593. *Magnetic Studies with Copper*(II) *Salts. Part V.*[1] *Binuclear Derivatives of Copper*(II) *Formate involving Covalent Copper-to-Copper δ-Bonds.*

By R. L. Martin and Hanneke Waterman.

The preparation of five novel derivatives of copper formate is described. They are the emerald-green heterocyclic monoamine copper(II) formates, $Cu(H{\cdot}CO_2)_2$,amine, where amine = pyridine, α-, β-, or γ-picoline, and the blue-green hemidioxan derivative, $Cu(H{\cdot}CO_2)_2,\frac{1}{2}C_4H_8O_2$. They provide the first examples in which copper formate has been " conditioned " into adopting the binuclear copper acetate-type structure, and their magnetic properties are remarkable, being zero below *ca.* 120° K, but rising to $\mu \simeq 1{\cdot}2$ B.M. at the decomposition temperature (*ca.* 360° K).

The anomalous temperature-variation of their magnetic susceptibilities provides strong evidence for their binuclear structures. The energy separation between singlet and triplet states, which arise from intramolecular exchange between pairs of contiguous copper atoms, is found to be twice that previously observed for anhydrous and hydrated copper(II) n-alkanoates (J *ca.* 600 cm.$^{-1}$ compared with 309 cm.$^{-1}$). This reflects an increase in binding energy of the postulated copper-to-copper covalent δ-bond in these compounds.

The compounds provide a unique opportunity for measuring directly the small temperature-independent contribution from copper to the paramagnetic susceptibility. Values for the four heterocyclic amine derivatives fall in the range, $N\alpha = 168\ (\pm 10) \times 10^{-6}$, while for the hemidioxan derivative a slightly smaller value, $N_\alpha = 128 \times 10^{-6}$, is observed.

The influence of both the amines and dioxan in " conditioning " copper formate so that it adopts the binuclear configuration is discussed.

Copper(II) formate displays[1] a marked reluctance to adopt the binuclear copper(II) acetate-type structure[2] (I) (p. 2966), which characterizes the cupric salts of the heavier homologues in the series of n-alkanoic acids. However, although anhydrous or hydrated binuclear copper(II) formate could not be isolated, strong evidence for the ephemeral existence of the binuclear species $[Cu_2(H{\cdot}CO_2)_4,L_2]$, where L is probably formic acid, water, or acetone, was provided by the absorption spectra in solution. These solutions exhibit an extra absorption band at 3700 Å which is not normally observed in the spectra of copper(II) compounds, but characterizes the spectra of the heavier binuclear copper(II) alkanoates. The blue-green solution obtained by dissolving copper carbonate in a mixture of formic acid and dioxan also exhibited this band at 3750 Å, but in this case dichroic blue-

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[1] Part IV, Martin and Waterman, *J.*, 1959, 1359.

[2] Bleaney and Bowers, *Proc. Roy. Soc.*, 1952, *A*, **214**, 451.

green crystals of copper formate containing dioxan could be isolated from solution. The magnetic moment, measured at room temperature, of the crystals,[3] $\mu \sim 1$ B.M., was considerably lower than the corresponding values for heavier copper n-alkanoates,[4] $\mu = 1{\cdot}38$ B.M., or for the other modifications of copper formate which lie in the range, $\mu = 1{\cdot}59$—$1{\cdot}93$ B.M.[1]

The binuclear structure (I), in which the two copper atoms are virtually contiguous [Cu–Cu = 2·64 Å in copper(II) acetate monohydrate] will be energetically unstable if a large residual electrostatic charge, of either sign, remains on the copper atoms after bonding to formate groups has taken place. Accordingly, the observed reluctance of anhydrous or hydrated copper formate to adopt this structure may well arise from the comparatively low σ-electron density on formate oxygen atoms, leading to a relatively large residue of positive charge on each copper atom after formation of the compound. If this is, in fact, the case, it should be possible considerably to reduce this excess of positive charge, and so favour structure (I) by forming a dative bond to copper in the terminal positions, L, by using a ligand of appropriate σ-electron charge density.

This hypothesis has now been tested with the ligands L = pyridine, α-, β-, and γ-picoline, aniline, and dioxan, and the experiments now described have led to the isolation and characterization of hitherto unknown binuclear derivatives of copper formate.

EXPERIMENTAL

Materials.—*Copper formate–hemidioxan.* Treatment of copper carbonate with a mixture of 98% formic acid and dioxan (1 : 2 v/v) yielded a dark green solution from which very small, dark dichroic blue-green rods of the hemidioxan derivative immediately crystallised. When reaction was complete, the crystals were washed and rapidly transferred to a desiccator, in which the adhering dioxan was removed at reduced pressure over calcium chloride. Although the *compound* was decomposed by moisture in the air, it was stable *in vacuo* at 150° (Found: C, 24·1; H, 2·85; Cu, 32·0. $CuC_4H_6O_5$ requires C, 24·3; H, 3·1; Cu, 32·2%); m. p. 190—200° (decomp.). A monodioxan compound could not be prepared.

Copper formate derivatives with amines. When anhydrous copper formate was dissolved at 70° in the appropriate freshly-distilled amine, a deep royal-blue solution was obtained. Slow evaporation at room temperature yielded royal-blue or violet crystals of the bisamine derivatives. When these were left for several days at reduced pressure over concentrated sulphuric acid, they lost one molecule of amine to form the corresponding emerald-green copper formate monoamine derivatives. The latter were insoluble in all non-donor solvents, and in acetone and alcohol, but very slightly soluble in dioxan. In water the complexes were destroyed, and in the appropriate amine, the tetrakisamine cupric complex was formed. The m. p.s of small quantities of the materials could be determined in capillary tubes, melting in each case being accompanied by loss of amine and reduction to copper. Surprisingly, the larger amounts contained in the Gouy tube during magnetic measurements decomposed rapidly at temperatures considerably below the m. p.

Copper formate–pyridine, m. p. 144° (Found: C, 36·0; H, 3·1; N, 6·2; Cu, 27·1. $C_7H_7O_4NCu$ requires C, 36·1; H, 3·0; N, 6·0; Cu, 27·3%). *Copper formate–α-picoline*, m. p. 135° (Found: C, 38·6; H, 3·7; N, 5·7; Cu, 25·5. $C_8H_9O_4NCu$ requires C, 39·0; H, 3·7; N, 5·7; Cu, 25·8%). *Copper formate–β-picoline*, m. p. 128° (Found: C, 38·8; H, 3·6; N, 5·55; Cu, 25·3%). *Copper formate–γ-picoline*, m. p. 126° (Found: C, 38·5; H, 3·8; N, 5·8; Cu, 25·4%). *Copper formate–bisaniline* separated as golden leaflets when benzene was added to a solution of copper formate in freshly distilled aniline at 70°. Attempts to transform the product into the monoaniline derivative were unsuccessful (Found: C, 49·2; H, 4·6; N, 8·3; Cu, 18·5. $C_{14}H_{16}O_4N_2Cu$ requires C, 49·5; H, 4·8; N, 8·2; Cu, 18·7%); m. p. 114° (decomp. at 120°).

Copper acetate derivatives of dioxan. Copper acetate–hemidioxan was prepared in hot solution by the method used for the corresponding formate. It so readily lost dioxan that complete analysis could not be carried out (Found: Cu, 28·8. $C_6H_{10}O_5Cu$ requires Cu, 28·2%). The hot mother-liquor from this preparation yielded large blue crystals of the *monodioxan derivative* on cooling. This was more stable than the hemidioxan compound, although it too decomposed on

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[3] Martin and Whitley, *J.*, 1958, 1394.
[4] Martin and Waterman, *J.*, 1957, 2545.

TABLE 1. *Experimental gram and molar susceptibilities (c.g.s., e.m.u.) and magnetic moments (B.M.) at various absolute temperatures.*

Copper formate–bisaniline

Temp. (°K)	$10^6\chi_g$	$10^6\chi_M$ *	μ (B.M.) *
100·5	12·2	4318	1·86
109·7	11·1	3943	1·85
124·6	9·78	3495	1·86
152·2	7·83	2833	1·85
173·7	6·59	2412	1·82
201·5	5·73	2119	1·83
247·9	4·65	1753	1·84
273·5	4·18	1592	1·84
295·7	3·87	1487	1·84
318·7	3·57	1386	1·85
342·5	3·30	1293	1·85
358·0	3·10	1226	1·84

* Diamagnetic correction, $10^6\Delta = -172$; $N\alpha = 60 \times 10^{-6}$.

Copper formate–pyridine

Temp. (°K)	$10^6\chi_g$	$10^6\chi_M$ †	μ (B.M.) ($N\alpha = 60 \times 10^{-6}$)	μ (B.M.) ($N\alpha = 168 \times 10^{-6}$)
85·9	0·258	156	0·255	0
92·8	0·275	160	0·274	0
100·0	0·264	157	0·280	0
116·0	0·254	155	0·298	0
138·0	0·333	173	0·355	0·075
166·1	0·653	248	0·502	0·327
194·5	0·935	314	0·631	0·479
226·5	1·24	385	0·770	0·630
257·6	1·54	454	0·905	0·771
295·0	1·78	510	1·04	0·902
325·0	1·95	550	1·13	1·00
351·0	2·01	564	1·20	1·06
359·5	2·03	568	1·21	1·07
370·3	2·01	564	1·23	1·09

† Diamagnetic correction, $10^6\Delta = -96$.

Copper formate–α-picoline

Temp. (°K)	$10^6\chi_g$	$10^6\chi_M$ *	μ (B.M.) ($N\alpha = 60 \times 10^{-6}$)	μ (B.M.) ($N\alpha = 168 \times 10^{-6}$)
84·3	0·278	177	0·282	0
89·0	0·274	176	0·289	0
95·0	0·238	167	0·286	0
101·4	0·238	167	0·296	0
107·0	0·235	166	0·303	0
118·4	0·227	164	0·315	0
128·5	0·246	169	0·336	0
144·5	0·326	188	0·386	0·153
170·0	0·544	242	0·500	0·318
197·0	0·824	311	0·632	0·477
229·6	1·17	397	0·790	0·651
264·7	1·46	468	0·933	0·800
297·8	1·71	530	1·06	0·953
320·0	1·83	559	1·13	1·00
341·0	1·89	574	1·19	1·06
349·2	1·91	579	1·21	1·08
355·0	1·93	584	1·23	1·09
360·0	1·94	587	1·24	1·10

Copper formate–β-picoline

Temp. (°K)	$10^6\chi_g$	$10^6\chi_M$ *	μ (B.M.) ($N\alpha = 60 \times 10^{-6}$)	μ (B.M.) ($N\alpha = 168 \times 10^{-6}$)
109·6	0·274	177	0·322	0
121·1	0·219	163	0·317	0
130·5	0·199	158	0·321	0
136·0	0·211	161	0·333	0
145·0	0·219	163	0·347	0
155·9	0·287	180	0·389	0·123
165·8	0·323	189	0·415	0·168
200·7	0·790	304	0·629	0·469
232·5	1·15	393	0·790	0·665
257·5	1·44	464	0·916	0·784
294·7	1·82	558	1·09	0·963
298·6	1·83	560	1·10	0·971
330·4	1·98	597	1·20	1·07
340·0	2·04	612	1·23	1·10
350·0	2·04	612	1·25	1·12
359·5	2·07	620	1·28	1·15
368·9	2·08	622	1·29	1·16

* Diamagnetic correction, $10^6\Delta = -108$.

Copper formate–γ-picoline *

85·0	0·281	177	0·272	0
120·6	0·263	173	0·324	0
130·0	0·282	178	0·337	0
151·3	0·267	174	0·363	0
193·0	0·697	280	0·585	0·418
221·1	1·17	397	0·776	0·639
244·8	1·45	466	0·895	0·767
259·9	1·52	483	0·942	0·813
295·5	1·70	527	1·05	0·925
319·8	1·82	557	1·13	1·00
345·2	1·85	564	1·18	1·05
355·1	1·92	582	1·22	1·09
364·9	1·89	574	1·23	1·09

* Diamagnetic correction, $10^6\Delta = -108$.

Copper formate–hemidioxan †

86·8	0·293	132	0·224	0
90·8	0·280	129	0·225	0
95·0	0·271	128	0·228	0
101·5	0·271	128	0·236	0
109·4	0·275	128	0·245	0
120·9	0·272	128	0·258	0
132·1	0·318	137	0·286	0·098
149·0	0·405	154	0·336	0·177
174·3	0·668	206	0·453	0·331
218·8	1·25	315	0·671	0·574
261·0	1·68	406	0·854	0·765
285·3	1·88	446	0·943	0·855
310·0	2·06	481	1·03	0·939
334·0	2·22	513	1·11	1·02
368·0	2·42	552	1·21	1·11

† Diamagnetic correction, $10^6\Delta = -74$.

Copper acetate–dioxan

Temp. (°K)	$10^6\chi_g$	$10^6\chi_M$ *	$\mu = 2{\cdot}839\,[(\chi_M - 60)T]^{\frac{1}{2}}$	Temp. (°K)	$10^6\chi_g$	$10^6\chi_M$ *	$\mu = 2{\cdot}839\,[(\chi_M - 60)T]^{\frac{1}{2}}$
88·0	−0·0838	100	0·169	173·6	1·50	528	0·809
95·2	−0·0126	120	0·215	198·6	1·84	619	0·946
103·0	0·161	166	0·297	224·6	2·13	698	1·08
121·0	0·483	253	0·434	258·0	2·34	754	1·20
151·4	1·11	422	0·665	295·0	2·41	773	1·30

* Diamagnetic correction, $10^6\Delta = -123$.

exposure to moist air (Found: C, 35·2; H, 5·1; Cu, 23·2. $C_8H_{14}O_6Cu$ requires C, 35·6; H, 5·2; Cu, 23·6%).

Magnetic Measurements.—The techniques and corrections applied in this work are essentially those described earlier. Previously, an allowance of $N\alpha = 60 \times 10^{-6}$ was made for the temperature-independent contribution to the paramagnetism per g.-ion of copper. This value was first calculated theoretically by Polder [6] for hexaquocupric ions, and later by Bleaney and Bowers [2] for copper(II) acetate monohydrate on the assumption that the ligand-field splittings are those present in Tutton's salts. The unusual absorption spectra [3,7] of binuclear copper(II) alkanoates provide strong evidence that this assumption is probably unjustified, and that the ligand-field splittings must be considerably modified in these compounds. Fortunately, it has been possible to measure $N\alpha$ directly with some of the compounds here described, the values being 2—3 times greater than those previously calculated. Accordingly, the effective magnetic moments quoted below have been calculated for two values of $N\alpha$; first, by assuming $N\alpha = 60 \times 10^{-6}$ for comparison with earlier data on compounds for which $N\alpha$ is not easily measured, and secondly, with the present experimental values. The experimental data for the compounds now described are tabulated.

DISCUSSION

This work has yielded several new derivatives of copper(II) formate, which at room temperature possess the magnetic properties shown in Table 2 (copper sulphate and copper acetate are included for comparison). The magnetic moments of the mono- and the hemi-dioxan compound of copper acetate fall in the range $\mu = 1{\cdot}34 \pm 0{\cdot}04$ B.M., which are closely similar to the values, $\mu = 1{\cdot}36$ B.M., determined for copper acetate dissolved in dioxan,[3,8] and $\mu = 1{\cdot}39$ B.M. for copper acetate itself.[5]

TABLE 2. *Room-temperature magnetic data.*

			Magnetic properties				
						$\mu = 2{\cdot}839\,[(\chi_M - N\alpha)T]^{\frac{1}{2}}$	
Compound *	Colour	Temp.	$10^6\chi_g$	$-10^6\Delta$	$10^6\chi_M$	$N\alpha = 60 \times 10^{-6}$	$N\alpha$ (expt.)
$CuSO_4,5H_2O$	Blue	20·0°	5·90	122	1595	1·91	—
$Cu(CH_3{\cdot}CO_2)_2,H_2O$...	Blue-green	21·0	4·03	85	889	1·40	—
$Cu(H{\cdot}CO_2)_2(an)_2$ ...	Gold lustre	22·7	3·87	172	1489	1·85	—
$Cu(H{\cdot}CO_2)_2$,py	Emerald-green	30·6	1·83	96	523	1·07	0·932
$Cu(H{\cdot}CO_2)_2$,α-pic ...	,,	23·6	1·71	108	530	1·06	0·932
$Cu(H{\cdot}CO_2)_2$,β-pic ...	,,	25·6	1·83	109	560	1·10	0·971
$Cu(H{\cdot}CO_2)_2$,γ-pic ...	,,	22·5	1·70	108	527	1·06	0·925
$Cu(H{\cdot}CO_2)_2,\frac{1}{2}$(diox)	Blue-green	17·0	1·92	74	453	0·96	0·872
$Cu(CH_3{\cdot}CO_2)_2,\frac{1}{2}$(diox)	Green	18·5	3·41	97	866	1·38	—
$Cu(CH_3{\cdot}CO_2)_2$,diox...	Blue-green	20·0	2·40	123	770	1·30	—

an = aniline, py = pyridine, pic = picoline, diox = dioxan.

These derivatives of copper formate fall naturally into two well-defined groups on the basis of their magnetic properties at room temperature. Members of the first group have magnetic moments in the range $\mu = 1{\cdot}9 \pm 0{\cdot}2$ B.M., the value normally observed for magnetically dilute compounds of bivalent copper. These are the well-known royal-blue or violet bisaminecupric compounds $Cu(H{\cdot}CO_2)_2(amine)_2$, and the golden bisaniline derivative.

The remaining derivatives comprise the second group, which is characterized by subnormal magnetic moments at room temperature (see Table 2). These are the four heterocyclic monoamine derivatives with moments in the range $\mu = 1{\cdot}08 \pm 0{\cdot}02$ B.M., and the hemidioxan compound with $\mu = 0{\cdot}96$ B.M., a value which may be compared with the magnetic moment of copper formate in dioxan solution, $\mu = 1{\cdot}01$ B.M.,[3] where solvation is probably increased to give $[Cu_2(H{\cdot}CO_2)_4(C_4H_8O_2)_2]$ molecules. These moments are even lower than those observed [4] for the heavier binuclear copper n-alkanoates, $\mu = 1{\cdot}38 \pm 0{\cdot}03$ B.M., and likewise are strongly dependent on temperature.

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[5] Figgis and Martin, *J.*, 1956, 3837.

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

[7] Tsuchida, Yamada, *et al.*, *Nature*, 1955, **176**, 1171; 1956, **178**, 1192; *Bull. Chem. Soc.* (*Japan*), 1957, **30**, 953; 1958, **31**, 303.

[8] Kondo and Kubo, *J. Phys. Chem.*, 1958, **62**, 468.

The anomalous temperature variation of the magnetic susceptibility exhibited by each of the compounds in the second group enables their molecular configuration to be readily deduced. Below about 120° K, only a small residual paramagnetism is observed, which is independent of temperature within experimental error, and the compounds have zero magnetic moment (cf. Figs. 1 and 2). At temperatures above *ca.* 120° K, the paramagnetic susceptibility steadily increases until the compounds decompose at 360—370° K. At the decomposition temperature the moments have risen to *ca.* 1·2 B.M.

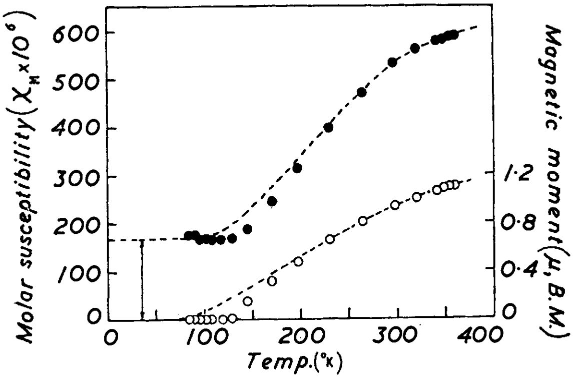


FIG. 1. [$Cu_2(H{\cdot}CO_2)_4(\alpha\text{-}Me{\cdot}C_5H_4N)_2$].
● χ_M ○ μ ---- Calculated.
The arrow represents $N\alpha = 168 \times 10^{-6}$ (exptl.).

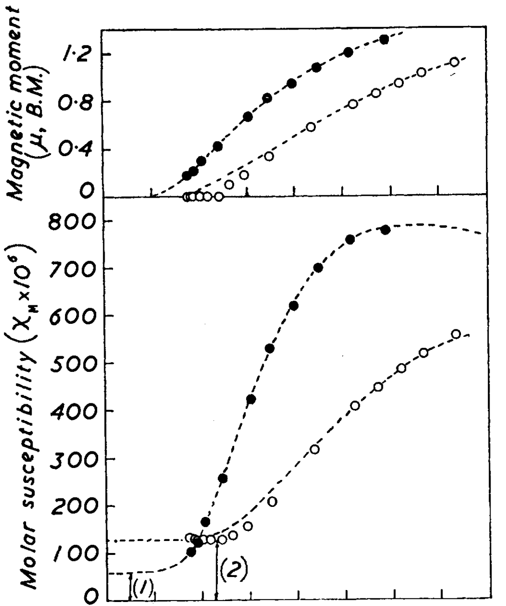


FIG. 2.
● [$Cu_2(Me{\cdot}CO_2)_4(C_4H_8O_2)_2$].
○ [$Cu_2(H{\cdot}CO_2)_4(C_4H_8O_2)$].
---- Calculated.
The arrows represent $N\alpha$ = (1) 60×10^{-6} (calc.) and (2) 128×10^{-6} (exptl.).

It is noteworthy that the only other diamagnetic complex of bivalent copper is the dark green binuclear bisdiazoaminobenzene derivative, $Cu_2(Ph{\cdot}N{\vdots}N{\cdot}NPh)_4$, recently reported by Harris and Martin.[9] This is believed to possess the structure (II), the diamagnetism arising from the presence of a strong copper-to-copper bond. Unlike the present compounds, bisdiazoaminobenzenecopper(II) is diamagnetic at all temperatures between 80° and 400° K. We believe that the anomalous magnetic properties of the monoamino- and hemidioxan derivatives of copper formate likewise reflect the presence of

[9] Harris and Martin, *Proc. Chem. Soc.*, 1958, 259.

a direct copper-to-copper exchange interaction arising from the binuclear molecular configuration shown in (I), where L = amine or dioxan.

The binuclear structure proposed for these derivatives of copper formate is supported by a comparison of the experimental susceptibility with that calculated on the basis of the copper acetate type model discussed[5] in Part I. There it was shown that the magnetic susceptibility, χ_M, could be related to the energy interval, J, between a lower singlet state ($S = 0$) and an upper triplet state ($S = 1$) (which arise from direct exchange between pairs of contiguous copper atoms in the molecule) by means of an expression, first derived by Bleaney and Bowers,[2] for copper(II) acetate monohydrate, *viz.*,

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

where J was evaluated from the relation, $J = 1{\cdot}6kT_c$, T_c representing the temperature at which the susceptibility attains its maximum value. Unfortunately, T_c cannot be measured for the present derivatives, since they decompose well below this temperature, and so g, the spectroscopic splitting factor, of necessity, has been taken to be the mean of the values obtained for the higher homologues, *i.e.*, $g = 2{\cdot}16$, and T_c obtained from it for each compound by substituting into the equation the value of χ_M at three temperatures, 150°, 250°, and 350° K. Thereby, it is found that J is not independent of temperature, as is assumed in the derivation of the above formula, but that it differs considerably at 150° from the values at 250° and 350°. The values at the two higher temperatures are, however, in close agreement and in the calculation of the theoretical susceptibility curves for the four amine derivatives, T_c and J are accordingly taken as the mean of the values obtained for the four compounds at 250° and 350° K. Table 3 contains the calculated values of T_c for the four amines and the dioxan compound at the three temperatures: the values at 150° will naturally show large scatter owing to the small magnitude of the susceptibility at such low temperatures.

The calculated susceptibility equations for the five compounds then become

$$[Cu_2(H{\cdot}CO_2)_4(\text{amine})_2]\ldots\ldots\ldots\chi_M = \frac{0{\cdot}585}{T}\left[1 + \tfrac{1}{3}\exp.\left(\frac{776}{T}\right)\right]^{-1} + 168 \times 10^{-6}$$

$$[Cu_2(H{\cdot}CO_2)_4(C_4H_8O_2)]\ldots\ldots\ldots\chi_M = \frac{0{\cdot}585}{T}\left[1 + \tfrac{1}{3}\exp.\left(\frac{794}{T}\right)\right]^{-1} + 128 \times 10^{-6}$$

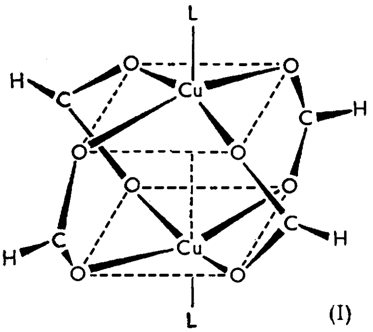
TABLE 3. *Calculated values of* T_c *at* 150°, 250°, *and* 350° K.

Derivative	T_c (calc.) 150°	 250°	 350°
Pyridine	569	489	495
α-Picoline	553	484	484
β-Picoline	—	484	461
γ-Picoline	628	480	491
Dioxan	565	502	497

The data for the α-picoline derivative are representative of the behaviour of the amine complexes, and are plotted in Fig. 1. The agreement between the calculated and experimental curves is quite good if allowance is made for the appreciable increase in magnitude of J as the temperature is lowered below 250° K. This agreement provides strong evidence that the compounds are indeed binuclear derivatives of copper formate with the structure (I), and should be properly formulated as $[Cu_2(H{\cdot}CO_2)_4am_2]$ and $[Cu_2(H{\cdot}CO_2)_4(C_4H_8O_2)]$.

Table 4 contains values, calculated from the expression $J = 1{\cdot}6kT_c$, for the separation between the singlet and triplet states. It will be seen that for these compounds J is of the order of 500—600 cm.$^{-1}$ (*i.e.*, 1·5—2·0 kcal. mole^{-1}), which is roughly twice the separation observed[4] in the heavier anhydrous and hydrated copper n-alkanoates, where $J = 309 \pm 31$ cm.$^{-1}$ $= 0{\cdot}88 \pm 0{\cdot}09$ kcal mole^{-1}. This is an indication that the intramolecular exchange interaction between copper atoms is considerably stronger in the formate series.

That this stronger interaction arises from the replacement of acetate by formate, and not by the insertion of amine or dioxan in the terminal positions, is demonstrated by direct comparison of the dioxan derivatives of copper formate and copper acetate. The susceptibility–temperature and magnetic moment–temperature curves for both $[Cu_2(H{\cdot}CO_2)_4(C_4H_8O_2)]$ and $[Cu_2(CH_3{\cdot}CO_2)_4(C_4H_8O_2)_2]$ are plotted together in Fig. 2. The magnetic moment of the acetate derivative rises from zero to 1·5 B.M. in the temperature range 50—400° K, in contrast to the moment of the formate derivative which is zero below 120° K, and has only increased to 1·2 B.M. at 400° K. Similarly, while the χ–T curve for acetate exhibits a well-defined maximum at 325° K, there is no evidence for a maximum in the formate curve up to 375° K, and, in fact, the calculated value is as high as 497° K. Evidently, replacement of acetate by the formate ion markedly increases the proposed $3d_\delta$–$3d_\delta$ orbital overlap, and thereby enhances the depression of the magnetic moment.



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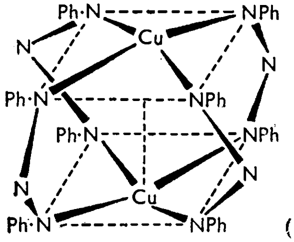
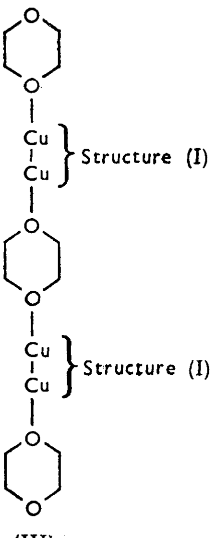


(II)



(III)

TABLE 4. *Calculated separation between singlet and triplet levels at* 150°, 250°, *and* 350° K, g *being assumed to be* 2·16.

Compound $[Cu_2(H{\cdot}CO_2)_4L_2]$	150°		250°		350°	
Singlet-triplet separation, J	cm.$^{-1}$	kcal. mole^{-1}	cm.$^{-1}$	kcal. mole^{-1}	cm.$^{-1}$	kcal. mole^{-1}
L = Pyridine	632	1·81	543	1·55	550	1·57
α-Picoline	614	1·75	538	1·54	538	1·54
β-Picoline	—	—	538	1·54	512	1·46
γ-Picoline	701	2·00	534	1·53	546	1·56
Mean for amine derivatives	649 ± 52	1·85 ± 0·15	538 ± 5	1·54 ± 0·01	537 ± 25	1·53 ± 0·07
L_2 = Dioxan	628	1·80	558	1·60	552	1·58

The shape of the susceptibility–temperature curves for the binuclear formate derivatives differs from that of the heavier alkanoates in one further significant feature, namely, the constant value recorded for the susceptibility below about 120° K. This value for the four amine complexes falls in the range $(168 \pm 10) \times 10^{-6}$, whilst for the hemidioxan compound a slightly smaller value, 128×10^{-6}, was recorded. The constant susceptibilities at low temperatures represent the temperature-independent paramagnetism associated with bivalent copper and will be discussed elsewhere.[10] The fact that this paramagnetism

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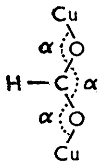
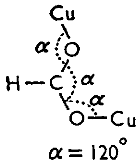
[10] Lark, Martin, and Waterman, unpublished data.

is being observed in the complete absence of spin paramagnetism shows that, at these temperatures, all the copper atoms are in diamagnetic singlet states, and that only above 120° K do the paramagnetic triplet states begin to be populated.



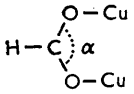
(IV)

anti-anti-Bridging arrangement



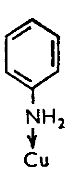
(V)

anti-syn-Bridging arrangement

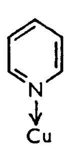


(VI)

syn-syn-Bridging arrangement



(VII)



(VIII)

(IX)

It is interesting that the dichroic dark blue-green dioxan derivative contains only one dioxan molecule per binuclear formate molecule. This immediately suggests that dioxan is utilizing both its oxygen atoms by co-ordinating with copper atoms from two different binuclear molecules. It would thus act as a novel type of " bridge " enabling the formate molecules to form infinite dioxan-bridged chains. The compound is surprisingly stable to heat, remaining unchanged *in vacuo* even at 150° C. This is in marked contrast to the thermo-sensitive heterocyclic amine derivatives and is quite possibly a consequence of the proposed polymeric structure illustrated in (III).

It is clear from these and earlier investigations that the terminal ligands, marked L in (I), exert such a highly specific influence on the bound copper atom that they largely determine whether the formate will adopt a binuclear configuration or not. It has already been pointed out [1] that the residual electrostatic charge on each copper atom, after bonding, must play an important rôle in deciding whether the bridged dimeric structure will be adopted preferentially. Thus a large residual charge, of either sign, will favour the *anti-anti-* or *anti-syn*-bridging arrangements (IV) and (V), in which bridged copper atoms are *ca.* 5·8 Å apart, rather than the *syn-syn*-arrangement (VI) in which these atoms are virtually contiguous, *i.e.*, *ca.* 2·6 Å apart. The higher acid dissociation constant of formic acid ($K_A = 1{\cdot}7 \times 10^{-4}$) than of, *e.g.*, acetic acid ($K_A = 1{\cdot}7 \times 10^{-5}$) reflects the smaller σ-electron charge density on the formate oxygen atoms. It seems not unreasonable to infer that the formate will therefore be less effective than acetate in reducing the positive charge on copper during the formation of the relevant copper n-alkanoate. This could well account for the reluctance of copper formate to crystallize from dilute formic acid solution with the binuclear configuration based on the *syn-syn*-configuration (VI). Nevertheless, the visible and ultraviolet spectra of such solutions do provide evidence for the ephemeral existence of such a species, even though it could not be isolated from solution either in hydrated or anhydrous forms.[1]

The remarkable " conditioning " influence exerted on copper formate by the pyridine bases and by dioxan, when occupying the terminal positions L in (I), can thus arise from the concomitant reduction in magnitude of the residual positive charge on each copper atom, to an extent sufficient for the *syn-syn*-bonding arrangement to become the favoured configuration. The fact that conversion of the violet bisamine cupric formates into the emerald-green monoamine derivates takes place so readily in the solid state, even under mild conditions, indicates that the binuclear configuration is much the preferred structure, provided that the magnitude of the electrostatic charge in copper has been reduced below some critical value. Since α-picoline is as efficient as pyridine in effecting this change, it is concluded that any inductive or steric effects due to the α-methyl group are either absent or very small.

The success of the pyridine-type bases contrasts with the failure of aniline in inducing the bridged configuration. However, pyridine co-ordinates to transition-metal ions, both more frequently and more strongly than aromatic amines, for whereas aniline can only form a classical co-ordinate link as in (VII), pyridine can form a multiple bond to the metal atom which involves both an $\overset{+}{\mathrm{N}}\rightarrow\overset{-}{\mathrm{M}}$ classical co-ordinate σ-linkage and a $\overset{+}{\mathrm{M}}\rightarrow\overset{-}{\mathrm{N}}$ ($3d_{\pi}\rightarrow 2p_{\pi}$) bond, through participation of the structures (VIII) and (IX). Double bonding between the metal and pyridine immediately provides a mechanism by which an excessive accumulation of negative charge on copper from the $\overset{+}{\mathrm{N}}\rightarrow\overline{\mathrm{Cu}}$ σ-bond can be partly alleviated by means of the $\overset{+}{\mathrm{Cu}}\rightarrow\overline{\mathrm{N}}$, π-bond, which has the reverse polarity. In the case of aniline no such mechanism exists.

In addition to double-bonding capacity, the subtle influence of the terminal ligand L must result from the accumulated influence of a variety of other factors. Both the electrostatic and orbital (*e.g.*, $3d_{z^2}$–$3d_{z^2}$) Cu–Cu repulsions, and the electronegativity, polarizability, σ-electron charge density, steric environment, and compatibility of L–Cu orbital overlap, of the ligating atom, are all factors which must contribute to its influence when co-ordinated to copper in this way. Obviously, it is impossible to disentangle the individual contributions of each effect from a magnetic moment which is indirectly related to the total accumulated contribution. The range of the positive and negative residual charges in which the *syn-syn*-arrangement is stable is probably narrow.

Finally, it is noteworthy that pyridine and its three methyl derivatives, and the cyclic aliphatic diether, dioxan, not only force copper formate to adopt the δ-bonded structure, but lead to the formation of a copper-to-coper δ-bond of greater binding energy than the δ-bond in heavier copper n-alkanoates. This is indicated by the much lower magnetic moment of the formate derivatives at room temperature (0·9 B.M. compared with 1·4 B.M.), and by the higher temperature of the maximum susceptibility (about 500° K compared with 270° K). In fact, the singlet–triplet separation, J, which provides a measure of the exchange energy associated with the δ-bond, is nearly twice that observed in copper n-alkanoates, reflecting a greatly enhanced lateral overlap between the Cu–Cu, $3d_{\delta}$–$3d_{\delta}$, orbitals.

The increased δ-overlap may arise as follows. First, it is possible that the Cu–Cu distance in the formate derivatives is decreased from the value of 2·64 Å observed in copper acetate monohydrate, towards the value 2·55 Å observed in metallic copper. It has already been pointed out [5] that orbital overlap between two δ-orbitals oriented with their lobar planes parallel will be particularly sensitive to the separation between their centres. Dr. G. A. Barclay and C. Kennard, of this department, are engaged on an *X*-ray structural investigation of the monopyridine derivative, in order to determine both the molecular geometry and the Cu–Cu bond length.

The second possibility assumes that the Cu–Cu distance remains 2·64 Å, as in the acetate, but that the $3d_{\delta}$–$3d_{\delta}$ overlap is considerably enhanced by the modified ligand field produced by the replacement of acetate by formate oxygen atoms and the presence of the terminal ligands. Thus, we [11] have recently prepared binuclear compounds of the type $[\mathrm{Cu_2(C_3H_7{\cdot}CO_2)_4py_2}]$ with a moment of 1·37 (20°) and $J = 300$ cm.$^{-1}$, which contrast with the corresponding aniline analogue $[\mathrm{Cu_2(C_3H_7{\cdot}CO_2)_4an_2}]$ which has a much higher moment 1·8 B.M. and lower $J = 100$ cm.$^{-1}$. Clearly, in this series, the terminal ligand is exerting a marked influence on the $3d_{\delta}$–$3d_{\delta}$ orbital overlap. The preparation of new binuclear derivatives of bivalent copper of general formula $[\mathrm{Cu_2(R{\cdot}CO_2)_4L_2}]$, and the effect of varying both R and L on the magnetic properties and on the binding energy of the Cu–Cu δ-bond, will be reported in a forthcoming publication.

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[11] Kokot and Martin, unpublished data.