by Fe^{2+}(aq), benzene-1,4-diol, and I^-(aq) have been analyzed[6] according to the scheme

$$CoOH^{2+}(aq) + Red \overset{fast}{\rightleftharpoons} CoOH^{2+}(aq), Red \qquad K_o \tag{10}$$

$$CoOH^{2+}(aq), Red \overset{fast}{\rightleftharpoons} (CoOH^{2+}, Red)^* \qquad K_d \tag{11}$$

$$(CoOH^{2+}, Red)^* \xrightarrow{k_{act}} (CoOH^{2+}, Red)^{\ddagger} \xrightarrow{fast} products \tag{12}$$

Here $CoOH^{2+}$, Red is the outer-sphere precursor formed between $CoOH^{2+}$(aq) and the reductant species Red, $(CoOH^{2+}(aq), Red)^*$ is a precursor form in which the distribution of OH^- in the inner coordination sphere is optimal for OH^--mediated electron transfer within the precursor and $(CoOH^{2+}, Red)^{\ddagger}$ is the transition state for electron transfer. According to this scheme $k_1K_h = K_oK_dK_hk_{act}$; i.e., $k_1 = K_oK_dk_{act}$. If k_{act} is essentially independent of the nature of Red,[6] then small variations in k_1K_h can be ascribed to minor variations in K_o and/or K_d.

However, examination of the activation parameters for reduction of $CoOH^{2+}$(aq) in Table III reveals substantial compensating variations of $\Delta H_b^{\ddagger}$ and $\Delta S_b^{\ddagger}$. These variations are presumably a reflection of the different enthalpy and entropy changes associated with equilibria 10 and 11 for different reductant species; unfortunately, current electrostatic models for precursor formation in (10),[5] which neglect any influence of the structure of Red on the stability of $CoOH^{2+}$, Red or the possibility of hydrogen bonding within such a precursor, are too crude for a more detailed and unambiguous analysis of these interesting activation parameter variations.[17]

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Registry No. Asc, 50-81-7; Co^{3+}(aq), 15275-05-5.

References and Notes

(1) (a) Adams State College. (b) Northeastern University.
(2) G. Davies and K. O. Watkins, *J. Phys. Chem.*, **74**, 3388 (1970).
(3) G. Davies and B. Warnqvist, *Coord. Chem. Rev.*, **5**, 349 (1970), and references therein.
(4) B. Warnqvist, *Inorg. Chem.*, **9**, 682 (1970).
(5) I. Bodek and G. Davies, *Coord. Chem. Rev.*, **14**, 269 (1974), and references therein.
(6) G. Davies, *Coord. Chem. Rev.*, **14**, 287 (1974), and references therein.
(7) G. Davies, *Inorg. Chem.*, **10**, 1155 (1971).
(8) E. Pelizzetti, E. Mentasti, and E. Paramauro, *J. Chem. Soc., Dalton Trans.*, 23, (1976).
(9) (a) W. G. Nigh in "Oxidation in Organic Chemistry", Vol. 5B, W. S. Trahanovsky, Ed., Academic Press, New York, N.Y., 1973, p 50; (b) A. E. Martell and M. M. T. Khan, *Inorg. Biochem.*, 676 ff (1973).
(10) D. A. Skoog and D. M. West, "Fundamentals of Analytical Chemistry", 3rd ed, Holt, Rinehart and Winston, New York, N.Y., 1976, pp 758–759.
(11) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).
(12) R. Stewart, "Oxidation Mechanisms", W. A. Benjamin, New York, N.Y., 1976, p 113; I. Yamazaki and L. H. Piette, *Biochim. Biophys. Acta*, **50**, 62 (1961).
(13) The acid dissociation constant of the neutral ascorbic acid molecule is 9×10^{-5} M at 0.1 M ionic strength and 25 °C: L. G. Sillen and A. E. Martell, "Stability Constants of Metal Ion Complexes", The Chemical Society, London, 1964, p 477.
(14) See Figure 2 of ref 7.
(15) E. Pelizzetti and E. Mentasti, *J. Chem. Soc., Dalton Trans.*, 2222 (1976).
(16) The redox couple evaluated must refer to that between the protonated ascorbic acid radical and ascorbic acid since k_0 is the rate constant at (hypothetical) infinite acidity, where Co^{3+}(aq) is the only cobalt(III) species and the radical produced by its reduction by ascorbic acid may be expected to be fully protonated.
(17) In addition to the uncertainties associated with a structureless model for precursor formation,[5] one would also have to contend with typical standard deviations of ±1.5 kcal mol^{-1} and ±7 cal deg^{-1} mol^{-1} in the activation enthalpies and entropies for reduction of $CoOH^{2+}$(aq) by benzenediols, which are somewhat higher than are those for ascorbic acid (present work).

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Magnetic Susceptibility of the Chloro(2-diethylaminoethanolato)copper(II) Tetramer

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In recent years there has been much interest in the magnetic properties of transition metal cluster complexes. The magnetic susceptibilities of copper tetramer complexes have been successfully described by the Heisenberg spin–spin exchange model with appropriate geometrical considerations. The series of $Cu_4OX_6L_4$ complexes where X = Cl or Br and L = pyridine,[1] $(C_6H_5)_3PO$,[2] or Cl,[3] for example, consist of a tetrahedral arrangement of copper ions bonded to a central oxygen atom, and the magnetic properties of many of these compounds can be described with T_d symmetry models although there are complications.[2] Other clusters with four copper(II) ions which have been studied include the basic quinoline adduct of copper trifluoroacetate $[Cu_2OH(O_2CCF_3)_3(quin)]_2$, an essentially symmetric linear[4] system, and several Schiff base complexes of copper.[5,6] These latter systems are formed by associated dimers. The magnetic properties of a new four-copper cluster formed from chloro(2-diethylaminoethanolato)copper(II) units, $[Cu(deae)Cl]_4$, are described here. X-ray structural studies have shown this cluster to consist of an approximately tetrahedral arrangement of copper ions bridged by ethanolate oxygens.[7,8] It has not been possible to explain the magnetic properties of $[Cu(deae)Cl]_4$ with the simple T_d model; however, we show in this report that it is possible to rationalize the magnetic properties of chloro(2-diethylaminoethanolato)-copper(II) in terms of a low-symmetry model.

Experimental Section

A sample of the complex chloro(2-diethylaminoethanolato)copper(II), $[Cu(deae)Cl]_4$, was prepared by mixing 1.34 g of copper(II) chloride in 150 mL of absolute alcohol with 2.34 g of 2-diethylaminoethanol in 50 mL of absolute alcohol. Dark green crystals formed after the solution was allowed to stand at room temperature for several days. Anal. Calcd for $Cu(C_6H_{14}NO)Cl$: C, 33.49; H, 6.55; N, 6.51; Cl, 16.47. Found: C, 33.53; H, 6.36; N, 6.54; Cl, 16.41. Magnetic susceptibilities were obtained using a Foner-type[9] vibrating-sample magnetometer,[10] calibrated with a nickel sphere at room temperature. The computer fits were made with an IBM 360/70 and a Raytheon 706 computer using a Simplex function minimization routine[11] and a standard least-squares procedure. The experimental magnetic susceptibilities were corrected for the diamagnetism of the constituent atoms and for temperature-independent paramagnetism, which was assumed to be 60×10^{-6} cgsu.[12]

Description of the Structure

The bond distances and bond angles which were reported for $[Cu(deae)Cl]_4$ are shown on the illustration of the structure in Figure 1. The x-ray crystal structure results reveal the presence of a C_2 axis, which passes through the centers of the Cu(1)–Cu(2) and the Cu(3)–Cu(4) faces. It will be seen below that this structural feature provides the unifying theme for the description of the magnetic properties.

Magnetic Susceptibility Theory

The Heisenberg spin–spin exchange Hamiltonian

$$H = -2 \sum_{i<j} J_{ij}\hat{S}_i \cdot \hat{S}_j \tag{1}$$

was adopted for the description of the magnetic properties. In the Hamiltonian (1) J_{ij} is the exchange constant and the subscripts i and j number the pairwise interacting magnetic

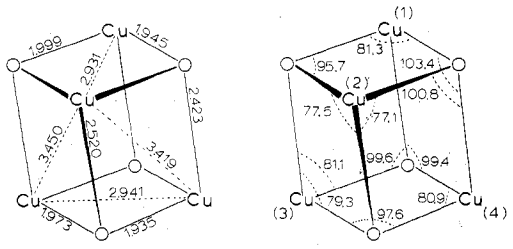

Figure 1. Bond distances and bond angles for the chloro(2-diethylaminoethanolato)copper(II) cluster.

Table I. Energy Levels for Four Interacting $S = {}^1/_2$ Ions with C_2 Symmetry

Quintet: $E_Q = -(J_1 + J_2 + 2J_3 + 2J_4)/2$

Triplets: $E_{T_1} = -(J_1 + J_2 - 2J_3 - 2J_4)/2$

$E_{T_2} = [J_1 + J_2 + 2((J_1 - J_2)^2 + (J_3 - J_4)^2)^{1/2}]/2$

$E_{T_3} = [J_1 + J_2 - 2((J_1 - J_2)^2 + (J_3 - J_4)^2)^{1/2}]/2$

Singlets: $E_{S_1} = [J_1 + J_2 + 2J_3 + 2J_4 + 2((J_1 + J_2 - J_3 - J_4)^2 + 3(J_3 - J_4)^2)^{1/2}]/2$

$E_{S_2} = [J_1 + J_2 + 2J_3 + 2J_4 - 2((J_1 + J_2 - J_3 - J_4)^2 + 3(J_3 - J_4)^2)^{1/2}]/2$

ions. For the interaction between four copper ions, the complete Hamiltonian is

$$H = -2(J_{12}\hat{S}_1\cdot\hat{S}_2 + J_{13}\hat{S}_1\cdot\hat{S}_3 + J_{14}\hat{S}_1\cdot\hat{S}_4 + J_{23}\hat{S}_2\cdot\hat{S}_3 + J_{24}\hat{S}_2\cdot\hat{S}_4 + J_{34}\hat{S}_3\cdot\hat{S}_4) \quad (2)$$

where, if we consider the tetramer as two consociated dimers and number the copper ions as shown in Figure 1, J_{12} is the interaction within one dimeric unit, J_{34} is the interaction within the other unit, and J_{13}, J_{14}, J_{23}, and J_{24} are the cross interactions. The presence of the C_2 axis simplifies the Hamiltonian and the energy levels can be derived exactly. Here, $J_{13} = J_{24}$ and $J_{14} = J_{23}$ and the reduced Hamiltonian is

$$H = -2(J_1\hat{S}_1\cdot\hat{S}_2 + J_2\hat{S}_3\cdot\hat{S}_4 + 2J_3\hat{S}_1\cdot\hat{S}_3 + 2J_4\hat{S}_1\cdot\hat{S}_4) \quad (3)$$

with $J_1 = J_{12}$, $J_2 = J_{34}$, $J_3 = J_{13} = J_{24}$, and $J_4 = J_{14} = J_{23}$. The solution of the 16 × 16 energy matrix yields one quintet level (S = 2), three triplet levels ($S = 1$) and two singlet levels ($S = 0$). The expressions for these energy levels are given in Table I in terms of J_1, J_2, J_3, and J_4.

There are four subgroups of the T_d group which retain a twofold axis. These are D_{2d}, D_2, C_{2v}, and C_2, and attempts were made to fit the magnetic susceptibility expressions for these cases to the experimental data. Two other possibilities were considered, these being separate and equal dimers, and separate but unequal dimers. The magnetic susceptibility expression for the dimer models is represented by the modified Van Vleck equation[13-16]

$$\chi_m^{cor} = \frac{Ng^2\beta^2}{3k(T-\Theta)}(1 + {}^1/_3\exp(-2J/kT))^{-1} \quad (4)$$

The general magnetic susceptibility expression which was derived from the Van Vleck equation is

$$\chi_m^{cor} = \frac{2Ng^2\beta^2}{kT}\frac{5\exp(-E_Q/kT) + \exp(-E_{T1}/kT) + \exp(-E_{T2}/kT) + \exp(-E_{T3}/kT)}{5\exp(-E_Q/kT) + 3\exp(-E_{T1}/kT) + 3\exp(-E_{T2}/kT) + 3\exp(-E_{T3}/kT) + \exp(-E_{S1}/kT) + \exp(-E_{S2}/kT)} \quad (5)$$

where E_Q, E_{T1}, E_{T2}, E_{T3}, E_{S1}, and E_{S2} are the energies of the quintet, the three triplets, and the two singlets, respectively.

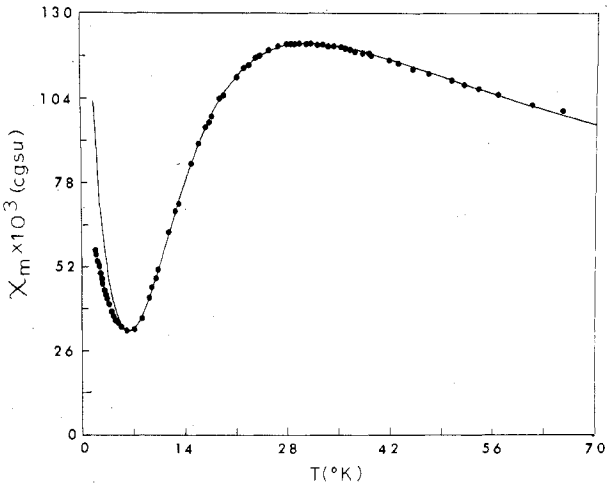

Figure 2. Temperature-dependent magnetic susceptibility of chloro(2-diethylaminoethanolato)copper(II). The solid line is the best fit to the C_{2v} model. A correction has been made for a 1% monomeric impurity.

The fits were made to the data points above 13 K with a correction for the small amount of monomeric impurity (1%) which appears below 7 K. In order to eliminate an overemphasis to the high-temperature data points and to evenly distribute the error, the criterion for the best fit was calculated from FIT = $\sum((\chi_{calcd} - \chi_{obsd})/\chi_{obsd})^2$. The procedure used to correct the magnetic data for monomer impurities as manifested by the minimum in χ_m at 7 K and subsequent increase with decrease in temperature has been described in detail.[17]

The investigation of the two dimer models revealed poor agreement between the observed and calculated susceptibilities. The experimental curve tends to be broader than what the equation predicts; this is an indication of some interaction between the two dimer pairs. The best fit g values obtained from these fits were 1.39 and 1.96, values which are too low for copper systems. When the parameter g was allowed to vary in the T_d, D_{2d}, and D_2 cases, the best fit g value obtained was consistently about 1.7. It is also interesting to note that there were little differences in the J values and the fits obtained in the T_d, D_{2d}, and D_2 models even though these models have one, two, and three parameters, respectively. For the C_{2v} and the C_2 models, however, the fit is dramatically improved. When g was allowed to vary, the best fit value was 2.11; this is indeed reasonable. Since the difference in the fit on lowering the symmetry from C_{2v} to C_2 is very small, the magnetic susceptibility can be explained with the C_{2v} tetramer model. The values of the exchange constant were calculated to be $J_1 = -14.9 \pm 1$ cm^{-1}, $J_2 = -60.3 \pm 2$ cm^{-1}, and $J_3 = J_4 = -36.2 \pm 2$ cm^{-1}. This excellent fit is shown in Figure 2.

The magnetism of chloro(2-diethylaminoethanolato)copper(II) can be satisfactorily described using the Heisenberg spin–spin exchange model with C_{2v} symmetry. This model now can be extended to other pseudotetrahedral complexes with increased confidence since the relative magnitudes of J_1 and J_2 are in agreement with the general trend which has been established for the relationship between the singlet–triplet splitting energies and the angle ϕ at the bridging oxygen atom in a series of di-μ-hydroxo-bridged copper(II) dimers.[18] However, the magnitudes of the antiferromagnetic coupling constants cannot be predicted from the $2J$ vs. ϕ relationship since the extent of the spin–spin coupling is markedly dependent on the nature of the chemical groups bonded to the bridging oxygen atom. In this molecule the bridge is an alkoxo oxygen atom which is simultaneously bonded to three copper ions. The magnitude of $J_3 = J_4$ is more difficult to explain

since there are no structural dimer models. We do note that the large angle at the bridge would imply a large antiferromagnetic J value, and the increase in the copper–oxygen bond distances would be expected to cause a decrease in the magnitude of J. Examples of dimers with these structural characteristics will have to be examined before the antiferromagnetic interaction can be understood.

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References and Notes

(1) R. F. Drake, V. H. Crawford, and W. E. Hatfield, *J. Chem. Phys.*, **60**, 4525 (1974).
(2) M. E. Lines, A. P. Ginsberg, R. L. Martin, and R. C. Sherwood, *J. Chem. Phys.*, **57**, 1 (1972).
(3) J. A. Barnes, G. W. Inman, Jr., and W. E. Hatfield, *Inorg. Chem.*, **10**, 1725 (1971).
(4) R. G. Little, J. A. Moreland, D. B. W. Yawney, and R. J. Doedens, *J. Am. Chem. Soc.* **96**, 3834 (1974).
(5) W. E. Hatfield and G. W. Inman, Jr., *Inorg. Chem.*, **8**, 1376 (1969).
(6) G. O. Carlisle, K. K. Ganguli, and L. J. Theriot, *Inorg. Nucl. Chem. Lett.*, **7**, 527 (1971).
(7) W. Hasse, *Chem. Ber.*, **106**, 3132 (1973).
(8) E. D. Estes and D. J. Hodgson, *Inorg. Chem.*, **14**, 334 (1975).
(9) S. Foner, *Rev. Sci. Instrum.*, **30**, 548 (1959).
(10) Princeton Applied Research Corp., Princeton, N.J.
(11) D. M. Olsson, *J. Quality Tech.*, **6**, 53 (1974); J. W. Hall, W. E. Estes, and W. E. Hatfield, to be submitted for publication.
(12) Landolt-Börnstein, "Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik", E. König, Ed., New Series, Group II, Vol. 2, Springer-Verlag, Berlin, 1966.
(13) J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities", Oxford University Press, London, 1932.
(14) B. Bleaney and K. Bowers, *Proc. R. Soc. London, Ser. A*, **214**, 451 (1952).
(15) J. A. Bertrand, A. P. Ginsberg, R. I. Kaplan, C. E. Kirkwood, R. L. Martin, and R. C. Sherwood, *Inorg. Chem.*, **10**, 240 (1971).
(16) A. P. Ginsberg and M. E. Lines, *Inorg. Chem.*, **11**, 2289 (1972).
(17) R. P. Eckberg and W. E. Hatfield, *J. Chem. Soc., Dalton Trans.*, 616 (1975).
(18) V. H. Crawford, H. W. Richardson, J. R. Wasson, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.*, **15**, 2107 (1976).