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Bis[μ -(benzoato-*O,O'*)]-bis(benzoato)-bis[μ -(2-dibutylaminoethanolato)]-bis(ethanol)tricopper(II)

BY HEIKKI MUHONEN, AARNE PAJUNEN AND REIJO HÄMÄLÄINEN

Department of Inorganic Chemistry, University of Helsinki, SF-00100 Helsinki 10, Finland

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Abstract. $[\text{Cu}_3(\text{C}_{10}\text{H}_{22}\text{NO})_2(\text{C}_7\text{H}_5\text{O}_2)_4(\text{C}_2\text{H}_6\text{O})_2]$, monoclinic, $P2_1/c$, $a = 8.210$ (9), $b = 29.77$ (5), $c = 12.71$ (1) Å, $\beta = 113.90$ (5)°, $V = 2839$ (6) Å³, $Z = 2$, $D_m = 1.30$ (the same as that of 1,2-dichlorobenzene by flotation), $D_c = 1.30$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 1.22$ mm⁻¹. The structure was solved from single-crystal diffractometer data. Three Cu atoms form a linear array with distances of 3.211 (6) Å. Aminoalcohol ligands and two of the four benzoato ligands form bridges between the Cu atoms. As a bridging group the benzoato ligand is bidentately coordinated through O atoms to different Cu atoms and shows a *syn-syn* configuration. The other two benzoato ligands are unidentately coordinated to the terminal Cu atoms. The coordination geometries are octahedral and square planar on the central and terminal Cu atoms, respectively, the ethanol O atoms occupying the axial coordination positions of the central Cu atom. The least-squares refinement led to a final R of 0.067. C atoms of the butyl chains and of ethanol, which have high thermal motions, could not be located satisfactorily.

Introduction. Only a few crystal structures of linear trinuclear oxygen-bridged Cu^{II} complexes have been described. The known Cu^{II} complexes of 2-dibutylaminoethanol are dimeric or tetrameric (Mergehenn & Haase, 1975, 1977; Mergehenn, Haase & Allmann, 1975). 1,3-Diamino-2-propanol, which contains three possible donor atoms, forms, in addition to mononuclear complexes (Pajunen & Kivekäs, 1974; Smolander, 1974; Bockelmann, Uggla, Orama & Böök, 1975;

Kivekäs, 1977), trinuclear complexes of two types (Bertrand, Marabella & Vanderveer, 1977; Kivekäs & Pajunen, 1977; Kivekäs, Pajunen & Smolander, 1977; Pajunen & Kivekäs, 1979; Näsäkkälä, 1977a; Kivekäs, 1978). However, the arrangement of the three Cu atoms in both types is triangular. Another aminoalcohol, 3-(*N,N*-diethylethylenediamine)-1-propanol [previously called *N,N*-diethyl-*N'*-(3-hydroxypropyl)-ethylenediamine], which also contains three possible donor atoms, forms both di- and trinuclear Cu^{II} complexes (Villa, Coghi, Manfredotti & Guastini, 1974; Matsumoto, Nishida, Kida & Ueda, 1976). The resulting trinuclear complex is linear. Among the iminoalcohols the condensation product of 3-amino-1-propanol with 2,4-pentanedione is capable of forming a linear trinuclear Cu^{II} complex acting as a quadridentate ligand (Baker & Helm, 1975). In this paper we describe the crystal structure determination of a linear trinuclear complex formed between Cu^{II} benzoate and 2-dibutylaminoethanol.

Blue needle-shaped crystals of the title compound were precipitated from an ethanol solution of 2-dibutylaminoethanol and Cu^{II} benzoate (molar ratio 2:1). Systematic absences from Weissenberg photographs (Cu $K\alpha$ radiation) showed the space group to be $P2_1/c$. The intensity data were collected on a Syntex $P2_1$ diffractometer. Calculation of the orientation matrix and refinement of cell parameters were carried out by the least-squares method from 9 automatically centred and indexed reflections. With the ω -scan technique, a variable scan rate from 3.0 to 30.0° min⁻¹ and graphite-monochromated Mo $K\alpha$ radiation ($\lambda =$

0.71069 Å), 3094 unique reflections with $5 < 2\theta < 45^\circ$ were collected. Of these, 1020 had $I > 3\sigma(I)$. Two standard reflections checked after every 98 intensity measurements revealed decomposition of the crystal. By the end of the data collection the standard reflection intensities had dropped by about 17%. A linear correction for the decrease of intensities was made in conjunction with Lp corrections with the aid of standard reflections. No absorption correction [$\mu(\text{Mo } K\alpha) = 1.22 \text{ mm}^{-1}$] was applied.

The Cu atom positions were solved with *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974) and other non-hydrogen atom positions through successive ΔF syntheses with XRAY 76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Location of C atoms in the butyl chains and the ethanol molecule caused difficulties similar to those encountered in the location of butyl C atoms in (2-dibutylaminoethanolato)(isocyanato)copper(II) and (2-dibutylaminoethanolato)(isothiocyanato)copper(II) (Merghehn & Haase, 1977). After refinement [isotropic temperature factors for atoms C(3)–C(10); otherwise anisotropic; $R = 0.075$] the C–C distances of the butyl groups were between 1.16 and 1.70 Å and the U_{iso} thermal parameters, except the value of 0.14 Å² for C(4), were in the range 0.22–0.31 Å². Anisotropic refinement using a large damping factor for the shifts resulted in a lower R value, but a better description of the butyl groups was not possible; the C–C distances were still far from the normal value. The block-diagonal least-squares cycles were continued until the shifts for the non-butyl parameters were less than their estimated standard deviations. As the final difference electron density synthesis revealed no peaks greater than 0.53 e Å⁻³, the structure analysis was considered complete. Unit weights were used for reflections with $F_o \leq 119.0$; otherwise the scheme $w = (119.0/F_o)^2$ was employed. An anomalous-dispersion correction was applied to the Cu atoms. The final R value was 0.067.* The large estimated standard deviations of the parameters are considered to be due to the large number of unobserved reflections, which are in turn a consequence of the high thermal motion of the C atoms. The final atomic coordinates and U_{eq} values (Hamilton, 1959) are given in Table 1. The U_{eq} values are in the range 0.062–0.179 Å² for well determined atoms, but other C atoms [C(2) and the poorly located butyl atoms C(3)–C(10), except C(4) of the aminoalcohol ligand, and C(25) and C(26) of the ethanol molecule] have U_{eq} values between 0.213 and 0.376 Å². Calculations were performed on a Univac 1108 computer.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35523 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final fractional coordinates and U_{eq} ($\times 10^2$) values

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} (Å ²)
Cu(1)	0.1198 (4)	−0.10334 (9)	0.0459 (3)	7.4
Cu(2)	0.0000	0.00000	0.0000	7.0
O(1)	0.150 (2)	−0.0474 (4)	−0.020 (1)	8.1
O(2)	0.133 (2)	0.1069 (5)	0.060 (1)	8.9
O(3)	0.213 (2)	0.0346 (5)	0.100 (1)	8.5
O(4)	0.096 (2)	−0.1577 (5)	0.121 (2)	10.8
O(5)	−0.048 (2)	−0.1266 (5)	0.216 (2)	11.4
O(6)	−0.006 (3)	−0.0425 (6)	0.170 (1)	12.8
N(1)	0.391 (2)	−0.1081 (6)	0.106 (2)	11.2
C(1)	0.328 (3)	−0.0391 (9)	−0.008 (3)	9.8
C(2)	0.439 (4)	−0.0743 (14)	0.038 (4)	23.5
C(3)	0.465 (5)	−0.1498 (14)	0.079 (4)	22.2
C(4)	0.387 (4)	−0.1846 (9)	0.025 (3)	13.7
C(5)	0.487 (6)	−0.2224 (15)	−0.008 (4)	25.4
C(6)	0.454 (5)	−0.2631 (13)	−0.026 (4)	22.6
C(7)	0.539 (7)	−0.1111 (25)	0.238 (5)	37.6
C(8)	0.460 (7)	−0.1039 (16)	0.300 (5)	25.4
C(9)	0.605 (6)	−0.0895 (19)	0.441 (4)	26.8
C(10)	0.735 (6)	−0.1109 (18)	0.508 (4)	25.8
C(11)	0.238 (3)	0.0782 (7)	0.120 (2)	6.7
C(12)	0.418 (3)	0.0894 (7)	0.217 (2)	6.2
C(13)	0.528 (3)	0.0581 (9)	0.287 (2)	9.3
C(14)	0.687 (4)	0.0718 (13)	0.376 (2)	12.4
C(15)	0.730 (5)	0.1195 (14)	0.401 (4)	17.9
C(16)	0.614 (4)	0.1493 (11)	0.325 (3)	13.9
C(17)	0.449 (4)	0.1371 (9)	0.229 (3)	10.7
C(18)	0.007 (3)	−0.1590 (8)	0.184 (2)	9.0
C(19)	−0.016 (3)	−0.2051 (7)	0.225 (2)	7.3
C(20)	−0.080 (4)	−0.2092 (12)	0.306 (3)	14.6
C(21)	−0.116 (4)	−0.2523 (16)	0.346 (3)	17.3
C(22)	−0.072 (4)	−0.2887 (11)	0.293 (3)	15.1
C(23)	−0.004 (4)	−0.2889 (8)	0.209 (3)	12.7
C(24)	0.024 (3)	−0.2441 (8)	0.166 (2)	10.0
C(25)	0.107 (5)	−0.0205 (14)	0.280 (4)	21.3
C(26)	−0.028 (6)	−0.0078 (14)	0.311 (4)	22.8

Discussion. The unit cell contains two linear trinuclear molecules between which there are no short contacts. One molecule is shown in Fig. 1 and bond lengths and angles are listed in Table 2. Three Cu atoms are arrayed in a straight line, with separations of 3.211 (6) Å. The middle Cu(2) atom lies at the centre of symmetry. The coordination around the two terminal Cu atoms is best described as a tetrahedrally distorted square-planar arrangement with the Cu–O bond lengths ranging from 1.93 (1) to 1.97 (1) Å and the Cu–N bond length 2.04 (2) Å. The deviations of atoms from the least-squares plane through N(1), O(1), O(4) and O(2¹) are −0.20 (2), 0.21 (2), 0.19 (2) and −0.20 (2) Å, respectively, for the plane atoms, and 0.15 (0) Å for Cu(1) not included in the calculation of the plane. The ethanol O atoms approach the bridging positions between the central and terminal Cu atoms. However, the Cu(1)–O(6) distance of 2.85 (2) Å is significantly longer than the Cu(2)–O(6) bond distance of 2.52 (2) Å, which with the centrosymmetrically related bond complete the octahedral environment around Cu(2) in the axial directions. The

Table 2. Bond lengths (Å) and angles (°)

The copper environments

Cu(1)—N(1)	2.04 (2)	Cu(2)—O(1)	1.96 (2)
Cu(1)—O(1)	1.93 (1)	Cu(2)—O(3)	1.98 (1)
Cu(1)—O(2) ⁱ	1.97 (1)	Cu(2)—O(6)	2.52 (2)
Cu(1)—O(4)	1.93 (2)		
O(1)—Cu(1)—N(1)	84.8 (7)	O(4)—Cu(1)—N(1)	94.0 (7)
O(1)—Cu(1)—O(2) ⁱ	91.9 (6)	O(1)—Cu(2)—O(3)	91.1 (6)
O(1)—Cu(1)—O(4)	176.5 (7)	O(1)—Cu(2)—O(6)	89.0 (7)
O(2) ⁱ —Cu(1)—N(1)	159.8 (9)	O(3)—Cu(2)—O(6)	91.7 (6)
O(2) ⁱ —Cu(1)—O(4)	90.3 (6)		

The aminoalcohol ligand

C(1)—O(1)	1.43 (3)	C(4)—C(5)	1.54 (6)
C(1)—C(2)	1.36 (4)	C(5)—C(6)	1.25 (6)
C(2)—N(1)	1.48 (5)	C(7)—C(8)	1.22 (10)
C(3)—N(1)	1.49 (5)	C(8)—C(9)	1.75 (7)
C(7)—N(1)	1.63 (6)	C(9)—C(10)	1.24 (6)
C(3)—C(4)	1.27 (5)		

Cu(1)—O(1)—Cu(2)	111 (1)	C(3)—N(1)—C(7)	89 (3)
C(1)—O(1)—Cu(1)	114 (1)	C(7)—N(1)—Cu(1)	129 (3)
C(1)—O(1)—Cu(2)	122 (1)	N(1)—C(3)—C(4)	130 (3)
C(2)—C(1)—O(1)	113 (3)	C(3)—C(4)—C(5)	122 (3)
C(1)—C(2)—N(1)	119 (3)	C(4)—C(5)—C(6)	131 (5)
C(2)—N(1)—Cu(1)	104 (1)	N(1)—C(7)—C(8)	106 (4)
C(2)—N(1)—C(3)	102 (3)	C(7)—C(8)—C(9)	112 (5)
C(2)—N(1)—C(7)	112 (3)	C(8)—C(9)—C(10)	128 (5)
C(3)—N(1)—Cu(1)	117 (2)		

The bidentate benzoato ligand

C(11)—O(2)	1.23 (2)	C(14)—C(15)	1.47 (6)
C(11)—O(3)	1.32 (2)	C(15)—C(16)	1.37 (5)
C(11)—C(12)	1.53 (3)	C(16)—C(17)	1.46 (4)
C(12)—C(13)	1.35 (3)	C(17)—C(12)	1.44 (3)
C(13)—C(14)	1.39 (3)		
C(11)—O(2)—Cu(1) ⁱ	132 (1)	C(12)—C(13)—C(14)	119 (2)
C(11)—O(3)—Cu(2)	131 (1)	C(13)—C(14)—C(15)	122 (3)
O(2)—C(11)—O(3)	123 (2)	C(14)—C(15)—C(16)	116 (3)
O(2)—C(11)—C(12)	124 (2)	C(15)—C(16)—C(17)	125 (3)
O(3)—C(11)—C(12)	113 (2)	C(16)—C(17)—C(12)	113 (2)
C(11)—C(12)—C(13)	123 (2)	C(17)—C(12)—C(13)	125 (2)
C(11)—C(12)—C(17)	112 (2)		

The unidentate benzoato ligand

C(18)—O(4)	1.28 (4)	C(21)—C(22)	1.40 (6)
C(18)—O(5)	1.20 (3)	C(22)—C(23)	1.39 (5)
C(18)—C(19)	1.51 (3)	C(23)—C(24)	1.50 (4)
C(19)—C(20)	1.34 (5)	C(24)—C(19)	1.49 (4)
C(20)—C(21)	1.45 (6)		
C(18)—O(4)—Cu(1)	122 (1)	C(19)—C(20)—C(21)	123 (3)
O(4)—C(18)—O(5)	125 (2)	C(20)—C(21)—C(22)	113 (3)
O(4)—C(18)—C(19)	115 (2)	C(21)—C(22)—C(23)	129 (3)
O(5)—C(18)—C(19)	120 (3)	C(22)—C(23)—C(24)	117 (3)
C(18)—C(19)—C(20)	119 (2)	C(23)—C(24)—C(19)	114 (3)
C(18)—C(19)—C(24)	117 (2)	C(24)—C(19)—C(20)	124 (2)

The ethanol ligand

C(25)—O(6)	1.47 (4)	C(25)—O(6)—Cu(2)	111 (2)
C(25)—C(26)	1.38 (7)	C(26)—C(25)—O(6)	97 (3)

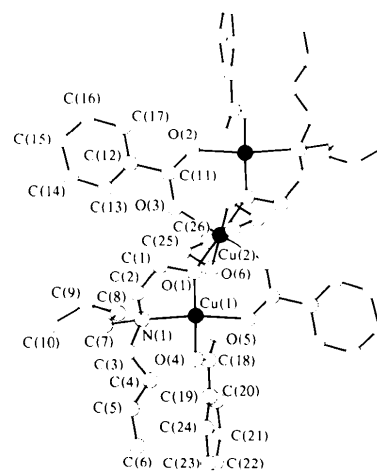
Symmetry code: (i) $-x, -y, -z$.

Fig. 1. View of the molecule showing the atomic labelling.

distance from the uncoordinated O(5) in the unidentate benzoato ligand to Cu(1) is 3.08 (2) Å. O(1) and O(3) together with their centrosymmetric atoms form the basal plane of the octahedron around Cu(2). The Cu(2)—O(1) and Cu(2)—O(3) distances are 1.96 (2) and 1.98 (1) Å respectively. The angle between the Cu(2)—O(6) bond and the normal of the plane through Cu(2), O(1) and O(3) is 2.0 (7)°.

As can be seen in Table 2 there is no significant difference in Cu—O bond lengths within the bridges. The bridging benzoato ligand has a *syn-syn* configuration with C(11)—O(3)—Cu(2) and C(11)—O(2)—Cu(1)ⁱ angles of 131 (1) and 132 (1)°. The corresponding angle, C(18)—O(4)—Cu(1), for the unidentate benzoato ligand is 122 (1)°. The dihedral angles between the phenyl ring and its carboxylic group are 11 (2) and 5 (2)° for the unidentate and bidentate benzoato ligands, respectively. The bridging angle Cu(1)—O(1)—Cu(2) at the aminoalcohol O atom is 111 (1)°.

The C(1)—C(2) bond of 1.36 (4) Å in the five-membered chelate ring is evidently too short. The larger than normal values of thermal parameters for C(2) ($U_{11} = 0.06$, $U_{22} = 0.26$, $U_{33} = 0.37$ Å²) suggest that it possesses some positional disorder. Short C—C bonds have also been observed in tetramethylethylenediamine and 1,3-diamino-2-propanol complexes (Näsäkkälä, 1977b). C(1) and C(2) are both below the plane through Cu(1), N(1) and O(1) at distances from the plane of 0.14 (3) and 0.37 (5) Å, respectively. Of the butyl chains one has a conformation halfway between *trans* and eclipsed (120°) about the C(4)—C(5) bond [154 (5)°], and the other has a *gauche* conformation about the C(8)—C(9) bond [55 (8)°].

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