width of the order $H_B(H_B/H_e)^n$ where H_B is a line-broadening term, H_e is a line-narrowing term, and n is equal to 1. If the off-axis interactions become quite small, then the line shape changes to the diffusive shape and the exponent n becomes $^1/_3$. Consider further the case when the line-broadening mechanism is anisotropic exchange. Then $H_B \simeq (\Delta g/g)^2 H_e$ and the overall line width goes as $(\Delta g/g)^{7/3} H_e$. Now for $\Delta g/g \simeq 0.1$ the first term is approximately 5×10^{-3}. If H_e is of the order of 10^7 G (500 K), then the line width would be about 5×10^4 G. This is about 2 orders of magnitude greater than that expected for the behavior when $n = 1$. Such a broad line would be very difficult to detect. It is not clear whether such a model could apply to $CuCl(tr)\cdot 2H_2O$ directly or not. The effects of significant short-range order[4b] at room temperature would also have to be taken into account in more detailed interpretation of the magnetic properties of this complex.

Still another possibility is that the line-broadening mechanism is dominated by antisymmetrical exchange and produces a line width of the order of $\Delta H \simeq (\Delta g/g)^2 H_e$. This is not significantly different from an ae mechanism with negligible interchain interactions. The data do not allow a choice between these models. Indeed, other mechanisms may be operative.

Finally, we note that in a recent study of a dimeric system, McGregor, Hodgson, and Hatfield[24] found a discrepancy between the calculated value of zero-field splitting due to dipolar and ae mechanisms and the observed value. In that case the antisymmetrical $\overline{D}\cdot\overline{S}_1 X \overline{S}_2$ term is ruled out by symmetry. Perhaps another line-broadening mechanism is responsible for some of the above observations but we are unable at present to suggest anything else.

Summary

In three heterocyclic amine–copper complexes the nonisotropic exchange interactions appear to play a significant role in the magnetic behavior. This work points out the deficiencies in the simple theory for accounting in detail for the absence of an observed line in $CuCl(tr)\cdot 2H_2O$ but suggests alternative explanations. For the other two complexes the ae provides a reasonable explanation for the data.

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Registry No. $CuCl_2(pnz)$, 61258-89-7; $Cu(tr)_2$, 3087-51-2; Cu(tr)Cl, 3087-52-3.

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Preparation and Properties of Copper(II) Complexes of 2,2'-Dicarboxyazobenzene. A New Series of Copper Acetate Like Dimers

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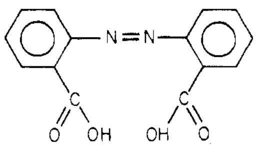
A 1:1 complex readily forms between copper(II) and 2,2'-dicarboxyazobenzene. The magnetic and spectroscopic properties of this material indicate the presence of copper(II) dimers structurally similar to those in copper(II) acetate monohydrate. The separation between the singlet ground state and the triplet excited state is approximately 315 cm^{-1}. The copper(II) azobenzoate complex will react with various difunctional amines to form mixed-ligand complexes. A 2:1 complex can be formed with ethanolamine while 1:1 complexes are observed with *N,N'*-dimethylethylenediamine, *N,N'*-dimethyl-1,3-propanediamine, and *N,N,N',N'*-tetramethylethylenediamine. The dimeric carboxylate structure persists in the complexes containing ethanolamine and *N,N'*-dimethyl-1,3-propanediamine but is lost in complexes of the other two amines.

Introduction

The copper(II) acetate monohydrate dimeric structure, containing a short Cu–Cu distance which results in antiferromagnetic exchange between the two copper(II) ions, can be easily characterized by its magnetic and EPR spectral properties.[2] The terminal H_2O molecules can be readily replaced by other ligands (pyridine, pyridine *N*-oxides, etc.) without destruction of the dimeric structure. The two copper(II) ions coupled by either dipolar and/or exchange interaction in the binuclear complex contain a diamagnetic singlet ground state ($S = 0$) populated at low temperature and a thermally accessible paramagnetic triplet excited state ($S = 1$). This accounts for the temperature dependence of their magnetic moment and their antiferromagnetic behavior. It has also been proposed that the magnetic properties of these dimers are influenced by an excited singlet state;[3] however this proposal has been challenged.[4-6]

Recent interest in polymeric materials containing copper(II) carboxylate dimers[7] prompts us to report work on complexes between copper(II) and 2,2′-dicarboxyazobenzene.



Most of the complexes that we have prepared appear to be highly polymeric.

The following points were of primary interest: (a) Can this dicarboxylate form stable Cu_2L_2 dimers structurally similar to those of copper acetate? (b) What types of complexes result when the azobenzoate complex is reacted with other polyfunctional ligands? (c) Under what circumstances can the polymeric structure of the copper(II) azobenzoate be broken down?

This paper describes the results obtained from this study.

Experimental Section

A. Organic Reagents. Common organic reagents required were purchased and used without further purification.

B. Preparations. 1. 2,2′-Dicarboxyazobenzene. A modified method of Bigelow and Robinson[8] for the preparation of azobenzene was used in the preparation of the dye. To a 300-ml three-necked flask fitted with a reflux condenser, thermometer, and magnetic stirrer, 60 ml of ethanol, 11 ml of water, 10 g of sodium hydroxide, 10 g of 2-nitrobenzoic acid, and 8 g of powdered zinc were added. The flask was then placed in a water bath at 95 °C. The reaction was allowed to proceed for 3 h. The inorganic residue was immediately filtered off and the ethanol distilled from the reaction mixture. The product was then acidified dropwise while being stirred until precipitation of the white impurity (corresponding hydroazobenzene) ceased. The impurity was filtered off and the filtrate further acidified until bright yellow crystals of 2,2′-dicarboxyazobenzene were obtained. The yellow product was recrystallized by dissolving in 1 N sodium hydroxide and reprecipitating with 3 N hydrochloric acid. The precipitate was then filtered, washed with water, and dried under vacuum. The melting point of the product was 236–237 °C (lit. mp 237 °C); Yield 75%. The azobenzoate is slightly soluble in boiling H_2O. Anal. Calcd for $C_{14}H_{10}O_4N_2$: C, 62.21; H, 3.70; N, 10.37. Found: C, 62.20; H, 3.70; N, 9.79.

2. Complexes with 2,2′-Dicarboxyazobenzene. a. The Copper(II)–Azobenzoate Complex. A 1.1-g (0.004-mol) sample of the azobenzoate was dissolved in 30 ml of 95% ethanol. An equivalent amount of 0.1 M (0.97 g) $Cu(NO_3)_2{\cdot}3H_2O$ in 30 ml of 95% ethanol was added and a light green precipitate formed. After 2 h of stirring the precipitate was filtered, washed several times with 50-ml portions of methanol and 50-ml portions of water, and dried in a vacuum desiccator. Analysis indicated the presence of three molecules of water.

Thermal analysis indicates that two molecules of H_2O come off first (maximum deflection at 106 °C). The other molecule follows in a second exotherm (maximum at 148 °C); dec pt 210 °C. Anal. Calcd for $(C_{14}H_8O_4N_2)Cu{\cdot}3H_2O$: C, 43.58; N, 7.24; H, 3.66; Cu, 16.47. Found: C, 43.90; N, 7.10; H, 3.40; Cu, 16.30.

b. The Copper(II)–Azobenzoate–*N,N′*-Dimethylethylenediamine–Dihydrate Complex. The copper(II)–azobenzoate complex was suspended in 50 ml of 95% ethanol and added to an ethanol solution of *N,N′*-dimethylethylenediamine (in slight molar excess). The suspension was stirred briskly overnight. A light yellowish green compound was isolated which was found to decompose at 238 °C. The compound is insoluble in most conventional solvents. Lengthy Soxhlet extraction with water was necessary to remove excess ligand. Thermal analysis indicated the presence of water. Anal. Calcd for $(C_{18}H_{20}N_4O_4)Cu{\cdot}2H_2O$: C, 47.48; H, 5.28; N, 12.03; Cu, 13.94. Found: C, 47.26; H, 4.65; N, 11.05; Cu, 14.12.

c. The Copper(II)–Azobenzoate–*N,N′*-Dimethyl-1,3-propanediamine–Hydrate Complex. The copper(II)–azobenzoate complex was suspended in 50 ml of ethanol and excess *N,N′*-dimethyl-1,3-propanediamine and allowed to react for 3 days with stirring. The resulting pale blue-green product was filtered and washed. It was found to decompose at 220 °C. The complex was found to be very slightly soluble in methanol; it was therefore Soxhlet-extracted for 3 days from this solvent and reprecipitated. A Soxhlet extraction with water followed to remove excess ligand. Thermal analysis indicated the presence of water. Anal. Calcd for $(C_{19}H_{22}N_4O_4)Cu{\cdot}1.5H_2O$: C, 49.50; H, 5.43; N, 12.18. Found: C, 49.75; H, 4.90; N, 12.05.

d. The Copper(II)–Azobenzoate–*N,N,N′,N′*-Tetramethylethylenediamine–Dihydrate Complex. The compound was prepared analogously to 2,2′-dicarboxyazobenzene-*N,N′*-dimethyl-1,3-propanediaminecopper(II). It is a deep blue complex having a decomposition point of 213 °C. It is slightly soluble in methanol and therefore was Soxhlet-extracted from methanol. The compound was then Soxhlet-extracted with water. Analysis indicated the presence of two molecules of water. Anal. Calcd for $(C_{20}H_{24}N_4O_4)Cu{\cdot}2H_2O$: C, 49.70; H, 5.80; N, 11.60; Cu, 13.14. Found: C, 49.62; H, 4.96; N, 11.59; Cu, 13.17.

e. The Copper(II)–Azobenzoate–Bis(ethanolamine) Complex. A 1.1-g (0.004-mol) sample of the azobenzoate was dissolved in 30 ml of ethanol. An equivalent amount of 0.1 M copper(II) nitrate in 25 ml of 95% ethanol was added and a light green precipitate formed. After 2 h of stirring a twofold excess of 0.1 M ethanolamine in ethanol was added to the suspension. Stirring was continued for 5 h; the precipitate was finally filtered, washed with several 50-ml portions of ethanol, and dried in a desiccator. The compound decomposed at 173 °C. Anal. Calcd for $(C_{18}H_{22}O_6N_4)Cu$: C, 47.62; N, 12.35; H, 4.90; Cu, 14.00. Found: C, 47.36; N, 11.82; H, 4.74; Cu, 13.91.

f. Reaction of Copper(II) Azobenzoate with Ethylenediamine. Attempts to replace one or both water molecules in the dimer complex with ethylenediamine were unsuccessful even when the mixture was stirred at 50 °C for several days. Analysis indicated that the compound consisted of the original triaquo complex with some adsorbed (maybe chemisorbed) ethylenediamine.

Thermal analysis always indicated a small amount of ethylenediamine coming off first (40 °C) followed by the typical decomposition described below for the triaquocopper–azobenzoate complex.

C. Infrared Spectra. The infrared spectra (4000–625 cm^{-1}) were obtained on a Beckman IR-8 spectrophotometer as potassium bromide disks. Data were collected on Nujol mulls supported between polyethylene windows in the region 700–300 cm^{-1} on a Perkin-Elmer Model 621 double-beam grating spectrophotometer. All spectra were calibrated with polystyrene film. Some data were also collected using a Beckman IR-11 spectrophotometer.

D. Electron Paramagnetic Resonance Spectra. The electron paramagnetic resonance spectra of powdered samples of the carboxylate complexes were studied at X- and Q-band frequencies. The X-band spectra were obtained using a Varian E-3 spectrometer while the Q-band spectra were recorded on a Varian E-15 spectrometer. Both instruments used 100 kHz modulation. Line positions were determined from the Fielddial reading when each resonance was carefully centered on the oscilloscope. Polycrystalline DPPH (diphenyldipicrylhydrazyl, $g = 2.0036$) was used as a g-value standard.

Values for the exchange parameter, J, for the magnetically coupled carboxylate complexes were obtained from the temperature dependence of the EPR spectra. The changes in intensity of the X-band spectrum between room and liquid nitrogen temperature were used to calculate J. A small amount of DPPH added to each sample served as an intensity reference.

E. Magnetic Susceptibility Measurements. The magnetic susceptibilities of powdered samples were determined at different temperatures on a Gouy balance standardized with $HgCo(SCN)_4$. The apparatus has been described previously.[9] The molar susceptibilities were corrected for diamagnetism using the values given by Mulay.[10] Since the gram-susceptibilities of the copper complexes are rather small, the susceptibility values are expected to only be accurate within 20–25%.

F. Thermal Stabilities. The thermal stabilities of the complexes were determined in a differential thermal analysis apparatus described previously.[11] This was connected through a bypass to a gas chromatograph.[11,12]

Results and Discussion

The Copper(II) Azobenzoate Trihydrate Complex. The magnetic susceptibility and EPR spectrum of the copper(II) complex of 2,2′-dicarboxyazobenzene clearly show that the material contains magnetically coupled pairs of copper(II) ions.

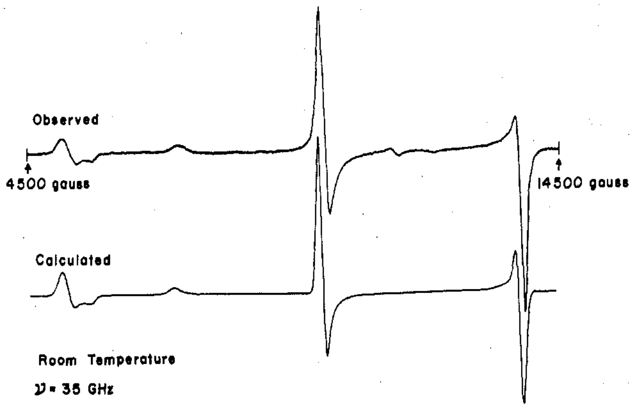


Figure 1. EPR spectrum of powdered $Cu^{II}(AB)\cdot 3H_2O$ (AB = azobenzoate) taken at Q-band frequency.

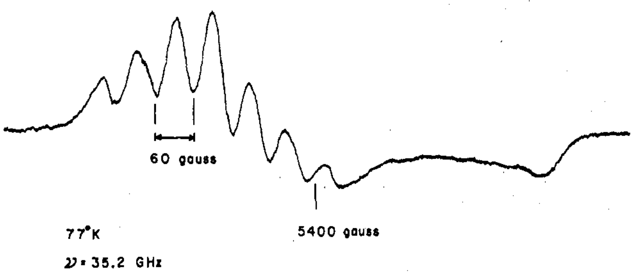


Figure 2. Low-field portion of the EPR spectrum of $Cu^{II}(AB)\cdot 3H_2O$ showing the copper hyperfine structure on the half-field ($\Delta M_S = 2$) transition.

Table I. EPR and Exchange Parameters of the Copper(II) Azobenzoate Trihydrate Dimer

$g_z = 2.37$

$g_{xy} = 2.06$

$A_z = 0.0066\ \mathrm{cm}^{-1}$

$A_{xy} = <0.0010\ \mathrm{cm}^{-1}$

$D = 0.36\ \mathrm{cm}^{-1}$

$E = <0.001\ \mathrm{cm}^{-1}$

$J = 315\ \mathrm{cm}^{-1}$

Table II. Infrared Data for the Copper(II) Complexes of 2,2′-Dicarboxyazobenzene

Compd[a]	Band energy, cm^{-1}	Assignment
2,2′-Dicarboxyazobenzene	1488, 1453 w	$\nu(N{=}N_{tr})$[19]
$Cu^{II}(AB)\cdot 3H_2O$	1485, 1455 w	$\nu(N{=}N_{tr})$
	670 s	$\delta\delta(CuO_2C)$[18]
$Cu^{II}(AB)(DMEN)\cdot 2H_2O$	1480, 1455 w	$\nu(N{=}N_{tr})$
	655 m	$\delta\delta(CuO_2C)$
$Cu^{II}(AB)(DMPN)\cdot 1.5H_2O$	1485, 1457 w	$\nu(N{=}N_{tr})$
	680 s	$\delta\delta(CuO_2C)$
$Cu^{II}(AB)(TMEDA)\cdot 2H_2O$	1485, 1450 w	$\nu(N{=}N_{tr})$
	660 m	$\delta\delta(CuO_2C)$
$Cu^{II}(AB)(EM)_2$	1488, 1470, 1451 w	$\nu(N{=}N_{tr})$
	670 s	$\delta\delta(CuO_2C$

[a] AB = azobenzoate; DMEN = *N,N′*-dimethylethylenediamine; DMPN = *N,N′*-dimethyl-1,3-propanediamine; TMEDA = *N,N,N′,N′*-tetramethylethylenediamine; EM = ethanolamine.

Although the data are somewhat crude, it appears that the magnetic susceptibility reaches a maximum between 200 and 300 K and diminishes as the temperature is lowered to 77 K. Similarly, the intensity of the EPR spectrum of the azobenzoate complex decreases drastically when the sample is cooled from room to liquid nitrogen temperature. The spectrum contains the features characteristics of a paramagnetic species containing two unpaired electrons ($S = 1$). This behavior is consistent with a dimeric system which has a singlet ground state and a thermally accessible triplet excited state.

At room temperature the EPR spectrum of the powdered azobenzoate complex exhibits the absorptions typical of a randomly oriented triplet state ($S = 1$) species having axial symmetry (see Figure 1). The half-field resonance ($\Delta M_s = \pm 2$) as well as the parallel (z) and perpendicular (xy) fine structure components resulting from the zero-field splitting can be readily identified.[13,14] At 77 K, the half-field resonance sharpens to the extent that the hyperfine structure due to the copper nuclei can be resolved. The seven-line pattern expected for two equivalent copper atoms ($I = {}^3/_2$ for both ^{63}Cu and ^{65}Cu) can be clearly seen (see Figure 2). The spectrum can be adequately described by the axial spin Hamiltonian

$$\begin{aligned}\mathcal{H} = {} & g_z\beta H_z\hat{S}_z + g_{xy}\beta(H_x\hat{S}_x + H_y\hat{S}_y) + D(\hat{S}_z{}^2 - {}^2/_3) \\ & + A_z\hat{S}_z(\hat{I}_{1z} + \hat{I}_{2z}) + A_{xy}\,[\hat{S}_x(\hat{I}_{1x} + \hat{I}_{2x}) \\ & + \hat{S}_y(\hat{I}_{1y} + \hat{I}_{2y})]\end{aligned}$$

The symbols $\hat{S}_z$ $\hat{S}_x$, and $\hat{S}_y$ correspond to the electron spin operators of the coupled dimer while $\hat{I}_1$ and $\hat{I}_2$ represent the individual nuclear spin operators of the two copper nuclei. The spin-Hamiltonian parameters can be calculated in a relatively straightforward manner from the observed spectrum.[14] The calculated parameters are presented in Table I. The calculated spectrum shown in Figure 1 was obtained from a computer simulation based on these spin-Hamiltonian parameters. The computational procedure is described in the Appendix. The close agreement between the observed and calculated spectra strongly supports the correctness of our interpretation. It is interesting to note that there is no evidence for a rhombic component in either the zero-field or g tensors.

The energy separation (J) between the triplet and singlet states can be determined from the temperature dependence of the intensity of the EPR resonance assuming that the populations of the two states are governed by Boltzmann statistics.[15-17] Using the EPR spectrum rather than the magnetic susceptibility to determine the triplet–singlet energy has the advantage that monomeric copper(II) impurities do not interfere. This is an important consideration for the copper(II) azobenzoate complex since the material contains a noticeable amount of monomeric impurity. By using the spectra at room and liquid nitrogen temperature, a triplet–singlet separation of 315 cm^{-1} is calculated. This exchange energy as well as the spin-Hamiltonian parameters is quite similar to that of copper(II) acetate and other related copper(II) carboxylates.[2]

The infrared spectrum (Table II) of the trihydrate is very complex but two frequencies could be assigned unambiguously. The first of these are the copper(II)–oxygen stretches[18] which are nearly identical with those in the much less complex copper(II) acetate monohydrate.

The other structural feature indicated by the IR spectrum is the trans structure of the azo group in the neat and complexed azobenzoate. The stretching vibrations of the azo group in aromatic azo compounds were established by Luttke and co-workers[19] resolving earlier controversies.[20-22] All of the complexes prepared in this study show medium bands in the 1480- and 1450-mμ region (Table II) and it appears that all of them contain the trans azo configuration. Comparison to the azobenzoate itself shows no shift, indicating that no coordination through the azo group occurs.

The thermal analysis of the copper(II) azobenzoate complex data indicates that two types of differently bonded H_2O molecules are present with a ratio of 2:1. The first two-thirds of H_2O molecules start to be liberated at a temperature of 76 °C with a maximum at 106 °C. The magnetic moment at 298 K remained the same as expected. The other one-third of H_2O started to be given off at 132 °C, maximum at 150 °C. The magnetic moment increased to about $\mu_{\mathrm{eff}}(295\ °C) = 1.85\ \mu_B$ at about 135 °C. The areas under each part of the curve correspond to a 2:1 ratio. This is the expected result since only two of the six H_2O molecules present in the dimer

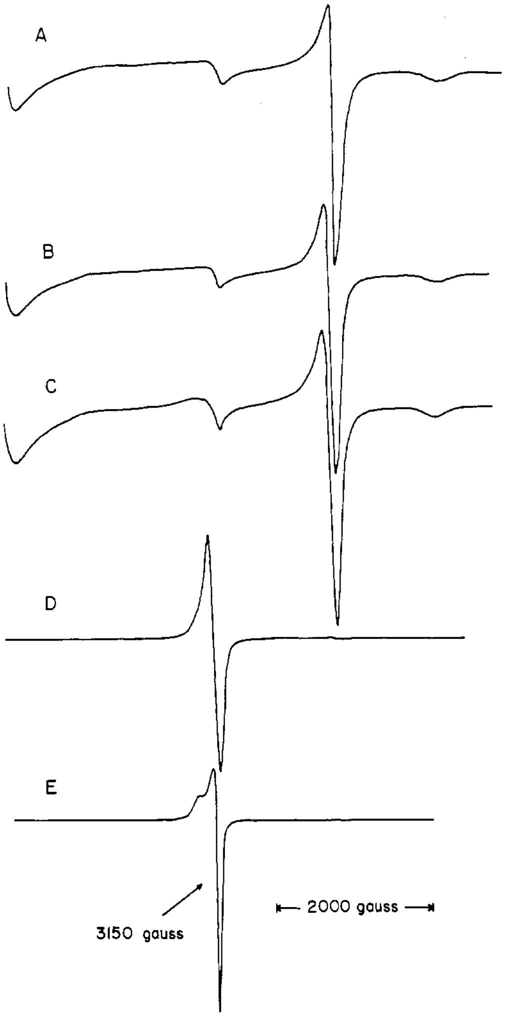


Figure 3. EPR spectra of powdered samples of the mixed-ligand complexes of copper(II) azobenzoate, recorded at room temperature at X-band frequency: A, $Cu^{II}(AB)\cdot 3H_2O$; B $Cu^{II}(AB)(DMPN)\cdot 1.5H_2O$; C, $Cu^{II}(AB)(EM)_2$; D, $Cu^{II}(AB)(DMEN)\cdot 2H_2O$; E, $Cu^{II}(AB)(TMEDA)\cdot 2H_2O$.

should be bonded strongly in the dimer as the moments confirm.

Considering the spectroscopic and magnetic data it seems virtually certain that the azobenzoate complex contains a dimeric unit structurally similar to that of copper(II) acetate monohydrate. Assuming that the ligand does have the trans azo linkage one would expect that the complex would consist of discrete Cu_2L_2 dimers or be polymeric. A discrete dimer would require both carboxylate groups of the ligand to be bound to the same pair of copper(II) ions. In a polymeric structure the carboxylate groups would coordinate to different pairs of copper(II) ions. Considering the insoluble nature of the azobenzoate complex, it would appear that a polymeric structure is more likely.

Reactions of the Copper Azobenzoate Complex with Polydentate Ligands. In general, the copper(II) azobenzoate complex is fairly unreactive toward other ligands. This is most likely due to the material's extreme insolubility. Prolonged exposure (8 h or more) to various bifunctional amines does, however, result in a measurable uptake of ligand by the complex. It has been possible to prepare 1:1 complexes between the copper(II) azobenzoate and a number of diamines while a 2:1 complex has been formed with ethanolamine. It is interesting to note that attempts to prepare a complex containing ethylenediamine by the same procedure were not successful. Since the copper(II) azobenzoate complex is insoluble, it is possible that the reaction of this material with these other ligands depends primarily on the ability of the ligand to penetrate the solid polymeric complex.

Table III. Magnetic Properties of $Cu^{II}(AB)(TMEDA)\cdot 2H_2O$

	Magnetic susceptibility Data			
EPR data	Temp, K	$10^6\chi$, esu/mol	$1/\chi$, mol/esu	μ_{eff}, μ_B
$g_z = 2.23$	295	1610	620	1.96
$g_{xy} = 2.06$	196	2290	435	
	77	5170	195	

The mixed-ligand complexes can be grouped into two categories: those in which the dimeric copper(II) carboxylate unit remains intact and those in which the dimer is lost. Since the EPR spectrum of a carboxylate dimer is so distinctive, the presence or absence of the dimer can readily be established. Figure 3 shows the EPR spectrum of the various mixed-ligand complexes. It is clear that the azobenzoate complexes containing *N,N'*-dimethyl-1,3-propanediamine and ethanolamine still retain the copper(II) carboxylate dimer. The spectra of both materials are essentially identical with that of the parent azobenzoate complex. A copper(II) acetate like dimer has only the two axial sites available for coordination by a second ligand (one site per copper(II) ion). Thus, it seems unlikely that all of the amine groups present in these two complexes are actually bound to the copper(II) ions. The ethanolamine and dimethylethylenediamine are probably absorbed into the polymeric azobenzoate complex without causing any significant structural modifications. In contrast to the spectra of these two materials, the spectra of the complexes with *N,N'*-dimethylethylenediamine and tetramethylethylenediamine (TMEDA) exhibit resonances characteristic of monomeric copper(II) species. Apparently the absorption of these diamine ligands in these cases has caused the decomposition of the carboxylate dimer.

Perhaps the most interesting of these mixed-ligand complexes is the TMEDA–azobenzoate complex since the properties of this material differ most noticeably from those of the parent complex. The TMEDA complex is blue and has a small but appreciable solubility in solvents such as methanol and acetone. The other mixed-ligand complexes as well as the parent complex are green and are quite insoluble in common solvents. The magnetic susceptibility of the TMEDA complex follows the Curie–Weiss law with a Weiss constant of approximately −20 °C. At room temperature the material has an effective magnetic moment of 1.96 μ_B which is typical of monomeric copper(II) complexes. The EPR spectrum of the powdered solid contains the features characteristic of an $S = {}^1/_2$ system with an axial **g** tensor. The parallel and perpendicular g values are in the range expected for copper(II) complexes which have a $d_{x^2-y^2}$ ground state (see Table III).[23] It is clear that coordination with TMEDA causes a considerable change in the structure of the copper(II) azobenzoate complex.

Conclusions

Copper(II) readily forms a 1:1 complex with 2,2'-dicarboxyazobenzene. This complex almost certainly contains dimeric units structurally similar to that of copper(II) acetate monohydrate. The physical properties of this material suggest that the material is polymeric. The azobenzoate complex will react with certain polyfunctional amines to form mixed-ligand complexes. In some cases the dimeric structure is maintained in the mixed-ligand complex while it is apparently lost in others.

Appendix

The simulated powder spectrum was obtained by numerically integrating the derivative spectrum of a single triplet species over all molecular orientations. The integration was carried out by using a five-point Gaussian quadrature. The resonances were assumed to have a Lorentzian shape. The widths were assumed to be anisotropic and were calculated according to

$$W(\theta) = (W_{\parallel}^2 \cos^2 \theta + W_{\perp}^2 \sin^2 \theta)^{1/2}$$

The angle θ is taken as the angle between the magnetic field and the principal symmetry axis of the triplet species. The simulated spectrum in Figure 1 was calculated with $W_{\parallel}$ and $W_{\perp}$ values of 220 and 120 G, respectively. It seems likely in this case that the primary contribution to the line widths is from unresolved hyperfine interactions. Thus, the use of an anisotropic width seems quite justified since the hyperfine interactions in most copper(II) complexes are quite anisotropic. The fields and intensities of the transitions between the spin states of the $S = 1$ manifold were calculated as a function of the angle θ using the spin-Hamiltonian parameters in Table II. The direct eigenfield method described by Belford and co-workers was used in this computation.[24-26]

Registry No. $Cu^{II}(AB)\cdot H_2O$, 61104-51-6; $Cu^{II}(AB)(DMEN)$, 61075-81-8; $Cu^{II}(AB)(DMPN)$, 61075-83-0; $Cu^{II}(AB)(TMEDA)$, 61104-48-1; $Cu^{II}(AB)(EM)$, 61075-85-2; 2,2′-dicarboxyazobenzene, 635-54-1; 2-nitrobenzoic acid, 552-16-9.

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Some Properties of Copper and Zinc Complexes of 2-Formylpyridine Thiosemicarbazone

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Substituted 2-formylpyridine thiosemicarbazones and some of their metal complexes are experimental antineoplastic agents. Formation constants for copper and zinc complexes of 2-formylpyridine thiosemicarbazone have been measured in aqueous solution together with other acid–base properties of these complexes and the half-wave reduction potential of the copper(II) complex. Logarithms of the formation constants of the 1:1 copper and zinc complexes are 16.90 and 9.18, respectively. The copper complex forms adducts with Lewis bases such as ethylenediamine (log $K^{\mathrm{CuL}}_{\mathrm{CuLen}} = 5.53$) as observed by electron paramagnetic resonance spectroscopy and in the determination of the formation constant for the copper chelate. Its $E_{1/2}$ is +2 mV. These results are compared with data for other related systems. Implications are then drawn about the possible reactions of these materials in biological systems.

Introduction

Recently the examination of the antitumor properties of α(N)-heterocyclic carboxaldehyde thiosemicarbazones has been extended to the consideration of some of their first-row transition metal complexes. Included have been the Fe(II), Cu(II), and Zn complexes of 1-formylisoquinoline thiosemicarbazone and the Fe(II) and Cu(II) complexes of 5-substituted-2-formylpyridine thiosemicarbazones.[1-5] Previously other bis(thiosemicarbazonato)copper and -zinc chelates had been shown to have substantial inhibitory effects against tumor cells.[6-8] Hence an investigation has begun of the chemical properties of metal complexes of 2-formylpyridine thiosemicarbazone to provide a basis for understanding their behavior in living systems. In this work the thermodynamics of ligand binding to Cu^{2+} and Zn^{2+} are described together with properties of the reduction of (2-formylpyridine thiosemicarbazonato)copper(II) to its copper(I) species.

Experimental Section

Materials and Solutions. 2-Formylpyridine thiosemicarbazone (HL) was generously supplied by Frederick A. French. Its copper complex (CuL^+) has been synthesized previously as the acetate salt.[5] Ethylenediamine (en), bp 118 °C, $n^{20}{}_{D}$ 1.4565, was purchased from Aldrich Chemical Co. and used without further purification. Dimethyl sulfoxide, Gold Label quality, was also obtained from Aldrich. Other chemicals were reagent grade materials. To obtain suitable solutions of CuL^+ it was first necessary to dissolve the solid complex in Me_2SO and then, adding this liquid to an aqueous solution, to obtain final concentrations of 0.10 M KCl and 1.0% v/v Me_2SO.

Formation Constants for CuL^+ and CuLen. The pH-independent formation constant, $K^{\mathrm{Cu}}_{\mathrm{CuL}}$, of CuL was determined by the method of competing equilibria, using ethylenediamine, a ligand of known