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Magnetic Studies on Basic Salts of Copper, Dicopper Arsenate Hydroxide, Dicopper Hydroxide Phosphate, and Dicopper Oxide Sulfate

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Magnetic susceptibilities, χ, of $Cu_2AsO_4(OH)$, $Cu_2(OH)PO_4$, and Cu_2OSO_4 have been measured from 4.2 to 360 K to establish the role of the OH^- and O^{2-} ions in the magnetic superexchange interaction. The former two compounds showed a broad maximum for χ at 118 and 110 K, respectively. Although the crystal structure is three-dimensional, only a tetramer model with two parameters can explain the temperature dependence of χ, since the hydroxide anion causes a strong magnetic interaction which is limited to four copper atoms between which the anion is intermediary. The magnetic susceptibility of Cu_2OSO_4 obeyed the Curie-Weiss law above 140 K with a Weiss constant of -56 K. At 16 K the compound transformed into a ferrimagnetic phase, the effective megneton number of which is 0.11 at 4.2 K. A canted ferrimagnetic structure has been proposed and the canting angle estimated. In the superexchange interaction, only hydroxide and oxide anions are significant and both anions behave similarly.

Copper oxide compounds are a group of substances whose magnetic behavior has been widely studied. The magnetic properties of many oxoacid copper salts have also drawn much interest and have been examined theoretically and magnetochemically. However, little work has been published on hydroxide compounds. Escoffier and Gauthier published the Curie and the Weiss constants for 15 basic copper salts.[1] Diot *et al.* studied copper hydroxide and found its transition to an antiferromagnetic phase at about 20 K from measurements of magnetic susceptibility and specific heat.[2] Abrahams *et al.* reported that $CuIO_3(OH)$ showed signs of a phase transition into an antiferromagnetic state at 162 K.[3] Hatfield and coworkers found a linear relationship between the exchange energy $2J$ and the bridging angle of the OH^- anion for a series of di-μ-hydroxocopper(II) complexes.[4] The observed correlation was explained quantitatively[5] as well as qualitatively[6] by means of MO's. All experiments indicated that the hydroxide anion has the potential to bring about a stronger magnetic interaction between copper(II) spins.

In order to elucidate the superexchange interaction *via* the hydroxide anion, the magnetic susceptibilities of three basic salts of copper, $Cu_2AsO_4(OH)$, $Cu_2(OH)PO_4$, and Cu_2OSO_4, have been measured from 4.2 to 360 K. The compounds have similar chemical compositions, and contain, as a common structural feature,[7,8] a trigonal bipyramid and an octahedron of oxygen atoms around a central copper atom. They were chosen as a suitable series of compounds to establish the magnetic behavior of the hydroxide and the oxide anions.

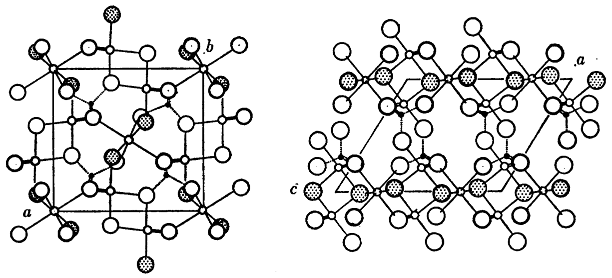
Experimental

Preparation. Samples of $Cu_2AsO_4(OH)$ and $Cu_2(OH)PO_4$ were prepared hydrothermally at 130—140 °C[9] and identified by X-ray diffraction.[7] Dicopper oxide sulfate, Cu_2OSO_4, was obtained by the thermal decomposition of $CuSO_4\cdot 5H_2O$ at 650 °C over 10 h.[10] During this process the reacting material was removed from the furnace, ground and re-heated several times. This technique was found necessary because, otherwise, the decomposition reaction proceeded only at the reagent surface owing to sintering of the product, Cu_2OSO_4, resulting in a mixture of $CuSO_4$, Cu_2OSO_4, and CuO. The product was identified by powder X-ray diffraction.[8] The reagent used are of superpure grade (Wako Pure Chemical Industries, Ltd.). Found: Cu, 44.89; As, 26.03%. Calcd for $Cu_2AsO_4(OH)$: Cu, 44.90; As, 26.47%. Found: Cu, 53.00; P, 12.88%. Calcd for $Cu_2(OH)PO_4$: Cu, 53.16; P, 12.96%.

Magnetic Measurements. The magnetic susceptibility was measured from 4.2 to 360K using powder samples. A Faraday balance was employed and calibrated for $CoHg(SCN)_4$.[11] Susceptibility values were corrected for diamagnetism; the values were -1.18, -1.02, and -0.93 mm^3 mol^{-1} for the arsenate, phosphate, and sulfate, respectively.[12] The temperature of the sample was measured by a calibrated 0.03% Co: Au or constantan *vs.* Cu thermocouple.

Results and Discussion

Crystal Structures.[7,8] The crystal structures of $Cu_2(OH)PO_4$ and Cu_2OSO_4 are projected in Fig. 1. As a common structural feature, they contain two kinds of oxygen polyhedra coordinating to the copper atoms; a trigonal bipyramid and an octahedron. In this paper the center of the trigonal bipyramid will be designated



(a) (b)

Fig. 1. Projection of the crystal structures of (a) $Cu_2(OH)PO_4$ and (b) Cu_2OSO_4. Symbols are Cu: middle circle, O: large circle and P or S: small solid circle. Oxygen atoms belonging to the hydroxide or the oxide anions are shaded. The octahedron in $Cu_2(OH)PO_4$ has the diad axis along the c axis, while that in Cu_2OSO_4 has a center of symmetry. They form a linear chain perpendicular to the projection plane.

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as site A and that of the octahedron as site B. The octahedron shares two opposite edges with two neighboring octahedra to form a linear chain. The two trigonal bipyramids constitute a dimer by sharing an edge. The dimeric unit, the linear chain of the octahedra, and the anion tetrahedra share corners thereby forming a three-dimensional network.

An oxide anion has the tendency to form tetrahedral bonds with four metallic cations.[13] Consequently, the oxide anion in Cu_2OSO_4 can occupy the position which lies on the shared edge of the linear chain and simultaneously on that of the dimer. The dimeric unit connects two linear chains by the oxide anions. Since other oxygen corners of the dimer are shared with the same linear chains, the two kinds of coordination polyhedra construct a two-dimensional network. This network is joined with neighboring ones only by the tetrahedra of an SO_4^{2-} anion, and as a result, each copper atom has 5 or 6 copper neighbors through the intermediate oxide anions.

In contrast, the hydroxide anion can make bonds with, at most, three metal atoms.[14] This limitation brings about a remarkable difference in the manner of linkage of the polyhedra between $Cu_2(OH)PO_4$ and Cu_2OSO_4. The hydroxide anion in $Cu_2(OH)PO_4$ lies on a shared edge of the linear chain, but in the dimer it is located on a corner not belonging to the shared edge. The dimer joins two linear chains by the hydroxide anions and two more chains by other oxygen atoms. In this case, therefore, a three-dimensional network is built of the coordination polyhedra, independent of the phosphate tetrahedra. Also in the phosphate the copper atom has 5 or 6 copper neighbors, two or three of which are connected with the copper atoms by the hydroxide anions.

The crystal structure of $Cu_2AsO_4(OH)$ is isomorphous with that of $Cu_2(OH)PO_4$.[15] The phosphate, however, belongs to the space group Pnnm and the arsenate to $P2_1nm$,[16] a subgroup of Pnnm, and so it appears necessary to take into account some deformation of the coordination polyhedra in $Cu_2AsO_4(OH)$.

Magnetic Properties of $Cu_2AsO_4(OH)$ and $Cu_2(OH)PO_4$. The magnetic susceptibilities, χV_m, of $Cu_2AsO_4(OH)$ and $Cu_2(OH)PO_4$ have been plotted as a function of temperature in Figs. 2 and 3. The two compounds exhibit a similar temperature dependence on χV_m; a broad maximum around 110 K accompanied by a large decrease below that temperature. The sharp increase of χV_m with decreasing temperature below 10 K has been attributed to paramagnetic impurities. There was, however, a distinct difference between the maximum susceptibilities, $\chi_{max} V_m$, for the arsenate and the phosphate, which were 39.8 and 49.7 mm³ mol⁻¹, respectively. The temperature, T_{max}, at which the susceptibility is a maximum, was 118 K for $Cu_2AsO_4(OH)$ and 110 K for $Cu_2(OH)PO_4$. Such large values of T_{max} indicate that the magnetic interaction between copper(II) spins is very strong in these compounds. Since the two values of T_{max} are similar, the large difference in $\chi_{max} V_m$ has been attributed to differences in the magnetic interaction and the g-factor.

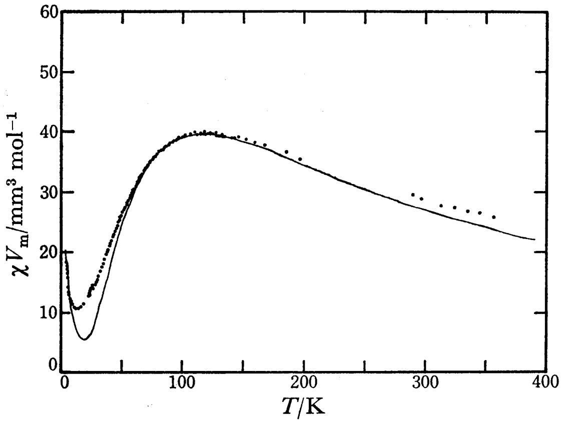

Fig. 2. Temperature dependence of the magnetic susceptibility of $Cu_2AsO_4(OH)$. The solid line shows the calculated susceptibility for the tetramer model with parameters of $g=2.02$, $J=-68$ K and $J'/J=-3.0$ plus a contribution from paramagnetic impurities.

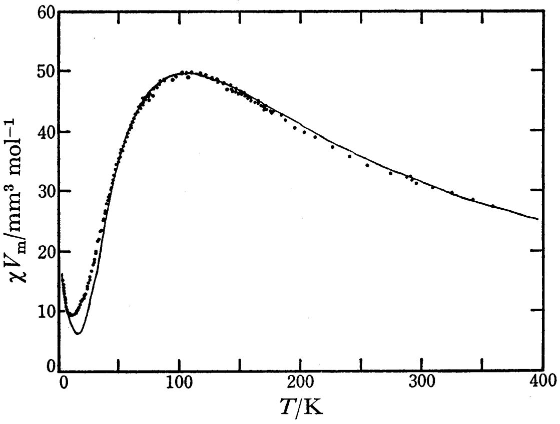

Fig. 3. Temperature dependence of the magnetic susceptibility of $Cu_2(OH)PO_4$. The solid line shows the calculated susceptibility for the tetramer model with parameters of $g=2.16$, $J=-62$ K and $J'/J=-2.4$ plus a contribution from paramagnetic impurities.

The susceptibility obeyed the Curie-Weiss law, $\chi V_m = C/(T-\theta)$, above 200 K. However, in the course of the analysis given below, the temperature of measurement was found so low that only formal values of the Curie and the Weiss constants were obtained.

Several magnetic models have been tested in order to investigate the magnetic interaction in these hydroxide compounds. However, since the susceptibility below T_{max} decreases significantly, only cluster models containing an even number of copper(II) spins are admissible. Furthermore, the possible models has been confined to the following two cases taking into account the symmetry relationship between the copper atoms.

(1) The tetramer model in which two copper atoms at site A and two at site B are connected by two hydroxide anions as depicted in Fig. 4. The interaction energy for this spin system may be written as follows:

$$H = -2J(S_1S_2+S_2S_3+S_3S_4+S_4S_1)-2J'(S_1S_3). \quad (1)$$

Solving the equation for the case of $S=1/2$ for all spins, the magnetic susceptibility is given by Eq. 2:[17]

$$\chi V_{\rm m} = \frac{Lg^2\mu_{\rm B}{}^2}{kT} \times \frac{\exp(x)+\exp(2x-x')+\exp(2x)+5\exp(3x)}{1+3\exp(x)+4\exp(2x-x')+3\exp(2x)+5\exp(3x)}, \quad (2)$$

where $x=2J/kT$ and $x'=2J'/kT$.[18]

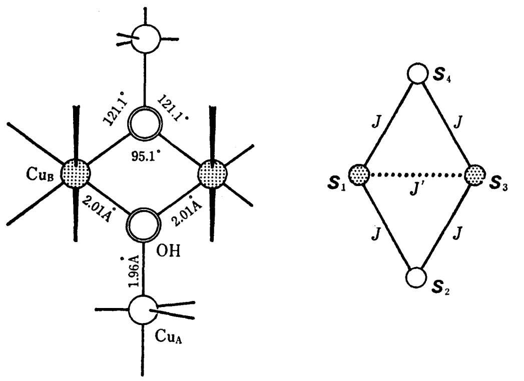

Fig. 4. Schematic drawing of the tetramer unit (left), and interaction scheme in it (right). The unit has a point symmetry of C_{2h} with the diad axis passing through the Cu_B atoms.

(2) Two kinds of dimers. One of the dimers is composed of two copper atoms on site A and the other on site B. The susceptibility for this system is obtained by adding the two Bleaney-Bowers equations with the respective values for the g-factor and J.[17,18]

$$\chi V_{\rm m} = (L\mu_{\rm B}{}^2/3kT)\sum_{\rm i=A,B} g_{\rm i}{}^2\left[1+\frac{1}{3}\exp(-2J_{\rm i}/kT)\right]^{-1} \quad (3)$$

The former model gave good agreement between the calculated and observed values, whereas in the latter $Cu_2(OH)PO_4$ gave an unreasonable value for the g-factor and $Cu_2AsO_4(OH)$ poorer agreement than in the tetramer model. Consequently the tetramer model has been thought suitable for these compounds. The values of g, J, and J'/J, which gave the best fit to the observed susceptibility, are 2.02 ± 0.04, -68 ± 1 K and <-1.5 for the arsenate, and 2.16 ± 0.04, -62 ± 2 K and -2.4 ± 1.5 for the phosphate. The susceptibilities calculated from these parameters are shown in Figs. 2 and 3. The large standard deviation of J'/J arises from Eq. 2 in that $\chi V_{\rm m}$ shows low sensitivity to J'/J when this parameter is less than -1. In the case of $Cu_2AsO_4(OH)$ the small g value further diminished the sensitivity to J'/J, which prevented the absolute value of this parameter being found.

As the large values of $T_{\rm max}$ suggest, the deduced values of J are very large. Such strong magnetic interaction must be brought about by a superexchange interaction *via* intermediate anions, since the separation between copper atoms exceeds 2.96 Å. It is also noteworthy that J and J' have opposite signs; the interaction between a copper spin on site A and that on site B is antiferromagnetic, whereas the interaction between two copper spins on site B is ferromagnetic (Fig. 4). It is widely recognized that there is a correlation between the parameter J and interatomic angle relevant to the superexchange interaction. The angle of Cu_B–OH–Cu_B' is 95.1° and that of Cu_A–OH–Cu_B is 121.1° in $Cu_2(OH)PO_4$ (Fig. 4), and consequently the signs expected from this correlation are consistent with those obtained from the present study.

As described earlier, the coordination polyhedra form a three-dimensional network and no isolated clusters are found in the crystal structure. Nevertheless, only the tetramer model could explain the temperature dependence of the magnetic susceptibility. This indicates that the hydroxide anion, which joins three copper atoms in the tetramer unit, makes the main contribution to the magnetic interaction between copper(II) spins, whereas the phosphate oxygen atoms have a negligible effect on the interaction. It is surprising that the difference between the roles is very large, because the interatomic distances and angles relevant to the superexchange interaction are similar for both types of oxygen atoms.

The susceptibility of $Cu_2AsO_4(OH)$ can be explained on the basis of the tetramer model. The magnitude of the obtained J value is similar to that of the phosphate and the signs of both J and J' are the same as those of the phosphate. This supports the assertion that the two compounds are isomorphous. Agreement between the observed and calculated susceptibility values was poorer for $Cu_2AsO_4(OH)$ than for $Cu_2(OH)PO_4$. Introduction of the anisotropic parameters, $J_{\parallel}$, $J_{\perp}$, $J_{\parallel}'$, and $J_{\perp}'$, into Eq. 1 proved no appreciable improvement. It appears, therefore, that the superexchange interaction through an arsenate oxygen atom makes some contribution to the magnetic behavior of $Cu_2AsO_4(OH)$.

In contrast with the values of J and J', the values of the g-factor differ from each other and this difference largely accounts for the difference in $\chi_{\rm max}V_{\rm m}$ between the two compounds. This indicates that the local environment at the copper site, and thus at the sites of the intermediary oxygen atoms in $Cu_2AsO_4(OH)$ vary considerably from those in $Cu_2(OH)PO_4$. This may explain the different effects of the arsenate and the phosphate oxygen atoms on the magnetic interaction. Further structural study is both necessary and desirable.

Magnetic Properties of Cu_2OSO_4. The magnetic susceptibility of Cu_2OSO_4 is shown in Figs. 5 and 6. It may be seen that as the temperature decreases, the

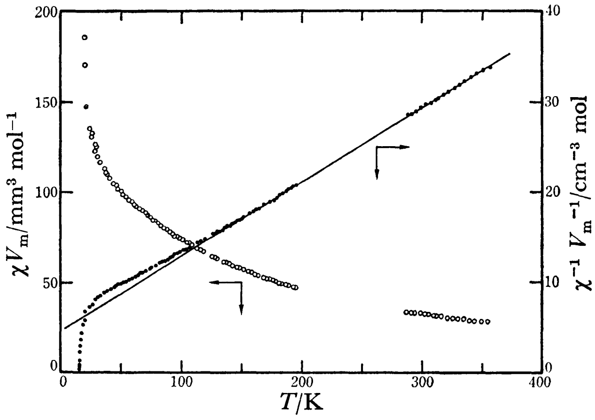

Fig. 5. Temperature dependence of the magnetic susceptibility (○) and its inverse (●) of Cu_2OSO_4 in the paramagnetic region. The solid line shows the Curie-Weiss relation obtained by the least-squares fit.

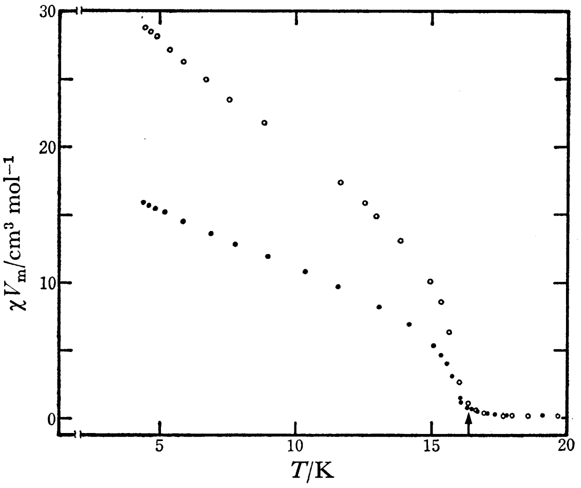

Fig. 6. Temperature dependence of the apparent magnetic susceptibility of Cu_2OSO_4 in the ordered phase. The arrow shows the transition temperature. ○: 22 kA m^{-1}, ●: 55 kA m^{-1}.

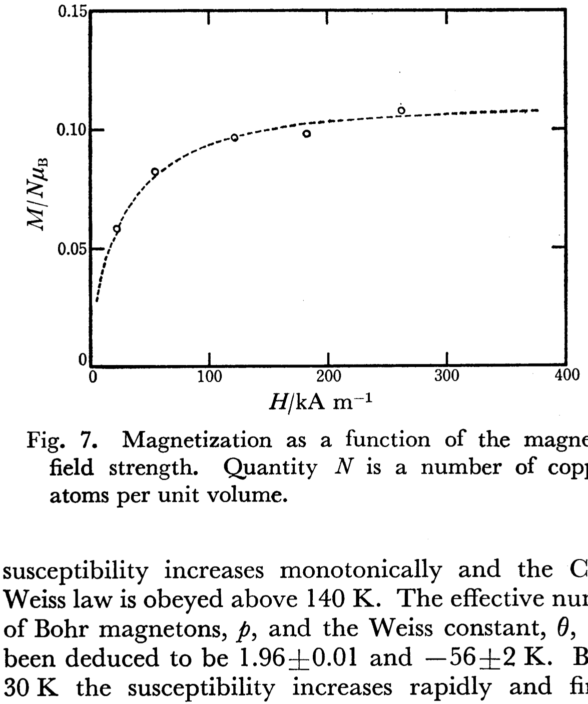

Fig. 7. Magnetization as a function of the magnetic field strength. Quantity N is a number of copper atoms per unit volume.

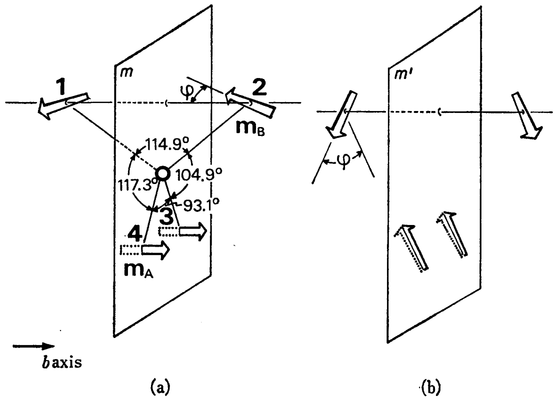

Fig. 8. Arrangement of the magenetic moments in the two possible magnetic space groups of (a) C2/m and (b) C2'/m'. Angles are the interatomic ones about the intermediary oxide anion.

susceptibility increases monotonically and the Curie-Weiss law is obeyed above 140 K. The effective number of Bohr magnetons, p, and the Weiss constant, θ, have been deduced to be 1.96 ± 0.01 and -56 ± 2 K. Below 30 K the susceptibility increases rapidly and finally becomes dependent on the magnetic field strength, indicating a transition to an ordered phase with spontaneous magnetization. The transition temperature was found to be 16 ± 1 K. In Fig. 7 the magnetization, M, at 4.2 K is plotted as a function of the magnetic field strength, H, and from this plot the effective magneton number, n_B, has been evaluated as 0.11 ± 0.01.

The small value of n_B and the negative value of θ indicate that the spin-ordered state is ferrimagnetic. In order to determine the ferrimagnetic structure, it has been assumed that the magnetic space group of Cu_2OSO_4 can be obtained by changing each element of the crystallographic space group, C2/m, for a primed or unprimed magnetic symmetry element. Thus the spontaneous magnetization can only arise in the magnetic space groups of C2/m and C2'/m'.[19] In Fig. 8 the arrangement of the magnetic moments is shown for the two space groups. In the case of C2/m, the moments of the copper cations on sites A, $\boldsymbol{m}_A$, are all parallel to the b axis. Those on sites B, $\boldsymbol{m}_B$, are divided into two sublattices. The components perpendicular to the b axis compensate for each other, whereas the components along the b axis remain unchanged. The net moment from $\boldsymbol{m}_B$ must be antiparallel to $\boldsymbol{m}_A$ so that the compound is ferrimagnetic. From the observed n_B the canting angle, φ, has been estimated as 38.7°, assuming that both m_A and m_B are equal to one μ_B. The discussion also holds in the case of C2'/m', except for the direction of the spontaneous magnetization and the value of φ (Fig. 8b).[20] Therefore this compound probably has a canted ferrimagnetic structure.[21]

As cited earlier, the coordination polyhedra in Cu_2OSO_4 form a two-dimensional network. In this network layer the copper atoms form a kagomé-like lattice and the oxide anion is intermediate in every pair of adjacent copper atoms. The magnetic interaction can extend through the layer, as expected from the presence of the ordered state, assuming the oxide anion plays an important role. Since the interatomic distance between copper atoms exceeds 2.9 Å, the superexchange interaction governs the magnetic behavior of Cu_2OSO_4. The sulfate oxygen atoms afford interaction paths with long Cu–O separations of 2.14 and 2.52 Å. On the other hand, the interatomic distances of Cu–O (oxide anion) are short; 1.87(×2), 1.91, and 2.01 Å. In addition, judging from the Cu–O distances in the coordination polyhedra, three copper atoms with a half-filled 3d orbital direct their lobes towards the oxide anion. For the magnetic interaction in Cu_2OSO_4, therefore, the oxide anion assumes important role, whereas the sulfate oxygen atoms contribute a negligible effect.

Since the four Cu–O (oxide anion) distances are similar, the sign and magnitude of the superexchange interaction appears to mainly depend on the interatomic angles Cu–O–Cu'. Then the following relations hold among the parameters, J_{ij}:

$$|J_{12}| > |J_{13}| = |J_{23}|, \quad J_{12} \approx J_{14} = J_{24},$$
$$\text{and } J_{12}, J_{13}, J_{23} < 0, \text{ and } J_{34} > 0$$

where the suffixes, i and j, refer to the numbering given in Fig. 8a. The statement that the interaction between copper(II) spins on sites B, J_{12}, is strong and antiferromagnetic appears, at first sight, to be conflicting with the ferrimagnetic structure discussed above, in which the main components of the $\boldsymbol{m}_B$'s are arranged ferromagnetically. However, this ferrimagnetic structure is a direct result of competing antiferromagnetic interactions. If the magnetic moments $\boldsymbol{m}_B$ are ordered antiferromagnetically, the interaction of $\boldsymbol{m}_A$ with two $\boldsymbol{m}_B$'s cancels out. Canting of $\boldsymbol{m}_B$'s brings the moment $\boldsymbol{m}_A$ some energy gain, which accompanies some energy loss for a pair of $\boldsymbol{m}_B$'s. The canting angle is thus determined by delicate balancing between energy loss and gain. The following simple formalism explains the canting angle quantitatively and supports the arguments made above. On the basis of the ferrimagnetic structure in Fig. 8 and including the interaction between the four copper moments, the interaction energy of the system, E, is given as a function of the angle, φ_{ij}, between the moments $\boldsymbol{m}_i$ and $\boldsymbol{m}_j$.

$$E = 2(N_{13}+N_{14})m^2\cos(180°-\varphi) + N_{12}m^2\cos(2\varphi) + N_{34}m^2 \tag{4}$$

The parameter, N_{ij}, is proportional to J_{ij}. The relationship of $N_{13}=N_{23}$ and $N_{14}=N_{24}$ holds on the basis of the symmetry, and $m_1=m_2=m_3=m_4=m$ is assumed. Setting $\partial E/\partial\varphi=0$, the canting angle is obtained.

$$\varphi = \cos^{-1}\{(N_{13}+N_{14})/2N_{12}\} \tag{5}$$

Substituting $\varphi=38.7°$, deduced from the magnetic space group of C2/m, and $N_{14}\approx N_{12}$, ratio of N_{13}/N_{12} is calculated to be 0.5. In the case of C2′/m′ it is in the range from 0.95 to 0.5 depending on the value of φ.[20] These values are comparable with the value of 0.5, obtained by application of the relationship between $2J$ and the bridging angle for the di-μ-hydroxo-copper(II) complexes.[4,6] The calculated values mean that both J_{12} and J_{13} have the same sign and that the interaction J_{12} is stronger than J_{13}.

Comparison of the Hydroxides and the Oxide. The magnetic behavior of the hydroxides, $Cu_2AsO_4(OH)$ and $Cu_2(OH)PO_4$, and the oxide, Cu_2OSO_4, are remarkably different; the former behaves like a cluster, whereas the latter like an ordered phase. This difference does not stem from the different roles in the magnetic behavior between the hydroxide and the oxide anions. On the contrary, the magnetic interaction induced by both anions has been explained qualitatively on the same principle. Rather the different magnetic behavior has its origin in the following: (1) mainly hydroxide or oxide anions contribute to the magnetic interaction, and (2) they are arranged in a different manner in the coordination polyhedra. The oxide anions occupy the trans positions in the octahedron and participate in every shared edge. Thus the interaction path extends infinately in the layer parallel to the (001) plane. The hydroxide anions occupy the cis positions in the octahedron and participate in every two shared edges. Moreover, it makes three bonds with copper atoms. Since other oxygen atoms give no appreciable effect, the magnetic interaction is localized within the four copper atoms bridged by two hydroxide anions. This explains the success of the tetramer model in spite of the three-dimensional network structure.

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