(16) R. J. Brotherton, A. L. McCloskey, L. L. Petterson, and H. Steinberg, *J. Amer. Chem. Soc.*, **82**, 6242 (1960).

(17) H. H. Schulbach and E. C. Goes, *Ber. Deut. Chem. Ges.*, **55**, 2889 (1922).

(18) A. A. Morton, J. B. Davidson, and B. L. Hakan, *J. Amer. Chem. Soc.*, **64**, 2242 (1942).

(19) R. Hoffman, *J. Chem. Phys.*, **40**, 2474 (1964); R. Hoffmann, *Advan. Chem. Ser.*, No. **42**, 78 (1964).

(20) R. L. Collins, *Acta Crystallogr.*, **5**, 431 (1952); **9**, 537 (1956).

(21) J. J. Rush, *J. Chem. Phys.*, **46**, 2285 (1967).

(22) H. Y. Ting, W. H. Watson, and H. C. Kelley, *Inorg. Chem.*, **11**, 375 (1972).

(23) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, No. **11** (1958).

(24) S. Geller and J. L. Hoard, *Acta Crystallogr.*, **4**, 399 (1951).

(25) W. J. McLean and G. A. Jeffrey, *J. Chem. Phys.*, **47**, 414 (1967).

(26) L. M. Trefonas, F. S. Mathews, and W. N. Lipscomb, *Acta Crystallogr.*, **14**, 273 (1961).

(27) K. Hedberg, V. Schomaker, and M. E. Jones, Second International Congress of Crystallography, Stockholm, Abstracts of Papers, 1951, E.D. 17, p 39.

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

Copper(II) Complexes of Amino Alcohols. Molecular Structures of Chloro(2-diethylaminoethanolato)copper(II) and Bromo(2-dibutylaminoethanolato)copper(II)

EVA DIXON ESTES and DEREK J. HODGSON*

Received July 15, 1974 AIC40473T

The crystal and molecular structures of chloro(2-diethylaminoethanolato)copper(II) and bromo(2-dibutylaminoethanolato)copper(II) have been determined from three-dimensional X-ray data collected by counter methods. The chloro complex crystallizes in the space group $P4_12_12$ (or $P4_32_12$) of the tetragonal system with 16 monomeric formula units in a cell of dimensions $a = 11.334$ (3) and $c = 27.791$ (8) Å. The observed and calculated densities are 1.59 and 1.602 g cm^{-3}, respectively. The bromo complex crystallizes in the space group $P2_12_12_1$ of the orthorhombic system with four formula units in a cell of dimensions $a = 21.16$ (2), $b = 15.15$ (2), and $c = 8.40$ (1) Å. The observed and calculated densities for this complex are 1.55 and 1.5 (1) g cm^{-3}, respectively. Least-squares refinement of the chloro and bromo structures has led to final values of the conventional R factor (on F) of 0.051 and 0.236, respectively. The chloro structure is tetranuclear with oxygen atoms bridging the adjacent copper(II) atoms. The bromo structure consists of oxygen-bridged, dimeric units. The analyses of these structures, therefore, support the classification by Uhlig and Staiger of complexes of the type Cu(OR)X (ROH = an amino alcohol) into three distinct structural classes and suggest that members of group 1 are dimeric while those in group 3 are tetrameric.

Introduction

The syntheses of a wide variety of compounds of the types CuCl(OR) and CuBr(OR), where ROH is an amino alcohol, have been reported by Hein and coworkers.[1,2] These workers postulated that the complexes should be formulated as dimers in which the amino alcohol acts as a chelating bridge, and this was recently confirmed by the report[3] of the structure of bromo(2-diethylaminoethanolato)copper(II). The geometry around the copper centers in this complex is roughly tetrahedral, with a Cu–O–Cu bridging angle, ϕ, of approximately 104.5°. More recently, Bertrand[4] has observed a similar dimeric unit in the structure of acetato(2-dibutylaminoethanolato)copper(II), with $\phi = 109°$. Uhlig and Staiger, however, have reported the room-temperature magnetic and spectroscopic properties of a number of compounds of this type[5,6] and deduced that they may be divided into three distinct groups according to their magnetic moments: (1) compounds which have greatly reduced moments at 20° (less than 1 BM); they assumed these to be oxygen-bridged dimers; (2) compounds which have normal magnetic moments; in this case the copper atom probably has a coordination number greater than 4; (3) compounds with only slightly reduced moments at 20° (about 1.5 BM); it was suggested[6] that these complexes might be tetrameric. It is noteworthy that Uhlig and Staiger placed bromo(2-diethylaminoethanolato)copper(II) in the first group, since the subsequent structure determination by Pajunen and Lehtonen lends credence to their scheme. The corresponding chloro complex ($\mu = 1.68$ BM) was assigned[5] to the third group, and Lehtonen later reported that the space group and cell constants are, in fact, different from those of the bromo complex; this strongly suggested that the two structures might be entirely different and that the chloro complex might not be an oxygen-bridged dimer.

In order to investigate further the structural properties of this class of complexes and especially to test the general classification of Uhlig and Staiger (*vide supra*), we have examined the crystal structures of two complexes of this type. One of the complexes chosen was chloro(2-diethylaminoethanolato)copper(II), which is in group 3, while the other was bromo(2-dibutylaminoethanolato)copper(II) which has been assigned[6] to group 1. The results of these structural investigations are reported here.

Experimental Section

(a) Chloro(2-diethylaminoethanolato)copper(II). The dark green chloro(2-diethylaminoethanolato)copper(II) was prepared by treating 1.34 g of copper(II) chloride (0.01 mol) in 150 ml of absolute ethanol with 2.34 g of 2-diethylaminoethanol (0.02 mol) in 50 ml of absolute ethanol. The reaction mixture was allowed to stand at room temperature. After several days dark green rhombic crystals formed. *Anal.* Calcd for $Cu(C_6H_{14}NO)Cl$: C, 33.49; H, 6.55; N, 6.51; Cl, 16.47; mol wt 860.70. Found: C, 33.53; H, 6.36; N, 6.54; Cl, 16.41.

On the basis of Weissenberg and precession photographs the crystals were assigned to the tetragonal system. The observed systematic absences of $h00$ for h odd and $00l$ for l not equal to $4n$ are consistent with the space groups $P4_32_12$ and $P4_12_12$; the latter assignment was chosen. The cell constants, obtained by the least-squares procedure of Busing and Levy,[7] are $a = 11.334$ (3) and $c = 27.791$ (8) Å. These are in agreement with the cell constants previously reported by Lehtonen.[8] A density of 1.602 g cm^{-3} calculated for 16 formula units in the cell agrees well with the value of 1.59 g cm^{-3} which Lehtonen obtained by flotation in carbon tetrachloride and toluene.[8]

Diffraction data were collected at 17° using a Picker four-circle automatic diffractometer. The wavelength was assumed to be λ(Mo Kα_1) 0.7093 Å. Two rhombic crystals with faces (011), $(0\bar{1}1)$, $(\bar{1}01)$, (101), $(0\bar{1}\bar{1})$, $(01\bar{1})$, $(10\bar{1})$, and $(\bar{1}0\bar{1})$ were chosen for data collection. The face–face distance was 0.04 cm for all opposite pairs of faces in both crystals. The crystals were mounted on glass fibers roughly normal to the (011) planes, and in this orientation intensity data were collected. The mosaicity of the crystals was examined by means of the narrow-source, open-counter ω-scan technique.[9] The width at half-height for a typical strong reflection was found to be 0.10°, and the general shape of the ω scans was symmetric and unsplit so we are confident that both are single. Twelve reflections, accurately centered through a narrow vertical slit at a takeoff angle of 0.8°, formed the basis for the least-squares refinement of cell parameters and orientation. The refinement was effected using the logic documented by Busing and Levy in the PDP-8/L computer.[7] This process was repeated for the second crystal.

Intensity data were collected at a takeoff angle of 0.8°; at this angle the peak intensity for a typical strong reflection was about 85% of the maximum value as a function of takeoff angle. The counter aperture was 5.0 mm high by 5.0 mm wide and was positioned 32.0 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 $K\alpha_1$ and $K\alpha_2$ radiations, the scan range for each reflection being from 0.7° below the calculated $K\alpha_1$ peak position to 0.7° above the calculated $K\alpha_2$ peak position.

Stationary-counter, stationary-crystal background counts of 10 sec were taken at each end of the scan. The diffracted beam was filtered through a 0.0015-in. Nb foil. The pulse height analyzer was set for approximately a 90% window, centered on the Mo $K\alpha$ peak.

A unique data set having $2\theta(\text{Mo}) < 50°$ was gathered, a total of 3537 independent intensities being recorded. The intensities of three standard reflections were measured after every 100 reflections, and after 926 data had been collected from the first crystal, it was apparent that decomposition was severe since the average intensity had dropped by 12%. The second crystal, therefore, was used for data with $30° \leq 2\theta(\text{Mo}) < 50°$; by the end of the run, the average intensity for this crystal had been attenuated by 10%. This decline of the intensity as a function of cumulative exposure time was allowed for in the data processing.

Data processing was carried out as described by Corfield, *et al.*[10] 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 0.05. This term in the expression prevents extremely high weight being given to very large reflections.[11] The values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects and for absorption factors.[12] The absorption coefficient for this compound for Mo $K\alpha$ radiation is 27.72 cm^{-1} and for the samples chosen the transmission coefficients ranged from 0.36 to 0.48. Of the 3537 independent reflections, 2498 were greater than 3 times their estimated standard deviations.

(b) Bromo(2-dibutylaminoethanolato)copper(II). The olive green bromo(2-dibutylaminoethanolato)copper(II) was prepared by a minor modification of the method of Uhlig and Staiger.[5] Copper(II) bromide (2.23 g, 0.01 mol) was dissolved in 300 ml of absolute ethanol, and to this solution was added a solution of 2-dibutylaminoethanol (3.47 g, 0.02 mol) in 30 ml of absolute ethanol. After standing for 1 day, the olive green crystals precipitated along with some microcrystalline material; Uhlig and Staiger have noted the existence of two isomeric forms of this complex, the olive green material being in group 1 and the light green material in group 2. The material whose structure we have investigated is the olive green complex.

On the basis of Weissenberg and precession photography the crystals were assigned to the orthorhombic system. The observed systematic absences of $h00$ for h odd, $0k0$ for k odd, and $00l$ for l odd are consistent with the space group $P2_12_12_1$, but in view of the poor quality of all crystals studied (*vide infra*), this assignment should be considered as only tentative. The cell constants, obtained as described above, are a = 21.16 (2), b = 15.15 (2), and c = 8.40 (1) Å. As a consequence of the apparent partial solubility of the crystals in all common solvents, it was not possible accurately to determine the density of the material, but a series of flotation experiments in dichloromethane–carbon tetrachloride demonstrated that the density is 1.5 (1) g cm^{-3}; this is consistent with the value of 1.55 g cm^{-3} calculated for four formula units in the cell. Hence, in space group $P2_12_12_1$, no crystallographic symmetry is imposed on the molecules.

Table I. Positional Parameters for Chloro(2-diethylaminoethanolato)copper(II)

Atom	x	y	z
Cu(1)	0.26070 (8)	0.10014 (9)	0.02559 (4)
Cu(2)	0.44406 (9)	0.46356 (9)	0.29551 (4)
Cl(1)	0.3352 (2)	0.3083 (2)	0.3162 (1)
Cl(2)	0.3242 (2)	0.0880 (2)	0.1016 (1)
O(1)	0.4019 (5)	0.4613 (4)	0.2257 (2)
O(2)	0.1269 (5)	0.2061 (5)	0.0395 (2)
N(1)	0.0622 (7)	0.0431 (6)	0.3977 (3)
N(2)	0.4103 (6)	0.0323 (7)	−0.0059 (3)
C(1)	0.0379 (10)	0.3887 (8)	0.0590 (3)
C(2)	0.0762 (10)	0.4067 (9)	0.2415 (4)
C(3)	0.1359 (9)	0.3048 (9)	0.0714 (3)
C(4)	0.3835 (10)	0.3575 (8)	0.1973 (3)
C(5)	0.0965 (13)	0.1606 (12)	0.3822 (5)
C(6)	0.4925 (13)	0.3237 (13)	0.1726 (5)
C(7)	0.4027 (10)	0.0188 (9)	0.2583 (5)
C(8)	0.2728 (10)	0.0119 (11)	0.2488 (6)
C(9)	0.4689 (15)	0.4753 (15)	0.1084 (5)
C(10)	0.4782 (13)	0.1649 (13)	0.4850 (5)
C(11)	0.1366 (13)	0.2483 (14)	0.4200 (5)
C(12)	−0.0049 (15)	0.0775 (17)	0.1660 (6)

The data were collected as described above, except that the radiation used was Cu $K\alpha$, filtered by 0.001-in. Ni foil, and the temperature was 20°. The crystal was coated in clear varnish to prevent decomposition. Examination of a large number of crystals by the ω-scan technique[9] indicated that all crystals were severely twinned. Numerous attempts to prepare crystals of higher quality by modification of the experimental conditions were unsuccessful, and it was determined to collect intensity data on the available twinned material in the hope of establishing the basic molecular geometry and mode of aggregation of this important complex. A unique data set having $2\theta(\text{Cu}) < 120°$ was collected, 2065 data being recorded; of these, only 812 were greater than 3 times their estimated standard deviations and 993 were greater than twice their esd's. The data were processed as above, except that no correction for crystal decomposition was necessary.

Solution and Refinement of Structure

All least-squares refinements in this analysis were carried out on F, the function minimized being $\sum w(|F_o| - |F_c|)^2$; 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 Br, Cu, Cl, and N were taken from Cromer and Waber,[13] those for O and C were taken from the tabulation of Ibers,[14] and those for hydrogen were taken from Stewart, Davidson, and Simpson.[15] The effects of the anomalous dispersion of Br, Cu, and Cl were included in calculations of F_c,[16] the values of $\Delta f'$ and $\Delta f''$ being taken from the tabulations of Cromer.[17]

(a) Chloro(2-diethylaminoethanolato)copper(II). The position of one Cu atom was determined from a three-dimensional Patterson function, and two cycles of least-squares refinement were run on this position. The usual agreement factors $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and R_2 (or weighted R factor) = $(\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2)^{1/2}$ were 0.565 and 0.591, respectively. A difference Fourier followed by a bond distance calculation revealed a roughly tetrahedral arrangement of Cu atoms approximately 3 Å apart. The remaining nonhydrogen atoms were found in subsequent difference Fourier maps and least-squares refinement of these atoms with isotropic thermal parameters yielded values of 0.080 and 0.094 for R_1 and R_2. Two further cycles in which the atoms were assigned variable anisotropic thermal parameters gave values of 0.057 and 0.070 for R_1 and R_2. Attempts to locate the hydrogen atoms were unsuccessful, as were least-squares refinements in which the hydrogen atoms were put in positions calculated on the basis of tetrahedral geometry at the methylene carbon atoms.

Since only one form (hkl) from two different crystals in this noncentrosymmetric space group had been collected, there were four possible combinations of anomalous dispersion corrections; least-squares refinements incorporating all possible combinations of signs of the Miller indices demonstrated that, in $P4_12_12$, the appropriate combination is that with ($+h,+k,+l$) assigned to the data collected from the first crystal and ($-h,-k,-l$) assigned to those from the second crystal. This assignment led to values of R_1 and R_2 of 0.054 and 0.065, respectively.

Examination of the data at this stage revealed that the low-order data were in much poorer agreement with the model than were the other data, presumably because of our failure to locate the hydrogen atoms. Hence, the 254 data for which $2\theta(\text{Mo}) < 20°$ were rejected from the next least-squares cycle; the resulting values of R_1 and R_2 of 0.051 and 0.056 support the validity of this decision. In the final

Table II. Thermal Parameters for Chloro(2-diethylaminoethanolato)copper(II)

Atom	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	0.00476 (10)	0.00624 (10)	0.00078 (1)	0.00023 (7)	−0.00031 (3)	0.00035 (3)
Cu(2)	0.00578 (10)	0.00603 (10)	0.00074 (1)	−0.00049 (7)	−0.00012 (3)	0.00038 (3)
Cl(1)	0.0095 (2)	0.0077 (2)	0.00142 (4)	−0.0016 (2)	0.0003 (1)	0.0011 (1)
Cl(2)	0.0090 (2)	0.0103 (3)	0.00092 (3)	−0.0005 (2)	−0.0013 (1)	0.0005 (1)
O(1)	0.0051 (4)	0.0047 (4)	0.0008 (1)	0.0006 (4)	0.0003 (2)	−0.0003 (2)
O(2)	0.0061 (5)	0.0040 (4)	0.0009 (1)	0.0009 (4)	−0.0006 (2)	−0.0002 (1)
N(1)	0.0100 (8)	0.0060 (6)	0.0012 (1)	0.0002 (6)	0.0009 (2)	0.0004 (2)
N(2)	0.0051 (6)	0.0089 (7)	0.0011 (1)	0.0005 (5)	−0.0002 (2)	0.0001 (2)
C(1)	0.0107 (10)	0.0067 (8)	0.0008 (1)	0.0016 (8)	−0.0003 (3)	−0.0006 (3)
C(2)	0.0096 (10)	0.0068 (8)	0.0013 (2)	−0.0009 (8)	0.0002 (3)	−0.0008 (3)
C(3)	0.0095 (10)	0.0080 (9)	0.0008 (1)	0.0009 (7)	−0.0009 (3)	−0.0010 (3)
C(4)	0.0101 (10)	0.0070 (8)	0.0008 (1)	0.0007 (7)	0.0002 (3)	−0.0010 (3)
C(5)	0.0141 (14)	0.0107 (12)	0.0018 (2)	−0.0036 (11)	0.0022 (4)	0.0002 (4)
C(6)	0.0134 (14)	0.0129 (14)	0.0022 (2)	−0.0010 (11)	0.0014 (5)	−0.0028 (5)
C(7)	0.0089 (10)	0.0071 (9)	0.0021 (2)	0.0014 (8)	0.0000 (4)	−0.0007 (4)
C(8)	0.0081 (10)	0.0114 (12)	0.0024 (2)	0.0027 (9)	−0.0006 (4)	−0.0005 (4)
C(9)	0.0192 (18)	0.0168 (17)	0.0015 (2)	0.0021 (15)	0.0000 (5)	0.0013 (5)
C(10)	0.0128 (14)	0.0128 (13)	0.0023 (3)	0.0058 (12)	−0.0004 (5)	0.0003 (5)
C(11)	0.0148 (15)	0.0136 (15)	0.0022 (2)	−0.0033 (13)	0.0003 (5)	−0.0014 (5)
C(12)	0.0137 (16)	0.0204 (20)	0.0024 (3)	0.0034 (14)	−0.0003 (5)	−0.0022 (6)

[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. Positional Parameters for Bromo(2-dibutylaminoethanolato)copper(II)

Atom	x	y	z
Br(1)	−0.262 (1)	0.241 (1)	0.454 (3)
Br(2)	−0.513 (1)	0.213 (1)	0.017 (2)
Cu(1)	0.045 (1)	0.243 (1)	0.221 (2)
Cu(2)	0.181 (6)	0.254 (1)	0.313 (2)
O(1)	0.106 (3)	0.262 (5)	0.383 (7)
O(2)	0.125 (3)	0.240 (6)	0.117 (9)
N(1)	−0.033 (4)	0.294 (6)	0.359 (10)
N(2)	0.248 (2)	0.220 (3)	0.160 (7)
C(1)	0.229 (4)	0.290 (6)	0.020 (12)
C(2)	0.001 (4)	0.230 (5)	0.523 (11)
C(3)	−0.435 (4)	0.212 (5)	0.445 (10)
C(4)	−0.347 (4)	0.270 (6)	0.029 (12)

cycle of least squares, no parameter exhibited a shift larger than 0.5 times its estimated standard deviation. Examination of the final values of $|F_o|$ and $|F_c|$ suggested that no correction for secondary extinction was necessary, perhaps partly as a result of our having eliminated the low-order data. A final difference Fourier map was featureless.

The positional and thermal parameters derived from the last cycle of least squares are given in Tables I and II. A table of observed and calculated structure amplitudes is available.[18]

(b) Bromo(2-dibutylaminoethanolato)copper(II). Examination of a three-dimensional Patterson function was inconclusive, so the structure was solved by direct methods using the procedure of Karle and Karle.[19] An E map revealed the locations of two copper and two bromine atoms, and isotropic least-squares refinement yielded values of 0.373 and 0.447. The oxygen, nitrogen, and methylene carbon atoms of the ligand were located in a difference Fourier map, and isotropic refinement of these 12 atoms using the data greater than 3σ yielded values of R_1 and R_2 of 0.236 and 0.299, respectively. A difference Fourier map computed at this stage showed many peaks in the vicinity of the nitrogen atoms, but these could not be interpreted in terms of any reasonable geometry for the butyl groups. Our failure to locate the butyl groups is not surprising in view of the quality of the crystal and consequent data set, of course. No further computations met with any success, so the refinement was terminated at this stage. The positional parameters obtained from this final refinement are listed in Table III. A table of structure amplitudes is available.[18]

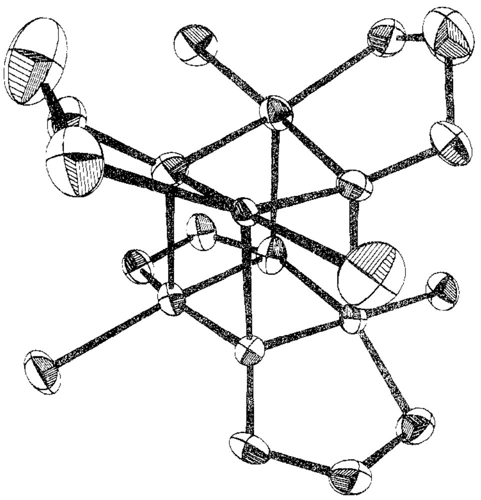

Figure 1. View of the tetrameric array in tetrakis[chloro(2-diethylaminoethanolato)copper(II)]. The ethyl groups and the hydrogen atoms have been omitted for clarity.

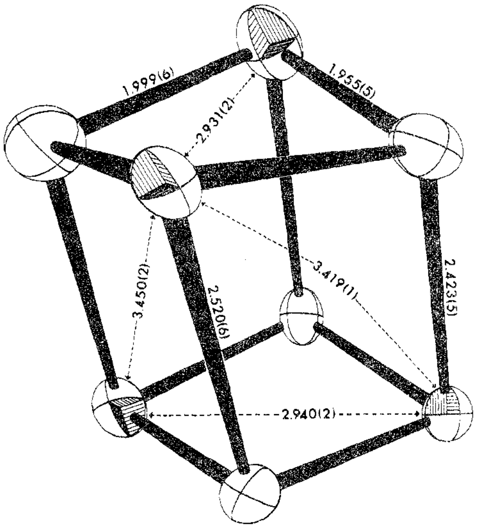

Figure 2. The bridging unit of copper and oxygen atoms in tetrakis[chloro(2-diethylaminoethanolato)copper(II)]. The copper atoms are shown as shaded ellipsoids.

Description of the Structures

(a) Chloro(2-diethylaminoethanolato)copper(II).[20] The structure consists of tetrameric tetrakis[chloro(2-diethylaminoethanolato)copper(II)] units, as is shown in Figure 1. The tetrameric array, which is more readily seen in Figure 2, consists of a roughly tetrahedral array of copper atoms which are bridged by an approximately tetrahedral array of oxygen atoms, giving rise to an approximately cubic array of alternating copper and oxygen atoms. Such a structure is not unique but is reminiscent of that found[21] for the related

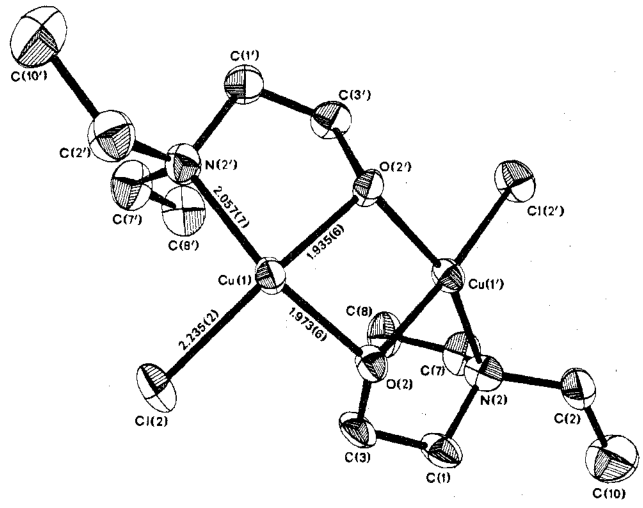

Figure 3. View of the bottom face of the tetrameric unit shown in Figure 1.

Table IV. Intramolecular Distances in Chloro(2-diethylaminoethanolato)copper(II)

Atoms	Distance, Å	Atoms	Distance, Å
Cu(1)–Cu(1′)	2.940 (2)	Cu(2)–Cl(1)	2.225 (3)
Cu(2)–Cu(2′)	2.931 (2)	C(3)–O(2)	1.432 (11)
Cu(1)–Cu(2)	3.450 (2)	C(4)–O(1)	1.432 (10)
Cu(1′)–Cu(2)	3.419 (1)	C(1)–N(2)	1.497 (12)
Cu(1)–Cu(2)	1.973 (6)	C(6)–N(1)	1.574 (18)
Cu(1)–O(2′)	1.935 (6)	N(2)–C(2)	1.486 (13)
Cu(2)–O(1)	1.955 (5)	N(2)–C(7)	1.487 (13)
Cu(2)–O(1′)	1.999 (6)	N(1)–C(5)	1.453 (14)
Cu(1)–O(1)	2.423 (5)	N(1)–C(9)	1.441 (17)
Cu(2)–O(2)	2.520 (6)	C(9)–C(12)	1.403 (22)
Cu(1)–N(2′)	2.057 (7)	C(5)–C(11)	1.515 (20)
Cu(2)–N(1′)	2.072 (7)	C(2)–C(10)	1.522 (18)
Cu(1)–Cl(2)	2.235 (2)	C(7)–C(8)	1.498 (17)

complex [Cu(EIA)]$_4$, where EIA is the Schiff base formed by the condensation of ethanolamine and acetylacetone.

The actual symmetry of the unit is much lower than tetrahedral, the only crystallographic symmetry being a twofold axis (C_2) which runs approximately vertically in Figure 2 and passes through the center of the top and bottom faces. The unit approximates C_{2v} (*mm*) symmetry, the Cu–Cu separation of 2.931 (2) Å in the top face being nearly equal to the value of 2.940 (2) Å in the bottom face, etc. The bond lengths and interatomic separations in the tetrameric bridging unit are shown in Figures 2 and 3, and all bond lengths and angles in the tetramer are listed in Tables IV and V. The in-plane Cu–O–Cu–O unit (*e.g.*, the bottom face in Figure 2) is somewhat similar to the dimeric unit found[3] in the corresponding bromo complex and is shown in Figure 3. The principal difference between this part of the tetramer and the dimeric bromo complex is in the Cu–O–Cu bridging angle, ϕ, which is 104.5 (4)° in the bromo complex[3] but only 97.6 (3) and 95.7 (2)° in the bottom and top halves of the tetramer, respectively. The in-plane Cu–O distances are in the range 1.935 (6)–1.999 (6) Å, which are longer than the values[3] of 1.904 (8) and 1.924 (8) Å in the bromo analog. The Cu–N distances of 2.057 (7) and 2.072 (7) Å are also longer than the value of 2.036 (8) Å in the bromo dimer but are in the range for Cu–N bonds reported in the literature. The Cu–Cl lengths of 2.225 (3) and 2.235 (2) Å are normal,[22] as are the chelating C(1)–C(3) and C(4)–C(6) bonds in the ligand.[3] The bond lengths associated with the ethyl groups are unreliable because of the absence of the contribution of the hydrogen atoms to the scattering.

The out-of-plane Cu–O distances of 2.423 (5) and 2.520 (6) Å are quite short for axial coordination to copper.[23] The out-of-plane Cu–Cu separations of 3.419 (1) and 3.450 (2) Å are longer than the in-plane distances but are well within the range observed for ligand-bridged systems.[24]

Table V. Intramolecular Angles in Chloro(2-diethylaminoethanolato)copper(II)

Atoms	Angle, deg	Atoms	Angle, deg
	In Plane		
Cu(1)–O(2)–Cu(1′)	97.6 (3)	C(6)–N(1)–C(5)	104.2 (9)
O(2)–Cu(1)–O(2′)	80.9 (2)	C(9)–N(1)–Cu(2)	111.4 (8)
Cu(2)–O(1)–Cu(2′)	95.7 (2)	C(5)–N(1)–C(9)	113.0 (9)
O(1)–Cu(2)–O(1′)	81.3 (2)	N(1)–C(5)–C(11)	118 (1)
O(2′)–Cu(1)–N(2′)	85.7 (3)	N(1)–C(9)–C(12)	116 (1)
O(2)–Cu(1)–Cl(2)	95.8 (2)	Cu(1′)–O(2)–C(3)	110.0 (5)
N(2′)–Cu(1)–Cl(2)	96.5 (2)	C(3)–C(1)–N(2)	111.2 (8)
O(1′)–Cu(2)–N(1′)	84.5 (3)	C(1)–N(2)–Cu(1′)	105.6 (6)
O(1)–Cu(2)–Cl(1)	96.2 (2)	C(1)–N(2)–C(2)	108.8 (8)
N(1′)–Cu(2)–Cl(1)	97.6 (2)	C(2)–N(2)–C(7)	108.5 (8)
Cu(2)–O(1)–C(4)	113.5 (5)	C(7)–N(2)–Cu(1)	112.6 (6)
O(1)–C(4)–C(6)	110.5 (9)	N(2)–C(7)–C(8)	113.4 (9)
C(4)–C(6)–N(1)	107 (1)	N(2)–C(2)–C(10)	118.1 (9)
	Out of Plane		
O(1′)–Cu(2)–O(2)	77.1 (2)	Cu(1′)–O(2)–Cu(2)	99.6 (2)
O(1)–Cu(2)–O(2)	77.5 (2)	Cu(1)–O(2)–Cu(2)	99.4 (2)
Cu(2)–O(1)–Cu(1)	103.4 (2)	Cl(1)–Cu(2)–O(2)	102.9 (1)
Cu(2′)–O(1)–Cu(1)	100.8 (2)	N(1)–Cu(2)–O(2)	120.9 (3)
O(2)–Cu(1)–O(1)	79.3 (2)	Cl(2)–Cu(1)–O(1)	102.6 (2)
O(2′)–Cu(1)–O(1)	81.1 (2)	N(2)–Cu(1)–O(1)	112.2 (2)

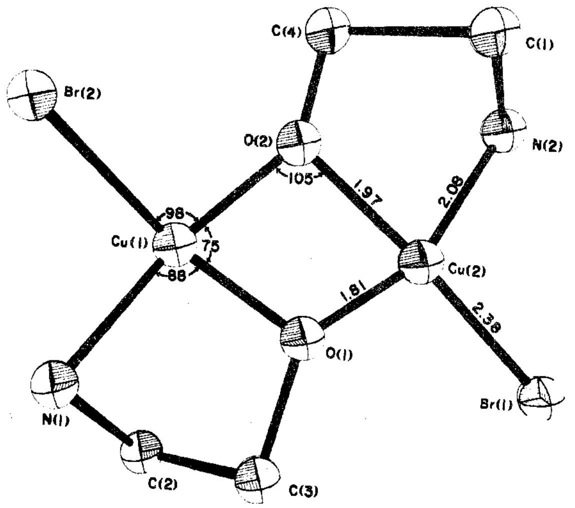

Figure 4. The inner coordination sphere in bis[bromo(2-dibutylaminoethanolato)copper(II)]. The distances and angles given are averaged values for chemically equivalent bonds. The isotropic thermal parameters have been artificially set to 3.0 Å^2.

(b) Bromo(2-dibutylaminoethanolato)copper(II). The structure consists of dimeric units as depicted in Figure 4. While the bond lengths and angles derived from this structural analysis based on data obtained from a severely twinned crystal are completely unreliable, the average values of chemically equivalent bond lengths and angles are shown in Figure 4. It should be noted that, although the quantitative aspects of the structure cannot be determined from this analysis, the qualitative description of this complex from group 1 as a dimer is reliable.

The results of these two structural analyses, therefore, strongly support the classification[5] of complexes of the type Cu(OR)X (where ROH is an amino alcohol) into distinct structural classes and endorse the suggestion[5,6] that members of group 1 are dimeric while those in group 3 are tetrameric.

Acknowledgment. We are grateful to our colleagues Professor W. E. Hatfield, Mr. W. E. Estes, and Dr. R. P. Eckberg for stimulating discussions concerning the magnetic

properties of these complexes. This research was supported by the National Science Foundation through Grant No. GP-38491X.

Registry No. Chloro(2-diethylaminoethanolato)copper(II), 51717-03-4; bromo(2-dibutylaminoethanolato)copper(II), 21331-08-8.

Supplementary Material Available. Listings 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 $4.00 for photocopy or $2.00 for microfiche, referring to code number AIC40473T.

References and Notes

(1) F. Hein and W. Beerstecher, *Z. Anorg. Allg. Chem.*, **282**, 93 (1955).
(2) F. Hein and W. Ludwig, *Z. Anorg. Allg. Chem.*, **338**, 63 (1965).
(3) A. Pajunen and M. Lehtonen, *Suom. Kemistilehti B*, **44**, 200 (1971).
(4) J. A. Bertrand, private communication.
(5) E. Uhlig and K. Staiger, *Z. Anorg. Allg. Chem.*, **346**, 21 (1966).
(6) E. Uhlig and K. Staiger, *Z. Anorg. Allg. Chem.*, **360**, 39 (1968).
(7) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **22**, 457 (1967).
(8) M. Lehtonen, *Suom. Kemistilehti B*, **43**, 198 (1970).
(9) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957.
(10) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
(11) W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).
(12) In addition to the local programs, the programs used in these analyses were local modifications of Hamilton's GONO9 absorption program, Ibers' NUCLS least-squares program, Dellaca and Robinson's FOURIER program, Busing, Martin, and Levy's ORFFE function and error program, Main, Germain, and Woolfson's MULTAN direct methods program, Johnson's ORTEP plotting program, and Doedens' RSCAN program.
(13) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
(14) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, Table 3.3.1A.
(15) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(16) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).
(17) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
(18) See paragraph at end of paper regarding supplementary material.
(19) J. Karle and I. L. Karle, *Acta Crystallogr.*, **21**, 849 (1966).
(20) A preliminary report of this structure has been presented elsewhere: E. E. Dixon, W. E. Hatfield, and D. J. Hodgson, 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 1973. After this report, the structure was independently published by W. Haase, *Chem. Ber.*, **106**, 3132 (1973); the results of our determination are in excellent agreement with those of Haase.
(21) J. A. Bertrand and J. A. Kelley, *Inorg. Chim. Acta*, **4**, 203 (1970).
(22) V. C. Copeland, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **12**, 1340 (1973), and references therein.
(23) A. Santoro, A. D. Mighell, and C. W. Riemann, *Acta Crystallogr., Sect. B*, **26**, 979 (1970).
(24) D. J. Hodgson, P. K. Hale, and W. E. Hatfield, *Inorg. Chem.*, **10**, 1061 (1971), and references therein.

Contribution from the Chemistry Departments, North Adams State College, North Adams,
Massachusetts 01247, and University of Massachusetts, Amherst, Massachusetts 01002

Crystal and Molecular Structure of Hexakis(pyridine *N*-oxide)cobalt(II) Perchlorate

TIMOTHY J. BERGENDAHL and JOHN S. WOOD*

Received July 15, 1974 AIC40474L

The crystal structure of hexakis(pyridine *N*-oxide)cobalt(II) perchlorate, $Co(C_5H_5NO)_6(ClO_4)_2$ has been determined from three-dimensional X-ray data collected on a three-circle automatic diffractometer using Mo Kα radiation. The complex crystallizes in the trigonal space group $R\bar{3}$ with cell constants $a = 12.512$ (3) and $c = 19.044$ (3) Å. The observed and calculated densities for three molecules per unit cell are 1.59 (2) and 1.601 g cm^{-3}, respectively. The structure was refined by full-matrix least squares to a final R value of 0.037 and a weighted R value of 0.052, for 590 independent reflections whose intensities were greater than twice their estimated standard deviations. The complex cation has S_6 ($\bar{3}$) symmetry and the coordination geometry about the cobalt atom is perfectly octahedral to within the estimated standard deviations, the Co–O distance being 2.088 (2) Å and the O–Co–O angles 89.97 (4) and 90.03 (4)°. The perchlorate ions have C_3 point symmetry and occupy the trigonal holes between the cations within each layer of the structure.

Introduction

Complexes of the transition metals with pyridine *N*-oxide and its substituted derivatives have been known for a decade or more and they have formed the subject of several recent reviews.[1] For the first-row metals several stoichiometries are known, but the series of hexakis complexes formed by these ligands are of considerable interest, in that they exhibit spectroscopic and magnetic properties indicative of large deviations from effective octahedral symmetry in their electronic structure.[2] For example, Lever and coworkers found appreciable splitting of the lower excited states in the spectra of the chromium(III) and nickel(II) complexes of the parent ligand, while the results of epr measurements on a variety of hexakis(pyridine oxide)manganese(II) complexes recently[3] are also consistent with a marked deviation from O_h symmetry as judged by the magnitude of the zero-field splitting.

In addition to the possibility of a large distortion from O_h (or near-octahedral) symmetry for the MO_6 moiety, a plausible explanation that has been advanced to account for these deviations is that they arise from the interactions of the metal d orbitals with the orbitals involving the ligand N–O bonds *via* the nonlinear M–O–N systems,[2] so that in crystal field terminology, the effective perturbing charges affecting the d orbitals are not centered at the coordinated oxygen atoms. As a large number of hexakis complexes, usually loosely described as octahedral, contain such nonlinear M–O–X groupings (X = C, S, P, N), it appeared appropriate to examine the molecular stereochemistry and electronic properties (in single-crystal form) of certain members of these series in some detail, to assess and develop various theoretical models useful in interpreting these properties. To date, few structural results on such species have been reported.

We have earlier investigated the stereochemistry and magnetic properties of the hexaurea complex of titanium, $Ti(OC(NH)_2)_6^{3+}$, which contains a nonlinear Ti–O–C system and a coordination polyhedron having D_3 symmetry.[4-6] In this instance, the deviation of the TiO_6 group from an octahedron is toward a trigonal prism, there being negligible distortion (*i.e.*, compression or extension) along the threefold axis. While the average magnetic properties were initially interpreted using a crystal field model based on the observed geometry,[6] sub-

---

* To whom correspondence should be addressed at the University of Massachusetts.