The higher number of molecules and their arrangement in the tetragonal unit cell for the Ga compound are possibly more advantageous for the abovementioned thermal cluster condensation for $M = \mathrm{Ga}$ than for $M = \mathrm{In}$ with starting material of the type $M_2\mathrm{Re}_4(\mathrm{CO})_{18}$.

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Structure of Tetrakis[μ_3-(2-diethylaminoethanolato-*O*)isocyanatocopper(II)]– Trichloromethane (1/1)

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Abstract. $\mathrm{C_{28}H_{56}Cu_4N_8O_8.CHCl_3}$, $M_r = 1006{\cdot}3$, monoclinic, $P2_1/c$, $a = 12{\cdot}861\ (3)$, $b = 14{\cdot}039\ (3)$, $c = 24{\cdot}236\ (5)$ Å, $\beta = 100{\cdot}39\ (1)°$, $V = 4303{\cdot}9$ Å^3, $Z = 4$, $D_m = 1{\cdot}54\ (3)$, $D_x = 1{\cdot}552$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 21{\cdot}07$ cm^{-1}, $F(000) = 2200$, $T = 297$ K, final $R = 0{\cdot}059$, 3828 unique reflections. The asymmetric part of the unit cell contains one tetrameric molecule of the cubane type with a $\mathrm{Cu_4O_4}$ core and one trichloromethane molecule, which occupies two positions with occupancy factors of 0·40 and 0·60 respectively. The coordination around the copper atom is fivefold amd may be described as between square pyramidal and trigonal bipyramidal.

Introduction. The crystal structure of the title compound without crystal solvent has been determined as part of our investigations of the magnetostructural properties of tetrameric copper(II) complexes (Merz & Haase, 1980, and references therein). The magnetic behaviour of the title complex has already been published (Schwabe & Haase, 1985*a*). Recently, the magnetic and structural behaviours of some tetrameric copper(II) compounds containing crystal solvent have been described as being completely different (Mergehenn, Merz, Haase & Allmann, 1976; Mergehenn, Merz & Haase, 1980) from the solvent-free forms (Haase, 1973; Bertrand & Kelley, 1970). In this paper we report the molecular structure of a tetrameric copper(II) complex with trichloromethane as crystal solvent. A solvent-free tetragonal modification of the title compound results on synthesis in methanol (Merz & Haase, 1978); recrystallization of this modification in benzene leads to another solvent-free triclinic form (Schwabe & Haase, 1985*b*).

Experimental. The solvent-free title compound was prepared following the procedure of Merz (Merz & Haase, 1978). Recrystallization from trichloromethane led to dark green orthorhombic crystals; D_m by flotation in $\mathrm{CHCl_3/CCl_4}$; cell constants and e.s.d.'s at 297 K from least-squares refinement of 2θ values of 16 reflections in range 13·4 to 15·8°. Data collected on Stoe Stadi 4 four-circle diffractometer. Dimensions of crystal used from faces to center: $\{101\}$ 0·324, $\{\bar{1}0\bar{1}\}$ 0·324, $\{\bar{1}\bar{1}2\}$ 0·171, $\{11\bar{2}\}$ 0·171, $\{1\bar{3}\bar{3}\}$ 0·438, $\{\bar{1}33\}$ 0·438 mm. 4417 intensities measured; $2\theta\,(\mathrm{max.}) = 45°$, $0 < h < 13$, $-14 < k < 3$, $-24 < l < 23$; 3 standard reflections (115, $31\bar{2}$, $15\bar{1}$), intensity variation $< 3\%$; 3828 unique reflections, $R_{\mathrm{int}} = 0{\cdot}0356$; 476 unobserved with $F_o < 4\sigma(F_o)$; 110 and $\bar{1}02$ reflections omitted due to error in data collection; numerical absorption correction, min. and max. transmission factors 0·2684 and 0·5113; direct methods (*F* refined) (*SHELX*76; Sheldrick, 1976); anisotropic refinement;

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$R = 0{\cdot}096$, $wR = 0{\cdot}095$, $1/w = \sigma(F_o)^2$; splitting of position of trichloromethane molecule (occupancy factors 0·4 and 0·6, respectively); positioning of hydrogen atoms with C—H distances 1·08 Å and fixed isotropic thermal parameters; final difference Fourier map max. positive 0·73 and max. negative $-0{\cdot}42$ e Å^{-3}; secondary-extinction coefficient $14{\cdot}6 \times 10^{-4}$. Final refinement, 532 variables, max. shift/e.s.d. 0·57 in copper complex and 3·3 in trichloromethane molecule, gave $R = 0{\cdot}059$, $wR = 0{\cdot}061$. The calculations were performed on an IBM 320/168 computer at the Technische Hochschule Darmstadt using updated version of *SHELX*76 (Sheldrick, 1976). Scattering factor of neutral Cu from Cromer & Mann (1968).

Discussion. The title compound $C_{28}H_{56}Cu_4N_8H_8$.-$CHCl_3$ crystallizes with four tetrameric molecules containing a Cu_4O_4 cubane-type core and four trichloromethane molecules in the unit cell. A perspective view of the tetrameric molecule is given in Fig. 1. The molecule possesses no symmetry elements; approximate S_4 symmetry is realized. In Table 1 the fractional atomic coordinates of all non-hydrogen atoms and U_{eq} values are listed.*

Some thermal parameters, especially those of the carbon atoms of the outer ethyl groups and the chlorine atoms of the trichloromethane molecules, are rather high and preclude a discussion of the bond lengths.

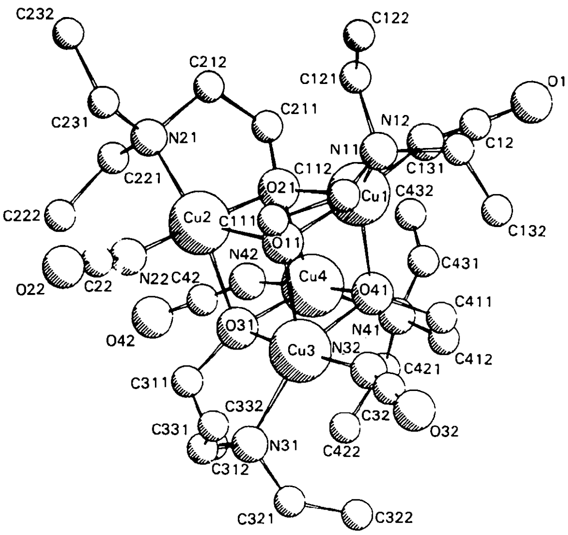

Fig. 1. Perspective view of the $C_{28}H_{56}Cu_4N_8O_8$ complex.

In Table 2 all distances and angles within the Cu_4O_4 core are given. The coordination around the copper atoms is fivefold and can be described as square pyramidal and trigonal bipyramidal. The oxygen atoms within the Cu_4O_4 core are nearly tetrahedral (mean 108·8°), as are the amino nitrogen atoms (mean 109·4°). The isocyanate groups are elongated with angle N(*I*2)—C(*I*2)—O(*I*2) (*I* = 1,2,3,4) 177·7° (mean).

The geometry of the tetrameric molecule described here is in good agreement with that of the triclinic solvent-free form (Schwabe & Haase, 1985*b*), but differs from the geometry of the tetragonal solvent-free one (Merz & Haase, 1978).

Table 1. *Atomic parameters of the nonhydrogen atoms*

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta).$$

	x	y	z	U_{eq}(Å^2)
Cu(1)	0·0950 (1)	0·3024 (1)	0·5610 (1)	0·069
Cu(2)	0·3338 (1)	0·3374 (1)	0·6161 (1)	0·069
Cu(3)	0·2827 (1)	0·2082 (1)	0·5067 (1)	0·076
Cu(4)	0·2303 (1)	0·1278 (1)	0·6201 (1)	0·069
O(11)	0·1851 (4)	0·2745 (4)	0·6316 (2)	0·060
O(12)	−0·1146 (7)	0·3433 (6)	0·4115 (4)	0·122
O(21)	0·2496 (4)	0·3449 (4)	0·5421 (2)	0·059
O(22)	0·4263 (8)	0·3396 (7)	0·7885 (3)	0·146
O(31)	0·1566 (4)	0·1711 (4)	0·5340 (2)	0·062
O(32)	0·5936 (8)	0·2421 (10)	0·4920 (5)	0·199
O(41)	0·3497 (4)	0·1872 (4)	0·5961 (2)	0·062
O(42)	−0·0041 (9)	−0·0034 (9)	0·6908 (4)	0·192
N(11)	−0·0125 (6)	0·3480 (6)	0·6083 (3)	0·071
N(12)	0·0171 (7)	0·3403 (7)	0·4907 (4)	0·085
N(21)	0·3901 (6)	0·4695 (5)	0·5981 (3)	0·067
N(22)	0·4058 (8)	0·3254 (7)	0·6912 (4)	0·095
N(31)	0·2267 (7)	0·1327 (7)	0·4367 (3)	0·084
N(32)	0·4144 (8)	0·2439 (7)	0·4866 (4)	0·104
N(41)	0·3358 (7)	0·0286 (6)	0·6560 (4)	0·069
N(42)	0·1048 (7)	0·0706 (7)	0·6374 (4)	0·089
C(12)	−0·0475 (10)	0·3404 (7)	0·4524 (5)	0·071
C(111)	0·1387 (8)	0·3056 (7)	0·6782 (4)	0·074
C(112)	0·0229 (12)	0·3088 (11)	0·6616 (5)	0·149
C(121)	−0·0132 (10)	0·4514 (7)	0·6058 (5)	0·097
C(122)	−0·0832 (11)	0·5022 (9)	0·6394 (6)	0·128
C(131)	−0·1288 (9)	0·3175 (9)	0·5819 (6)	0·120
C(132)	−0·1425 (10)	0·2209 (9)	0·5674 (6)	0·118
C(22)	0·4147 (8)	0·3328 (7)	0·7382 (6)	0·083
C(211)	0·2600 (7)	0·4312 (6)	0·5125 (4)	0·069
C(212)	0·2998 (9)	0·5046 (7)	0·5532 (4)	0·094
C(221)	0·4846 (9)	0·4614 (9)	0·5732 (5)	0·101
C(222)	0·5760 (9)	0·4086 (11)	0·6096 (5)	0·127
C(231)	0·4028 (10)	0·5348 (7)	0·6467 (4)	0·096
C(232)	0·4283 (13)	0·6395 (9)	0·6362 (6)	0·142
C(32)	0·5014 (13)	0·2413 (9)	0·4895 (5)	0·107
C(311)	0·0896 (8)	0·1102 (7)	0·4965 (4)	0·081
C(312)	0·1419 (18)	0·0854 (17)	0·4534 (7)	0·345
C(321)	0·3072 (12)	0·0681 (13)	0·4169 (7)	0·177
C(322)	0·3638 (17)	0·0081 (14)	0·4594 (8)	0·240
C(331)	0·1681 (16)	0·1895 (12)	0·3921 (8)	0·233
C(332)	0·2270 (13)	0·2611 (10)	0·3665 (8)	0·176
C(42)	0·0526 (10)	0·0365 (9)	0·6634 (5)	0·090
C(411)	0·4482 (7)	0·1400 (7)	0·6147 (4)	0·072
C(412)	0·4251 (11)	0·0463 (13)	0·6308 (9)	0·232
C(421)	0·3081 (14)	−0·0653 (11)	0·6455 (8)	0·202
C(422)	0·2504 (10)	−0·1082 (9)	0·5997 (5)	0·115
C(431)	0·3566 (16)	0·0379 (16)	0·7120 (7)	0·255
C(432)	0·2947 (10)	0·0683 (9)	0·7525 (5)	0·110
The two trichloromethane positions				
Cl(1)	0·2738 (15)	0·7564 (17)	0·2978 (9)	0·241
Cl(2)	0·1555 (19)	0·8181 (20)	0·2093 (8)	0·245
Cl(3)	0·2865 (9)	0·9580 (7)	0·2753 (4)	0·152
Cl(4)	0·1010 (6)	0·7020 (6)	0·2125 (3)	0·155
Cl(5)	0·1293 (11)	0·8914 (8)	0·2486 (4)	0·206
Cl(6)	0·3103 (8)	0·7621 (8)	0·2658 (4)	0·162
C(6)	0·1946 (46)	0·8581 (23)	0·2726 (13)	0·134
C(7)	0·1905 (37)	0·8261 (45)	0·2187 (24)	0·200

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* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles and H-atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42758 (79 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

A more detailed discussion of the structural properties related to the magnetic behaviour of the different modifications, considering magnetostructural correlations in particular, will be published (Schwabe & Haase, 1986). This publication will also include the magnetic behaviour and structural properties of two modifications containing tetrachloromethane as solvent, so at least five different modifications of the tetrameric copper(II) complex, $C_{28}H_{56}Cu_4N_8O_8$, are available to give magnetostructural correlations. In the trichloromethane molecule, which occupies two neighbouring positions [C(6)—C(7) 1·4 Å] with occupancy factors 0·4 and 0·6 respectively, the values of the C—Cl distances of one position are of the expected order of magnitude. For the second position the bond distances differ remarkably from these values and the Cl—C—Cl angles differ from tetrahedral, corresponding to the high thermal parameters. This problem is well known in the literature (Dubler, Textor, Oswald & Jameson, 1983; Gjoystdal & Romming, 1977), where structures with integrated BF_4 anions are reported. Other structures with incorporated $FeCl_4$ (Figgis, Reynolds & Lehner, 1983), PF_6 (Gourdon & Prout, 1983) and ClO_4 anions (Escobar & Wittke, 1983) show the same disorder for these groups, which could be reduced by X-ray data collection at low temperatures.

Table 2. *All distances* (Å) *and angles* (°) *within the* Cu_4O_4 *core of the* $C_{28}H_{56}Cu_4N_8O_8$ *complex with e.s.d.'s in parentheses*

Cu(1)–O(11)	1·927 (5)	Cu(3)–O(31)	1·929 (6)
Cu(1)–O(21)	2·203 (6)	Cu(3)–O(21)	2·172 (5)
Cu(1)–O(31)	2·156 (6)	Cu(3)–O(41)	2·203 (5)
Cu(1)–N(11)	2·052 (9)	Cu(3)–N(31)	2·020 (8)
Cu(1)–N(12)	1·889 (8)	Cu(3)–N(32)	1·915 (11)
Cu(2)–O(21)	1·925 (5)	Cu(4)–O(41)	1·925 (6)
Cu(2)–O(11)	2·202 (6)	Cu(4)–O(31)	2·216 (5)
Cu(2)–O(41)	2·184 (5)	Cu(4)–O(11)	2·167 (6)
Cu(2)–N(21)	2·068 (8)	Cu(4)–N(41)	2·032 (8)
Cu(2)–N(22)	1·896 (8)	Cu(4)–N(42)	1·910 (10)
O(11)–Cu(1)–O(21)	79·6 (2)	O(31)–Cu(3)–O(41)	80·2 (2)
O(11)–Cu(1)–O(31)	84·2 (2)	O(31)–Cu(3)–O(21)	82·4 (2)
O(11)–Cu(1)–N(11)	85·8 (3)	O(31)–Cu(3)–N(31)	87·2 (3)
O(11)–Cu(1)–N(12)	173·8 (3)	O(31)–Cu(3)–N(32)	174·7 (3)
O(21)–Cu(1)–O(31)	76·8 (2)	O(41)–Cu(3)–O(21)	78·6 (2)
O(21)–Cu(1)–N(11)	139·4 (3)	O(41)–Cu(3)–N(31)	140·7 (3)
O(21)–Cu(1)–N(12)	94·9 (3)	O(41)–Cu(3)–N(32)	94·5 (3)
O(31)–Cu(1)–N(11)	139·2 (3)	O(21)–Cu(3)–N(31)	136·6 (3)
O(31)–Cu(1)–N(12)	97·5 (3)	O(21)–Cu(3)–N(32)	96·5 (3)
N(11)–Cu(1)–N(12)	96·6 (4)	N(31)–Cu(3)–N(32)	97·1 (4)
O(21)–Cu(2)–O(11)	79·7 (2)	O(41)–Cu(4)–O(31)	80·0 (2)
O(21)–Cu(2)–O(41)	84·5 (2)	O(41)–Cu(4)–O(11)	82·9 (2)
O(21)–Cu(2)–N(21)	85·1 (3)	O(41)–Cu(4)–N(41)	85·5 (3)
O(21)–Cu(2)–N(22)	174·6 (4)	O(41)–Cu(4)–N(42)	175·0 (3)
O(11)–Cu(2)–O(41)	76·5 (2)	O(31)–Cu(4)–O(11)	77·4 (2)
O(11)–Cu(2)–N(21)	138·3 (3)	O(31)–Cu(4)–N(41)	137·4 (3)
O(11)–Cu(2)–N(22)	94·9 (3)	O(31)–Cu(4)–N(42)	95·1 (3)
O(41)–Cu(2)–N(21)	140·4 (3)	O(11)–Cu(4)–N(41)	140·1 (3)
O(41)–Cu(2)–N(22)	94·4 (3)	O(11)–Cu(4)–N(42)	96·5 (3)
N(21)–Cu(2)–N(22)	99·0 (3)	N(41)–Cu(4)–N(42)	98·1 (4)
Cu(1)–O(11)–Cu(2)	99·6 (2)	Cu(3)–O(31)–Cu(4)	98·9 (2)
Cu(1)–O(11)–Cu(4)	102·3 (2)	Cu(3)–O(31)–Cu(1)	104·5 (2)
Cu(1)–O(11)–C(111)	111·7 (5)	Cu(3)–O(31)–C(311)	113·0 (5)
Cu(2)–O(11)–Cu(4)	95·7 (2)	Cu(4)–O(31)–Cu(1)	93·8 (2)
Cu(2)–O(11)–C(111)	120·6 (5)	Cu(4)–O(31)–C(311)	122·9 (5)
Cu(4)–O(11)–C(111)	123·1 (5)	Cu(1)–O(31)–C(311)	119·9 (5)
Cu(2)–O(21)–Cu(1)	99·6 (2)	Cu(4)–O(41)–Cu(3)	99·4 (2)
Cu(2)–O(21)–Cu(3)	101·7 (2)	Cu(4)–O(41)–Cu(2)	103·8 (3)
Cu(2)–O(21)–C(211)	115·4 (4)	Cu(4)–O(41)–C(411)	114·3 (5)
Cu(1)–O(21)–Cu(3)	95·3 (2)	Cu(3)–O(41)–Cu(2)	93·0 (2)
Cu(1)–O(21)–C(211)	120·4 (5)	Cu(3) O(41) C(411)	122·7 (5)
Cu(3)–O(21)–C(211)	120·4 (5)	Cu(2)–O(41)–C(411)	119·6 (5)

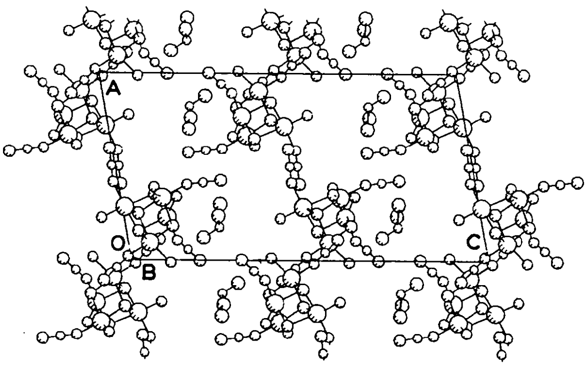

Fig. 2. Projection of the unit cell along the *b* axis.

The crystal packing is shown in Fig. 2, in which the outer ethyl groups of the tetrameric molecule and one position of the trichloromethane molecule are omitted for clarity.

No bonding between the tetrameric copper(II) complexes and the trichloromethane molecules could be detected (minimum intermolecular distance between non-hydrogen atoms = 4·96 Å).

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