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The Crystal Structure of Cyanato(2-dimethylaminoethanolato)copper(II), $C_5H_{10}N_2O_2Cu$

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The title compound is monoclinic, space group $P2_1/c$, with $a = 18.57(2)$, $b = 17.29(2)$, $c = 19.87(2)$ Å, $\beta = 98.2(1)^\circ$, $Z = 32$. The structure has been refined to a final R of 0.091 for 4138 independent counter reflexions. Two crystallographically different but very similar cubane-like tetramers are built up from two dimers. The mean values for the intramolecular Cu–Cu separations are 2.92 (inside a dimer) and 3.44 Å (between two dimers). The Cu coordination is approximately square pyramidal with Cu bonded to two O atoms (inside the dimer, mean Cu–O 1.96 Å), the amino N atom (mean Cu–N 2.05 Å), and the N of the cyanato group (mean Cu–N 1.88 Å). The apical position of the pyramid is occupied by one O atom of the second dimer (mean Cu–O 2.48 Å).

Introduction

Different types of structures in the solid state have been found to be built up by thiocyanato(2-dialkylaminoethanolato)copper(II) complexes. Polymeric structures have been reported for the complexes containing *N,N*-dimethylamino (Haase, Mergehenn & Krell, 1976) and *N,N*-diethylamino (Pajunen & Smolander, 1974) groups; a tetrameric cubane-like structure is realized by thiocyanato(2-dibutylaminoethanolato)copper(II) (Mergehenn & Haase, 1977b). These structural properties are analogous to those of the halogeno complexes (e.g. Matsumoto, Ueda, Nishida & Kida, 1976; Mergehenn, Haase & Allmann, 1975). Here we present the first structural investigation of complexes of the cyanato series, which are found to be tetrameric in most cases (Merz & Haase, 1977; Mergehenn & Haase, 1977b), but with different molecular properties.

Experimental

The preparation of cyanato(2-dimethylaminoethanolato)copper(II) followed closely that reported by Lehtonen, Luukkonen & Uggla (1971). Instead of KSCN an equivalent amount of KOCN was used and the precipitate recrystallized from methanol.

A needle-like crystal with the following dimensions was used for the structure determination: $\{100\} - \{100\} = \{010\} - \{0\bar{1}0\} = 0.15$, $\{001\} - \{00\bar{1}\} = 0.87$ mm (distances from face to face). The measurements were carried out on a computer-controlled Stoe four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation.

Cell dimensions and the orientation matrix were obtained by a least-squares fit of 20 strong reflexions to the setting angles. For the intensity collection the $\omega/2\theta$ scan technique was used ($3^\circ \leq 2\theta \leq 42^\circ$); the measuring time for the reflexions (60 s) was twice the time for

measuring background (2×30 s). 6790 reflexions were measured, from which 2650 were rejected because $I \leq 3\sigma(I)$. Lorentz-polarization and absorption corrections (256 grid points) were applied to the remaining 4138 unique reflexions.

Structure solution and results

The positions of eight Cu atoms were derived by direct methods. This partial structure refined well and the remaining non-hydrogen atoms could be located after several ΔF syntheses and successive least-squares cycles. The concluding refinement with full-matrix least squares could only be done by refining one quarter (with isotropic temperature factors) or one eighth (with anisotropic temperature factors for all atoms) of the total parameters (80 atoms + overall scale = 721 free

parameters) with a large damping factor for the shifts. Continued refinement reduced R to a final value of 0.091 with no shift greater than the estimated standard deviation.

The final atom parameters are given in Table 1; positions of H atoms were not determined.*

All calculations were performed with a program for crystal structure analysis by G. M. Sheldrick (Cambridge) on the IBM 370/168 computer of the Technische Hochschule Darmstadt. The scattering factor for Cu was taken from Cromer & Mann (1968). The remaining bond distances (Table 2) and interbond

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32354 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Positional parameters* ($\times 10^4$, $\times 10^3$ for C)

Molecule I	<i>x</i>	<i>y</i>	<i>z</i>	Molecule II	<i>x</i>	<i>y</i>	<i>z</i>
Cu(1)	-1247 (1)	2019 (1)	5161 (1)	Cu(5)	3664 (1)	2064 (1)	-206 (1)
Cu(2)	-1702 (1)	1998 (1)	3698 (1)	Cu(6)	3469 (1)	2169 (1)	1234 (1)
Cu(3)	-609 (1)	3555 (1)	4297 (1)	Cu(7)	4506 (1)	3624 (1)	683 (1)
Cu(4)	-2085 (1)	3667 (1)	4613 (1)	Cu(8)	2952 (1)	3746 (1)	216 (1)
O(1)	-793 (6)	2112 (7)	4337 (6)	O(5)	4259 (6)	2161 (7)	669 (6)
O(2)	-2128 (6)	2236 (7)	4492 (6)	O(6)	2903 (6)	2347 (6)	333 (6)
O(3)	-1597 (7)	3483 (7)	3826 (6)	O(7)	3621 (6)	3566 (6)	1091 (6)
O(4)	-1128 (6)	3398 (6)	5098 (6)	O(8)	3809 (6)	3426 (6)	-162 (5)
O(11)	-2651 (9)	1578 (9)	6556 (9)	O(51)	2227 (11)	1203 (12)	-1808 (10)
O(21)	-250 (10)	1295 (11)	2453 (10)	O(61)	5058 (10)	1477 (10)	2784 (9)
O(31)	1069 (9)	4624 (9)	5494 (9)	O(71)	5977 (9)	4631 (9)	-351 (8)
O(41)	-3922 (11)	4786 (12)	3715 (11)	O(81)	1463 (9)	5173 (10)	828 (9)
N(1)	-272 (8)	1582 (9)	5600 (9)	N(5)	4557 (9)	1574 (10)	-514 (10)
N(2)	-2749 (9)	1739 (11)	3257 (9)	N(6)	2482 (9)	1964 (9)	1554 (8)
N(3)	-306 (10)	3832 (10)	3375 (8)	N(7)	4996 (8)	3944 (10)	1644 (8)
N(4)	-2288 (9)	4034 (10)	5545 (9)	N(8)	2555 (9)	4049 (8)	-764 (7)
N(11)	-1706 (9)	1783 (10)	5915 (9)	N(51)	3043 (9)	1837 (10)	-1023 (8)
N(21)	-1281 (10)	1732 (12)	2944 (10)	N(61)	4007 (11)	1919 (12)	2082 (10)
N(31)	323 (12)	3751 (14)	4808 (11)	N(71)	5339 (11)	3737 (12)	268 (11)
N(41)	-3010 (9)	3996 (11)	4155 (10)	N(81)	2143 (9)	4121 (12)	584 (9)
C(1)	-213 (1)	173 (1)	623 (1)	C(5)	255 (1)	156 (2)	-137 (1)
C(11)	25 (1)	170 (1)	510 (1)	C(51)	516 (1)	165 (2)	8 (1)
C(12)	-14 (1)	162 (1)	437 (1)	C(52)	488 (1)	166 (1)	74 (1)
C(13)	3 (1)	198 (1)	625 (1)	C(53)	441 (1)	76 (1)	-71 (1)
C(14)	-35 (1)	73 (1)	570 (1)	C(54)	480 (1)	199 (2)	-108 (1)
C(2)	-80 (2)	152 (2)	270 (1)	C(6)	454 (1)	169 (2)	244 (1)
C(21)	-315 (1)	185 (2)	384 (2)	C(61)	190 (1)	217 (1)	97 (1)
C(22)	-286 (1)	188 (1)	454 (1)	C(62)	220 (1)	196 (1)	30 (1)
C(23)	-278 (1)	96 (2)	295 (1)	C(63)	245 (1)	110 (1)	172 (1)
C(24)	-302 (1)	227 (1)	276 (1)	C(64)	233 (1)	243 (1)	216 (1)
C(3)	67 (1)	421 (2)	515 (1)	C(7)	559 (1)	417 (2)	-2 (1)
C(31)	-100 (1)	376 (1)	286 (1)	C(71)	437 (1)	395 (1)	206 (1)
C(32)	-165 (1)	397 (1)	323 (1)	C(72)	365 (1)	408 (1)	168 (1)
C(33)	24 (1)	330 (1)	316 (1)	C(73)	532 (1)	473 (1)	164 (1)
C(34)	-3 (1)	465 (1)	335 (1)	C(74)	553 (1)	337 (1)	194 (1)
C(4)	-340 (2)	437 (2)	395 (1)	C(8)	180 (1)	464 (2)	72 (1)
C(41)	-165 (1)	384 (1)	607 (1)	C(81)	313 (1)	381 (1)	-121 (1)
C(42)	-96 (1)	387 (1)	570 (1)	C(82)	386 (1)	387 (1)	-78 (1)
C(43)	-239 (1)	492 (1)	550 (1)	C(83)	245 (1)	492 (1)	-82 (1)
C(44)	-295 (1)	365 (1)	576 (1)	C(84)	187 (1)	366 (1)	-102 (1)

Table 2. Bond distances (Å)

	Molecule I				Molecule II			
	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 7$	$n = 8$
	$m = 2$	$m = 1$	$m = 4$	$m = 3$	$m = 6$	$m = 5$	$m = 8$	$m = 7$
	$p = 4$	$p = 3$	$p = 1$	$p = 2$	$p = 8$	$p = 7$	$p = 5$	$p = 6$
Cu(<i>n</i>)—O(<i>n</i>)	1.95 (1)	1.91 (1)	1.94 (1)	1.95 (1)	1.93 (1)	1.97 (1)	1.94 (1)	1.94 (1)
Cu(<i>n</i>)—O(<i>m</i>)	1.99 (1)	1.97 (1)	1.99 (1)	1.94 (1)	1.95 (1)	1.97 (1)	2.00 (1)	2.01 (1)
Cu(<i>n</i>)—O(<i>p</i>)	2.40 (1)	2.59 (1)	2.52 (1)	2.49 (1)	2.37 (1)	2.45 (1)	2.57 (1)	2.43 (1)
Cu(<i>n</i>)—N(<i>n</i>)	2.04 (1)	2.07 (2)	2.05 (2)	2.04 (2)	2.03 (2)	2.05 (2)	2.07 (1)	2.05 (1)
Cu(<i>n</i>)—N(<i>n</i> 1)	1.87 (2)	1.85 (2)	1.91 (2)	1.91 (2)	1.90 (1)	1.88 (2)	1.86 (2)	1.88 (2)
N(<i>n</i> 1)—C(<i>n</i>)	1.07 (3)	1.14 (3)	1.17 (3)	1.02 (3)	1.05 (3)	1.20 (3)	1.09 (3)	1.15 (3)
C(<i>n</i>)—O(<i>n</i> 1)	1.27 (3)	1.25 (3)	1.18 (3)	1.24 (3)	1.24 (3)	1.16 (3)	1.31 (3)	1.16 (3)
N(<i>n</i>)—C(<i>n</i> 1)	1.50 (3)	1.48 (4)	1.53 (3)	1.50 (2)	1.52 (3)	1.50 (2)	1.52 (3)	1.52 (3)
C(<i>n</i> 1)—C(<i>n</i> 2)	1.53 (3)	1.42 (4)	1.54 (3)	1.58 (3)	1.48 (4)	1.57 (3)	1.46 (3)	1.51 (3)
C(<i>n</i> 2)—O(<i>n</i>)	1.48 (2)	1.50 (2)	1.45 (2)	1.45 (2)	1.44 (2)	1.46 (2)	1.46 (3)	1.46 (2)
N(<i>n</i>)—C(<i>n</i> 3)	1.50 (3)	1.49 (3)	1.47 (3)	1.54 (3)	1.47 (3)	1.53 (3)	1.48 (3)	1.52 (3)
N(<i>n</i>)—C(<i>n</i> 4)	1.49 (2)	1.40 (3)	1.52 (3)	1.50 (3)	1.47 (3)	1.51 (2)	1.48 (3)	1.47 (3)

Table 3. Interbond angles (°)

	Molecule I				Molecule II			
	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 7$	$n = 8$
	$m = 2$	$m = 1$	$m = 4$	$m = 3$	$m = 6$	$m = 5$	$m = 8$	$m = 7$
	$p = 4$	$p = 3$	$p = 1$	$p = 2$	$p = 8$	$p = 7$	$p = 5$	$p = 6$
	$q = 3$	$q = 4$	$q = 2$	$q = 1$	$q = 7$	$q = 8$	$q = 6$	$q = 5$
O(<i>n</i>)—Cu(<i>n</i>)—O(<i>m</i>)	80.6 (5)	82.2 (5)	81.1 (5)	82.1 (5)	81.4 (5)	80.0 (5)	81.8 (5)	81.4 (5)
—O(<i>p</i>)	79.6 (5)	74.9 (5)	80.2 (5)	79.9 (5)	80.4 (4)	78.2 (4)	78.1 (5)	78.3 (4)
—N(<i>n</i>)	85.8 (6)	85.5 (6)	86.8 (6)	84.2 (6)	85.4 (6)	85.6 (5)	85.1 (6)	84.8 (6)
—N(<i>n</i> 1)	171.8 (7)	177.9 (7)	172.5 (8)	176.4 (7)	172.3 (7)	175.7 (7)	176.5 (7)	176.4 (7)
O(<i>m</i>)—Cu(<i>n</i>)—O(<i>p</i>)	81.4 (5)	78.0 (5)	75.9 (6)	76.8 (6)	79.5 (4)	80.4 (5)	74.3 (5)	77.9 (4)
—N(<i>n</i>)	161.9 (6)	164.3 (6)	166.3 (6)	161.5 (6)	162.7 (6)	160.8 (5)	165.5 (6)	162.7 (6)
—N(<i>n</i> 1)	98.6 (6)	97.2 (6)	96.0 (7)	99.0 (7)	97.0 (6)	99.5 (7)	97.2 (7)	98.4 (6)
O(<i>p</i>)—Cu(<i>n</i>)—N(<i>n</i>)	107.9 (5)	108.1 (5)	108.4 (5)	112.9 (5)	109.3 (6)	109.2 (5)	109.1 (6)	109.4 (5)
—N(<i>n</i> 1)	108.3 (6)	107.0 (6)	106.0 (6)	103.6 (7)	106.8 (6)	106.0 (7)	104.9 (7)	105.2 (7)
N(<i>n</i>)—Cu(<i>n</i>)—N(<i>n</i> 1)	93.1 (7)	94.8 (8)	95.1 (8)	94.0 (8)	94.5 (7)	93.9 (8)	95.5 (8)	94.7 (7)
Cu(<i>n</i>)—O(<i>n</i>)—Cu(<i>q</i>)	95.7 (5)	96.5 (5)	96.8 (5)	94.8 (5)	97.8 (5)	97.2 (5)	95.0 (5)	95.4 (5)
—Cu(<i>q</i>)	100.6 (5)	106.4 (5)	99.4 (5)	100.3 (5)	100.0 (5)	102.7 (4)	102.6 (5)	101.7 (5)
—C(<i>n</i> 2)	111.5 (11)	116.4 (11)	107.9 (11)	110.6 (11)	112.6 (11)	109.4 (10)	111.5 (11)	109.0 (10)
Cu(<i>m</i>)—O(<i>n</i>)—Cu(<i>q</i>)	100.7 (5)	96.4 (5)	101.8 (5)	103.7 (5)	97.6 (5)	99.0 (5)	100.7 (4)	104.9 (4)
—C(<i>n</i> 2)	126.5 (11)	123.0 (11)	125.5 (12)	120.7 (11)	126.9 (12)	124.6 (10)	122.9 (11)	120.1 (10)
Cu(<i>q</i>)—O(<i>n</i>)—C(<i>n</i> 2)	117.1 (11)	114.9 (11)	120.1 (11)	121.8 (11)	117.3 (11)	119.8 (9)	119.9 (11)	121.2 (10)
Cu(<i>n</i>)—N(<i>n</i>)—C(<i>n</i> 1)	106.3 (12)	101.1 (13)	105.6 (13)	109.6 (13)	106.0 (15)	107.2 (12)	103.4 (12)	107.0 (11)
—C(<i>n</i> 3)	113.7 (12)	110.8 (13)	113.5 (13)	106.9 (13)	110.4 (13)	107.3 (12)	111.7 (12)	110.3 (11)
—C(<i>n</i> 4)	109.1 (11)	112.7 (14)	112.7 (13)	112.5 (13)	112.9 (13)	115.3 (12)	112.0 (13)	113.1 (12)
C(<i>n</i> 1)—N(<i>n</i>)—C(<i>n</i> 3)	108.2 (15)	116.9 (19)	107.5 (16)	109.9 (15)	111.5 (17)	110.1 (14)	109.6 (17)	107.9 (15)
—C(<i>n</i> 4)	107.7 (16)	107.0 (19)	108.4 (15)	107.2 (16)	106.6 (17)	107.1 (15)	108.1 (16)	108.5 (15)
C(<i>n</i> 3)—N(<i>n</i>)—C(<i>n</i> 4)	111.6 (16)	108.2 (18)	108.9 (17)	110.9 (17)	109.3 (18)	109.8 (15)	111.7 (15)	109.9 (15)
Cu(<i>n</i>)—N(<i>n</i> 1)—C(<i>n</i>)	159.7 (18)	151.4 (19)	144.4 (22)	157.4 (23)	160.5 (21)	153.3 (21)	138.9 (22)	149.1 (20)
N(<i>n</i> 1)—C(<i>n</i>)—O(<i>n</i> 1)	171.3 (25)	177.0 (28)	174.9 (28)	174.5 (34)	176.3 (32)	178.3 (28)	172.5 (29)	176.7 (28)
N(<i>n</i>)—C(<i>n</i> 1)—C(<i>n</i> 2)	111.0 (17)	126.8 (21)	107.5 (16)	106.4 (16)	112.1 (19)	107.6 (15)	115.6 (20)	107.6 (15)
C(<i>n</i> 1)—C(<i>n</i> 2)—O(<i>n</i>)	105.3 (16)	100.4 (19)	106.5 (16)	105.5 (16)	107.6 (17)	105.9 (13)	104.3 (18)	106.2 (16)

angles (Table 3) have estimated standard deviations that are too small, because they are not determined from the full variance-covariance matrix.

Structural description and discussion

Two crystallographically different cubane-type molecules with very similar molecular geometries

[molecule I consists of Cu(1) to C(44), molecule II of Cu(5) to C(84) (Table 1)] are built up from cyanato(2-dimethylaminoethanolato)copper(II) with molecular symmetry approximately S_4 (exact symmetry C_1). No direct bonding exists between the two crystallographically different cubane-type clusters. More favourable packing in $P2_1/c$ is the only reason that the substance does not crystallize in the orthorhombic space group $Pbca$, which may be used to describe the

approximate crystal structure with only one cubane-type molecule in the asymmetric unit. It may be derived from Table 1 by application of the operation $0.5 + x$, y , $0.5 - z$ to the coordinates of (I), resulting in approximate coordinates for (II), and *vice versa*.

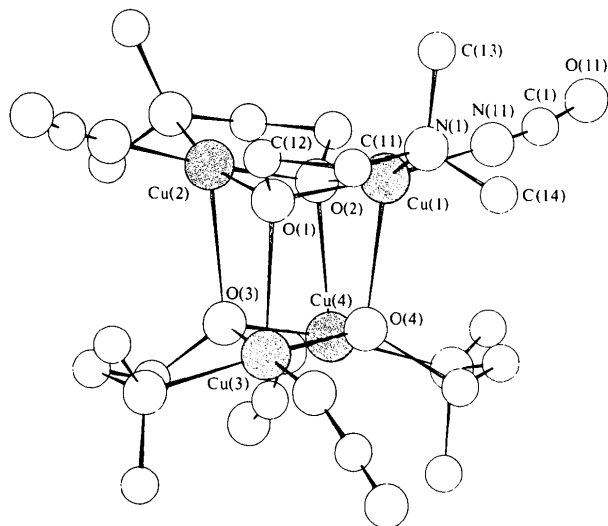


Fig. 1. Molecular structure of cyanato(2-dimethylaminoethanolato)copper(II).

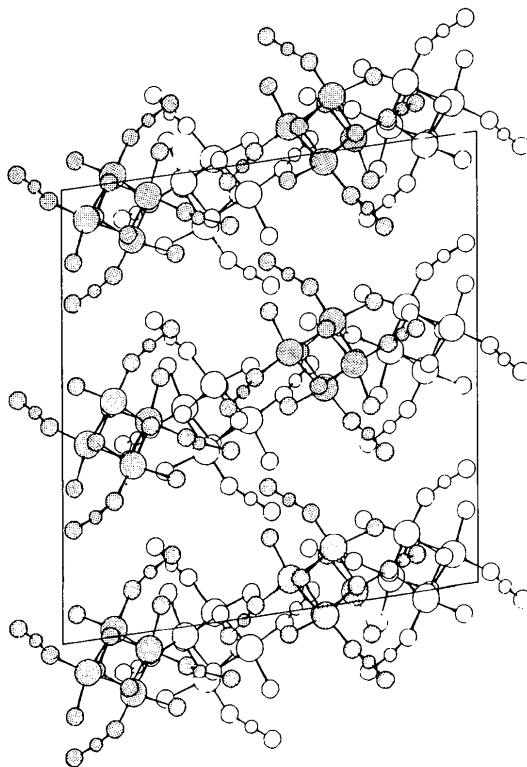


Fig. 2. Projection of the unit cell showing the arrangement of the molecules in the ac plane. Molecules with hatched circles are placed nearly in $y = 0.75$, molecules with empty circles nearly in $y = 0.25$. C atoms of the dimethylamino groups are omitted for clarity.

The projection of (I) nearly along c (Fig. 1) and the Cu—O distances (Table 2) show that the cubane-type molecule may be thought of as formally built up from two dimers with eight short (1.96 Å, mean) and four long (2.48 Å, mean) Cu—O bonds. The arrangement of the molecules in the cell is approximately such that all best planes through the Cu and O atoms of the pseudodimers are nearly parallel to the ac plane, and all long Cu—O bonds are parallel to b (Fig. 2).

The equations of the best planes through the dimers and the distances of several atoms from these planes are given in Table 4. All Cu atoms are placed 0.14 Å (mean) outside the best cluster faces (Cu_2O_2 faces) and the O atoms the same distance inside. These deviations result in relatively large dihedral angles in the dimers: 22.4 [Cu(1)O₂Cu(2)], 23.0 [Cu(3)O₂Cu(4)], 25.5 [Cu(5)O₂Cu(6)] and 18.6° [Cu(7)O₂Cu(8)]. The mean values for each cluster are nearly the same (22.7 and 22.0°). The mean values of the angles between the best cluster faces are 2.3° (3 × parallel, molecule I), 90.6° (12 × perpendicular, molecule I) and 1.9° (3 × parallel, molecule II), 89.7° (12 × perpendicular, molecule II).

The main difference between the two cluster molecules is that (II) is more compact than (I). This can be seen from the distances between the Cu atoms in each cluster (Table 5).

Table 4. Equations of the best planes through the dimers and distances (Å) of several atoms from these planes

Plane 1: Cu(1) O(1) Cu(2) O(2)				
	$1.502x + 17.232y - 0.687z = 4.582$			
Plane 2: Cu(3) O(3) Cu(4) O(4)				
	$1.435x + 17.223y + 0.674z = 7.613$			
Plane 3: Cu(5) O(5) Cu(6) O(6)				
	$2.583x + 17.120y - 0.877z = 4.620$			
Plane 4: Cu(7) O(7) Cu(8) O(8)				
	$1.848x + 17.166y - 1.637z = 6.776$			

Molecule I

	Distances from plane 1		Distances from plane 2		Mean values (abs.)
	$n = 1$ $p = 4$	$n = 2$ $p = 3$	$n = 3$ $p = 1$	$n = 4$ $p = 2$	
Cu(n)	-0.142	-0.146	0.149	0.146	0.146
O(n)	0.143	0.145	-0.145	-0.151	0.146
N(n)	-0.779	-0.720	0.816	0.605	0.730
N(n 1)	-0.669	-0.491	0.553	0.653	0.592
O(p)	2.255	2.419	-2.329	-2.360	2.341

Molecule II

	Distances from plane 3		Distances from plane 4		Mean values (abs.)
	$n = 5$ $p = 8$	$n = 6$ $p = 7$	$n = 7$ $p = 5$	$n = 8$ $p = 6$	
Cu(n)	0.164	0.165	-0.118	-0.122	0.142
O(n)	-0.165	-0.164	0.119	0.121	0.142
N(n)	0.772	0.648	-0.753	-0.703	0.719
N(n 1)	0.598	0.582	-0.482	-0.599	0.565
O(p)	-2.265	-2.390	2.325	2.243	2.306

Table 5. Cu—Cu distances (Å)

Molecule I		Molecule II	
Cu(1)—Cu(2)	2.910 (3)	Cu(5)—Cu(6)	2.941 (3)
—Cu(3)	3.461 (3)	—Cu(7)	3.471 (3)
—Cu(4)	3.353 (3)	—Cu(8)	3.350 (3)
Cu(2)—Cu(3)	3.477 (3)	Cu(6)—Cu(7)	3.441 (3)
—Cu(4)	3.536 (3)	—Cu(8)	3.450 (3)
Cu(3)—Cu(4)	2.904 (4)	Cu(7)—Cu(8)	2.911 (3)

In (I) the mean value of the short Cu—Cu distances (2.907 Å) is 0.02 Å less than in (II) (2.926 Å) and the long Cu—Cu distance in (I) (3.457 Å, mean) is 0.03 Å greater than in (II) (3.428 Å). The same behaviour may be derived from the short and long Cu—O distances (mean): 1.96 and 2.50 Å for (I); and 1.96 and 2.45 Å for (II). The coordination around each Cu atom is distorted square pyramidal with O(*n*), O(*m*), N(*n*) and N(*n*1) in the basal plane and O(*p*) at the top of the pyramid. The mean value for the angles O(*p*)—Cu(*n*)—L [*L* = O(*n*), O(*m*), N(*n*), N(*n*1)] is 94.3°, and the mean values for the basal angles are 169.1 (2×) and 89.5° (4×).

Much the same structure is built up by chloro(2-diethylaminoethanolato)copper(II) (Haase, 1973; Estes & Hodgson, 1975) and the Cu—Cu, Cu—N(amino) and Cu—O distances are in good agreement with those reported here. The Cu(*n*)—N(*n*1)(cyanato) distance of 1.8 Å (mean) is in good agreement with the values found for cyanato(2-dibutylaminoethanolato)copper(II) (Mergehenn & Haase, 1977*b*) and cyanato(2-diethylaminoethanolato)copper(II) (Merz & Haase,

1977). The O atoms of the ethanolato group are mainly *sp*³ hybridized, but two angles are far from the value of an idealized tetrahedron: Cu(*n*)—O(*n*)—Cu(*m*) 96.2° (mean, inside the dimer) and Cu(*m*)—O(*n*)—C(*n*2) 123.8°. *sp*³ hybridization is also true for the amino-nitrogen, with a mean angle of 109.5°.

Some difficulties arose in the determination of the cyanato group (both the O and N atoms are able to coordinate to Cu). If O is coordinated directly to Cu, its hybridization should be mainly *sp*², and therefore the angle Cu(*n*)—O(*n*1)—C(*n*) would be about 120°. This is in contrast to the observed angle of 151.8° (mean) which is halfway to *sp* hybridization. In accordance with the shorter N(*n*1)—C(*n*) distances [1.11 Å mean O(*n*1)—C(*n*) 1.23 Å, mean] we propose that N is directly coordinated to Cu.* This is in agreement with cyanato(2-dibutylaminoethanolato)copper(II) and cyanato(2-diethylaminoethanolato)copper(II).

Temperature factors of the cyanato O atoms are relatively high but similar to those of other structures which also contain single coordinated cyanato groups.

A summary of all investigated crystal structures of halogeno- and pseudohalogeno(2-dialkylaminoethanolato)copper(II) complexes is presented in Table 6. These substances form dimeric, polymeric and tetrameric molecules in the solid state and the tetramers are different in their molecular type. The subdivision into tetrameric I and tetrameric II results from the different arrangement of the longest Cu—O bonds. We

* Hence the ligands 'cyanato' and 'thiocyanato' are strictly 'isocyanato' and 'isothiocyano'.

Table 6. Summary of all known crystal structures of Cu[N(C₂H₄O)L₂]X complexes (*L* = CH₃, C₂H₅, *n*-C₃H₇, *n*-C₄H₉; *X* = Cl, Br, NCO, NCS) and their classification into groups (Uhlig & Staiger, 1966; Nishida & Kida, 1976)

<i>L</i>	<i>X</i>	Molecular type	Classification		References	
			Uhlig	Nishida		
CH ₃	NCO	Tetrameric I*	—	—	This work	
	NCS	Polymeric	—	C(b)	Haase, Mergehenn & Krell (1976)	
C ₂ H ₅	Cl	Tetrameric I	3	C(a)	Haase (1973); Estes & Hodgson (1975)	
		Tetrameric II†	—	—	Mergehenn & Haase (1977 <i>a</i>)	
	Br	Dimeric	1	—	Pajunen & Lehtonen (1971); Haase (1973)	
		Polymeric	—	—	Mergehenn, Merz & Haase (1975)	
		Tetrameric II	—	—	Mergehenn & Haase (1977 <i>a</i>)	
<i>n</i> -C ₃ H ₇	NCO	Tetrameric II (→I)	—	—	Merz & Haase (1977)	
	NCS	Polymeric	—	C(b)	Pajunen & Smolander (1974)	
	Cl	Tetrameric II (→I)	—	C(a)	Matsumoto, Ueda, Nishida & Kida (1976)	
<i>n</i> -C ₄ H ₉	Cl	Tetrameric II	2	B	Mergehenn, Haase & Allmann (1975)	
		Tetrameric II	2	B	Mergehenn, Haase & Allmann (1975)	
	Br	Dimeric	1	A	Mergehenn & Haase (1975)	
		NCO	Tetrameric I (→II)	—	—	Mergehenn & Haase (1977 <i>b</i>)
		NCS	Tetrameric I (→II)	—	C(a)	Mergehenn & Haase (1977 <i>b</i>)

* Tetrameric I means the four longest Cu—O bonds parallel.

† Tetrameric II means two of the longest Cu—O bonds perpendicular to the other two longest Cu—O bonds.

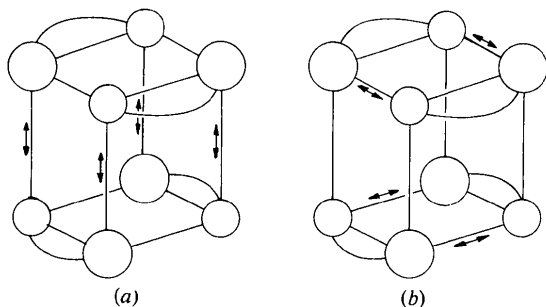


Fig. 3. Cu_4O_4 core. (a) Four stretching directions parallel. (b) Two stretching directions perpendicular to the other two.

distinguish between two extreme types, both derived from an idealized Cu_4O_4 cube by stretching four edges. That with all four stretching directions parallel (Fig. 3a) forms molecules nearly realized by cyanato(2-dimethylaminoethanolato)copper(II) (this work) and chloro(2-diethylaminoethanolato)copper(II) (Haase, 1973; Estes & Hodgson, 1975); that with two stretched edges perpendicular to the other two (Fig. 3b) forms molecules nearly realized by chloro- or bromo(2-dibutylaminoethanolato)copper(II) (Mergenhenn, Haase & Allmann, 1975) and chloro- or bromo(2-diethylaminoethanolato)copper(II). CCl_4 (Mergenhenn & Haase, 1977a). Some tetrameric molecules symbolized by tetrameric I (\rightarrow II) and tetrameric II (\rightarrow I) (Table 6) build up structures between these extreme types.

Other substances which also contain a Cu_4O_4 core closely follow this behaviour (Pajunen & Nieminen, 1975); the so-called CuEIA is able to build up both types of structures (Bertrand & Kelley, 1970; Mergenhenn, Merz, Haase & Allmann, 1976).

The characterization of the different cubane types by molecular magnetism (Merz, Haase & Keller, 1976; Merz & Haase, 1976) demonstrates that the possible six Cu—Cu interactions are of different strength and therefore molecular antiferromagnetism or ferromagnetism results in the spin ground state. A more detailed interpretation of the relation between

molecular geometries and magnetic properties will be given later.

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