Magnetic Exchange in Cis-bis(glycinato)aquocopper(II), Bis-(hydrogen-o-phthalato)diaquocopper(II), (o-phthalato)aquocopper(II) and the Corresponding Dehydrated Complexes. A Possible Correlation Between Copper(II)–Water Bond Lengths and the Ability of Hydrated Copper(II) Carboxylates to Form Magnetically-subnormal Anhydrous Complexes

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The temperature dependence of the magnetic susceptibility has been determined for several hydrated copper(II) carboxylate complexes. The susceptibility–temperature data for the hydrates bis(glycinato)aquocopper(II), bis(hydrogen-o-phthalato)diaquocopper(II) and o-phthalatoaquocopper(II) are described by the Curie–Weiss Law $[\Theta(^\circ K) = -7 \pm 6, -0.6 \pm 3.3$ and -26 ± 7, respectively]. Additional epr studies suggest the presence of a low dimensional pathway for interactions between copper(II) ions in (o-phthalato) aquocopper(II) but only very weak interactions in bis (hydrogen-o-phthalato)diaquocopper(II). The anhydrous bis(glycinato)copper(II) also exhibits Curie–Weiss behavior $(\Theta = -21 \pm 4^\circ K)$ but the anhydrous o-phthalatocopper(II) has a susceptibility maximum at about $250^\circ K$ and the susceptibility – temperature data may be fit to the Bleaney–Bowers' equation $(J \sim 280$ $cm^{-1})$. Thermogravimetric analyses and differential scanning calorimetry have been used to characterize the dehydration process in the hydrated complexes. A possible correlation between copper–water bond lengths and the ability of a hydrated copper(II) carboxylate to form magnetically subnormal anhydrous complexes is proposed. Specifically, dehydration of magnetically normal hydrated copper(II) carboxylates, where water molecules occupy one or more of the short contact positions, tends to produce a magnetically subnormal anhydrous complex.

Introduction

During the past two decades there has been considerable interest in copper(II) carboxylate complexes because of the common occurrence of a binuclear structure with strong magnetic coupling between pairs of copper(II) ions.[1–4] For bridged copper(II) dimers that do not contain a carboxylate anion, correlations

between magnetic properties and structural factors have been proposed.[5,6]

Recently we noted that drastic changes in the magnetic behavior accompany the dehydration process for copper(II) hippurate tetrahydrate.[7] Additional epr studies[8] and magnetic susceptibility measurements in the very low temperature range[9] confirm that the hydrated complex consists of rather weakly coupled pairs of copper(II) ions compared to the strongly coupled pairs that occur in the anhydrous complex. This change in magnetic behavior during dehydration is accompanied by concurrent structural change within the first coordination sphere of the paramagnetic ion resulting in the formation of the copper(II) acetate-type binuclear complex (see Figure 1).

Other hydrated copper(II) complexes that are magnetically normal and contain the carboxylate moiety undergo similar changes upon dehydration to produce magnetically subnormal anhydrous complexes.[10,11] There have been no reports of a systematic study of the relationship between the bond lengths in magnetically normal hydrated copper(II) carboxylates and the
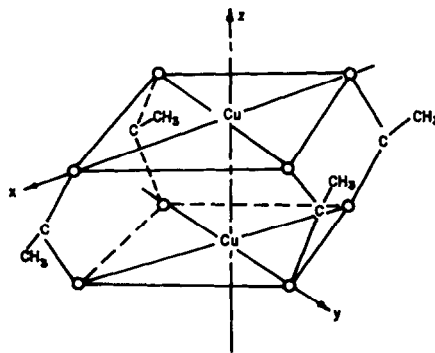

Figure 1. Schematic representation of the copper acetate dimer.

ability of these complexes to form magnetically sub-normal complexes upon dehydration. We have initiated such a study with this investigation of the thermal, epr and bulk magnetic behavior or three hydrated copper (II) complexes, cis-bis(glycinato)aquocopper(II), [Cu(gly)$_2 \cdot$H$_2$O], bis(hydrogen-o-phthalato)diaquocopper (II), [Cu(Hphth)$_2 \cdot$2H$_2$O], (o-phthalato)aquocopper (II), [Cu(phth)$\cdot$H$_2$O], and their corresponding anhydrous complexes.

Experimental

Preparative

The syntheses of the three complexes that form between ortho-phthalic acid and copper(II) ions have been previously reported.[12,13] Phthalatoaquocopper (II) was prepared following a slightly modified procedure where the copper(II) to hydrogen o-phthalate ratio was 1:1 in place of the reported 0.33:1. Under these conditions it was not necessary to concentrate the reaction mixture in order to obtain the desired light blue crystals. Anal. Calc. for [Cu(C$_8$I$_4$O$_4$)(H$_2$O)] : Cu, 25.86; H$_2$O, 7.33. Found: Cu, 25.80; H$_2$O, 7.44.

Bis(hydrogen-o-phthalato)diaquocopper(II) was prepared by adding small portions of basic copper carbonate (a slight excess over 0.1 mol) to a solution of phthalic acid formed by boiling 29.6 g (0.2 mol) phthalic acid anhydride in 500 ml of water. The initial precipitate that forms is removed by filtration and discarded. The filtrate is allowed to evaporate until blue rod-like crystals form. These are collected by filtration and washed with a small quantity of cold water. Anal. Calc. for [Cu(C$_8$H$_5$O$_4$)$_2 \cdot$(H$_2$O)$_2$] : Cu, 14.78; Found: Cu, 14.91.

Phthalatocopper(II) was prepared by a hot solvent procedure although the same complex may be prepared by heating Cu(Hphth)$_2 \cdot$2H$_2$O or Cu(phth)$\cdot$H$_2$O. A solution of 8.3 g (0.025 mol) of copper(II) sulfate pentahydrate in 100 ml of boiling water is mixed with a hot solution of 20 g (0.1 mol) of potassium hydrogen-o-phthalate in 200 ml of water. The resulting solution turned a deep blue and a light blue precipitate formed within 5 min. Upon continued boiling a green precipitate forms. To insure complete conversion to the green complex, the reaction mixture was heated for a total of 6 hr. The green anhydrous complex was collected by filtration, washed with ethanol and dried in a vacuum desiccator overnight. Anal. Calc. for [Cu(C$_8$H$_4$O$_4$] : Cu, 27.91. Found: Cu, 27.83. Analytical results, visual inspection and electronic spectra (Nujol mulls: maximum, 670 nm; minimum, 500 nm; shoulder, 360 nm) suggest that the anhydrous Cu(phth) complexes are identical whether prepared by direct heating of the hydrate or by the hot solvent method. This same conclusion has been reached by other workers[12] who characterized the anhydrous complexes more extensi-

vely (infrared and electronic spectra, and X-ray powder patterns).

The complex cis-bis(glycinato)aquocopper(II) was prepared following published procedures.[14] The anhydrous complex resulted when the hydrate was heated at 175°C for several hours. Anal. Calc. for [Cu(C$_2$NH$_4$O$_2$)$_2 \cdot$H$_2$O] : Cu, 27.66; H$_2$O, 7.84. Found: Cu, 27.53; H$_2$O, 8.11.

Thermal Analyses

Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TG) were used to characterize the dehydration process. The effect of various methods of sample containment on the detailed thermal behavior was investigated using available procedures.[15] A description of the instrumentation, calibration and procedures used in the thermal studies has been reported previously.[7]

Magnetic Susceptibility Measurements

Measurements for the complexes were obtained over the range 115–340° K. At each temperature, measurements were obtained at 10 different field strengths. The absolute Gouy method was used with magnetic fields determined as previously described.[16] The method of temperature variation has been described.[17] Samples were in the form of finely ground powders.

Electron Paramagnetic Resonance Measurements

Data were obtained at room temperature (295° K) at 9, 14 and 25 GHz and at liquid nitrogen temperature at 9 GHz for Cu(phth)$\cdot$H$_2$O and Cu(Hphth)$_2 \cdot$2H$_2$O. The spectrometers were constructed in this laboratory (SUNY Plattsburgh) and used a 1000 Hz modulation frequency. The magnetic field was monitored with a Varian Mark II fieldial but g-values were determined from field measurements made with an nmr gaussmeter.

Results

Thermal Analysis

A previous investigation[12] of the dehydration of Cu(phth)$\cdot$H$_2$O and Cu(Hphth)$_2 \cdot$2H$_2$O reported only that the former complex loses one mole of water by gradual heating up to 210°C while the latter complex loses both water and phthalic acid at the same time by heating up to 210°C. These qualitative results are in reasonable agreement with our more quantitative measurements that appear in Table I.

Simple dehydration of Cu(Hphth)$_2 \cdot$2H$_2$O should result in the formation of a complex of stoichiometry Cu(Hphth)$_2$. Thermogravimetric curves for this complex did not indicate a well defined plateau after the initial dehydration of the complex. A complex, isolated by heating the Cu(Hphth)$_2 \cdot$2H$_2$O complex at

TABLE I. Thermal Analysis Results for the Hydrated Copper (II)–Phthalic Acid Complexes. Initial Weight-loss Temperatures (t_i), DTG Peak Temperatures (t_m), and Enthalpy of Dehydration (ΔH).

Complex	ΔH (cal/ g)[a]	Dehydration (°C)		Complex Decomposition (°C)	
		t_i	t_m	t_i	t_m
$Cu(Hphth) \cdot 2H_2O$	59[b]	122	150	260	311
$Cu(phth) \cdot H_2O$	32	200	238	280	312

[a] Obtained by use of a value of 6.8 cal/g for the standard Indium reference material. [b] For this complex contained in a regular sample pan concurrent sublimation of free phthalic acid prevented a quantitative calculation of the heat of dehydration. The value shown was obtained when the complex was enclosed in a volatile sample pan with a small pin hole.

about 125° C until the weight loss indicated the loss of two water molecules per copper ion, gave a reasonable analysis for the stoichiometry $Cu(Hphth)_2$. However, the magnetic behavior of the complex was similar to that of $Cu(phth)$ and the complex was shown to contain free phthalic acid. This indicates that the complex isolated is better described as a mixture of $Cu(phth)$ and H_2phth. The free phthalic acid sublimes upon heating this mixture and hence no well defined plateau occurs in the TG curve after the dehydration process.

The higher derivative thermogravimetry (DTG) peak temperatures that are associated with the decomposition of the dehydrated complexes are identical for both $Cu(Hphth)_2 \cdot 2H_2O$ and $Cu(phth) \cdot H_2O$. This is consistent with formation of the same anhydrous $Cu(phth)$ before ultimate decomposition. Presumably final decomposition results in the formation of copper metal as has been found for the decomposition of copper(II) oxalate complexes.[18,19]

Some preliminary experiments on the effect of sample containment on the observed enthalpy changes for Cu $(Hphth)_2 \cdot 2H_2O$ indicate that enclosure of the complex in a sealed volatile sample pan[15,20] results in a transition ($\Delta H = 41$ cal/g) that does not involve the loss of water and may imply structural rearrangement.[7]

Magnetic Studies

The gram susceptibilities, molar susceptibilities corrected for diamagnetism, and magnetic moments for the complexes investigated are reported at various temperatures in Table II. The diamagnetic corrections used for $Cu(phth)$, $Cu(phth) \cdot H_2O$, $Cu(Hphth)_2 \cdot 2H_2O$, $Cu(gly)_2$ and $Cu(gly)_2 \cdot H_2O$ are $(-90.5, -103.5, -200.1, -87.6$ and $-100.6) \times 10^{-6}$ cgsu, respectively. These values were calculated from the free ligand values available in the literature[21] and by the method of Pascal.[22] Magnetic moments were calculated by use of the equation $\mu = 2.828 \ (\chi_M'T)^{1/2}$ where χ_M' is

TABLE II. Gram Susceptibilities, Corrected Molar Susceptibilities and Magnetic Moments for the Complexes.

Complex	Temp., °K	$10^6 \chi_g$	$10^6 \chi_M'$	μ
$Cu(gly)_2$	294	6.67	1500	1.88
	288	6.87	1542	1.88
	269	7.27	1627	1.87
	251	7.75	1729	1.86
	233	8.34	1853	1.86
	211	9.05	2004	1.84
	188	9.98	2201	1.82
	168	11.14	2446	1.81
	150	12.51	2736	1.81
	140	13.32	2908	1.80
	128	14.42	3141	1.79
	115	15.68	3407	1.77
$Cu(phth)$	333	3.79	953	1.59
	317	3.96	992	1.59
	298	4.03	1008	1.55
	281	4.06	1015	1.51
	261	4.10	1024	1.46
	243	4.10	1024	1.41
	227	4.07	1017	1.36
	212	3.99	1000	1.30
	190	3.82	960	1.21
	172	3.57	903	1.11
	153	3.16	809	0.99
	133	2.61	685	0.85
	114	2.14	578	0.73
$Cu(phth) \cdot H_2O$	339	5.14	1366	1.92
	319	5.43	1439	1.92
	297	5.82	1533	1.91
	278	6.07	1596	1.88
	259	6.45	1688	1.87
	240	6.97	1816	1.87
	220	7.58	1965	1.86
	198	8.44	2179	1.86
	176	9.34	2399	1.84
	154	10.51	2685	1.82
	133	12.00	3055	1.80
	114	13.78	3490	1.78
$Cu(Hphth)_2 \cdot 2H_2O$	319	3.02	1498	1.95
	297	3.28	1608	1.95
	278	3.50	1703	1.95
	259	3.77	1818	1.94
	240	4.14	1979	1.95
	220	4.50	2133	1.94
	198	5.05	2370	1.94
	176	5.69	2646	1.93
	154	6.55	3013	1.93
	133	7.69	3504	1.93
	114	9.27	4182	1.95

the molar susceptibility corrected for diamagnetism but not for temperature-independent paramagnetism. The magnetic data for $Cu(gly)_2 \cdot H_2O$ are those of Bair and Larsen[23,24] and have been used to calculate the magnetic parameters g and Θ by the procedures discussed below.

The temperature-susceptibility data for all of the complexes except Cu(phth) could be fit to a Curie–Weiss law of the form:

$$\chi_M' = \frac{Ng^2\beta^2}{4k(T-\Theta)} + N\alpha = \frac{0.09383\ g^2}{(T-\Theta)} + N\alpha \qquad (1)$$

where χ_M' is the molar susceptibility corrected for diamagnetism and the other symbols have their usual meanings. With the form of the Curie–Weiss law used here, a negative Θ value would imply the existence of antiferromagnetic coupling between paramagnetic centers. This could be verified only by the observation of a susceptibility maximum at temperatures much lower than those investigated in this study. The method of data treatment employed the usual linear regression analysis on the $1/\chi_M''$ versus $T(^\circ K)$ data where χ_M'' is the molar susceptibility corrected for both diamagnetism and an assumed value of 60×10^{-6} cgsu for the $N\alpha$ term. The results of this data treatment are presented in Table III. For the complexes where the anisotropic g values have been independently measured by epr experiments, an average g value was calculated[25], and Θ and $N\alpha$ were permitted to vary to produce the best fit of the experimental data to equation (1) by minimizing the sum of the squares of the differences between the experimental $\chi_M'(T)$ and the corresponding value of the fitted curve. The values of Θ and $N\alpha$ determined by this procedure varied insignificantly from those determined in the previous manner when experimental uncertainties were considered.

TABLE III. The Values of g and Θ that Produce the Best Fit of the Experimental Susceptibilities to Equation (1) with $N\alpha = 60 \times 10^{-6}$.

Complex	g, 95%CI(N)[a]	$\Theta(^\circ K)$, 95%CI(N)[a]
Cu(phth)·H$_2$O	2.24 ± 0.03(12)	−26 ± 7(12)
Cu(Hphth)$_2$·2H$_2$O	2.21 ± 0.02(11)	−0.6 ± 3.3(11)
Cu(gly)$_2$·H$_2$O	2.18 ± 0.03(6)	−7 ± 6(6)
Cu(gly)$_2$	2.20 ± 0.02(12)	−21 ± 4(12)

[a] The N value listed in parentheses indicates the number of data points.

For the anhydrous complex Cu(phth) a maximum susceptibility was observed at about 250° K when the corrected molar susceptibility is plotted versus temperature. One interpretation of this susceptibility maximum is that the copper(II) ions interact as strongly coupled pairs as in anhydrous copper(II) acetate.[26] This implies that the $\chi_M'(T)$ data should be described by the Bleaney–Bowers' equation:[27]

$$\chi_M' = \frac{Ng^2\beta^2}{3kT}[1 + 0.333\exp(J/kT)]^{-1} + N\alpha \qquad (2)$$

where J is the parameter that defines the energy separation between the singlet and triplet states and is a measure of the magnitude of the spin-spin interaction. With the convention used in equation (2) a positive J value implies antiferromagnetic coupling and that the singlet state lies below the triplet state. The other commonly used convention is that the coupling energy between pairs of paramagnetic centers is given by an energy of the form $-2J$ and a negative J implies antiferromagnetism. The susceptibility–temperature data for Cu(phth) was fit to this three parameter (g, J, Nα) equation by use of a nonlinear least-squares computer analysis described previously.[28] The values of J and Nα were permitted to vary to obtain the best fit with the value of g fixed at a value of 2.17. The procedure of using a fixed value for g should result in the most meaningful estimate of J.[29] The above treatment produces an estimate of J = 280 cm^{-1} and Nα = 139 $\times$ 10^{-6} cgsu when g is fixed at the value of 2.17 (see Table IV). This J value is nearly identical to the value that would be estimated from the temperature of the susceptibility maximum, J = 1.6 T(max).

The possiblity that the experimental $\chi_M'(T)$ data for Cu(phth) might be more appropriately described by interacting copper(II) centers along a chain rather than as strongly coupled pairs was investigated by fitting the data to:[30]

$$\chi_M' = \frac{Ng^2\beta^2}{4kT}\exp(-J'/2kT) + N\alpha \qquad (3)$$

where the symbols have been previously defined (J' = −J). Jotham[30,31] has recently suggested that equation (3) appears to provide a reasonable description

TABLE IV. The Values of J and Nα that Provided the Best Fit of the Susceptibility–Temperature Data for Cu(phth) to Equations (2) and (3) with g = 2.17.

Complex	Equation 2			Equation 3		
	J, cm^{-1}	10$^9\sigma^a$	10^{6}Nα, cgsu	−J', cm^{-1}	10$^9\sigma^a$	10^{6}Nα, cgsu
Cu(phth)[b]	280	1	139	490	56	569
Cu(phth)[c]	299	15	263	732	1720	1108

[a] Unweighted sum of the squares of the deviations. [b] Prepared anhydrous by a hot solvent preparation. [c] Prepared by heating a hydrate (see text).

of the experimental data of linear-chain complexes. A better fit of the experimental data to equation (3) would suggest that the dimer model is inappropriate. The results of the nonlinear least-squares computer analysis that provided the best fit of our experimental data to equation (3) when g is fixed are shown in Table IV.

EPR Studies

The epr results could be analyzed following the methods outlined by Hathaway and Billings.[32] The g values were found to be independent of frequency. For $Cu(phth) \cdot H_2O$ we find $g_\perp = 2.081 \pm 0.002$ and $g_{\parallel} = 2.325 \pm 0.005$ while for $Cu(Hphth)_2 \cdot 2H_2O$ $g_\perp = 2.066 \pm 0.003$ and $g_{\parallel} = 2.327 \pm 0.002$. The low temperature value for $g_{\parallel}$ in the latter complex could not be previously determined because the parallel portion of the spectrum broadened considerably and was barely detectable. However, a value in the range 2.32 to 2.35 is consistent with our observation and essentially the same as the room temperature result. The value of $g_\perp$ is the same as at room temperature. The linewidths were determined in the perpendicular direction with existing methods.[32] Here we report the half width at half height assuming a Lorentzian shaped line. For the parallel portion of the spectrum we report the half width at half height in the derivative presentation. For Cu $(phth) \cdot H_2O$ at $295° K$ we have $\Delta H_\perp = 110 \pm 8$ gauss, $\Delta H_{\parallel} = 66 \pm 5$ gauss, while at $77° K$ $\Delta H_\perp = 61 \pm 8$ gauss and $\Delta H_{\parallel} = 44 \pm 5$ gauss. For $Cu(Hphth)_2 \cdot 2H_2O$ the values at $295° K$ are $\Delta H_\perp = 77 \pm 6$ gauss, $\Delta H_{\parallel} = 110 \pm 10$ gauss while at $77° K$ $\Delta H_\perp = 107 \pm 10$ gauss and $\Delta H_{\parallel}$ is over 300 gauss.

The g values for $Cu(Hphth) \cdot 2H_2O$ are in good agreement with the data reported earlier[33]: $g_x = 2.080 \pm 0.002$, $g_y = 2.063 \pm 0.002$, $g_z = 2.328 \pm 0.002$, $A_{zz} = 0.0149$ cm^{-1} and $A_{xx} \approx A_{yy} < 0.0025$ cm^{-1}. Magnetic results for the anhydrous material are available in the literature.[34,35]

Discussion

Both DSC and TG results were used to monitor the dehydration process in order to establish the optimum conditions for preparing dehydrated complexes by heating. Fountain and Hatfield[36] found that dehydration by heating had an adverse effect on the magnetic properties of several dehydrated copper(II) arylcarboxylates. It was suggested that decarboxylation possibly occurred upon heating the hydrates. This resulted in the formation of CuO and the loss of volatile organic decomposition products.

In order to investigate the possibility that the magnetic properties of anhydrous Cu(phth) might vary with the method of dehydration, the magnetic parameters of our hot solvent preparation of Cu(phth) are
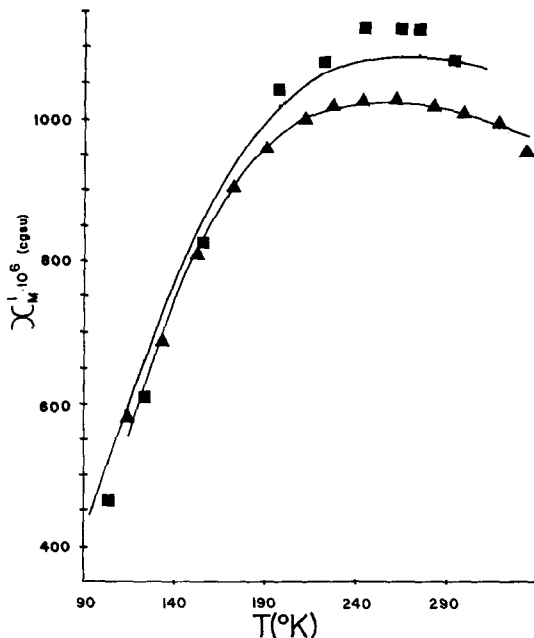

Figure 2. Plot of the corrected molar susceptibility versus temperature for the Cu(phth) complexes. The squares represent the data of reference 34 and the triangles are the data of Table II. The lines represent the best fit of the experimental data to equation (2) with the value of g, J and Nα from Table IV.

compared with those reported for the same complex prepared by heating a hydrated form of the complex to constant weight at 120–130° C.[34] The experimental susceptibility–temperature curves for both forms of the anhydrous complex are shown in Figure 2. The magnetic parameters that produce the best fit of the experimental data to the dimer model [equation (2)] are compared in Table IV. Fair agreement is indicated but the parameters for the Cu(phth) prepared by the hot solvent procedure clearly produce a better fit to equation (2). In addition, the presence of several percent of a paramagnetic impurity was suggested when the data for the heat dehydrated complex was fit to a modified form of the Bleaney–Bowers' equation.[28] Independent epr measurements in our laboratories and by other workers[35] also indicate the presence of a paramagnetic impurity (an S = 1/2 signal at liquid nitrogen temperatures) and a much lower g value of 2.12[35] (use of this value for g resulted in a poorer fit to the experimental data). The slight difference observed in the magnetic parameters and the T_{max}'s for the two different preparations of the anhydrous complex might be ascribed to dehydration by heating or simply to experimental uncertainties. In any case these effects are not nearly as adverse as those previously found for certain arylcarboxylate complexes of copper(II).[36] We believe the effect of heat dehydration on the magnetic

properties of anhydrous metal complexes should be further investigated by use of complimentary thermal and magnetic studies.

Although it may be difficult to distinguish between the linear and binuclear model without structural evidence[37], the magnetic parameters of Table IV suggest that equation (2) provides a better fit to the experimental data than equation (3). This implies the occurrence of strongly coupled pairs of copper(II) ions rather than chains. Hence the structure proposed for Cu(phth) is one in which two phthalate anions bind two adjacent copper ions such that each phthalate ion forms two *syn–syn* bridges with the same two copper ions to give a structure similar to that found in anhydrous copper(II) acetate[26] (see Figure 1).

Structurally[13] the complex Cu(phth)·H_2O contains two crystallographically independent copper atoms. Each possesses a distorted CuO_6 octahedral first coordinate sphere. The adjacent independent copper atoms are linked into zig-zag chains by bridging phthlate ions and water molecules. A particularly interesting bridging arrangement is formed by a carboxyl group that bridges two adjacent copper atoms with a carboxyl oxygen atom and simultaneously forms a *syn–syn* bridge to a third copper atom by means of a carboxylate bridge. The phthlate ligands also link the chains into sheets which are held together by hydrogen bonding. The presence of bridging atoms suggests the possible occurrence of spin–spin coupling between adjacent copper atoms. A simplified schematic representation for the structure of the Cu(phth)·H_2O complex is shown in Figure 3.

The experimental Weiss constant Θ = –26 ± 7°K (95% CI, N = 12) suggests the presence of a weak antiferromagnetic interaction in Cu(phth)·H_2O. The epr results can be used to gain further insight into the long range dimensionality of this interaction. If the interaction proceeds in three dimensions then the linewidth is related to the dipolar width and the exchange field by:

$$\Delta H = K \frac{(H_d)^2}{H_e}$$

where H_d is the dipolar linewidth which may be estimated from crystallographic data[8,13] and ΔH is the experimental value here taken as 61 gauss from the perpendicular region of the 77°K spectrum. This value is chosen to minimize: (1) the effect of hyperfine interactions which contribute to the parallel region and (2) possible contributions to the linewidth at room temperature from spin–lattice relaxation effects. The value K may vary from 10/3 to 1 depending on whether or not the nonsecular terms in the dipolar Hamiltonian contribute to the linewidth. We find an effective exchange field of about 2500 gauss. This may be converted to an estimate for the Curie–Weiss constant by $g\beta H_e \sim k\Theta$ to give a value of $\Theta \sim 0.4$°K.
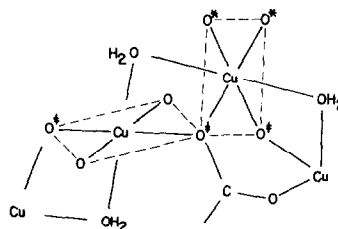

Figure 3. Simplified schematic representation of Cu(phth)·H_2O. The O^+'s represent carboxylate oxygens that bridge copper atoms along a chain, the O*'s represent carboxylate oxygens that bridge copper atom in adjacent chains and O's represent nonbridging carboxylate oxygen. All water molecules bridge copper atoms in the same chain.

This value is considerably below the susceptibility data quoted earlier and suggests the possibility of a low dimensional interaction.[8] The theory of Richards and coworkers[38,39] can be used to provide some estimate of H_e and Θ for low dimensional cases.

In two dimensions the equation is:

$$\Delta H = K \frac{(H_d)^2}{H_e} \ln \left(\frac{H_e}{H_d}\right)$$

while for one dimension the equation is:

$$\Delta H = \frac{H_d^{4/3}}{H_e^{1/3}}$$

The K appears in the first but not the second equation since two dimensional behavior[40] can retain some nonsecular components. In the one dimensional case the appearance of these components may be associated with significant off-chain interactions and thus the equation quoted above would no longer be applicable.[39,40] The value for H_e and Θ are in the range 7000 to 23,000 gauss and 1°K to 3°K for two dimensional behavior and about 100,000 gauss and 15°K for one dimensional behavior. These results are more nearly in accord with the susceptibility data especially since the nature of the approximations used in obtaining these estimates could produce an uncertainty of nearly one order of magnitude.

The question as to whether coupling is best described by copper atoms interacting in pairs with a coupling between these pairs[8] along a chain or by a more complicated two dimensional situation can not be answered in detail, but the presence of a low dimensional pathway for interactions between metal ions seems likely.

A distorted octahedral CuO_6 stereochemistry is also found in the complex Cu(Hphth)$_2$·$2H_2O$.[33,41] Each copper atom is bound to two hydrogen phthalate ions and two water molecules. Two carboxyl oxygens from the two different hydrogen phthalate ions and the two oxygen atoms of the two different water molecules form the 4 close contacts in the distorted CuO_6 unit. The long contacts are formed by the remaining two oxygen
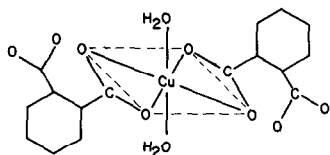
Figure 4. Schematic representation of Cu(Hphth)$_2 \cdot$2H$_2$O.

atoms of the coordinated carboxyl group. A distorted 4-membered chelate ring is thus formed by each unprotonated carboxyl group which hence does not act to bridge adjacent copper atoms. The remaining protonated carboxyl group is also unavailable for bridging adjacent metal atoms since it is involved in strong intramolecular hydrogen bonds. The structure for Cu (Hphth)$_2 \cdot$2H$_2$O is shown in Figure 4.

Although the coordinated water molecules form hydrogen bonds to a hydrogen phthalate group bound to a second copper atom, no bridging atoms or groups serve to link adjacent copper atoms. The structure prevents the existence of appreciable magnetic coupling by a superexchange pathway between metal atoms. This is confirmed by a Weiss constant of zero within experimental uncertainty, $\Theta = -0.6 \pm 3.3°$ K (95% CI, N = 11). The epr data can also be analyzed according to the method outlined above. The three dimensional formula produces a Θ of less than 0.5° K in good agreement with the Curie–Weiss constant. This suggests only very weak interactions between metal ions. The rather

pronounced broadening of the parallel portion of the spectrum at low temperatures may be due to a partial resolution of the hyperfine compounds under these conditions. Such an analysis would be generally consistent with very weak interactions as well.

Finally, these results seem consistent with general trends relating the magnetic and structural parameters of other related systems. Magnetic parameters for some hydrated copper(II) carboxylates of known crystal structures are tabulated in Table V. In constructing this table, only hydrated complexes were selected that form between copper(II) and simple carboxylate ligands and that have a normal magnetic moment at room temperature. Also included are two hydrates that have the quite common binuclear structure (acetate and succinate) or a more complicated bridging structure (formate tetrahydrate) and exhibit subnormal moments. Inspection of the table reveals certain correlations between the copper–water bond distance in the normal hydrates and the ability to form subnormal anhydrous complexes by dehydration of the complex. Presumably this subnormal complex has the copper acetate-type binuclear structure. Specifically in all but one of the normal hydrates where water molecules occupy one or more of the short contact positions (less than 2.05 Å) in the distorted CuO$_6$ octahedron, dehydration (by direct heating or by refluxing) produces a magnetically subnormal complex. The one exception is the Cu (Hmal)$_2 \cdot$4H$_2$O complex (mal = maleate anion). The

TABLE V. Magnetic Parameters for Some Hydrated and Dehydrated Copper(II) Carboxylates.

Hydrate Formula[a]	System	Bond Length	Crystal Structure Reference	Bulk Magnetic[c] Parameter of Hydrate	Bulk Magnetic[c] Parameter of Anhydrous	Reference for Magnetic Parameters
Cu(ben)$_2 \cdot$3H$_2$O	CuO$_6$	1.97(2) 2.51(2)	42	$\Theta = 40°$ K	J = 312 cm^{-1}	43
Cu(succ)$\cdot$2H$_2$O	CuO$_5$	2.10(1)	44	J = 331 cm^{-1} J = 242° K	J = 312 cm^{-1} J = 230° K	11 10
Cu(form)$_2 \cdot$4H$_2$O	CuO$_6$	2.36(2)	45	$\Theta = -175°$ K	$\Theta = -175$	46
Cu(form)$_2 \cdot$2H$_2$O	CuO$_6$	1.97(2) 2.02(2)	47	$\Theta = 0$	$\Theta = -175$	46
Cu(sal)$_2 \cdot$4H$_2$O	CuO$_6$	1.92(2)	48	$\mu(22°) = 1.92$	$\mu(25°) = 1.41$	49
Cu(gly)$_2 \cdot$H$_2$O	CuN$_2$O$_4$	2.40(1)	50	$\Theta = -7 \pm 6°$ K	$\Theta = -21 \pm 4$	This work
Cu(hip)$_2 \cdot$4H$_2$O	CuO$_5$	2.00(2)	51	$\Theta = -33 \pm 10°$ K J = 4 cm^{-1}	J = 327 cm^{-1}	7 9
Cu(Hphth)$_2 \cdot$2H$_2$O	CuO$_6$	1.97(2)	41	$\Theta = -0.3 \pm 6°$ K	J = 280 cm^{-1}	This work
Cu(phth)$\cdot$H$_2$O	CuO$_6$	1.96(2)	13	$\Theta = -26 \pm 7°$ K	J = 280 cm^{-1}	This work
Cu(Hmal)$_2 \cdot$4H$_2$O	CuO$_6$	1.93(2) 1.96(2) 2.68(2)	52	$\mu(20°) = 1.97$	$\mu(20°) = 1.89$	53
Cu(mal)$\cdot$H$_2$O	CuO$_5$	2.26(1)	52	$\mu(20°) = 2.00$	$\mu(20°) = 1.91$	53
Cu(ac)$_2 \cdot$H$_2$O	CuO$_5$	2.20(1)	54	J = 284 cm^{-1}	J = 302 cm^{-1}	27

[a] The following ligand abbreviations have been used: ben=benzoate, succ=succinate, form=formate, sal=salicylate, gly=glycinate, hip=hippurate, Hphth=hydrogen o-phthalate, phth=o-phthalate, Hmal=hydrogen maleate, mal=maleate, ac=acetate. [b] The number in parentheses is the number of water molecules at the given bond length.
[c] The sign and definition of J and Θ have been changed to conform to the definition used in this work (see text).

complex produced by direct heating has been assigned the formula $Cu(Hmal)(mal)_{1/2}$ and has a normal magnetic moment.[53] Since maleate anions coordinate to copper as a seven-membered chelate ring[52] similar to that found with succinate and phthalate anions (both of which have hydrates that produce subnormal complexes upon dehydration), further attempts at dehydration (such as prolonged heating at reduced pressures) may produce the predicted subnormal anhydrous complex. That such a complex may exist is evident from the preparation of subnormal $[Cu_2(Hmal)_4] \cdot H_2mal \cdot 4EtOH$ that loses EtOH upon heating to form another subnormal complex.[53] The correlation that exists appears to be related to the unique stability of the binuclear copper acetate structure and the inability of the carboxylate group to form stable four-member chelate structures.

Thermal dehydration of hydrates where the water is bound to the copper atom by long bonds (greater than 2.05 Å) results in little structural rearrangement and little change in the bulk magnetic properties. Hence dehydration of the hydrated binuclear copper(II) acetate or succinate results in the binuclear structure being retained. For the CuN_2O_4 system, $Cu(gly)_2 \cdot H_2O$, dehydration of the magnetically normal long-bond hydrate results in a normal anhydrous complex with retention of the five-membered chelate ring.

Acknowledgments

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