Chart I. Structural Possibilities for the Tris-Chelate Copper(II) Complexes

(A) dynamic Jahn-Teller
$Cu(ompa)_3(ClO_4)_2$[30]
$Cu(en)_3SO_4$[31]

(B) static structure
$Cu(bipy)_3(ClO_4)_2$
$Cu(phen)_3(ClO_4)_2$

(C) static–three equal structures
$Cu(ompa)_3(ClO_4)_2$[30]
$Cu(en)_3SO_4$[31]

(D) fluxional behavior
$Cu(hfacac)_2(py)_2$[24]

(E) static–one dominant structure
$Cu(hfacac)_2py_2$[24]

namely, $d_{xy} > d_{z^2} > d_{x^2-y^2} \approx d_{xz} \approx d_{yz}$, and within this sequence the effect of the different chelate ligands will only change the energies of the one-electron orbitals in a minor way. The in-plane chelate, N(1)-N(4), may effect the energies of the d_{xz} and d_{yz} orbitals and the out-of-plane chelate ligands N(2)-N(5) and N(3)-N(6) may limit the extent of the axial elongation possible[1] (restricted tetragonal distortion) and reduce the separation of the d_{z^2} and d_{xy} levels.

These results question the earlier suggestion that the $Cu(bipy)_3^{2+}$, $Cu(phen)_3^{2+}$, and $Cu(en)_3^{2+}$ cations will always involve a D_3 symmetry and undergo a dynamic Jahn-Teller distortion. The latter will only arise when these cations are present in high-symmetry crystal lattices, such as trigonal or hexagonal, in which the copper(II) ion may occupy a special position of D_3 symmetry. When these cations are present in lower symmetry crystals, such as monoclinic and triclinic, where the copper(II) ion does not occupy a special position, the more usual[4] static elongated rhombic octahedral stereochemistry will be present and no genuine dynamic Jahn-Teller effect will operate. The most likely structure will represent one of the three equally possible dynamic Jahn-Teller states as in $Cu(bipy)_3(ClO_4)_2$ and $Cu(phen)_3(ClO_4)_2$. A less likely possibility is that a mixture of all three possible structures may be observed in equal distribution as for $Cu(ompa)_3(ClO_4)_2$[30] and $Cu(en)_3SO_4$[31] or in unequal distribution as in $Cu-Zn(hfacac)_2(py)_2$.[24] These various possibilities are summarized in Chart I.

Acknowledgment. The authors thank University College, Cork, for a demonstratorship (P. G. H.) and the Department of Education for a studentship (P. C. P.).

Registry No. $Cu(phen)_3(ClO_4)_2$, 36502-34-8; $Cu(bipy)_3(ClO_4)_2$, 14375-99-6; $(C_{14}H_{19}N_2)Cu(hfacac)_3$, 31117-62-1.

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Copper Halide Adducts of Copper Schiff Base Complexes. Structure and Magnetic Properties

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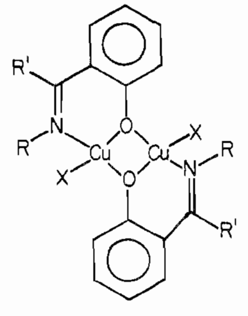
The complete crystal and molecular structures of four complexes, dichlorobis (*N*-methylsalicylaldimino)dicopper(II), dichlorobis (*N*-ethylsalicylaldimino)dicopper(II), dibromobis (*N*-ethylsalicylaldimino)dicopper(II), and dichloro[*N,N'* ethylenebis(2-hydroxyacetophenimino)copper(II)]copper(II) have been determined by X-ray diffraction analyses. The magnetic moments of the complexes are dependent on temperature but not pressure, indicating the absence of any significant volume changes, in agreement with the X-ray data. The magnetic properties are found to be more a function of structure than of the electronic properties of the ligands. In each case, increased distortion of the copper environment from planar is accompanied by reduced antiferromagnetic interaction between the pairs of copper atoms. Replacement of chlorine atoms attached directly to the interacting copper atoms has no significant effect on the magnetic properties in dichlorobis-(*N*-ethylsalicylaldimino)dicopper(II). Using these results and the magnetic properties, the copper environments may now be deduced in a series of analogous binuclear copper complexes.

Introduction

Binuclear complexes, **1**, exhibit an antiferromagnetic coupling, $|J|$, between the copper atoms and fall phenomenologically into two general groups according to the nitrogen substituent R. When R is bulky or methyl, $|J|$ is much less than for R = *n*-alkyl, and distortion from planar toward tetrahedral copper, as indicated by the electronic spectra, is slightly greater than for R = *n*-alkyl.[2a] These data suggest that dis-



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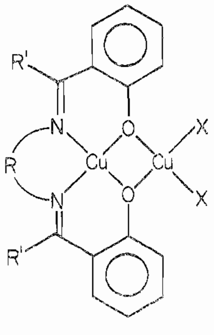
[1] (a) University of Canterbury; (b) University of Virginia.

[2] (a) C. M. Harris and E. Sinn, *J. Inorg. Nucl. Chem.*, **30**, 2723 (1968); (b) E. Sinn and W. T. Robinson, *J. Chem. Soc., Chem. Commun.*, 359 (1972).

tortion from planar copper environments in this series leads to smaller values of $|J|$ and that bulkiness of R produces such distortions. However, the methyl complex does not fit into the series as it has a relatively small $|J|$ value and its spectrum suggests a greater distortion toward tetrahedral copper environment than the other complexes with R = *n*-alkyl. X-Ray data, given in a preliminary report,[2b] confirm the earlier observations, and detailed molecular structures and their relation to the magnetic properties in the series 1 will be here discussed in detail.

For a second series of binuclear copper(II) complexes, 2,



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the structures were similarly assigned from the magnetic and spectroscopic properties[3] and the assignments were confirmed for three complexes of this type by single-crystal X-ray studies.[2b,4] The correlation of the magnetic and spectroscopic properties in the series with these structures is also reported here, together with the detailed crystal and molecular structure of dichloro[*N,N'*-ethylenebis(2-hydroxyacetophenimino)copper(II)]copper(II).

Four compounds have been examined crystallographically: dichlorobis(*N*-ethylsalicylaldimino)dicopper(II) (the "chloroethyl complex," 3), dichlorobis(*N*-methylsalicylaldimino)dicopper(II) (the "chloromethyl complex," 4), dichloro[*N,N'*-ethylenebis(2-hydroxyacetophenimino)copper(II)]copper(II) (the (CuEHA)$CuCl_2$ complex, 5), and dibromobis(*N*-ethylsalicylaldimino)dicopper(II) (the "bromoethyl complex," 6).

Experimental Section

Magnetic susceptibilities were measured as a function of temperature[2a] and pressure[5] using the Gouy method as previously described. The temperature and pressure ranges were 80–360°K and 1–3000 atm.

Values of J, the antiferromagnetic exchange or coupling constant, and g, the effective Lande g factor, were estimated as previously described from the fit of the magnetic data to the spin-only dimer model,[6,7] using the equation

$$\chi = \frac{Ng^2\beta^2}{3kT}\left(1 + {}^1/_3{}^{-2J/kT}\right)^{-1} + N\alpha$$

based on the Hamiltonian $\mathcal{H} = -2J\mathbf{S}_1\cdot\mathbf{S}_2 + g\beta\mathbf{H}\cdot(\mathbf{S}_1 + \mathbf{S}_2)$, where the symbols have their usual meanings. The temperature-independent paramagnetism, $N\alpha$, is given its usual value of 6×10^{-5} cgsu. In cases where the susceptibility maximum occurs within the experimental temperature range, the value of J can be obtained directly from the maximum, and accuracy is better than ±3 cm^{-1}, both in the present data and in the literature results cited. For large $|J|$, the maximum may be unobservable, and errors up to ±10 cm^{-1} are possible, though relative magnitudes of J can be determined to better accuracy by comparing the change in slope of χ *vs.* T for various compounds.

All compounds were prepared by published methods[2a,3] and the four compounds examined crystallographically were obtained as well-formed black crystals. Single crystals of the chloromethyl (3) and bromoethyl (6) complexes and fragments obtained by crushing large crystals of the chloroethyl complex (4) and (CuEHA)$CuCl_2$ were examined by precession photography. Cell dimensions (Table I) were obtained by least-squares refinement of the setting angles of 12 reflections accurately centered in a 3.5 mm diameter circular receiving aperture on a Hilger and Watts four-circle, computer-controlled diffractometer (λ(Mo K$\bar{\alpha}$) 0.7107).[8] The digits in parentheses in Table I, and elsewhere in this paper, are estimated standard deviations in the least significant figures quoted and were usually derived from the inverse matrix in the course of normal least-squares refinement calculations.

Densities were measured by suspension of the crystals in bromoform–acetone mixtures of uniform density and by the density gradient method.

Collection and Reduction of Intensity Data. Diffraction data were collected from small well-formed cuboid crystals of centric habit. The bounding faces were identified and their distances from an arbitrary origin in the crystal measured using a calibrated graticule in a binocular microscope. The maximum and minimum crystal dimensions and the volumes are given in Table I.

The mosaicity of each crystal was examined by means of open-counter scans at a take-off angle of 3°; the widths at half-height for strong low angle reflections were 0.08, 0.18, 0.15, and 0.4° for crystals 3, 4, 5, and 6, respectively. Zirconium-filtered Mo Kα X-radiation and the θ–2θ scan techniques were used to record the intensities of all reflections for which $0 \leqslant 2\theta \leqslant 50°$, $0 \leqslant 2\theta \leqslant 40°$, $0 \leqslant 2\theta \leqslant 45°$, and $0 \leqslant 2\theta \leqslant 38°$ for 3, 4, 5, and 6, respectively. The symmetric scan ranges of 1.20° in 2θ (60 steps of 1 sec duration), 1.44° (72 steps, 1 sec), 1.44° (72 steps, 1 sec), and 2.40° (120 steps, 0.7 sec) for 3, 4, 5, and 6, respectively, were centered on the calculated peak positions (λ(Mo Kα) 0.7107 Å). Stationary-crystal, stationary-counter background measurements of 15, 18, 21, and 18 sec were recorded at each end of the scan range.

For 3 and 5, attenuators, and therefore separate scaling, were required respectively for 17 and 12 reflections to bring these within the linear response range of the scintillation counter, which was located with its 5-mm receiving aperture 230 mm from the crystal.

The intensities of three standard reflections for each compound, monitored at regular intervals, showed no greater fluctuations than those expected from the Poisson statistics during the data collections. Data were corrected for *LP* and then for absorption in each of the four complexes (μ(Mo Kα) is 26.0 cm^{-1} for 3, 28.2 for 4, 26.0 for 5, and 65.0 for 6) using Gaussian integration.[9] Maximum and minimum transmission coefficients were 0.811 and 0.744 for 3, 0.871 and 0.657 for 4, 0.661 and 0.585 for 5, and 0.661 and 0.344 for 6. After averaging the intensities of equivalent reflections, the data were reduced to 1677, 817, and 924 independent reflections of which 1316, 514, and 579 had $F^2 > 3\sigma_{F^2}$ for 3, 4, and 6, respectively, where σ_{F^2} was estimated from counter statistics as detailed in ref 10. Of the 2563 independent reflections collected for 5, 1713 had $F^2 > 3\sigma_{F^2}$.[10] These were the data used in the final refinements of the structure parameters.

Solution and Refinement of the Structures. Full-matrix least-squares refinements were based on F, and the function was minimized[11] as $\Sigma w(|F_o| - |F_c|)^2$. The weights w were taken as $4F_o^2/\sigma_{F_o^2}{}^2$ where $|F_o|$ and $|F_c|$ are observed and calculated structure factor amplitudes. The atomic scattering factors for nonhydrogen at-

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(9) Calculations were carried out at the University of Canterbury using an IBM 360/44 computer, with 32K words of core storage and twin 2315 disk drives. The data processing program HILGOUT is based on programs DRED (J. F. Blount) and PICKOUT (R. J. Doedens). Numerical absorption corrections are applied using program DABS which is a modified version of DATAPH (P. Coppens). Mathematical methods are fully described in "Crystallographic Computing," Munksgaard, Copenhagen, 1970.

(10) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967).

(11) Structure factor calculations and least-squares refinements were carried out using program CUCLS and Fourier summations using program FOURIER. These are highly modified versions of the well-known programs ORFLS (W. R. Busing, K. O. Martin, and H. A. Levy) and FORDAP (A. Zalkin), respectively.

Table I. Crystallographic Data (Distances in Å, Angles in Degrees, Esd's in Parentheses)

	Compd			
	3	4	5	6
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a	9.989 (1)	6.998 (2)	7.639 (2)	10.069
b	7.441 (1)	10.165 (2)	18.527 (3)	7.674
c	8.396 (1)	7.189 (2)	14.633 (3)	8.380
α	122.56 (1)	90.32 (1)	90	121.40
β	98.74 (1)	105.77 (1)	116.93 (1)	97.92
γ	104.28 (1)	115.51 (1)	90	106.43
z	1	1	4	1
No. of reflections	1316	514	1713	579
R_1	0.039	0.046	0.056	0.068
R_2	0.052	0.058	0.071	0.083
No. of crystal faces	6	7	12	6
Max crystal dimension, mm	0.12	0.13	0.20	0.11
Min crystal dimension, mm	0.09	0.05	0.11	0.06
Crystal vol, mm^3	0.0011	0.00087	0.00210	0.00145
Density, g cm^{-3}	1.714 ± 0.003	1.762 ± 0.003	1.76 ± 0.01	2.01 ± 0.01
Calcd density, g cm^{-3}	1.72	1.76	1.77	1.99

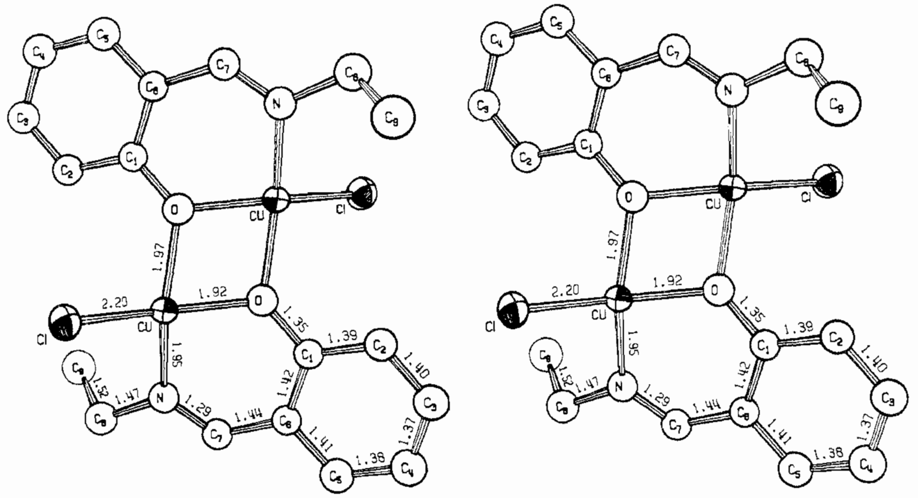

Figure 1. Complex 3.

oms were taken from Cromer and Waber[12] and those for hydrogen from Stewart.[13]

The effects of anomalous dispersion of copper, chlorine, and bromine were included in F_c[14] using Cromer's values[15] for $\Delta f'$ and $\Delta f''$. Agreement factors are defined as $R_1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$.

A position for the one independent copper atom was obtained in each of 3 and 4 from the $2x$, $2y$, and $2z$ peak in a three-dimensional Patterson synthesis. Refinement of the copper coordinates and isotropic temperature factor gave values for R_1 and R_2 of 0.452 and 0.511 for 3. For 4, these values were 0.407 and 0.469. A difference Fourier synthesis showed the positions of all remaining nonhydrogen atoms apart from the ethyl carbon atom in 3 which was found from a second difference Fourier synthesis. Using isotropic temperature factors, refinement of the models converged with $R_1 = 0.077$ and $R_2 = 0.095$ for 3, $R_1 = 0.081$ and $R_2 = 0.092$ for 4. Examination of residual electron density maps suggested that the thermal motion of the copper and chlorine atoms in 3 and 4 might be better described by anisotropic temperature factors. The precise positions of the nonmethyl hydrogen atoms indicated on these maps were calculated using a hydrogen–carbon bond length of 1.00 Å along the bisectors of C–C–C angles, with isotropic temperature factors of 7.5, in subsequent refinement cycles. The positions of the copper atoms for 5 were found from an E map obtained by direct phasing of the 242 reflections having a normalized structure factor greater than 1.300.[16] Refinement of these positions and successive difference Fourier maps showed all the remaining nonhydrogen atoms. This model converged with $R_1 = 0.093$ and $R_2 = 0.133$ using isotropic temperature factors. The copper and chlorine atoms were then refined using anisotropic temperature factors. For 6, the unit cell was indexed to correspond to that of 3, and least-squares refinement was carried out beginning with the final atomic positions obtained for 3. Refinement of these models ultimately converged with R_1 and R_2 values listed in Table I. Shifts in the last cycle of refinement were all less than half of their estimated standard deviations.

Final difference Fourier calculations gave peaks approximately one-tenth the height at which nonhydrogen atoms had been located earlier in the analysis. The relative weighting schemes are satisfactory in that averaged values of the minimized function appear to be independent of $|F_o|$ and $\lambda^{-1} \sin \theta$. The error in an observation of unit weight is 1.477 for 3, 1.461 for 4, 2.084 for 5, and 1.555 for 6. Structure factor calculations in 3, 4, 5, and 6 for the 361, 303, 850, and 345 reflections having $F_o < 3\sigma_{F_o}{}^2$ show that none has $|F_o{}^2 - F_c{}^2| > 3\sigma_{F_o}{}^2$. There is no evidence of secondary extinction among the strong low-angle reflections.

Results and Discussion

Final positional and thermal parameters for the atoms are given in Table II, and thermal parameters for anisotropic atoms are given in Table III. Bond lengths and angles are given in Tables IV and V.

Figures 1 and 2 are stereoscopic pairs for the dimeric structures of the chloroethyl complex (3) and the chloromethyl

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(12) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 511 (1965).

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(14) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).

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(16) Program SHNORM, derived from NRC-4 (S. R. Hall and F. R. Ahmed), was used to calculate normalized structure factors and symbolic addition was carried out using SAP, also derived from NRC-4. Refinement with the tangent formula was carried out with DPHASE, derived from NRC-5.

Table II. Final Positional and Thermal Parameters

(a) For Chloromethyl Complex (**4**, $Cu_2C_{16}H_{16}N_2O_2Cl_2$), Chloroethyl Complex (**3**, $Cu_2C_{18}H_{20}N_2O_2Cl_2$), and Bromoethyl Complex (**6**, $Cu_2C_{18}H_{20}N_2O_2Br_2$)

Atom		**3** (chloroethyl)	**4** (chloromethyl)	**6** (bromoethyl)	Atom		**3** (chloroethyl)	**4** (chloromethyl)	**6** (bromoethyl)
Cu	*X*	0.16600 (6)	−0.0436 (3)	0.1661 (2)	C7	*X*	0.2313 (6)	0.065 (2)	0.225 (2)
	Y	0.1309 (1)	−0.1563 (2)	0.1247 (4)		*Y*	0.2295 (9)	−0.169 (1)	0.224 (3)
	Z	0.11243 (9)	0.0353 (2)	0.1106 (3)		*Z*	0.5026 (8)	0.443 (2)	0.504 (3)
	B	[a]	[a]	[a]		*B*	2.74 (9)	3.5 (3)	3.6 (4)
Cl or Br	*X*	0.3438 (1)	−0.0686 (6)	0.3572 (3)	C8	*X*	0.4227 (6)	−0.202 (2)	0.424 (2)
	Y	0.3384 (2)	−0.3430 (4)	0.3468 (3)		*Y*	0.167 (1)	−0.403 (1)	0.165 (3)
	Z	0.0805 (2)	−0.1435 (5)	0.0775 (3)		*Z*	0.369 (8)	0.259 (2)	0.372 (3)
	B	[a]	[a]	[a]		*B*	3.4 (1)	4.2 (3)	5.0 (5)
N	*X*	0.2784 (5)	−0.054 (2)	0.274 (2)	C9	*X*	0.4053 (7)		0.399 (2)
	Y	0.1838 (7)	−0.244 (1)	0.182 (2)		*Y*	−0.073 (1)		−0.070 (4)
	Z	0.3555 (6)	0.274 (2)	0.357 (2)		*Z*	0.197 (1)		0.200 (3)
	B	2.80 (8)	2.9 (2)	3.7 (3)		*B*	4.2 (1)		5.7 (5)
O	*X*	−0.0162 (4)	0.128 (1)	−0.016 (1)	H2	*X*	−0.2410	0.4562	
	Y	0.0590 (6)	0.0416 (8)	0.062 (2)		*Y*	0.1396	0.3024	
	Z	0.1582 (5)	0.167 (1)	0.155 (2)		*Z*	0.2498	0.3212	
	B	2.78 (6)	3.2 (2)	4.2 (3)		*B*	7.5	7.5	
C1	*X*	−0.0279 (5)	0.254 (2)	−0.030 (2)	H3	*X*	−0.2599	0.6696	
	Y	0.1652 (8)	0.081 (1)	0.171 (3)		*Y*	0.3341	0.3784	
	Z	0.3421 (7)	0.355 (2)	0.340 (3)		*Z*	0.5774	0.6637	
	B	2.41 (8)	3.1 (3)	4.1 (4)		*B*	7.5	7.5	
C2	*X*	−0.1560 (6)	0.424 (2)	−0.155 (2)	H4	*X*	−0.0650	0.6067	
	Y	0.1962 (9)	0.228 (1)	0.202 (3)		*Y*	0.4580	0.2135	
	Z	0.3690 (7)	0.420 (2)	0.364 (3)		*Z*	0.8610	0.8886	
	B	2.75 (9)	3.8 (3)	4.11 (4)		*B*	7.5	7.5	
C3	*X*	−0.1671 (6)	0.549 (2)	−0.170 (2)	H5	*X*	0.1567	0.3301	
	Y	0.3073 (9)	0.272 (1)	0.309 (3)		*Y*	0.4048	−0.0358	
	Z	0.5604 (8)	0.616 (2)	0.554 (3)		*Z*	0.8227	0.7902	
	B	3.2 (1)	3.9 (3)	5.2 (5)		*B*	7.5	7.5	
C4	*X*	−0.0544 (6)	0.514 (2)	−0.046 (2)	H7	*X*	−0.0066	0.0421	
	Y	0.382 (1)	0.178 (1)	0.388 (4)		*Y*	0.1736	−0.2258	
	Z	0.7245 (9)	0.744 (2)	0.725 (3)		*Z*	0.4046	0.5601	
	B	3.4 (1)	4.2 (3)	5.2 (5)		*B*	7.5	7.5	
C5	*X*	0.0740 (6)	0.356 (2)	0.074 (2)	H81	*X*	0.4895		
	Y	0.3512 (9)	0.035 (1)	0.350 (3)		*Y*	0.2872		
	Z	0.7018 (8)	0.688 (2)	0.698 (3)		*Z*	0.3619		
	B	3.1 (1)	3.9 (3)	4.9 (5)		*B*	7.5		
C6	*X*	0.0918 (5)	0.226 (2)	0.089 (2)	H82	*X*	0.4692		
	Y	0.2469 (8)	−0.018 (1)	0.239 (3)		*Y*	0.2001		
	Z	0.5123 (7)	0.0490 (2)	0.509 (3)		*Z*	0.5017		
	B	2.46 (9)	2.7 (3)	3.6 (4)		*B*	7.5		

(b) For $(CuEHA)CuCl_2$ (**5**, $Cu_2C_{18}H_{18}N_2O_2Cl_2$)

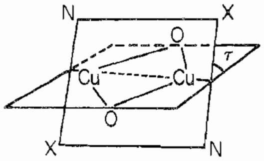
Atom	*X*	*Y*	*Z*	*B*	Atom	*X*	*Y*	*Z*	*B*
Cu1	0.2572 (2)	0.01706 (6)	0.14701 (8)	[a]	C6	0.253 (1)	0.0276 (5)	0.3695 (7)	3.0 (2)
Cu2	0.3757 (2)	−0.13775 (7)	0.20225 (9)	[a]	C7	0.257 (1)	0.0955 (5)	0.3185 (7)	2.9 (2)
Cl1	0.6637 (5)	−0.1559 (2)	0.3311 (2)	[a]	C8	0.272 (2)	0.1668 (6)	0.3753 (8)	4.0 (2)
Cl2	0.2629 (4)	−0.2444 (1)	0.1406 (2)	[a]	C9	0.255 (2)	0.1674 (6)	0.1802 (8)	3.7 (2)
O1	0.296 (1)	−0.0507 (3)	0.2492 (5)	3.6 (1)	C10	0.191 (2)	0.1580 (5)	0.0628 (8)	3.6 (2)
O2	0.2782 (9)	−0.0664 (3)	0.0776 (5)	3.1 (1)	C11	0.216 (2)	0.0674 (5)	−0.0484 (7)	3.0 (2)
N1	0.245 (1)	0.0969 (4)	0.2286 (6)	3.0 (2)	C12	0.177 (2)	0.1283 (6)	−0.1262 (8)	4.1 (2)
N2	0.227 (1)	0.0827 (4)	0.0401 (6)	2.7 (1)	C13	0.243 (1)	−0.0058 (5)	−0.0777 (7)	2.9 (2)
C1	0.269 (1)	−0.0427 (5)	0.3338 (7)	2.9 (2)	C14	0.243 (2)	−0.0160 (6)	−0.1741 (8)	3.7 (2)
C2	0.257 (2)	−0.1052 (6)	0.3828 (8)	3.8 (2)	C15	0.263 (2)	−0.0850 (6)	−0.2080 (8)	4.0 (2)
C3	0.229 (2)	−0.1002 (6)	0.4732 (8)	4.4 (3)	C16	0.288 (2)	−0.1460 (6)	−0.1466 (7)	3.5 (2)
C4	0.218 (2)	−0.0309 (6)	0.5097 (8)	4.2 (2)	C17	0.296 (5)	−0.1375 (5)	−0.0492 (7)	3.3 (2)
C5	0.227 (2)	0.0294 (6)	0.4599 (8)	3.9 (2)	C18	0.270 (2)	−0.0690 (5)	−0.0159 (7)	3.0 (2)

[a] See Table III.

complex (**4**), and Figure 3 shows the $(CuEHA)CuCl_2$ complex (**5**). Although complexes **3** and **4** appear approximately flat, it is clear from Figures 1 and 2, and from selected least-squares planes in Table VI, that distortion from the planar copper(II) environment is significant.

Hitherto unreported magnetic susceptibilities as a function of temperature are given in Table VII. The exchange integrals *J* between the copper atoms in each complex are based on the fit of the experimental magnetic data to the spin-only model.[6,7]

Comparison of Figures 1 and 2 and the data in Table V relating to the copper environment indicates that the distortion from planar toward tetrahedral stereochemistry is greater in the chloromethyl complex than in the chloroethyl. Perhaps the best direct measure of the relative degrees of distortion of the complexes is the dihedral angle, τ, between



the planes formed by Cu_2O_2 and $Cu_2N_2X_2$. This is greater

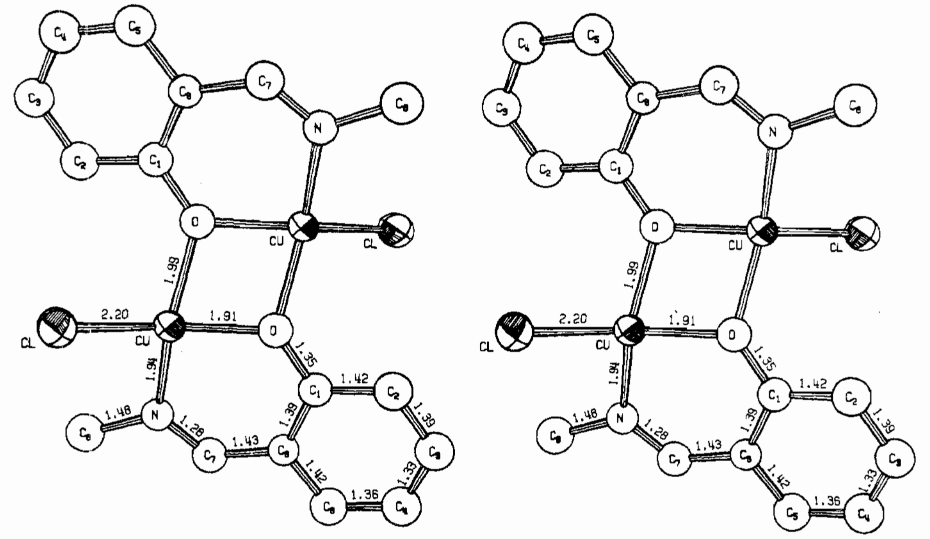


Figure 2. Complex **4**.

Table III [a]

Thermal Parameters for Anisotropic Atoms

Compd	Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
4	Cu	0.0235 (6)	0.0070 (3)	0.0145 (5)	0.0037 (3)	0.0026 (4)	0.0024 (2)
4	Cl	0.042 (2)	0.0107 (6)	0.017 (1)	0.0102 (8)	0.006 (1)	0.0015 (6)
3	Cu	0.00592 (8)	0.0215 (2)	0.0105 (2)	0.0037 (1)	0.00227 (8)	0.0078 (1)
3	Cl	0.0088 (2)	0.0242 (4)	0.0182 (3)	0.0032 (2)	0.0051 (2)	0.0112 (3)
5	Cu1	0.0200 (4)	0.00147 (4)	0.00384 (8)	0.0001 (1)	0.0043 (1)	0.00015 (4)
5	Cu2	0.0262 (4)	0.00162 (4)	0.00424 (1)	0.0011 (1)	0.0048 (2)	0.0000 (5)
5	Cl1	0.029 (1)	0.0030 (1)	0.0050 (2)	0.0023 (3)	0.0027 (4)	−0.0005 (4)
5	Cl2	0.0307 (9)	0.00168 (9)	0.0053 (2)	0.0002 (2)	0.0052 (3)	−0.0001 (1)
6	Cu	0.0129 (5)	0.028 (1)	0.0154 (7)	0.0076 (5)	0.0011 (4)	0.0123 (7)
6	Br	0.0152 (4)	0.0284 (9)	0.0231 (7)	0.0070 (5)	0.0043 (6)	0.0147 (6)

Root-Mean-Square Amplitude of Vibration (Å)

Compd	Atom	Min	Intermed	Max
4	Cu	0.166 (3)	0.180 (3)	0.240 (3)
4	Cl	0.200 (6)	0.207 (6)	0.285 (6)
3	Cu	0.151 (1)	0.163 (1)	0.206 (1)
3	Cl	0.177 (2)	0.199 (2)	0.237 (2)
5	Cu1	0.158 (2)	0.179 (2)	0.218 (2)
5	Cu2	0.162 (2)	0.189 (2)	0.255 (2)
5	Cl1	0.201 (4)	0.211 (4)	0.308 (4)
5	Cl2	0.171 (4)	0.212 (4)	0.276 (4)
6	Cu	0.168 (5)	0.227 (4)	0.276 (4)
6	Br	0.224 (4)	0.231 (4)	0.267 (3)

[a] The form of the anisotropic ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

for the chloromethyl complex (39.3°) than for the chloroethyl (33.1°). Fully planar and tetrahedral configurations would have $\tau = 0$ and 90°, respectively. Thus there is no deviation from the general observation[2a,7] that the magnitude of the $|J|$ values decreases as the copper environment in this series is moved from the planar toward tetrahedral.

There has been considerable discussion in the literature on the mechanism of the exchange interactions in such systems[7,17-19] though without complete agreement, and detailed speculations will not be undertaken here. If an important exchange pathway here is superexchange involving the copper $d_{x^2-y^2}$ and oxygen p_x orbitals, distortion from planarity would reduce the overlap of these orbitals, thereby weakening the exchange interaction. Then the great change in $|J|$ values between the two complexes (240 cm^{-1} in the chloroethyl (**3**) and 146 cm^{-1} in the chloromethyl (**4**)) reflects the extreme sensitivity of this overlap to very small angular changes in the copper environment. For symmetry reasons, identical changes are made in the environments of both copper atoms of the binuclear molecules. Unfortunately, we cannot isolate the effect of the copper geometries because the Cu-O-Cu′ angle must also affect the overlap, and this angle does change between the two complexes, albeit by only a small amount (about 1°).

If the bromoethyl complex is included in the comparison, there is an apparent correlation between $|J|$ and τ (Table VIII). Another complex related to **1**, dibromobis(*N*-*n*-butyl-5-chloro-2-oxybenzophenimino)dicopper(II), $Cu_2(BuCBP)_2Br_2$,[20] conforms to this expected trend. It does not appear to be significant whether Cl or Br is bonded to the Cu atom. There is no consistent trend of $|J|$ with Cu-O-Cu angle, probably because the variation of this angle over the compounds considered is not large enough to be important.

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Table IV. Bond Distances (Å) and Selected Interatomic Distances

(a) For 3, 4, and 6

	3 (chloroethyl)	4 (chloromethyl)	6 (bromoethyl)
Cu-Cu	3.051 (1)	3.041 (1)	3.05 (1)
Cu-O′	1.923 (3)	1.915 (7)	1.89 (1)
Cu-N	1.950 (4)	1.94 (1)	1.95 (2)
Cu-Cl (Br)	2.202 (1)	2.202 (4)	2.34 (3)
Cu-O	1.966 (3)	1.992 (7)	1.96 (1)
N-C7	1.291 (7)	1.28 (1)	1.30 (2)
N-C8	1.468 (7)	1.48 (1)	1.52 (2)
O-C1	1.346 (6)	1.34 (1)	1.38 (2)
C1-C2	1.386 (7)	1.42 (2)	1.36 (2)
C1-C6	1.424 (7)	1.39 (2)	1.46 (2)
C2-C3	1.400 (7)	1.39 (2)	1.42 (3)
C3-C4	1.368 (7)	1.32 (2)	1.47 (3)
C4-C5	1.381 (8)	1.36 (2)	1.36 (2)
C5-C6	1.411 (7)	1.42 (2)	1.41 (2)
C6-C7	1.441 (7)	1.43 (2)	1.41 (2)
C8-C9	1.516 (9)		1.54 (3)

(b) For 5

Cu1-Cu2	3.006	C6-C7	1.47 (1)
Cu1-O1	1.871 (6)	C7-C8	1.54 (1)
Cu1-O2	1.896 (6)	C7-N1	1.28 (1)
Cu1-N1	1.928 (8)	N1-C9	1.50 (1)
Cu1-N2	1.910 (7)	C9-C10	1.57 (1)
Cu2-O1	1.952 (7)	C10-N2	1.49 (1)
Cu2-O2	2.097 (6)	N2-C11	1.29 (1)
Cu2-Cl1	2.180 (3)	C11-C13	1.47 (1)
Cu2-Cl2	2.181 (3)	C11-C12	1.53 (1)
O1-C1	1.35 (1)	C13-C14	1.42 (1)
C1-C2	1.39 (1)	C14-C15	1.40 (1)
C2-C3	1.44 (1)	C15-C16	1.40 (1)
C3-C4	1.41 (1)	C16-C17	1.41 (1)
C4-C5	1.35 (1)	C17-C18	1.41 (1)
C5-C6	1.43 (1)	C18-C13	1.44 (1)
C6-C1	1.43 (1)	C18-O2	1.34 (1)

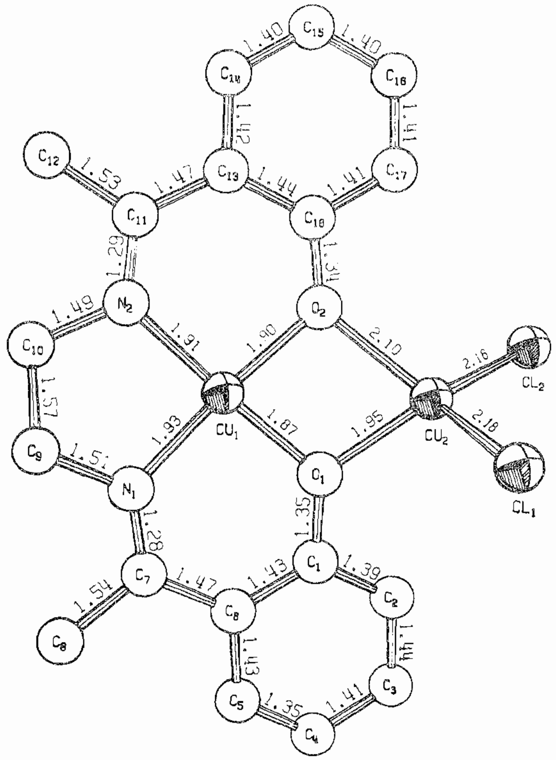

Figure 3. Complex 5.

Table V. Bond Angles (deg)

(a) For 3, 4, and 6

	3 (chloroethyl)	4 (chloromethyl)	6 (bromoethyl)
O-Cu-O′	76.7 (2)	77.8 (2)	75.4 (2)
Cu-O-Cu′	103.3 (2)	102.2 (2)	104.6 (2)
O′-Cu-N	92.1 (2)	94.5 (4)	92.6 (5)
N-Cu-Cl (Br)	99.2 (1)	97.5 (3)	99.8 (4)
O′-Cu-Cl (Br)	154.0 (1)	149.1 (1)	150.7 (4)
C7-N-C8	118.9 (4)	119 (1)	119 (1)
C8-N-Cu	117.9 (3)	118.6 (8)	117 (1)
C7-N-Cu	123.2 (4)	122.1 (8)	124 (1)
C1-O-Cu	123.8 (3)	125.4 (8)	124 (1)
O-C1-C2	120.8 (4)	119 (1)	122 (2)
O-C1-C6	120.2 (4)	122 (1)	117 (2)
C2-C1-C6	119.1 (4)	118 (1)	121 (2)
C1-C2-C3	120.4 (5)	120 (1)	121 (2)
C2-C3-C4	121.3 (5)	121 (1)	118 (2)
C3-C4-C5	119.6 (5)	121 (1)	120 (2)
C4-C5-C6	121.0 (5)	121 (1)	123 (2)
C5-C6-C1	118.6 (4)	121 (1)	117 (2)
C5-C6-C7	117.7 (4)	117 (1)	117 (2)
C1-C6-C7	123.7 (4)	124 (1)	126 (2)
N-C7-C6	126.2 (5)	128 (1)	126 (2)
N-C8-C9	110.2 (5)		110 (2)
O-Cu-Cl	100.7 (1)	102.1 (1)	102.2 (2)
O-Cu-N	154.1 (2)	153.2 (4)	153.5 (2)

(b) For 5

O1-Cu1-O2	81.9 (3)	C2-C1-C6	122.3 (9)
O1-Cu1-N2	176.5 (3)	C1-C2-C3	120 (1)
O1-Cu1-N1	93.2 (3)	C2-C3-C4	118 (1)
O2-Cu1-N2	95.1 (3)	C3-C4-C5	122 (1)
O2-Cu1-N1	174.9 (3)	C4-C5-C6	123 (1)
N2-Cu1-N1	89.8 (3)	C5-C6-C1	115.6 (9)
O1-Cu2-O2	75.0 (3)	C5-C6-C7	119.6 (9)
O1-Cu2-Cl1	100.1 (3)	C1-C6-C7	124.8 (8)
O1-Cu2-Cl2	140.0 (2)	C6-C7-C8	118.3 (8)
O2-Cu2-Cl1	132.2 (2)	C6-C7-N1	122.1 (9)
O2-Cu2-Cl2	107.0 (2)	C8-C7-N1	119.6 (9)
Cl1-Cu2-Cl2	105.8 (1)	N1-C9-C10	111.2 (8)
C1-O1-Cu1	128.4 (6)	C9-C10-N2	110.5 (8)
C1-O1-Cu2	127.9 (6)	N2-C11-C12	119.1 (9)
Cu1-O1-Cu2	103.7 (3)	N2-C11-C13	122.9 (9)
C18-O2-Cu1	126.8 (6)	C12-C11-C13	118.0 (8)
C18-O2-Cu2	134.3 (6)	C11-C13-C14	118.4 (9)
Cu1-O2-Cu2	97.5 (3)	C11-C13-C18	124.7 (9)
C11-N2-C10	119.7 (8)	C14-C13-C18	116.9 (9)
C11-N2-Cu1	127.6 (7)	C13-C14-C15	121.2 (9)
C10-N2-Cu1	112.3 (6)	C14-C15-C16	121 (1)
C7-N1-C9	120.4 (8)	C15-C16-C17	119.3 (9)
C7-N1-Cu1	128.4 (7)	C16-C17-C18	120.3 (9)
C9-N1-Cu1	110.4 (6)	C17-C18-C13	121.2 (9)
O1-C1-C2	117.1 (9)	C13-C18-O2	122.7 (8)
O2-C1-C6	120.6 (8)	C17-C18-O2	116.0 (8)

In view of the large Cu-Cu distances (3 Å), it seems unlikely that direct exchange due to overlap of copper d orbitals is significant.[7]

The present selection of four compounds is too small to permit detailed generalization about the relation between $|J|$ and τ, and further X-ray structural studies and more accurate magnetic susceptibility determinations are required, but the decrease in $|J|$ with increasing distortion from planar to tetrahedral geometry is confirmed.

It is now possible in retrospect to assign copper stereochemistries for the entire series of chloride complexes 1 (X = Cl). In agreement with the expectations from the electronic spectra, small $|J|$ and hence greater distortions from planar stereochemistry are associated with R = methyl and bulky R groups, while larger $|J|$ values and hence smaller distortions are associated with R = *n*-alkyl. We can now also use the same reasoning in the analogous bromide series 1 (X = Br) to assign copper stereochemistries from the J values as listed in Table VII. We find that there is the same dependence upon bulkiness of R groups, with R = methyl again an exception. The magnetic data indicate significant amounts of paramagnetic impurities in this compound, which is expected to introduce considerable error into the experimental g

Table VI. Coefficients of Least-Squares Planes $AX + BY + CZ = D$ for Chloroethyl Complex (**3**, $Cu_2C_{18}H_{20}N_2O_2Cl_2$), Chloromethyl Complex (**4**, $Cu_2C_{16}H_{16}N_2O_2Cl_2$), Bromoethyl Complex (**6**, $Cu_2C_{18}H_{20}N_2O_2Br_2$), and for $CuEHACuCl_2$ Complex (**5**)

	Atoms in plane	Complex	A	B	C	D
I	CuXNCu'X'N'	3	−0.5532	0.5952	0.5828	0
		4	0.9061	0.2849	0.3128	0
		6	−0.5679	0.5915	0.5724	0
II	CuOO'Cu'	3	−0.3658	0.9179	0.1536	0
		4	−0.9286	−0.1394	0.3440	0
		6	−0.3424	0.9325	0.1145	0
	$Cu_1O_1O_2Cu_2$	5	0.9000	0.2574	0.3518	1.6411
III	CuXN	3	−0.5884	0.5820	0.5613	−0.1085
		4	−0.8927	−0.3385	−0.2977	0.1482
		6	−0.6217	0.5776	0.5290	−0.1823
IV	$C_1C_2C_3C_4C_5C_6$	3	0.0904	0.9805	0.1747	−0.1966
		4	0.9575	−0.2261	−0.1792	0.1951
		6	0.11806	0.98062	0.15638	−0.18842
		5	0.8265	0.0182	0.5627	2.3004
V	CuXNOO'	3	−0.6255	0.6566	0.4216	−0.2094
		4	0.9078	0.4079	0.0978	−0.2563
		6	−0.5573	0.7221	0.4009	−0.0575
VI	$CuNOC_1C_2C_7$	3	0.1657	−0.9037	−0.3949	−0.4224
		4	0.9934	−0.1037	−0.0496	0.4430
		6	0.1342	−0.9496	−0.2834	−0.1369
	$Cu_1N_1O_1C_1C_6C_7$	5	0.8978	0.1006	0.4288	1.7460
VII	$CuN_2O_2C_{11}C_{13}C_{18}$	5	0.9055	0.1253	0.4054	1.7142
VIII	$Cu_2Cl_1Cl_2$	5	0.7853	0.0706	−0.6150	−0.6022
IX	$CuO_1O_2N_1N_2$	5	0.9107	0.1239	0.3940	1.6995

	Dihedral Angles between the Planes			
	3	4	6	5
I, II	33.05	39.33	35.74	
II, III	33.31	39.31	35.69	
II, VI	18.05	22.33	15.44	
IV, VI	19.91	10.43	14.81	
VI, VII				2.00
II, VIII				120.57
VIII, IX				118.79
II, IX				8.05

Table VII. Magnetic Data for Bromo Complexes

Dibromo(*N*-methylsalicylaldimino)dicopper(II), $J = -140$ cm^{-1}, $g = 2.03$

T, °K	80.2	84.8	109.1	152.0	193.8	216.5	237.8	275.2	301.5	350.0
χ_M, cgs	524	458	522	638	713	737	742	736	730	710
μ_{eff}, BM	0.54	0.53	0.63	0.83	1.00	1.08	1.13	1.21	1.27	1.35

Dibromobis(*N*-ethylsalicylaldimino)dicopper(II), $J = -205$ cm^{-1}, $g = 2.18$

T, °K	82.5	117.0	141.5	178.9	222.4	247.0	292.0	323.0	356.5
χ_M, cgs	133	183	257	392	527	597	649	680	687
μ_{eff}, BM	0.21	0.34	0.47	0.69	0.91	1.03	1.17	1.26	1.34

Dibromobis(*N*-*n*-octylsalicylaldimino)dicopper(II), $J = -175$ cm^{-1}, $g = 2.10$

T, °K	82.2	114.7	142.8	197.4	239.6	285.5	327.8
χ_M, cgs	336	361	457	637	688	695	698
μ_{eff}, BM	0.42	0.52	0.67	0.95	1.09	1.20	1.29

Dibromobis(*N*-*sec*-butylsalicylaldimino)dicopper(II), $J = -160$ cm^{-1}, $g = 2.04$

T, °K	119.1	154.3	212.0	247.0	304.7	330.2
χ_M, cgs	297	441	658	723	753	740
μ_{eff}, BM	0.47	0.68	1.00	1.14	1.29	1.34

Table VIII. Dihedral Angles, J Values (cm^{-1}), and Cu-O-Cu Angles

	τ	J	Cu-O-Cu
3	33.1	240[a]	103.3
6	35.7	205[b]	104.6
$Cu_2(BuCBP)_2Br_2$	35.5	220[c]	101.2
4	39.3	146[a]	102.2

[a] Reference 7. [b] This work. [c] Reference 20.

value but less error into J. The g value is not estimated and J is estimated from the susceptibility maximum and is significantly lower than for the other compounds. We therefore conclude that the bromomethyl complex, like the chloromethyl, exhibits greater distortions than the other *n*-alkyl analogs. The correlation between the bulkiness of R and increasing distortion from planarity can in general be attributed to steric crowding, except for the methyl complexes. More accurate magnetic studies than are currently available would be very useful for more detailed correlation of magnetic properties with molecular structure. Such studies are contemplated.

In the second series of complexes, **2**, the crystal structures, like the spectra, indicate increasing distortion from planarity of the copper atoms with lengthening of the R group, which is again correlated with a decrease in $|J|$ values;[2b-4] here we compare the complexes **5** and dichlorobis[*N*,*N*'-1,3-propylenebis(salicylaldimino)copper(II)]copper(II) (**7**). Another complex, dichlorobis[*N*,*N*'-ethylenebis(salicylaldimino)copper(II)]copper(II) (**8**), has a different structure and therefore does not form part of the series **2** with increasing distortion for **5** to **6**. In complex **8**, the possibility[21] of linkage

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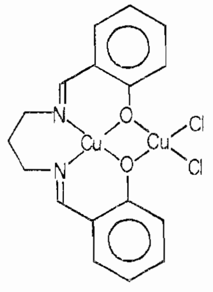
[21] C. M. Harris, J. M. James, P. J. Milham, and E. Sinn, *Inorg. Chim. Acta*, **3**, 81 (1969).



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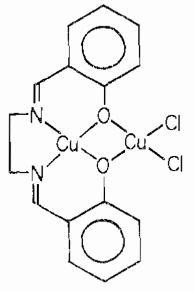

8

through the halogen atoms of adjacent molecules was realized, making one copper atom five coordinate and simultaneously weakening one of the Cu–O bonds (2.3 Å). In this case, there is a weaker antiferromagnetic interaction in 8 than in its analog 5, which must be attributed to the structural effect of weakening the Cu–Cu bridging linkages, since there are no other significant differences between molecules 5 and 8.

Although the magnetic properties of the complexes are very dependent upon temperature, there is no pressure dependence within experimental error, up to 3000 atm, indicating that there is little difference in volume between the singlet and triplet forms of the molecules. This compares interestingly with the lack of volume change on electron pairing in the antiferromagnetic copper(II) acetate[22] and the dramatic volume decrease upon electron pairing in ferric dithiocarbamates.[23,24] At very high pressures (~10^5 atm), a phase change analogous to the tetrahedral → planar transition in $\mathrm{CuCl_4^{2-}}$ and $\mathrm{CuBr_4^{2-}}$ may be expected.[25]

In agreement with the pressure effect, the complexes 3 and 4 have different bond angles but essentially the same bond lengths and therefore essentially the same volumes for corresponding molecular fragments despite the fact that 3 contains twice as many triplet state molecules as 4. Thus a single important factor exists between the pairs of copper atoms. This factor is the angular arrangement of the ligand atoms about the copper, and variation of these angles to correspond to tetrahedral distortions from planarity leads to rapid weakening of the interactions.

Purely inductive effects, when the R group is changed, have not been invoked in the discussion, and they are not considered to be large, because changing of R consists of altering a substituent atom three bond distances away from the copper. This is especially so if our conclusion is valid, that it makes little difference whether the substituent X directly on the copper is Cl or Br.

Registry No. 3, 21465-68-9; 4, 21044-53-1; 5, 19362-09-5; 6, 26194-16-1.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers of this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W. Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy, or $2.00 for microfiche, referring to code number INORG-74-2013.

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[22] A. H. Ewald and E. Sinn, *Inorg. Chem.*, 8, 537 (1969).

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Mossbauer Spectra of *cis*-Dicyanoethylene-1,2-dithiolatotin(IV) Complexes[1]

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The Mossbauer spectra of a variety of formally four-, five-, and six-coordinate dicyanoethylene-1,2-dithiolato (mnt) complexes of tin(IV) have been obtained. Evidence is presented for polymeric $\mathrm{R_2Sn(mnt)}$ ($\mathrm{R = CH_3, C_6H_5}$) species and for monodentate coordination of the mnt unit in the $\mathrm{R_3Sn(mnt)^-}$ ion ($\mathrm{R = CH_3, C_6H_5}$). The $\mathrm{R_2Sn(mnt)X^-}$ ($\mathrm{R = CH_3}$, X = Cl, Br, I; $\mathrm{R = C_6H_5}$, X = Cl) complexes appear to be authentic five-coordinate species. The cis configuration is assigned to the $\mathrm{R_2Sn(mnt)_2^{2-}}$ ($\mathrm{R = CH_3, C_6H_5}$) ions. The isomer shift of the $\mathrm{Sn(mnt)_3^{2-}}$ ion shows a marked cation dependence and is interpreted in terms of distortions in the coordination sphere. The mnt complexes are compared to the corresponding toluenedithiolato and dithiocarbamato complexes whenever possible.

Introduction

Recent reports from this laboratory have shown that the *cis*-dicyanoethylene-1,2-dithiolate (mnt)[2] ion forms a wide variety of complexes with group IVb metal ions.[3-5] Although these complexes have been characterized by a variety of techniques,[3-6] several questions concerning the geometrical and electronic structures of the species in question still remain unanswered. Mossbauer spectroscopy has proved to be a useful technique in formulating solutions to problems of this sort for a wide variety of tin compounds.[7,8] Therefore, we have examined the Mossbauer spectra of a series of $\mathrm{Sn^{IV}}$-mnt complexes in order to understand better the interaction of dithiolato ligands with posttransition elements.

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[2] mnt is an abbreviation of the trivial name maleonitrile-dithiolate for the dicyanoethylene-1,2-dithiolate ion.

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