

Copper(II) Complexes of *p*-Nitrophenaceturic Acid: Magnetic and Thermal Behavior of Copper(II) *p*-Nitrophenacetate Dihydrate, Anhydrous Copper(II) *p*-Nitrophenacetate and the Corresponding Methanol Adduct

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Received July 28, 1980

A hydrated copper(II) p-nitrophenacetate complex, an anhydrous analogue and a methanol adduct were prepared and examined by various physical methods in order to test proposed structure-rearrangement criteria. The desolvation processes were investigated by thermal gravimetric analysis. Magnetic measurements were made by the absolute Guoy method over the temperature range of 112–342 K. The UV, visible and IR spectra of solid samples of the complexes were recorded. X-ray diffraction was used to obtain powder patterns of the complexes.

The hydrated complex and the methanol adduct exhibit normal paramagnetic behavior. Two separate preparations of the anhydrous complex indicate that its paramagnetic susceptibility is slightly field dependent and that the magnitude of its susceptibility varies from sample to sample. The temperature dependence of the susceptibility of the anhydrate indicates antiferromagnetism. The IR spectra suggest that coordination occurs through the carboxylate group only. Comparison of the X-ray powder patterns of the hydrated and anhydrous complexes indicates that rearrangement accompanies dehydration. From consideration of the results it appears that the structure-rearrangement criteria that were previously suggested are valid for the preparation of the anhydrous compound.

Introduction

In previous studies we have been concerned with structural changes that accompany the loss of coordinated water molecules from hydrated copper(II) carboxylate complexes [1–3]. Results to date have encouraged us to propose a relationship between copper–water bond lengths in the hydrated complex and the structure of the resulting dehydrated complex [2]. Our structure-rearrangement criteria are:

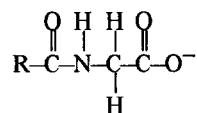
1) Hydrated copper(II) carboxylates that possess the caged-dimer structure dehydrate with retention of this structure.

2) Magnetically-normal complexes with short copper–water bonds dehydrate to form magnetically-subnormal caged dimers.

3) Magnetically-normal complexes with long copper–water bonds dehydrate to form magnetically-normal complexes that are not caged dimers.

Here we have used magnetically-normal to mean the Weiss constant is small ($\theta \sim 0 \pm 20$ K) and short bonds to mean less than 2.05 Å. In the several systems so far investigated, where a dramatic change in magnetic properties accompanies dehydration, the magnetically-subnormal anhydrous complex that forms is thought to possess the caged-dimer structure typified by copper(II) acetate monohydrate [4]. The observed structural rearrangements that accompany desolvation appear to be related to the unique stability at elevated temperatures of the binuclear structure, the usual reluctance of the carboxylate moiety to form stable four-membered chelate rings with a single copper(II) ion and the ‘plasticity’ of the coordination polyhedra of copper(II) complexes [5].

The structures of the hydrated complexes that form between copper(II) and α -amidoamino acid anions (I) are widely varied. For the hippurate anion



I

(see I, $\text{R} = \text{C}_6\text{H}_5$) a tetrahydrate forms that consists of dimeric units with carboxylate-oxygen bridges [6]. The magnetically-normal [2, 7, 8] five coordinate copper ion is in a distorted square pyramidal configuration. With $\text{R} = \text{CH}_3$ (acetylglycinate) a magnetically-normal [3, 9] blue tetrahydrate is again isolated but it is not isostructural with the hippurate analog. The acetylglycinate complex is not dimeric and the coordination about the copper ion is square

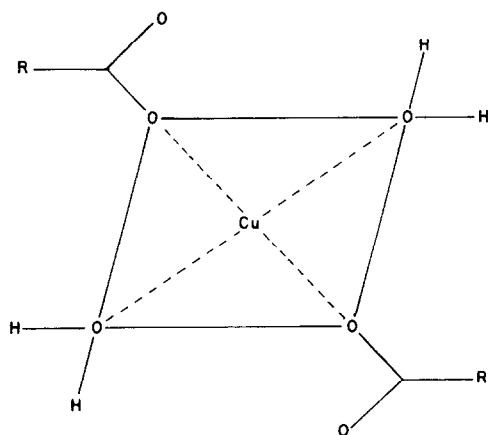


Fig. 1. The square planar structure of $\text{Cu}(\text{npaa})_2 \cdot 2\text{H}_2\text{O}$ with a copper-water bond length of 1.96 Å.

planar with two long contacts involving the remaining carboxylate oxygen of the coordinated anion [10]. The structure [11] of the magnetically-normal [12] blue bis(*p*-nitrophenacetate)diaquocopper(II) ($\text{R} = \text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{CH}_2$ and see Fig. 1) is similar to that of the corresponding acetylglycinate complex but the two uncoordinated water molecules are absent.

In the present study we have used a multi-technique approach in our investigation of the structure of anhydrous copper(II) *p*-nitrophenacetate. We report the infrared and electronic spectra, and X-ray powder patterns of both the hydrated and anhydrous complexes as well as the temperature dependence of the magnetic susceptibility of the hydrated and anhydrous complex, and the corresponding methanol adduct.

Experimental

Preparative Methods

N-phenylacetyl glycine (phenaceturic acid) was prepared by the method reported by Ford [13]. The IR spectrum of the recrystallized acid matched that given in the Sadtler Standard Infrared Prism Spectra.

Nitration [14] of the acid was accomplished by dissolving 10 g of the acid in 40 ml of concentrated sulfuric acid. Concentrated nitric acid was added dropwise with shaking until a total of 40 ml had been added. The reaction mixture was placed in an ice bath for 45 minutes, then poured over 250 g of ice. The precipitate was collected by filtration and recrystallized in dilute ethanol. The melting point, 173 °C, and the appearance (fine white hair-like crystals) of the acid agreed with that reported in the literature [15] for N-acetyl-2-(*p*-nitrophenyl)-

glycine (abbreviated Hnpaa) and see I with $\text{R} = \text{NO}_2-\text{C}_6\text{H}_4\text{CH}_2$.

$\text{Cu}(\text{npaa})_2 \cdot 2\text{H}_2\text{O}$ was prepared by adding 5 g (0.021 mol) of Hnpaa to 75 ml of 50% methanol in water. A stoichiometric volume (21 ml) of 1 *N* NaOH was added with stirring. The resulting yellow solution was filtered to remove any undissolved acid. To the filtrate, 2.6 g (0.007 mol) of copper(II) perchlorate hexahydrate was slowly added with stirring. Initially the mixture produced a green precipitate but upon further addition of the copper salt the precipitate turned blue. The mixture was permitted to stir for 2 hr to insure conversion to the blue form. After standing in the coldroom overnight, the blue precipitate was filtered and left to air-dry for a day.

There were two separate preparations of the anhydrous complex $\text{Cu}(\text{npaa})_2$. Both were obtained by heating the dihydrate in a vacuum oven. Preparation A resulted from heating the dihydrate several times for 4–5 hr at $130 \pm 10^\circ\text{C}$ and preparation B resulted from heating the dihydrate several times for 4–5 hr at $110 \pm 10^\circ\text{C}$.

Bis[N-(4-nitrophenylacetyl)glycinato]dimethanolcopper(II), $[\text{Cu}(\text{npaa})_2 \cdot 2\text{CH}_3\text{OH}]$ was prepared from $\text{Cu}(\text{OH})_2$ and Hnpaa in a solvent composed of equal amounts of absolute ethanol and methanol. The $\text{Cu}(\text{OH})_2$ was prepared from a warm aqueous solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ by the addition of 10% ammonia until the deep blue color of the tetrammine complex appeared. At this point a stoichiometric amount of NaOH was added. The freshly precipitated $\text{Cu}(\text{OH})_2$ was collected by filtration, washed several times with warm water, and added to a hot solution of 5 g (0.021 mol) Hnpaa in 150 ml of absolute ethanol. A pale blue precipitate appeared that was most likely $\text{Cu}(\text{npaa})_2 \cdot 2\text{H}_2\text{O}$. The reaction mixture was then placed in a 300 ml round bottomed flask and connected to a Soxhlet extractor which contained activated 3 Å molecular sieves in the porous thimble. The mixture was heated and a volume (150 ml) of methanol was added to the flask. The mixture refluxed overnight and in the morning the flask contained a white precipitate in a green liquid. The precipitate was collected by filtration and washed with dry ether. This compound was very sensitive to air moisture so it was kept in a vacuum desiccator and handled in a dry glove bag. Iodometric and thermal analysis indicate the formula $\text{Cu}(\text{npaa})_2 \cdot 2\text{CH}_3\text{OH}$ for this compound. The green filtrate from the preparation was evaporated to 30 ml and left to stand. A pale blue precipitate formed and this was identified as $\text{Cu}(\text{npaa})_2 \cdot 2\text{H}_2\text{O}$ by its IR spectrum.

Compounds were analyzed for percent copper by iodometric titrations. The percent water in the hydrated complexes was determined by thermogravimetric analysis and by the weight losses recorded during the vacuum oven preparations of the anhydrous

TABLE I. Gram Susceptibilities, Corrected Molar Susceptibilities and Magnetic Moments for the Complexes.^a

Complex	Temp. (K)	$10^6 \chi_g$	$10^6 \chi'_M$	μ (BM)
Cu(npaa) ₂ ·2H ₂ O	342	1.815	1.302	1.89
	324	1.960	1.385	1.89
	307.5	2.072	1.449	1.89
	299	2.109	1.471	1.88
	283.5	2.236	1.544	1.87
	268	2.380	1.626	1.87
	252	2.570	1.735	1.87
	232	2.842	1.891	1.88
	215	3.080	2.027	1.87
	194.5	3.470	2.251	1.87
	177	3.819	2.452	1.86
	156.5	4.305	2.730	1.85
	135	5.055	3.160	1.85
	342 ^b	1.710	1.306	1.89
	324 ^b	1.817	1.371	1.88
Cu(npaa)·2CH ₃ OH	307.5	1.899	1.420	1.87
	299	1.974	1.465	1.87
	297	1.980	1.469	1.87
	283.5	2.106	1.547	1.87
	268	2.240	1.626	1.87
	252	2.405	1.721	1.86
	232	2.602	1.851	1.85
	215	2.799	1.963	1.84
	194.5	3.180	2.191	1.85
	177	3.548	2.412	1.84
	156.5	3.970	2.666	1.83
	135	4.670	3.087	1.83
	112	5.708	3.712	1.82
	342	1.726	1.163	1.78
	324	1.779	1.191	1.76
Cu(npaa) ₂ ^c (preparation A)	307.5	1.832	1.220	1.73
	297	1.836	1.222	1.70
	283.5	1.905	1.259	1.69
	268	1.925	1.270	1.65
	252	1.960	1.288	1.61
	232	1.970	1.294	1.55
	215	1.972	1.295	1.49
	194.5	1.964	1.291	1.42
	177	1.923	1.269	1.34
	156.5	1.846	1.227	1.24
	135	1.689	1.143	1.11
	112	1.469	1.025	0.96
	297	1.548	1.067	1.59
	297	1.542	1.064	1.59
	268	1.619	1.105	1.54
(preparation B)	232	1.687	1.142	1.46
	194.5	1.720	1.159	1.34
	156.5	1.746	1.174	1.21
	112	1.820	1.213	1.04

^aThe molar susceptibility (χ'_M) is corrected for the diamagnetism of the complex $[(-261, -277 \text{ and } -235) \times 10^{-6} \text{ cgs/mol for Cu(npaa)}_2 \cdot 2\text{H}_2\text{O, Cu(npaa)}_2 \cdot 2\text{CH}_3\text{OH and Cu(npaa)}_2$, respectively]. The magnetic moment is calculated as $\mu = 2.828 (\chi'_M T)^{1/2}$. ^bMolar susceptibilities at these two temperatures were not used in evaluating θ for the Curie-Weiss Law since some loss of methanol from the adduct

rous complexes. Analyses of the copper(II) complexes are as follows: (Calcd. for Cu(npaa)₂·2H₂O: Cu, 11.1; H₂O, 6.28 and Found: Cu, 11.0; H₂O, 6.50. Calcd. for anhydrous Cu(npaa)₂: Cu, 11.8; C, 44.6; H, 3.35; N, 10.4 and Found: for preparation A: Cu, 12.0; C, 44.5; H, 3.49; N, 10.3 and for preparation B: Cu, 11.4; C, 44.4; H, 3.70; N, 10.2. Calcd. for Cu(npaa)₂·2CH₃OH; Cu, 10.6; CH₃OH, 10.6 and Found: Cu, 10.5; CH₃OH 10.5).

EPR Spectra

EPR spectra were recorded at X-band frequencies on a Varian E-9 spectrometer for both preparations of the anhydrous compound. Measurements were obtained at both room temperature and approximately 90 K.

Thermal Analysis

Thermal gravimetric analysis and derivative thermogravimetry (DTG) results were obtained in a nitrogen atmosphere on the Perkin-Elmer TGS-1 Thermobalance. A scan rate of 10°/min and a purge rate of 60 ml/min were used. The sample temperature was estimated by use of the magnetic transitions suggested by the manufacturer. Temperatures for the maximum rate of weight loss for desolvation as determined by DTG were 128 and 153 °C for Cu(npaa)₂·2CH₃OH and Cu(npaa)₂·2H₂O, respectively. The corresponding temperature for the decomposition of anhydrous Cu(npaa)₂ occurred at 236 °C.

Magnetic Measurements

Magnetic susceptibilities were measured in a nitrogen atmosphere by the absolute Gouy method over the temperature range 112 to 358 K. Measurements were made in 1000 gauss intervals between 0 and 10,000 gauss at each temperature. Samples were kept at each temperature for 30 min before the magnetic measurements were made. The variable temperature unit employed has been described previously [16].

Spectroscopic Measurements

Visible and UV spectra were measured on the Cary 14 Spectrophotometer. Spectra of the solid complexes were obtained from nujol mulls of the samples using filter paper as a support. IR spectra were recorded on the Perkin-Elmer 621 Grating Spectrophotometer, in the 4000 to 340 cm⁻¹ region. Samples were run as KBr pellets and as nujol mulls between sodium chloride plates. Identical spectra for the compounds were obtained by the two sampling techniques.

was noticed. ^cThe susceptibilities of both preparations exhibit a slight field dependence. The values presented herein correspond to those at our strongest magnetic field (10,000 gauss).

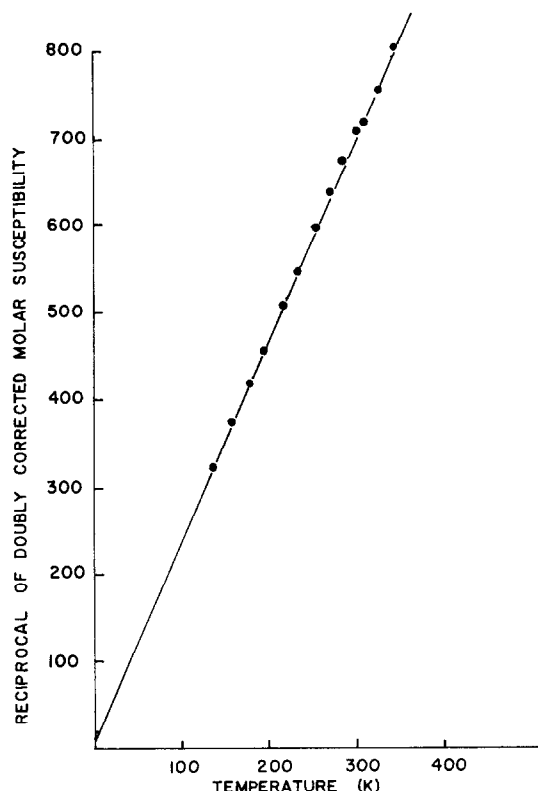


Fig. 2. Curie-Weiss plot of the reciprocal of the molar susceptibility of $\text{Cu}(\text{npaa})_2 \cdot 2\text{H}_2\text{O}$ corrected for both diamagnetism and temperature-independent paramagnetism versus temperature.

X-ray Powder Diffraction

The Debye-Scherrer method was used to obtain the X-ray powder diffraction patterns of several samples. A Picker Model 809B X-ray Diffraction Unit and a Picker Style No. 3591A Cylindrical Powder Camera were employed. The unit utilized a copper target to produce unfiltered copper K_α radiation. Samples were run as ground powders packed in 0.5 mm (i.d.) glass capillaries.

The angles corresponding to 2θ were measured on the developed films as described by Azaroff and Buerger [17]. The values for the interplanar spacings were taken from tables [18] of 'd' versus 2θ for copper K_α radiation. The intensities of the lines were determined by visual inspection and assigned a rating from the following five-point arbitrary scale: very dark (vd), dark (d), gray (g), light (l), or very light (vl).

Results and Discussion

The results of the magnetic measurements are presented in Table I. For $\text{Cu}(\text{npaa})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Cu}(\text{npaa})_2 \cdot 2\text{CH}_3\text{OH}$, the values shown at any particular

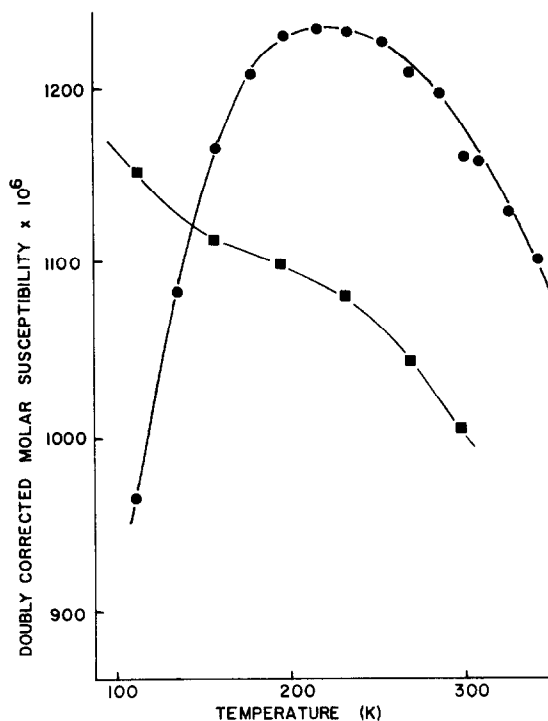


Fig. 3. Plot of the doubly corrected molar susceptibility of anhydrous $\text{Cu}(\text{npaa})_2$ versus temperature. The circles represent preparation A and the squares preparation B.

temperature are the averages from the five highest magnetic field strengths. Since both preparations of anhydrous $\text{Cu}(\text{npaa})_2$ had magnetic susceptibilities that exhibited a field dependence, the results given are those obtained at the highest field strength only. For these two samples, the values for χ_g increased by approximately 8 percent as the field strength increased from 5,000 to 10,000 gauss.

Figure 2 is a Curie-Weiss plot of $1/\chi_M^C$ vs. T for $\text{Cu}(\text{npaa})_2 \cdot 2\text{H}_2\text{O}$. Here χ_M^C represents the molar susceptibility corrected for both diamagnetism and temperature-independent paramagnetism (60×10^{-6} cgs/mol). A similar linear plot is obtained for $\text{Cu}(\text{npaa})_2 \cdot 2\text{CH}_3\text{OH}$ hence we conclude that these substances behave as normal paramagnetic species in the temperature range investigated. From these plots values for g and θ may be obtained from the slope and intercept by use of the equations: $g = [(1/\text{slope}) \times 10.658]^{1/2}$ and $\theta = -(\text{y intercept}/\text{slope})$. The values for g are 2.1 ± 0.1 (uncertainties represent standard deviation) for both $\text{Cu}(\text{npaa})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Cu}(\text{npaa})_2 \cdot 2\text{CH}_3\text{OH}$ and are typical for paramagnetic $\text{Cu}(\text{II})$ species. The values for θ in degrees Kelvin are -3 ± 6 and -6 ± 7 for $\text{Cu}(\text{npaa})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Cu}(\text{npaa})_2 \cdot 2\text{CH}_3\text{OH}$ respectively, and indicate that there is little interaction between copper ions in either complex.

TABLE II. Electronic Spectra of the Solid Complexes.

Compound	Color	$\lambda_{\max}$, nm	Ref.
Cu(npaa) ₂ · 2H ₂ O	blue	615	a
Cu(npaa) ₂	green	690	a
Cu(ag) ₂ · 4H ₂ O	blue	620 780(sh)	9
Cu(ag) ₂ · H ₂ O	green	370(sh) 720	9
Cu(OAc) ₂ · H ₂ O	blue-green	365(sh) 690	a,b

^aThis work. ^bThese values are in reasonable agreement with 699 and 370 nm previously reported [22].

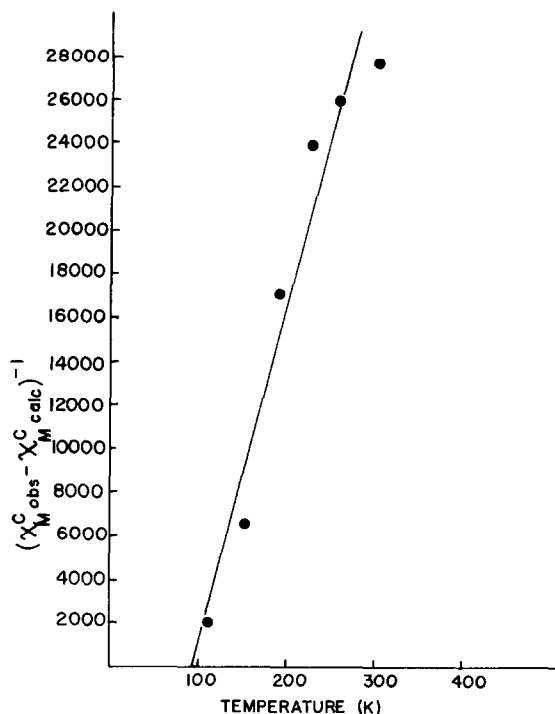


Fig. 4. Plot of the reciprocal of the difference between the observed magnetic susceptibility of anhydrous Cu(npaa)₂ and that calculated by use of $T_{\max}$, versus temperature.

The magnetic properties of anhydrous Cu(npaa)₂ are complicated and were found to vary from preparation. The temperature dependences of χ_M^C for both preparations are shown in Fig. 3. For preparation A the maximum in the plot suggests that this complex is antiferromagnetic. Preparation B does not exhibit a maximum in its susceptibility-temperature plot although a shoulder does appear. A plot of the difference between the experimental molar susceptibility for preparation B and that calculated by use of equation 1 with $J = 236 \text{ cm}^{-1}$ (the singlet-triplet separation estimated from the temperature at which the maximum susceptibility occurs for preparation A and the approximation that $-2J = 1.6 kT_{\max}$), $g = 2.17$ and $N\alpha = 60 \times 10^{-6}$ is shown in Fig. 4.

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

The linearity of the plot suggests the presence of a paramagnetic impurity. The presence of such an impurity is not uncommon for dimer copper(II) carboxylate complexes and may be adequately treated by including a parameter (Y) in eqn. 1 to estimate the fraction of monomeric copper(II) present [19].

$$\chi_M = \frac{Ng^2\beta^2}{3kT} [1 + (1/3) \exp(-2J/kT)] (1 - Y) + \frac{0.448Y}{T} + N\alpha \quad (2)$$

A nonlinear least-squares analysis of eqn. 2 results in the following values of the four parameters: (preparation A: $g = 2.34 \pm 0.10$, $-2J = (273 \pm 6) \text{ cm}^{-1}$, $N\alpha = (157 \pm 71) \times 10^{-6}$, and $Y = 0.11 \pm 0.02$; preparation B: $g = 2.17 \pm 0.25$, $-2J = (318 \pm 6) \text{ cm}^{-1}$, $N\alpha = (120 \pm 160) \times 10^{-6}$ and $Y = 0.22 \pm 0.03$). These results clearly indicate that the magnetic behaviors of the anhydrous Cu(npaa)₂ preparations are typical of that of binuclear copper(II) carboxylate complexes that possess the caged-dimer structure. For these compounds, $-2J$ values fall in the range 278 to 358 cm^{-1} with $g = 2.17 \pm 0.02$ [20]. Our two preparations of the anhydrous compound simply differ in the amount of monomeric copper(II) present. The magnetic behavior of our anhydrous system is similar to that observed for Cu(C₂O₄)₂ · 3H₂O whose susceptibility has been found to depend on the method of preparation, exhibit a maximum near 300 K and possess a field dependency. In view of these complications we only estimate the magnitude of $-2J \sim 300 \text{ cm}^{-1}$ for anhydrous Cu(npaa)₂ and note that preparation by heat dehydration of the hydrate does not appear to offer in this case a good method for the synthesis of the magnetically-pure binuclear copper(II) carboxylate.

Additional support for the presence of a monomeric copper(II) impurity arises from the interpretation of the EPR spectra. These spectra are similar to

TABLE III. Amide and Carboxylate Stretches of the Solid Complexes.

Complex	Coord ^a	Amides Stretches (cm ⁻¹) NH(CO)	Carboxylate Stretches ^b (cm ⁻¹) asy(sym)	$\Delta\nu$ (cm ⁻¹)	Shift ^d of asy(sym)	Ref.
Cu(NPAA) ₂ ·2H ₂ O	mo	3359(1650sh ^f)	1621(1392)	229	+ (-)	e
Cu(NPAA) ₂ ·2CH ₃ OH	mo	3315(1640sh)	1605(1390)	215	+ (-)	e
Cu(NPAA) ₂	—	3310(1640sh)	1610(1411)	199	+ (+)	e
Cu(AG) ₂ ·4H ₂ O	mo	3310(1613)	1614(1397)	216	+ (-)	9
Cu(AG) ₂ ·H ₂ O	br	3350(1640sh)	1625(1415)	210	+ (+)	9
Cu(OAc) ₂ ·H ₂ O	br	—	1605(1421)	184	+ (+)	27
Cu(OAc) ₂	br	—	1592(1421)	174	+ (+)	27
NaNPAA·2H ₂ O ^g	io	3335(1643)	1593(1398)	195		e
NaAG	io	3320(1630)	1600(1400)	200		9
NaOAc	io	—	1578(1414)	164		25

^aType of carboxylate coordination is indicated by mo = monodentate, br = bridging, and io = ionic. ^bCarboxylate stretches given are asy = asymmetric and sym = symmetric. ^c $\Delta\nu$ equals the difference between the asy and sym carboxylate stretches. ^dChange in the carboxylate stretches relative to the ionic salt. ^eThis work. ^fThe abbreviation for shoulder is sh. ^gA dihydrate is indicated by TG measurements.

those reported for anhydrous copper(II) hippurate [21]. In both samples an absorption is found near 3100 G and is attributed to mononuclear impurities of spin $S = \frac{1}{2}$. At the lower temperature the intensity of this absorption increases as is expected. In addition, the copper(II) hyperfine coupling is observed at the lower temperature. Two other absorptions were noted in each spectrum and these are assigned to the caged dimer of spin $S = 1$. The intensities of these are diminished at the lower temperature.

The electronic spectra of the npaa complexes and some structurally similar copper(II) complexes are collected in Table II. In each case both charge-transfer and d-d transitions are observed. The UV-Vis spectrum of solid Cu(npaa)₂·2H₂O consists of a very intense band that begins near 420 nm and extends into the UV region. This can be assigned to a charge-transfer transition and it is observed in the spectrum of each copper(II) complex studied herein. In the Cu(npaa)₂·2H₂O there is a second broad band that is centered at 615 nm and results from a d-d transition.

The electronic spectrum of anhydrous Cu(npaa)₂ consists of a charge-transfer band and a broad weak band that is centered around 690 nm. This latter band is in the appropriate position to be assigned as band I in a caged-dimer structure [22]. The shift of the d-d band from 615 nm in the dihydrate to 690 nm in the anhydrous complex indicates that either the coordination site previously occupied by water has been filled by a group that has a lower ligand field strength or that the geometry about the metal ion has changed. The shift in the wavelength

maximum that we observe for Cu(npaa)₂·2H₂O is similar to that reported for the isostructural complex, Cu(ag)₂·4H₂O, when it is dehydrated to form the caged dimer [23], Cu(ag)₂·H₂O (see Table II). Band II is found near 370 nm in the dimeric Cu(ag)₂·H₂O and Cu(OAc)₂·H₂O complexes [9, 22] and originally was taken to be indicative of the caged-dimer structure. The observation that band II appears in nondimeric complexes and that it is often difficult to locate or obscured by the charge-transfer bands [22] indicates that our inability to locate band II for anhydrous Cu(npaa)₂ cannot be used as evidence to eliminate the caged-dimer structure for this compound.

The relevant IR bands are reported in Table III. The assignment of bands was based on those reported for the isostructural complex Cu(ag)₂·4H₂O [9]. The IR spectrum of Cu(npaa)₂·2H₂O indicates that the N-H stretch occurs at nearly the same frequency as in the free acid. This suggests that the hydrogen bonding of the amide group's nitrogen and hydrogen are comparable to that found in the free acid. The appearance of the N-H stretch also indicates that the amide nitrogen is not coordinated to the copper. An amide nitrogen binds a metal only when the process is accompanied by the dissociation of the amide proton [24].

Two criteria used in predicting the mode of binding of the carboxylate group (monodentate, bidentate, or bridging) are the direction of the shifts, relative to the free carboxylate ion value, of the asymmetric and symmetric carboxylate stretching frequencies and the frequency difference ($\Delta\nu$) between them [25]. These values are given in Table

III for the complexes studied herein. We assume that the IR spectrum of the sodium salt of the acid corresponds to the ionic form of the carboxylate group. The asymmetric CO stretch is shifted to a higher frequency and the symmetric CO stretch to a lower frequency for $\text{Cu}(\text{npaa})_2 \cdot 2\text{H}_2\text{O}$, $\text{Cu}(\text{npaa})_2 \cdot 2\text{CH}_3\text{OH}$ and $\text{Cu}(\text{ag})_2 \cdot 4\text{H}_2\text{O}$ compared to the sodium salts of the acids. This is indicative of monodentate coordination [25] by the carboxylate group and agrees with the reported crystal structure for the two hydrated compounds.

The N-H stretch for $\text{Cu}(\text{npaa})_2 \cdot 2\text{CH}_3\text{OH}$ is shifted to a frequency 45 cm^{-1} lower in value. This indicates a weakening of that bond and is probably due to increased hydrogen bonding by the nitrogen or the involvement of the proton in hydrogen bonding. As in the dihydrate, the position of the amide CO stretch and the appearance of the N-H stretch suggest the absence of coordination through the amide group. When the methanol adduct was mixed with nujol in the ambient atmosphere, the observed IR spectrum was identical to that of the dihydrate. This facile replacement of loosely held organic ligands, such as alcohols and ketones, by atmospheric water has been observed by other workers [26].

The appearance of both the amide N-H and CO stretches in the IR spectrum of anhydrous $\text{Cu}(\text{npaa})_2$ again is evidence that the amide linkage is not coordinated to the copper atom. The fact that the asymmetric and symmetric carboxylate stretches are shifted in the same direction and that the value of the frequency difference between the two stretches is comparable to that in the ionic salt, indicates bidentate or bridging coordination by the carboxylate group [25]. Table III indicates that similar features are found in the IR spectra [27] of the compounds known to have the caged-dimer structure, anhydrous $\text{Cu}(\text{OAc})_2$, $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ and $\text{Cu}(\text{ag})_2 \cdot \text{H}_2\text{O}$. As has been clearly demonstrated [22], the use of IR spectroscopy to assign a binuclear structure must be supplemented by magnetic data, as in our current investigation.

The X-ray powder pattern ('d' spacings and intensities) of anhydrous $\text{Cu}(\text{npaa})_2$ bears no resemblance to that of the hydrate and we take this as evidence to support our contention that the mononuclear $\text{Cu}(\text{npaa})_2 \cdot 2\text{H}_2\text{O}$ undergoes considerable structural rearrangement upon dehydration to form the caged dimer, $\text{Cu}(\text{npaa})_2$.

Our structure-rearrangement criteria appear to be further supported in the present work and in several other studies that have appeared since we first noted the possible existence of such an occurrence [2]. A detailed review [28] of much of the chemical literature indicates that there are very few systems where both the crystal structure of the hydrate and the magnetic behavior of the heat-dehydrated com-

pound have been determined. Both types of data are necessary to test the proposed criteria and are available for magnetically-normal $\text{Cu}(\text{lactate})_2 \cdot 1.5\text{H}_2\text{O}$. The structure data [29] locates the coordinated water molecule at a distance of $2.30\text{ \AA}$ from the copper(II) ion. Heat dehydration of this compound produces a normal paramagnetic anhydrous compound with a room temperature magnetic moment of 1.92 B.M. [30] and this is as expected by use of our structure-rearrangement criteria.

Our observation that heat dehydration of magnetically-normal $\text{Cu}(\text{ag})_2 \cdot 4\text{H}_2\text{O}$ produced an anhydrous compound with magnetic properties consistent with the caged-dimer structure [3] resulted in the suggestion that water coordinated to copper occurs in the tetrahydrate at a short contact distance ($<2.05\text{ \AA}$). The subsequent determination of the structure of this hydrate indicates that two water molecules are found at $1.95\text{ \AA}$ from the copper(II) ion [10].

Popovich and Mirel [31] dried at 160°C magnetically-normal copper(II) *p*-nitrobenzoate adducts (adduct ligand = water, CH_3OH or DMSO) and indicated that the anhydrous $\text{Cu}(\text{p-NO}_2\text{C}_6\text{H}_4\text{COO})_2$ compound that formed possessed the dimer structure. In each case a subnormal magnetic moment of 1.45 B.M. and EPR signals of $S = 1$ species were observed. Although structural data for the adducts are not available, the results do suggest the possibility that our structure-rearrangement criteria may be applicable to systems that contain volatile ligands other than water bound to the copper(II) ion.

Patel and coworkers [31-33] have investigated the magnetic behavior of both the hydrated and the corresponding heat-dehydrated anhydrous copper(II) halosubstituted acetates. Although structural data is not available for the hydrates, several recurring observations appear relevant to the present discussion. Firstly, the monosubstituted hydrates are assigned the caged-dimer structure on the basis of the fit of their χ'_M vs. T behavior to the dimer equation and they undergo dehydration to form anhydrous complexes that are assumed via their magnetism to be dimers or monomer/dimer mixtures. This is as suggested by our structure-rearrangement criteria that indicates that the caged-dimer structure should be retained upon dehydration. A possible exception is the $\text{Cu}(\text{F}_2\text{CHCOO})_2 \cdot \text{H}_2\text{O}$ compound, where the anhydrous complex has a higher magnetic moment than the hydrate, but in this case the magnetic behavior of the hydrate is complicated due to the presumed presence of monomeric impurities. Secondly, the higher halosubstituted complex may well be magnetically-normal monomeric copper(II) complexes but they appear to form anhydrous compounds which are most conveniently classified as monomer/dimer mixtures. Without structural data for these hydrates, the results cannot be used to test our proposed structure-rearrangement criteria.

The problem that persists is the difficulty of preparing, by simple heat dehydration, anhydrous copper(II) carboxylates free of monomeric and/or ferromagnetic impurities. In our previous studies, we were able to prepare anhydrous complexes by heat dehydration with little or no monomeric impurity for the copper(II) complexes with phthalate or acetylglycinate anions but for the hippurate, a measurable monomeric impurity appeared to be present. In the present study, the magnetic behavior of the anhydrous $\text{Cu}(\text{npaa})_2$ complex prepared by heat dehydration is complicated by the presence of both ferromagnetic and paramagnetic impurities. Attempts to prepare the anhydrous complex in dry methanol or ethanol were unsuccessful. At present we are working to develop alternative procedures to synthesize and purify anhydrous complexes suitable for structural studies and to use EPR studies to carefully monitor the presence of such impurities in analytically pure anhydrous complexes.

The synthetic utility of our structure-rearrangement criteria is demonstrated by the work of Moreland and Doedens [35]. Although the stability of caged-dimer copper(II) carboxylates decreases as the number of halosubstituents on the acetate anion increases, the first example of a copper(II) caged-dimer trihaloacetate adduct has been prepared by procedures that involve heating a magnetically normal copper(II) carboxylate. The monoadduct $\text{Cu}(\text{CF}_3\text{-COO})_2 \cdot \text{quinoline}$ results when the bisadduct is heated at 80 °C. Soxhlet extraction and recrystallization from benzene produced crystals suitable for structure analysis. Although structural data is not available for the bisadduct, our criteria would suggest that the N atom of the quinoline molecule is located at a short contact position in the first coordination sphere of the copper(II) ion.

Acknowledgement

The authors gratefully acknowledge partial financial support by a research grant from the Research Foundation of the State University of New York.

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