C. Chow, R. Caputo, R. D. Willet, and B. C. Gerstein, *ibid.*, **61**, 271 (1974); (d) C. Chow, R. D. Willet, and B. C. Gerstein, *Inorg. Chem.*, **14**, 205 (1975).

(17) (a) M. Textor, E. Dubler, and R. Oswald, *Inorg. Chem.*, **13**, 1361 (1974); (b) M. V. Hanson, C. B. Smith, and G. O. Carlisle, *Inorg. Nucl. Chem. Lett.*, **12**, 917 (1976).

(18) D. Y. Jeter, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chim. Acta*, **5**, 257 (1971).

(19) D. W. Smith, *Coord. Chem. Rev.*, **21**, 93 (1976), and references therein. See also J. R. Wasson, H. W. Richardson, and W. E. Hatfield, *Z. Naturforsch., B*, **32**, 551 (1977).

(20) G. O. Doak, G. G. Long, and L. D. Freedman, *J. Organomet. Chem.*, **12**, 443 (1968).

(21) J. R. Wasson, *Chemist-Analyst*, **56**, 36 (1967).

(22) D. P. Landau, B. E. Keen, B. Schneider, and W. P. Wolf, *Phys. Rev. B*, **12**, 1908 (1972), and references therein.

(23) D. B. Losee and W. E. Hatfield, *Phys. Rev. B*, **10**, 212, 1122 (1974).

(24) L. N. Mulay, "Magnetic Susceptibility", reprint monograph, Wiley-Interscience, New York, N.Y., 1966.

(25) R. P. Scaringe, Ph.D. Dissertation, University of North Carolina, 1976.

(26) J. W. Hall, W. E. Estes, and W. E. Hatfield, to be submitted for publication.

(27) W. Ludwig and M. Textor, *Helv. Chim. Acta*, **54**, 1143 (1971).

(28) R. L. Harlow, W. J. Wells III, G. W. Watt, and S. H. Simonsen, *Inorg. Chem.*, **14**, 1768 (1975).

(29) A. M. Heyns and C. J. H. Schutte, *J. Mol. Struct.*, **8**, 339 (1971).

(30) E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964), and the references therein.

(31) R. L. Carlin, *J. Chem. Educ.*, **43**, 521 (1966).

(32) P. Erdos, *J. Phys. Chem. Solids*, **27**, 1705 (1966).

(33) A. Abragam and B. Bleaney, "Electron Paramagnetic Resonance of Transition Ions", Oxford University Press, London, 1970, p 506 ff.

(34) J. H. van der Waals and M. S. de Groot, *Mol. Phys.*, **2**, 333 (1959).

(35) C. A. Hutchinson and B. W. Mangum, *J. Chem. Phys.*, **34**, 908 (1961).

(36) J. R. Wasson, C. Shyr, and C. Trapp, *Inorg. Chem.*, **7**, 469 (1968), and references therein.

(37) T. Lund and W. E. Hatfield, *J. Chem. Phys.*, **59**, 885 (1973), and references therein.

(38) R. M. Golding and W. C. Tennant, *Mol. Phys.*, **25**, 1163 (1973).

(39) R. K. Cowsik and R. Srinivasan, *Pramana*, **1**, 177 (1973).

(40) K. T. McGregor and W. E. Hatfield, *J. Chem. Phys.*, **65**, 4155 (1976), and references therein.

(41) R. L. Carlin, *J. Chem. Educ.*, **43**, 521 (1966).

(42) The expressions for the average susceptibility of a $S = {}^1/_2$ dimer with zero-field splitting included are in error in ref 16d since the perpendicular energies were ignored by their calculation.

(43) W. E. Estes, R. P. Scaringe, J. W. Hall, and W. E. Hatfield, to be submitted for publication.

(44) J. S. Smart, "Effective Field Theories of Magnetism", W. B. Saunders, Philadephia, Pa., 1966.

(45) R. L. Carlin, *Acc. Chem. Res.*, **9**, 67 (1976).

(46) A. P. Ginsberg, R. L. Martin, R. W. Brookes, and R. C. Sherwood, *Inorg. Chem.*, **11**, 2884 (1972).

(47) K. T. McGregor and Z. Soos, submitted for publication.

(48) T. D. Smith and J. R. Pilbrow, *Coord. Chem. Rev.*, **13**, 173 (1974).

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

(50) G. R. Wagner, R. T. Schumacher, and S. A. Friedberg, *Phys. Rev.*, **150**, 226 (1966).

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Spin–Spin Coupling in the Nitrogen-Bridged Dimer Formed by Sodium (Glycylglycylglycinato)cuprate(II) Monohydrate

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The magnetic properties of the unique nitrogen-bridged dimer sodium (glycylglycylglycinato)cuprate(II) monohydrate ($Na_2[Cu(ggg)H_2O]_2$) have been measured as a function of temperature (1.6–160 K) and magnetic field strength (10–50 kOe). The data indicate that the copper(II) ions are exchange coupled with the exchange coupling constant, J, being approximately -1.2 cm^{-1}. In addition, there are extensive intercluster interactions which are sensitive to the strength of the applied field and vary from -0.30 to -0.63 cm^{-1} (for $Z' = 4$). The EPR results indicate that an upper limit for the zero-field splitting of the triplet state is approximately $|D| = 0.27$ cm^{-1}. The intra- and intercluster superexchange pathways are postulated from the available crystallographic data.

Introduction

Since copper(II) ions are widely distributed in biological systems,[1-4] a significant amount of current research has centered around the search for relatively simple copper(II) complexes which may display some of the properties of the metalloproteins.[5-8] At least several native copper-containing proteins are known to contain more than one copper ion per enzyme unit.[1,5,8] Furthermore, there is growing experimental evidence that suggests there may be cluster formation among copper(II) ions within these macromolecules. Since copper(II) ions are widely known to exist in small exchange-coupled clusters in "normal complexes", dimeric complexes of copper(II) with small peptides are of considerable interest. The properties of sodium (glycylglycylglycinato)cuprate(II) monohydrate, $Na_2[Cu(ggg)H_2O]_2$, are of interest in this regard since Freeman et al.[11] have shown that the structure of this compound consists of dimeric clusters of copper(II) ions. Also, this compound is the only reported copper(II) dimer known to be bridged by nitrogen atoms. Results of spectral and magnetic studies on this unusual dimeric cluster are reported in this paper.

Experimental Section

Preparation of $Na_2[Cu(ggg)H_2O]_2$. The preparations described in the literature[11,12] were not adequate for our work, and, therefore, the procedure that we used is described in detail here.

Copper(II) chloride dihydrate was obtained from J. T. Baker Chemical Co. (ACS reagent grade) and used without further purification. Triglycine was obtained from Aldrich Chemical Co. and also used without additional purification.

To a stirred solution of 0.91 g (5 mmol) of $CuCl_2 \cdot 2H_2O$ in 75 mL of distilled water was added 0.99 g (5 mmol) of solid triglycine. The resulting light blue solution was stirred for several minutes and then filtered. The pH of this mixture was about 3.2 (Corning Model 7 pH meter). The pH of this mixture was then carefully adjusted to 9.3 by titration with 0.1 N NaOH. At this point the solution was deep bluish purple. The solution was then covered with Parafilm and allowed to evaporate slowly in a desiccator over solid NaOH. The pH of the mixture was checked periodically and readjusted when necessary. Crystals grew slowly over a period of several weeks, and the dark bluish purple prisms showed the morphology found earlier.[11] Anal. Calcd for $Na_2[Cu(C_6H_8N_3O_4) \cdot H_2O]_2$: C, 24.79; H, 3.47; Cu, 21.86. Found: C, 24.41, 24.20; H, 3.50, 3.50; Cu, 21.28, 21.19. Carbon and hydrogen duplicate analyses were performed by Integral Microanalytical Laboratories, Inc. (Raleigh, N.C.). Copper analyses were determined by EDTA titrations using a SNAZOX indicator.[13]

Physical Measurements. Magnetization measurements at constant applied field (isooestic) and susceptibility experiments (1.6–160 K) were carried out on a PAR Model 155 vibrating-sample magnetometer (VSM) operating at a field strength of 10 kOe. Temperatures were measured with a calibrated GaAs diode using techniques described in detail elsewhere.[14] High-field isothermal magnetization measurements were obtained on a PAR Model 150-A VSM equipped with a Westinghouse superconducting solenoid capable of attaining 50 kOe.

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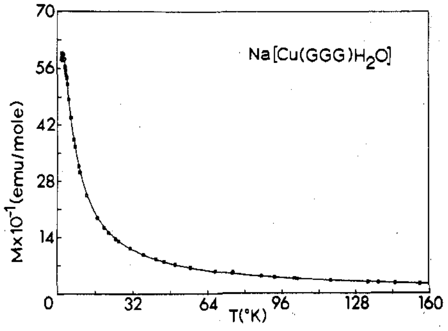

Figure 1. Constant-field magnetization (10 kOe) vs. absolute temperature for $[Cu(ggg)^-]_2$. Solid lines are best fit to eq 4 and 5 (see text and Table I for parameters).

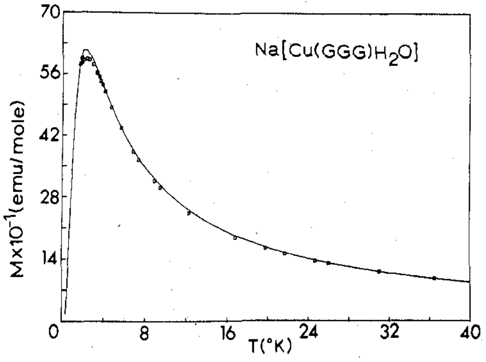

Figure 2. Expanded-scale view of the lowest temperatures of the data in Figure 1.

At 4.2 K, the magnetization data were simply collected by flooding the sample zone with liquid He, energizing the solenoid to the desired value of the applied field, placing the magnet in the persistent mode, and taking each data point individually. For isotherms measured below 4.2 K, the temperature was monitored by the vapor pressure of liquid helium. A detailed description of the experimental procedures has been given.[14]

EPR spectra were obtained at room temperature and 77 K with a Varian E-3 X-band spectrometer (~9.5 GHz) as described previously.[15] Polycrystalline powders and the "pH 9.3" mother liquor were examined. DPPH ($g = 2.0035$) was used as a field marker in all cases.

Electronic spectra were obtained from Nujol mulls on a Cary 17 spectrometer.[16]

Diamagnetic corrections due to the ligands were estimated from Pascal's constants. A value of 60×10^{-6} emu/mol was assumed for the TIP of copper(II) ions.[17]

Results

The experimental magnetization data (10 kOe) are shown in Figure 1. At first sight the data appear quantitatively like those expected of a simple paramagnet (simple $1/T$ dependence), but a closer examination of the lower temperature data in Figure 2 reveals a change in slope and a maximum in the magnetization near 2 K. Since our samples of $Na_2[Cu(ggg)H_2O]_2$ were small (~70 mg), it was necessary to use strong magnetic fields to increase the precision of the measurements. Since the interaction between copper(II) ions is very small ($T_{max} = 2$ K), the Zeeman energy of the applied magnetic field will be very important (10 kOe ≈ 1 cm⁻¹) in the treatment of the data. To investigate this behavior further, high-field isothermal magnetization data were obtained at temperatures of 4.2 K (boiling liquid helium) and at 1.72 K. These data are shown in Figure 3.

The constant-field (10 kOe) data above 30 K were fitted to the Curie–Weiss law

$$\chi = M_{obsd}/H = Ng^2\beta^2S(S+1)/3k(T-\Theta) \qquad (1)$$

An estimate of $\langle g \rangle$ obtained from eq 1 was $\langle g \rangle = 2.01$ while the Weiss constant, Θ, was calculated to be −2.9 K. This estimate of the average g value is substantially different from that observed by resonance techniques; this discrepancy will be discussed below.

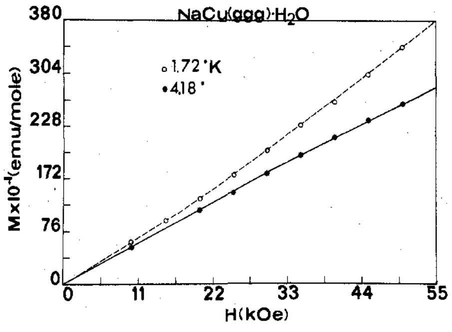

Figure 3. High-field isothermal magnetization for the complex. The dashed and solid lines are best-fit curves to eq 4 and 5, and parameters are listed in Table I.

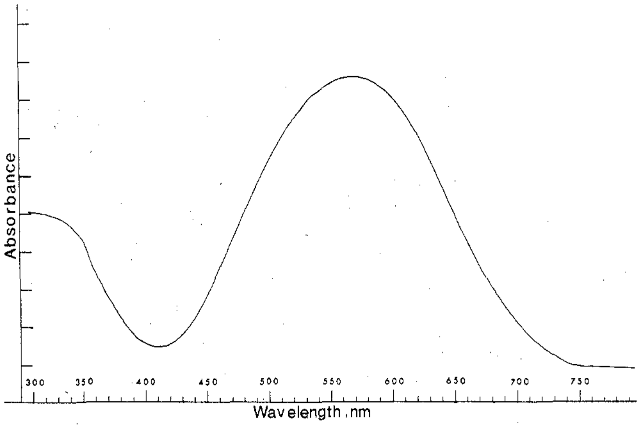

Figure 4. Solid-state electronic spectrum of $NaCu(ggg)H_2O$ recorded from a Nujol mull.

The electronic spectra of solid $Na_2[Cu(ggg)H_2O]_2$ are shown in Figure 4. A broad symmetrical band in the visible region was observed near 570 nm, and the position of this band is in good agreement with the reported value observed in solution studies of the complex. In addition, the onset of another band in the UV was detected near 290 nm.

In the range 77 K to room temperature the EPR spectrum of the pure solid material is essentially that characteristic of a tetragonal system. From these spectra, we calculate apparent values of $g_{\parallel} = 2.20$, $g_{\perp} = 2.05$, and $g_{av} = 2.10$. Careful examination of the low-field region near g(apparent) = 4 revealed an additional weak line characteristic of exchange-coupled copper(II) ions. Additional spectra were recorded up to about 6500 Oe in attempts to locate the high-field resonances expected for a triplet-state species. However, no additional resonances were observed above the high-field line centered at $g = 2.05$. Frozen solution spectra were obtained on samples of the mother liquor from which the crystals were harvested. Excellent agreement with previously reported work was obtained,[18] but we were unable to make any definite triplet-state assignments owing to very intense doublet absorptions. Low-field spectra of the frozen solutions again revealed a very weak line centered near 1565 Oe; no fine structure could be resolved on this resonance.

Small deviations between average g values determined from bulk magnetization studies and from EPR measurements are not uncommon and frequently arise from experimental vagaries such as sample purity, miscalibrations of instrumental devices, and preferential orientation of crystallites in the magnetic field. Since the small deviation obtained here did not affect our analysis of exchange-coupling mechanism, it may be ignored.

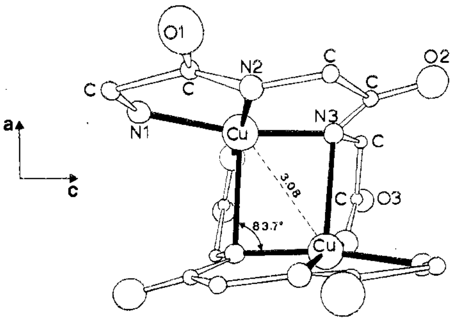

Figure 5. ORTEP drawing of the parallel-planar nitrogen-bridged dimer in $[Cu(ggg)^-]_2$. The sodium ions and the water molecules have been omitted. Peptide to copper bonds are blackened for clarity while the rest of the backbone is unshaded. The view is along the crystallographic twofold axis.

Discussion

An ORTEP[19] drawing of the dimeric structure of $Na_2[Cu(ggg)H_2O]$[11] is shown in Figure 5. Each peptide molecule binds copper with three nitrogen atoms and a second copper with a carboxyl oxygen. The fifth coordination site about copper is formed by an apical bond to a nitrogen (N3′) belonging to the neighboring copper ion. Thus a unique nitrogen-bridged parallel-planar dimer results.[9,10,20] The copper–nitrogen (N3) in-plane bond distance is 2.0 Å, the copper–nitrogen (N3′) out-of-plane bond distance is 2.6 Å, the copper–copper separation is 3.08 Å, and the Cu–N3′–Cu angle is 83.70°. In Figure 5 we have emphasized the parallel nature of the planes of the four short bonds about a given copper ion; the bonds about a given copper ion are blackened in for clarity while those of the peptide "backbone" are unshaded.

Since the observed maximum in the susceptibility (as $\chi = M/H$) occurs at very low temperature, the singlet–triplet splitting must be very small. In a situation such as this, the usual zero-field Heisenberg Hamiltonian given by (2) is no

$$H_0 = -2J\hat{S}_1\cdot\hat{S}_2 \tag{2}$$

longer applicable since the Zeeman energy of the applied field is comparable to the exchange energy.[21-23] Thus, eq 2 must be modified to include a Zeeman term, thereby giving

$$H = -2J\hat{S}_1\cdot\hat{S}_2 + g\beta H\hat{S}_t \tag{3}$$

where $\hat{S}_1 = \hat{S}_2$ are the spin operators of the individual ions, $\hat{S}_t$ is the total spin ($\hat{S}_t = \hat{S}_1 + \hat{S}_2$), and g is assumed to be isotropic. With this formulation one can readily derive the exact expression for the magnetization per mole of $S = {}^1/_2$ ions,[23] that expression being

$$M = \frac{Ng\beta \sinh (g\beta H/kT)}{\exp(-2J/kT) + 2 \cosh (g\beta H/kT) + 1} \tag{4}$$

Any additional interactions which are ignored by eq 3 can be estimated by a molecular field correction of the form

$$H_{\text{eff}} = H + \gamma M \tag{5}$$

where H is the applied magnetic field, H_{eff} is the effective molecular field, and M is the magnetization resulting from the effective field and the exchange interaction. For excellent accounts of the qualitative features of eq 4 and 5 see ref 15 and 23.

We have fitted the experimental isooestic magnetization data in Figures 1 and 2 to the magnetization expressions in eq 4 and 5. Initial attempts to interpret the observed data were made using eq 4 alone to see if the simple pair model would be adequate. However, this approach proved to be rather fruitless since the "best fit" g value was always approximately 1.78, an unreasonable value for copper complexes. By assuming that an *intercluster* term can be accounted for by eq 5, the next fits were performed by fixing g at 2.10 from the EPR data and allowing J and γ to vary freely. The best fit from this approach yielded $J = -1.8$ cm^{-1} and $\gamma = -4.0$, but the parameters are rather highly correlated. A final fit was performed by allowing g, J, and γ to vary simultaneously. This fit converged rapidly to $g = 2.00 \pm 0.005$, $J = -1.26 \pm 0.004$, and $\gamma = -2.33 \pm 0.054$. In Figures 1 and 2, the theoretical curves corresponding to these parameters are compared with the experimental data. The fit is seen to be excellent over the whole temperature range, with there being significant deviations only at the very lowest temperatures.

Since the parameters obtained from the constant-field measurements suggested that the single–triplet splitting was very small ($2J = -2.52$ cm^{-1}), additional measurements were made in strong magnetic fields to search for a triplet to singlet "crossover". This "crossover" phenomenon occurs when the applied magnetic field is strong enough to split the lowest level of the excited triplet state ($M_S = -1$) down past the singlet ground state, i.e., when the Zeeman energy exceeds the exchange energy at $H_{\text{cross}} \gtrsim |2J|/g\beta$.[15,23] If one then fits the isothermal high-field magnetization data (Figure 3), then an independent determination of the value of the single–triplet splitting is possible.[4] This approach has an additional advantage in that it also eliminates temperature errors which will be catastrophic in systems in which the exchange energy is very small. Unfortunately, in eliminating one potentially troublesome error, one may introduce an additional complication which arises from the change in ground-state multiplicity. The new "ground state" induced by strong fields will now be paramagnetic and capable of experiencing exchange interactions with other such "triplets" if a convenient superexchange pathway exists.[24,25] Furthermore, it would therefore seem reasonable that these additional exchange interactions will most likely induce a temperature dependence of the pair-exchange constant and will almost certainly yield larger intercluster interactions at very low temperatures.[25]

Analysis of the isothermal data in Figure 3 confirms the hypotheses outlined above. The data along the $T = 4.2$ K isotherm yield best-fit parameters $g = 2.0$, $J = -1.12$ cm^{-1}, and $\gamma = -4.13$. Thus, while the singlet–triplet splitting, $2J$, is hardly affected, the molecular field term increases by a factor of about 2. The data at still lower temperatures ($T = 1.72$ K) also reveal a similar trend, with a slight increase in J being obtained: $g = 2.0$, $J = -1.20$ cm^{-1}, and $\gamma = -4.85$. Within the framework of molecular field[24] theory, the values of the *interpair* exchange may be estimated from eq 6 where

$$J' = \gamma N g^2\beta^2/2Z' \tag{6}$$

the symbols have their usual meaning, and Z' represents the number of nearest-neighbor copper ions to a given cluster. The structural data[11] suggest that each cluster will have four or perhaps six nearest neighbors. It is important to note that the dimers within the unit cell are extensively hydrogen bonded via their "free" carboxyl oxygen atoms and water molecules to the sodium ions which essentially occupy holes between the dimeric units. Thus the deviations from the simple pair model, eq 4, are not so surprising. The various magnetic and spectral parameters for $[Cu(ggg)]_2^{2-}$ are collected in Table I.

There is considerable interest in the correlation of magnetic and structural parameters of small cluster systems.[9,10,26,27] In systems such as the "parallel planar" dimers present in $Na_2[Cu(ggg)H_2O]_2$, the exchange between metal centers is expected to be smaller than that observed for edge-shared systems.[26] First, since the unpaired spins are expected to be in the plane of the four short bonds, the orbitals which bridge metal centers are often nearly orthogonal, and hence one predicts weak ferromagnetic exchange,[9,10,21] Hay et al.[28] have

Table I

electronic spectra λ_{max}, nm	EPR g_{av}	Curie-Weiss law		magnetization parameters				
		g_{av}	Θ, K	$2J$, cm^{-1}	$\langle g \rangle$ best fit	γ	$J'(Z' = 4)$, cm^{-1}	method
570[a]	2.10[a]	2.01 ± 0.01	−2.9 ± 0.2	−2.52 ± 0.008	2.00 ± 0.005	−2.33 ± 0.05	−0.30	M vs. T
555[b]	2.10[c]			−2.24 ± 0.10	2.00 ± 0.01	−4.13 ± 0.1	−0.53	M vs. H ($T = 4.2$ K)
				−2.41 ± 0.20	2.00 ± 0.03	−4.85 ± 0.2	−0.63	M vs. H ($T = 1.72$ K)

[a] This work. [b] Reference 18. [c] Reference 17.

recently presented some evidence in support of this from molecular orbital calculations on several hypothetical examples. Second, since the out-of-plane bonds of the bridge are considerably longer than the in-plane bonds (2.6 vs. 2 Å for $[Cu(ggg)]_2^{2-}$), a considerable reduction in the exchange is expected. This conclusion is in reasonable accord with experimental and theoretical predictions of the superexchange interaction since Boch[29] has shown that J varies roughly as r^{-10} (r being the metal–metal separation).

The absence of readily discernible triplet-state resonances in the pure solid and in frozen solutions makes an analysis of the EPR spectrum very difficult.[30] However, the observation of a very weak line in the "$\Delta M_S = \pm 2$" region of both the pure solid and the frozen solution does allow us to estimate the triplet-state zero-field parameters.[31] From the spin Hamiltonian in eq 7, the resonance field for the forbidden $\Delta M_S =$

$$H_{S=1} = g\beta H\cdot\hat{S} + D(S_z^2 - S(S+1)/3) + E(S_x^2 + S_y^2) \tag{7}$$

±2 transition (assuming g to be isotropic) is given by

$$H_{\min} = \frac{1}{g\beta}\left(\frac{h^2\nu^2}{4} - \frac{D^2 + 3E^2}{3}\right)^{1/2} \tag{8}$$

Taking $\langle g \rangle = 2.10$,[18] we can estimate $(D^2 + 3E^2)^{1/2}$ after the method of Kottis and Lefebvre[31] to be $D^* = (D^2 + 3E^2)^{1/2} \approx 0.27\ cm^{-1}$. Since this estimate does not allow one to determine the relative signs of D and E, very little information other than an order of magnitude is possible. The observation that D is less than $h\nu$ at X band is quite reasonable since the contribution to the zero-field splitting from the anisotropic exchange interaction is approximated in this situation by

$$D_{ex} \approx \left[\frac{g_{av} - g_e}{g_e}\right]^2 J \tag{9}$$

where g_e is the free electron g value, g_{av} is the observed average g value, and J is the isotropic exchange coupling constant. The relatively large copper–copper distance also ensures that the dipolar contribution to the zero-field splitting, D_{dd}, is small.[32]

Conclusions

We have shown that the unique nitrogen-bridged dimeric copper(II) complex $Na_2[Cu(ggg)H_2O]_2$ is very weakly exchange coupled with an excited triplet state being about 2.5 cm^{-1} above the ground-state singlet. Since this unusual complex is the only structurally characterized nitrogen-bridged copper(II) dimer, no precise comparisons can be made to other similar compounds by way of structural and/or magnetic correlations. However, it is of interest to compare the magnitude of the exchange constant in the $[Cu(ggg)]_2^{2-}$ ion with those found in other parallel-planar dimer complexes.

In general, exchange coupling constants are rather small in dimeric complexes in which the copper ions are in quasi-tetragonal-pyramidal environments where the dimer is formed by edge sharing of a common apical to basal edge. There are two features of the structure which lead to these small $2J$ values. First, the bridge is usually unsymmetrical with one copper–bridge atom bond being significantly longer than the other. The short bond invariably lies in the basal plane of the tetragonal-pyramidal coordination while the long bond is formed with atom in the apical position. Since the spin–spin coupling mechanism is highly dependent on bond distances in the superexchange pathway, it is easy to understand how this structural feature tends to minimize $|2J|$ values. The second feature is a result of the electronic structure of the copper(II) ions. The unpaired electrons which are involved in the exchange coupling occupy σ^* orbitals which lie in the basal planes. For the case of a 90° angle at the bridge atom, the σ^* orbital is orthogonal to the orbitals of the bridge atom which provide the superexchange pathway, and only potential exchange is possible. As the angle deviates from 90°, kinetic exchange terms may contribute to the exchange process, but these are weighted by overlap integrals which are small. Kinetic exchange terms can be larger than potential exchange terms, and when these terms are allowed by symmetry, $|2J|$ can become very large, even when the superexchange pathway involves several atoms as in the imidazolate-bridged copper systems.[33]

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Registry No. $Na_2[Cu(ggg)H_2O]_2$, 64653-43-6.

References and Notes

(1) J. A. Fee, *Struct. Bonding* (*Berlin*), **23**, 1 (1975).
(2) J. Peisach, P. Aizen, and W. Blumberg, Eds., "The Biochemistry of Copper", Academic Press, New York, 1966.
(3) D. C. Wharton in "Metal Ions in Biological Systems", Vol. 3, H. Siegel, Ed., Marcel Dekker, New York, 1974, Chapter 5.
(4) R. Lontie and L. Vanquickenbourne, ref 3, Chapter 6.
(5) R. Osterberg, *Coord. Chem. Rev.*, **12**, 309 (1974).
(6) R. P. Martin and J. P. Scharff in "An Introduction to Bio-Inorganic Chemistry", D. R. Williams, Ed., Charles C. Thomas, Springfield, Ill., 1976, Chapter 6.
(7) H. C. Freeman, *Adv. Protein Chem.*, **22**, 257 (1967).
(8) H. B. Gray, *Adv. Chem. Ser.*, **No. 100**, Chapter 17 (1971).
(9) D. J. Hodgson, *Prog. Inorg. Chem.*, **19**, 173 (1975).
(10) W. E. Hatfield in "Theory and Applications of Molecular Paramagnetism", L. Mulay and E. Boudreaux, Ed., Wiley, New York, 1976, Chapter 7.
(11) H. C. Freeman, J. C. Schoone, and J. G. Sime, *Acta Crystallogr.*, **18**, 381 (1965).
(12) M. Rising, F. Parker, and D. Gaston, *J. Am. Chem. Soc.*, **56**, 1178 (1934).
(13) G. Guerin, M. Sheldon, and C. N. Reilley, *Chemist-Analyst*, **49**, 36 (1960).
(14) D. B. Losee and W. E. Hatfield, *Phys. Rev. B*, **10**, 212 (1974).
(15) K. T. McGregor, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.*, **15**, 421 (1976).
(16) J. R. Wasson, *Chemist-Analyst*, **56**, 36 (1967).
(17) E. König, "Magnetic Properties of Coordination and Organometallic Transition Metal Compounds", Springer-Verlag, West Berlin, 1966.
(18) A. K. Wiersema and J. J. Windle, *J. Phys. Chem.*, **68**, 2316 (1964).
(19) C. K. Johnson, "ORTEP—A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations", Document ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.
(20) W. E. Hatfield, *Inorg. Chem.*, **11**, 216 (1972), and references therein.
(21) K. T. McGregor, J. A. Barnes, and W. E. Hatfield, *J. Am. Chem. Soc.*, **95**, 7993 (1973).
(22) E. D. Estes, W. E. Estes, R. P. Scaringe, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **14**, 2564 (1975).
(23) B. E. Meyers, L. Berger, and S. A. Friedberg, *J. Appl. Phys.*, **40**, 1149 (1969).
(24) W. E. Estes and W. E. Hatfield, to be submitted for publication.

(25) M. Tachihi and T. Yamada, *J. Phys. Soc. Jpn.*, **28**, 1413 (1970).
(26) V. H. Crawford, H. W. Richardson, J. R. Wasson, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.*, **15**, 2107 (1976).
(27) W. E. Estes, E. D. Estes, D. J. Hodgson, and W. E. Hatfield, to be submitted for publication.
(28) P. J. Hay, J. C. Thibeault, and R. Hoffmann, *J. Am. Chem. Soc.*, **97**, 4884 (1975).
(29) D. Bloch, *J. Phys. Chem. Solids*, **27**, 881 (1966).
(30) J. E. Wertz and J. R. Bolton, "Electron Spin Resonance", McGraw-Hill, New York, 1972, Chapter 10, p 242 ff.
(31) P. Kottis and R. Lefebvre, *J. Chem. Phys.*, **39**, 393 (1963).
(32) C. Chow and R. D. Willet, *J. Chem. Phys.*, **59**, 5903 (1973), and references therein.
(33) G. Kolks and S. J. Lippard, *J. Am. Chem. Soc.*, **99**, 5804 (1977).

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Central Role of the $S_3N_3^-$ and $S_4N_5^-$ Ions in the Deprotonation of Tetrasulfur Tetraimide and in the Reductive or Nucleophilic Degradation of Tetrasulfur Tetranitride

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$K^+S_3N_3^-$ has been isolated and characterized as the major product from the deprotonation of $S_4N_4H_4$ with potassium hydride. Salts of the $S_3N_3^-$ ions are also formed as the final products in the chemical reduction of S_4N_4 with potassium metal in 1,2-dimethoxyethane and in the electrochemical reduction of S_4N_4 in ethanol. The formation of $S_3N_3^-$ in these reduction processes supports an earlier proposal that the initially formed radical anion $S_4N_4^-\cdot$ decomposes by an intramolecular bond rupture. S_4N_4 reacts with liquid ammonia or secondary amines to give salts of the $S_4N_5^-$ ion but in the presence of sodium amide an $S_3N_3^-$ salt is the major product. The reaction of S_4N_4 with potassium cyanide in ethanol or dimethylformamide also produces $K^+S_4N_5^-$, in addition to potassium thiocyanate. Previous claims of sulfur–nitrogen anions derived from S_4N_4 are critically evaluated in the light of these results.

Introduction

The reduction of S_4N_4 with potassium metal in dimethoxyethane at room temperature has been reported by Chapman and Massey to produce a series of color changes attributed to ions of the type $S_4N_4^{n-}$ (n = 1–4).[1] A nine-line ESR spectrum was observed and assigned to the radical anion $S_4N_4^-\cdot$.[1] In a subsequent electrochemical study,[2] Meinzer and co-workers observed a *different* nine-line ESR spectrum for the primary reduction product of S_4N_4. Theoretical calculations supported the assignment of this spectrum to $S_4N_4^-\cdot$ with a similar structure to S_4N_4. It was further demonstrated that this radical anion is only stable at temperatures below ca. −25 °C and that, above 0 °C, rapid decomposition occurs. In a more detailed electrochemical investigation, using the techniques of controlled-potential electrolysis and cyclic voltammetry, Prater and co-workers conclusively identified the $S_4N_4^-\cdot$ radical and showed that it decays by a first-order rate law.[3] The activation energy for this process was estimated to be ca. 11 kcal mol^{-1} and it was suggested that decomposition takes place via an intramolecular bond rupture.

Investigations of the deprotonation of $S_4N_4H_4$ are also relevant to a discussion of S–N anions derived from S_4N_4. For example, the orange-red product of the reaction of $S_4N_4H_4$ with triphenylmethyl sodium is claimed to be the sodium salt of the $S_4N_4^{4-}$ anion, although the evidence presented is unconvincing.[4] Similarly, the color changes observed in the deprotonation of $S_4N_4H_4$ with n-butyllithium have been attributed to ions of the type $S_4N_4H_{4-n}^{n-}$ (n = 1–4).[5] It is difficult to reconcile these claims with the demonstrated instability of $S_4N_4^-\cdot$.

Very recent studies of S–N anions by Scherer and Wolmershäuser[6a,b] and by the present authors[7] have led to the structural characterization of the $S_4N_5^-$[6b] and $S_3N_3^-$[7c] ions. These are the only binary S–N anions whose structures are known, although the dark blue S_4N^- anion has been isolated as its tetra-n-butylammonium salt.[8] Scherer and Wolmershäuser have referred to the ubiquitous presence of $S_4N_5^-$ among the products of reactions of various sulfur compounds with ammonia.[9] In a preliminary communication,[7a] we referred to the likely formation of $S_3N_3^-$ in the electrochemical reduction of S_4N_4. In this paper we discuss in detail the role of $S_3N_3^-$ in the chemical and electrochemical reduction of S_4N_4 and in the deprotonation of $S_4N_4H_4$. We also describe the formation of this ion and $S_4N_5^-$ in a variety of reactions of S_4N_4 with nucleophiles. The results of these studies necessitate a reconsideration, and in most cases a reinterpretation, of previous work related to S–N anions derived from S_4N_4.

Experimental Section

Reagents and General Procedures. Absolute ethanol was refluxed with magnesium turnings and a few crystals of iodine for 4 h and distilled immediately prior to use. Absolute methanol was distilled from Drierite. 1,2-Dimethoxyethane was distilled from Drierite, then refluxed over sodium for 6 h, and finally distilled into a flask containing freshly cut sodium. n-Pentane (Caledon laboratories) was distilled from calcium hydride, and tetrahydrofuran (Fisher) and diethyl ether (Mallinckrodt) were distilled from $LiAlH_4$. Methylene chloride (Fisher) was distilled from P_2O_5. Anhydrous ammonia (Matheson) was distilled from sodium directly into the reaction tube. All distillations of solvents and reactions and manipulation of $S_3N_3^-$ salts were carried out in flame-dried apparatus under N_2 (99.99% purity) passed through Ridox and silica gel.

S_4N_4 (mp 179 °C) was prepared according to the literature,[10] recrystallized twice from benzene, and checked for the absence of c-S_8 by mass spectroscopy. $S_4N_4H_4$ (mp 151 °C) was prepared by the literature method.[11] CCl_3COCl (Eastman), mercury (Johnson, Matthey and Mallory), mercurous chloride (BDH, >99.6%), potassium chloride (Baker, 99.7%), and dimethylamine (Matheson, anhydrous) were used as received. Potassium hydride (Alfa, 22.7% in mineral oil) was handled using the procedure described by Brown.[12] Potassium metal (BDH) was washed with dry n-pentane and cut in a drybox to expose the clean metal surface. Anhydrous Me_4NCl was prepared by the neutralization of Me_4NOH (Eastman, 25% in methanol) by 6.0 M aqueous HCl, followed by drying in vacuo (50 °C (10^{-2} mmHg) for 24 h). Piperidine (Fisher) was stored over 4-Å molecular sieves and distilled before use. Piperidyllithium was obtained as a white solid from the reaction of n-butyllithium with piperidine in n-hexane.

Instrumentation. Infrared spectra (4000–250 cm^{-1}) were recorded as Nujol mulls (CsI optics) on a Perkin-Elmer 467 spectrophotometer. Mass spectra were recorded on a Varian CH5 instrument operating at 70 eV. Electrochemical reductions were performed in a two-compartment, three-electrode cell using a PAR 176 potentiostate/galvanostat. UV–visible spectra were obtained in a 1-cm cell, with

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