746. *Magnetic Studies with Copper*(II) *Salts. Part I. Anomalous Paramagnetism and δ-Bonding in Anhydrous and Hydrated Copper*(II) *Acetates.*

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The temperature variation of the magnetic susceptibilities of anhydrous and hydrated copper(II) acetates has been determined between 90° and 400° K. The results establish well-defined maxima in the susceptibility curves at 270° and 255° K from which an exchange interaction between adjacent copper atoms in each of the binuclear molecules may be calculated to be 302 and 286 cm.$^{-1}$ respectively. These values indicate the existence of very weak covalent copper–copper bonds in which the exchange contribution to the total bond energy is approx. 1 kcal. mole^{-1}.

The nature of the bond is discussed from the valency-bond point of view and it is suggested that a δ-bond is formed between adjacent copper atoms by lateral overlap of $3d_{x^2-y^2}$ orbitals, the z-axis being taken as along the line joining the copper atoms. Copper acetate, according to this hypothesis, is the first case in which a δ-bond is the sole direct link between two atoms.

The diamagnetism reported for the isostructural chromous acetate is consistent with the presence of weak σ-, π-, and δ-bonds between each pair of chromium atoms.

The experimental susceptibilities for the copper acetates agree with those calculated theoretically from an expression similar to one first developed by Bleaney and Bowers.[1] Some discrepancies below 200° K in two earlier determinations of the susceptibility of hydrated copper acetate are discussed.

THE magnetic behaviour of crystalline cupric acetate monohydrate $Cu(CH_3 \cdot CO_2)_2,H_2O$ has excited considerable interest since Lifschitz and Rosenbohm [2] in 1915, using the Curie method, found that the molar susceptibility χ_M at room temperature was much less than the value, $10^6 \times \chi_M \sim 1600$, usually observed for copper salts. With the exception of some measurements by Bhatnagar, Singh, and Ghani [3] in 1932, all subsequent investigations [4, 5, 6, 7, 8] have confirmed that the susceptibility of copper acetate at room temperature is anomalously low.

The first study of the temperature variation of the susceptibility of a single crystal of the hydrate (between 83° and 304° K) was made in 1951 by Guha.[6] Instead of obeying some form of the expected Curie–Weiss law, the susceptibility was found to pass through a probable maximum near 270° K and to fall rapidly below this temperature, the extrapolated value being zero at 20° K. The main features of Guha's curve were confirmed by Foex, Karantassis, and Perakis [7] for the powdered hydrate between 87° and 288° K. However, below *ca.* 200° K considerable discrepancies exist between the results from these two schools, so that re-investigation seemed necessary before an attempt to correlate experiment and theory quantitatively. In addition, the higher temperature used did not establish the maximum unequivocally or enable the form of the susceptibility curve at, say, 150° above the maximum to be assessed. Further, extrapolation of Guha's results leads to $\chi_M = 0$ at *ca.* 20° K whereas Foex *et al.* report 75° K.

Evidence that this anomalous magnetic behaviour arises from some form of strong coupling between the unpaired electrons on adjacent copper atoms through exchange forces was obtained from the anomalous behaviour of both powdered [9] and single crystal

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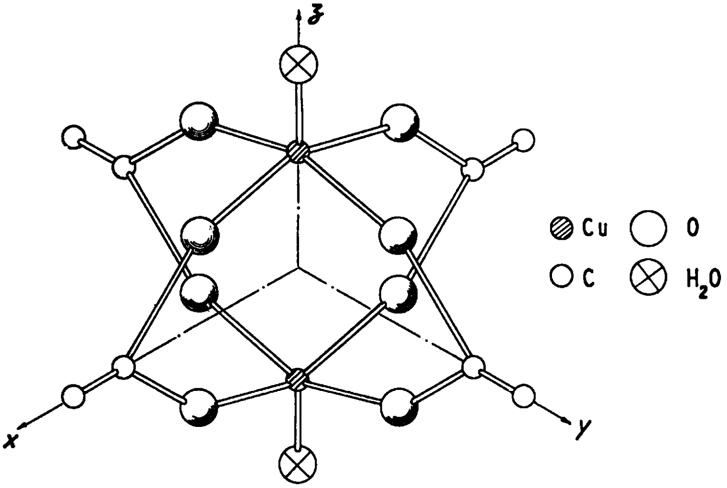
[1] Bleaney and Bowers, *Proc. Roy. Soc.*, 1952, *A*, **214**, 451.
[2] Lifschitz and Rosenbohm, *Z. Electrochem.*, 1915, **21**, 499.
[3] Bhatnagar, Singh, and Ghani, *Indian J. Phys.*, 1932, **7**, 323.
[4] Amiel, *Compt. rend.*, 1938, **207**, 1097.
[5] Mookerjee, *Indian J. Phys.*, 1945, **19**, 63.
[6] Guha, *Proc. Roy. Soc.*, 1951, *A*, **206**, 353.
[7] Foex, Karantassis, and Perakis, *Compt. rend.*, 1953, **237**, 982.
[8] Gauthier, *ibid.*, 1954, **238**, 1999.
[9] Lancaster and Gordy, *J. Chem. Phys.*, 1951, **19**, 1181.

specimens [1,10,11,12] of copper acetate towards paramagnetic resonance absorption of microwaves in the range 9—50 kMc./sec. (λ = 0·6—3·3 cm.). In particular, Bleaney and Bowers[1] explained convincingly both the susceptibility curves obtained by Guha and the paramagnetic absorption data by suggesting that isolated pairs of copper atoms interact strongly through exchange forces, each pair forming a lower singlet state and an upper triplet state, only the latter being paramagnetic. As the temperature is lowered the singlet level becomes increasingly populated at the expense of the triplet level so that the susceptibility decreases steadily, eventually to zero. In the absence of either crystallographic data or isomorphous diamagnetic dilution data (as suggested by Mookerjee [5]) they were unable to decide whether direct spin interaction occurred between adjacent copper atoms or whether the interaction forces were of Kramer's super-exchange type,[13] [14] acting through intermediate oxygen atoms.

The latter problem has been recently resolved by Niekerk and Schoening's complete structure determination [15] which shows that copper acetate monohydrate is a binuclear molecule $Cu_2(CH_3{\cdot}CO_2)_4,2H_2O$ in which copper atoms are bridged in pairs by four acetate groups with two water molecules occupying the terminal positions (cf. Fig. 1).

FIG. 1. *Structure of the cupric acetate monohydrate molecule.*



A remarkable feature of the structure is the close distance of approach of the two copper atoms (2·64 Å) which is only slightly greater than the interatomic distance in metallic copper (2·56 Å). Clearly, the postulated exchange interaction between electron spins is of a direct nature rather than of the super-exchange type, and may be described as the overlap of atomic orbitals of the two copper atoms.

The present work was undertaken as part of a programme of cryomagnetic investigations on polycrystalline inorganic compounds in which exchange interactions of an antiferromagnetic nature play an important role.[16] The specific objects were : First, as mentioned above, a re-investigation of the temperature dependence of the susceptibility of $Cu(CH_3{\cdot}CO_2)_2,H_2O$, to resolve discrepancies in and to extend earlier measurements. Secondly, to evaluate directly the magnitude of the exchange energy, J, in preference to the procedure employed by Bleaney and Bowers in which they chose an empirical value for J which gave the best fit to Guha's susceptibility data (the latter now seem to be up to 100% in error at the lower temperatures). Thirdly, to examine in detail the nature of

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[10] Bleaney and Bowers, *Phil. Mag.*, 1952, **43**, 372.
[11] Kumagai, Abe, and Shimada, *Phys. Rev.*, 1952, **87**, 385.
[12] Abe and Shimada, *ibid.*, 1953, **90**, 316.
[13] Anderson, *ibid.*, 1950, **79**, 350.
[14] Lidiard, *Reports Progr. Phys.*, 1954, **17**, 201.
[15] Nierkerk and Schoening, *Acta Cryst.*, 1953, **6**, 227.
[16] Martin, Nyholm, and Stephenson, *Chem. and Ind.*, 1956, 83.

the bonding orbitals used by each copper atom, and to extend the examination to the isostructural diamagnetic chromous acetate. In addition, the temperature variation of the susceptibility of anhydrous copper acetate was studied to determine whether the magnitude of the exchange interaction was altered by the concomitant modification of the crystalline field acting on each copper atom.

EXPERIMENTAL

Materials.—Large single crystals of cupric acetate monohydrate were obtained by recrystallization of " AnalaR " copper acetate from dilute acetic acid. They were transparent green or blue diamond-shaped plates. Grinding the crystals with an agate pestle and mortar gave an opaque blue-green powder which was used in the magnetic measurements: its water content was determined by the Fischer method and by dehydration over phosphoric oxide *in vacuo* at 118°. The anhydrous acetate is similar in colour to the hydrated form. Copper was determined by electrolytic deposition on a platinum electrode, the carbon and hydrogen contents by the conventional micro-methods (Anhydrous copper acetate—Found: Cu, 34·9; C, 26·4; H, 3·27. Calc. for $CuC_4H_6O_4$: Cu, 35·0; C, 26·4; H, 3·33%. Hydrated copper acetate—Found: Cu, 31·7; C, 24·4; H, 4·18; H_2O, 9·0. Calc. for $CuC_4H_6O_4,H_2O$: Cu, 31·8; C, 24·1; H, 4·04; H_2O, 9·0%).

Magnetic Measurements.—The magnetic susceptibilities of the anhydrous and the hydrated powdered specimens were determined by the Gouy method, in nitrogen between 90° and 400° K, an apparatus developed by Figgis and Nyholm [17] being used. The specimen was maintained at within ±0·05° for 1—2 hr. at each temperature before measurement. The field strength employed was about 8000 gauss, ±0·1%. The chief source of error arose from the packing of the powder in the Gouy tube and, for this reason, the absolute accuracy of the determinations was no better than ±1%, even though the self-consistency of the measurements was much better.

Results.—The values obtained are contained in Tables 1 and 2. The molar susceptibility χ_M (per mole of copper ions) includes a diamagnetic correction of -72×10^{-6} (cf. Mookerjee [5]) for $Cu(CH_3{\cdot}CO_2)_2$, and -85×10^{-6} for the hydrated salt. The effective magnetic moment μ has been calculated at each temperature from the expression $\mu = 2{\cdot}839[(\chi_M - N\alpha)T]^{0{\cdot}5}$, where $N\alpha$ represents the temperature-independent paramagnetism associated with the copper ion. In the present work, a value $N\alpha = 60 \times 10^{-6}$ has been used (cf. refs. 1 and 18).

TABLE 1. *Experimental gram and molar susceptibilities and magnetic moments of* $Cu(CH_3{\cdot}CO_2)_2$.

Temp. (K)	93·0°	105·5°	126·0°	153·2°	182·8°	211·5°
$10^6 \times \chi_g$ (c.g.s., e.m.u.)	0·890	1·30	2·04	2·96	3·71	4·18
$10^6 \times \chi_M$ (c.g.s., e.m.u.)	234	309	442	609	745	831
μ (B.M.)	0·361	0·460	0·623	0·824	1·01	1·15
Temp. (K)	240·5°	268·5°	295·4°	332·6°	398·9°	
$10^6 \times \chi_g$ (c.g.s., e.m.u.)	4·36	4·43	4·39	4·33	4·05	
$10^6 \times \chi_M$ (c.g.s., e.m.u.)	865	877	869	858	808	
μ (B.M.)	1·25	1·33	1·39	1·46	1·55	

TABLE 2. *Experimental gram and molar susceptibilities and magnetic moments of* $Cu(CH_3{\cdot}CO_2)_2,H_2O$.

Temp. (K)	93·5°	100·1°	120·2°	143·5°	160·5°	181·0°	200·9°	220·0°
$10^6 \times \chi_g$ (c.g.s., e.m.u.)	0·907	1·09	1·83	2·64	3·14	3·52	3·77	3·95
$10^6 \times \chi_M$ (c.g.s., e.m.u.)	266	302	451	612	712	787	837	873
μ (B.M.)	0·39	0·44	0·62	0·80	0·92	1·03	1·12	1·20
Temp. (K)	239·7°	258·6°	277·9°	294·2°	300·3°	321·3°	349·5°	396·5°
$10^6 \times \chi_g$ (c.g.s., e.m.u.)	4·05	4·07	4·06	4·03	4·02	3·96	3·85	3·57
$10^6 \times \chi_M$ (c.g.s., e.m.u.)	893	898	895	889	878	876	854	797
μ (B.M.)	1·27	1·32	1·37	1·40	1·42	1·45	1·50	1·54

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[17] Figgis and Nyholm, unpublished work.

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

The present room-temperature susceptibilities are compared in Table 3 with earlier values. The agreement is good except with that by Bhatnagar, Singh, and Ghani[3] now thought to be erroneous.

The variation with temperature, of the molar susceptibility and the magnetic moment, is shown in Figs. 2 and 3. The susceptibility curve of hydrated copper acetate exhibits a broad maximum in the region of 250° K, whereas the corresponding temperature for the anhydrous compound is some 20° higher. The exact positions of the maxima were established from graphical plots of $\delta\chi/\delta T$ against the temperature T, the intercept on the axis $\delta\chi/\delta T = 0$ being taken as the critical temperature T_c. In this way, values of 270° and 255° K were obtained for the anhydrous and hydrated compounds. Above the critical temperature T_c, the susceptibility

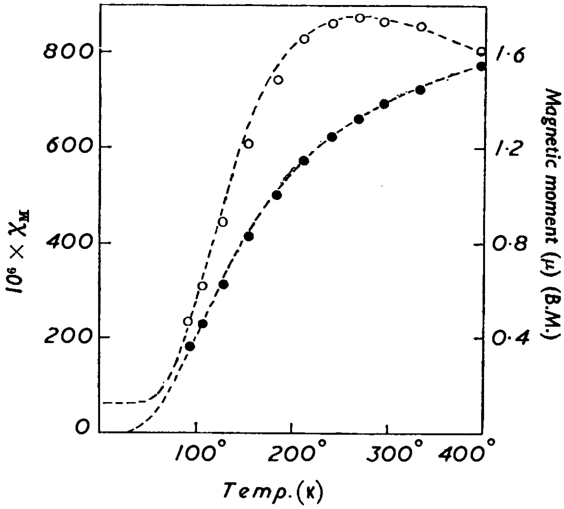


FIG. 2. *Experimental and calculated magnetic susceptibilities and moments of anhydrous cupric acetate.*

○ *Experimental susceptibility,* $10^6 \times \chi_M$.
● *Experimental moment,* μ.
– – – – *Calc. from eqn.* 4.

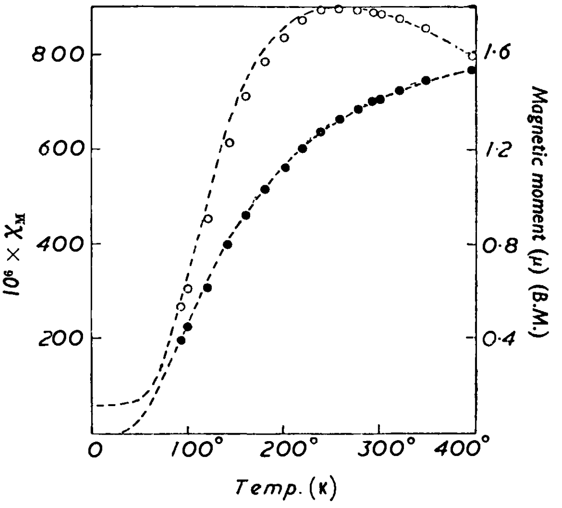


FIG. 3. *Experimental and calculated magnetic susceptibilities and moments of cupric acetate monohydrate.*

○ *Experimental susceptibility,* $10^6 \times \chi_M$.
● *Experimental moment,* μ.
– – – – *Calc. from eqn.* 5.

TABLE 3. *Comparison of room-temperature molar susceptibilities* ($10^6 \times \chi_M$, c.g.s., e.m.u.; temp. in parentheses).

$Cu(CH_3{\cdot}CO_2)_2$: 869 (22·2°) *; 885 (20°).[4]
$Cu(CH_3{\cdot}CO_2)_2,H_2O$: 889 (21·0°) *; 1024 (18°)[2]; 1585 (?)[3]; 890 (20°)[4]; 852 (30°)[5]; 858 (31·2°)[6]; 879 (14·6°)[7]; 905 (16°).[8]

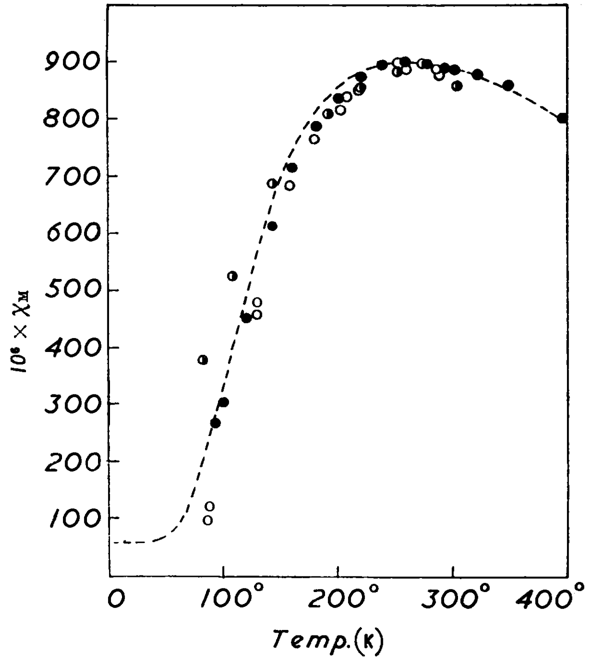
* Present work.

fell gradually but Curie–Weiss law behaviour had not been established at 400° K. Below T_c the susceptibility fell rapidly, so that at 90° K it was only one-quarter of the maximum value. For both compounds, the magnetic moment (μ) rises steadily from $\sim$0·4 at 90° K to $\sim$1·6 at 400° K. The spin-only value $\mu = 1{\cdot}73$ would be attained at *ca.* 500° K, but, unfortunately, thermal decomposition at these temperatures would vitiate direct measurement.

The present values for $Cu(CH_3{\cdot}CO_2)_2,H_2O$ agree well (see Fig. 4) with those obtained by Guha and by Foex *et al.* at 200—300° K, but below 200° K Guha's results are too high, suggesting the presence of a paramagnetic impurity in his material, and at their lowest recorded temperature (87° K) Foex *et al.* give $10^6 \times \chi_M = 98$ compared with the present value of 230.

FIG. 4. *Comparison of magnetic susceptibilities of cupric acetate monohydrate.*

● *Present work.*
○ Foex *et al.*
◑ Guha.
– – – – *Calc. from eqn.* 5.



DISCUSSION

Bleaney and Bowers [1] first accounted for the anomalous susceptibility of hydrated copper acetate (using Guha's results) in terms of two hypotheses : (*a*) " that isolated pairs of copper ions interact strongly through exchange forces, each pair forming a lower singlet and an upper triplet state, only the latter being paramagnetic " and (*b*) " that the crystalline field acting on each copper ion is similar to that in other salts such as Tutton's salts." The latter hypothesis has recently been shown to be substantially correct by the *X*-ray evidence of Niekerk and Schoening.[15] However, in order adequately to fit Guha's data to their theoretical expression an empirical value for the exchange integral was necessary, *viz.*, $J = 315$ cm.$^{-1}$, whereas their paramagnetic resonance experiments had led to $J = 259 \pm 26$ cm.$^{-1}$. It will be shown below that the exchange integral can be related directly to the critical temperature T_c, so that it may be determined directly from the magnetic data.

The spectroscopic ground state of a free Cu^{++} ion is $^2D_{5/2}$ corresponding to a fully occupied 3*d* shell minus one electron. The *D*-state is five-fold degenerate in the free ion if electron spin is neglected. Bethe [19] has shown that under the influence of a cubic crystalline field (as occurs when the Cu^{++} ion is at the centre of a perfect octahedron of oxygen atoms) this degeneracy is partly removed and the multiplet is split into two levels, one two-fold degenerate *A*, *C* and the other three-fold degenerate *B*, *D*, *E* with an energy difference of

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[19] Bethe, *Ann. Physik*, 1929, **3**, 133.

about 13,000 cm.$^{-1}$. In the present case, there is a departure from cubic symmetry owing to some distortion of the octahedral co-ordination of each Cu^{++} along the z-axis (cf. Fig. 1), but to a first approximation the symmetry may be regarded as equivalent to that obtained by imposing a component of tetragonal symmetry on the cubic field. In a field of this symmetry with the z-axis as symmetry axis, the level A, C is split up into two non-degenerate levels A and C, whereas the level B, D, E is split into a non-degenerate level D and a two-fold degenerate level B, E, each orbital level having, of course, an additional double degeneracy with respect to a magnetic field associated with the electron spin of $\frac{1}{2}$. The level B,E is further split when spin–orbit interaction is taken into account. Polder [18] has estimated the energy separation of the levels under these conditions to be as shown in Fig. 5.

The situation in each $Cu_2(CH_3\cdot CO_2)_4,2H_2O$ molecule is modified owing to the overlap of the orbital wave functions belonging to neighbouring copper ions which are only 2·64 Å apart. Following the argument development by Bleaney and Bowers, the number of orbital levels now becomes $5 \times 5 = 25$, each with a degeneracy in spin of $2 \times 2 = 4$. The lowest of these " molecular " states may be denoted by C_1C_2 since its wave function is the product of the individual wave functions C for the ions Cu_1^{++} and Cu_2^{++}. The four-fold spin degeneracy is partly removed by the exchange interaction which splits the level into a singlet and a triplet with an energy separation equal to J. The singlet is diamagnetic with $S = 0$ and is the ground state, whereas the triplet level is paramagnetic and behaves like a state of spin $S = 1$. Under the influence of an applied magnetic field H, the degeneracy in the triplet is lifted, the level splitting into three levels of energy separation equal to $g\beta H$ where g is the spectroscopic splitting factor and β is the Bohr magneton. The splitting of the molecular C_1C_2 level by the exchange interaction is shown diagrammatically in Fig. 6.*

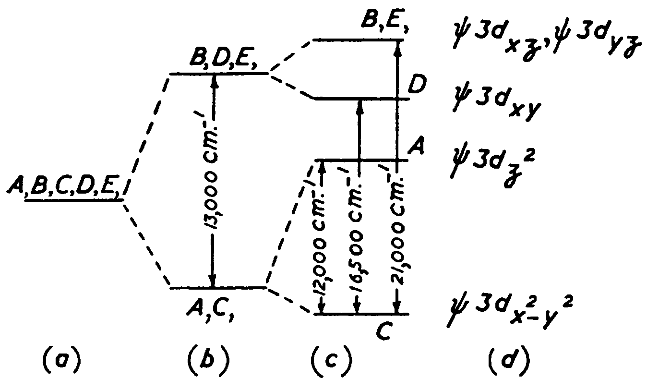

FIG. 5. *Energy level diagram for the d^9 configuration of* Cu^{2+}.

(*a*) *^2D state of the free ion.*
(*b*) *splitting of the orbital levels in an electric field of cubic symmetry.*
(*c*) *further splitting due to tetragonal component of the field.*
(*d*) *wave functions for each orbital level.*

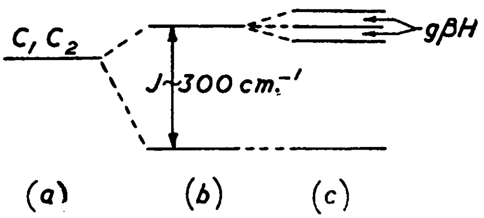

FIG. 6.

(*a*) *Lowest energy level of a system of two interacting* Cu^{++}–Cu^{++} *ions under the influence of a cubic and tetragonal field.*
(*b*) *Splitting into a singlet and a triplet due to the exchange interaction.*
(*c*) *Further splitting of the triplet in a magnetic field.*

The magnetic properties of hydrated copper acetate will be primarily determined by the energy-level diagram illustrated in Fig. 6. In a general way, it will be seen that, as the temperature is raised above the absolute zero, the paramagnetic triplet level becomes

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* The effect of spin–orbit coupling, and the zero field splitting of the triplet level into a singlet and a doubtlet, which it is not essential to mention here, are discussed in the paper by Bleaney and Bowers.[1]

populated at the expense of the diamagnetic singlet level so that the susceptibility rapidly increases until a maximum value is reached at T_c. Above this temperature the usual decrease in susceptibility with rise in temperature is observed.

An expression for the molar susceptibility can be readily obtained from Van Vleck's basic formula :[20]

$$\chi_{\mathrm{M}} = \frac{N\sum_{mn}\left\{\dfrac{{E_{nm}^{(1)}}^2}{kT} - 2E_{nm}^{(2)}\right\}\exp\left(-E_n^{(0)}/kT\right)}{\sum_n g_n \exp\left(-E_n^{(0)}/kT\right)} \quad . \ . \ . \ . \ . \quad (1)$$

where $E_n^{(0)}$ denotes energy levels under no applied magnetic field and $E_{nm}^{(1)}$ and $E_{nm}^{(2)}$ denote coefficients of the first- and second-order Zeeman displacements of levels defined by the relation,

$$E_{nm} = E_n^{(0)} + E_{nm}^{(1)}H + E_{nm}^{(2)}H^2$$

The magentic field removes the spin degeneracy of g_n of level n and these sublevels are specified by the magnetic quantum number m. Terms in H^2 do not change the separation of the four orbital levels but introduce a temperature-independent term $N\alpha$ into the susceptibility which is not affected by the relative distribution of Cu^{++} ions between the singlet and the triplet state. Thus, to the first order of the magnetic field,

$$\chi_{\mathrm{M}} = \frac{2g^2N\beta^2}{3kT}\cdot\frac{1}{1+\frac{1}{3}\exp\left(J/kT\right)} \quad . \ . \ . \ . \ . \ . \ . \quad (2)$$

If the magnetic moment arises from spin alone, then $g = 2$ and

$$\chi_{\mathrm{M}} = \frac{0{\cdot}500}{T}\cdot\frac{1}{1+\frac{1}{3}\exp\left(J/kT\right)} + N\alpha \quad . \ . \ . \ . \ . \ . \ . \quad (3)$$

$N\alpha$ is included to represent the temperature-independent paramagnetism per mole of Cu^{++} ions. It follows that $\chi_{\mathrm{M}} = N\alpha$ when $T = 0$, and rises to a maximum value at $T_c \simeq 5J/8k$, so that the exchange energy can be determined directly from the temperature of the maximum, $J = 1{\cdot}6kT_c$. The Curie–Weiss law will not be strictly obeyed until $T \gg T_c$ when $\theta \simeq 0{\cdot}4T_c$.[14]

Comparison of Experimental and Theoretical Data.—Susceptibility maxima in anhydrous and hydrated copper acetates were observed at 270° K and 255° K, leading to the values 432° K (= 302 cm.$^{-1}$) and 408° K (= 286 cm.$^{-1}$) for the respective exchange interactions. The latter figure is in fair agreement with Bleaney and Bowers's estimate of $J = 259 \pm 26$ cm.$^{-1}$ from paramagnetic resonance experiments. If it is assumed that $N\alpha = 60 \times 10^{-6}$ and that J is effectively independent of temperature, the splitting factor g can be calculated by substituting the experimental values of the maximum susceptibility at T_c into equation (2). In this way, values $g = 2{\cdot}17$ and $2{\cdot}13$ are obtained for the anhydrous and the hydrated compounds respectively. The latter figure may be compared with those obtained by Bleaney and Bowers, $g = 2{\cdot}19$, and Abe and Shimada,[12] $g = 2{\cdot}16$, from paramagnetic resonance experiments. The resulting susceptibility equations are :

$$Cu(CH_3{\cdot}CO_2)_2 :\ 10^6 \times \chi_{\mathrm{M}} = \frac{0{\cdot}586}{T}\cdot\frac{1}{1+\frac{1}{3}\exp\left(432/T\right)} + 60 \quad . \ . \quad (4)$$

$$Cu(CH_3{\cdot}CO_2)_2,H_2O :\ 10^6 \times \chi_{\mathrm{M}} = \frac{0{\cdot}568}{T}\cdot\frac{1}{1+\frac{1}{3}\exp\left(408/T\right)} + 60 \quad . \ . \quad (5)$$

The experimental results are compared in Figs. 2 and 3 with those calculated from these equations. The agreement is remarkably good, even though the values below T_c tend to

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[20] Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford Univ. Press, 1932, p. 182.

lie slightly below the calculated curves. Contrary to Bleaney and Bowers's view this indicates that anisotropic thermal expansion along the z-axis produced by an increase in temperature decreases the overlap of $3d$ wave functions on neighbouring Cu^{++} ions, and the exchange interaction would accordingly be lowered. This is in harmony with the calculations of the overlap integral $S(3d_{x^2-y^2}-3d_{x^2-y^2})$ by Craig *et al.*[21] which show, for example, that a 10% increase in the Cu–Cu distance of 2·64 Å would halve the overlap integral.

The deviation of the g-values from the free-spin value, $g = 2$, indicates that spin-orbit coupling cannot here be neglected, and that an orbital contribution to the magnetic moment arises from mixing of some of the upper " molecular " states of the binuclear molecule into the ground C_1C_2 level.

The small increase in J of 16 cm.$^{-1}$ observed on dehydration of copper acetate may well be a real effect, even though small. The X-ray data have indicated a small displacement (0·22 Å) of each Cu atom out of its CuO_4 plane, indicating a repulsion between neighbouring Cu atoms, probably due to overlap of their filled $3d_{z^2}$, $3d_{xz}$, and $3d_{yz}$ orbitals. However, on removal of the terminal water molecules, overlap along the z-axis will be decreased, and the concomitant decrease in the Cu–Cu distance will result in an increased $3d_{x^2-y^2}-3d_{x^2-y^2}$ exchange interaction.

The Nature of the Cu–Cu *Bond in Copper Acetate.*—The bonding orbitals in each binuclear $Cu_2(CH_3{\cdot}CO_2)_4,2H_2O$ unit are best described in valency-bond rather than molecular-orbital language since the overlap integral $S(3d_{x^2-y^2}-3d_{x^2-y^2})$ is small. In each molecule, two square pyramidal CuO_5 groups are held together, base to base, by four bridging acetate groups, the fifth oxygen atom belonging to a terminal water molecule (cf. Fig. 1). The bonding orbitals used by each copper atom are best described as four square planar $4s4p^24d$ hybrid orbitals, together with a fifth $4p$ orbital lying along the z-axis at right angles to the CuO_4 plane. This agrees better with the observed Cu–O distances (Cu–O in the planar CuO_4 group = 1·97 Å whereas $Cu-H_2O$ = 2·20 Å) than an alternative description involving s-character in all five bonds. The use of " upper " d-orbitals in copper(II) compounds is well recognized where the ligands are highly electronegative, as in the present compound (cf. Craig *et al.*[21]).

Of particular interest in the present work is the nature of the bond between the neighbouring copper atoms in each binuclear molecule. The bond type (*i.e.*, σ, π, δ, etc.) will be determined by the particular $3d$-orbital occupied by an unpaired electron in the ground state, whereas the bond energy will be determined, in part, by the magnitude of the overlap of these $3d$-orbitals. If the electron configuration $3d^9$ is considered as a fully filled $3d$ level containing one " positive hole," it follows that the ground state will correspond to the " positive hole " occupying that $3d$ orbital which has its lobes in the direction of the negative, and hence electron-repelling, ligands. This corresponds to the $3d_{x^2-y^2}$ orbital, a conclusion which has been verified theoretically by the work of Polder (cf. Fig. 5). Polder has estimated that the $3d_{z^2}$ orbital level in the $[Cu(H_2O)_6]^{++}$ ion lies 12,000 cm.$^{-1}$ above the $3d_{x^2-y^2}$ level owing to an elongation of the CuO_6 octahedron along the z-axis. Further destabilization of the $3d_{z^2}$ orbital arises, in the present compound, from replacement of a highly electronegative oxygen ligand by a weakly electronegative copper atom on the z-axis. It might be argued that if a Cu–Cu bond arising from " end-on " overlap of two $3d_{z^2}$ orbitals along the z axis were sufficiently stronger than one resulting from lateral overlap of two $3d_{x^2-y^2}$ orbitals, then the former would become the favoured bond type, in spite of the separation of 12,000 cm.$^{-1}$ referred to above. However, an evaluation of the overlap integral, $S(3d_{z^2}-3d_{z^2}) = 0{\cdot}046$ (see next section), does not support this possibility, but indicates that such a bond, while certainly stronger than that arising from $3d_{x^2-y^2}-3d_{x^2-y^2}$ overlap, is quite unlikely to be sufficiently strong to be preferred on energy grounds. It is therefore concluded that the observed exchange interaction between unpaired spins on adjacent copper atoms arises from lateral overlap of $3d_{x^2-y^2}$ orbitals oriented with their lobar planes parallel. The link between neighbouring copper atoms may be described as a δ-bond : it is illustrated in Fig. 7.

Calculation of the overlap integral, S, using the expression quoted by Craig *et al.*,

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[21] Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332.

gives a value consistent with the above conclusion that $3d_\delta$–$3d_\delta$ overlap is involved. Thus a value $S(3d_\delta–3d_\delta) = 0{\cdot}003$ is obtained by using the values $t = 0$ and $p = 12$, where t and p are independent variables giving a measure of nuclear asymmetry and internuclear distance respectively of the bond. This value may be compared, for example, with the π-overlap in a homonuclear bond such as C=C where $S(2p_\pi–2p_\pi) \sim 0{\cdot}2$—$0{\cdot}3$, indicating that the present exchange energy is very much smaller. The exchange energies determined from the magnetic data (286 and 302 cm.$^{-1}$) are equivalent to an energy contribution of slightly less than 1 kcal. mole^{-1}. Although the weakly electronegative copper ligands will favour the formation of a δ-bond between themselves, it must of necessity be very weak because of the dependence of the wave function $\psi_{3d_{x^2-y^2}}$ on $\sin^2 \theta$ which concentrates the orbital function in the xy plane. This minimizes the overlap with a parallel function except at internuclear distances much smaller than 2·64 Å.

Copper acetate, according to the above hypothesis, is the first case in which a δ-bond is the sole direct link between two atoms. However, the bond is so weak that the configuration of the binuclear molecule can only be maintained by the four bridging acetate groups. Reference to the bond as a " metallic " copper–copper bond (cf. refs. 22 and 23) seems to us inappropriate, and the more accurate description as " a very weak covalent δ-bond " between two copper atoms is preferable.

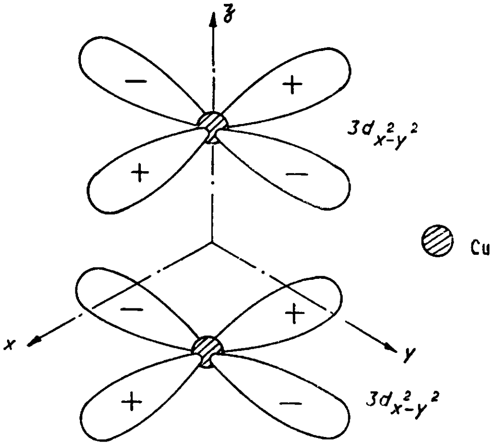

FIG. 7. *δ-Bonding arising from lateral overlap of two $3d_{x^2-y^2}$ orbitals oriented with their lobar planes parallel.*

This type of bonding is not confined to copper acetate alone, and experimental evidence will be presented in Part II of this series which indicates that probably all copper(II) salts of straight-chain fatty acids are binuclear molecules of general formula $Cu_2(C_nH_{2n+1}{\cdot}CO_2)_4,xH_2O$ where x is generally 0 or 2. The behaviour of single crystals of copper propionate to paramagnetic resonance absorption of microwaves strongly resembles that of the acetate, and has led to the proposal that strong exchange interactions are also present in this compound.[24] Polarized absorption spectra in the visible and the near-ultraviolet region have recently been reported for both copper acetate and copper propionate, and the presence of a new absorption band at 80 × 10^{13} c./sec. (3750 Å) has been taken as a further indication of a direct linkage between two copper atoms in these compounds.[25] The apparently anomalous variation of magnetic susceptibility with temperature of copper laurate reported [26] in 1953 can now also be safely ascribed to a further example of δ-bonding between two copper atoms in a fatty acid salt.

Diamagnetism of Chromous Acetate.—The magnetic behaviour of chromous acetate is of interest in the present connection. King and Garner [27] have shown that both anhydrous

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[22] Niekerk and Schoening, *Nature*, 1953, **171**, 36.
[23] Speakman, *Ann. Rep.*, 1954, **51**, 390.
[24] Abe, *Phys. Rev.*, 1953, **92**, 1572.
[25] Tsuchida and Yamada, *Nature*, 1955, **176**, 1171.
[26] Gilmour and Pink, *J.*, 1953, 2198.
[27] King and Garner, *J. Chem. Phys.*, 1950, **18**, 689.

and hydrated chromous acetate are diamagnetic, and, in the absence of *X*-ray data, interpreted this result as the first example of tetrahedral $3d^34s$-bond hybridization. However, a recent *X*-ray structure determination [22, 28] invalidated their conclusion and showed that chromous acetate is also a binuclear molecule $Cr_2(CH_3{\cdot}CO_2)_4,2H_2O$ isostructural with copper acetate.

In its simple and complex salts with highly electronegative ligands chromium(II) normally exhibits a magnetic moment corresponding to the presence of four unpaired electrons,[29] so that the observed diamagnetism is, at first sight, surprising. However, it is explained if both the directional properties of the chromium $3d$-orbitals and the short Cr–Cr internuclear distance are taken into account. If, as in the case of the copper analogue, four $4s4p^24d$ chromium orbitals are used for bonding each planar CrO_4 group and the remaining $4p$ orbital is used for bonding a terminal water molecule, then four unpaired electrons occupy $3d$ levels in each chromium atom. Orgel [30] has pointed out that the energy diagram for the quintet *D* states of the d^4-configuration is identical with that of the d^9-arrangement (cf. Fig. 5), so that it seems probable that the ground state will correspond with zero electron density in the $3d_{x^2-y^2}$ orbital, the remaining four $3d$ electrons occupying $3d_{z^2}$, $3d_{xz}$, $3d_{yz}$, and $3d_{xy}$ orbitals in accordance with Hund's rule. Owing to the abnormally close distance of approach between chromium atoms (2·64 Å) in each binuclear molecule, overlap of adjacent $3d_{z^2}$–$3d_{z^2}$, $3d_{xz}$–$3d_{xz}$, $3d_{xz}$–$3d_{yz}$, and $3d_{xy}$–$3d_{xy}$ orbitals can occur, so that one *schedo*-σ-bond,*, two π-bonds, and one δ-bond are formed. Since the internuclear Cr–Cr distance is identical with that observed in copper acetate the bonds are unlikely to be strong. This conclusion is supported by evaluation of the overlap integrals *S*. Using the formulæ of Craig *et al.* with $t = 0$ and $p = 12$ as the appropriate independent variables, one obtains values $S(3d_\pi–3d_\pi) = 0{\cdot}021$ and $S(3d_\delta–3d_\delta) = 0{\cdot}003$. If, as with the copper compound, the δ-bond contributes approximately 1 kcal. mole^{-1} to the Cr–Cr bond energy, then the contribution from each π-bond is probably of the order of 5 kcal. mole^{-1}. The *schedo*-σ-bond resulting from " end-on " overlap of two $3d_{z^2}$ orbitals along the internuclear axis is slightly stronger with $S(3d_{r^2}–3d_{z^2}) = 0{\cdot}046$ (see Appendix). However, even this overlap is small when compared with the σ overlap in a homonuclear bond such as C–C where $S(2sp^3{}_\sigma–2sp^3{}_\sigma) = 0{\cdot}64$ at 1·54 Å.[31] On this basis, the Cr–Cr bond must be regarded as weak, although it is probably considerably stronger than its Cu–Cu counterpart, the bonds in both cases being supported by the bridging acetate groups. The resulting exchange is apparently sufficient effectively to pair the spins of the eight electrons occupying $3d$ levels in each chromous acetate molecule and to account for the observed diamagnetism.

APPENDIX

We are indebted to Mr. E. A. Magnusson for evaluating the overlap integral for the *schedo*-σ-type bond resulting from " end-on " overlap of two $3d_{z^2}$ orbitals along a common *z*-axis. This integral has not previously been evaluated, for this is probably the first compound in which this type of overlap appears to play a significant part in the bonding of two atoms.

The explicit expression for the overlap integral (using the nomenclature of Craig *et al.*) is :

$$S(3d_{z^2}–3d_{z^2}) = \frac{(1-t^2)^{7/2}p^7}{1152}[A_0(-9B_2+6B_4-B_6)+A_2(9B_0-3B_4+6B_6) + A_4(-6B_0+3B_2-9B_6)+A_6(B_0-6B_2+9B_4)]$$

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* The nomenclature follows that suggested by Craig *et al.*

[28] Niekerk, Schoening, and de Wet, *Acta Cryst.*, 1953, **6**, 501.

[29] Hume and Stone, *J. Amer. Chem. Soc.*, 1941, **63**, 1200.

[30] Orgel, *J. Chem. Phys.*, 1955, **23**, 1004.

[31] Mulliken, Reike, D. Orloff, and H. Orloff, *J. Chem. Phys.*, 1949, **17**, 1248.