charge on the central copper ion and so reduce the radial extension of copper 3d orbitals and thereby lower the concomitant singlet–triplet separation.[32] That is, for the dimer the order of spectrochemical effects is dioxane $\sim$ water $\sim$ ethanol $<$ aniline $<$ pyridine, whereas the order of singlet–triplet reducing power is pyridine $<$ dioxane $\sim$ water $\sim$ ethanol $<$ aniline.

The insensitivity of band II to these ligands is at variance with the original proposal of Yamada, *et al.*,[35] that this band is "an indication of the linkage between the two copper atoms." Nor can it be assigned to an internal transition in the partly filled d shell, and we have commented elsewhere[26] on other evidence which precludes such an assignment. We have recently completed molecular orbital calculations in the Hückel approximation of the π system of the copper(II) acetate dimer and have concluded that band II may either arise from electron transfer from the highest filled π-nonbonding orbital of the ligand to the empty σ-antibonding $d_{x^2-y^2}$ orbital on copper or possibly from the filled d_{xy} orbital of copper to the empty π-antibonding orbital of the acetate ligands.[36] The appearance of a similar near-ultraviolet band in the electronic spectra of monomeric copper(II) acetylacetonate[37] and of planar-bridged dimers[38] such as 8-hydroxyquinolinatocopper(II) is not unexpected, for closely related copper–ligand π systems are present for each compound.

The reflectance spectra of copper(II) malonate and copper(II) oxalate are atypical of the dicarboxylates in having a single broad region of absorption occurring at 775 and 730 mμ, respectively (see Table II). The absence of band II from the spectra is expected from the magnetic properties of these two derivatives and reinforces our view that this band originates in the π system of the copper acetate dimer.

Acknowledgment.—The authors thank Dr. Ernest Challen of the University of New South Wales for carbon, hydrogen, and nitrogen microanalyses.

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CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY,
THE UNIVERSITY OF WESTERN AUSTRALIA, NEDLANDS, W.A., AUSTRALIA

The Magnetic Properties and Structure of the Cupric α,ω-Dicarboxylates

BY B. N. FIGGIS AND D. J. MARTIN

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The magnetic susceptibilities of five of the cupric α,ω-dicarboxylates have been measured between about 80 and 300°K. The results confirm that, with the exception of the malonate, the structures of the compounds are based upon the dimeric unit found in the cupric monocarboxylates. The succinate, and probably the glutarate and suberate, are formed of chains of magnetically isolated dimeric units joined by $-(CH_2)_n-$ bridges. The oxalate shows most anomalous magnetic behavior, and this is believed to follow from a three-dimensional cross-linked arrangement of the dimers.

The magnetic moments of a considerable number of complexes of bivalent copper are below the more normal value of about 1.9 B.M.[1] and indeed are below the spin-only value for one unpaired electron, 1.73 B.M. In most of the compounds the reduction in the magnetic moment is attributed to magnetic exchange of an antiferromagnetic nature consequent upon either the formation of a weak bond between two or more copper atoms[2] or a superexchange process *via* intervening oxygen or other atoms.[3] The most notable instance concerns the acetate and higher monocarboxylic acid derivatives, $Cu_2(RCOO)_4 \cdot 2H_2O$. That series of compounds is based upon the dimeric structure which is established for the acetate by X-ray single-crystal analysis.[4] The four acetate groups bridge the two copper atoms. One oxygen atom from each forms part of the square plane about each copper. The octahedral stereochemistry of each copper atom is completed by a water molecule and the other copper atom.

The variation of magnetic susceptibility of the cupric monocarboxylates with temperature is accurately of the form required for magnetic interaction between two sites of spin $^1/_2$ with exchange integral J.[2,5] The susceptibility should obey the relationship

$$\chi_{\mathrm{Cu}} = 3g^2 \frac{N\beta^2}{3kT}[3 + \exp(-2J/kT)]^{-1} + N\alpha \qquad (1)$$

where g is the Lande splitting factor (near 2.2 for most cupric complexes) and $N\alpha$ is the temperature-independent paramagnetism (about 60×10^{-6} c.g.s./mole for most cupric complexes).[6] $Cu_2(CH_3COO)_4 \cdot 2H_2O$ is accounted for with $J = -204°$, $g = 2.13$, and $N\alpha =$

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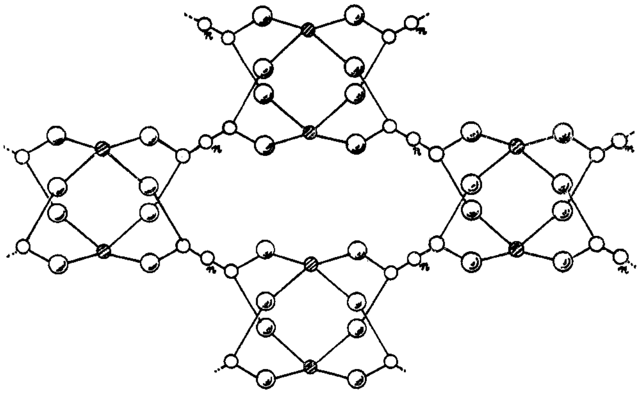

Figure 1.—Previously proposed[13,14] two-dimensional linkage of cupric acetate type dimers in the cupric α,ω-dicarboxylates.

60×10^{-6} c.g.s./mole.[7] At room temperature the magnetic moment of the compound is about 1.4 B.M.

The spectra of the monocarboxylates of bivalent copper, in solution in dioxane, etc., show, in addition to the band at about 13,000 cm.$^{-1}$ normal for cupric complexes, a band at about 25,000 cm.$^{-1}$. This band has been correlated with the presence of the copper–copper bond in the dimeric unit.[8,9] Theoretical considerations have been advanced to account for the magnitude of the exchange integral and the position of the new band in the cupric acetate dimer.[10–12]

The α,ω-dicarboxylates of bivalent copper [Cu(OOC$(CH_2)_n$COO)] also possess subnormal magnetic moments at room temperature.[13,14] With the exception of the first two members of the series, the oxalate ($n = 0$, $\mu_{\text{eff}}^{300^\circ\text{K.}} = 1.2$ B.M.) and the malonate ($n = 1$, $\mu_{\text{eff}}^{300^\circ\text{K.}} = 1.7$ B.M.), the magnetic moments are close to 1.4 B.M. The structure set out in Figure 1, based upon a two-dimensional array of linked cupric acetate type dimers, has been suggested by these earlier workers. The near-normal moment of the malonate was explained by the difficulty of obtaining an even approximately linear bridge from one $-CH_2-$ group.

This paper presents measurements of the magnetic susceptibilities of several of the cupric α,ω-dicarboxylates as a function of temperature, undertaken to find whether their description as systems of magnetically isolated dimeric units is valid. If it is, behavior of the form of the cupric monocarboxylates, eq. 1, should appear. The search for a band in the region of 25,000 cm.$^{-1}$ is also reported.

Concomitant with this research, the determination of the structure of cupric succinate is being carried out by other workers.[15]

Experimental Section

Magnetic susceptibilities at room temperature were determined on a conventional Gouy balance, employing a small electromagnet. Water was used as the calibrant substance. The susceptibilities are estimated to be accurate to ±2%.

Variation of magnetic susceptibility with temperature was carried out between 80 and 300°K. by the Gouy method on apparatus previously described,[16] using a magnetic field of about 5000 gauss. The temperature calibration of the equipment was obtained by the measurement of the magnetic susceptibility of $(NH_4)_2Cu(SO_4)_2\cdot 6H_2O$, which obeys a Curie–Weiss law, with $\theta = 0.3°$.[17] The accuracy of the measurement of relative susceptibility at different temperatures is estimated to be better than 0.5%, and of temperature better than 0.2°.

The spectrum of a single crystal of cupric succinate in the region of 25,000 cm.$^{-1}$ was obtained with the aid of a microscope attached to a manually operated monochromator. No attempt to obtain a value for the extinction coefficient of the band was made.

Analyses for copper were performed by electrodeposition after destruction of the compound with sulfuric acid. Analytical data for the preparations are listed in Table II.

Cupric oxalate was prepared by the slow addition of a solution of oxalic acid (6 g.) in water (100 ml.) to a boiling solution of $CuSO_4\cdot 5H_2O$ (8 g.) in water (300 ml.), with vigorous stirring. The very fine pale blue powder was dried *in vacuo* to yield a material of variable water content, $Cu(C_2O_4)\cdot {\sim}1H_2O$. (The literature generally reports $Cu(C_2O_4)\cdot 0.5H_2O$.) Drying this compound at 100° gave the nearly anhydrous compound, $Cu(C_2O_4)\cdot 0.3H_2O$ (I).

A specimen of apparently larger particle size was obtained by very slow precipitation in the following manner: $CuSO_4\cdot 5H_2O$ (2.48 g.) and oxalic acid (1.6 g.) were dissolved in a solution of sulfuric acid (73.5 g.) made up to 400 ml. with water. To this saturated solution of cupric oxalate,[18] urea (45 g.) was added. The solution was thermostated at 55° for 4 weeks. The hydrolysis of the urea gradually neutralized the sulfuric acid and cupric oxalate separated out. It was dried at 110°. It analyzed as $Cu(C_2O_4)\cdot 0.3H_2O$ (II).

Both the preparations, I and II, appeared to be amorphous on examination under the microscope, but showed well-defined X-ray powder photographs. Many attempts were made, using different precipitation techniques and nonaqueous solvents, to obtain macrocrystalline material, but without success.

Cupric malonate monohydrate ($Cu(C_3H_2O_4)\cdot H_2O$) was prepared by the method of Britton and Jarrett.[19] It was recrystallized from very dilute malonic acid solution.

Cupric succinate dihydrate was prepared by direct precipitation (I) and in crystalline form (II) by the method attempted for the oxalate. A solution of $CuSO_4\cdot 5H_2O$ (5 g.), succinic acid (3.2 g.), and urea (4 g.) in water (250 ml.) was thermostated at 55°. After about 3 days green-blue fibrous needles commenced to separate out. These were washed with water and dried in air, to give $Cu(C_4H_4O_4)\cdot 2H_2O$. Anhydrous cupric succinate was prepared by heating the dihydrate at 120°.

Cupric glutarate was prepared by the same methods as used for the succinate, employing an equivalent amount of glutaric acid. Direct precipitation (I) gave a green anhydrous powder, $Cu(C_5H_6O_4)$. The urea method gave, after drying at 110°, a crystalline preparation (II).

Cupric suberate was prepared by the direct precipitation method as for the succinate, giving a green-blue powder, $Cu(C_8H_{12}O_4)$.

Results

The magnetic moments of the cupric α,ω-dicarboxylates at 300°K. are listed in Table I, together with the

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(7) In order to conform with the more usual definition of the exchange integral, J, $-2J$ is used wherever J appeared in ref. 2.

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Table I

The Magnetic Moments of Cupric α,ω-Dicarboxylates at 300°K.

Compound	n^a	Diam. cor., c.g.s./mole × 10^6	$\mu_{\text{eff}}^{300°\text{K.}}$ B.M., this work	Previous work[12,13] μ_{eff}, B.M.	Previous work[12,13] T, °K.
Oxalate·0.3H_2O	0	−25	1.25[b,c]	1.20	288
Malonate	1	−34	1.86	1.76	
Succinate	2	−46	1.40[d]	1.40	299
Succinate·2H_2O	2	−72	1.40	1.40	298
Glutarate	3	−57	1.40	1.45	300
Suberate	6	−93	1.45	1.44	288

[a] n = number of $-CH_2-$ groups in the acid. [b] This moment varies between 1.30 and 1.25 B.M. as the magnetic field strength in the Gouy method varies from 3900 to 8400 gauss. [c] The moment is the same for both preparations I and II. [d] This value is for preparation II. The value for preparation I was about 1.5 B.M., but varied somewhat from sample to sample.

Table II

Analytical Data for the Cupric α,ω-Dicarboxylates

Formula		Calcd., % Cu	Calcd., % C	Calcd., % H	Found, % Cu	Found, % C	Found, % H
$Cu(C_2O_4)\cdot 0.3H_2O$	(I)	40.65	15.30	...	40.6	15.38	...
	(II)				40.3	15.24	...
$Cu(C_3H_2O_4)\cdot H_2O$		34.61	19.62	2.19	34.6	19.80	2.30
$Cu(C_4H_4O_4)$			26.75	2.23		27.26	2.55
$Cu(C_4H_4O_4)\cdot 2H_2O$		29.47	22.27	3.74	29.42	22.43	3.98
$Cu(C_5H_6O_4)$	(I)	32.82	31.02	3.11	32.4	31.40	3.42
	(II)				32.4	31.35	3.06
$Cu(C_8H_{12}O_4)$		26.96	40.77	5.12	26.7	40.37	5.22

Table III

Smoothed Values of χ_{Cu} for Some of the Cupric α,ω-Dicarboxylates at Fixed Temperature Intervals[a]

T, °K.	Copper succinate dihydrate	Copper succinate	Copper malonate	Copper glutarate	Copper suberate
325	809	793	1320	808	870
300	820	804	1444	819	878
275	817	808	1564	830	881
250	795	795	1723	830	880
225	762	766	1918	800	860
200	709	719	2135	745	790
150	470	522	2790	532	570
100	200	172	4430	201	230
75	140	100	6100	100	100

[a] The units are c.g.s. × 10^6.

values reported by previous workers. In general, the agreement is good. The magnetic susceptibilities for the compounds, except the oxalate, at several fixed temperatures are given in Table III. These values were obtained by interpolation of the smoothed experimental curves. The corresponding values are not quoted for the oxalate because of the anomalous behavior. Data given recently for the oxalate and succinate[20] do not agree with our results in detail. Except for the malonate, the behaviors of the magnetic susceptibilities of the compounds as a function of temperature are given in Figures 2 and 3. The spectrum of a single crystal of cupric succinate dihydrate in the region of 25,000 cm.$^{-1}$ is given in Figure 4.

Cupric succinate dihydrate belongs to the space group $P\bar{1}$: a = 6.44 Å., b = 7.62 Å., c = 8.08 Å., α = 104.24°, β = 73.11°, γ = 98.62°. The crystals grow in laths whose long dimension is the a axis. Preliminary interpretation of three-dimensional X-ray data[15] shows that the molecular structure of the compound is based upon chains of cupric acetate type dimers along the a axis. The individual dimeric units in the chain are joined by two $-CH_2CH_2-$ bridges from opposite corners. The Cu–Cu separation within a dimeric unit is 2.61 Å. (it is 2.64 Å. in cupric acetate monohydrate). The Cu–Cu separation between nearest copper atoms in

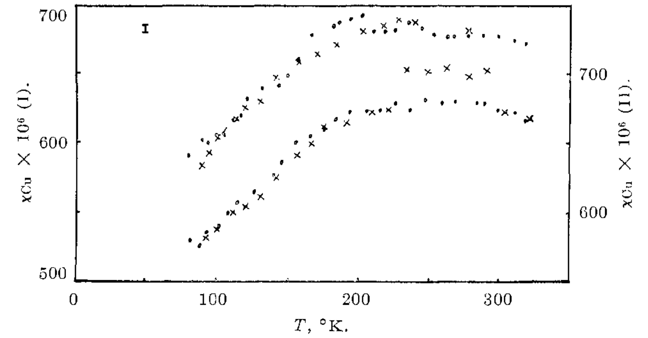

Figure 2.—The magnetic susceptibility of cupric oxalate as a function of temperature, for two different preparations: I, estimated experimental error; ●, decreasing temperature; ×, increasing temperature.

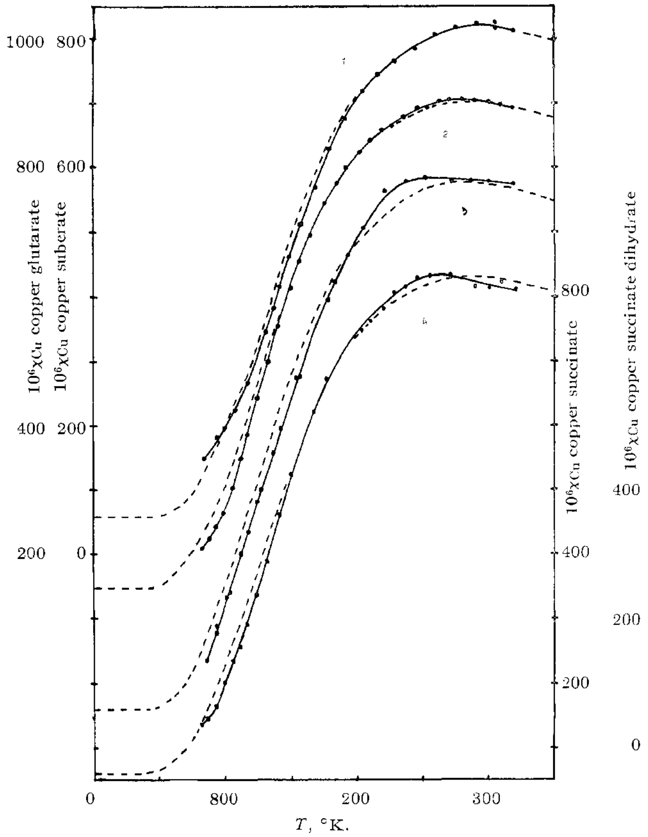

Figure 3.—The magnetic susceptibilities some cupric α,ω-dicarboxylates as a function of temperature. The dotted lines give the results of eq. 1 evaluated for the sets of parameters listed: 1, copper succinate dihydrate: J = −242°, g = 2.20, $N\alpha$ = 60 × 10^{-6} c.g.s./mole; 2, copper succinate: J = −230°, g = 2.12, $N\alpha$ = 60 × 10^{-6} c.g.s./mole; 3, copper suberate: J = −225°, g = 2.16, $N\alpha$ = 60 × 10^{-6} c.g.s./mole; 4, copper glutarate: J = −230°, g = 2.16, $N\alpha$ = 60 × 10^{-6} c.g.s./mole.

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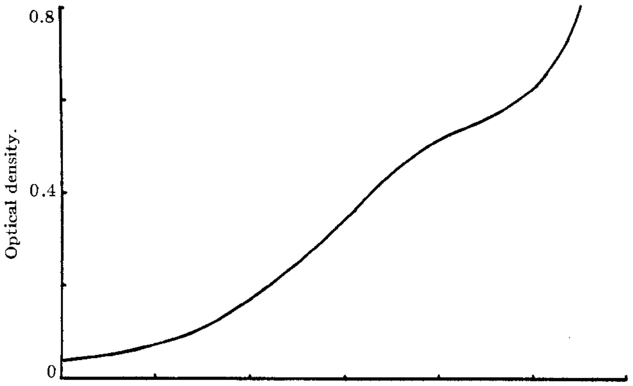

Figure 4.—The spectrum of a single crystal of cupric succinate dihydrate down, approximately, the c axis.

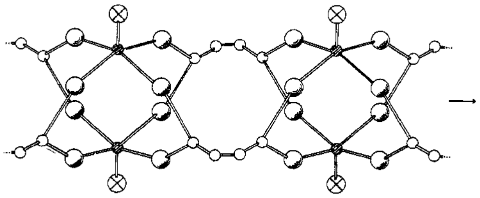

Figure 5.—Two units in the chain structure of copper succinate dihydrate. The water molecule not coordinated to copper is omitted. The arrow indicates the a axis.

TABLE IV

THE PARAMETERS OF EQ. 1 WHICH DESCRIBE THE VARIATION OF THE MAGNETIC SUSCEPTIBILITIES OF SOME OF THE CUPRIC α,ω-DICARBOXYLATES WITH TEMPERATURE[a]

	Cupric succinate dihydrate	Cupric succinate	Cupric glutarate	Cupric suberate
J, °K.	−242	−230	−230	−225
g	2.20	2.12	2.16	2.16

[a] In each case $N\alpha$ is taken to be 60×10^{-6} c.g.s./mole.

adjacent units in the chain is 6.44 Å. The main features of the structure are outlined in Figure 5. One of the water molecules is not coordinated to a copper atom, but forms hydrogen bonds between oxygen atoms of carbonyl groups in adjacent chains. It is not shown in Figure 5.

The magnetic susceptibility of cupric malonate obeys the Curie–Weiss law ($\chi_{Cu} \propto (T + \theta)^{-1}$) with $\theta = -2°$.

Cupric succinate dihydrate shows a variation of magnetic susceptibility with temperature (Figure 3) very similar to that of cupric acetate. The susceptibility passes through a broad maximum at about 270°K. The results can be accounted for by eq. 1 with the values of the parameters given in Table IV. The exchange integral, J, is some 20% larger in absolute magnitude (−242° as against −204°) than in cupric acetate monohydrate. This increase in the exchange integral could be an obvious consequence of the closer approach of the two copper atoms of the dimeric unit, from 2.64 to 2.61 Å. However, the uncertainties in the determination of the Cu–Cu separation in the acetate may be sufficiently large to make this comparison unreliable. More recent neutral diffraction studies[21] have indicated that the separation in that compound is also 2.61 Å. The behavior of anhydrous cupric succinate is very similar (Figure 3 and Table IV). In contrast to the cupric acetate system, where there is a small increase, the loss of the water molecule coordinated to each copper atom causes a small decrease in $|J|$ in the cupric succinate system.

The susceptibility of cupric glutarate varies with temperature in much the same way as the acetate, a broad maximum appearing at about 270°K. (Figure 3). The results cannot be fitted to eq. 1 with quite the same accuracy as is possible for the succinate. The results are best fitted by the set of parameters given in Table IV, which are very close to those for the succinate. The susceptibility of cupric suberate appears to be passing through a broad maximum at about 300°K. (Figure 3). The behavior is again of the form of cupric acetate, but the data cannot be described by eq. 1 with high accuracy. The set of parameters for closest fit is given in Table IV, and they are close to the values for the succinate.

The magnetic susceptibility of cupric oxalate and its variation with temperature present some remarkable features. There is some resemblance to the behavior of cupric acetate, in that the Curie law is not followed, and there is a broad maximum in the susceptibility at about 300°K. However, the fall in the susceptibility at lower temperatures is much less than required by eq. 1.

At room temperature the susceptibility of the oxalate depends somewhat on the strength of the magnetic field used for the measurement. Since the Gouy method was used, a quantitative examination of the variation of susceptibility with field strength would not have been useful. As the temperature is reduced below 300°K. the susceptibility falls only slightly and with a certain amount of irregularity. On increasing the temperature from 80°K. the susceptibility rises, to about the initial value at 300°K. However, the two curves, one for falling and one for rising temperature, do not match accurately; only the general features are reproduced. Furthermore, although the general fall of susceptibility with decreasing temperature is maintained with different preparations of the compound, the details of the variation are not. Figure 2 shows the results for cupric oxalate prepared by the two methods, I and II, given in the Experimental Section. The samples show differences and both show the thermal hysteresis at lower temperatures.

The spectrum of a single crystal of cupric succinate, down the c axis, approximately, indicates the presence of a weak, broad absorption band centered at about 28,000 cm.$^{-1}$ (Figure 4).

Discussion

The behavior of the magnetic susceptibilities of cupric succinate and of its dihydrate are in accord with an isolated system of cupric acetate dimeric units. Such a system is indeed present in the chain structure deduced from the X-ray single-crystal analysis. Evidently the inter-unit Cu–Cu separation is sufficient to

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(21) R. Chidambaram and G. M. Brown, *Am. Cryst. Assn. Program Abstr.* (1965).

prevent magnetic interaction between them. The presence of the band at 28,000 cm.$^{-1}$ in this substance confirms its correlation with the dimeric unit,[22] although a similar band has been found in cupric compounds which do not possess that feature.[23] In view of the fact that cupric glutarate and suberate also show behavior fairly close to that for a system of the isolated dimers, it is likely that they also possess the cupric acetate structural feature, with linking of the units by means of $-(CH_2)_3-$ and $-(CH_2)_6-$ bridges, respectively. Indeed, it is possible to substantiate this hypothesis for the glutarate, with some certainty. X-Ray analysis of a single crystal of cupric glutarate shows that, like the succinate, it is triclinic, and the dimensions of the unit cell are very similar. The exception to this statement is that the *a* axis is elongated relative to the succinate by 1.6 Å. It is along the *a* axis that linkage of the dimeric units by means of $-(CH_2)_2-$ groups takes place in the succinate. The increased *a* dimension corresponds accurately to the insertion of the additional $-CH_2-$ group in the linkage to form the glutarate. The substances are all very insoluble in water, the succinate being the most soluble (0.03 g./100 ml.).

Cupric malonate is, magnetically, a perfectly normal bivalent copper complex. The magnetic moment, 1.86 B.M., is very much as expected, and the variation of the susceptibility with temperature is essentially the usual Curie law. This compound cannot possess the dimeric structural unit of cupric acetate and is presumably monomeric. The much greater solubility in water (2.6 g./100 ml.) supports this thesis.

Cupric oxalate is quite insoluble in water. It defied all attempts to obtain a crystalline material. Since the compound showed at least some of the features of the variation of magnetic susceptibility with temperature characteristic of cupric acetate, it is likely that it, too, possesses the dimeric unit structure in some form. However, it is obvious that the bridging arrangement between the dimeric units must be very complicated. Such a state of affairs does not arise from a model in which the cross-linking between the dimeric units forms a two-dimensional array, as in Figure 2. The complicated magnetic behavior of cupric oxalate indicates that the dimeric units are not magnetically isolated. There must be magnetic exchange between adjacent units. It is not difficult to invoke superexchange *via* –O–C–C–O– bridges to explain the interaction. The mechanism may be similar to that proposed for the exchange in one of the forms of cupric formate.[3] It is likely that the bridging arrangement between the dimeric units in cupric oxalate is of lower symmetry than suggested in Figure 1 and that it extends into three dimensions. This statement is made because of the similarity of the magnetic behavior to that of many "metamagnetic" substances. These "metamagnetic" substances, such as FeF_3, give rise to magnetic exchange in lattices of low symmetry. The magnetic behavior is complicated and shows features of both ferromagnetism and antiferromagnetism.[24] The high symmetry of the array of Figure 1 would probably lead to behavior closer to that of true antiferromagnetism, with a sharp break in the χ *vs.* T curve, the susceptibility falling rapidly below the Curie temperature.

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