vents, but does not isomerize in the class B type solvents $CHCl_3$, CH_2Cl_2, $ClCH_2CH_2Cl$, CH_3CN, and CH_3NO_2. They cited this as evidence for a solvent effect which is in opposition to that reported earlier by us[6] and discussed in greater detail herein.

We have investigated their system in detail,[24] and find that they have completely misinterpreted their results, insofar as a solvent effect is concerned. While it is true that the S-bonded isomer does not isomerize to an appreciable extent in chloroform solution at room temperature over a period of 1 month, we have found that this is *also* true for the N isomer. However, an S→N-bonded isomerization can be effected in this solvent by refluxing the solution. The difference in behavior of the complex in DMF *vs.* chloroform in this case is therefore due to kinetic effects, not thermodynamic effects, as is the case in our system. The relatively high dielectric constant of DMF lowers the activation energy for the isomerization, which undoubtedly proceeds *via* a dissociative or ion-pair mechanism, by providing for better solvation of the free ion (a relatively large concentration of noncoordinated NCS^- is formed in the DMF solution, but none is observed in the chloroform solution). Comparable behavior is observed in DMSO, which also has a relatively high dielectric constant.

Despite the fact that it is not always of preponderant importance, the synthetic and theoretical ramifications of the solvent effect promise to be greater than any of the ambidentate ligand bonding mode determinants yet discovered.

Acknowledgments.—The authors wish to express their gratitude to the National Science Foundation for its support of this research (Grant No. GP-8327 and GP-20607) and to Professor G. Klopman for stimulating and rewarding discussions.

[24] R. L. Hassel and J. L. Burmeister, *Chem. Commun.*, 568 (1971).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, NORTH CAROLINA 27514

Spin–Spin Coupling in Magnetically Condensed Complexes. XI. Out-of-Plane Interactions and Triplet Ground State in Tetrakis(*N*,*N*-diethyldithiocarbamato)dicopper(II)

BY JUAN F. VILLA AND WILLIAM E. HATFIELD*

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The electronic nature of tetrakis(*N*,*N*-diethyldithiocarbamato)dicopper(II) is characterized by a best-fit convergence study of the magnetic parameters. It is shown that this compound possesses a triplet ground state 24.0 cm^{-1} below the singlet. There are, also, some additional weak lattice antiferromagnetic interactions observable at low temperatures. The spin coupling mechanism is seen to be of the superexchange σ-orbital type *via* the out-of-plane bonds, with interatomic electron transfer and intraatomic orbital coupling.

Introduction

The compound tetrakis(*N*,*N*-diethyldithiocarbamato)dicopper(II), $[Cu(edtc)_2]_2$, is composed of dimers[1] where, as shown in Figure 1, the sulfur atoms act as bridges. The copper ions are in a distorted tetragonal-pyramidal environment with four sulfur atoms comprising the basal plane at distances ranging from 2.30 to 2.34 Å and a fifth apical sulfur atom at 2.85 Å. The Cu–Cu distance is 3.54 Å. Some attention has been given to the magnetic properties of this complex[2,3] in the temperature region from 77 to 300°K. However, since it is below 77°K where the magnetic parameters change dramatically with temperature (therefore providing better data to characterize the type of magnetic interaction), we undertook the investigation of the magnetic susceptibility of tetrakis(*N*,*N*-diethyldithiocarbamato)dicopper(II) from 4.2 to 56°K. We had recently demonstrated[4] by epr measurements that there was spin–spin coupling in this system and proposed that it was transmitted through the orbitals of the sulfur atoms. We also gave recently a preliminary account of this work,[5] where it was reported that the spin coupling constant was positive. Now we present the complete data, a best-fit study of the data, comparisons to the previously available magnetic susceptibility and epr data, and a theoretical model for the coupling in this biologically related[6,7] compound.

Experimental Section

$[Cu(edtc)_2]_2$ was prepared by mixing water solutions of $CuCl_2$ and sodium *N*,*N*-diethyldithiocarbamate (excess of edtc). The dark brown precipitate which formed immediately was filtered, washed repeatedly with water, and dried at 110°. *Anal.* Calcd for $Cu(C_5H_{10}NS_2)_2$: C, 33.33; H, 5.60; N, 7.78. Found: C, 33.39; H, 5.74; N, 7.58.

The magnetic measurements were carried out with a Foner-type[8] vibrating-sample magnetometer from Princeton Applied Research, Inc. We used a sample size of about 0.1 g and a previously calibrated germanium resistor thermometer from Scientific Instruments, Inc. The field was held constant at 10,000 G with a Ventron Instruments Corp. power supply equipped with

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[1] M. Bonamico, G. Dessy, A. Mugnoli, A. Vaciago, and L. Zambonelli, *Acta Crystallogr.*, **19**, 886 (1965).

[2] A. K. Gregson and S. Mitra, *J. Chem. Phys.*, **49**, 3696 (1968).

[3] K. Hara, W. Mori, M. Inoue, M. Kishita, and M. Kubo, *Bull. Chem. Soc. Jap.*, **42**, 576 (1969).

[4] J. F. Villa and W. E. Hatfield, *Inorg. Chim. Acta*, **5**, 145 (1971).

[5] J. F. Villa and W. E. Hatfield, *Chem. Commun.*, 101 (1971).

[6] R. West and F. W. Sunderman, *Amer. J. Med. Sci.*, **236**, 15 (1958).

[7] G. D. Thorn and R. A. Ludwig, "The Dithiocarbamates and Related Compounds," American Elsevier, New York, N. Y., 1962.

[8] S. Foner, *Rev. Sci. Instrum.*, **30**, 548 (1959).

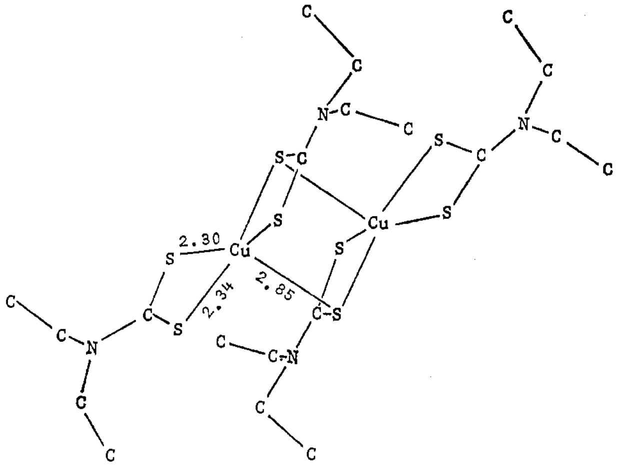

Figure 1.—Schematic structure of [Cu(edtc)$_2$]$_2$. Hydrogens were left out for clarity.

a field control unit. Prior to the runs, the magnetometer was calibrated with samples of pure nickel and with Hg[Co(CNS)$_4$]. A diamagnetic correction for the sample rod and empty sample holder were obtained and applied to the data. The usual Pascal constants[9] was used to correct for the diamagnetism of the sample (202 × 10^{-6} cgsu). Corrections were also applied for the TIP (100 × 10^{-6} cgsu).

The calculations were carried out with the Raytheon 706 computer of our Chemistry Department with an SCC-DTC-132 input–output system.

Results

The data are shown in Figure 2. It was determined that the system could best be described as composed of two coupled spins and that the effective Hamiltonian (1) holds for the system, where $2J$ is the energy separation between the triplet state and the singlet state, as shown in Figure 3, and S_i are the respective spins of the copper ions. It should be noted that a positive $2J$ value is indicative of a triplet ground state (Figure 3a).

$$H = -2J\vec{S}_1\cdot\vec{S}_2 \qquad (1)$$

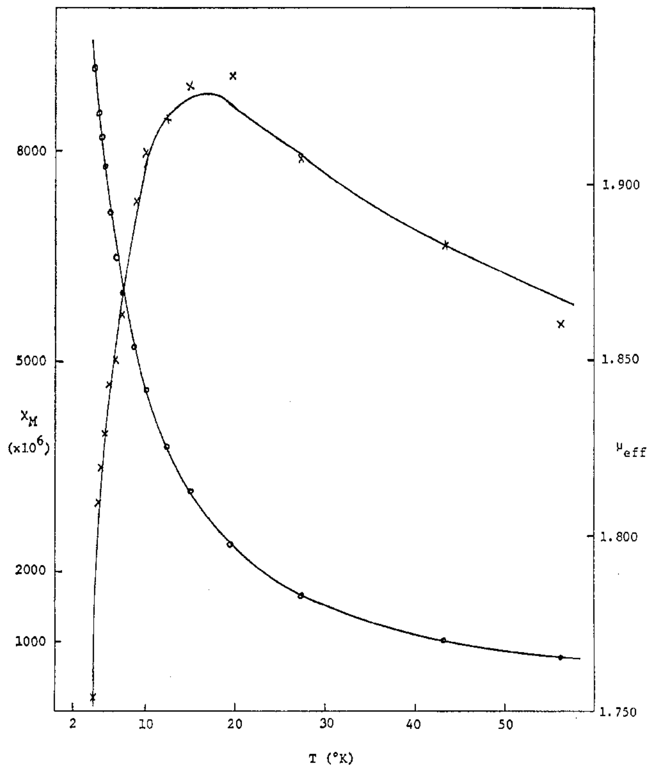

Figure 2.—Experimental and calculated (lines) molar magnetic susceptibility and effective magnetic moments of [Cu(edtc)$_2$]$_2$.

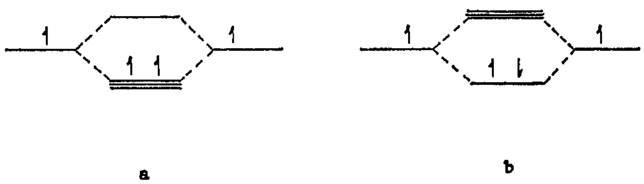

Figure 3.—Spin–spin interaction in a system with two spins of $^1/_2$

The data were interpreted with the modified Langevin equation (eq 2) and with eq 3 where all of the

$$\chi = \frac{Ng^2\beta^2}{3k(T-\Theta)}[1 + (1/3)e^{-2J/kT}]^{-1} \qquad (2)$$

$$\mu_{\text{eff}} = 2.83(\chi T)^{1/2} \qquad (3)$$

symbols have their usual meaning and Θ is a constant equivalent to the Weiss constant in the Curie–Weiss law equation.

A Fortran IV program were written to calculate the best fit of the data using a constant value of Θ and allowing g and $2J$ to vary. The calculated lines for the best fit of the χ_M and μ_{eff} are shown as solid lines, also in Figure 2. The criterion used to determine the best fit was an additional parameter, A, defined as shown in eq 4. It was felt that this type of fitting parameter was

$$A = \sum_i(\text{square of deviation})_i T_i \qquad (4)$$

needed when the triplet state is lowest in energy because the susceptibility increases considerably as the temperature decreases. If the sum of the squares of deviations is not weighted with temperature, the low-temperature susceptibilities have an unduly large effect on the best fit obtained.

In order to extract the magnetic parameters from the data, a contour map was built, Figure 4, where the points with the same A value are connected with a contour line. The parameters show an excellent convergence to the values of $g^2 = 4.1657$ ($g = 2.041$), $2J = +24.0$ cm^{-1}, and $A = 1.849 \times 10^{-4}$, with a constant value of $\Theta = -1.37°$. Other contour maps would have to be constructed to determine the suitability of the Θ parameter, but this work was avoided by noting that for values of Θ of -1.36 and $-1.38°$ the parameter A was 1.850×10^{-4} for the best fits, indicating that the values of the parameters obtained with $\Theta = -1.37°$ gives the overall best fit. Other values of Θ above and below 1.37° were also tried to avoid an artificial minimum. However, in these cases the values of A changed rapidly to larger values, corroborating the best fit.

Discussion

It is very interesting that the Hamiltonian of eq 1 can be used to interpret the results. This means that there is an interaction between the spins on the two adjacent copper ions. Furthermore, the value of $2J$ is positive

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[9] J. Lewis and R. G. Wilkins, "Modern Coordination Chemistry," Interscience, New York, N. Y., 1960, p 403.

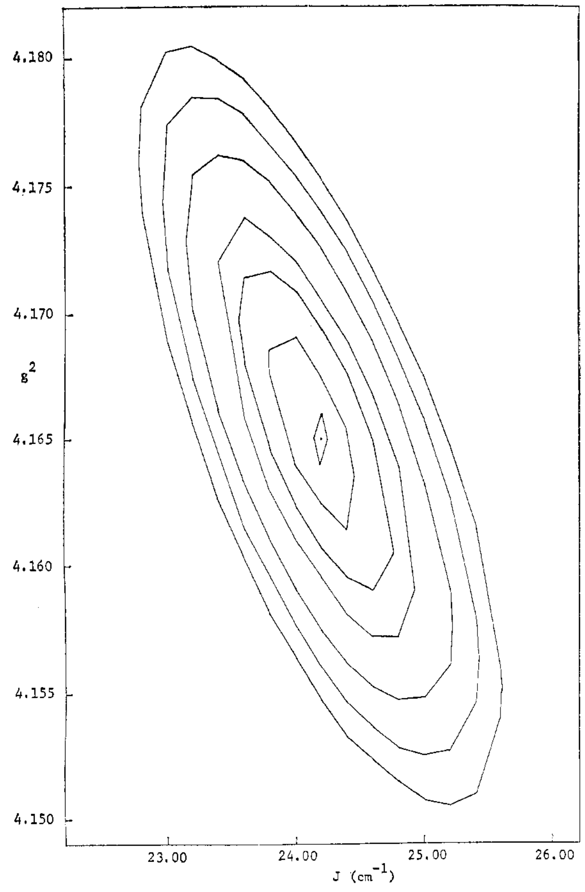

Figure 4.—Contour map defining best fit of the magnetic parameters for $[Cu(edtc)_2]_2$. $\Theta = -1.37°$ and $A_{best} = 1.849 \times 10^{-4}$.

indicating a triplet ground state. This type of behavior has been observed very recently in compounds of copper with oxygen-bridged ligands[10,11] but never in sulfur-bridged ones.

There are two possible mechanisms to account for this type of coupling. One is the magnetic dipolar coupling which gives rise to a tensor, D_{dd}, pointing along the line between the two copper ions. In this case D_{dd} is about 0.024 cm^{-1}. This value is obtained from eq 5 using the known values for $r = 3.54$ Å, $\alpha = 40°$,

$$D_{dd} = \frac{0.325 g_{\parallel}^2(1 - 3\cos^2\alpha)}{r^3} \qquad (5)$$

and $g_{\parallel} = 2.093$.

The relatively small magnitude of the D_{dd} tensor and the absence of a rhombic component in the g tensors are indicative that the dipolar exchange plays, as expected, a small role in the coupling mechanism in $[Cu(edtc)_2]_2$.

The second mechanism of spin coupling is that of σ-orbital superexchange, similar to the 90° interaction discussed by Goodenough and Anderson.[12,13] The model proposed is shown in Figure 5. It can be observed that there will be two different transmitting effects acting in this model of superexchange. One is the partial electron transfer between overlapping orbitals and the second is the intraatomic coupling between orthogonal orbitals. The former effect is acting between the copper 1 and the sulfur p_x orbitals (a–b in Figure 5) and between the sulfur p_y orbitals and the copper d_{z^2} orbitals (e–f), while the latter effect occurs between the sulfur p_x and p_y orbitals (c–d). The end result is the production of a triplet state. Apparently, this superexchange mechanism is of the utmost importance in the present case since the only other additional coupling mechanism that could be effective here is the "direct superexchange" which on the basis of the Cu–Cu distance would be expected to be less important.

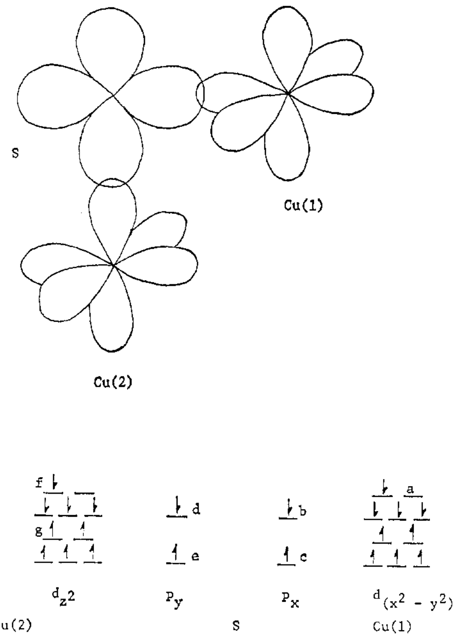

Figure 5.—Model for out-of-plane interactions in $[Cu(edtc)_2]_2$.

It should be noticed that the superexchange mechanism works through the out-of-plane bonds. These out-of-plane interactions have usually being disregarded in the interpretation of the electronic properties of coordination compounds. However, this is one example where these interactions play a key role. Furthermore, very recently we have reported[14] that these out-of-plane bonds are also relatively strong in the zinc analog of $[Cu(edtc)_2]_2$, in which these bonds hold even in pressures down to 10^{-7} Torr.

Our g value of 2.041 compares very favorably with the g value of 2.049 previously obtained by epr.[2] However, the $2J$ value previously reported[2] does not agree very well with the value obtained here. The reasons for this discrepancy are twofold. First, the magnetic parameters are not as responsive in the higher temperature range as they are in the temperature range used in this investigation. We determined that in this system the magnetic susceptibility changed by about 12-fold from 4 to 55°K, while it changed by only fourfold from 77 to 300°K. This allowed us to determine the value of $2J$ with a higher degree of certainty. Second, we included the parameter Θ in our calculations. We think this allows a more correct determination of the parameter $2J$, as will be shown below.

There is still another method of estimating $2J$ avail-

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[10] W. E. Hatfield, J. A. Barnes, D. Y. Jetter, R. Whyman, and E. R. Jones, Jr., *J. Amer. Chem. Soc.*, **92**, 4982 (1970).

[11] J. F. Villa and W. E. Hatfield, *J. Chem. Phys.*, in press.

[12] J. B. Goodenough, *Phys. Rev.*, **100**, 564 (1955).

[13] P. W. Anderson, "Magnetism," Vol. I, G. T. Rado and H. Suhl, Ed., Academic Press, New York, N. Y., 1963, p 201.

[14] J. F. Villa, M. M. Bursey, and W. E. Hatfield, *Chem. Commun.*, 307 (1971).

able to us. This is by using the Bleaney–Bowers approximation,[15] where it is assumed that J_1 and J_2 (from excited states) in eq 6 are equal to each other and equal

$$D_{\text{exch}} = -(1/8)[(J_1(g_{\parallel} - 2)^2/4) - J_2(g_{\perp} - 2)^2] \quad (6)$$

to the ground-state $2J$ value. D_{exch} is calculated from eq 7, D_{dd} was calculated above using eq 5, and D_{exptl} is

$$D_{\text{exptl}} = D_{\text{dd}} + D_{\text{exch}} \quad (7)$$

obtained from epr data ($D_{\text{exptl}} = 0.028$). It can also be assumed that D_{exch} and D_{dd} have opposite signs.[16] The range of values of $|2J|$ calculated is 21–293 cm^{-1}. Our value of $+24.0$ cm^{-1} is located at the low end of that range.

The use of the modified Langevin equation (eq 2) should be reviewed. If the constant Θ has a finite value, it means that there are additional interactions present, most likely lattice (or sublattice) effects. A negative Θ indicates that the lattice tends to line the spins among the dimers in an antiparallel fashion. It should be obvious that the use of the Langevin equation without Θ would assume the nonexistence of any additional lattice effects and would actually lump all the additional effects together with the pairwise interaction in the value of $2J$. If, as is the case here, there are additional lattice antiferromagnetic effects, one would expect a smaller calculated value of $2J$ if Θ is disregarded That is what is seen, with the absolute values of $2J$ from ref 2 quite a bit lower than ours (7 and 1 *vs.* $+24.0$ cm^{-1}).

The energy value for this lattice interaction is small, about 1 cm^{-1}, but is quite noticeable at low temperatures, where the values of kT approach that value. It is interesting to note that the only other compound[17] with a positive $2J$ value reported outside this laboratory where appropriate data are available, bis(acetylacetonato)nickel(II), also shows a weak lattice antiferromagnetism at low temperatures. In that case $2J = +37$ cm^{-1} and $\Theta = -0.2°$. It appears, then, to be advisable when working in the low-temperature range, to test the experimental fit by using the Weiss constant Θ.

The biological implications of the type of spin interactions described here for $[\text{Cu(edtc)}_2]_2$ are not completely apparent at the present time. However, this same type of behavior might be displayed by other compounds of biological importance, where the out-of-plane coupling has been assumed weak or nonimportant. We are presently engaged in the study of some of these systems, in particular of tetrakis(tyrosinato)dicopper(II)[18] in order to shed some additional light on this important question.

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[15] B. Bleaney and K. D. Bowers, *Proc. Roy. Soc., Ser. A*, **214**, 451 (1952).

[16] G. F. Kokoszka, M. Linzer, and G. Gordon, *Inorg. Chem.*, **7**, 1730 (1968).

[17] A. P. Ginsberg, R. L. Martin, and R. C. Sherwood, *ibid.*, **7**, 932 (1968).

[18] S. H. Laurie, *Aust. J. Chem.*, **20**, 2609 (1967).

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
MONASH UNIVERSITY, CLAYTON, VICTORIA, AUSTRALIA 3168

Proton Knight Shifts and Antiferromagnetic Exchange in Binuclear Oxo-Bridged Iron(III) Porphyrins

BY P. D. W. BOYD AND T. D. SMITH*

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The temperature dependence of the Knight shifts of the pyrrole protons in the binuclear porphyrins μ-oxo-tetraphenylporphineiron(III) and μ-oxo-tetra(p-methylphenyl)porphineiron(III) have been used as a direct measure of the isotropic exchange parameter J. The values obtained are somewhat larger than those obtained from magnetic susceptibility data obtained for similar compounds in the solid phase. It is proposed that the reason for the increased value of J is the slight increase in the Fe(III)–O–Fe(III) bond angle which it is considered could occur when these binuclear chelates exist in solution.

The solvent conditions permitting hemin aquation or heme autoxidation may frequently lead to the formation of binuclear oxo-bridged iron(III) porphyrins.[1] The synthesis, characterization, and structure of μ-oxo-bis(tetraphenylporphine)iron(III) was studied by Fleischer and Srivastava.[2] The magnetic data for this compound gave $\mu_{\text{eff}} = 1.15$ BM, clearly indicating an antiferromagnetic interaction between the iron(III) atoms. The Fe–O–Fe bond angle was found to be 168° involving a tilting of the porphyrin rings though the remainder of the tetraphenylporphyrin structure is much the same as for other porphyrins. The room-temperature magnetic data for μ-oxo-bis(tetraphenylporphineaquoiron(III)) ions reported by Cohen,[3] who determined μ_{eff} to be 1.74 BM per ion and interpreted the results of previous magnetic studies of hemins in terms of mixtures of high-spin hydroxo and low-spin oxo binuclear species.

The nmr spectra of iron(III) porphyrins have been studied to measure Fermi contact shifts,[4] contact shift

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[1] N. Sadasivan, H. I. Eberspaecher, W. H. Fuchsman, and W. S. Caughey, *Biochemistry*, **8**, 536 (1969).

[2] E. B. Fleischer and T. S. Srivastava, *J. Amer. Chem. Soc.*, **91**, 2403 (1969).

[3] I. A. Cohen, *ibid.*, **91**, 1980 (1969).

[4] D. R. Eaton and E. A. Lalancette, *J. Chem. Phys.*, **41**, 3534 (1961).