type of chelation would feature an eight-member ring. (An analogous complex has been proposed for $\mathrm{Cu}(N^{\alpha}\text{-dodecanoyl-L-histidinol})_2{}^{2+}$[6]). On the other hand, Cu(II) may bind the ligand only at the thioether sulfur. We favor the former possibility because, where sterically feasible, chelation is a favored process on the basis of entropy considerations.

Jones et al. have reported molar extinction coefficients of $\sim 1 \times 10^3$ for the d–d transition of Cu(II) bound to cyclic thioethers.[27] We have calculated a rough estimate for the extinction coefficient of the d–d transition in the Cu(II)/*N*-dodecanoyl-L-methioninol system. The EPR spectrum in Figure 6 permits one to partition the available Cu(II) into three species, each present in more or less equal amounts. Thus, about two-thirds of the Cu(II) is bound to the ligand, yet the measured extinction for this system is less than 30 (Figure 7). Therefore, in our system the extinction coefficient for 1 mol of Cu(II)–thioether interactions would not exceed 60.[28]

The side chains of both glutamine and methionine contain functional groups which are very weak ligands for Cu(II). Apparently, these two side chains would provide a ligand site for a metal only in an environment essentially free of competing ligands, even bulk water. Such an environment is feasible within the metal binding site of a metalloprotein. The initial, "trapping" interaction between the protein and the metal presumably would involve side chains with strong donor groups, however.

Finally, the present studies demonstrate both the utility and the versatility of an oil continuous microemulsion for studying metal–ligand complexes. By substantially reducing the water content of the microemulsion, an interaction between Cu(II) and the side chains of both glutamine and methionine was forced to occur. To date, published studies on the interaction of metals with these two side chains are rare.

Registry No. $\mathrm{Cu^{II}}(N^{\alpha}\text{-dodecanoyl-L-lysinol})_4$, 61278-46-4; $\mathrm{Cu^{II}}(N^{\alpha}\text{-dodecanoyl-L-glutaminol})$, 61278-47-5; N^{α}-dodecanoyl-L-methioninol, 61259-54-9; Cu, 7440-50-8.

References and Notes

(1) This work was supported by grants from the NIH (HL 14590, to S.L.H.) and the NSF (CHE76-00183, to S.L.H. and R.E.B.). R.E.B. is the recipient of an NIH Research Career Development Award (GM 00246). A portion of this material was presented at the Symposium on Biological Inorganic Models, 3rd Rocky Mountain Regional Meeting of the American Chemical Society, Laramie, Wyo., 1976.
(2) Visiting Professor, Spring 1975, from the Department of Chemistry, Florida State University, Tallahassee, Fla. 32306.
(3) To whom correspondence should be addressed at the Department of Chemistry, University of Wyoming.
(4) E. H. Cordes, Ed., "Reaction Kinetics in Micelles", Plenum Press, New York, N.Y., 1973.
(5) J. H. Fendler, *Acc. Chem. Res.*, **9**, 153 (1976).
(6) G. D. Smith, B. B. Garrett, S. L. Holt, and R. E. Barden, *J. Phys. Chem.*, **80**, 1708 (1976).
(7) (a) For a discussion of microemulsions, see L. M. Prince in "Emulsions and Emulsion Technology", Vol. 6, K. J. Lissant, Ed., Marcel Dekker, New York, N.Y., 1974, Part I, p 125. (b) U. K. A. Klein and D. J. Miller, *Ber. Bunsenges. Phys. Chem.*, **80**, 113 (1976); A. Kitahara, O. Ohashi, and K. Kon-no, *J. Colloid Interface Sci.*, **49**, 108 (1974).
(8) E. Schröder and K. Lübke, "The Peptides", Vol. I, Academic Press, New York, N.Y., 1965, p 151 ff.
(9) A. Kjaer and P. O. Larsen, *Acta Chem. Scand.*, **15**, 750 (1961).
(10) L. Benoiton, *Biochem. Prep.*, **11**, 80 (1966).
(11) G. D. Smith, C. E. Donelan, and R. E. Barden, *J. Colloid Interface Sci.*, in press.
(12) J. T. Edsall, G. Felsenfeld, D. S. Goodman, and F. R. N. Gurd, *J. Am. Chem. Soc.*, **76**, 3054 (1954).
(13) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution", P. Haase and Son, Copenhagen, 1941.
(14) A. S. Brill, R. B. Martin, and R. J. P. Williams, in "Electronic Aspects of Biochemistry", B. Pullman, Ed., Academic Press, New York, N.Y., 1964.
(15) H. R. Gersmann and J. D. Swalen, *J. Chem. Phys.*, **36**, 3221 (1962).
(16) A. Abragam and B. Bleaney, "Electron Paramagnetic Resonance of Transition Ions", Clarendon Press, Oxford, 1970, Chapter 20.
(17) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants", McGraw-Hill, New York, N.Y., 1961, pp 71–72.
(18) *Chem. Soc., Spec. Publ.*, **No. 25**, 272 (1971).
(19) B. L. Vallee and W. E. C. Wacker, *Proteins*, **5**, 121 (1970).
(20) H. Porter in "The Biochemistry of Copper", J. Peisach, P. Aisen, and W. E. Blumberg, Ed., Academic Press, New York, N.Y., 1966, pp 159–174.
(21) T. Nakamura and Y. Ogura, ref 20, pp 389–405.
(22) C. J. Ballhausen, "Introduction to Ligand Field Theory", McGraw-Hill, New York, N.Y., 1962.
(23) B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, **5**, 143 (1970).
(24) (a) B. L. Vallee and W. E. C. Wacker, *Proteins*, **5**, Chapter 4 (1970); (b) D. E. Schmidt, Jr., and F. H. Westheimer, *Biochemistry*, **10**, 1249 (1971), and references therein.
(25) No evidence of metal binding to the alcohol moiety of the ligand molecules has been observed in any system studied to date.
(26) *Chem. Soc., Spec. Publ.*, **No. 25**, 272 (1971).
(27) T. E. Jones, D. B. Rorabacher, and L. A. Ochrymowycz, *J. Am. Chem. Soc.*, **97**, 7485 (1975).
(28) In this calculation, we have assumed that, to a first approximation at least, the distribution of Cu(II) in the quick-frozen microemulsion is the same as that in the system at room temperature.

Contribution from the Departments of Chemistry, State University of New York, Plattsburgh, New York 12901, and State University of New York, Oswego, New York 13126

Anisotropic Exchange in Heterocyclic Amine–Copper(II) Complexes

M. LYNCH, K. E. HYDE,*[1a] P. L. BOCKO, and G. F. KOKOSZKA*[1b]

Received August 9, 1976 AIC60567Y

The purpose of this paper is to report high-temperature magnetic susceptibility and EPR data for three systems, bis(1,2,4-triazolato)copper(II) [$\mathrm{Cu(tr)_2}$], dichloro(phenazene)copper(II) [$\mathrm{CuCl_2(pnz)}$], and chloro(1,2,4-triazolato)copper(II) dihydrate [$\mathrm{CuCl(tr)\cdot 2H_2O}$], and to relate these data to the anisotropic exchange which may be experimentally observed when the isotropic exchange is fairly large. The strength of the isotropic exchange term is related to the high-temperature Curie–Weiss constant and is −49 K for $\mathrm{CuCl_2(pnz)}$ and −97 K for $\mathrm{Cu(tr)_2}$. A larger isotropic exchange field is believed to be present in $\mathrm{CuCl(tr)\cdot 2H_2O}$. The anisotropic exchange is related to the EPR line width and is expected to be proportional to the isotropic exchange with a constant proportionally of about 10^{-4}. This simple model is consistent with the data for $\mathrm{Cu(tr)_2}$ and $\mathrm{CuCl_2(pnz)}$. Possible alternative mechanisms for the data on $\mathrm{CuCl(tr)\cdot 2H_2O}$ are considered as the simple model seems inadequate.

Introduction

Recent studies of spin-exchange interactions $(\overline{S_1}{:}\mathrm{J}{:}\overline{S_2})$ in clusters, semidilute systems, and concentrated paramagnetic systems have considerably extended our knowledge in this area.[2–6] While the dominant interaction in systems with little orbital magnetism appears to be an isotropic coupling $(J\overline{S_1}\cdot\overline{S_2})$ between spins, there is increasing interest in the temperature dependence[5,7–9] of J and in anisotropic exchange (ae) between spins.[10] Two recent papers[4] provide a detailed review of the theory and a critical evaluation of existing data concerning the role played by the ae term in linear-chain copper(II) coordination complexes with extended interactions. In particular the ae term is an EPR line-broadening mechanism whereas the isotropic interaction is a line-narrowing term. Moriya[10] has estimated that the line width contribution from ae goes as $(\Delta g/g)^2 H_e$ where Δg is the difference between maximum and minimum g values, g is their average value, and H_e is effective isotropic exchange field ($\simeq J/g \simeq k\Theta/g$). The second moment for ae is $(\Delta g/g)^4 H_e^2$, and in cases where this term dominates[4] the observed line width should be

$$\Delta H = M_2^{\mathrm{ae}}/H_e \simeq (\Delta g/g)^4 H_e$$

McGregor and Soos[4b] have studied the temperature and frequency dependence of polycrystalline $Cu(C_2O_4)\cdot{}^1/_3H_2O$ and have confirmed that the ae term makes a major contribution to the line width in that one-dimensional antiferromagnetic Heisenberg chain where $J = -130$ cm^{-1}. There have been very few examples of the evaluation of ae terms in copper(II) complexes[4,11] and the purpose of this paper is to report high-temperature magnetic susceptibility and EPR data for three other systems: bis(1,2,4-triazolato)copper(II) [$Cu(tr)_2$], dichloro(phenazine)copper(II) [$CuCl_2(pnz)$], and chloro(1,2,4-triazolato)diaquocopper(II) [$CuCl(tr)\cdot 2H_2O$]. The first two of these compounds have been studied by various methods by Kubo and co-workers.[12]

These three compounds have relatively large internal magnetic fields at room temperature as determined by magnetic susceptibility and rather different EPR behavior. In all cases the ae term is expected to make a major contribution to the line width. In $CuCl_2(pnz)$, the agreement between the simple theory and the experimental result is quite good. For $Cu(tr)_2$, the experimental line width is somewhat larger than the simple theory predicts but the agreement is still reasonable. Finally, in $CuCl(tr)\cdot 2H_2O$ the line is so broad that it cannot be observed. Here the possibility of antisymmetric exchange or "pure" one-dimensional behavior may be playing a role.

Experimental Section

Preparation. The complexes $Cu(tr)_2$, $CuCl(tr)\cdot 2H_2O$, and $CuCl_2(pnz)$ were prepared as described previously.[12,13] The polycrystalline materials have good analyses for the two anhydrous complexes. Anal. Calcd for $Cu(tr)_2$: Cu, 31.8; C, 24.1; H, 2.0; N, 42.1. Found: Cu, 30.9; C, 24.3; H, 2.3; N, 42.2. Calcd for $CuCl_2(pnz)$: Cu, 20.2. Found: Cu, 19.6. The analytical results for the $CuCl(tr)\cdot 2H_2O$ complex were sensitive to drying procedures.

The analyses of four different samples of $CuCl(tr)\cdot 2H_2O$ were in good agreement but suggest that the complex has between 1.5 and 2 waters of hydration. Heating this hydrate at 110 °C for approximately 48 h resulted in a color change from blue to green and a 17.2% weight loss.

Magnetic Susceptibility Measurements. The absolute Gouy method was used with magnetic fields and temperatures determined as previously described.[14,15] At each temperature magnetic data were obtained at 10 different field strengths in the range 1000–10 000 G. Samples were in the form of finely ground powders. Corrected molar susceptibilities were calculated by the use of Pascal's constants.[16] Doubly corrected molar susceptibilities (χ_M'') refer to corrected molar susceptibilities less the assumed contribution from temperature-independent paramagnetism, $N\alpha$, of copper(II) (60×10^{-6} cgsu/Cu atom). The gram-susceptibilities and magnetic moments for the three complexes are in good agreement with those previously reported near room temperature.[12a,13] Plots of the reciprocal of the doubly corrected molar susceptibilities vs. temperature are shown in Figure 1.

Electron Paramagnetic Resonance Measurements. EPR measurements were carried out with a Varian V-4501 spectrometer at X band (9 GHz), a simple reflection spectrometer operating at 14 GHz and utilizing 1000-Hz modulation, and a 3-GHz spectrometer with a 35-Hz field modulation frequency. At X band for the $Cu(tr)_2$ complex the line width was measured at room temperature, liquid nitrogen temperature, and 430 ± 10 K. The latter temperature was obtained by heating mineral oil.

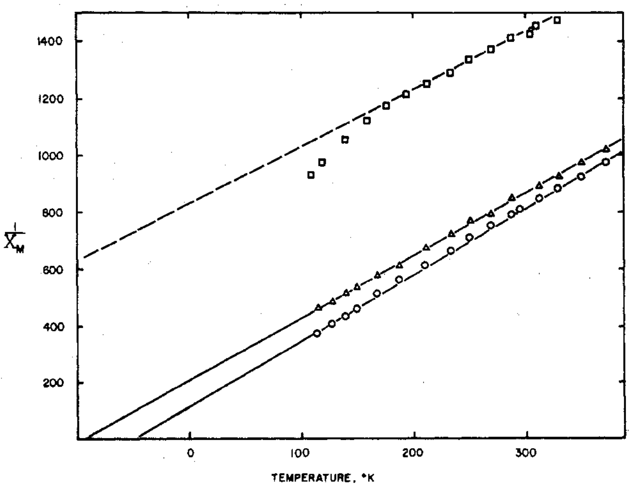

Figure 1. Plot of the reciprocal of the doubly corrected molar susceptibilities vs. temperature for (○) $CuCl_2(pnz)$, (△) $Cu(tr)_2$, and (□) $Cu(tr)Cl\cdot 2H_2O$.

Results and Discussion

Dichloro(phenazine)copper(II). In the temperature range 115–375 K, the $CuCl_2(pnz)$ complex obeys a Curie–Weiss law of the form $\chi_M'' = C/(T - \Theta)$ with bulk magnetic parameters $\Theta = -49 \pm 5$ K and $g = 2.13 \pm 0.02$ (95% confidence interval for 16 points). The EPR spectrum was characteristic of the three g value case with $g_1 = 2.034$, $g_2 = 2.085$, and $g_3 = 2.163$ (all values ±0.004). The data were collected at X band and no temperature variation was noted. The line width was taken as equal to the width from the low-field peak to the half-height value in the derivative spectrum. The value obtained was about 35 G. This value would also be about the same in the case of the high-field peak. A detailed computer fit was not attempted since the purpose of this investigation requires only that the line width be known to within say 10% and this condition is adequately fulfilled (vide infra).

Complexes of the stoichiometry $CuCl_2L_2$ where L_2 represents two monodentate or one bidentate ligand are found to exist in several structural forms. For the dichloro-bridged dimers Hatfield[2] has initiated an investigation of the correlation of structure and magnetic properties. The bridging geometries for the dimers of known structure have been summarized.[17] Complexes of the above stoichiometry may also occur as chains of copper(II) ions bridged by chloride ions as in $CuCl_2(py)_2$.[18] In these cases the major magnetic interactions are intrachain and are via the bridging chloride ions[19] but bidentate ligands such as pyrazine[20] or 1,2,4-triazine[21] provide for the possibility of additional exchange pathways that may be intra- or interchain. The $CuCl_2(pnz)$ complex investigated in this study is of unknown structure although it has been suggested that it possess a high degree of distortion relative to the tetragonally distorted octahedral structure of $CuCl_2(py)$ and may possess a square-pyramidal or essentially square-planar structure.[13] With the limited susceptibility–temperature data reported here and the unknown structure, no correlation between structure and magnetism may be inferred. Although the Weiss constant was calculated from data in the high-temperature range, $\Theta = -49$ K appears to be somewhat larger than those reported for other complexes of this stoichiometry and of known structure.

The EPR studies support the idea of a cross-linked structure and the relatively high value of the exchange field H_e ($\simeq k\Theta/g\beta$) of some 3×10^5 G suggests that anisotropic exchange may be making a dominant contribution to the line width. In order to test this idea we use the equation listed in the Introduction. With $\Delta g/g \simeq 0.1$ and $H_e \approx 3 \times 10^5$ G, the expected line width is about 30 G and in order of magnitude agreement with the experimental value. The close correspondence between the value calculated and the experimental value is regarded as fortuitous.

Other line-broadening mechanisms such as dipolar and hyperfine fields would be expected to contribute at most a few gauss to the line width and may be safely neglected.[4b] Purely one-dimensional behavior seems to be ruled out on the basis of the cross-linking mentioned above which would provide pathways to limit the characteristic long-time diffusional behavior in "pure" one-dimensional systems.[6] Antisymmetrical exchange seems unlikely to provide an explanation for the line width because it is often associated with a pronounced temperature dependence and, in any event, produces a line width of the order of $(\Delta g/g)^2 H_e$.[6] In this case that would be some 3000 G, well above the observed value.

Bis(triazolato)copper(II). The complex $Cu(tr)_2$ also obeys a Curie–Weiss law in the temperature range investigated. The bulk magnetic parameters $\Theta = -97 \pm 5$ K and $g = 2.21 \pm 0.02$ (95% confidence interval for 15 points) for $Cu(tr)_2$ imply that the antiferromagnetic interaction is approximately twice as strong as that present in $CuCl_2(pnz)$, $\Theta = -49 \pm 5$ K. No deviations from Curie–Weiss behavior are observed in the temperature range studied and this would suggest that neither simple coupled pairs nor chains of copper(II) ions are present. If either were the case a maximum would be expected in the susceptibility in the temperature range investigated since $T_{max} \simeq \Theta$(chain) or 2.5Θ(dimer).

The EPR data obtained at X band revealed a peak-to-peak line width of 693 ± 30 G at 295 K and a value of 701 ± 25 G at 430 ± 15 K. At 77 K the line width is 803 ± 30 G. The uncertainty in the line width reflects the average deviation for five runs while that in the temperature is the maximum deviation before and after the spectral tracing. Other runs in the 400–500 K range confirmed the temperature independence of the line width in the high-temperature region (300–450 K). Room-temperature measurements at 3 and 14 GHz indicate no frequency dependence of the line width although the uncertainty in these measurements is somewhat greater than that listed above. The overall experimental situation then is a temperature- and frequency-independent line width (700 G) in the high-temperature region. This behavior is to be contrasted with that observed by McGregor and Soos[4b] in which a nearly linear line width increase with temperature is observed. We believe this is associated with the lack of development of significant short-range order in this temperature region. Here kT/J should be in the region of 5–10 while McGregor and Soos studied the line width for kT/J in the range of about 0.02–2. Further, as indicated below this system is likely not to be a simple one-dimensional system.

The compound has been the subject of two earlier investigations in which Kubo and co-workers reported the synthesis, room-temperature magnetic moments, and broad-line proton NMR.[12] The latter study is of particular importance since two proton resonances were observed while the only protons in the system are those occupying the 3 and 5 positions in the five-membered triazole ring. Kubo and co-workers proposed two alternative structures which were consistent with this finding. The first consists of a two-dimensional array in which the protonic inequivalence is associated with intermolecular hydrogen bonding and metal–metal interaction proceeds via a planar Cu–N–C–N–Cu pathway. In the second structure they suggested a linear-chain arrangement in which the bridging groups alternate between two N–N linkages and a single-nitrogen bridge. These two different bridging groups are thus associated with triazoles along and perpendicular to the chain axis. This second structure is consistent with alternating values of the isotropic coupling constant J. In both structures the copper(II) ions are taken as square planar. Weaker intersheet or interchain coupling is possible in either of the proposed structures and other coordination geometries might also be suggested. Either of the structures would be consistent with the bulk susceptibility behavior reported herein.

The order of magnitude of the line width calculated on the basis of the major effect associated with ae is

$$\Delta H = (\Delta g/g)^4 (H_e)$$

With $H_e \simeq 6 \times 10^5$ and $\Delta g/g \simeq 0.1$, we find $\Delta H = 60$ G. For $\Delta g/g \simeq 0.15$ the line width is about 300 G. Since the EPR powder data do not give the g-value anisotropy for such a broad line, a single-crystal study could be quite useful. Still a spread in g values of 0.30 or even 0.35 is not unreasonable for copper(II) complexes. A line width of about 300 G is in the order of magnitude agreement with the experimental results. Again, the dipolar and hyperfine contributions to the line width can be neglected. Finally, the lack of a frequency dependence to the line width indicates no direct contribution to the line width from nonequivalent complexes as found by McGregor and Soos[4b] at very low temperatures. The increase in line width at 77 K is not fully understood. It may simply be a reflection of a temperature-dependent J. Alternatively an antisymmetrical contribution to the line width may be present, but this normally produces a decrease in line width with decreasing temperature rather than the inverse behavior.[6]

Chloro(triazolato)diaquocopper(II). As shown in Figure 1 the susceptibility–temperature data for the complex $CuCl(tr)\cdot 2H_2O$ is complicated. At the higher temperatures the Curie–Weiss law appears to be obeyed but this fact should be regarded with caution due to the experimental scatter at the very highest temperatures where the complex undergoes slow dehydration (above 305 K) and the limited temperature range. The approximately linear behavior at the higher temperatures also was observed for a second preparation of the complex measured on another Gouy system. Although deviations from the Curie–Weiss law are expected as the temperature of measurement approaches the critical temperature of an antiferromagnetic system, the deviations from linearity observed in the $CuCl(tr)\cdot 2H_2O$ complex are in the opposite direction as those expected for such a situation. Without structural information and additional magnetic measurements over a much wider temperature range only limited statements may be made with respect to the susceptibility–temperature behavior for $CuCl(tr)\cdot 2H_2O$.

The effective internal magnetic field at room temperature is approximately 5 times higher than in $Cu(tr)_2$ and 10 times higher than in $CuCl_2(pnz)$. This remarkably high value would be expected to cause a considerable broadening in the EPR signal. In fact no signal was observed! This result is the same for samples dried by different procedures and on spectrometers of quite high sensitivity. A simple estimate of the line width made in the same way as above suggests a value in the range 300–1500 G. Such a line width should be observable.

The lack of an EPR spectrum in copper(II) complexes is rare indeed. Aside from exchange-coupled dimers with very large J where the disappearance is associated with a very small paramagnetic population[3] the only other example in the literature is $CsCuCl_3$ where dilution studies suggest the origin is associated with a very large line width.[22] This material is of the general type ABX_3 and such complexes have been widely investigated.[23] The famous $(CH_3)_4NMnCl_3$, a "pure" one-dimensional system, is a member of this class of compounds.

A possible mechanism for the origin of very large line widths in one-dimensional systems can be developed in the following way. For most cases, the interchain interactions in nearly one-dimensional systems produce a Lorentzian line shape of 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.

Acknowledgment. It is a pleasure to acknowledge correspondence from Professor Z. G. Soos and to thank him for preprints of his work. Acknowledgment is made to the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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

References and Notes

(1) (a) State University of New York, Oswego, N.Y. (b) State University of New York, Plattsburgh, N.Y.

(2) W. E. Hatfield, *ACS Symp. Ser.*, **No. 5** (1974).

(3) G. Kokoszka and R. Duerst, *Coord. Chem. Rev.*, **5**, 209 (1970).

(4) (a) K. T. McGregor and Z. G. Soos, *J. Chem. Phys.*, **64**, 2506 (1976); (b) K. T. McGregor and Z. G. Soos, *Inorg. Chem.*, **15**, 2159 (1976).

(5) D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, **13**, 2929 (1974).

(6) Reviews of EPR of low-dimensional systems appear in "Low Dimensional Cooperative Phenomena", H. J. Keller, Ed., Plenum Press, New York, N.Y., 1975: Z. G. Soos, p 45; P. M. Richards, p 147; G. F. Kokoszka, p 171.

(7) K. W. Plumlee, B. M. Hoffman, J. A. Ibers, and Z. G. Soos, *J. Chem. Phys.*, **63**, 1926 (1975).

(8) H. T. Witteveen, B. Nievwenhuijse, and J. Reedijk, *J. Inorg. Nucl. Chem.*, **35**, 1535 (1974).

(9) M. Kurzynski, *J. Phys. C.*, **8**, 2749 (1975).

(10) T. Moriya, *Phys. Rev.*, **120**, 91 (1960).

(11) K. E. Hyde, G. Gordon, and G. F. Kokoszka, *J. Inorg. Nucl. Chem.*, **31**, 1193 (1969).

(12) (a) M. Inoue, M. Kishita, and M. Kubo, *Inorg. Chem.*, **4**, 626 (1965); (b) M. Inoue and M. Kubo, *ibid.*, **5**, 70 (1966).

(13) D. E. Billing and A. E. Underhill, *J. Inorg. Nucl. Chem.*, **30**, 2147 (1968).

(14) K. E. Hyde, B. C. Quinn, and I. P. Yang, *J. Inorg. Nucl. Chem.*, **33**, 2377 (1971).

(15) K. E. Hyde, *J. Chem. Educ.*, **49**, 69 (1972).

(16) The calculated diamagnetic susceptibilities for the complexes $Cu(tr)_2$, $CuCl(tr){\cdot}2H_2O$, and $CuCl_2(pnz)$ are (−89, −104, and −180) $\times 10^{-6}$ cgsu, respectively.

(17) E. D. Estes, W. E. Estes, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **14**, 106 (1975).

(18) J. D. Dunitz, *Acta Crystallogr.*, **10**, 307 (1957).

(19) M. Matsuura, *Phys. Lett. A*, **34**, 274 (1971).

(20) H. W. Richardson, W. E. Hatfield, H. J. Stoklosa, and J. R. Wasson, *Inorg. Chem.*, **12**, 2051 (1973).

(21) J. A. J. Jarvis, *Acta Crystallogr.*, **15**, 964 (1962).

(22) N. Achiwa, *J. Phys. Soc. Jpn.*, **27**, 561 (1969).

(23) J. F. Ackerman, G. M. Cole, and S. L. Holt, *Inorg. Chim. Acta*, **8**, 323 (1974).

(24) K. McGregor, D. Hodgson, and W. Hatfield, *Inorg. Chem.*, **15**, 421 (1976).

Contribution from the Department of Chemistry, Tulane University, New Orleans, Louisiana 70118,
and School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

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

C. J. DOUMIT, G. L. McPHERSON, R. L. BELFORD, S. B. LANOUX, and H. B. JONASSEN*[1]

Received August 9, 1976 AIC60570H

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