CLARK, G. R. & ORBELL, J. D. (1974). *J. Chem. Soc. Chem. Commun.* pp. 139–140.

CLARK, G. R. & ORBELL, J. D. (1975). *J. Chem. Soc. Chem. Commun.* pp. 697–698.

COLLINS, A. D., DE MEESTER, P., GOODGAME, D. M. L. & SKAPSKI, A. C. (1975). *Biochim. Biophys. Acta,* **402,** 1–6.

FISCHER, B. E. & BAU, R. (1977). *J. Chem. Soc. Chem. Commun.* pp. 272–273.

GOODGAME, D. M. L., JEEVES, I., PHILLIPS, F. L. & SKAPSKI, A. C. (1975). *Biochim. Biophys. Acta,* **378,** 153–157.

GOODGAME, D. M. L., JEEVES, I., REYNOLDS, C. D. & SKAPSKI, A. C. (1975a). *Nucleic Acid Res.* **2,** 1375–1379.

GOODGAME, D. M. L., JEEVES, I., REYNOLDS, C. D. & SKAPSKI, A. C. (1975b). *Biochem. J.* **151,** 467–468.

HATHAWAY, B. J. (1973). *Struct. Bonding (Berlin),* **14,** 49–67.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

IZATT, R. M., CHRISTENSEN, J. J. & RYTTING, J. H. (1971). *Chem. Rev.* **71,** 439–481.

JARDETSKY, C. D. (1960). *J. Am. Chem. Soc.* **82,** 229–233.

KIM, S. H., SUDDATH, F. L., QUIGLEY, G. J., MCPHERSON, A., SUSSMAN, J. L., WANG, A. H. J., SEEMAN, N. C. & RICH, A. (1974). *Science,* **185,** 435–440.

LADNER, J. E., JACK, A., ROBERTUS, J. D., BROWN, R. S., RHODES, D., CLARK, B. F. C. & KLUG, A. (1975). *Nucleic Acid Res.* **2,** 1629–1637; *Proc. Natl Acad. Sci. USA,* **72,** 4414–4418.

LOUIE, S. & BAU, R. (1977). *J. Am. Chem. Soc.* **99,** 3874–3876.

MEESTER, P. DE, GOODGAME, D. M. L., JONES, T. J. & SKAPSKI, A. C. (1974a). *Biochem. J.* **139,** 791–792.

MEESTER, P. DE, GOODGAME, D. M. L., JONES, T. J. & SKAPSKI, A. C. (1974b). *C. R. Acad. Sci. Sér. C,* **279,** 667–669.

MEESTER, P. DE, GOODGAME, D. M. L., JONES, T. J. & SKAPSKI, A. C. (1974c). *Biochim. Biophys. Acta,* **353,** 392–394.

MEESTER, P. DE, GOODGAME, D. M. L., SKAPSKI, A. C. & SMITH, B. T. (1974). *Biochim. Biophys. Acta,* **340,** 113–115.

OGAWA, M. & SAKAGUCHI, T. (1971). *Yakugaku Zasshi,* **91,** 750–754.

SHEFTER, E. & TRUEBLOOD, K. N. (1965). *Acta Cryst.* **18,** 1067–1077.

SLETTEN, E. & LIE, B. (1976). *Acta Cryst.* B**32,** 3301–3304.

SUNDARALINGAM, M. & JENSEN, L. H. (1965). *J. Mol. Biol.* **13,** 914–929.

SUSSMAN, J. L. & KIM, S. H. (1976). *Biochem. Biophys. Res. Commun.* **68,** 89–96.

The Crystal Structures of Two Modifications of Isocyanato(2-dipropylaminoethanolato)copper(II)

BY L. MERZ AND W. HAASE

Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstrasse 20, D-6100 Darmstadt, Federal Republic of Germany

The structures of two modifications of isocyanato(2-dipropylaminoethanolato)copper(II) [$C_{18}H_{36}N_4O_4Cu_2$ (*A*), $C_{36}H_{72}N_8O_8Cu_4$ (*B*)] have been determined by single-crystal X-ray diffraction methods from 1793 (*A*) and 1390 (*B*) independent reflections. (*A*) crystallizes as monoclinic crystals of space group $P2_1/n$ [a = 10·469 (7), b = 12·742 (8), c = 8·695 (6) Å, β = 95·92 (1)°, Z = 2]; (*B*) crystallizes as orthorhombic crystals of space group *Pnna* [a = 12·83 (1), b = 19·03 (2), c = 19·28 (2) Å, Z = 4]. Both structures were solved from three-dimensional Patterson and electron density maps and refined by least-squares methods to a final R of 0·035 (*A*) and 0·077 (*B*). The monoclinic modification is built up from discrete centrosymmetric oxygen-bridged dimeric molecules with an intramolecular Cu–Cu separation of 3·010 (1) Å and Cu–O separations of 1·891 (2) and 1·924 (2) Å. The orthorhombic modification consists of oxygen-bridged cubane-type tetramers with Cu–Cu separations (mean values) of 3·168 (2×) and 3·202 Å (4×) and Cu–O separations (mean values) of 1·923 (4×), 2·230 (4×) and 2·154 Å (4×). The different structural features are responsible for the different magnetic properties. Whereas the dimeric compound shows strong antiferromagnetic interaction, the tetrameric compound has a normal magnetic moment at room temperature.

Introduction

Alkoxo-bridged Cu^{II} complexes with N,N-dialkyl-aminoethanols, $Cu(R_2NCH_2CH_2O)X$ (where R = CH_3, C_2H_5, C_3H_7, C_4H_9; X = Cl^-, Br^-, NCS^-) have been investigated by a number of research workers (Uhlig & Staiger, 1968; Nishida & Kida, 1976; Mergehenn & Haase, 1977a, and references therein) and have been shown to be built up of dimeric, polymeric and tetrameric structures in the solid state. Recently, these investigations have been extended to complexes where $X = NCO^-$ and the structures of two members of this series (R = CH_3, C_4H_9) have been reported (Mergehenn & Haase, 1977a,b). A marked change occurs in the structure of these complexes on going from the NCS^- to the NCO^- series. Whereas the members of the first series mainly possess polymeric structures with alternating alkoxo and NCS^- bridges (Pajunen & Smolander, 1974; Haase, Mergehenn & Krell, 1976; Mikuriya, Nishida & Kida, 1977), tetrameric structures predominate in the NCO^- series. This general behaviour is confirmed by the compound with R = C_2H_5, X = NCO^- (Merz & Haase, 1978a). The complex with R = C_3H_7, X = NCO^- exists in two isomeric modifications with different magnetic properties. The structural differences between these modifications will be discussed in this paper.

Experimental

The preparation of isocyanato(2-dipropylamino-ethanolato)copper(II) followed closely the procedure described by Lehtonen, Luukkonen & Uggla (1971). KOCN was used instead of KSCN. As it is very sparingly soluble in methanol, solid KOCN was added to a methanolic solution of copper(II) acetate mono-hydrate and 2-dipropylaminoethanol. It dissolved when the reaction mixture was heated on a water bath. Upon standing over night, crystals of the two isomers resulted. Recrystallization from methanol on rapid cooling gave exclusively light-green, needle-like crystals of (B) suitable for X-ray analysis. Upon standing in methanolic solution for some days the light-green crystals dissolved and dark-green crystals (A) resulted.

Besides the structurally known (A) and (B), there exist further modifications of isocyanato(2-dipropyl-aminoethanolato)copper(II) of unknown structure combined with solvent molecules. This can be demonstrated by recrystallization of (A) or (B) from benzene or CCl_4. Crystals with the formulae $(C_9H_{18}N_2O_2-Cu).\frac{1}{2}C_6H_6$ and $(C_9H_{18}N_2O_2Cu).CCl_4$ resulted. Upon standing in air they lose the solvent molecules and a light-green powder results. Debye–Scherrer photographs of the powder showed it to be (B).

The orientation matrix and cell dimensions were obtained by a least-squares fit of 20 (A), 24 (B) strong reflections to the setting angles on a computer-controlled Stoe four-circle diffractometer.

Crystal data

(A) $C_{18}H_{36}N_4O_4Cu_2$, M_r = 499·6, monoclinic, $P2_1/n$, a = 10·469 (7), b = 12·742 (8), c = 8·695 (6) Å, β = 95·92 (1)°, Z = 2, U = 1154 Å³, D_o = 1·43 (1) (by flotation), D_c = 1·436 g cm⁻³, μ(Mo $K\alpha$) = 18·0 cm⁻¹. Crystal dimensions: 0·25 × 0·25 × 0·25 mm.

(B) $C_{36}H_{72}N_8O_8Cu_4$, M_r = 999·2, orthorhombic, $Pnna$, a = 12·83 (1), b = 19·03 (2), c = 19·28 (2) Å, Z = 4, U = 4710 Å³, D_o = 1·40 (1) (by flotation), D_c = 1·409 g cm⁻³, μ(Mo $K\alpha$) = 17·7 cm⁻¹. Crystal dimensions: 0·11 × 0·12 × 0·36 mm.

Intensities were collected ($\omega/2\theta$ scan) in the range 3° $\leq 2\theta \leq$ 50° (A) and 3° $\leq 2\theta \leq$ 40° (B) on the Stoe four-circle diffractometer with graphite-mono-chromated Mo $K\alpha$ radiation; measuring time for the reflections (60 s) was twice the time for measuring background. Three strong reflections were monitored every 50 reflections and showed no significant change in intensity. 2035 (A) and 2205 (B) reflections were measured; those with $I \leq 3\sigma(I)$ and some weak reflections (B) were treated as unobserved. The remaining 1793 (A), 1390 (B) reflections were corrected for Lorentz and polarization effects. Absorption correction was only applied for (B).

Structure solution and results

All calculations were performed with the program $SHELX$ 76 (Sheldrick, 1976) on the IBM 370/168 computer of the Technische Hochschule Darmstadt. The scattering factor for Cu^{II}, which is not stored in the program, was taken from Cromer & Mann (1968).

Table 1. *Positional parameters* $(\times 10^4)$ *for all non-hydrogen atoms of* (A) *, with their estimated standard deviations in parentheses*

	x		y		z	
Cu	753·8	(0·3)	810·6	(0·3)	969·8	(0·4)
O(1)	958	(2)	−459	(2)	−102	(3)
N(1)	2650	(2)	597	(2)	1740	(3)
N(2)	420	(3)	2144	(2)	1791	(4)
C(2)	−210	(3)	2746	(3)	2272	(4)
O(2)	−838	(4)	3411	(3)	2786	(6)
C(11)	2182	(3)	−926	(2)	24	(4)
C(12)	3143	(3)	−70	(2)	519	(4)
C(21)	2731	(3)	6	(3)	3238	(4)
C(22)	2050	(5)	486	(4)	4465	(5)
C(23)	2014	(5)	−223	(4)	5857	(5)
C(31)	3345	(3)	1624	(2)	1856	(4)
C(32)	4772	(4)	1565	(3)	2405	(5)
C(33)	5403	(4)	2634	(4)	2262	(6)

Table 2. *Positional parameters* $(\times 10^4)$ *for the hydrogen atoms of* (A)

$U_{iso} = 0.052$ Å^2 (chelate-group H atoms), 0.103 Å^2 (propyl H atoms). The first two numbers refer to the C atom to which the H is attached.

	x	y	z
H(111)	2235 (3)	−1564 (2)	845 (4)
H(112)	2435 (3)	−1209 (2)	−1075 (4)
H(121)	3250 (3)	479 (2)	−405 (4)
H(122)	4067 (3)	−404 (2)	914 (4)
H(211)	3733 (3)	−131 (3)	3612 (4)
H(212)	2255 (3)	−735 (3)	2987 (4)
H(221)	2540 (5)	1232 (4)	4571 (5)
H(222)	1068 (5)	606 (4)	3987 (5)
H(231)	1516 (5)	112 (4)	6767 (5)
H(232)	3011 (5)	−342 (4)	6275 (5)
H(233)	1582 (5)	−966 (4)	5507 (5)
H(311)	3214 (3)	1968 (2)	716 (4)
H(312)	2900 (3)	2118 (2)	2657 (4)
H(321)	4927 (4)	1411 (3)	3631 (5)
H(322)	5220 (4)	957 (3)	1785 (5)
H(331)	6397 (4)	2619 (4)	2740 (6)
H(332)	4892 (4)	3220 (4)	2856 (6)
H(333)	5347 (4)	2825 (4)	1047 (6)

Table 3. *Positional parameters* $(\times 10^4)$ *for* (B), *with their standard deviations in parentheses*

	x	y	z
Cu(1)	286 (1)	1680 (1)	2622 (1)
Cu(2)	2069 (1)	2382 (1)	1683 (1)
O(11)	411 (6)	2508 (4)	3196 (4)
O(21)	1945 (6)	1797 (5)	2486 (4)
N(11)	−805 (9)	1344 (6)	3351 (6)
N(21)	3132 (10)	1641 (7)	1360 (6)
N(12)	146 (13)	958 (7)	1989 (7)
C(12)	15 (15)	544 (9)	1657 (8)
O(12)	−96 (14)	27 (8)	1278 (7)
N(22)	2224 (12)	3027 (8)	956 (7)
C(22)	2267 (12)	3352 (9)	494 (8)
O(22)	2344 (11)	3723 (7)	−21 (6)
C(111)	−215 (11)	2496 (8)	3805 (7)
C(112)	−1049 (16)	1996 (10)	3728 (10)
C(121)	−1766 (16)	1033 (12)	3072 (9)
C(122)	−2314 (17)	1368 (11)	2476 (10)
C(123)	−3270 (17)	1033 (13)	2217 (12)
C(131)	−413 (17)	832 (12)	3848 (10)
C(132)	277 (16)	285 (10)	3626 (10)
C(133)	728 (19)	−207 (11)	4157 (11)
C(211)	2597 (12)	1186 (8)	2482 (8)
C(212)	3474 (17)	1286 (12)	1987 (10)
C(221)	4095 (16)	1911 (11)	1073 (11)
C(222)	4634 (14)	2524 (11)	1339 (10)
C(223)	5512 (17)	2830 (12)	970 (12)
C(231)	2703 (19)	1140 (11)	933 (12)
C(232)	2126 (16)	1376 (10)	302 (8)
C(233)	1658 (24)	867 (12)	−153 (14)

The positions of the Cu atoms could be derived from a sharpened Patterson map for both compounds. Successive least-squares calculations and ΔF syntheses revealed all the non-hydrogen atoms. The concluding refinement with blocked full-matrix least squares could only be done by refining one half of the parameters (14 atoms + H atoms + overall scale = 153 free parameters) (A) and one third of the total parameters (28 atoms + overall scale = 253 free parameters) (B).

Continued refinement with anisotropic temperature parameters of all non-hydrogen atoms led to an R of 0·052 (A). At this stage of refinement the positions of the H atoms were calculated with a C—H distance of 1·08 Å and a staggered conformation assumed. These positions corresponded to maxima in the concluding ΔF calculation. Further refinement now including H atoms as rigid groups riding on the corresponding C atoms and two common isotropic temperature factors (one for the chelate group and one for the propyl H atoms) reduced R to 0·035 with no shift greater than the estimated standard deviation. A ΔF map at this stage showed no peak greater than 0·5 e Å^{-3}. The final positional parameters for all non-hydrogen atoms are given in Table 1,* those for H in Table 2.

In the case of (B) continued refinement reduced R to a final value of 0·077 with no significant shifts in the parameters. Final positional parameters are given in Table 3;* the positions of the H atoms have not been

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33461 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
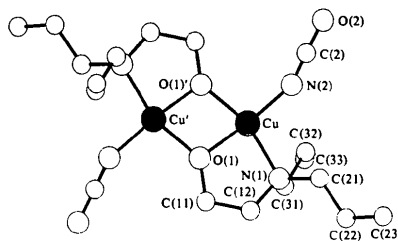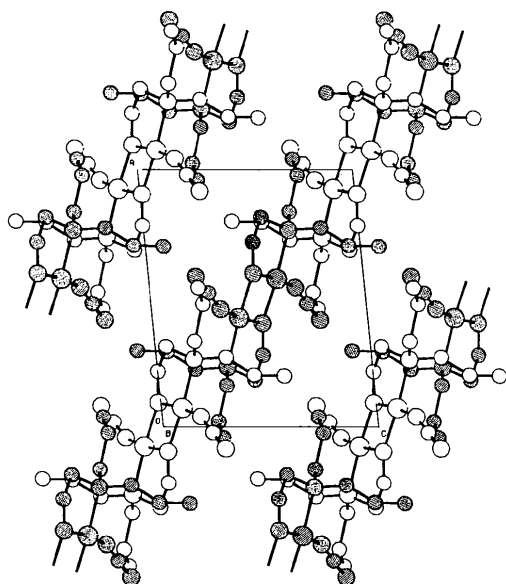

Fig. 1. Molecular structure of dimeric isocyanato(2-dipropylamino-ethanolato)copper(II) (A).

determined. A ΔF synthesis at this point showed no peak greater than 0·5 e Å^{-3}.

Discussion

The monoclinic modification (A) essentially consists of alkoxo-O bridged, centrosymmetric binuclear units (Figs. 1, 2). Each Cu atom is coordinated by amino and cyanate N atoms and two alkoxo O atoms. The central four-membered Cu_2O_2 ring is exactly planar, because the Cu and O atoms are related by an inversion centre. The coordination around Cu is distorted square planar (Tables 4 and 5) and the deviations of the coordinating N atoms from the plane of the Cu_2O_2 ring are only small (Table 6). The coordination around the bridging

Fig. 2. Projection of the unit cell of the dimeric form (A) along the monoclinic axis. The molecule with hatched circles is placed at 0·5, 0·5, 0·5.

Table 4. Bond distances (Å)

The symmetry code denoted by a prime is $\bar{x}, \bar{y}, \bar{z}$ (A); x, $0·5 - y$, $0·5 - z$ (B).

		(B)	
	$(A)^{*}$	$m = 1, n = 2$	$m = 2, n = 1$
Cu(m)—Cu(m)'	3·010 (1)	3·155 (4)	3·181 (3)
—Cu(n)		3·208 (2)	3·196 (2)†
—O(m1)	1·891 (2)	1·932 (8)	1·913 (8)
—O(m1)'	1·924 (2)	2·214 (8)	2·244 (8)
—O(n1)		2·157 (8)	2·150 (8)†
—N(m1)	2·047 (2)	2·085 (12)	2·059 (13)
—N(m2)	1·890 (3)	1·848 (14)	1·876 (14)
N(m2)—C(m2)	1·120 (5)	1·03 (2)	1·09 (2)
C(m2)—O(m2)	1·188 (6)	1·23 (2)	1·22 (2)
O(m1)—C(m11)	1·407 (4)	1·42 (2)	1·43 (2)
N(m1)—C(m12)	1·493 (4)	1·47 (2)	1·45 (2)
—C(m21)	1·500 (4)	1·47 (2)	1·45 (3)
—C(m31)	1·497 (4)	1·46 (2)	1·38 (3)
C(m11)—C(m12)	1·517 (4)	1·44 (3)	1·49 (3)
C(m21)—C(m22)	1·476 (6)	1·49 (3)	1·45 (3)
C(m22)—C(m23)	1·515 (7)	1·47 (3)	1·45 (3)
C(m31)—C(m32)	1·523 (5)	1·43 (3)	1·49 (3)
C(m32)—C(m33)	1·525 (6)	1·50 (3)	1·44 (3)

* In this case m should be omitted.
† The second atom should be the symmetry-related one.

O is nearly planar with C(11) only deviating 0·11 Å from the plane of the Cu_2O_2 ring.

The geometry within the Cu_2O_2 four-membered ring is very similar to that in other alkoxo-bridged dimeric Cu^{II} complexes. The Cu—Cu distance of 3·010 (1) Å agrees well with the values found for $(CuPIA)_2$: 3·026 (6) Å (Bertrand & Kelley, 1970), bromo(2-diethyl-

Table 5. Interbond angles (°)

		(B)	
	$(A)^{*}$	$m = 1,$ $n = 2$	$m = 2,$ $n = 1$
O(m1)—Cu(m)—O(m1)'	75·8 (1)	80·4 (4)	79·8 (4)
—O(n1)		84·5 (3)	83·6 (3)†
—N(m1)	83·8 (1)	85·4 (4)	84·3 (4)
—N(m2)	172·2 (1)	173·5 (5)	174·4 (5)
O(n1)—Cu(m)—O(m1)'		76·7 (3)	77·6 (3)†
—N(m1)		141·0 (4)	139·1 (4)†
—N(m2)		95·3 (6)	97·0 (6)†
N(m1)—Cu(m)—O(m1)'	158·4 (1)	138·1 (4)	137·8 (4)
—N(m2)	102·0 (1)	98·7 (6)	98·7 (6)
N(m2)—Cu(m)—O(m1)'	99·0 (1)	93·2 (4)	94·8 (4)
Cu(m)—O(m1)—Cu(m)'	104·2 (1)	98·9 (2)	99·5 (2)
—Cu(n)'		103·0 (2)	103·9 (2)†
Cu(m)—O(m1)'—Cu(n)		94·6 (2)	93·1 (2)†
Cu(m)—O(m1)—C(m11)	118·2 (2)	114·4 (8)	114·8 (8)
Cu(m)—N(m2)—C(m2)	153·6 (3)	175·4 (17)	172·7 (15)
N(m2)—C(m2)—O(m2)	177·4 (4)	176·4 (22)	178·1 (19)
Cu(m)—N(m1)—C(m12)	103·8 (2)	102·5 (10)	105·5 (10)
—C(m21)	108·5 (2)	116·1 (9)	116·0 (11)
—C(m31)	110·7 (2)	114·6 (11)	113·0 (12)
C(m12)—N(m1)—C(m21)	109·9 (2)	110·0 (14)	103·0 (14)
—C(m31)	110·1 (2)	108·2 (13)	107·3 (15)
C(m21)—N(m1)—C(m31)	113·4 (2)	105·2 (14)	111·0 (15)
O(m1)—C(m11)—C(m12)	106·9 (2)	110·2 (12)	109·9 (14)
N(m1)—C(m12)—C(m11)	110·1 (3)	116·8 (15)	111·4 (16)
—C(m21)—C(m22)	115·5 (3)	120·4 (17)	123·8 (17)
—C(m31)—C(m32)	115·6 (3)	120·3 (16)	118·5 (17)
C(m21)—C(m22)—C(m23)	112·6 (4)	118·0 (18)	121·1 (18)
C(m31)—C(m32)—C(m33)	110·5 (3)	119·2 (17)	120·1 (18)

* In this case m should be omitted.
† All atoms with $n = 1$ should read as the symmetry-related ones.

Table 6. Equations for the best planes defined by copper and bridging oxygen atoms and distances (Å) of some atoms of interest

(A) Plane defined by Cu, O(1), Cu', O(1)'
$$-2·3699X - 6·5863Y + 7·3472Z = 0·0$$
N(1) 0·258, N(2) —0·196, C(11) 0·110

(B) Plane I defined by Cu(1), O(11), Cu(1)', O(11)'
$$12·834X = 0·4473$$

Plane II defined by Cu(2), O(21), Cu(2)', O(21)'
$$12·834X = 2·5753$$

Plane III defined by Cu(1), O(11), Cu(2)', O(21)
$$0·9451X - 12·582Y + 14·398Z = 1·5878$$

Plane IV defined by Cu(1)', O(11), Cu(2)', O(21)'
$$-0·9620X + 14·317Y + 12·623Z = 7·6552$$

	Distances from plane I $m = 1, n = 2$	Distances from plane II $m = 2, n = 1$
Cu(m)	—0·081	0·079
O(m1)	0·081	—0·079
N(m1)	—1·481	1·444
N(m2)	—0·260	0·279
C(m11)	—0·723	0·758
O(n1)	2·049	—2·047

aminoethanolato)copper(II): 3·026 (2) Å (Pajunen & Lehtonen, 1971; Haase, 1973), and α-bromo(2-dibutyl-aminoethanolato)copper(II): 3·019 (4) Å (Mergehenn & Haase, 1975). Cu—O distances (1·891, 1·924 Å) differ only slightly and are in the range of those of the alkoxo-bridged dimeric complexes cited above.

The NCO⁻ group is nearly linear (N—C—O = 177·4°) and of nearly the same structure as found for other alkoxo-bridged complexes containing an NCO⁻ group (Mergehenn & Haase, 1977a,b). The angle Cu—N(2)—C(2) of 153·6° deviates from 180° and is nearly the same as found in isocyanato(2-dimethylamino-ethanolato)copper(II) (Mergehenn & Haase, 1977a), a tetrameric cubane-type cluster, which can be thought of as built up from dimeric moieties. This angle becomes closer to 180° with the tetrameric modification and with isocyanato(2-dibutylaminoethanolato)copper(II) (Mergehenn & Haase, 1977b).

The unit cell of (B) contains four cubane-type clusters (Fig. 3) with a Cu_4O_4 core. The symmetry of the cluster is C_2 with the C_2 axis parallel to the crystallographic a axis (Fig. 4). The same symmetry is found in the related compounds chloro(2-diethyl-aminoethanolato)copper(II) (Haase, 1973) and chloro-(2-dipropylaminoethanolato)copper(II) (Matsumoto, Ueda, Nishida & Kida, 1976). There are only small deviations from the higher possible symmetry S_4 which is reached in the alkoxo-bridged compounds (CuEIA)₄ (Bertrand & Kelley, 1970), chloro(bromo)(2-diethyl-aminoethanolato)copper(II).CCl₄ (Mergehenn & Haase, 1978), and the closely related compound isocyanato(2-diethylaminoethanolato)copper(II) (Merz & Haase, 1978a). Less favourable packing effects, on going from ethyl to propyl, seem to be the only reason why S_4 symmetry is not reached. As can be seen from the differences in the densities of the dimeric and the tetrameric modifications, these unfavourable steric conditions in the tetrameric compound may cause the existence of the more dense dimeric modification and of
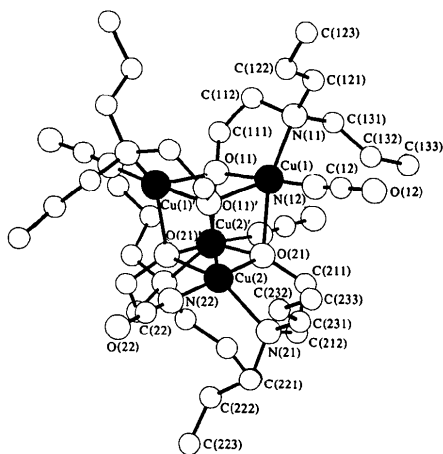

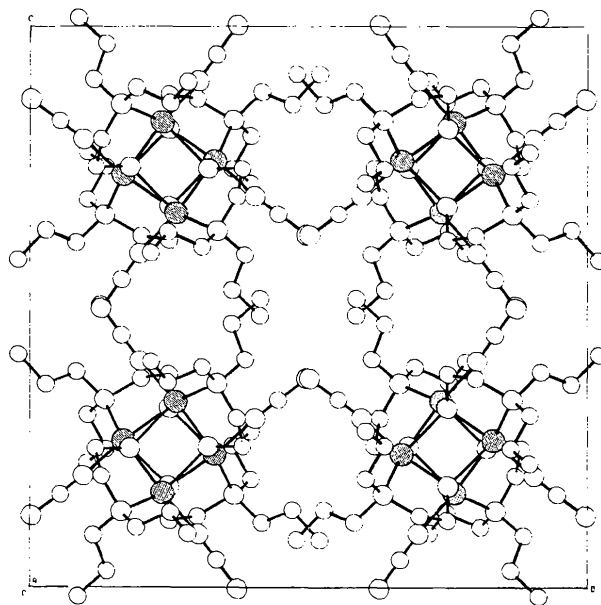Fig. 3. Molecular structure of tetrameric isocyanato(2-dipropyl-aminoethanolato)copper(II) (B).

Fig. 4. Projection of the unit cell of the tetrameric form (B) along a.

the tetrameric modifications with included solvent molecules.

The compound can be thought of as two 'dimers' (formed from the atoms related by the C_2 axis) held together by out-of-plane Cu—O bonds; but this model is not as good as for the related isocyanato(2-dimethyl-aminoethanolato)copper(II) (Mergehenn & Haase, 1977a), as can be seen from the nearly equal Cu—Cu separations 3·155, 3·181 Å within the 'dimers' and 3·208, 3·196 Å (2×) between the 'dimers'. This geometry of the Cu₄ tetrahedron is thus very similar to that of chloro(2-dipropylaminoethanolato)copper(II) and should, according to Mergehenn, be classified as I (→ II), a transition type between the extremes isocyanato(2-dimethylaminoethanolato)copper(II) and chloro(bromo)(2-dibutylaminoethanolato)copper(II) (Mergehenn & Haase, 1978).

The best planes through the Cu₂O₂ four-membered rings (Table 6) constitute a nearly regular cube, with all the O atoms within this cube and the Cu atoms outside. The angles between the planes are I–III: 85·8, I–IV: 94·3, III–IV: 90·8, III'–IV: 89·8°.

Changes within the Cu₂O₂ four-membered rings occur on going from the dimeric (A) to the tetrameric (B) modification. The Cu—O distances within the pseudodimers are no longer approximately equal. Whereas the Cu—O distance within the five-membered chelate ring maintains its (mean) value of 1·92 Å, the non-chelate-bonded Cu—O bond length is much elongated: mean value 2·23 Å. The Cu—O out-of-plane distance, 2·15 Å (4×) (mean value), is intermediate between these values, a typical property of the transition type. The extent of bending of the pseudo-

dimer unit is indicated by the dihedral angles 11·8 [Cu(1)O$_2$Cu(1)'] and 11·6° [Cu(2)O$_2$Cu(2)'].

The coordination number of Cu^{II} changes from 4 (A) to 5 (B) and the coordination from distorted square planar to distorted trigonal bipyramidal with the chelate-bonded O and cyanate N at the vertical axis [O—Cu—N = 174° (mean value)] and with amino N and the other two coordinating O atoms in the equatorial plane. The interbond angles within this plane deviate rather strongly from the ideal value of 120° [76·7, 138·1, 141·0° (mean values)]. The mean value of the equatorial angles is 118·6°, while the mean value of the six angles between the equatorial and axial atoms is 89·6°. Much the same situation is found with isocyanato(2-dibutylaminoethanolato)copper(II) [axial angle 175·6°, equatorial angles 78·6, 130·9, 145·5° (mean values)] and with chloro(2-dipropylamino-ethanolato)copper(II).

The coordination around the bridging O is distorted tetrahedral indicating that O has sp^3 hybridization. This is confirmed by the fact that the mean value of the interbond angles at O is 108·8°, though the individual values are in the range from 93·1 to 123·9°, with only the angle within the chelate group Cu—O—C (114·4, 114·8°) of the correct magnitude. The angle at the bridging O within the dimers is much smaller (99·2°, mean value) than in the dimeric modification (104·2°). This is the general trend with alkoxo-bridged compounds on going from dimerics to tetramerics.

The geometry within the nearly linear NCO$^-$ group lies in the range found for the other members of this series. The change in the Cu—N—C interbond angle from 153·6 (A) to 174·1° (mean value) (B) is accompanied by a shortening of the C—N bond length of the cyanate group from 1·12 (A) to 1·06 Å (mean value) (B), as is to be expected when hybridization at the cyanate N becomes closer to sp.

The change in structural properties of the two modifications of isocyanato(2-dipropylaminoethano-lato)copper(II) accompanies a change in magnetic properties. The effective magnetic moment* of (A), μ(298 K) = 0·72 BM, is strongly reduced and reaches zero at the temperature of liquid nitrogen. These results show that there exist strong exchange interactions between the O-bridged Cu^{II} ions, a commonly observed effect. For a recent review on magnetic interaction see Hatfield (1976).

Fitting the experimental susceptibility data in the range from 77–300 K to the well known Bleaney–Bowers equation for spin-coupled Cu^{II} complexes gave good agreement and yielded a value of the singlet–triplet splitting $2J = -670$ cm^{-1}. A linear relation between the Cu—O—Cu bridging angle and the singlet–triplet splitting has been found for several hydroxy-bridged dimeric Cu^{II} complexes, and the mechanisms

of superexchange have been discussed (Hatfield, 1976, and references therein).

A similar relation seems to be true for alkoxo-bridged Cu^{II} dimers. The Cu—O—Cu bridging angle 104·2 (1)° (A) is below the value of 105·0 (6)° (Haase, 1973) found for bromo(2-diethylaminoethanolato)-copper(II) in agreement with the values of the singlet–triplet splitting −670 and −800 cm^{-1} (Uhlig & Staiger, 1968).

The effective magnetic moment of (B), μ(298 K) = 1·89 BM, indicates normal paramagnetic behaviour at room temperature. It decreases slightly with decreasing temperature to μ(78 K) = 1·46 BM. Thus, the overall antiferromagnetic exchange interactions in (B) are only small. Determination of the exchange integrals by extending the susceptibility measurements to the temperature of liquid helium and a discussion of their relation to structural details will be given later (Merz & Haase, 1978b).

References

BERTRAND, J. A. & KELLEY, J. A. (1970). Inorg. Chim. Acta, 4, 203–209.

CROMER, D. T. & MANN, J. B. (1968). Acta Cryst. A24, 321–324.

HAASE, W. (1973). Chem. Ber. 106, 3132–3148.

HAASE, W., MERGEHENN, R. & KRELL, W. (1976). Z. Naturforsch. Teil B, 31, 85–89.

HATFIELD, W. E. (1976). Theory and Applications of Molecular Paramagnetism, edited by E. A. BOUDREAUX & L. N. MULAY, pp. 349–449. New York: Interscience.

LEHTONEN, M., LUUKONEN, E. & UGGLA, R. (1971). Suom. Kemistil. B, 44, 399–403.

MATSUMOTO, N., UEDA, I., NISHIDA, Y. & KIDA, S. (1976). Bull. Chem. Soc. Jpn, 49, 1308–1312.

MERGEHENN, R. & HAASE, W. (1975). Z. Naturforsch. Teil B, 30, 155–158.

MERGEHENN, R. & HAASE, W. (1977a). Acta Cryst. B33, 1877–1882.

MERGEHENN, R. & HAASE, W. (1977b). Acta Cryst. B33, 2734–2739.

MERGEHENN, R. & HAASE, W. (1978). To be published.

MERZ, L. & HAASE, W. (1978a). J. Chem. Soc. Dalton. In the press.

MERZ, L. & HAASE, W. (1978b). In preparation.

MIKURIYA, M., NISHIDA, Y. & KIDA, S. (1977). Acta Cryst. B33, 538–540.

NISHIDA, Y. & KIDA, S. (1976). J. Inorg. Nucl. Chem. 38, 451–457.

PAJUNEN, A. & LEHTONEN, M. (1971). Suom. Kemistil. B, 44, 200–206.

PAJUNEN, A. & SMOLANDER, K. (1974). Finn. Chem. Lett. pp. 67–70.

SHELDRICK, G. M. (1976). SHELX 76. Program for crystal structure determination. Univ. of Cambridge, England.

UHLIG, E. & STAIGER, K. (1968). Z. Anorg. Allg. Chem. 360, 39–49.

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* Experimental susceptibility data were obtained by the Faraday method using HgCo(SCN)$_4$ as a calibrating standard.