

- (19) R. J. Campion, unpublished observations, quoted in ref 15.  
 (20) A value  $19.2 \text{ M}^{-1} \text{ s}^{-1}$  was extrapolated to zero ionic strength; since  $w_{11} = 5.6$  ( $r = 4.5 \text{ \AA}$ ),  $\Delta G^{**} = 7.4 \text{ kcal mol}^{-1}$ .<sup>21</sup>  
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 (22)  $\Delta E^\circ = 0.09 \text{ V}$  as derived from data in ref 12.  
 (23) B. M. Gordon, L. L. Williams, and N. Sutin, *J. Am. Chem. Soc.*, **83**, 2061 (1961).  
 (24)  $\Delta E^\circ = 0.52 \text{ V}$ , by assuming  $E^\circ = 0.88 \text{ V}$  for  $\text{IrCl}_6^{2-/3-}$  from the data at low ionic strength and acidity reported by P. George, G. I. H. Hanania, and D. H. Irvine, *J. Chem. Soc.*, 3048 (1957), and  $E^\circ = 0.36 \text{ V}$  for  $\text{Fe}(\text{CN})_6^{3-/4-}$  at very low ionic strength.<sup>17</sup>  
 (25)  $\Delta E^\circ = 0.247 \text{ V}$ , by assuming the reduction potential of  $\text{IrCl}_6^{2-/3-}$  quoted by R. Cecil, J. S. Littler, and G. Easton, *J. Chem. Soc. B*, 626 (1970).  
 (26) The calculations referred to  $\text{IrCl}_6^{2-}$  oxidation of  $\text{Mo}(\text{CN})_8^{4-}$  in  $0.50 \text{ M H}_2\text{SO}_4$ <sup>15</sup> and were reported in a previous paper;<sup>12</sup> they show also a moderate agreement with the present conclusions.

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### Evidence of the Higher Order Spin Coupling in an Antiferromagnetic Oligomer Complex

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The magnetic susceptibility measurement of the dimeric complex of iron  $[\text{FeS}_4\text{C}_4(\text{CF}_3)_4]_2$  has been reported by Dance together with the theoretical account for the observations.<sup>1</sup> The dimerization of this oligomeric complex occurs through the two Fe-S bonds bridging the two equivalent monomeric  $[\text{FeS}_4\text{C}_4(\text{CF}_3)_4]$  chelate units. Assuming that this oligomer bonding utilizes a sulfur lone pair of electrons and an empty orbital at iron, the number of singly occupied orbitals at each submolecule must be even. Accordingly, each submolecule is supposed to have a spin of 1. However, the usual Heisenberg-type exchange Hamiltonian between two submolecule spins  $S_a$  and  $S_b$  ( $S_a = S_b = 1$ ) has turned out to be inappropriate to account for the experimental data.

The theoretical model, in which two singly occupied orbitals at each submolecule are involved and all exchange interactions for the four electrons are explicitly included, has been proposed by Dance.<sup>1</sup> Possible sets of the exchange parameters  $J_{ij}$  between two electrons each located on the orbitals  $i$  and  $j$  were derived reproducing well the  $\chi_M$ - $T$  data. This fact, however, may not necessarily give a basis for withdrawal of the exchange model between submolecule spins  $S_a$  and  $S_b$ .

In the general theory of the exchange interaction for a many-electron system,<sup>2,3</sup> there has been pointed out that besides the bilinear Heisenberg-type exchange interaction, the higher order spin coupling such as a type among the three spins  $(s_i \cdot s_j)(s_j \cdot s_k)$  or a type among the four spins  $(s_i \cdot s_j)(s_j \cdot s_m)$  etc. can be obtained successively as a series expansion of the energy eigenvalue with regard to the overlap integrals between atomic wave functions. For spins of  $1/2$ , the so-called biquadratic exchange interaction reduces to a bilinear one by eq 1.

$$(s_i \cdot s_j)^2 = 3/16 - 1/2(s_i \cdot s_j) \quad (1)$$

Let the singly occupied orbitals at each submolecule be  $\psi_1$ ,  $\psi_2$  and  $\psi_1'$ ,  $\psi_2'$  and the corresponding spin operators be  $s_1$ ,  $s_2$  and  $s_1'$ ,  $s_2'$ , respectively. Then, from the general theory we may have the Hamiltonian

$$H = -2K_0 \{(s_1 \cdot s_2) + (s_1' \cdot s_2')\} - 2K_1 \{(s_1 \cdot s_1') + (s_1 \cdot s_2') + (s_2 \cdot s_1') + (s_2 \cdot s_2')\} - K_2 \{(s_1 \cdot s_1')(s_1 \cdot s_2') + (s_2 \cdot s_1')(s_2 \cdot s_2') + (s_1 \cdot s_1')(s_2 \cdot s_1') + (s_1 \cdot s_2')(s_2 \cdot s_2') + \text{HC}\} - K_2'' \{(s_1 \cdot s_1')(s_1 \cdot s_2) + (s_1 \cdot s_2)(s_2 \cdot s_2') + (s_1 \cdot s_1')(s_1' \cdot s_2') + (s_2 \cdot s_2')(s_2' \cdot s_1') + \text{HC}\} - K_2''' \{(s_1 \cdot s_2)(s_1 \cdot s_2') + (s_1 \cdot s_2)(s_2 \cdot s_1') + (s_2 \cdot s_1')(s_1' \cdot s_2') + (s_1 \cdot s_2')(s_2' \cdot s_1') + \text{HC}\} - 2K_3 \{(s_1 \cdot s_1')(s_2 \cdot s_2') + (s_1 \cdot s_2')(s_2 \cdot s_1')\} - 2K_3' \{(s_1 \cdot s_2)(s_1' \cdot s_2')\} \quad (2)$$

where HC denotes the part of Hermitian conjugate. The two terms of mutually Hermitian conjugate can be reduced to a bilinear term by using the relation

$$(s_i \cdot s_j)(s_i' \cdot s_k) + (s_i' \cdot s_k)(s_i \cdot s_j) = 1/2(s_j \cdot s_k) \quad (3)$$

If we assume that  $K_2'' = K_2'''$  and neglect the term of  $K_3'$ , eq 2 can be rewritten as

$$\tilde{H} = -(2K_0 + K_2') \{(s_1 \cdot s_2) + (s_1' \cdot s_2')\} - (2K_1 + K_2'') \{(s_1 \cdot s_1') + (s_1 \cdot s_2') + (s_2 \cdot s_1') + (s_2 \cdot s_2')\} - 2K_3 \{(s_1 \cdot s_1')(s_2 \cdot s_2') + (s_1 \cdot s_2')(s_2 \cdot s_1')\} \quad (4)$$

With the spin operators  $S_a$  and  $S_b$  which are defined as

$$S_a = s_1 + s_2 \quad S_b = s_1' + s_2' \quad (5)$$

eq 4 can further be simplified as

$$H = -2J(S_a \cdot S_b) - 2J'(S_a \cdot S_b)^2 \quad (6)$$

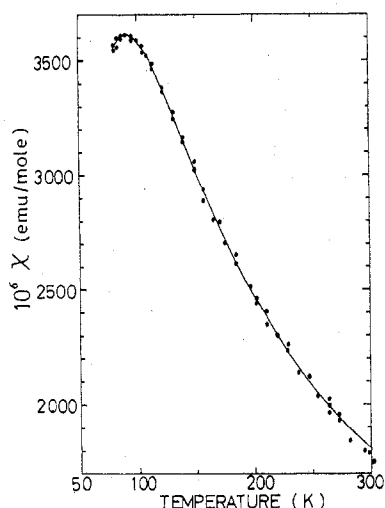
In other words, the Hamiltonian for the present four-electron system will generally be given by the customary Heisenberg exchange interaction and the biquadratic one between the submolecule spins  $S_a$  and  $S_b$ .

The calculation of the molar susceptibility  $\chi_M$  for the Hamiltonian (eq 6) can be done straightforwardly using the vector model.<sup>4</sup> The spin states have total spin  $S' = S_a + S_b$  ( $S' = 0, 1, 2$ ) with relative energies  $E(S')$ . For the antiferromagnetic sign of  $J$ , we have the ground state  $S' = 0$ ,  $E(0) = 0$  and the excited states  $S' = 1$ ,  $E(1) = -2J + 6J'$  and  $S' = 2$ ,  $E(2) = -6J + 6J'$ . The experimental data will be compared with the well-known susceptibility formula

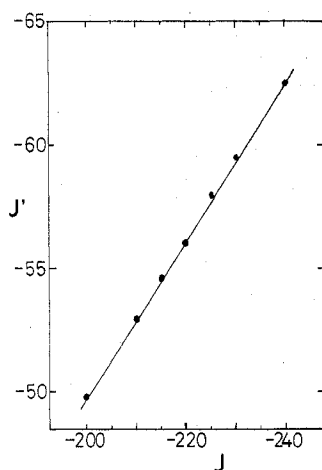
$$\chi_M = \frac{Ng^2\mu_B^2}{3kT} \frac{\sum_S S'(S'+1)(2S'+1) \exp\{-E(S')/kT\}}{\sum_S (2S'+1) \exp\{-E(S')/kT\}} + \chi_{\text{const}} \quad (7)$$

where  $N$  is Avogadro's number,  $g$  is the  $g$  factor,  $\mu_B$  is the Bohr magneton, and  $\chi_{\text{const}}$  represents both the Van Vleck high-frequency part and the diamagnetic contributions of the magnetic susceptibility.

With the use of the FACOM 230-75 computing facility, the temperature dependence of the susceptibility has been calculated for various sets of values of parameters in the ranges of  $-200$  to  $-250 \text{ cm}^{-1}$  for  $J$  and  $-40$  to  $-70 \text{ cm}^{-1}$  for  $J'$ , taking  $g = 2.00$ . For no positive values of parameters will this model reproduce the observations. We could find several sets of values which show an excellent agreement with Dance's data. In Figure 1, the calculation for the case (A)  $J = -210 \text{ cm}^{-1}$ ,  $J' = -53 \text{ cm}^{-1}$ ,  $\chi_{\text{const}} = -500 \times 10^{-6} \text{ cgsu}$  is shown and compared with the experimental data. The other set of values, for example (B)  $J = -220 \text{ cm}^{-1}$ ,  $J' = -56 \text{ cm}^{-1}$ ,  $\chi_{\text{const}} = -430 \times 10^{-6} \text{ cgsu}$  or (C)  $J = -225 \text{ cm}^{-1}$ ,  $J' = -58 \text{ cm}^{-1}$ ,  $\chi_{\text{const}} = -500 \times 10^{-6} \text{ cgsu}$ , also gives a nice fitting with the observations. The theoretical curves for the cases (B) and (C) practically coincide with the curve in Figure 1. Therefore, it may be concluded that the present simple model is quite useful to account for the magnetic behaviors of the oligomer complex of iron and is equally significant as the more complicated theoretical



**Figure 1.** Calculated susceptibility of the oligomer complex  $[\text{FeS}_4\text{C}_4(\text{CF}_3)_4]_2$  compared with the experimental data by Dance. The calculation is made with the values of the parameters  $J = -210 \text{ cm}^{-1}$ ,  $J' = -53 \text{ cm}^{-1}$ , and  $\chi_{\text{const}} = -500 \times 10^{-6} \text{ cgsu}$ .



**Figure 2.** The relation of  $J$  and  $J'$  which reproduces the observation. The numerical values are in units of  $\text{cm}^{-1}$ .

treatment. The coefficient  $J'$  of the biquadratic exchange interaction is related to the coefficient  $K_3$  of the higher order spin coupling which depends strongly on the overlap integrals between wave functions of electrons participating in the exchange interaction.<sup>3</sup> The unusually large relative value of  $J'$  is not so unreasonable in the present oligomeric complex as considerable amounts of the overlap between wave functions may be expected in this case.

In the present fitting procedures, the parameter  $J'$  seems to change linearly with the parameter  $J$  as shown in Figure 2. Since the strength of the biquadratic exchange interaction may usually be estimated as 20–30% at most of that of the Heisenberg exchange,<sup>5</sup> the relation of  $J$  and  $J'$  shown in Figure 2 may not be extended so far. As we have pointed out in the previous studies,<sup>6</sup> the biquadratic exchange interaction may be important for binuclear complex compounds. For tri- or quadrinuclear complex compounds, generally the other types of the higher order spin couplings may appear.<sup>7,8</sup> In the present studies, however, the origin of the biquadratic exchange interaction has been elucidated in relation to the general exchange mechanism of many-electron system.

**Registry No.**  $[\text{FeS}_4\text{C}_4(\text{CF}_3)_4]_2$ , 41959-83-5.

## References and Notes

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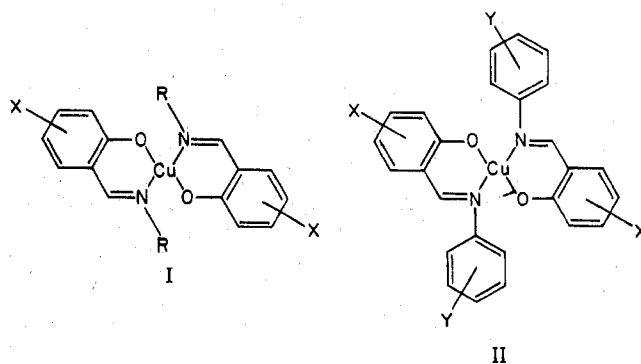
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## Lewis Acid Properties of Copper(II) in $\text{Cu}(\text{II})\text{-N}_2\text{O}_2$ -Chelate Complexes

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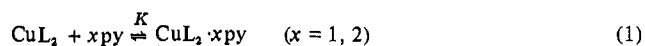
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Copper(II) readily forms neutral bis complexes  $\text{CuL}_2$  with Schiff bases prepared from salicylaldehyde and aliphatic (see I) or aromatic amines (see II). Kinetic studies of the metal<sup>1</sup>



and ligand exchange<sup>2</sup> behavior of  $\text{CuL}_2$  in organic solvents have led to the conclusion that substituent effects, as introduced by variation of X and Y, are kinetically operative only when changes in electron density at donor oxygen are involved. Variation of Y and, hence, changes of electron density at donor nitrogen seem to contribute kinetically only via corresponding changes at donor oxygen.<sup>1b</sup> The interesting questions are, therefore, in which way X and Y affect the electron density of O and N and in which way the electron density at the central copper is involved.

In noncoordinating solvents the copper in  $\text{CuL}_2$  is four-coordinated,<sup>3</sup> the coordination geometry varying between square planar and pseudotetrahedral,<sup>4</sup> depending on the nature of X and R. Coordinating solvents like pyridine cause spectral changes due to the formation of five- or six-coordinated copper(II) species.<sup>5</sup> Therefore, the equilibrium constant  $K$  of this Lewis acid–base reaction (as described by eq 1) is a



quantitative measure of the electron density available at the  $d_{z^2}$  orbital of Cu(II). On the basis of spectrophotometric studies, we report the effect of the parameters X, Y, and R on  $K$ .

## Experimental Section

The bis(salicylaldiminato)copper(II) complexes  $\text{CuL}_2$  were prepared by standard procedures.<sup>3</sup> The results of elemental analysis were in good agreement with theoretical data. Analytical grade toluene and pyridine (E. Merck, Darmstadt) were used as solvents without further purification. The absorption spectra were recorded with a Zeiss DMR 22 spectrometer at 400–800 nm in thermostated quartz cells of 2- and 10-cm path length. The temperature inside the cells was controlled with a thermocouple.

In each case 20 solutions of the complex in toluene were prepared ( $[\text{CuL}_2] = \text{constant}$ ;  $[\text{py}] = 0\text{--}12.4 \text{ M}$ ) and their spectra recorded at 298, 313, and 333 K. For all complexes and temperatures an