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The Crystal Structures of Isocyanato(2-dibutylaminoethanolato)copper(II) and Isothiocyanato(2-dibutylaminoethanolato)copper(II)

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The structures of isocyanato- and isothiocyanato(2-dibutylaminoethanolato)copper(II), $(C_{10}H_{22}NOCuY)_4$, Y = NCO (A), NCS (B), have been determined by single-crystal X-ray diffraction methods from 2875 (A) and 4192 (B) independent reflexions. The isomorphous substances belong to space group $P\bar{1}$ with (A): a = 12·14 (1), b = 13·09 (1), c = 19·69 (2) Å, α = 72·2 (1), β = 103·5 (1), γ = 106·5 (1)° and (B): a = 12·34 (2), b = 13·53 (2), c = 20·33 (3) Å, α = 73·8 (1), β = 107·6 (1), γ = 109·0 (1)°. Tetrameric cubane-type molecules with intramolecular Cu–Cu separations (mean values) of 3·052 (5) (A), 3·034 (5) (B) (2×) and 3·252 (4) (A), 3·242 (3) Å (B) (4×) are built up in the solid state. They are new examples of the variability of Cu_4O_4 core clusters which differ in their magnetic and optical properties and their molecular structures. Refinement by Fourier and least-squares techniques led to final R's of 0·096 (A) and 0·105 (B), although some C atoms of the butyl groups, which have high thermal motions, could not be located satisfactorily.

Introduction

Halogeno(2-dialkylaminoethanolato)copper(II) complexes, first described by Hein & Beerstecher (1955), are able to form different types of molecular structures in the solid state [a summary of all known structures is given by Mergehenn & Haase (1977*a*)]. There are dimeric, polymeric and tetrameric cubane-like molecules and different tetrameric Cu_4O_4 clusters exist. For a more detailed interpretation of the different magnetic and optical properties, it is necessary to know the structure of these substances.

The two extreme types of tetrameric molecules differ in the arrangement of the short (~1·9–2·0 Å) and long (~2·4–2·5 Å) Cu–O bonds and one type may be interpreted as formally being built up from two dimeric moieties (all four long Cu–O bonds parallel). In contrast to this formalism the other type may be considered to be derived from an eight-membered Cu_4O_4 ring, folded in a boat-like conformation.

Recently, intermediate forms of Cu_4O_4 clusters have been investigated. Chloro(2-dipropylaminoethanolato)copper(II) (Matsumoto, Ueda, Nishida & Kida, 1976) and isocyanato(2-diethylaminoethanolato)- and isocyanato(2-dipropylaminoethanolato)copper(II) (Merz & Haase, 1977) have structures which may be interpreted as transition types on the way from the boat-like type to the type formally thought of as being built up of two dimeric moieties. The transition type in the reverse direction is formed by isocyanato- and isothiocyanato(2-dibutylaminoethanolato)copper(II). The structural differences between these intermediate types will be discussed in this paper.

Experimental

The preparation of the substances followed the procedure described by Lehtonen, Luukkonnen & Uggla (1971). For the isocyanato complex instead of KSCN an equivalent amount of KOCN was used. Crystals could be obtained from methanol and two with the following distances from face to face were used in the X-ray analysis: $\{001\}$–$\{00\bar{1}\}$ = 0·16, $\{101\}$–$\{\bar{1}0\bar{1}\}$ = 0·22, $\{100\}$–$\{\bar{1}00\}$ = 0·22, $\{10\bar{1}\}$–$\{\bar{1}01\}$ = 0·19, $\{011\}$–$\{0\bar{1}\bar{1}\}$ = 0·24, $\{010\}$–$\{0\bar{1}0\}$ = 0·30 mm (A) and $\{001\}$–$\{00\bar{1}\}$ = 0·56, $\{100\}$–$\{\bar{1}00\}$ = 0·26, $\{10\bar{1}\}$–$\{\bar{1}01\}$ = 0·31, $\{011\}$–$\{0\bar{1}\bar{1}\}$ = 0·26, $\{00\bar{1}\}$–$\{0\bar{1}1\}$ = 0·46, $\{\bar{1}11\}$–$\{1\bar{1}\bar{1}\}$ = 0·41 mm (B). Unit-cell dimensions were determined by least squares from the measurement of 20 strong reflexions and their setting angles on a computer-controlled Stoe four-circle diffractometer.

Intensities were collected ($\omega/2\theta$ scan) in the range $3° \leq 2\theta \leq 42°$ with graphite-monochromated Mo $K\alpha$ radiation; measuring time for the reflexions (40 s) was twice the time for measuring background. 5272 (A) and 5360 (B) reflexions were measured; those with $I \leq 3\sigma(I)$ were treated as unobserved. The remaining 2875 (A) and 4192 (B) reflexions were corrected for Lorentz, polarization and absorption effects.

Structure solution and results

Solution of the structure was carried out independently for both substances. Intensity statistics led to space group $P\bar{1}$ and the positions of four Cu atoms could be

Table 1. *Positional parameters* (×10³)

	x	y	z		x	y	z
Cu(1)	−12·2 (2)	272·4 (2)	−224·0 (2)	C(21)	25 (2)	366 (2)	−451 (1)
	−17·4 (2)	266·6 (2)	−230·7 (1)		10 (2)	362 (2)	−449 (1)
Cu(2)	129·1 (3)	239·5 (2)	−322·0 (2)	C(22)	−38 (2)	372 (2)	−393 (1)
	112·1 (2)	236·7 (2)	−325·9 (1)		−47 (2)	367 (1)	−393 (1)
Cu(3)	264·9 (2)	289·0 (2)	−168·0 (1)	C(211)	−39 (2)	148 (2)	−426 (1)
	261·0 (2)	282·3 (2)	−171·0 (1)		25 (2)	205 (2)	−476 (1)
Cu(4)	188·8 (3)	479·5 (2)	−287·3 (1)	C(212)	−120 (3)	137 (3)	−483 (2)
	188·9 (2)	467·3 (2)	−281·4 (1)		−97 (2)	137 (2)	−436 (1)
O(1)	95·5 (10)	186·5 (10)	−214·6 (7)	C(213)	−185 (3)	13 (2)	−466 (2)
	85·8 (9)	182·9 (8)	−224·0 (6)		−146 (3)	25 (2)	−462 (2)
O(2)	48·3 (11)	347·8 (10)	−325·0 (7)	C(214)	−278 (3)	19 (2)	−503 (2)
	38·6 (9)	341·6 (8)	−324·5 (6)		−270 (3)	−37 (2)	−446 (2)
O(3)	281·5 (11)	353·5 (10)	−267·2 (7)	C(221)	209 (2)	310 (2)	−463 (2)
	272·1 (9)	346·0 (8)	−266·8 (5)		201 (2)	316 (2)	−454 (1)
O(4)	151·6 (10)	394·1 (10)	−192·7 (6)	C(222)	229 (3)	364 (2)	−530 (2)
	151·6 (9)	385·1 (8)	−193·9 (6)		199 (2)	363 (2)	−528 (2)
O(11)	−253 (2)	441 (2)	−229 (1)	C(223)	367 (3)	362 (3)	−524 (2)
S(11)	−237·0 (9)	466·5 (8)	−213·2 (6)		347 (2)	377 (2)	−524 (1)
O(21)	278 (2)	−18 (2)	−302 (1)	C(224)	363 (3)	440 (3)	−581 (2)
S(21)	253·9 (7)	−37·4 (5)	−330·7 (4)		347 (3)	449 (2)	−608 (2)
O(31)	240 (2)	161 (2)	48 (1)	C(3)	244 (2)	200 (2)	−17 (1)
S(31)	284·1 (9)	185·1 (8)	66·9 (4)		257 (2)	209 (1)	−18 (1)
O(41)	306 (2)	659 (2)	−480 (1)	C(31)	452 (2)	286 (2)	−231 (1)
S(41)	337·3 (7)	669·3 (7)	−470·7 (4)		441 (2)	273 (2)	−227 (1)
N(1)	−112 (2)	127 (1)	−171 (1)	C(32)	401 (2)	376 (2)	−283 (1)
	−115 (1)	127 (1)	−181 (1)		393 (2)	367 (2)	−276 (1)
N(2)	67 (2)	261 (1)	−433 (1)	C(311)	506 (2)	282 (2)	−99 (2)
	56 (2)	271 (1)	−431 (1)		508 (2)	292 (2)	−98 (1)
N(3)	424 (2)	253 (2)	−156 (1)	C(312)	525 (2)	407 (2)	−116 (1)
	417 (1)	249 (1)	−156 (1)		521 (2)	396 (2)	−109 (1)
N(4)	203 (1)	615 (1)	−248 (1)	C(313)	635 (2)	450 (2)	−58 (2)
	214 (1)	598 (1)	239 (1)		631 (2)	423 (2)	−40 (2)
N(11)	−109 (2)	366 (2)	−240 (1)	C(314)	667 (2)	561 (2)	−75 (2)
	−116 (1)	357 (1)	−242 (1)		639 (2)	523 (8)	−51 (2)
N(21)	194 (2)	122 (2)	−313 (1)	C(321)	387 (2)	112 (2)	−128 (1)
	177 (1)	125 (1)	−322 (1)		373 (2)	109 (2)	−133 (1)
N(31)	250 (2)	236 (2)	−72 (1)	C(322)	470 (2)	53 (2)	−121 (1)
	252 (1)	231 (1)	−76 (1)		454 (2)	56 (2)	−127 (1)
N(41)	224 (2)	561 (2)	−382 (1)	C(323)	404 (2)	−71 (2)	−101 (1)
	226 (1)	549 (1)	−379 (1)		382 (2)	−70 (2)	−98 (1)
C(1)	−173 (2)	402 (2)	−234 (1)	C(324)	469 (3)	−136 (2)	−112 (2)
	−165 (2)	405 (2)	−230 (1)		452 (2)	−117 (2)	−111 (2)
C(11)	−60 (2)	41 (2)	−179 (1)	C(4)	265 (2)	606 (2)	−425 (1)
	−70 (2)	42 (2)	−193 (1)		278 (2)	595 (2)	−413 (1)
C(12)	63 (2)	68 (2)	−176 (1)	C(41)	230 (2)	571 (2)	−167 (1)
	51 (2)	69 (1)	−194 (1)		240 (2)	550 (1)	−162 (1)
C(111)	−235 (2)	106 (2)	−203 (2)	C(42)	147 (2)	460 (2)	−143 (1)
	−247 (2)	111 (2)	−208 (1)		153 (1)	447 (1)	−145 (1)
C(112)	−273 (2)	128 (2)	−278 (1)	C(411)	302 (2)	715 (2)	−274 (1)
	−285 (2)	118 (2)	−282 (1)		310 (1)	696 (1)	−257 (1)
C(113)	−394 (2)	129 (2)	−309 (2)	C(412)	420 (2)	684 (2)	−255 (1)
	−405 (2)	123 (2)	−310 (1)		428 (2)	666 (1)	−240 (1)
C(114)	−443 (2)	155 (2)	−381 (2)	C(413)	497 (2)	792 (2)	−311 (1)
	−455 (3)	152 (2)	−381 (2)		519 (2)	777 (2)	−274 (1)
C(121)	−97 (2)	112 (2)	−95 (1)	C(414)	599 (3)	774 (2)	−284 (2)
	−84 (2)	106 (2)	−101 (1)		630 (2)	749 (2)	−263 (1)
C(122)	−106 (2)	209 (2)	−69 (1)	C(421)	83 (2)	641 (2)	−281 (1)
	−93 (2)	204 (2)	−82 (2)		97 (1)	625 (1)	−272 (1)
C(123)	−85 (2)	190 (2)	10 (2)	C(422)	66 (2)	720 (2)	−245 (1)
	−84 (2)	171 (2)	2 (2)		77 (2)	698 (1)	−234 (1)
C(124)	−81 (2)	297 (2)	35 (2)	C(423)	−52 (2)	753 (2)	−295 (1)
	−72 (2)	275 (2)	29 (2)		−32 (2)	736 (2)	−283 (1)
C(2)	231 (2)	55 (2)	−310 (1)	C(424)	−81 (2)	821 (2)	−263 (2)
	209 (2)	58 (1)	−327 (1)		−55 (2)	807 (2)	−242 (1)

Table 2. *Bond distances* (Å)

	$n = 1$ $m = 2$ $p = 4$		$n = 2$ $m = 1$ $p = 3$		$n = 3$ $m = 4$ $p = 1$		$n - 4$ $m = 3$ $p = 2$	
	$X = $ O	$X = $ S	$X = $ O	$X = $ S	$X = $ O	$X = $ S	$X = $ O	$X = $ S
Cu(*n*)–O(*n*)	1·90 (2)	1·92 (1)	1·92 (2)	1·93 (1)	1·91 (1)	1·93 (1)	1·94 (1)	1·92 (1)
–O(*m*)	2·13 (1)	2·10 (1)	2·11 (1)	2·08 (1)	2·09 (1)	2·11 (1)	2·14 (2)	2·11 (1)
–O(*p*)	2·26 (1)	2·24 (1)	2·30 (1)	2·28 (1)	2·28 (1)	2·27 (1)	2·23 (1)	2·21 (1)
–N(*n*)	2·06 (2)	2·06 (1)	2·10 (2)	2·01 (2)	2·06 (2)	2·04 (2)	2·10 (2)	2·07 (2)
–N(*n*1)	1·85 (2)	1·92 (2)	1·86 (2)	1·90 (2)	1·84 (2)	1·89 (2)	1·92 (2)	1·93 (2)
O(*n*)–C(*n*2)	1·48 (2)	1·47 (2)	1·51 (2)	1·50 (2)	1·49 (3)	1·49 (2)	1·51 (3)	1·46 (3)
N(*n*1)–C(*n*)	1·05 (4)	1·12 (3)	1·08 (4)	1·14 (3)	1·05 (3)	1·13 (3)	1·02 (3)	1·16 (3)
X(*n*1)–C(*n*)	1·25 (4)	1·57 (3)	1·19 (4)	1·59 (2)	1·24 (3)	1·61 (2)	1·23 (3)	1·52 (2)
N(*n*)–C(*n*1)	1·50 (4)	1·53 (4)	1·51 (3)	1·43 (3)	1·50 (3)	1·47 (3)	1·50 (3)	1·51 (2)
–C(*n*11)	1·46 (3)	1·52 (3)	1·64 (3)*	1·33 (4)*	1·38 (3)*	1·47 (3)	1·55 (2)	1·50 (2)
–C(*n*21)	1·43 (3)	1·53 (3)	1·82 (3)*	1·84 (3)*	1·72 (3)*	1·76 (2)*	1·54 (3)	1·51 (2)
C(*n*1)–C(*n*2)	1·42 (3)*	1·41 (3)*	1·54 (4)	1·54 (4)	1·49 (3)	1·54 (3)	1·52 (3)	1·48 (2)
C(*n*11)–C(*n*12)	1·40 (4)*	1·42 (4)*	1·32 (4)*	1·77 (4)*	1·52 (4)	1·33 (3)*	1·54 (3)	1·55 (3)
C(*n*21)–C(*n*22)	1·54 (4)	1·53 (4)	1·34 (4)*	1·45 (4)	1·40 (4)*	1·36 (4)*	1·50 (4)	1·53 (3)
C(*n*12)–C(*n*13)	1·46 (4)	1·44 (4)	1·56 (4)	1·61 (4)	1·63 (4)	1·66 (3)*	1·70 (3)*	1·67 (3)*
C(*n*22)–C(*n*23)	1·48 (4)	1·62 (4)	1·67 (5)*	1·76 (4)*	1·56 (3)	1·68 (3)*	1·62 (3)	1·55 (3)
C(*n*13)–C(*n*14)	1·37 (4)*	1·38 (4)*	1·20 (4)*	1·56 (4)	1·35 (4)*	1·28 (4)*	1·29 (4)*	1·48 (4)
C(*n*23)–C(*n*24)	1·60 (5)	1·61 (5)	1·26 (4)*	1·72 (4)*	1·40 (5)*	1·34 (5)*	1·40 (5)*	1·56 (4)

Table 3. *Interbond angles* (°)

	$n = 1$ $m = 2$ $p = 4$ $q = 3$		$n = 2$ $m = 1$ $p = 3$ $q = 4$		$n = 3$ $m = 4$ $p = 1$ $q = 2$		$n = 4$ $m = 3$ $p = 2$ $q = 1$	
	$X = $ O	$X = $ S	$X = $ O	$X = $ S	$X = $ O	$X = $ S	$X = $ O	$X = $ S
O(*n*)–Cu(*n*)–O(*m*)	80·6 (6)	80·6 (5)	80·5 (6)	80·8 (5)	82·3 (6)	81·6 (5)	80·3 (6)	81·7 (5)
–O(*p*)	82·3 (5)	83·3 (4)	81·9 (5)	81·2 (4)	83·6 (5)	82·7 (4)	83·5 (5)	82·3 (4)
–N(*n*)	84·9 (7)	84·8 (6)	87·4 (7)	86·3 (7)	85·7 (7)	86·8 (6)	84·0 (6)	84·7 (5)
–N(*n*1)	174·4 (7)	176·4 (6)	172·9 (7)	175·0 (6)	176·5 (8)	175·5 (6)	178·6 (7)	179·7 (2)
O(*m*)–Cu(*n*)–O(*p*)	78·6 (5)	77·8 (4)	78·6 (5)	79·2 (4)	77·9 (9)	78·5 (4)	79·1 (5)	78·9 (4)
–N(*n*)	140·2 (7)	143·4 (6)	149·6 (6)	153·2 (6)	154·7 (6)	154·3 (5)	137·6 (5)	138·8 (5)
–N(*n*1)	94·2 (7)	95·9 (6)	94·3 (7)	94·9 (6)	95·2 (8)	95·1 (7)	98·9 (8)	98·2 (7)
O(*p*)–Cu(*n*)–N(*n*)	135·8 (6)	133·6 (5)	127·3 (5)	122·0 (5)	122·8 (7)	122·8 (6)	137·7 (6)	137·2 (5)
–N(*n*1)	94·7 (6)	94·8 (5)	101·8 (7)	100·4 (5)	98·4 (6)	99·7 (5)	95·3 (6)	97·4 (5)
N(*n*)–Cu(*n*)–N(*n*1)	100·5 (8)	98·7 (7)	94·9 (9)	96·7 (8)	95·7 (8)	95·1 (7)	97·3 (8)	95·5 (7)
Cu(*n*)–O(*n*)–Cu(*m*)	99·0 (5)	98·6 (4)	97·7 (5)	97·6 (4)	97·6 (7)	97·2 (6)	98·4 (6)	97·6 (6)
–Cu(*q*)	102·0 (6)	101·0 (5)	103·6 (6)	103·3 (5)	100·8 (5)	100·7 (4)	100·5 (5)	101·7 (5)
–C(*n*2)	116·5 (1·2)	117·2 (1·1)	113·2 (1·4)	111·7 (1·2)	115·2 (1·0)	111·9 (9)	115·3 (1·0)	115·3 (8)
Cu(*m*)–O(*n*)–Cu(*q*)	95·7 (5)	96·3 (4)	95·8 (6)	97·1 (5)	94·4 (5)	95·5 (4)	96·7 (5)	96·0 (4)
–C(*n*2)	122·3 (1·3)	121·4 (1·1)	119·7 (1·2)	121·6 (1·0)	123·6 (1·0)	123·9 (9)	123·6 (1·0)	124·0 (8)
Cu(*q*)–O(*n*)–C(*n*2)	117·3 (9)	118·1 (8)	122·6 (1·0)	121·5 (8)	120·4 (1·2)	122·6 (1·1)	118·0 (1·0)	118·0 (9)
Cu(*n*)–N(*n*1)–C(*n*)	162·2 (1·8)	162·7 (1·6)	177·1 (2·1)	172·1 (1·4)	175·5 (2·5)	172·1 (1·3)	164·8 (1·9)	161·7 (1·6)
N(*n*1)–C(*n*)–*X*(*n*1)	177·2 (2·7)	177·2 (1·8)	174·4 (2·9)	177·7 (1·7)	177·9 (2·4)	172·3 (1·7)	174·8 (2·6)	170·8 (2·3)
Cu(*n*)–N(*n*)–C(*n*1)	103·0 (1·3)	102·4 (1·3)	101·1 (1·5)	107·8 (1·6)	105·4 (1·3)	106·4 (1·2)	103·1 (1·3)	101·1 (1·0)
–C(*n*11)	114·3 (1·2)	113·5 (1·1)	96·6 (1·2)	127·3 (1·5)	116·1 (2·0)	112·5 (1·6)	113·5 (1·5)	117·9 (1·3)
–C(*n*21)	113·8 (1·4)	116·0 (1·1)	96·9 (1·1)	98·1 (1·0)	100·6 (1·1)	99·8 (1·0)	100·0 (1·2)	101·5 (1·0)
C(*n*1)–N(*n*)–C(*n*11)	108·5 (1·9)	113·6 (1·6)	113·5 (1·7)	120·9 (1·8)	121·0 (1·8)	120·5 (1·5)	109·7 (1·4)	110·9 (1·1)
-C(*n*21)	104·7 (1·8)	100·5 (1·6)	103·1 (1·5)	107·2 (1·4)	108·8 (1·9)	105·9 (1·6)	119·3 (1·7)	117·6 (1·5)
C(*n*11)–N(*n*)–C(*n*21)	111·5 (2·0)	109·9 (1·8)	137·4 (2·0)	86·5 (1·9)	102·9 (1·9)	109·5 (1·3)	110·8 (1·4)	108·0 (1·2)
N(*n*)–C(*n*11)–C(*n*12)	123 (2)*	113 (2)	119 (2)*	86 (2)*	105 (2)	109 (2)	112 (2)	110 (1)
C(*n*11)–C(*n*12)–C(*n*13)	123 (3)*	113 (3)	106 (2)	104 (2)	108 (2)	99 (2)*	100 (2)	104 (1)
C(*n*12)–C(*n*13)–C(*n*14)	129 (3)*	124 (3)*	101 (3)	112 (3)	111 (2)	97 (2)*	98 (2)*	106 (2)
N(*n*)–C(*n*21)–C(*n*22)	117 (2)	105 (2)	126 (2)*	115 (2)	119 (2)*	117 (2)	107 (2)	112 (1)
C(*n*21)–C(*n*22)–C(*n*23)	114 (2)	104 (2)	101 (2)	98 (2)*	105 (2)	101 (2)	101 (2)	105 (2)
C(*n*22)–C(*n*23)–C(*n*24)	112 (2)	108 (2)	83 (3)*	96 (2)*	110 (2)	96 (2)*	106 (2)	105 (2)
N(*n*)–C(*n*1)–C(*n*2)	116 (2)	118 (2)	114 (2)	113 (2)	116 (2)	112 (2)	110 (2)	111 (1)
C(*n*1)–C(*n*2)–O(*n*)	107 (2)	107 (2)	103 (2)	104 (2)	105 (2)	106 (1)	105 (2)	105 (2)

derived from a sharpened Patterson map for *A*. Direct methods were applied to *A* and *B* and the positions of all Cu and ethanolato O atoms could be determined for both. With these positions the peaks in the sharpened Patterson map of *B* could be interpreted. The partial structures refined well and most non-hydrogen atoms could be located after several ΔF syntheses and successive least-squares cycles.

Greater difficulties arose in the determination of the butyl groups bonded to N(2) and N(3). Refinement of the most probable peaks in the ΔF syntheses, interpreted as C atom positions of the butyl group or of the positions calculated for an all-*trans* conformation of the butyl group with normal N–C and C–C bonds, did not lead to satisfactory C–C and C–N distances. Refinement of all positions with isotropic temperature parameters until all shifts were less than the estimated standard deviation resulted in C–C distances between 0·95 and 1·70 Å, whilst the N–C distances were in the range of 1·30 to 1·94 Å. The temperature factors of butyl C atoms were very high [$U_{\rm iso}$max: 0·31 (*A*) and (*B*)]. At this stage *R* reached values of 0·125 (*A*) and 0·167 (*B*). Anisotropic refinement from an earlier stage (R = 0·20) first for all non-carbon atoms and subsequently for all C atoms should result in a better description of the butyl groups. Although *R* reached lower values, an accurate description of the butyl groups was not possible [$U_{\rm max}$: 0·23 (*A*), 0·34 (*B*)]. Because the parameters for the other atoms did not vary significantly, refinement was stopped when the shifts of all non-butyl parameters except the temperature parameters of the isocyanato O and the isothiocyanato S atoms were less than the estimated standard deviations. The concluding positional parameters are given in Table 1.* Because of the very high temperature parameters (up to 0·20) of the butyl C atoms the C–C and N–C distances (Table 2) and the N–C–C and C–C–C angles (Table 3) are not reliable. Additionally the O atoms of the isocyanato groups and the S of the isothiocyanato groups have very high temperature factors. Because of the large number of parameters (577 for all atoms with anisotropic temperature parameters) proof of vibration would only be possible if the intensity measurements were repeated at low temperatures.

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 all parameters with a large damping factor for the shifts and interchanging the atoms in the refining groups.

All calculations were performed on the IBM 370/168 computer of the Technische Hochschule Darmstadt with a program for crystal structure analysis written by G. M. Sheldrick (Cambridge University, England). The scattering factor for Cu was taken from Cromer & Mann (1968), the others were used as stored in the program.

Discussion

The unit cell contains two tetrameric molecules [$(C_{10}H_{22}NOCuY)_4$, Y = NCO, NCS] of cubane-type clusters (Fig. 1) with a Cu_4O_4 core. The dimensions of the Cu_4 tetrahedron (Table 4) are in the expected range with two short [3·052 (*A*) and 3·034 Å (*B*)] and four long [3·252 (*A*) and 3·242 Å (*B*), mean values] intramolecular Cu–Cu separations. The geometry of the Cu_4O_4 core is similar to the type formally thought of as being built up of two 'dimeric moieties'. The first dimeric moiety consists of all atoms having 1 or 2 as the first index in their atom number (Table 1). The equations of the best planes through the Cu and O atoms of the two moieties with the deviations of several atoms from these planes are given in Table 5. The four longest Cu–O bonds arranged between the two dimeric moieties [2·27 (*A*) and 2·25 Å (*B*)] are nearly parallel, but their mean values are about 0·22 Å less than the value found in chloro(2-diethylaminoethanolato)-(Haase, 1973; Estes & Hodgson, 1975) and isocyanato-(2-dimethylaminoethanolato)copper(II) (Mergehenn & Haase, 1977*a*), which represent the extreme type. In

Table 4. Cu–Cu *separations* (Å)

	A	*B*
Cu(1)–Cu(2)	3·053 (5)	3·034 (4)
–Cu(3)	3·254 (4)	3·237 (3)
–Cu(4)	3·253 (4)	3·233 (3)
Cu(2)–Cu(3)	3·256 (4)	3·244 (3)
–Cu(4)	3·265 (4)	3·253 (3)
Cu(3)–Cu(4)	3·051 (4)	3·034 (3)

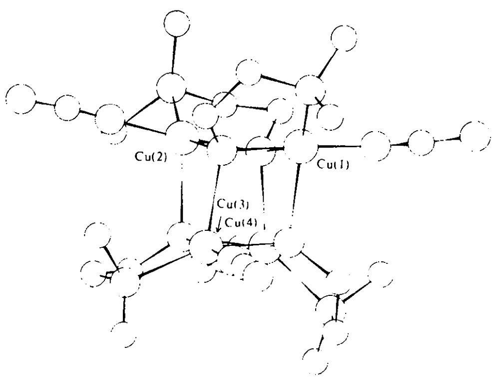

Fig. 1. Molecular structure of isocyanato(2-dibutylaminoethanolato)copper(II). Only the first carbon atoms of the butyl groups have been plotted for clarity.

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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 32648 (45 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 5. *Equations of best planes through the 'dimeric moieties' and distances* (Å) *of atoms from these planes*

Plane I: Cu(1), O(1), Cu(2), O(2)

A: $6{\cdot}93x + 7{\cdot}19y + 7{\cdot}56z = 7{\cdot}84$
B: $6{\cdot}92x + 6{\cdot}68y + 7{\cdot}31z = 7{\cdot}39$

Plane II: Cu(3), O(3), Cu(4), O(4)

A: $6{\cdot}71x + 7{\cdot}45y + 7{\cdot}64z = 10{\cdot}20$
B: $6{\cdot}71x + 6{\cdot}99y + 7{\cdot}33z = 9{\cdot}71$

	Distances from plane I				Distances from plane II				Mean values (absolute)	
	$n = 1$	$p = 4$	$n = 2$	$p = 3$	$n = 3$	$p = 1$	$n = 4$	$p = 2$		
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
Cu(*n*)	−0·10	−0·10	−0·10	−0·10	0·08	0·09	0·08	0·09	0·09	0·10
O(*n*)	0·10	0·10	0·10	0·10	−0·08	−0·09	−0·08	−0·09	0·09	0·10
N(*n*)	−1·44	−1·35	−1·21	−1·04	0·97	1·01	1·49	1·48	1·28	1·22
N(*n*1)	−0·22	−0·26	−0·43	−0·37	0·32	0·36	0·21	0·27	0·29	0·31
O(*p*)	2·15	2·13	2·19	2·17	−2·17	−2·13	−2·13	−2·11	2·16	2·14

accordance with this shortening, the values of the Cu—O bonds inside the 'dimer', which are not bridged by the alkoxy groups [2·12 (*A*) and 2·10 Å (*B*)], are about 0·16 Å longer than in the extreme type. The mean of all different Cu—O bonds is the same as found in chloro(2-dipropylaminoethanolato)- (Matsumoto, Ueda, Nishida & Kida, 1976) and isocyanato(2-diethylaminoethanolato)copper(II) (Merz & Haase, 1977), but in these molecules the arrangement of the single Cu—O bonds tends to the second extreme type [represented by chloro-(bromo)-(2-dibutylaminoethanolato)- (Mergehenn, Haase & Allmann, 1975) and chloro-(bromo)-(2-diethylaminoethanolato)copper(II) (Mergehenn & Haase, 1977*b*)]. The longest Cu—O bonds (2·24 Å) are inside the dimer, whereas the intermediate values (2·16 Å) are between the two dimeric moieties. Therefore the main structural difference between the two 'transition-type' molecules is that the long Cu—O bonds (2·12 and 2·26 Å) change their places.

The coordination of Cu is between square pyramidal and trigonal bipyramidal. One angle, O(*n*)—Cu(*n*)—N(*n*1), with a mean value of 175·6 (*A*) and 176·7° (*B*), is nearly linear. If the coordination around Cu is interpreted as trigonal bipyramidal, the axial angles, which should be in the range of 120°, are different and deviate widely from the expected value. The mean values of two axial angles [O(*m*)—Cu(*n*)—N(*n*) and O(*p*)—Cu(*n*)—N(*n*)] are nearly the same (138·2° for both substances), and each dimer contains one Cu whose angles are both in this range, but for the other Cu atom one of these angles is about 15° greater [O(*m*)—Cu(*n*)—N(*n*)] whereas the other [O(*p*)—Cu(*n*)—N(*n*)] is 15° less than the mean angle. The third axial angle [O(*m*)—Cu(*n*)—O(*p*)] is about 78·6° for both substances.

The mean values of the Cu—*L* bonding distances are in good agreement with other Cu_4O_4 cubane-like structures, Cu—N: 2·08 (*A*), 2·05 (*B*) (amino); Cu—N: 1·97 (isocyanato), 1·91 (isothiocyanato); Cu—O: 1·92 (*A*) and 1·93 Å (*B*) (alkoxy).

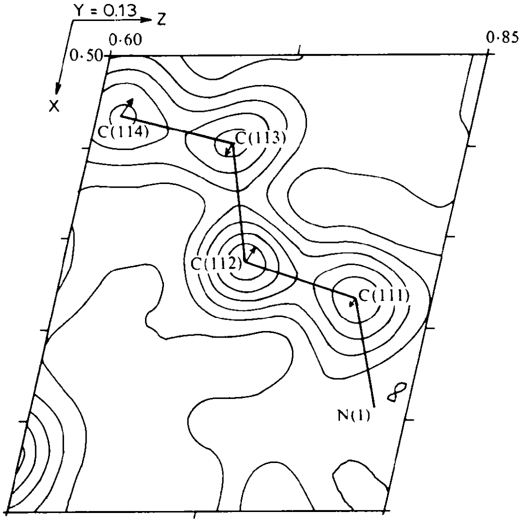

Fig. 2. Picture of the ΔF map (*A*) in a stage in which all non-butyl atoms have been located ($R = 0{\cdot}18$). The section shows the arrangement of the butyl group C(111) to C(114) and has been generated from a printout of the ΔF map (1250 grid points).

The N atoms of the isocyanato and isothiocyanato groups possess mainly *sp* hybridization as can be seen from the mean Cu(*n*)—N(*n*1)—C(*n*) angles of 169·9 (*A*) and 167·2° (*B*) and from the N—C distances of 1·05 (*A*) and 1·14 Å (*B*). The mean C—O distance of 1·23 Å is in good agreement with the values found in isocyanato(2-dimethylaminoethanolato)- (Mergehenn & Haase, 1977*a*) and isocyanato(2-diethylaminoethanolato)copper(II) (Merz & Haase, 1977). The mean C—S distance of 1·57 Å of the isothiocyanato group is the same as in (iso)thiocyanato(2-dimethylaminoethanolato)- (Haase, Mergehenn & Krell, 1976) and (iso)thiocyanato(2-diethylaminoethanolato)copper(II) (Pajunen & Smolander, 1974).

The difficulties in the determination of the butyl C atoms have been described above and in many cases the tabulated N—C and C—C distances and N—C—C and C—C—C angles are far from normal.

The strongly deviating bond distances and angles are marked with an asterisk (Tables 2, 3). We believe that very high thermal motions of some butyl groups or of single C atoms of these groups cause these deviations. The positions of C(111) to C(114) (Fig. 2) were moving in the direction of the arrows during the least-squares refinement for example. Similar problems in the location of C atoms occurred in chloro-(2-dipropylaminoethanolato)copper(II) (Matsumoto, Ueda, Nishida & Kida, 1976). The C—C distances reported there are in the range of 1·27 to 1·71 Å.

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Structures des Oxo-3 et Oxo-6 Cyclobarbitals

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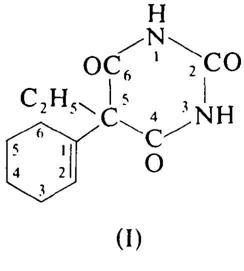
X-ray structure determinations show that the photochemical (P_p) and metabolic (P_m) oxidation products of cyclobarbital are respectively 6-oxocyclobarbital and 3-oxocyclobarbital. The crystal data are: $a = 9{\cdot}719$, $b = 17{\cdot}081$, $c = 12{\cdot}273$ Å, $\beta = 143{\cdot}11°$, space group $P2_1/c$, $Z = 4$ for P_p and $a = 8{\cdot}822$, $b = 10{\cdot}072$, $c = 6{\cdot}848$ Å, $\beta = 104{\cdot}07°$, space group $P2_1$, $Z = 2$ for P_m. In both structures the two rings are almost perpendicular to each other, a conformation already found in cyclobarbital.

Introduction

Le cyclobarbital (I) (Phanodorme®), ou (cyclohexen-1 yl-1)-5 éthyl-5 pyrimidinetrione-2,4,6(1*H*,3*H*), est un barbiturique à action relativement courte qui s'altère facilement.

Sa structure a été décrite par Bideau & Artaud (1970). Le produit pur jaunit rapidement et son point de fusion (171–174°C) tombe aux environs de 150°C.



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