

Contribution from the Dipartimento di Chimica and Istituto di Mineralogia e Cristallografia, Università di Perugia, 06100 Perugia, Italy, and the Department of Chemistry, The University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27514

Exchange Interaction in Multinuclear Transition-Metal Complexes. 3.¹ Synthesis, X-ray Structure, and Magnetic Properties of $\text{Cu}_2\text{L}(\text{CH}_3\text{COO})_2 \cdot 2\text{CH}_3\text{OH}$ (L^{2-} = Anion of N,N' -Bis(2-((*o*-hydroxybenzhydrylidene)amino)ethyl)-1,2-ethanediamine), a One-Dimensional Heisenberg Antiferromagnet Having Through-Bond Coupled Copper(II) Ions

B. CHIARI,[†] W. E. HATFIELD,[‡] O. PIOVESANA,*[†] T. TARANTELLI,[†] L. W. TER HAAR,[‡] and P. F. ZANAZZI[†]

Received November 9, 1982

The synthesis, crystal structure, and magnetic properties are reported for the new compound $\text{Cu}_2\text{L}(\text{CH}_3\text{COO})_2 \cdot 2\text{CH}_3\text{OH}$, where L^{2-} is the hexadentate anion of N,N' -bis(2-((*o*-hydroxybenzhydrylidene)amino)ethyl)-1,2-ethanediamine, $[(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4\text{OH})\text{C}=\text{N}-(\text{CH}_2)_2-\text{NH}-\text{CH}_2-]_2$. The compound crystallizes in the triclinic space group $P\bar{1}$. Cell dimensions are $a = 8.080$ (3) Å, $b = 8.166$ (3) Å, $c = 16.688$ (4) Å, $\alpha = 91.33$ (2)°, $\beta = 113.86$ (2)°, and $\gamma = 107.29$ (2)°. The structure was solved by full-matrix least-squares techniques to a conventional R value of 0.068. In the dinuclear molecule each copper atom is bonded to two cis nitrogens and one phenolic oxygen of L^{2-} , and a fourth coordination site, to make an approximate plane, is furnished by one oxygen atom of an acetate anion. The second oxygen of each acetate ligand is strongly hydrogen bonded to a methanol molecule but is not involved in any bonding to the copper atom. A 1,2-ethanediamine fragment of L^{2-} bridges in an extended fashion the two copper atoms, with the Cu-N directions, when viewed along an N-C bond, forming an angle of 13.8° with the C-C bond. The dinuclear molecules are stacked along the crystallographic b axis. Adjacent molecules along this axis are linked by Cu_2O_2 bridging units that involve the coordinated oxygen atoms of the acetate anions. A zigzag chain is formed in which the copper atoms are alternately spaced and alternately ligand bridged. In the strictly planar Cu_2O_2 bridging units the angle at the oxygen atom is 98.3 (5)° and the Cu-O distance is 2.495 (6) Å. The magnetic susceptibility of the compound has been examined between 4.2 and 80 K. A maximum in the susceptibility at 14.2 K is indicative of antiferromagnetic exchange interaction. The best fit of the magnetic susceptibility data by alternating-chain theory yields values for the exchange coupling constants of -7.88 and -1.50 cm^{-1} , with use of the experimental ESR g value of 2.109. The effectiveness of the 1,2-ethanediamine bridges in propagating magnetic exchange between the copper(II) ions through a σ type of exchange pathway is discussed.

Introduction

Dinuclear and polymeric copper(II) compounds in which the metal centers are bridged by pyrazine (pyz) or 1,4-diazabicyclo[2.2.2]octane (Dabco) have occupied considerable experimental and theoretical work. The basic question under study is the effectiveness of polyatomic bridging ligands in propagating magnetic exchange between transition-metal ions through a σ type of exchange pathway.

Hoffmann et al.² have analyzed the magnetic exchange interactions for a variety of Cu(II) dimers in terms of pairwise interactions of dimeric molecular orbitals. According to this approach (which has recently been disputed³), since the through-bond coupling of the N lone pairs in pyz and Dabco is large, producing splittings between symmetric and anti-symmetric lone pair combinations of 1-2.5 eV,⁴ metal centers coordinated to such systems with the appropriate symmetry should respond to the energy splitting by showing a sizable antiferromagnetic coupling.

This view is not supported by the experimental evidence that is so far available. The magnetic susceptibility data that have been reported for copper(II) complexes bridged by Dabco,^{5,6} having a σ framework only, do not reveal any sign of exchange interaction down to 4.2 or 1.8 K. On the other hand, it seems to be well established with structural data that the weak antiferromagnetic⁵⁻¹¹ or ferromagnetic¹² interactions observed for several pyz-bridged copper(II) complexes and related systems, in which both σ and π mechanisms are available for spin exchange, are determined by the orientation of the π system of pyz relative to the copper(II) ion coordination plane. It has been deduced⁶ from CNDO/2 molecular orbital cal-

culations for the pyrazine molecule that its apparent inability to support exchange interaction between σ -bonded copper(II) ions is attributable to a small contribution of the carbon 2p _{σ} orbitals to the highest occupied a_g orbital (D_{2h} symmetry), the one that should be the main propagator of interaction.

As in the case of pyz and Dabco, photoelectron spectroscopy has provided abundant evidence for the splitting of the lone-pair levels of 1,2-ethanediamine.² With the aim of providing some answers to questions regarding the effectiveness of σ -orbital pathways in supporting spin-spin coupling, we here report the preparation, single-crystal X-ray structure, and magnetic properties of a new system having $\text{Cu}_2(1,2\text{-ethanediamine})$ bridging units, this being $\text{Cu}_2\text{L}(\text{CH}_3\text{COO})_2 \cdot 2\text{CH}_3\text{OH}$, where L^{2-} is the hexadentate anion of N,N' -bis(2-((*o*-hydroxybenzhydrylidene)amino)ethyl)-1,2-ethanediamine,

- (1) Part 2: Chiari, B.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F. *Inorg. Chem.* **1982**, *21*, 2444.
- (2) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884.
- (3) de Loth, P.; Cassoux, P.; Daudey, J. P.; Malrieux, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 4007.
- (4) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1. Gleiter, R. *Angew. Chem.* **1974**, *86*, 770.
- (5) Richardson, H. W.; Wasson, J. R.; Hatfield, W. E. *Inorg. Chem.* **1977**, *16*, 484.
- (6) Haddad, M. S.; Hendrickson, D. N.; Cannady, J. P.; Drago, R. S.; Bielsza, D. S. *J. Am. Chem. Soc.* **1979**, *101*, 898.
- (7) Villa, J. F.; Hatfield, W. E. *J. Am. Chem. Soc.* **1971**, *93*, 4091.
- (8) Losee, D. B.; Richardson, H. W.; Hatfield, W. E. *J. Chem. Phys.* **1973**, *59*, 3600.
- (9) Richardson, H. W.; Hatfield, W. E. *J. Am. Chem. Soc.* **1976**, *98*, 835.
- (10) Richardson, H. W.; Hatfield, W. E.; Stoklosa, H. J.; Wasson, J. R. *Inorg. Chem.* **1973**, *12*, 2051.
- (11) (a) Stoklosa, H. J.; Wasson, J. R.; Brown, E. W.; Richardson, H. W.; Hatfield, W. E. *Inorg. Chem.* **1975**, *14*, 2378. (b) Richardson, H. W.; Wasson, J. R.; Hatfield, W. E.; Brown, E. W.; Plas, A. *Ibid.* **1976**, *15*, 2916.
- (12) O'Connor, C. J.; Klein, C. L.; Majeste, R. J.; Trefonas, L. M. *Inorg. Chem.* **1982**, *21*, 64.

* To whom correspondence should be addressed at the Dipartimento di Chimica, Università di Perugia.

[†] Università di Perugia.

[‡] University of North Carolina.

$[(C_6H_5)(C_6H_4OH)C=N-(CH_2)_2-NH-CH_2-]_2$.

The system is of further interest since its X-ray structure shows that adjacent copper(II) ions of different dinuclear molecules are linked by Cu_2O_2 units. A polymeric one-dimensional structure is attained in which the exchange integral alternates periodically between two values. Few transition-metal compounds with alternating structures have been reported.¹³ Materials of this type are important theoretically and experimentally since they represent simple magnetic systems with extended interactions.¹⁴

Experimental Section

$Cu_2L(CH_3COO)_2 \cdot 2CH_3OH$. A 0.005-mol quantity of triethylenetetramine was added to a warm solution of 0.01 mol of 2-hydroxybenzophenone in 50 mL of methanol. The reaction mixture was heated at $\sim 70^\circ C$ for 30 min; then an additional 120 mL of warm methanol was added. To the clear, hot solution was added 0.01 mol of $Cu(CH_3COO)_2 \cdot H_2O$. The addition was made over a period of 20 min, with constant stirring. The resulting clear solution was stirred for an additional 1.5 h at $70^\circ C$. After cooling of the solution to room temperature, crystallization was allowed to continue for ~ 12 h before green-blue, microcrystalline $Cu_2L(CH_3COO)_2 \cdot 2CH_3OH$ was collected by filtration, washed with methanol, and dried under vacuum; yield 1.6 g (39%). The product softens at $\sim 210^\circ C$, without melting. Anal. Calcd for $C_{38}H_{46}N_4O_8Cu_2$: C, 56.08; H, 5.70; N, 6.88; O, 15.73; Cu, 15.61. Found: C, 55.92; H, 5.76; N, 6.94; O, 15.52; Cu, 15.74.

Crystals suitable for X-ray analysis were obtained, with a lower yield, by adding a filtered solution of 7.5 mmol of $Cu(CH_3COO)_2 \cdot H_2O$ in 200 mL of methanol to a warm solution of 5 mmol of triethylenetetramine and 10 mmol of 2-hydroxybenzophenone in 50 mL of methanol. The reaction mixture was heated for 1 h, and it was then allowed to cool to room temperature. Green-blue crystals were formed.

The title compound is air stable. It is generally sparingly soluble in organic solvents so as to prevent significant solution measurements. It presents a very slight solubility in methanol, where it exhibits a strictly nonelectrolytic behavior.

Chemical Analyses. These were performed by Mikroanalytisches Laboratorium, Elbach, West Germany.

Conductivity Measurements. These were made with a Philips PW 9501 apparatus.

ESR Spectra. These were obtained with a Varian E-109 spectrometer, operated at X-band, with diphenylpicrylhydrazyl (DPPH) free radical as internal reference.

Magnetic Measurements. Magnetic susceptibility data were collected on powdered samples of the compound with use of a Princeton Applied Research Model 155 vibrating-sample magnetometer and procedures that have been described elsewhere.¹³ Susceptibilities were corrected for the diamagnetism of the ligand system (-198×10^{-6} cgsu/Cu atom) and for the temperature-independent paramagnetism, $N\alpha$, of copper(II) (estimated to be 60×10^{-6} cgsu/Cu atom).

X-ray Data and Structure Solution. A crystal of $Cu_2L(CH_3COO)_2 \cdot 2CH_3OH$ with dimensions $0.4 \times 0.1 \times 0.1$ mm was mounted on a Philips PW 1100 four-circle diffractometer equipped with Mo radiation and a graphite monochromator. The crystal was determined to be triclinic. The centrosymmetric space group $P\bar{1}$ was assumed on the basis of intensity statistics and was later confirmed by the structure analysis. Cell dimensions, as determined by least-squares fitting of the angular ϑ , χ , and φ values of 25 reflections, are $a = 8.080$ (3) Å, $b = 8.166$ (3) Å, $c = 16.688$ (4) Å, $\alpha = 91.33$ (2)°, $\beta = 113.86$ (2)°, $\gamma = 107.29$ (2)°. For a cell content of $C_{36}H_{38}O_6N_4Cu_2 \cdot 2CH_3OH$ the calculated density is $D = 1.423$ g·cm⁻³, and the asymmetric unit of the structure is half of the molecule; i.e., the molecule must lie on a crystallographic inversion center.

The intensity data were measured with the ω - 2ϑ scan technique up to $\vartheta = 25^\circ$. The scan speed was 0.05° min⁻¹ and the scan width 1.4° . As a general check on the experimental conditions, the intensities of three reflections were monitored every 180 min. No significant variations during the period of data collection were detected. A total of 3254 independent reflections were measured; of these, 1594, having $I \leq 3\sigma(I)$,¹⁵ were considered as "unobserved". The intensities were

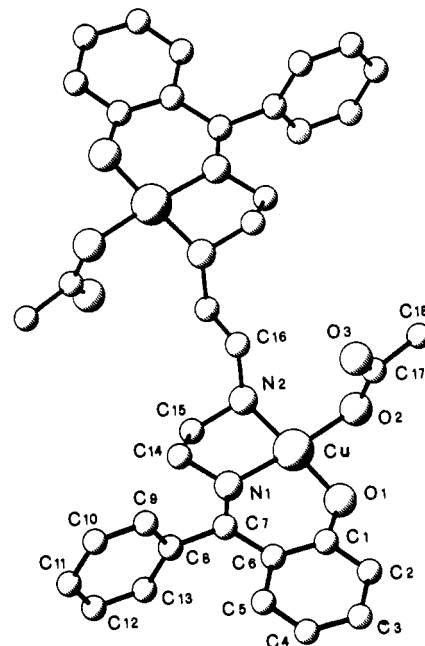


Figure 1. Molecular structure of $Cu_2L(CH_3COO)_2 \cdot 2CH_3OH$. The solvent molecules and hydrogen atoms are not shown for clarity.

corrected for Lorentz and polarization factors but not for absorption ($\mu = 11.51$ cm⁻¹ for Mo $K\alpha$).

The structure was solved by the direct multisolution method with the centrosymmetric routine of the SHELX-76 set of programs.¹⁶ The E map for the best solution showed the position of the Cu atom at the asymmetric unit and part of the coordination sphere around the metal atom. The structure was completed by successive Fourier syntheses, which also showed the presence of solvent molecules hydrogen bonded to the complex. The refinement was carried out with the full-matrix least-squares method. The phenyl rings of the ligand moiety were constrained to perfect hexagons with C-C distances of 1.395 Å and C-C-C angles of 120° and were refined with their H atoms as rigid groups. The other H atoms were included at their expected positions. The distances from the bonded atoms were imposed as 1.08 Å. The H atoms of methyl groups were refined as rigid groups starting from the staggered position. All non-hydrogen atoms were refined isotropically, except for the Cu atom, and the O and N atoms of the copper coordination sphere, for which anisotropic thermal parameters were refined.

An overall isotropic thermal parameters $U = 0.11$ Å² was imposed on the hydrogen atoms. The refinement was stopped when all shift/esd ratios were less than 0.1. The R value¹⁷ converged to 0.068 for 1660 observed reflections and 114 parameters; R_w was 0.074. The atomic scattering factors of neutral O, N, C, and H were those of the SHELX system of programs. The Cu scattering curve was taken from ref 18. A correction for anomalous dispersion was applied. Lists of observed and calculated structure factors and the calculated hydrogen coordinates are available as supplementary material.

Results

Description of the Structure. Final positional and thermal parameters for $Cu_2L(CH_3COO)_2 \cdot 2CH_3OH$ are given in Table I. The dinuclear molecule and labeling scheme are shown in Figure 1. Tables II and III contain the bond lengths and angles, respectively. The ligand environments of the two copper atoms are identical owing to crystallographic inversion

(13) Hall, J. W.; Marsh, W. E.; Weller, R. R.; Hatfield, W. E. *Inorg. Chem.* **1981**, *20*, 1033 and references therein.

(14) Bonner, J. C. *J. Magn. Magn. Mater.* **1980**, *15-18*, 1003.

(15) Standard deviations on intensities were computed as $\sigma(I) = [P + 0.25(T_p/T_B)^2(B_1 + B_2) + (0.02I)^2]^{1/2}$, where P is the total peak count in a scan of time T_p , B_1 and B_2 are the background counts each in a time T_B (5 s), and I is the intensity equal to $P - 0.5(T_p/T_B)(B_1 + B_2)$.

(16) Sheldrick, G. M. "SHELX-76, a Program for Crystal Structure Determination"; University of Cambridge: Cambridge, England, 1976.

(17) The R index is defined as $\sum(|F_o| - |F_c|)/\sum|F_o|$ and R_w as $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, where the weighting factor w is $1/(\sigma^2(F) + 0.0013F^2)$.

(18) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 99.

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for $\text{Cu}_2\text{L}(\text{CH}_3\text{COO})_2 \cdot 2\text{CH}_3\text{OH}^a$

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> , Å ²
Cu	0.6287 (2)	0.1329 (2)	0.0994 (1)	
O(1)	0.7520 (11)	-0.0278 (9)	0.1479 (5)	
O(2)	0.6764 (9)	0.1064 (8)	-0.0051 (4)	
O(3)	0.9517 (11)	0.3156 (11)	0.0597 (5)	
N(1)	0.5840 (11)	0.1769 (10)	0.2027 (5)	
N(2)	0.4754 (13)	0.2890 (13)	0.0426 (6)	
C(1)	0.7896 (9)	-0.0732 (8)	0.2279 (4)	0.045 (2)
C(2)	0.7365 (9)	-0.0135 (8)	0.2897 (4)	0.039 (2)
C(3)	0.7805 (9)	-0.0738 (8)	0.3708 (4)	0.056 (3)
C(4)	0.8776 (9)	-0.1938 (8)	0.3901 (4)	0.062 (3)
C(5)	0.9307 (9)	-0.2534 (8)	0.3282 (4)	0.063 (3)
C(6)	0.8867 (9)	-0.1931 (8)	0.2471 (4)	0.055 (3)
C(7)	0.6344 (13)	0.1141 (12)	0.2743 (6)	0.038 (2)
C(8)	0.5883 (9)	0.1681 (8)	0.3474 (4)	0.045 (2)
C(9)	0.7150 (9)	0.3185 (8)	0.4085 (4)	0.053 (3)
C(10)	0.6755 (9)	0.3723 (8)	0.4767 (4)	0.065 (3)
C(11)	0.5091 (9)	0.2758 (8)	0.4838 (4)	0.068 (2)
C(12)	0.3823 (9)	0.1254 (8)	0.4227 (4)	0.074 (3)
C(13)	0.4219 (9)	0.0715 (8)	0.3545 (4)	0.059 (3)
C(14)	0.4869 (15)	0.3072 (14)	0.1916 (7)	0.055 (3)
C(15)	0.3600 (17)	0.2882 (15)	0.0926 (7)	0.066 (3)
C(16)	0.5753 (16)	0.4570 (15)	0.0327 (8)	0.067 (3)
C(17)	0.8295 (16)	0.2085 (14)	-0.0039 (7)	0.051 (3)
C(18)	0.8540 (18)	0.1967 (16)	-0.0893 (8)	0.077 (4)
O(4)	1.0099 (21)	0.4523 (19)	0.2172 (10)	0.159 (5)
C(19)	1.1287 (28)	0.3939 (25)	0.2793 (12)	0.133 (6)

atom	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Cu	0.047 (1)	0.043 (1)	0.039 (1)	0.022 (1)	0.024 (1)	0.009 (1)
O(1)	0.094 (6)	0.067 (5)	0.060 (5)	0.054 (5)	0.047 (4)	0.022 (4)
O(2)	0.048 (4)	0.048 (4)	0.050 (4)	0.005 (3)	0.033 (4)	0.008 (3)
O(3)	0.048 (5)	0.087 (6)	0.070 (5)	0.003 (4)	0.015 (4)	-0.012 (5)
N(1)	0.046 (5)	0.042 (5)	0.048 (5)	0.029 (4)	0.023 (4)	0.012 (4)
N(2)	0.067 (6)	0.093 (7)	0.052 (6)	0.046 (6)	0.038 (5)	0.029 (5)

^a The anisotropic temperature factors of Cu, O, and N atoms are in the form $\exp(-2\pi^2(\sum_i \Sigma_j h_i h_j a_i^* a_j^* U_{ij}))$.

Table II. Bond Lengths (Å) for $\text{Cu}_2\text{L}(\text{CH}_3\text{COO})_2 \cdot 2\text{CH}_3\text{OH}$

Cu-O(1)	1.882 (7)	C(14)-C(15)	1.525 (15)
Cu-O(2)	1.952 (6)	C(15)-N(2)	1.480 (13)
Cu-O(2) ^a	2.495 (6)	N(2)-C(16)	1.422 (13)
Cu-N(1)	1.944 (7)	C(16)-C(16) ^b	1.623 (22)
Cu-N(2)	2.026 (9)	C(17)-O(2)	1.262 (12)
O(1)-C(1)	1.331 (8)	C(17)-O(3)	1.210 (12)
C(2)-C(7)	1.478 (10)	C(17)-C(18)	1.520 (15)
C(7)-C(8)	1.504 (10)	O(4)-C(19)	1.309 (19)
C(7)-N(1)	1.271 (11)	O(4)···O(3)	2.632 (10)
N(1)-C(14)	1.473 (12)		

^a Symmetry 1 - *x*, -*y*, -*z*. ^b Symmetry 1 - *x*, 1 - *y*, -*z*.

Table III. Bond Angles (deg) in $\text{Cu}_2\text{L}(\text{CH}_3\text{COO})_2 \cdot 2\text{CH}_3\text{OH}$

O(1)-Cu-O(2)	90.0 (3)	C(3)-C(2)-C(7)	116.9 (8)
O(1)-Cu-N(1)	93.4 (3)	C(2)-C(7)-N(1)	122.9 (8)
O(1)-Cu-N(2)	175.3 (4)	C(2)-C(7)-C(8)	117.2 (7)
O(1)-Cu-O(2) ^a	91.5 (3)	N(1)-C(7)-C(8)	119.9 (8)
O(2)-Cu-N(1)	175.8 (3)	C(7)-N(1)-Cu	128.3 (6)
O(2)-Cu-N(2)	90.1 (3)	C(7)-N(1)-C(15)	120.7 (8)
O(2)-Cu-O(2) ^a	81.7 (3)	C(15)-N(1)-Cu	110.9 (6)
N(1)-Cu-N(2)	86.7 (3)	N(1)-C(15)-C(14)	109.1 (9)
N(1)-Cu-O(2) ^a	100.6 (4)	C(14)-N(2)-Cu	104.4 (6)
N(2)-Cu-O(2) ^a	83.9 (4)	C(14)-N(2)-C(16)	114.7 (9)
C(1)-O(1)-Cu	127.0 (5)	Cu-N(2)-C(16)	117.6 (7)
O(1)-C(1)-C(2)	125.3 (8)	N(2)-C(16)-C(16) ^b	110.3 (9)
C(1)-C(2)-C(7)	123.1 (8)		

^a Symmetry 1 - *x*, -*y*, -*z*. ^b Symmetry 1 - *x*, 1 - *y*, -*z*.

symmetry. Each copper atom is bonded to two cis nitrogens (Cu-N(1) = 1.944 (7) Å, Cu-N(2) = 2.026 (9) Å) and one phenolic oxygen (Cu-O(1) = 1.882 (7) Å) of hexadentate L²⁻, and a fourth coordination site, to complete an approximate coordination plane, is furnished by one oxygen atom of an acetate anion (Cu-O(2) = 1.952 (6) Å). Detailed atomic

Table IV. Deviations of Atoms from the Least-Squares Plane through the Square around Cu^a

$$4.567x + 4.197y + 0.609z = 3.475^b$$

atom	Δ	atom	Δ	atom	Δ
Cu	0.015 Å	O(2)	0.058	N(2)	-0.065
O(1)	-0.066	N(1)	0.058		

^a Esd's are less than 0.01 Å. ^b Equation of the plane (in the form $Ax + By + Cz = D$) in direct space.

deviations from the least-squares plane are in Table IV. A 1,2-ethanediamine fragment of L²⁻ bridges in an extended fashion the two copper atoms, with the Cu-N directions, when viewed along an N-C bond, forming an angle of 13.8° with the C-C bond. The second oxygen of each acetate ligand, O(3), is strongly hydrogen bonded to the oxygen atom, O(4), of a CH₃OH molecule, with an O(3)-O(4) separation of 2.632 (10) Å. Both Cu-O(3) and Cu-O(4) distances, 2.934 (7) and 3.200 (7) Å, respectively, are long with respect to bonding. Bond distances and angles of the L²⁻ ligand are normal.

As schematically shown in Figure 2, the dinuclear molecules are stacked along the crystallographic *b* axis. Adjacent molecules along this axis are linked by Cu₂O₂ bridging units that involve the coordinated oxygen atoms of the acetate anions. Therefore, each bridging oxygen simultaneously occupies an equatorial position on the copper atom of one molecule and an apical position on the adjacent copper atom of the successive molecule. The result is a zigzag chain in which the copper atoms are alternately spaced and alternately bridged. The copper-copper distances in the Cu₂(1,2-ethanediamine) and Cu₂O₂ units are 7.352 (2) and 3.383 (2) Å, respectively. Surprisingly, the small displacement (0.015 Å) of the copper atom from the principal ligand plane is on the opposite side of the axial oxygen atom. From the inter-

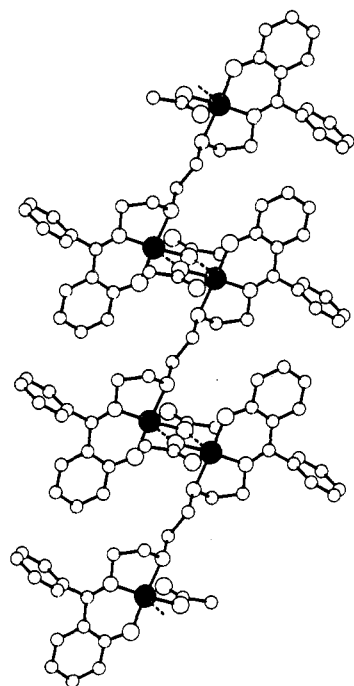


Figure 2. View of the structure $\text{Cu}_2\text{L}(\text{CH}_3\text{COO})_2 \cdot 2\text{CH}_3\text{OH}$ that shows the alternating $\text{Cu}_2(1,2\text{-ethanediamine})$ and Cu_2O_2 bridges.

chain contacts, which are longer than the sums of van der Waals radii, it appears that the individual chains in the structure are effectively isolated, leading to 1-D magnetic behavior.

The four-membered Cu_2O_2 bridging units are strictly planar, owing to inversion symmetry. The bridging angle at oxygen is $98.3(5)^\circ$. The Cu–O bridging distance is $2.495(6) \text{ \AA}$, in the range reported for structures involving parallel planar units linked by relatively long out-of-plane bonds.^{19–21}

The unusual one-atom acetate bridging in the present compound is similar to that recently observed²¹ for $[\text{Cu}(\text{L}')\text{-CH}_3\text{COO}]_2 \cdot \text{H}_2\text{O} \cdot \text{C}_2\text{H}_5\text{OH}$, where $\text{L}'\text{H} = N\text{-}(1,1\text{-dimethyl-2-hydroxyethyl})\text{salicylaldimine}$.

Magnetic Properties. In agreement with the coordination geometry revealed by the X-ray structure, the X-band ESR spectra of powdered samples of $\text{Cu}_2\text{L}(\text{CH}_3\text{COO})_2 \cdot 2\text{CH}_3\text{OH}$ are axial with $g_{\parallel} = 2.219$ and $g_{\perp} = 2.054$ ($g_{\text{av}} = 2.109$). There is no appreciable change in the spectrum in changing the temperature of the sample from room temperature to 77 K. Corrected magnetic susceptibility data are given in Figure 3. The maximum at 14 K in the χ_M vs. T curve clearly indicates the presence of an antiferromagnetic interaction.

The X-ray results for the compound show that the copper(II) ions are alternately spaced and alternately ligand bridged along the crystallographic b axis, with essentially no interaction between chains.

An appropriate Hamiltonian for such a system, in the Heisenberg model, may be written as

$$H = -2J \sum_{i=1}^{n/2} [\hat{S}_{2i} \hat{S}_{2i-1} + \alpha \hat{S}_{2i} \hat{S}_{2i+1}] \quad (1)$$

where J is the exchange integral between a spin and one of its nearest neighbors, and αJ is the exchange integral of the same spin with the other nearest neighbor in the chain. The case of immediate interest is for $J < 0$ (antiferromagnetic interaction) and $0 \leq \alpha \leq 1$. The model reproduces the dimeric

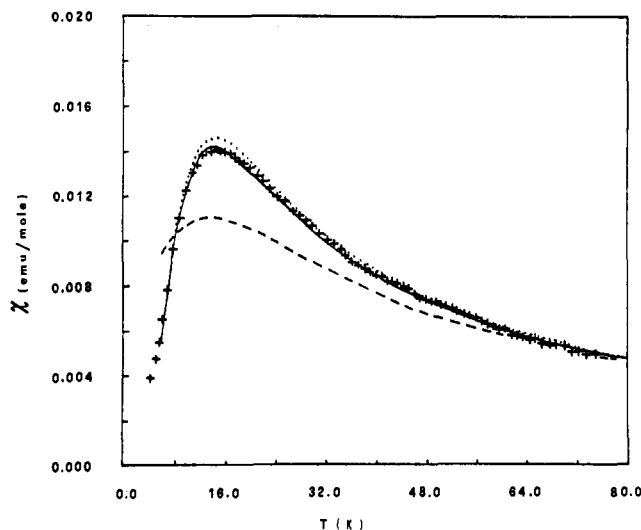


Figure 3. Magnetic susceptibility data for $\text{Cu}_2\text{L}(\text{CH}_3\text{COO})_2 \cdot 2\text{C}_2\text{H}_5\text{OH}$, between 4.2 and 80 K. The solid line through the data was generated by the expression given in the text for Heisenberg exchange in an alternately spaced chain with an exchange coupling constant of -7.88 cm^{-1} and an alternating parameter of 0.19. The best fit to the data obtained for (---) $\alpha = 1$ ($J = -7.63 \text{ cm}^{-1}$) and (···) $\alpha = 0$ ($J = -8.01 \text{ cm}^{-1}$) are also shown. The theoretical curves stop at ~ 6 K since below this temperature $kT/|J| < 0.5$.

case for $\alpha = 0$ and the uniform Heisenberg chain for $\alpha = 1$.

Solutions of the Hamiltonian (1) have been investigated by many authors,^{13,22–24} at various levels of approximation. Notable success was achieved by Bonner and Fisher²⁵ in inferring the physical properties of long regular chains of $S = 1/2$ spins by extrapolating from the behavior calculated for short chains of 2–11 spins. Duffy and Barr²² have applied the same approach to the alternating chain ($\alpha < 1$). Recently, Hatfield et al.^{13,24} have repeated the calculations reported by Duffy and Barr for the latter model system and obtained numerical data for the generation of the magnetic susceptibility in terms of the exchange coupling constant J and the alternation parameter α . The equation is

$$\chi_M = \frac{(Ng^2\mu_B^2/kT)[A + Bx + Cx^2][1 + Dx + Ex^2 + Fx^3]^{-1}}{\quad} \quad (2)$$

where $x = -J/kT$, and constants A – F are power series in terms of α .^{13,24} The expression is only valid for $kT/|J| > 0.5$ and for negative J values.

Equation 2 was used to fit the experimental data for $\text{Cu}_2\text{L}(\text{CH}_3\text{COO})_2 \cdot 2\text{CH}_3\text{OH}$. The function that was minimized in curve fitting, with use of a Simplex²⁶ nonlinear fitting routine, was

$$F = \sum_i (\chi_i^{\text{obsd}})^{-1} (\chi_i^{\text{obsd}} - \chi_i^{\text{calcd}})^2$$

The experimentally determined ESR g value of 2.109 was held

- (19) Hatfield, W. E. *Inorg. Chem.* **1972**, *11*, 216.
 (20) Brown, J. N.; Trefonas, L. M. *Inorg. Chem.* **1973**, *12*, 1730.
 (21) Greenaway, A. M.; O'Connor, C. J.; Overman, J. W.; Sinn, E. *Inorg. Chem.* **1981**, *20*, 1508.

- (22) Duffy, W.; Barr, K. P. *Phys. Rev.* **1968**, *165*, 647 and references therein.
 (23) Bonner, J. C.; Friedberg, S. A.; Kobayashi, H.; Meyers, B. E. *Proc. Int. Conf. Low Temp. Phys.* **1971**, *12*, 691. Bonner, J. C.; Friedberg, S. A. "Proceedings of the International Conference on Phase Transitions and their Applications in Material Science"; Hanish, H. K., Roy, R.; Cross, L. E., Eds.; Pergamon Press: New York, 1973; p 429. Bonner, J. C.; Blote, H. W. J.; Bray, J. W.; Jacobs, I. S. *J. Appl. Phys.* **1979**, *50*, 1810. Diederix, K. M.; Blote, H. W. J.; Groen, J. P.; Klaassen, T. O.; Poullis, N. *J. Phys. Rev. B: Condens. Matter* **1979**, *19*, 420.
 (24) Hatfield, W. E. *J. Appl. Phys.* **1981**, *52*, 1985.
 (25) Bonner, J. C.; Fisher, M. E. *Phys. Rev. [Sect.] A* **1964**, *135*, 640 and references therein.
 (26) Spendley, W.; Hext, G. R.; Himsworth, F. R. *Technometrics* **1962**, *4*, 441. Neider, J. A.; Mead, R. *Computer J.* **1965**, *7*, 308.

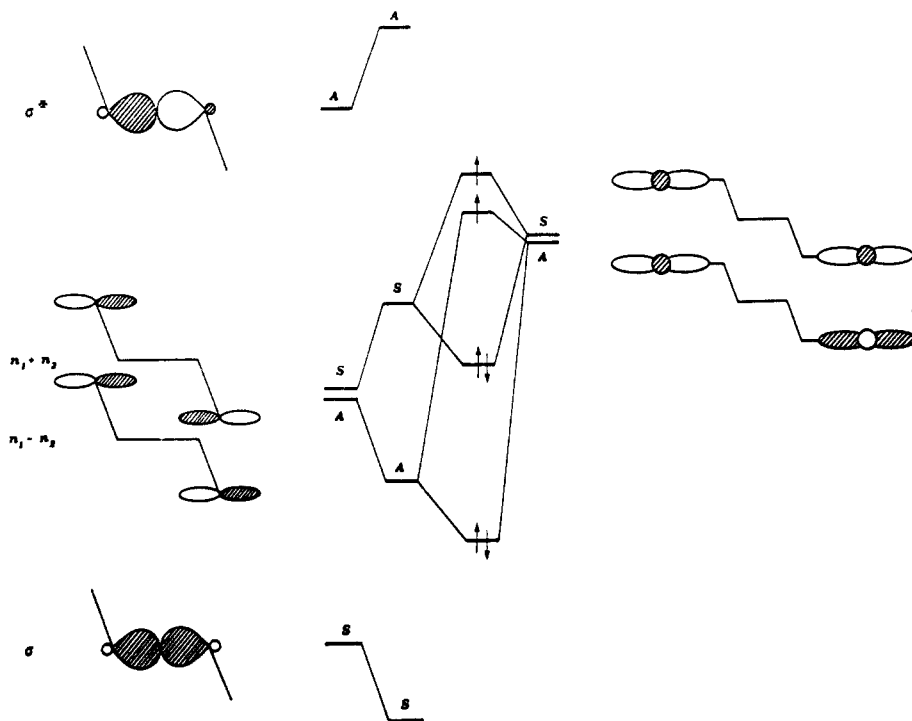


Figure 4. Hoffmann's orbital model applied to the $\text{Cu}_2(1,2\text{-ethanediamine})$ unit (labels S and A refer to inversion symmetry): (left) coupling of the $n_1 \pm n_2$ combinations of the N lone pairs (only the p component is shown) with the C-C σ bond orbitals; (right and center) S and A combinations of the $d_{x^2-y^2}$ -like orbitals and their interaction with the nitrogen orbitals. The square of the energy separation between the S and A antibonding MO's is used as a measure of the difference in energy between the triplet (shown) and singlet molecular states.

constant during all the fitting calculations. The best fit to the data yielded $J = -7.88 \pm 0.01 \text{ cm}^{-1}$ and $\alpha = 0.19$. This fit is illustrated in Figure 3. Data below 6 K are not significant to the fit since $kT/|J| < 0.5$. Figure 3 also shows, for purpose of comparison, the best fits that have been obtained through the use of either the uniform Heisenberg chain model or the dimer model. The uniform-chain model is clearly inadequate to explain the data, which appears to reflect the quite different nature of the alternating ligand bridges in the individual chains. The dimer model gives a fit that, although statistically rather close to the fit obtained for the alternating chain, poorly reproduces the susceptibility data in the temperature region where the maximum susceptibility is observed. It is well-known, on both experimental and theoretical grounds, that the principal effect of slightly increasing the alternation parameter from the limiting zero value is to shift the susceptibility peak to a lower temperature and to reduce its height.²² Although the differences in the susceptibility maxima between the curve calculated from the dimer model and the experimental curve are small (as expected for a small value of the alternation parameter), they strictly conform to this pattern.

Discussion

Strongly alternating antiferromagnetic spin chains, with J values of -7.88 and -1.50 cm^{-1} , account rather well for the magnetic behavior of $\text{Cu}_2\text{L}(\text{CH}_3\text{COO})_2 \cdot 2\text{CH}_3\text{OH}$. Corroborating crystal structure studies for the compound support this interpretation in showing 1-D behavior with alternate oxygen and 1,2-ethanediamine bridges. There seems to be little doubt, therefore, that the $\text{Cu}_2(1,2\text{-ethanediamine})$ bridging unit is antiferromagnetically coupled and, since the 1,2-ethanediamine framework lacks a π system, the exchange pathway must be of σ type. It can be seen from Figure 4 that the $\text{Cu}_2(1,2\text{-ethanediamine})$ unit strictly conforms to Hoffmann's design² of a σ -bonded antiferromagnetically coupled dimer. The ESR spectrum for the compound clearly indicates a σ -type $d_{x^2-y^2}$ ground state, and as mentioned above, the Cu-N(2) direction, when viewed along the N(2)-C(16) bond, forms an angle of only 13.8° with the crucial coupling C(16)-C(16)^b bond. The

unpaired electron is in an orbital that has the correct symmetry to interact with the through-bond coupled 1,2-ethanediamine lone pairs.

The present magnetic and structural data, therefore, represent direct evidence supporting the view that through-bond coupling can provide a mechanism for propagating magnetic exchange. However, although Hoffmann's theoretical analysis predicts the correct sign for the exchange interaction, its magnitude, as judged from a J value of either -7.88 or -1.50 cm^{-1} , appears to be weaker than was proposed.

In order to compare the effectiveness of the 1,2-ethanediamine bridge in propagating magnetic exchange to that of other polyatomic bridges, it would be clearly desirable to know whether the J value of -7.88 or -1.50 cm^{-1} pertains to the diamino bridge. In speculation of this point, it may be useful to consider what may be expected for the other bridging unit in the chain, the one involving the coordinated acetate oxygen atoms. The magnetic and structural properties of two other compounds are of particular interest in this respect: $[\text{Cu}(\text{L}')\text{CH}_3\text{COO}]_2 \cdot \text{H}_2\text{O} \cdot \text{C}_2\text{H}_5\text{OH}$ ²¹ ($\text{L}'/\text{H} = N\text{-(1,1-dimethyl-2-hydroxyethyl)salicylaldimine}$) and the hippurato derivative $[\text{Cu}[(\text{C}_6\text{H}_5)\text{CONHCH}_2\text{COO}]_2(\text{H}_2\text{O})_2]_2 \cdot 4\text{H}_2\text{O}$.^{20,27} These two dinuclear complexes are structurally related to our compound in that they have the copper atoms bridged through two coordinated oxygen atoms of the carboxylate anions, with each bridging oxygen simultaneously occupying an equatorial position on one copper atom and an apical position on the other copper atom in the dimer. In comparison to $\text{Fe}_2\text{L}(\text{CH}_3\text{COO})_2 \cdot 2\text{CH}_3\text{OH}$ the hippurato compound, showing a J value of -2.15 cm^{-1} , exhibits a larger bridging angle at oxygen, ϕ , of 101.0° and a shorter O-Fe bridging distance of 2.37 \AA . The (L')⁻ derivative has inequivalent ϕ angles of 102.7 and 95.7° , bridging distances of 2.446 and 2.651 \AA , and a J value of $+0.63 \text{ cm}^{-1}$. Smooth correlations of J with the quotient ϕ/R^0 (R^0 = long, out-of-plane Cu-X interatomic contact connecting

(27) Estes, E. D.; Estes, W. E.; Scaringe, R. P.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1975**, *14*, 2564.

planar units into dimers or extended chains) have been found for parallel-planar chloro- and sulfur-bridged copper complexes.²⁸ On the basis of the ϕ/R^0 quotient of 39.4 for the Cu_2O_2 unit in $\text{Cu}_2\text{L}(\text{CH}_3\text{COO})_2 \cdot 2\text{CH}_3\text{OH}$, as compared to the corresponding values of 42.6 for the hippurato compound and 35.0 (mean value) for the $(\text{L}')^-$ derivative, it may be tentatively suggested that a J value of -1.50 cm^{-1} , intermediate between those for the other two compounds, would not be

inappropriate for the Cu_2O_2 unit in the present system.

Acknowledgment. O.P. thanks W.E.H. for his hospitality during his stay at The University of North Carolina at Chapel Hill.

Registry No. $\text{Cu}_2[(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4\text{O})\text{C}=\text{N}(\text{CH}_2)_2\text{NHCH}_2-]_2(\text{C}-\text{H}_3\text{COO})_2 \cdot 2\text{CH}_3\text{OH}$, 84928-97-2.

Supplementary Material Available: Listings of the hydrogen atom coordinates and the observed and calculated structure factor amplitudes for $\text{Cu}_2\text{L}(\text{CH}_3\text{COO})_2 \cdot 2\text{CH}_3\text{OH}$ (11 pages). Ordering information is given on any current masthead page.

(28) Hatfield, W. E. *Comments Inorg. Chem.* 1981, 1, 105.

Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Canada S7N 0W0, and the Hahn-Meitner-Institut für Kernforschung Berlin GmbH, Bereich Strahlenchemie, D-1000 Berlin 39, Federal Republic of Germany

Pulsed-Laser Photochemical Study of Tris(2,2'-bipyridine)chromium(III) Ion in Acidic and Alkaline Aqueous Media

JOCHEN LILIE^{1a} and WILLIAM L. WALTZ^{*1b}

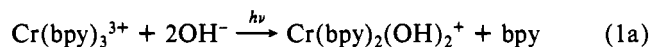
Received August 10, 1982

The photochemistry and photophysics of tris(2,2'-bipyridine)chromium(III) ion, $\text{Cr}(\text{bpy})_3^{3+}$, following pulsed-laser excitation at 347 nm, have been studied in acidic (pH 2.3–5.4) and alkaline (pH 9.4–11.0) aqueous media by using conductivity and visible optical detection methods. Evidence is presented to show that the lowest doublet excited state(s) is primarily responsible for chemical change, where in basic solution it accounts for about 93% of the photoaquation reaction. This state exhibits phosphorescence emission at 727 nm and an excited-state absorption band with a peak at 380 nm and a molar absorption coefficient of about $7000 \text{ M}^{-1} \text{ cm}^{-1}$. The decay of the absorption band and that of emission obey first-order rate laws with the respective rate constants of 1.5×10^4 and $1.6 \times 10^4 \text{ s}^{-1}$. The concomitant change in conductivity also follows a first-order rate law ($k \approx 1.8 \times 10^4 \text{ s}^{-1}$). In acidic media, the change involves an increase in conductivity associated with release of proton with a quantum yield of ca. 0.08. At longer times, the conductivity decreases, and this is described by a two-term rate law: $k_{\text{obsd}}(\text{acid}) = k_i' + k_a[\text{H}^+]$, with $k_i' = 39 \pm 9 \text{ s}^{-1}$ and $k_a = (8.7 \pm 0.4) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. In basic solution, the conductivity decreases in two stages and leads to net chemical change. The slower stage exhibits a two-term rate law: $k_{\text{obsd}}(\text{base}) = k_i + k_b[\text{OH}^-]$, with $k_i = 0.75 \pm 0.08 \text{ s}^{-1}$ and $k_b = (3.8 \pm 0.1) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$. Two possible mechanistic interpretations of the results are presented, one of which invokes the participation of an electronically excited intermediate that undergoes acidic dissociation with a $\text{p}K_a$ value less than 2.

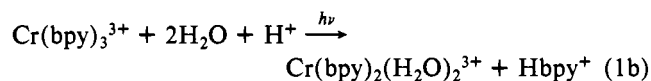
Introduction

A number of studies have appeared within recent years on the photochemistry and photophysics of aqueous and non-aqueous solutions containing chromium(III) complex ions with nitrogen heterocyclic ligands, the premier example being tris(2,2'-bipyridine)chromium(III), $\text{Cr}(\text{bpy})_3^{3+}$.²⁻¹⁹ Interest

in this and related systems derives both from the fundamental chemical and spectroscopic opportunities afforded by their study and from their relevance to solar energy conversion processes. Several excellent reviews have appeared recently covering these aspects.²⁻⁴ The results reported here focus on the photoaquation reaction of $\text{Cr}(\text{bpy})_3^{3+}$ where the overall process is in basic media



and in acidic solution



The photochemical and photophysical details of this and related complex ions provide intriguing differences from those of the other major type of chromium(III) complex ions so far studied, namely systems with NH_3 , amine, halogen, and pseudohalogen ligands. For $\text{Cr}(\text{bpy})_3^{3+}$, the photoaquation quantum yield attains a maximum limiting value in base (Φ_{bpy}

- (1) (a) Hahn-Meitner-Institut. (b) University of Saskatchewan.
- (2) Jamieson, M. A.; Serpone, N.; Hoffman, M. Z. *Coord. Chem. Rev.* 1981, 39, 121.
- (3) Kirk, A. D. *Coord. Chem. Rev.* 1981, 39, 225.
- (4) Kemp, T. J. *Prog. React. Kinet.* 1980, 10, 301.
- (5) Bolletta, F.; Maestri, M.; Balzani, V. *J. Phys. Chem.* 1976, 80, 2499.
- (6) Ferraudi, G. J.; Endicott, J. F. *Inorg. Chim. Acta* 1978, 37, 219.
- (7) Henry, M. S.; Hoffman, M. Z. *Adv. Chem. Ser.* 1978, No. 168, 91.
- (8) Maestri, M.; Bolletta, F.; Moggi, L.; Balzani, V.; Henry, M. S.; Hoffman, M. Z. *J. Am. Chem. Soc.* 1978, 100, 2694.
- (9) Jamieson, M. A.; Serpone, N.; Henry, M. S.; Hoffman, M. Z. *Inorg. Chem.* 1979, 18, 214.
- (10) Serpone, N.; Jamieson, M. A.; Henry, M. S.; Hoffman, M. Z.; Bolletta, F.; Maestri, M. *J. Am. Chem. Soc.* 1979, 101, 2907.
- (11) Sriram, R.; Henry, M. S.; Hoffman, M. Z. *Inorg. Chem.* 1979, 18, 1727.
- (12) Walters, R. T.; Adamson, A. W. *Acta Chem. Scand., Ser. A* 1979, A33, 53.
- (13) Allsopp, S. R.; Cox, A.; Kemp, T. J.; Reed, W. J.; Sostero, S.; Traverso, O. *J. Chem. Soc., Faraday Trans. 1* 1980, 76, 162.
- (14) Kirk, A. D.; Porter, G. B. *J. Phys. Chem.* 1980, 84, 887.
- (15) Kirk, A. D.; Porter, G. B. *J. Phys. Chem.* 1980, 84, 2998.
- (16) Sasseville, R. L. P.; Langford, C. H. *Inorg. Chem.* 1980, 19, 2850.

- (17) Sriram, R.; Hoffman, M. Z.; Jamieson, M. A.; Serpone, N. *J. Am. Chem. Soc.* 1980, 102, 1754.
- (18) Serpone, N.; Jamieson, M. A.; Emmi, S. S.; Fuchi, P. G.; Mulazzani, Q. G.; Hoffman, M. Z. *J. Am. Chem. Soc.* 1981, 103, 1091.
- (19) Sriram, R.; Hoffman, M. Z.; Serpone, N. *J. Am. Chem. Soc.* 1981, 103, 997.