

C2	0.0822 (5)	-0.0425 (7)	0.6304 (4)	5.3 (2)
C3	0.0781 (5)	-0.1397 (7)	0.5743 (4)	6.0 (2)
C4	-0.0144 (5)	-0.1824 (7)	0.5497 (4)	5.7 (2)
C5	-0.1025 (5)	-0.1268 (6)	0.5809 (3)	4.4 (1)
C6	-0.2015 (5)	-0.1652 (7)	0.5593 (4)	5.3 (1)
C7	-0.2839 (5)	-0.1081 (7)	0.5908 (4)	5.2 (1)
C8	-0.2748 (4)	-0.0071 (6)	0.6473 (3)	4.2 (1)
C9	-0.3574 (5)	0.0576 (7)	0.6815 (4)	5.2 (2)
C10	-0.3415 (5)	0.1532 (6)	0.7351 (4)	5.2 (2)
C11	-0.2423 (5)	0.1849 (6)	0.7543 (4)	4.7 (1)
C12	-0.1779 (4)	0.0331 (6)	0.6708 (3)	3.6 (1)
C13	-0.0900 (4)	-0.0290 (6)	0.6375 (3)	3.7 (1)

Table 2. Selected geometric parameters (Å, °)

Cu—N1	2.020 (7)	C4—C5	1.402 (9)
Cu—N2	2.132 (5)	C5—C6	1.415 (9)
Cu—N3	2.217 (5)	C5—C13	1.403 (8)
S—C1	1.625 (8)	C6—C7	1.35 (1)
N1—C1	1.150 (8)	C7—C8	1.419 (9)
N2—C2	1.311 (8)	C8—C9	1.404 (9)
N2—C13	1.361 (8)	C8—C12	1.404 (8)
N3—C11	1.303 (8)	C9—C10	1.357 (9)
N3—C12	1.359 (8)	C10—C11	1.39 (1)
C2—C3	1.38 (1)	C12—C13	1.442 (9)
C3—C4	1.366 (9)		
N1—Cu—N1'	93.2 (4)	N2—C2—C3	124.3 (7)
N1—Cu—N2	168.4 (2)	C2—C3—C4	118.6 (7)
N1—Cu—N2'	89.0 (2)	C3—C4—C5	119.8 (7)
N1—Cu—N3	91.5 (2)	C4—C5—C6	123.8 (7)
N1—Cu—N3'	99.3 (2)	C4—C5—C13	117.0 (6)
N2—Cu—N2'	91.1 (3)	C6—C5—C13	119.2 (6)
N2—Cu—N3	76.9 (2)	C5—C6—C7	121.6 (7)
N2—Cu—N3'	92.0 (2)	C6—C7—C8	121.2 (6)
N3—Cu—N3'	164.4 (3)	C7—C8—C9	124.1 (6)
Cu—N1—C1	161.0 (6)	C7—C8—C12	119.0 (6)
Cu—N2—C2	127.4 (5)	C9—C8—C12	116.9 (6)
Cu—N2—C13	115.1 (4)	C8—C9—C10	120.0 (7)
C2—N2—C13	117.5 (5)	C9—C10—C11	118.3 (7)
Cu—N3—C11	130.1 (4)	N3—C11—C10	124.7 (6)
Cu—N3—C12	112.5 (4)	N3—C12—C8	122.8 (6)
C11—N3—C12	117.3 (5)	N3—C12—C13	117.6 (5)
C8—C12—C13	119.6 (5)	N2—C13—C12	117.8 (5)
N2—C13—C5	122.8 (6)	C5—C13—C12	119.4 (6)
S—C1—N1	178.9 (6)		

Symmetry code: (i)  $-x, y, \frac{3}{2} - z$ .

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *MolEN*. Molecular graphics: *SHELXTL/PC*, *ORTEP* (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1208). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Cu<sub>3</sub>(bdmap)<sub>4</sub>Cl<sub>2</sub>(CH<sub>3</sub>OH), bdmap = 1,3-Bis(dimethylamino)-2-propanolato. A Clamp-Shaped Molecule

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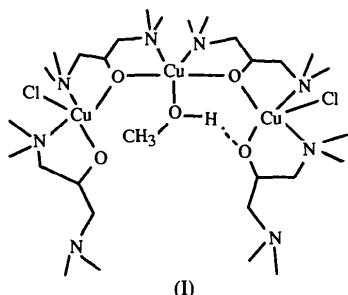
## Abstract

The title structure, bis[ $\mu$ -1,3-bis(dimethylamino)-2-propanolato]-1 $\kappa$ N:2 $\kappa$ N',1:2 $\kappa^2$ O;1 $\kappa$ N:3 $\kappa$ N',1:3 $\kappa^2$ O-bis[1,3-bis(dimethylamino)-2-propanolato]-2 $\kappa$ N,2 $\kappa$ O;3 $\kappa$ N,3 $\kappa$ O-dichloro-2 $\kappa$ Cl,3 $\kappa$ Cl-methanol-1 $\kappa$ O-tricopper(II), [Cu<sub>3</sub>-Cl<sub>2</sub>(C<sub>7</sub>H<sub>17</sub>N<sub>2</sub>O)<sub>4</sub>(CH<sub>3</sub>O)], contains discrete molecules with C<sub>2</sub> crystallographic symmetry and a non-linear Cu<sub>3</sub> arrangement. Each Cu atom is five-coordinate. The central Cu atom is coordinated by a methanol molecule and is bridged by one bdmap ligand [bdmap = 1,3-bis(dimethylamino)-2-propanolato] to each of the outer Cu atoms, which are additionally coordinated by a Cl atom and a chelating bdmap ligand.

## Comment

We have been investigating the coordination chemistry of copper(II) with bidentate and tridentate aminoalcohol ligands. Aminoalcohol ligands have been found to be

able to bind to two or more metal centres, forming homonuclear or heteronuclear complexes involving copper(II) ions (Waltz, Paulus & Haase, 1985; Wang, Pang, Smith & Wagner, 1994). Two classes of copper(II) complexes with the 1,3-bis(dimethylamino)-2-propanolato (bdmap) ligand have been observed. The first class has the general composition  $\text{Cu-bdmap-X}$  ( $X = \text{halide}$ ) (Wang, Pang, Zheng & Wagner, 1993) and the second class has the general composition  $\text{Cu-bdmap-RCO}_2^-L$  ( $L = \text{H}_2\text{O}, \text{OH}^-$ ). Herein, the structure of a new copper(II) compound,  $\text{Cu}_3(\text{bdmap})_4\text{Cl}_2(\text{CH}_3\text{OH})$ , (I), is reported.



This trinuclear copper complex has an unusual clamp shape with two pendant amino groups. The three  $\text{Cu}^{2+}$  ions have a triangular arrangement with a non-bonded  $\text{Cu}(1)\cdots\text{Cu}(2)$  distance of  $3.506(2)\text{ \AA}$  and a  $\text{Cu}(1)\cdots\text{Cu}(2)\cdots\text{Cu}(1')$  angle of  $140.63(7)^\circ$ . The molecule has a  $C_2$  axis and half of the molecule is in the asymmetric unit. The bdmap ligand has two bonding modes. Two of the bdmap ligands function as bridges and are bound to two Cu-atom centres *via* both O and N atoms, while each of the other two bdmap ligands functions as a chelate ligand and binds to one Cu-atom centre only. One of the dimethylamino groups of the chelate bdmap ligand is uncoordinated. Such a bidentate bonding mode of the bdmap ligand has been observed previously in a  $\text{BaCu}_4$  complex (Wang, Trepanier & Wagner, 1993). A methanol solvent molecule is bound to the central Cu atom with a normal Cu—O bond length [ $\text{Cu}(2)\text{—O}(3) = 2.06(1)\text{ \AA}$ ]. This methanol ligand is disordered over two positions related by a twofold rotation axis. The acidic proton [H(38)] of the methanol, located directly from a difference Fourier map, forms a hydrogen bond with the O(1') atom of the chelating bdmap ligand, as evidenced by the  $\text{O}(1')\cdots\text{O}(3)$  distance of  $2.52(2)\text{ \AA}$  and the  $\text{H}(38)\cdots\text{O}(1')$  distance of  $1.77\text{ \AA}$  [ $\text{O}(3)\text{—H}(38) = 0.94\text{ \AA}$ ]. If only one of the coordination sites for the disordered methanol is taken into consideration, the central Cu atom has an approximately trigonal bipyramidal environment with O(2) and O(2') in the axial positions [ $\text{O}(2)\text{—Cu}(2)\text{—O}(2') = 179.3(4)^\circ$ ]. The terminal Cu atom has square-pyramidal coordination geometry with N(4) occupying an axial position [ $\text{Cu}(1)\text{—N}(4) = 2.35(1)\text{ \AA}$ ].

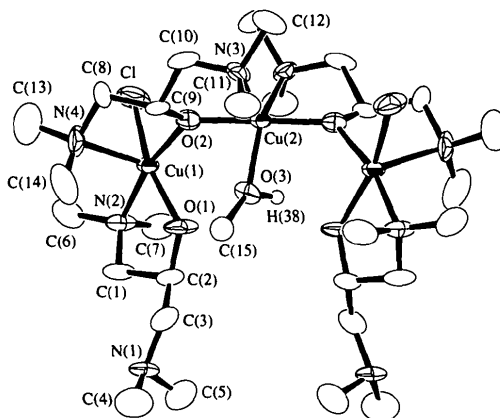


Fig. 1. The molecular structure with atom-labelling scheme and 50% probability ellipsoids. H atoms are omitted for clarity.

## Experimental

The complex  $\text{Cu}_3(\text{bdmap})_4\text{Cl}_2(\text{CH}_3\text{OH})$  was synthesized *via* the reaction of bdmapH with  $\text{CuCl}_2$  and  $\text{Cu}(\text{OCH}_3)_2$  in methanol in a 4:1:2 ratio at 300 K under a nitrogen atmosphere for 24 h. The solution was filtered and concentrated under vacuum. The blue–green crystals of  $\text{Cu}_3(\text{bdmap})_4\text{Cl}_2(\text{CH}_3\text{OH})$  were obtained directly from the concentrated  $\text{CH}_3\text{OH}$  solution after a few days standing at 300 K. A single rectangular-shaped crystal was mounted on a glass fibre and sealed with epoxy.

### Crystal data

$[\text{Cu}_3\text{Cl}_2(\text{C}_7\text{H}_{17}\text{N}_2\text{O})_4(\text{CH}_4\text{O})]$

$M_r = 874.48$

Orthorhombic

*Pbcn*

$a = 14.341(5)\text{ \AA}$

$b = 12.451(7)\text{ \AA}$

$c = 23.866(13)\text{ \AA}$

$V = 4262(2)\text{ \AA}^3$

$Z = 4$

$D_x = 1.363\text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71073\text{ \AA}$

Cell parameters from 20 reflections

$\theta = 13\text{--}30^\circ$

$\mu = 1.65\text{ mm}^{-1}$

$T = 293\text{ K}$

Rectangular

$0.40 \times 0.20 \times 0.20\text{ mm}$

Blue–green

### Data collection

Rigaku AFC-6S diffractometer

$\omega/2\theta$  scans

Absorption correction:

$\psi$  scan (TEXSAN;

Molecular Structure

Corporation, 1992)

$T_{\min} = 0.50$ ,  $T_{\max} = 0.72$

3189 measured reflections

3189 independent reflections

1562 observed reflections

$[I > 3\sigma(I)]$

$\theta_{\max} = 25^\circ$

$h = 0 \rightarrow 17$

$k = 0 \rightarrow 15$

$l = 0 \rightarrow 28$

3 standard reflections

monitored every 150

reflections

intensity decay: 4.8%

### Refinement

Refinement on  $F$

$R = 0.068$

$wR = 0.052$

$S = 2.42$

1562 reflections

$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.62\text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.71\text{ e \AA}^{-3}$

Extinction correction: none

217 parameters  
H-atom parameters not  
refined

Atomic scattering factors  
from Cromer & Waber  
(1974)

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$B_{\text{iso}}$  for C(15);  $B_{\text{eq}} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$  for all others.

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}/B_{\text{iso}}$
Cu(1)	0.55216 (9)	0.23527 (10)	0.61531 (5)	2.70 (3)
Cu(2)	1/2	0.3301 (1)	3/4	2.54 (4)
Cl	0.6455 (2)	0.3695 (3)	0.5814 (1)	5.23 (10)
O(1)	0.5081 (6)	0.1151 (5)	0.6604 (3)	4.4 (2)
O(2)	0.4868 (5)	0.3292 (5)	0.6698 (3)	2.8 (2)
O(3)†	0.4300 (7)	0.1858 (10)	0.7473 (7)	3.8 (4)
N(1)	0.4814 (7)	-0.1739 (7)	0.6273 (4)	3.6 (3)
N(2)	0.6258 (7)	0.1193 (7)	0.5728 (4)	3.5 (3)
N(3)	0.3735 (6)	0.4266 (7)	0.7460 (4)	3.5 (2)
N(4)	0.4257 (8)	0.2833 (9)	0.5582 (4)	4.4 (3)
C(1)	0.5710 (8)	0.0211 (9)	0.5810 (5)	4.0 (3)
C(2)	0.5413 (8)	0.0120 (10)	0.6431 (5)	3.8 (3)
C(3)	0.4641 (8)	-0.0691 (10)	0.6521 (5)	4.4 (4)
C(4)	0.3998 (10)	-0.241 (1)	0.6305 (5)	6.8 (4)
C(5)	0.562 (1)	-0.227 (1)	0.6541 (5)	7.1 (5)
C(6)	0.6373 (9)	0.1348 (10)	0.5133 (5)	5.4 (4)
C(7)	0.7161 (8)	0.1135 (10)	0.5998 (5)	5.2 (4)
C(8)	0.3940 (9)	0.377 (1)	0.5916 (5)	4.4 (4)
C(9)	0.3964 (9)	0.3517 (9)	0.6528 (5)	3.5 (3)
C(10)	0.3628 (9)	0.4486 (9)	0.6867 (5)	4.6 (4)
C(11)	0.2925 (8)	0.3645 (10)	0.7660 (5)	5.5 (4)
C(12)	0.3755 (9)	0.5272 (10)	0.7804 (5)	5.6 (4)
C(13)	0.4453 (10)	0.320 (1)	0.5011 (5)	7.8 (5)
C(14)	0.3548 (10)	0.197 (1)	0.5585 (5)	6.8 (5)
C(15)†	0.355 (1)	0.114 (2)	0.7342 (9)	3.1 (5)

† 50% occupancy.

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Cu(1)—Cl	2.289 (3)	Cu(1)—O(1)	1.948 (7)
Cu(1)—O(2)	1.984 (6)	Cu(1)—N(2)	2.057 (9)
Cu(1)—N(4)	2.35 (1)	Cu(2)—O(2)	1.924 (6)
Cu(2)—O(3)	2.06 (1)	Cu(2)—N(3)	2.178 (9)
O(1)—C(2)	1.43 (1)	O(2)—C(9)	1.39 (1)
O(3)—C(15)	1.43 (2)		
Cl—Cu(1)—O(1)	161.0 (3)	Cu(2)—O(3)—C(15)	157 (1)
Cl—Cu(1)—O(2)	94.4 (2)	O(1)—Cu(1)—N(2)	84.3 (3)
Cl—Cu(1)—N(2)	92.2 (3)	O(2)—Cu(1)—N(2)	168.5 (4)
Cl—Cu(1)—N(4)	93.5 (3)	O(2)—Cu(1)—N(4)	82.2 (3)
O(1)—Cu(1)—O(2)	86.4 (3)	N(2)—Cu(1)—N(4)	106.8 (4)
O(1)—Cu(1)—N(4)	105.4 (4)	O(2)—Cu(2)—O(2')	179.3 (4)
O(1)—N(2)—C(1)	104.2 (6)	O(2)—Cu(2)—O(3')	94.3 (5)
Cu(1)—N(2)—C(6)	116.8 (8)	Cu(2)—N(3)—C(10)	103.6 (7)
Cu(1)—N(2)—C(7)	105.9 (8)	Cu(2)—N(3)—C(11)	110.7 (6)
O(2)—Cu(2)—O(3)	85.1 (5)	Cu(2)—N(3)—C(12)	114.9 (8)
O(2)—Cu(2)—N(3)	83.0 (3)	O(3)—Cu(2)—N(3')	152.7 (4)
O(2)—Cu(2)—N(3')	97.4 (3)	N(3)—Cu(2)—N(3')	113.1 (5)
O(3)—Cu(2)—O(3')	58.5 (6)	Cu(1)—N(4)—C(13)	118.1 (8)
O(3)—Cu(2)—N(3)	94.2 (4)	Cu(1)—O(1)—C(2)	115.0 (6)
Cu(1)—O(2)—Cu(2)	127.5 (4)	Cu(1)—N(4)—C(8)	97.2 (7)
Cu(1)—O(2)—C(9)	111.6 (6)	Cu(1)—N(4)—C(14)	110.1 (7)
Cu(2)—O(2)—C(9)	112.5 (6)		

The metal-atom positions were determined by direct methods. The methanol ligand was disordered over two sites related by a twofold rotation axis. The occupancy factor of the methanol ligand for each site is 50%. All non-H atoms except C(15) of the disordered methanol were refined anisotropically. The positions of H atoms except H(38) were calculated and their isotropic displacement factors were tied to the corresponding C atom's isotropic displacement factor (multiplied by 1.2). H(38) was located directly from the difference Fourier map and its position was not refined.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *TEXSAN*. Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *TEXSAN*.

These studies were supported by the Natural Science and Engineering Research Council of Canada.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1030). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## A Tetracarboxylatobenzene-Bridged Binuclear Copper(II) Complex

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## Abstract

The tetracarboxylatobenzene tetraanion in  $\mu$ -(1,2,4,5-benzenetetracarboxylato- $O^1:O^4$ )bis[aqua(4-azaheptane-1,7-diamine-*N,N',N''*)copper(II)] octahydrate, [ $\{\text{Cu}$