Contribution from the Department of Chemistry,
The University of North Carolina, Chapel Hill, North Carolina 27514

Molecular Structure of Bis[dichloro(*N*,*N*,*N'*,*N'*-tetramethylethylenediaminecopper(II)], $[Cu(tmen)Cl_2]_2$

EVA DIXON ESTES, WILLIAM E. ESTES, WILLIAM E. HATFIELD, and DEREK J. HODGSON*

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The crystal and molecular structure of bis[dichloro(*N*,*N*,*N'*,*N'*-tetramethylethylenediamine)copper(II)], $[Cu(tmen)Cl_2]_2$, has been determined from three-dimensional X-ray data collected by counter methods. The material crystallizes in space group $P\bar{1}$ of the triclinic system with one dimeric formula unit in a cell of dimensions $a = 7.713$ (7), $b = 8.560$ (8), and $c = 9.249$ (8) Å; $\alpha = 98.44$ (6), $\beta = 94.39$ (7), and $\gamma = 118.63$ (5)°. The observed and calculated densities are 1.59 and 1.591 g cm^{-3}, respectively. Least-squares refinement of the structure based on 1451 independent intensities has led to an R factor (on F) of 0.040. The structure consists of weakly bound chloro-bridged dimers, the out-of-plane Cu–Cl distance being 3.147 (4) Å while the Cu–Cu' separation is 4.089 (4) Å and the Cu–Cl–Cu' angle is 96.8 (1)°. The coordination about copper is a distorted tetragonal pyramid, with two chlorine and two nitrogen atoms in the base and the out-of-plane chlorine atom at the apex. The structure is quite similar to that of the corresponding bromo complex.

Introduction

There has been considerable recent research activity in the area of the correlation of the structural and magnetic properties of bridged copper(II) dimers,[1] and qualitative and quantitative correlations between various structural features and magnetic behavior have been postulated by several groups for the cases where the bridging atom is a first-row (typically oxygen) atom.[2-4] The relatively simple concepts which have been successfully used for these cases, however, may not be directly applicable to halogen-bridged systems because of the presence, in this latter case, of relatively low-lying d orbitals on the bridging atom.

There is a surprising paucity of structural data for dichloro-bridged copper(II) dimers, with only five complete structures known to us;[5-9] the situation for dibromo-bridged copper(II) dimers is even worse, with only two known structures.[10,11] This lack of data, together with an associated lack of detailed magnetic information, has rendered impossible the correlation of magnetic and structural properties in these systems. We are continuing, therefore, our structural investigations in this area and report here the complete three-dimensional structure of the *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (tmen) complex, $[Cu(tmen)Cl_2]_2$.

Data Collection and Reduction

Blue crystals of $[Cu(tmen)Cl_2]_2$ were prepared by the method of Lemmetti, *et al.*[12] On the basis of precession and Weissenberg photographs the crystals were assigned to the triclinic system. No systematic absences were observed, which implies that the space group is either $P1$ or $P\bar{1}$. The latter space group was chosen and subsequent refinement indicated that this choice is the correct one. The cell constants, obtained by the least-squares method described previously,[13] are $a = 7.713$ (7), $b = 8.560$ (8), and $c = 9.249$ (8) Å; $\alpha = 98.44$ (6), $\beta = 94.39$ (7), and $\gamma = 118.63$ (5)°. The observations were made at 23.5° with the wavelength assumed as $\lambda(\text{Cu K}\alpha_1) = 1.5405$ Å. A density of 1.591 g cm^{-3} calculated for one dimeric formula unit in the cell is in good agreement with the value of 1.59 g cm^{-3} obtained by flotation by Lemmetti, *et al.*[12] Hence, in the centrosymmetric space group $P\bar{1}$, the dimer is constrained to lie on a crystallographic inversion center. The space group and cell volume obtained here are in agreement with those reported by Lemmetti, *et al.*[12]

Diffraction data were collected from a parallelepiped-shaped crystal with faces (110), $(\bar{1}\bar{1}0)$, $(\bar{1}10)$, $(1\bar{1}0)$, (001), and $(00\bar{1})$. The separations between opposite pairs of faces were as follows: (110) and $(\bar{1}\bar{1}0)$, 0.014 cm; $(\bar{1}10)$ and $(1\bar{1}0)$, 0.010 cm; (001) and $(00\bar{1})$, 0.070 cm. The crystal was mounted on a glass fiber normal to the (001) planes, and in this orientation intensity data were collected on a Picker four-circle automatic diffractometer using Cu Kα radiation filtered through a 0.5-mil Ni foil. The mosaicity of the crystal was examined by means of the narrow-source, open-counter, ω-scan technique and was judged to be acceptable. Twelve reflections from the crystal were accurately centered through a narrow vertical slit at a takeoff angle of 3.0°. These formed the basis for the least-squares refinement of cell parameters and orientation using the logic documented by Busing and Levy[13] for the PDP-8/L computer.

Intensity data were collected at a takeoff angle of 3.0°; at this angle the peak intensity of a typical strong reflection was approximately 90% as a function of takeoff angle. The receiving aperture was 5.0 mm high by 5.0 mm wide and was positioned 32 cm from the crystal. The data were collected by the θ–2θ scan technique at a scan rate of 1°/min. Allowance was made for the presence of both Kα_1 and Kα_2 radiations, the peaks being scanned from −0.75° in 2θ below the calculated Kα_1 peak position to +0.75° in 2θ above the calculated Kα_2 position. Stationary-counter, stationary-crystal background counts of 10 sec were taken at each end of the scan. The pulse height analyzer was set for approximately a 90% window centered on the Cu Kα peak.

A unique data set having $3° \leq 2\theta \leq 120°$ was gathered; a total of 1628 independent intensities was recorded. The intensities of three standard reflections, measured after every 100 reflections, showed only the deviations from the mean predicted from counting statistics.

Data processing was carried out as described by Corfield, *et al.*[14] After correction for background, the intensities were assigned standard deviations according to the formula $\sigma(I) = [C + 0.25(t_s/t_b)^2(B_H + B_L) + (pI)^2]^{1/2}$ and the value of p was selected as 0.045. The values of I and $\sigma(I)$ were corrected for Lorentz–polarization effects and for absorption factors. The absorption coefficient for this compound for Cu Kα radiation is 72.6 cm^{-1}, and for the crystal chosen the transmission coefficients evaluated by numerical integration were found to range from 0.311 to 0.532. Of the 1628 independent reflections, 1451 were greater than 3 times their estimated standard deviations.

Solution and Refinement of Structure

The positions of the copper atom and the bridging chlorine atom were determined from a three-dimensional Patterson function. Two cycles of least-squares refinement of these positions were run.[15] All least-squares refinement in this analysis were carried out on F, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$; the weights w were taken as $4F_o^2/\sigma^2(F_o^2)$. In all calculations of F_c the atomic scattering factors for Cu, Cl, and N were taken from Cromer and Waber,[16] that for C was taken from the tabulation of Ibers,[17] and that for H was taken from Stewart, Davidson, and Simpson.[18] The effects of anomalous dispersion were included in calculations of F_c,[19] the values of $\Delta f'$ and $\Delta f''$ being taken from the tabulations of Cromer and Liberman.[20] Only the 1451 independent intensities which were greater than 3 times their estimated standard deviations were used in the refinement of the structure.

Initially, the copper and chlorine atoms were assigned isotropic thermal parameters. After two cycles of least-squares refinement, the usual agreement factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2)^{1/2}$ were 0.487 and 0.572, respectively. A difference Fourier synthesis revealed the positions of the other chlorine atom and the two carbon and two nitrogen atoms in the tmen chelate ring. Two further cycles of least-squares refinement yielded values of R_1 and R_2 of 0.260 and 0.364, respectively.

A difference Fourier map revealed the positions of all remaining

Table I. Positional Parameters for $[Cu(tmen)Cl_2]_2$

Atom	x	y	z
Cu	0.06003 (7)	0.00893 (6)	−0.21105 (6)
Cl(1)	−0.2358 (1)	−0.1352 (1)	−0.1301 (2)
Cl(2)	−0.0030 (2)	−0.2285 (1)	0.2716 (1)
N(1)	0.3485 (4)	0.1371 (4)	−0.2527 (4)
N(2)	0.0829 (4)	−0.2258 (4)	−0.2447 (3)
C(1)	0.4257 (6)	0.0139 (6)	−0.2271 (6)
C(2)	0.2745 (7)	−0.1765 (6)	−0.3007 (6)
C(3)	0.3561 (8)	0.1671 (8)	−0.4058 (6)
C(4)	0.4786 (8)	0.3165 (7)	−0.1524 (6)
C(5)	−0.0857 (7)	−0.3739 (6)	−0.3558 (5)
C(6)	0.0819 (7)	−0.2915 (7)	−0.1057 (5)
H(1A)	−0.442 (6)	0.055 (5)	−0.255 (5)
H(1B)	0.456 (6)	0.033 (6)	−0.126 (6)
H(2A)	0.326 (7)	−0.243 (6)	−0.287 (6)
H(2B)	0.245 (9)	−0.185 (8)	−0.413 (8)
H(3A)	0.313 (7)	0.255 (7)	−0.415 (6)
H(3B)	0.497 (9)	0.212 (7)	−0.432 (7)
H(3C)	0.286 (9)	0.064 (8)	−0.461 (7)
H(4A)	0.428 (7)	0.384 (7)	−0.160 (6)
H(4B)	−0.392 (7)	0.367 (6)	−0.163 (5)
H(4C)	0.475 (7)	0.299 (6)	−0.055 (6)
H(5A)	−0.076 (7)	−0.342 (6)	−0.452 (6)
H(5B)	−0.199 (6)	−0.385 (5)	−0.319 (5)
H(5C)	−0.075 (6)	−0.481 (7)	−0.374 (6)
H(6A)	−0.046 (7)	−0.317 (6)	−0.075 (5)
H(6B)	0.174 (7)	−0.207 (6)	−0.035 (6)
H(6C)	0.085 (7)	−0.389 (7)	−0.129 (6)

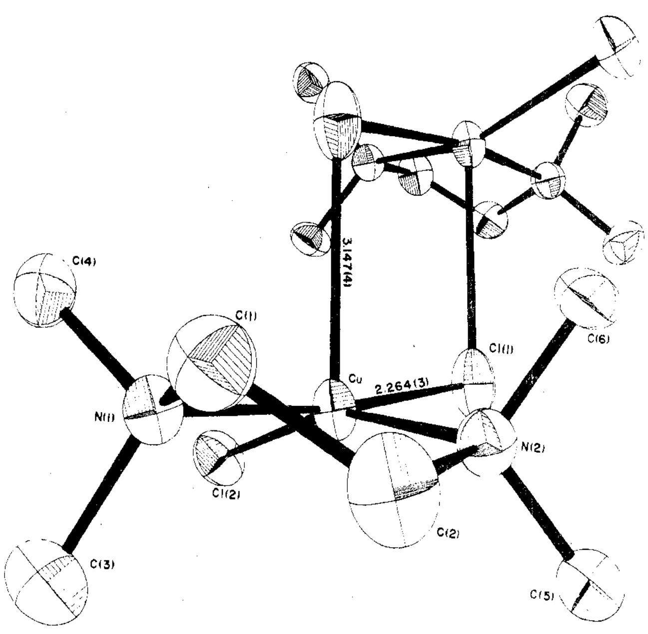

Figure 1. View of the $[Cu(tmen)Cl_2]_2$ dimeric unit. Hydrogen atoms have been omitted for clarity.

nonhydrogen atoms. Least-squares refinement of the parameters derived from this Fourier map yielded values of 0.138 and 0.207 for R_1 and R_2.

The absorption correction was then applied (*vide supra*), and four further cycles of least-squares refinement with anisotropic thermal parameters assigned to all atoms yielded values of $R_1 = 0.061$ and $R_2 = 0.101$. The 16 hydrogen atoms were located in a difference Fourier map, and two further least-squares cycles were run in which the nonhydrogen atoms were assigned anisotropic thermal parameters and the hydrogen atoms were assigned isotropic thermal parameters. This reduced the values of the agreement factors to 0.044 and 0.057. An examination of the final values of $|F_o|$ and $|F_c|$ suggested that the data were suffering from secondary extinction, and a correction of the type described by Zachariasen[21–23] was applied; the value of the extinction coefficient was 1.1 (1) × 10^{-7}. In the last cycle of least-squares refinement, the greatest shift in any parameter was 0.7 times its estimated standard deviation, which is taken as evidence that the refinement had converged. The positional and thermal parameters derived from the last cycle of least-squares refinement, along with their associated standard deviations as estimated from the inverse matrix, are presented in Tables I and II. A table of observed and calculated structure factors is available.[24] The final values of R_1 and R_2 were 0.040 and 0.054.

Description of the Structure

The complex consists of discrete dimeric $[Cu(tmen)Cl_2]_2$ units which are well separated from each other; the structure of the dimer is shown in Figure 1. The bridging Cu–Cl(1)–Cu′–Cl(1)′ unit is strictly planar, there being a crystal-

Table II. Thermal Parameters for $[Cu(tmen)Cl_2]_2$

Atom	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Atom	B, Å^2
Cu	0.0162 (2)	0.0123 (1)	0.0131 (1)	0.0079 (1)	0.0057 (1)	0.0052 (1)	H(1A)	3.3 (8)
Cl(1)	0.0200 (3)	0.0182 (2)	0.0247 (2)	0.0108 (2)	0.0121 (2)	0.0089 (2)	H(1B)	3.4 (9)
Cl(2)	0.0308 (3)	0.0181 (2)	0.0137 (2)	0.0162 (2)	0.0072 (2)	0.0074 (1)	H(2A)	4.3 (10)
N(1)	0.0172 (7)	0.0150 (6)	0.0105 (4)	0.0059 (6)	0.0039 (5)	0.0044 (4)	H(2B)	7.2 (15)
N(2)	0.0178 (7)	0.0130 (6)	0.0102 (4)	0.0087 (5)	0.0039 (4)	0.0029 (4)	H(3A)	5.4 (12)
C(1)	0.0150 (9)	0.0230 (10)	0.0143 (8)	0.0102 (8)	0.0044 (7)	0.0057 (7)	H(3B)	7.1 (14)
C(2)	0.0233 (11)	0.0195 (9)	0.0169 (8)	0.0147 (9)	0.0087 (7)	0.0057 (7)	H(3C)	7.3 (17)
C(3)	0.0271 (13)	0.0247 (12)	0.0121 (7)	0.0121 (11)	0.0085 (8)	0.0075 (8)	H(4A)	5.1 (13)
C(4)	0.0226 (12)	0.0162 (9)	0.0130 (7)	0.0016 (9)	0.0041 (7)	0.0035 (7)	H(4B)	4.6 (10)
C(5)	0.0244 (11)	0.0157 (9)	0.0102 (6)	0.0095 (8)	0.0036 (7)	0.0032 (6)	H(4C)	5.0 (10)
C(6)	0.0283 (13)	0.0165 (9)	0.0091 (6)	0.0133 (9)	0.0022 (7)	0.0037 (6)	H(5A)	5.1 (10)
							H(5B)	3.2 (8)
							H(5C)	4.5 (10)
							H(6A)	3.4 (9)
							H(6B)	3.8 (10)
							H(6C)	5.1 (12)

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

Table III. Bridging Geometry in Dichloro-Bridged Copper(II) Dimers

	$[Cu_2Cl_8]^{4-}$	$[Cu(guan)Cl_2]$	$[Cu_2Cl_6]^{2-}$ [a]	$[Cu(DMG)Cl_2]_2$	$[Cu(pic_2)Cl_2]_2$	$[Cu(tmen)Cl_2]_2$
Cu–Cu′, Å	3.72	3.58	3.37	3.45	4.41	4.09
Cu–Cl′ (out of plane), Å	2.70	2.45	2.33[b]	2.70	3.37	3.15
Cu–Cl–Cu′, deg	95.2	98	93.5	88	101.4	96.8
Geometry at Cu	TBP[c]	TBP[c]	Tet[d]	TP[e]	TP[e]	TP[e]
Ref	5	8	9	7	6	This work

[a] Values cited are the averages of the two independent measurements. [b] Longer bridging distance. [c] TBP = trigonal bipyramidal. [d] Tet = tetrahedral. [e] TP = tetragonal pyramidal.

Table IV. Internuclear Distances in $[Cu(tmen)Cl_2]_2$

Atoms	Dist, Å	Atoms	Dist, Å
Cu-Cu'	4.089 (4)	C(2)-H(2A)	0.85 (5)
Cu-Cl(1)	2.264 (3)	C(2)-H(2B)	1.03 (7)
Cu-Cl(1)'	3.147 (4)	C(3)-H(3A)	0.96 (5)
Cu-Cl(2)	2.259 (2)	C(3)-H(3B)	1.03 (6)
Cu-N(1)	2.054 (4)	C(3)-H(3C)	0.84 (6)
Cu-N(2)	2.081 (3)	C(4)-H(4A)	0.85 (5)
N(1)-C(1)	1.475 (5)	C(4)-H(4B)	0.90 (5)
N(1)-C(3)	1.477 (6)	C(4)-H(4C)	0.94 (6)
N(1)-C(4)	1.479 (6)	C(5)-H(5A)	0.96 (6)
N(2)-C(2)	1.488 (5)	C(5)-H(5B)	0.93 (4)
N(2)-C(5)	1.479 (6)	C(5)-H(5C)	0.95 (5)
N(2)-C(6)	1.477 (5)	C(6)-H(6A)	0.98 (5)
C(1)-C(2)	1.488 (7)	C(6)-H(6B)	0.87 (5)
C(1)-H(1A)	0.98 (4)	C(6)-H(6C)	0.84 (5)
C(1)-H(1B)	0.92 (5)		

Table V. Internuclear Angles in $[Cu(tmen)Cl_2]_2$

Atoms	Angle, deg	Atoms	Angle, deg
Cu(1)-Cu-Cl(1)'	83.2 (1)	Cu-N(1)-C(4)	113.3 (3)
Cu-Cl(1)-Cu'	96.8 (1)	C(1)-N(1)-C(3)	111.0 (4)
N(1)-Cu-N(2)	85.3 (1)	C(1)-N(1)-C(4)	108.8 (4)
N(1)-Cu-Cl(2)	92.4 (1)	C(3)-N(1)-C(4)	107.0 (4)
Cl(2)-Cu-Cl(1)	93.6 (1)	Cu-N(2)-C(2)	106.3 (2)
Cl(1)-Cu-N(2)	91.8 (1)	Cu-N(2)-C(5)	111.3 (3)
Cl(1)'-Cu-Cl(2)	105.9 (1)	Cu-N(2)-C(6)	111.1 (3)
Cl(1)'-Cu-N(1)	88.4 (1)	C(2)-N(2)-C(5)	109.4 (3)
Cl(1)'-Cu-N(2)	96.4 (1)	C(2)-N(2)-C(6)	110.9 (3)
N(1)-Cu-Cl(1)	170.8 (1)	C(5)-N(2)-C(6)	107.9 (3)
N(2)-Cu-Cl(2)	157.5 (1)	N(1)-C(1)-C(2)	109.8 (3)
Cu-N(1)-C(1)	104.7 (2)	N(2)-C(2)-C(1)	109.0 (4)
Cu-N(1)-C(3)	112.1 (3)		

lographic inversion center in the middle of the dimer. The bridging geometry is compared with that of the other known dichloro-bridged dimers in Table III. The Cu–Cu' and out-of-plane Cu–Cl(1)' distances of 4.089 (4) and 3.147 (4) Å, respectively, and the Cu–Cl(1)–Cu' bridging angle of 96.8 (1)° all fall within the ranges observed for these other complexes.[5-9] The bond lengths and angles in the dimer are listed in Tables IV and V.

The in-plane Cu–Cl distances of 2.259 (2) and 2.264 (3) Å are normal, with the distance to the bridging chlorine atom slightly the longer, as expected. The Cu–N bond lengths of 2.054 (4) and 2.081 (3) Å are slightly longer than those in most copper–amine complexes[3,25,26] but are similar to those in the bromo analog.[11] The bond lengths and angles associated with the tmen ligands are normal for such complexes;[3,11,27] the presence of the inversion center contrains each dimer to contain one δ and one λ ring.[28]

The geometry at the copper centers is best described as tetragonal pyramidal, with N(1), N(2), Cl(1), and Cl(2) forming the base and Cl(1)' occupying the apical site. The four basal atoms are not coplanar, however; N(1) and Cl(1) lie 0.31 and 0.26 Å, respectively, above the best least-squares plane through the four atoms while N(2) and Cl(2) lie 0.30 and 0.26 Å, respectively, below it. The copper atom is 0.13 Å above the plane, *i.e.*, toward the apical atom Cl(1)'; this is the usual situation in tetragonal-pyramidal complexes.[29,30]

As can be seen in Table III, the Cu–Cu' separation, the out-of-plane Cu–Cl(1)' distance, and the bridging Cu–Cl(1)–Cu' angle in this complex are all intermediate between the values for the two other tetragonal pyramidal dichloro-bridged dimers. For $[Cu(DMG)Cl_2]_2$ (DMG = dimethylglyoxime), the Cu–Cu' and Cu–Cl(1)' distances are[7] 3.45 and 2.70 Å; these short separations might lead one to expect considerable magnetic exchange, but the bridging angle of 88° presumably precludes much orbital overlap, and the observed[31] value of the singlet–triplet splitting, $2J$, is $+6.3$ cm^{-1}. In $[Cu(pic)_2Cl_2]_2$ (pic = 2-methylpyridine) the Cu–Cu and Cu–Cl(1)' separations are very long,[6] but the bridging angle is increased to 101.4°; this increased bridging angle brings about a more antiferromagnetic interaction, whose magnitude is greater than the ferromagnetic effect observed in $[Cu(DMG)Cl_2]_2$; the value of $2J$ for $[Cu(pic)_2Cl_2]_2$ is -7.4 cm^{-1}.[32] The present structural data, therefore, should allow insight into the relative roles of the out-of-plane separation and the bridging angle in determining the magnitude and sign of the magnetic interaction in dimers of this type once complete magnetic data become available; unfortunately, only the room-temperature magnetic moment is known at present.

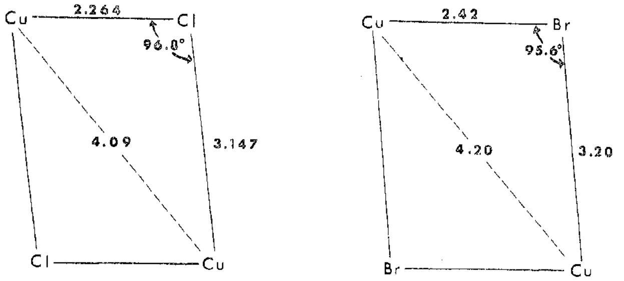

Figure 2. A comparison of the bridging geometries of $[Cu(tmen)Cl_2]_2$ and $[Cu(tmen)Br_2]_2$. Data for $[Cu(tmen)Br_2]_2$ are from ref 11.

The bridging geometry of this dimer is compared with that of the bromo analog[11] in Figure 2. Since the covalent radius[33] of Br is 0.15 Å larger than that of Cl while the out-of-plane separation in the bromo analog is only 0.05 Å longer than that in the chloro, we conclude that the bridging interaction is stronger in the bromo complex than in the chloro complex. Since the bridging angles are very similar, we would anticipate that the magnitude of $2J$ for the bromo complex will prove to be greater than that of the chloro complex. It is noteworthy that, in the case of the 2-methylpyridine complexes, the structural interaction in the bromo complex[10] is weaker than that in the chloro complex,[6] and the magnitude of J is greater for the chloro complex than for the bromo analog.

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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 in 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 AIC40510G.

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Contribution from the Department of Chemistry,
University of Virginia, Charlottesville, Virginia 22901

Solvated Tris(4-morpholinecarbodithioato-*S*,*S*') Complexes of Iron(III) and Cobalt(III). Direct Comparison of d^5 and d^6 Analogs and Study of Solvation Effects

P. C. HEALY and E. SINN*

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A number of tris(dithiocarbamato)iron(III) and -cobalt(III) solvate complexes have been examined. Inclusion of polar solvent molecules appears to be the common norm in crystals of these complexes. The decomposition points, at which all the solvent suddenly escapes, breaking up the crystal lattices, are well above the boiling points of the particular solvents. The iron(III) complexes retain the solvent molecules less well, and in many cases, solvent is lost on standing, a fact that may explain a number of the difficulties in earlier attempts at structural analysis. The strong trend to form solvates is the probable cause of anomalous nmr spectra observed in several of the cobalt complexes. Crystal structures of the dichloromethane solvates of the title complexes were determined from three-dimensional counter data at room temperature. Both compounds crystallize in space group $P\bar{1}$, $Z = 2$. The lattice constants are $a = 13.088$ (3) Å, $b = 10.693$ (1) Å, $c = 11.499$ (1) Å, $\alpha = 116.08$ (1)°, $\beta = 104.97$ (1)°, and $\gamma = 99.49$ (2)° for the iron complex and $a = 13.079$ (1) Å, $b = 10.682$ (1) Å, $c = 11.493$ (1) Å, $\alpha = 116.03$ (1)°, $\beta = 105.04$ (1)°, and $\gamma = 99.45$ (1)° for the cobalt complex. The data were refined by block-diagonal least squares to $R = 6.3\%$ (iron) and 4.2% (cobalt). The molecular geometry of the CoS_6 in the cobalt is identical with previous cobalt tris(dithio chelate) structures with $\langle Co–S \rangle = 2.27$ Å and $\langle S_{i1}–Co–S_{i2} \rangle = 76.1°$. The values of 2.44 Å and 72.5° for $\langle Fe–S \rangle$ and $\langle S_{i1}–Fe–S_{i2} \rangle$ in the iron complex are atypical and the linear relationship previously postulated for the magnetic moments and Fe–S bond length in iron tris(dithio chelate) complexes does not seem to be universally applicable. The solvent molecules are orientated so as to minimize electrostatic repulsions with the complex. However, no strong hydrogen bonding interactions exist.

Introduction

Structures of metal(III) dithiocarbamate complexes have been of considerable interest but have presented unusual difficulty. For example, Ewald, *et al.*,[1] commented on microscopic disorder in the iron(III) complexes after observing powder X-ray patterns from apparently well-formed crystals. Bernal, *et al.*,[2] were forced to abandon attempts to collect single-crystal X-ray data on several iron(III) dithiocarbamates because of extensive changes destroying the lattices within hours of withdrawing the crystals from the mother liquor. Similar difficulties occur in the cobalt(III) complexes in addition to a tendency to form twinned crystals. Part of the problem may be the escape of solvent molecules included or adducted in the crystals. It appears that well-formed single crystals of tris(dithiocarbamates) are more likely to be produced from solvated than from unsolvated complexes. The situation is further complicated by the $^6A_1$–$^2T_2$ electronic equilibrium in the iron(III) complexes, so that the spin state and the metal–ligand bond lengths depend on temperature, pressure, and other external factors.[3,4]

We report here the crystal structures of two analogous solvated complexes, tris(4-morpholinecarbodithioato-*S*,*S*')-iron(III)–dichloromethane and tris(4-morpholinecarbodithioato-*S*,*S*')cobalt(III)–dichloromethane. These two represent a transition from d^5 to d^6 electronic configuration in an otherwise unaltered molecule, thereby permitting observation of the structural effect of inserting a single electron. Detailed comparison of the metal–ligand distances and angles is important to an understanding of the d-electron involvement in the bonding. For dithiocarbamates, the equilibrium between high spin and low spin must also affect the metal–ligand bonding and intercomparison between ferric complexes having different proportions of high- and low-spin components is important.

Further interest in tris(dithiocarbamate) solvates stems from two other observations: the nmr spectra, particularly in deuterated chloroform, show nonequivalencies in the R groups of many $Co(S_2CNR_2)_3$ complexes;[5] lattice effects were found to be of considerable importance in determining the position of the $^6A_1$–$^2T_2$ crossover,[2] and such lattice-disturbing phenomena as the presence or absence of solvates must strongly influence the magnetic properties. A detailed study in the range 1–200°K on the tris(pyrrolidinecarbodithioate-*S*,*S*') has shown this to be the case; the precise magnetic properties depend dramatically on the presence or absence of a solvent molecule in the lattice.[5]

Experimental Section

The unsolvated complexes were prepared as previously described.[6] Evaporation of an equimolar mixture of dichloromethane–cyclohexane gave well-formed crystals of the solvated complexes. Analogs with other solvents were prepared in a like manner.

Low-resolution mass spectral data for these complexes were run on a Hitachi Perkin-Elmer RMU-6E mass spectrometer. Infrared spectra were recorded as Nujol mulls between potassium bromide plates over the range 4000–400 cm^{-1} on a Perkin-Elmer 521 grating ir spectrophotometer. Densities were determined by flotation in aqueous potassium iodide. Melting points were measured on a Fisher-Johns melting point apparatus.

Collection and Treatment of X-Ray Diffraction Data. The crystal selected for the diffraction study on the cobalt complex was mounted on a glass fiber, normal to the (100) plane and attached to a eucentric goniometer head. The crystal was a parallelepiped bound by the (100) faces, 0.24 mm apart, the (010) faces, 0.20 mm apart, and the (001) faces, 0.20 mm apart. Crystals of the iron complex deteriorated rapidly in the atmosphere and the crystal used in data collection was