

the complex has not been formed with 100% stereospecificity.

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Correspondence

Spin-Spin Coupling in Magnetically Condensed Complexes. IX. Exchange Coupling Constants for Tetranuclear Schiff's Base Complexes of Copper(II)¹

Sir:

Tridentate Schiff's base ligands derived from acetylacetone or salicylaldehydes and *o*-aminophenol form copper(II) complexes with unusual magnetic properties.² Although acetylacetonemono(*o*-hydroxyanil)copper(II) is reported to exhibit temperature-dependent magnetism which, like dimeric copper(II) acetate monohydrate, can be described by the exchange-coupled dimer equation for a singlet ground state and low-lying triplet state,³ other similar complexes have shown complex magnetic behavior.⁴ Barclay and Hoskins⁵ have noted that some of these latter compounds exhibit antiferromagnetism but that there are features which are different from copper acetate. A clue to the source of the deviation is found in the description of the crystal structure of acetylacetonemono(*o*-hydroxyanil)-copper(II).⁵ Although the molecule has frequently been described as a dimer, it is actually *tetrameric*. As shown schematically in Figure 1, the dimeric units are associated into pairs by coordination of bridging oxygen atoms to copper ions in adjacent molecules. The purpose of this correspondence is to show that the magnetic behavior can be described if electron spin-spin interactions among all four copper ions are taken into account. Intermolecular effects between tetramers would have to be transmitted through contacts of copper atoms 3 and 4 with carbon atoms of tetramers in adjacent unit cells. Since the Cu-C internuclear distances of 3.22 Å are on the order observed for the van der Waals forces, it is not expected that important spin-spin interactions will be transmitted through these linkages.

The arrangement of the magnetic ions presents a four-spin problem similar in essential details to the A_2X_2 problem in high-resolution nuclear magnetic resonance.⁶ Four exchange coupling constants are required to describe the spin-spin interactions; these are $J_{13} = J_{24}$, $J_{23} = J_{14}$, J_{12} , and J_{34} . Although the numbering of the

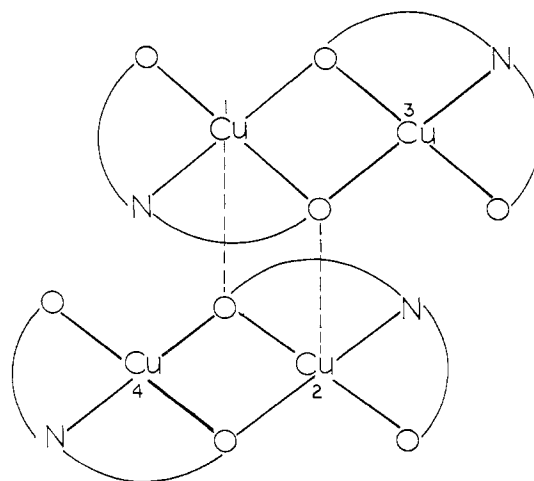


Figure 1.—A schematic representation of the structure of acetylacetonemono(*o*-hydroxyanil)copper(II).

copper ions in Figure 1 is arbitrary, once they are numbered it is then possible to associate a specific coupling constant with the corresponding spin-spin interaction.⁷ The Hamiltonian appropriate for the problem is

$$H = -2J_{12}S_1 \cdot S_2 - 2J_{13}(S_1 \cdot S_3 + S_2 \cdot S_4) - 2J_{14}(S_1 \cdot S_4 + S_2 \cdot S_3) - 2J_{34}S_3 \cdot S_4$$

Spin wave functions and the elements of the energy matrix are given in Table I. The energy matrix factors into one 4×4 matrix, $Q(i, j)$, five 2×2 matrices, and two 1×1 matrices. While algebraic expressions in terms of the exchange coupling constants can be written for the 12 energy levels resulting from the 2×2 and 1×1 matrices, it is necessary to solve the 4×4 matrix $Q(i, j)$ in terms of choices of J parameters in order to obtain the remaining four eigenvalues.

Eigenvalues calculated for choices of the exchange coupling constants and the first-order Zeeman terms, $E_n^{(1)}$, equal to $M_n g \beta$ were substituted into the Van Vleck susceptibility expression yielding eq 1 per gram-atom of copper. The Landé g factor, temperature independent paramagnetism TIP, and the coupling constants J_{12} , J_{13} , J_{14} , and J_{34} were varied systematically, and a set of temperature-dependence-of-susceptibility curves was compiled for graphical comparison. The calculations were performed by a program written in Fortran IV for the IBM 360/75 computer of the University of North Carolina Computation Center, and the calculated and experimental curves were drawn by the Calcomp plotter.

(7) See ref 6, p 138 ff.

(1) Supported by the National Science Foundation under Grant GP-7400.

(2) M. Kishita, Y. Muto, and M. Kubo, *Australian J. Chem.*, **10**, 386 (1957).

(3) G. A. Barclay, C. M. Harris, B. F. Hoskins, and E. Kokot, *Proc. Chem. Soc.*, 264 (1961).

(4) W. E. Hatfield and E. L. Bunger, *Inorg. Chem.*, **5**, 1161 (1966).

(5) G. A. Barclay and B. F. Hoskins, *J. Chem. Soc.*, 1979 (1965).

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TABLE I
 SPIN WAVE FUNCTIONS AND ELEMENTS OF THE ENERGY MATRIX^a

Wave Function	M_s	Diagonal elements	Off-diagonal elements
1. $\alpha\alpha\alpha\alpha$	2	$(-K/2) - N$	
2. $(1/\sqrt{2})(\alpha\beta + \beta\alpha)\alpha\alpha$	1	$-K/2$	$\langle 2 H 3 \rangle = -N$
3. $(1/\sqrt{2})\alpha\alpha(\alpha\beta + \beta\alpha)$	1	$-K/2$	
4. $\beta\beta\alpha\alpha$	0	$(-K/2) + N$	$\langle 4 H 5 \rangle = 0, \langle 5 H 6 \rangle = -L$
5. $\alpha\alpha\beta\beta$	0	$(-K/2) + N$	$\langle 4 H 6 \rangle = -L, \langle 5 H 7 \rangle = -N$
6. $1/2(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)$	0	$3K/2$	$\langle 4 H 7 \rangle = -N, \langle 6 H 7 \rangle = L$
7. $1/2(\alpha\beta + \beta\alpha)(\alpha\beta + \beta\alpha)$	0	$-K/2$	
8. $(1/\sqrt{2})(\alpha\beta + \beta\alpha)\beta\beta$	-1	$-K/2$	$\langle 8 H 9 \rangle = -N$
9. $(1/\sqrt{2})\beta\beta(\alpha\beta + \beta\alpha)$	-1	$-K/2$	
10. $\beta\beta\beta\beta$	-2	$(-K/2) - N$	
11. $(1/\sqrt{2})(\alpha\beta - \beta\alpha)\alpha\alpha$	1	$(+K/2) + M$	$\langle 11 H 12 \rangle = L$
12. $(1/\sqrt{2})\alpha\alpha(\alpha\beta - \beta\alpha)$	1	$(+K/2) - M$	
13. $1/2(\alpha\beta + \beta\alpha)(\alpha\beta - \beta\alpha)$	0	$(+K/2) - M$	$\langle 13 H 14 \rangle = L$
14. $1/2(\alpha\beta - \beta\alpha)(\alpha\beta + \beta\alpha)$	0	$(+K/2) + M$	
15. $(1/\sqrt{2})(\alpha\beta - \beta\alpha)\beta\beta$	-1	$(+K/2) + M$	$\langle 15 H 16 \rangle = L$
16. $(1/\sqrt{2})\beta\beta(\alpha\beta - \beta\alpha)$	-1	$(+K/2) - M$	

^a $K = J_{12} + J_{34}$; $L = J_{14} - J_{13}$; $M = J_{12} - J_{34}$; $N = J_{14} + J_{13}$.

$$\chi_M = \frac{3 g^2}{32 T} \frac{10 \exp\{[(K/2) + N]/kT\} + 2 \exp\{[(K/2) - N]/kT\} + 2 \exp\{[(-K/2) + \sqrt{M^2 + L^2}]/kT\} + 2 \exp\{[(-K/2) - \sqrt{M^2 + L^2}]/kT\}}{4 \exp\{[(K/2) + N]/kT\} + \exp\{[(K/2) - N]/kT\} + \exp\{Q(1,1)/kT\} + \exp\{Q(2,2)/kT\} + \exp\{Q(3,3)/kT\} + \exp\{Q(4,4)/kT\} + 3 \exp\{[(-K/2) + \sqrt{M^2 + L^2}]/kT\} + 3 \exp\{[(-K/2) - \sqrt{M^2 + L^2}]/kT\}} + \text{TIP} \quad (1)$$

The magnetic susceptibility⁸ of acetylacetonemono-(2-hydroxy-5-nitroanil)copper(II) is typical. The susceptibility increases from 432×10^{-6} cgsu at 96°K to a broad maximum of $\sim 1050 \times 10^{-6}$ cgsu over the temperature range $240\text{--}340^\circ\text{K}$. As demonstrated in Figure 2, the susceptibility data may be adequately de-

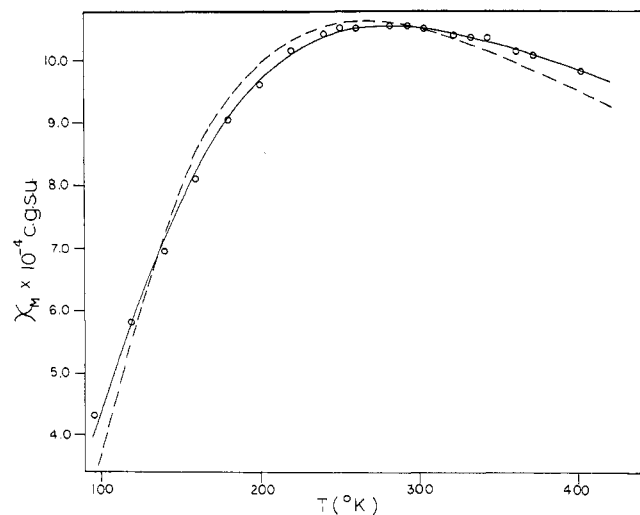


Figure 2.—The temperature dependence of magnetic susceptibility of tetrameric acetylacetonemono(*o*-hydroxy-5-nitroanil)-copper(II). Experimental points are compared to calculated values: —, tetramer equation; ----, dimer equation.

scribed using the tetramer equation and the coupling constants $J_{13} = -140$, $J_{12} = -48$, $J_{14} = 134$, and $J_{34} = 0 \text{ cm}^{-1}$, respectively. Values of 2.33 for g and 100×10^{-6} cgsu for TIP resulted from the graphical fitting process. After initial agreement of experimental and

(8) F. L. Bunger and W. E. Hatfield, unpublished observations.

calculated curves was obtained from graphical comparison, the set of parameters given above was obtained from a least-squares refinement. The sum of the squares of the deviations was 1.37×10^{-9} . By experimentation, other sets of parameters were found to give agreement with experiment; however, these fits usually obtained with absurd values⁹ for one or more of the parameters and could be discarded. The final choice was dictated by agreement with parameters for interactions between copper ions in structurally similar units.

The best fit of the magnetic data to the equation for exchange-coupled copper ions in a dimeric molecule yields $J_{12} = -148 \text{ cm}^{-1}$, $g = 2.31$, and $\text{TIP} = 100 \times 10^{-6}$ cgsu. A comparison of the experimental data with the susceptibilities calculated from the dimer equation is set out in Figure 2, where it can be seen that the agreement between experimental and calculated values is much less satisfactory.

The sign and magnitude of the coupling constants are consistent with the following mechanisms:¹⁰ (1) antiferromagnetic superexchange between adjacent ion pairs 1-3, 2-4, and 1-2; (2) ferromagnetic superexchange between ion pairs 1-4 and 2-3.

As noted above coupling constants obtained for this tetrameric molecule are comparable to those found for less complicated dimeric copper compounds. For example, J_{13} is related to the spin-exchange process in pyridine N-oxide-copper chloride complexes, where the

(9) For example, the next best fit, as determined by $\Sigma \delta_i$, gave $J_{12} = -259$, $J_{34} = 185$, $J_{14} = 331$, and $J_{13} = 8.3 \text{ cm}^{-1}$. Surely the interaction between copper ions 3 and 4 cannot be many times greater than the interaction between the adjacent copper ions 1 and 3.

(10) (a) P. W. Anderson, *Phys. Rev.*, **115**, 2 (1959). (b) See, for example, A. P. Ginsberg, R. L. Martin, and R. C. Sherwood, *Inorg. Chem.*, **7**, 932 (1968), for a related discussion on $[\text{Ni}(\text{acac})_2]_2$.

antiferromagnetic coupling constants range from 72 to 1075 cm^{-1} depending on pyridine ring substituents.¹¹ In the binuclear pyridine N-oxide complexes both bridging oxygen atoms may transmit magnetic effects; however, in this case the fourth pair of electrons on one bridging oxygen atom is tied up in out-of-plane bond formation with a copper ion in an adjacent binuclear fragment. A simple model for the ferromagnetic interactions between pairs 1-4 and 2-3 may also exist. The pyridine N-oxide complex of copper nitrate, $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_2(\text{NO}_3)_2]_2$, is binuclear, with a structure which may be described as two tetragonal pyramids sharing a base-to-apex edge.¹² If the copper ions in this binuclear molecule are coupled, the tem-

perature-independent moment of 1.9 BM per copper ion in $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})_2(\text{NO}_3)_2]_2$ shows that the triplet state lies lowest and that the exchange integral is positive. Thus it has been possible to account for the magnetic properties of acetylacetonemono(2-hydroxy-5-nitroanil)copper(II) in terms of its tetrameric structure and to choose meaningful exchange-coupling constants by reference to simple molecules with common structural features.

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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NORTH CAROLINA
CHAPEL HILL, NORTH CAROLINA 27514

WILLIAM E. HATFIELD
GUY W. INMAN, JR.¹³

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