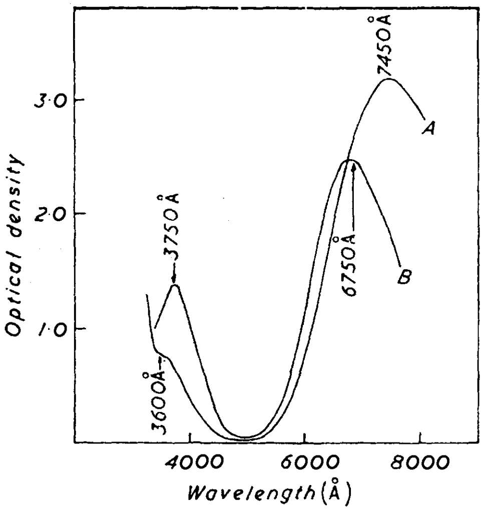
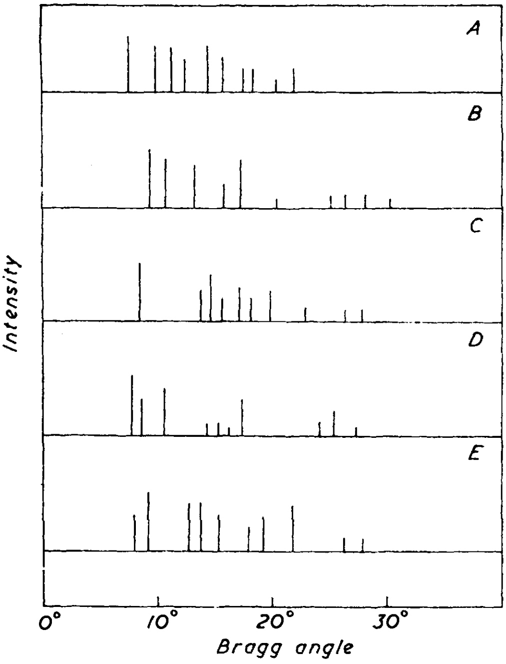


FIG. 2. X-*Ray diffraction of A, copper formate tetrahydrate; B, copper formate dihydrate; C, anhydrous copper formate from the tetrahydrate; D, anhydrous copper formate from the dihydrate; E, royal-blue anhydrous copper formate.*



(c) *Copper formate dihydrate.* This was prepared by rapidly filtering the blue-green solution described in (a) into a large volume of ether (Found: C, 13·0; H, 3·20; Cu, 33·7. Calc. for $CuC_2H_2O_4,2H_2O$: C, 12·7; H, 3·17; Cu, 33·5%). The very pale blue needles of the dihydrate lose water of crystallisation after standing for some hours in air.

(d) *Anhydrous copper formate.* A powder-blue form was readily produced by dehydrating the tetrahydrate for several days over calcium chloride at reduced pressure. As the water of hydration is removed, the crystals become opaque and their faces lustrous, but the external crystal shape is retained (Found: C, 15·6; H, 1·25; Cu, 41·3. Calc. for $CuC_2H_2O_4$: C, 15·6; H, 1·31; Cu, 41·4%).

A pale turquoise modification was obtained by heating the dihydrate at 100° under vacuum over phosphoric oxide. The product again retained the external crystal shape and readily absorbed moisture on exposure to air (Found: C, 15·6; H, 1·51; Cu, 40·9%).

A royal-blue modification, crystallising in small, well-defined rods, was produced when the blue-green solution described in (a) was heated at 100° for several hours. It was formed more slowly when the blue-green solution was allowed to stand for several days at room temperature (Found: C, 15·8; H, 1·20; Cu, 41·5%).

(e) *Copper formate–tetraformic acid.* Pale blue plates of copper formate, probably containing four molecules of formic acid, were the initial product deposited from the unstable blue-green solution discussed in (a) when it was kept at room temperature. [After standing for a much longer period, the crystals lose their co-ordinated formic acid and are converted into the royal-blue crystalline anhydrous compound described in (d).] These crystals rapidly decompose as their mother liquor evaporates. Accordingly, the crystals were analysed while still moist (Found: Cu, 17·6. Calc. for $CuC_2H_2O_4,4CH_2O_2$: Cu, 18·8%).

X-Ray Diffraction Photographs.—These were taken of powders of the various modifications of copper formate and its hydrates, a Philips unit type PW1010 and an 11·5 cm. diam. camera being used. The strongest lines are illustrated in Fig. 2, their visually estimated intensities being plotted as a function of Bragg angle. Clearly the five modifications differ fundamentally in their structures.

Magnetic Measurements.—Apparatus and methods described in earlier papers were used. Diamagnetic corrections both for attached groups and for cupric ion were made, and, in

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

Compound	Temp.	$10^6\chi_g$	$-10^6\Delta$	$10^6\chi_M$	μ (B.M.).
$CuSO_4,5H_2O$ (calibrant)	20·0°	5·90	122	1595	1·91
$Cu(H\cdot CO_2)_2$ (royal-blue)	22·6	9·88	48	1566	1·90
$Cu(H\cdot CO_2)_2,2H_2O$	18·0	8·00	74	1591	1·90
$Cu(H\cdot CO_2)_2$ (turquoise)	18·0	8·52	48	1357	1·75
$Cu(H\cdot CO_2)_2,4H_2O$	15·5	4·95	100	1218	1·64
$Cu(H\cdot CO_2)_2,4H\cdot CO_2H$	17·1	2·87	138	1173	1·61
$Cu(H\cdot CO_2)_2$ (blue)	16·2	7·33	48	1174	1·61

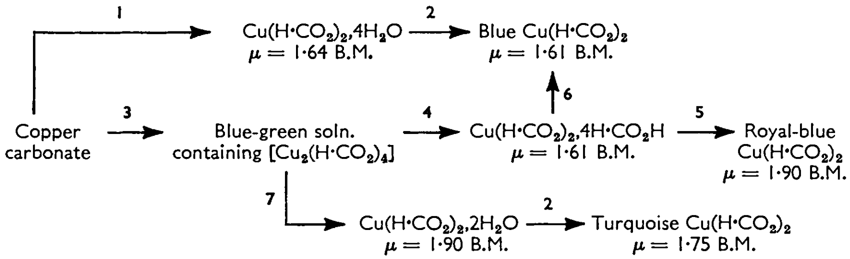
TABLE 2. *Experimental gram and molar susceptibilities* (*c.g.s., e.m.u.*) *and magnetic moments* (*B.M.*), *at various absolute temperatures.*

Temp. (°K)	$10^6\chi_g$	$10^6\chi_M$	μ (B.M.)	Temp. (°K)	$10^6\chi_g$	$10^6\chi_M$	μ (B.M.)
Anhydrous copper(II) *formate: blue modification from tetrahydrate*							
82·7	12·0	1897	1·11	184·3	9·11	1448	1·44
89·5	11·9	1877	1·15	212·8	8·50	1353	1·49
95·2	11·8	1867	1·18	245·0	7·90	1261	1·54
101·5	11·8	1853	1·21	272·2	7·39	1182	1·57
108·7	11·5	1816	1·24	291·8	7·10	1139	1·60
125·8	11·0	1743	1·31	304·5	6·94	1113	1·61
154·1	10·2	1618	1·39	333·6	6·48	1043	1·63
Anhydrous copper(II) *formate: turquoise modification from dihydrate*							
97·3	14·8	2322	1·33	227·5	9·98	1581	1·67
111·4	13·9	2183	1·38	258·6	9·34	1482	1·72
130·4	13·1	2060	1·45	290·5	8·48	1350	1·74
146·7	12·5	1968	1·50	314·5	8·25	1316	1·78
173·2	11·6	1830	1·57	338·5	7·83	1251	1·80
197·8	10·6	1677	1·61	359·2	7·41	1187	1·81
Anhydrous copper(II) *formate: royal-blue crystalline modification*							
100·5	31·8	4932	1·99	243·6	12·0	1891	1·90
121·0	25·9	4026	1·97	290·5	9·99	1583	1·89
152·3	19·7	3074	1·92	295·6	9·88	1564	1·89
177·3	16·7	2613	1·91	329·0	8·64	1375	1·87
199·4	14·9	2337	1·91				
Copper(II) *formate tetrahydrate*							
87·5	9·13	2165	1·22	204·5	6·07	1473	1·53
101·0	8·57	2038	1·27	233·0	5·61	1371	1·57
115·5	8·12	1937	1·32	263·3	5·13	1260	1·60
143·4	7·33	1758	1·40	288·5	4·95	1220	1·64
172·8	6·75	1627	1·48	296·4	4·89	1207	1·66
Copper(II) *formate dihydrate*							
102·5	23·6	4539	1·92	207·9	11·2	2197	1·89
110·6	21·6	4171	1·91	229·2	9·99	1968	1·88
129·7	18·5	3583	1·92	249·5	9·26	1820	1·88
159·9	14·7	2861	1·90	266·5	8·61	1706	1·88
191·1	12·3	2406	1·90	291·5	8·00	1591	1·90

addition, a correction of 60×10^{-6} c.g.s., e.m.u. for the temperature-independent paramagnetism associated with cupric ion. The room-temperature moments are collected in Table 1, the measurements with copper formate–tetraformic acid being on crystals moistened in the minimum quantity of their mother liquor. The dependence of susceptibility and magnetic moment upon temperature (80—360° K) is listed in Table 2. Each sample was studied at two different field strengths between 5000 and 8000 gauss, the mean of the two susceptibilities being taken.

DISCUSSION

This work reveals that, apart from the tetrahydrate which is well known, several forms of copper(II) formate can be prepared from aqueous formic acid, depending upon the conditions of their isolation. Their interrelation is conveniently summarised by the annexed scheme. When copper carbonate is dissolved in concentrated formic acid the resulting solution has a blue-green colour, reminiscent of the colour of binuclear copper acetate. This colour persists for several minutes, then changes to blue, and pale blue square plates crystallise. The absorption spectrum, in the visible and ultraviolet regions, of the blue-green solution is characterised by an absorption band at 3600 Å in addition to the usual " copper band " at 7450 Å (Fig. 1). Tsuchida *et al.*[14,15] ascribed the unusual absorption band at 3750 Å, which appears in the spectra of the heavier binuclear copper alkanoates, to the inherent copper–copper linkage, so the present band at 3600 Å provides strong evidence for the existence of binuclear copper(II) formate in solution, most probably in $[Cu_2(H{\cdot}CO_2)_4(H{\cdot}CO_2H)_2]$ molecules with structure (II). Unfortunately measurement of the magnetic moment of the cupric ion in the blue-green solution was impossible, owing to the ephemeral nature of the binuclear derivative, and to the rapid growth of crystals a few minutes after the carbonate has dissolved.

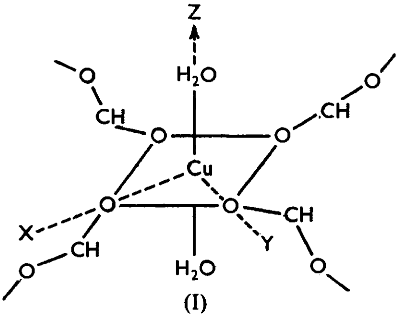


Reagents, etc.: 1, Dil. $H{\cdot}CO_2H$. 2, $-H_2O$. 3, Conc. $H{\cdot}CO_2H$. 4, Standing. 5, 100°. 6, $-H{\cdot}CO_2H$. 7, Ether.

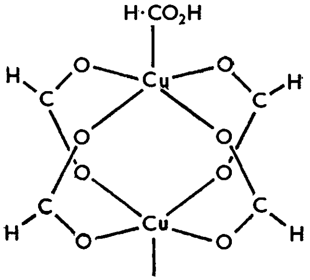
Attempts to stabilise the blue-green solution, and to isolate the binuclear compound (II) by replacing water with acetone, were unsuccessful. However, the resultant particularly well-defined absorption maximum at 3750 Å, coupled with a displacement of the " copper band " from 7450 Å to 6750 Å, suggests that acetone molecules have replaced formic acid (or possibly water) from the terminal positions in structure (II) to form $[Cu_2(H{\cdot}CO_2)_4(CH_3{\cdot}CO{\cdot}CH_3)_2]$ molecules.

The pale blue square plates which crystallise so quickly from the solution are unstable in the absence of their mother liquor. Several copper analyses of crystals still moist indicated that they most probably contained four molecules of formic acid per copper atom. The compound, which has a sub-normal room-temperature magnetic moment (1·61 B.M.) like the tetrahydrate (1·64 B.M.), readily loses formic acid to give the same modification of anhydrous copper formate (μ = 1·61 B.M.) as is obtained from the tetrahydrate. Clearly, $Cu(H{\cdot}CO_2)_2,4H{\cdot}CO_2H$, is probably the solvate analogue of $Cu(H{\cdot}CO_2)_2,4H_2O$, which has a particularly open structure. The bulky nature of the formic acid molecule compared with the water molecule could account for the rapid decomposition in the absence of formic acid.

Royal-blue anhydrous copper formate crystallises in well-defined rods when the blue-green solution is heated at 100° for several hours. This modification has a normal magnetic moment (1·90 B.M.), but its insolubility in organic solvents precludes molecular weight, electrical conductivity, or cryoscopic measurements and suggests a polymeric structure. The same compound is also formed when the blue-green solution stands for several days at room temperature. The pale blue square plates of the tetraformic acid derivative which initially deposit gradually lose their acid in favour of the royal-blue anhydrous compound.



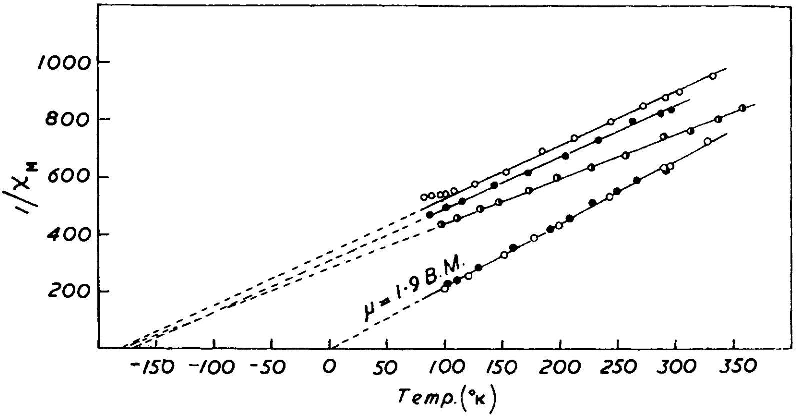
(I)



(II)

The best known form of copper formate is the tetrahydrate, which readily crystallises from slightly acid aqueous solutions. Its room-temperature magnetic moment is low, $\mu = 1{\cdot}64$ B.M. The blue-green solution is the source of a second hydrate, obtained when the solution is quickly poured into ether. Microscopic needles of dihydrate are formed having a magnetic moment as required for one unpaired electron (1·90 B.M.). Both the tetra- and the di-hydrate lose water of crystallisation to form anhydrous salts. The former yields powder-blue opaque crystals ($\mu = 1{\cdot}61$ B.M.) which retain the shape of the parent hydrate, while the latter forms a pale turquoise product ($\mu = 1{\cdot}75$ B.M.). It is unusual to find three inorganic compounds of the same empirical formula. Even so, the different appearances, magnetic properties, and *X*-ray powder diffraction patterns (Fig. 2) leave little doubt that the structures of the three modifications are different. That attempts to isolate a dihydrate by careful dehydration of the tetrahydrate were

FIG. 3.



Upper three curves.
○ Dehydrated $Cu(H{\cdot}CO_2)_2,4H_2O$.
● $Cu(H{\cdot}CO_2)_2,4H_2O$.
◑ Dehydrated $Cu(H{\cdot}CO_2)_2,2H_2O$.

Bottom curve.
○ Royal-blue $Cu(H{\cdot}CO_2)_2$.
● $Cu(H{\cdot}CO_2)_2,2H_2O$.

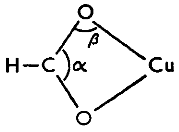
unsuccessful suggests that the dihydrate differs fundamentally in structure from the tetrahydrate.

These compounds fall naturally into two groups on the basis of their magnetic properties. The dihydrate and the royal-blue crystalline anhydrous formate have normal moments which show practically no variation with temperature. Their reciprocal molar susceptibilities vary linearly with temperature, the curves intercepting the temperature axis very close to the origin (Fig. 3). These are magnetically dilute compounds obeying a simple Curie law of the form, $\chi \propto T^{-1}$. In contrast the tetrahydrate, and both the blue and the turquoise form of anhydrous cupric formate, possess sub-normal moments which are strongly dependent on temperature (see Fig. 5). Although their reciprocal susceptibilities vary linearly with temperature, the intercepts of the curves with the temperature abscissa are far from the origin, in the direction of negative temperatures (Fig. 3). These compounds obey Curie–Weiss laws of the form $\chi \propto (T - \theta)^{-1}$ where θ, the Weiss constant, has large values of the order of $-175°$, which is further indication of interaction between the magnetic centres. The marked jump in magnetic moment from 1·61—1·75 to 1·9 B.M. which occurs when the three compounds are dissolved in water[1] further confirms the presence of exchange interactions in the solid state. Although these moments are smaller than those usually observed for magnetically dilute cupric compounds, they are not depressed to the value (1·38 B.M.) observed[2,9] for the heavier binuclear homologues where direct copper–copper intramolecular exchange demagnetisation takes place.

The experimental negation of the rule, so often tacitly assumed, that " the greater the degree of hydration, the greater the magnetic dilution " is noteworthy. Copper formate tetrahydrate, the most highly hydrated formate, is undoubtedly magnetically concentrated compared with both the dihydrate and the royal-blue anhydrous salt.

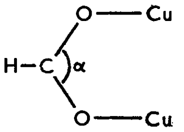
Clearly it is impossible to establish the origin of these sub-normal moments in the absence of structural information. The present *X*-ray powder diffraction data, while establishing that the various forms of copper formate differ, provide few clues to their actual structures. However, complete crystallographic information is available for the tetrahydrate on which to base an analysis of the magnetic data.

We first consider some of the bonding potentialities of the formate ion. Utilisation of pure *p*-orbitals of oxygen would favour the monomeric chelate structure (III), proposed first by Lowry and French[16] and later by Amiel.[9] Although four-membered rings can undoubtedly occur with some chelates, they are generally less stable than five- or six-membered rings, and in the present case considerable steric strain would be present. On the other hand, a pure sp^2-hybridisation of oxygen orbitals would lead to two bonding arrangements, both of which, in contrast to (III), involve one formate group bridging two copper atoms.



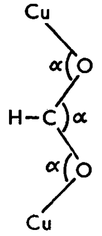
(III)

Lowry and French arrangement



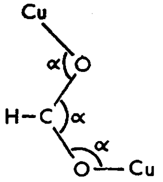
(IV)

syn–syn-Bridging arrangement



(V)

anti–anti-Bridging arrangement



(VI)

anti–syn-Bridging arrangement

$\alpha = 120°$; $\beta = 90°$.

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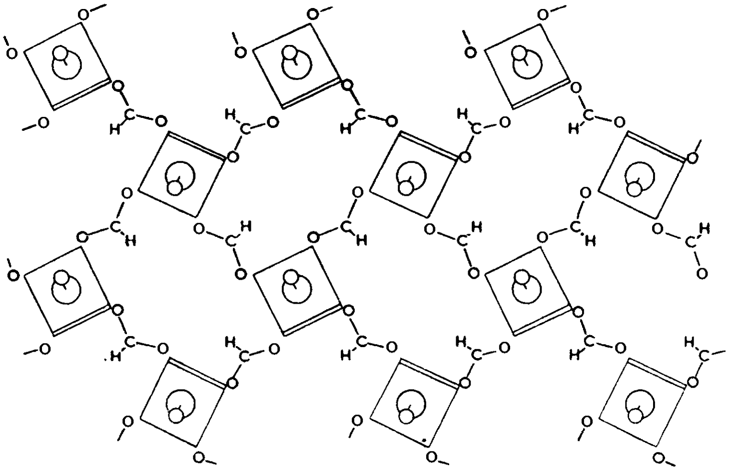
[16] Lowry and French, *Proc. Roy. Soc.*, 1924, *A*, **106**, 489.

In the first arrangement, two parallel sp^2-hybrid orbitals from the formate oxygen atoms are used to bond two copper atoms, approximately 2·6 Å apart, in a *syn-syn* * bridging arrangement as in (IV). Four such bridging groups are known to support two contiguous copper atoms in binuclear copper(II) acetate monohydrate.[17] In the second arrangement, two opposed sp^2-hybrid orbitals bridge two copper atoms, approximately 5·8 Å apart, in an *anti-anti* bridging arrangement as in (V). A further bonding arrangement based on sp^2-hybridisation of oxygen orbitals would be the *anti-syn* bridging arrangement (VI). The possibility of copper–copper exchange interaction is obvious in the *syn-syn* structure (IV), but is not immediately apparent in the *anti-anti* or *anti-syn* arrangements (V) and (VI).

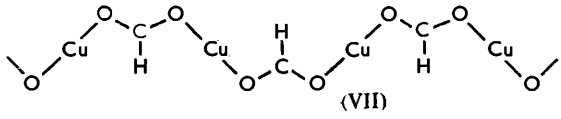
The complete *X*-ray analysis by Kiriyama *et al.*[7] reveals that the layer structure of the tetrahydrate is based on the *anti-anti* bonding arrangement (V). Each layer is very open, and is composed of elongated CuO_6 octahedra (I) which are linked together, in an infinite two-dimensional array, by sharing corners *via* bridging formate groups. Two water molecules co-ordinated to each copper atom lie one above and one below each layer. The CuO_4 planes, formed by the four co-ordinated formate oxygen atoms of each CuO_6 octahedron, do not quite lie in the plane of the copper atoms which provide the framework of each layer. Adjacent octahedra are also slightly rotated contrariwise to one another. The essential structural features of each layer are apparent in Fig. 4.

FIG. 4.



Large circles, copper; small circles, water.

The remaining two water molecules are not linked directly to copper atoms, but are hydrogen-bonded between adjacent layers which are 6·2 Å apart. The easy cleavage, the spontaneous tendency to effloresce, and the possibility of accommodating four molecules of formic acid to give the apparently related compound $Cu(H{\cdot}CO_2)_4,4H{\cdot}CO_2H$ are all consequences of the inherent openness of the tetrahydrate structure.



(VII)

Cu–Cu = 5·8 Å.

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* This nomenclature is a convenient extension of that currently employed in organic chemistry to describe the somewhat similar stereochemical configurations which occur in oximes and diazoates.

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

The interlayer separation of 6·2 Å precludes direct interlayer exchange interaction, and indicates that the sub-normal magnetic moment originates from magnetic interactions occurring wholly within each layer. At first sight it appears that each copper atom is magnetically well shielded from its nearest copper neighbour at 5·8 Å by the four intervening diamagnetic atoms of each formate group. Closer inspection reveals that the copper atoms form infinite linear chains linked by formate groups, whose C–H bonds approximately bisect the line joining adjacent copper atoms as in (VII). Fig. 4 shows that each copper atom lies at the point of intersection of two such linear chains.

This characteristic recalls corresponding features in the compound $KCuF_3$, in which CuF_6 octahedra share corners to form a distorted perovskite lattice involving infinite linear F–Cu–F–Cu–F–Cu–F chains extending throughout the crystal. Although in this compound also the cupric ions are approximately 5·7 Å apart, *i.e.*, too far for direct interaction, the low room-temperature moment, 1·46 B.M., and the Curie–Weiss temperature-dependence of the susceptibility with a large negative value of θ, almost certainly reflect antiferromagnetic interactions occurring *via* intermediate fluoride ions.[18]

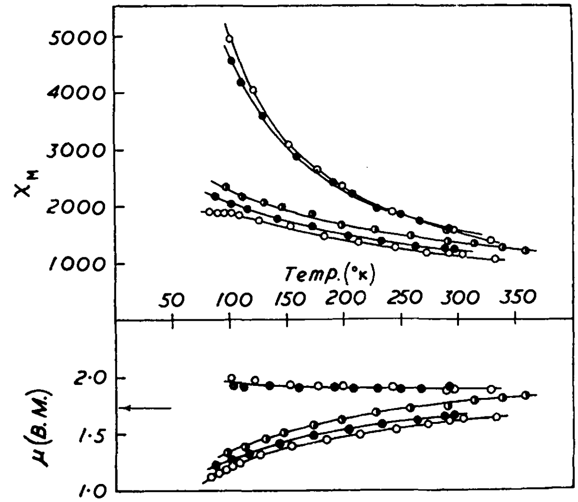

FIG. 5.

Upper curves in each section.
○ Royal-blue $Cu(H{\cdot}CO_2)_2$.
● $Cu(H{\cdot}CO_2)_2,2H_2O$.

Lower curves in each section.
○ Dehydrated $Cu(H{\cdot}CO_2)_2,4H_2O$.
● $Cu(H{\cdot}CO_2)_2,4H_2O$.
◑ Dehydrated $Cu(H{\cdot}CO_2)_2,2H_2O$.

The arrow represents the "spin-only" value of μ = 1·73 B.M.

It is suggested that the magnetic anomalies of the tetrahydrate arise from antiferromagnetic exchange interactions between copper atoms through intervening formate groups. If this is correct, then the formate group is functioning in a novel fashion as a polyatomic counterpart of the monatomic ions fluoride, chloride, and oxide which are generally associated with antiferromagnetism.

Antiferromagnetic compounds are characterised magnetically by an angular maximum in their susceptibility–temperature curves, and generally they obey Curie–Weiss laws considerably above the temperature at which the maximum susceptibility occurs (Néel temperature). Spin-aligning forces, acting from one cation to another through an intermediate diamagnetic anion, divide the magnetic ions into two equivalent interpenetrating ferromagnetic sub-lattices. Below the Néel temperature an ordered condition exists in which the spins on one sub-lattice are coupled antiparallel to those on the other; above the Néel temperature, the spins are randomly oriented.

Although the tetrahydrate and the blue and the turquoise modification of anhydrous copper formate, exhibit just those features (sub-normal room temperature moments, temperature-dependent moments, large negative values for θ) which normally characterise antiferromagnetism, susceptibility maxima were not observed down to 80° K. However, an incipient maximum is just evident in the susceptibility curve for the

[18] Martin, Nyholm, and Stephenson, *Chem. and Ind.*, 1956, 83.

dehydrated tetrahydrate (see Fig. 5), which suggests that the Néel temperature should not be very far below 80° K for this compound.

The mechanism by which the spin moment of an electron on one Cu^{2+} cation is coupled antiparallel to the moment of an electron on a neighbouring Cu^{2+} cation separated from it by an intermediate diamagnetic $H{\cdot}CO_2^-$ anion to give rise to antiferromagnetism, is called "superexchange."

In a binary antiferromagnetic compound such as manganese(II) oxide, there is evidence that the interaction between two Mn^{2+} ions is strongest when the bonds to the intervening oxide ion are collinear, and accordingly it has been inferred [19] that the superexchange is principally due to the $2p_\sigma$-electrons of the oxide ion. In contrast, we suggest that in copper formate tetrahydrate the superexchange is primarily due to the delocalised π-electron cloud, which arises from overlapping of $2p_\pi(O)$–$2p_\pi(C)$–$2p_\pi(O)$ atomic orbitals associated with the resonating $^-O{-}CH{=}O/O{=}CH{-}O^-$ anion system. This delocalised π-type molecular orbital, which extends over the three nuclei, is believed to provide a low-energy path for migration of electrons * along the infinite linear chains represented in (VII).

Although we regard the delocalised π-electron cloud associated with formate ion as the most likely transmission medium for the postulated superexchange, several other possibilities must be considered. In finding the path of lowest energy for migration of the $3d$-positive electron hole associated with each copper atom, three factors appear of prime importance. They are (*a*) the relative energies of alternative paths offered by each formate ion; (*b*) the "transmission probability" associated with each path, which will be determined by the magnitude of orbital overlap between copper and formate oxygen atoms; (*c*) the relative energies of the ground and excited states of copper under the influence of the ligand field.

The formate ion provides two alternatives for migration of a positive electron hole, either *via* the π-electron cloud, or *via* the σ-bonding electron orbitals of the OCO nuclei. The respective combinations of atomic orbitals appropriate to each path [with axial directions locally defined for each copper nucleus as shown in (I)] are as follows:

$$\pi\text{-path}\ \begin{cases}(a)\ 3d_{xz}(\mathrm{Cu})\text{–}2p_z(\mathrm{O})\text{–}2p_z(\mathrm{C})\text{–}2p_z(\mathrm{O})\text{–}3d_{xz}(\mathrm{Cu})\\ (b)\ 3d_{yz}(\mathrm{Cu})\text{–}2p_z(\mathrm{O})\text{–}2p_z(\mathrm{C})\text{–}2p_z(\mathrm{O})\text{–}3d_{yz}(\mathrm{Cu})\end{cases}$$

$$\sigma\text{-path}\ \begin{cases}(c)\ 3d_{x^2-y^2}(\mathrm{Cu})\text{–}2sp_\sigma^2(\mathrm{O})\text{–}2sp_\sigma^2(\mathrm{C})\text{–}2sp_\sigma^2(\mathrm{O})\text{–}3d_{x^2-y^2}(\mathrm{Cu})\\ (d)\ 3d_{xy}(\mathrm{Cu})\text{–}2sp_\sigma^2(\mathrm{O})\text{–}2sp_\sigma^2(\mathrm{C})\text{–}2sp_\sigma^2(\mathrm{O})\text{–}3d_{xy}(\mathrm{Cu})\\ (e)\ 3d_{z^2}(\mathrm{Cu})\text{–}2sp_\sigma^2(\mathrm{O})\text{–}2sp_\sigma^2(\mathrm{C})\text{–}2sp_\sigma^2(\mathrm{O})\text{–}3d_{z^2}(\mathrm{Cu})\end{cases}$$

Utilisation of the σ-path with its high charge localised between oxygen and carbon nuclei would almost certainly be associated with a gross energy barrier. No such restriction would apply to the π-path involving delocalised π-electrons.

Finally, Polder [20] has calculated the ligand-field splittings for the d^9-configurations of octahedrally oxygen-co-ordinated cupric ion, and has shown that with respect to the positive electron hole their stability decreases in the sequence $3d_{x^2-y^2}$, $3d_{z^2}$, $3d_{xy}$, $3d_{xz}$, and $3d_{yz}$, the overall splitting being estimated to be of the order of 21,000 $cm.^{-1}$. Clearly the choice of a σ- versus a π-pathway for the superexchange rests on whether the promotional enery involved in the $3d_{x^2-y^2} \longrightarrow 3d_{xz};3d_{yz}$ transition for copper is greater or less than the energy barrier to mobility of a positive hole offered by the highly localised σ-bonding orbitals of the OCO framework. Although this energy barrier is difficult to estimate, we believe that "preconditioning" copper may well be energetically easier than "preconditioning" the σ-pathway, and accordingly we favour the π-cloud as the probable "transmission medium."

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* Careful dehydration of crystalline copper formate tetrahydrate can produce crystal faces which often possess an almost metallic lustre. This may well originate from the delocalized π-electrons which would possess unrestricted mobility throughout the whole of each layer.

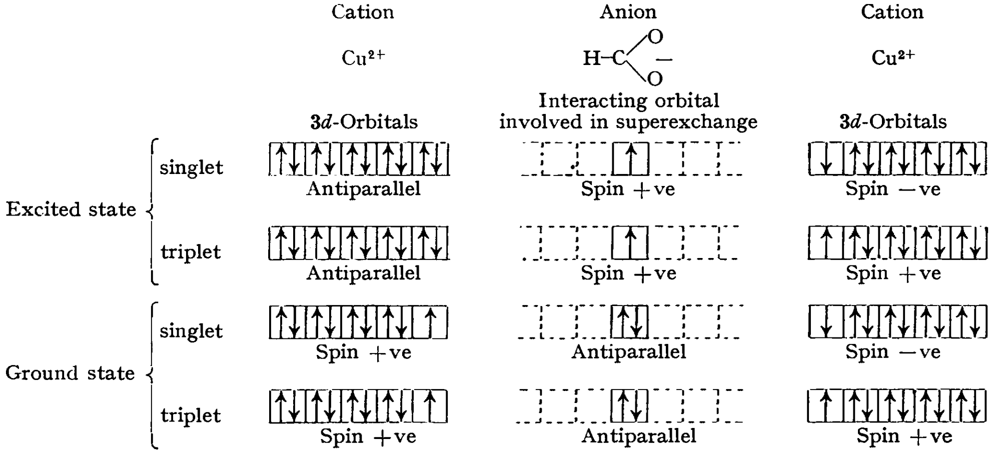
[19] Lidiard, *Reports Progr. Phys.*, 1954, **17**, 201.

[20] Polder, *Physica*, 1942, **9**, 709.

The geometric location of a C–H group approximately mid-centre between copper atoms could also conceivably give rise to superexchange through the C–H bonding pair of electrons. This again appears unattractive, for the excited state necessitates a one-electron C–H bond, and the localised nature of the C–H bonding orbital would render favourable overlap with copper 3*d*-orbitals extremely unlikely.

By using Anderson's [21] method of presentation, the interaction scheme associated with the postulated superexchange can be represented in a manner which is independent of which of the above mechanisms is correct. This is illustrated in Table 3.

TABLE 3. *Interaction scheme in superexchange.*



This scheme qualitatively indicates the process involved in the spin-coupling between formate-bridged cupric ions which gives rise to antiferromagnetic behaviour in copper(II) formate tetrahydrate. In particular, it illustrates that a completely bivalent-ionic description of the molecule as $Cu^{2+}(H{\cdot}CO_2^-)_2$ is inadequate, and that a consideration of other configurations, such as $Cu^+(H{\cdot}CO_2)(H{\cdot}CO_2^-)$, can provide a mechanism for superexchange. Further, it illustrates that, contrary to cases in which direct intramolecular exchange between paramagnetic atoms takes place [*e.g.*, $Fe_2(CO)_9$; $W_2Cl_9^{2-}$; $Cu_2(CH_3{\cdot}CO_2)_4(H_2O)_2$], the total spin remains unaltered, so that the effective magnetic moment of cupric ion will not be too greatly diminished by the superexchange coupling.

A study of the magnetic susceptibility of copper(II) formate below 80° K is now needed to test our hypothesis of antiferromagnetism. If an angular maximum in susceptibility is found, the measurements could be profitably extended to single crystals, for the tetrahydrate should be markedly magnetically anisotropic, exhibiting two-dimensional antiferromagnetism in the layer plane but paramagnetism in the direction perpendicular to the layers.

Corresponding structural information is not available for formates other than the tetrahydrate. The retention of external crystalline form on dehydration suggests that the four water molecules are easily removed from between the layers, and that the layers come together without any significant change in the relative orientation of the copper atoms with respect to attached formate groups. If this is so the superexchange within each layer would continue, and account for the persistence of the low room-temperature moment on dehydration of the tetrahydrate. The incipient maximum in magnetic susceptibility which occurs at the lowest temperatures attainable with our apparatus certainly suggests antiferromagnetism (Fig. 5).

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[21] Anderson, *Phys. Rev.*, 1950, **79**, 350.

Any suggestions concerning the magnetic properties of the dihydrate and the two remaining anhydrous modifications are inevitably speculative in the absence of structural data. The cupric ions, in both the royal-blue and the dihydrate structure, are magnetically well shielded from one another, but dehydration of the latter modifies the structure so as to introduce magnetic interactions which are reflected in the decrease in moment from 1·90 to 1·75 B.M. The argument that a moment of 1·75 B.M. is still greater than the spin-only value for cupric ion, 1·73 B.M., and that the decrease does not necessarily indicate a magnetically concentrated compound, is valid, and stresses the weakness of deductions based on a single magnetic measurement at room temperature. Fig. 3 shows that the reciprocal susceptibility curve for the dehydrated dihydrate, quite fortuitously, has the same value of the susceptibility as the parent dihydrate just above room temperature. The slope of its susceptibility curve (proportional to its magnetic moment) is, however, much less than that of the dihydrate. Further, the temperature at which the reciprocal susceptibility becomes zero, changes from zero (Curie law behaviour) for the dihydrate to approximately $-175°$ (Curie–Weiss behaviour) on dehydration. It is these features, rather than the value of the room-temperature moment, which provide significant confirmation of magnetic concentration in the dehydrated dihydrate.

It is of interest to enquire why copper formate differs from its homologues by not adopting the binuclear structure (II) for its stable configuration. Lowering of the total energy by the formation of an extra bond, *i.e.*, the postulated copper–copper δ-bond, can be disregarded, first because its binding energy will be very small, and secondly because it appears to be a consequence, rather than a cause, of the bridged structure. The most obvious difference between the copper derivatives of formic and of other *n*-alkanoic acids is the one between dissociation constants of the parent acids. The heavier alkanoic acids with values of $K_a \simeq 1{\cdot}7 \times 10^{-5}$ are considerably weaker than formic acid with $K_a = 1{\cdot}7 \times 10^{-4}$, reflecting the greater σ-electron density on their hydroxyl-oxygen atoms due to inductive effects of *n*-alkyl groups. As a result, acetate ion, for example, will be more effective than formate ion in reducing the positive charge on the cupric ion in copper alkanoates, and, in fact, it reduces the electrostatic copper–copper repulsion sufficiently for the binuclear configuration to be favoured. On the other hand, with copper formate, the residual positive charge on each cupric ion remains sufficiently large for the *anti-anti* bridging arrangement to be favoured, since it increases the separation between the charged copper atoms from 2·6 to 5·8 Å, and thereby alleviates electrostatic copper–copper repulsion. Consideration of this electrostatic factor alone is an oversimplification; other factors must be taken into account. Even so, it seems that the magnitude of the residual charge on each cupric ion after bonding may well be the most important factor in deciding which of the bonding arrangements (IV) or (V) is likely to be adopted. The question is being pursued.

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