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Acta Cryst. (1999). **C55**, 1652–1654

Bis{(μ -nitrato)[μ -bis(salicylidene)-1,3-propanediaminato]copper(II)}zinc(II)†

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(Received 26 April 1999; accepted 23 June 1999)

Abstract

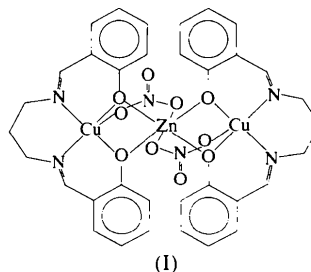
The title compound, [Zn{Cu(NO₃)(C₁₇H₁₆N₂O₂)}₂], has the central Zn²⁺ ion located on an inversion centre, with four bridging O atoms from two *N,N'*-bis(salicylidene)-1,3-propanediaminate (SALPD²⁻) ligands and one O atom from each bridging nitrate group as nearest neighbours. This arrangement constitutes a distorted octahedral coordination around the Zn²⁺ ion. The inversion-related terminal Cu²⁺ ions have irregular square-pyramidal coordinations involving two O and two N atoms of a SALPD²⁻ ligand and one O atom from a nitrate group in the axial position. The Zn—Cu pairs are triple bridged by the SALPD²⁻ O atoms and by the O—N—O atoms of the nitrate groups. The Zn···Cu bridging distance is 3.0017 (6) Å.

† Alternative name: bis(μ -nitrato)-1:3 κ^2 O:O':2:3 κ^2 O:O'-bis{ μ -2,2'-(1,3-propanediyl)bis(nitrilomethylidene)diphenolato}-1 κ^4 N,N',O,O':-3 κ^2 O:O':2 κ^4 N,N',O,O':3 κ^2 O,O'-zinc(II)dicopper(II).

Comment

The structure and magnetic properties of the trinuclear complex [Zn{Cu(CH₃CO₂)(SALPD)}₂] have been reported previously (Fukuhara *et al.*, 1990). Similar examples of trihomo- and heteronuclear complexes have been prepared in our laboratory using different metal ions, acetate or nitrite groups, and the ligand *N,N'*-bis(salicylidene)-1,3-propanediamine. The structures of these complexes have also been described (Ülkü, Tahir *et al.*, 1997; Ülkü, Ercan *et al.*, 1997; Ercan *et al.*, 1998; Tahir *et al.*, 1998; Atakol *et al.*, 1999). These triple-bridged linear complexes are of interest because of their magnetic properties.

We report here a new heterometallic trinuclear complex, [Zn{Cu(NO₃)(C₁₇H₁₆N₂O₂)}₂], (I), which, in addition to the two O-atom bridges between a pair of metal ions, has a third bridge provided by an NO₃ group. In our previously reported complexes, the third bridge was either an acetate or a nitrite group.



The central Zn²⁺ ion, located on an inversion centre, has a distorted octahedral coordination involving four bridging O atoms from two SALPD²⁻ ligands in the equatorial plane [O1, O2, O1' and O2'; symmetry code: (i) $-x, -y, -z$] and an O atom from each of the two bridging nitrate groups occupying the apical positions (Fig. 1). The Zn—O1, Zn—O2 and Zn—O3 bond lengths are 2.063 (2), 2.055 (2) and 2.188 (2) Å, respectively. The O—Zn—O bond angles within the distorted octahedra range from 76.04 (9) to 93.74 (9)°. Owing to the inversion centre, the Zn²⁺ ion is in the equatorial plane.

The coordination around the terminal Cu²⁺ ions, related by the inversion centre, is an irregular square pyramid. The basal plane, defined by the O1, O2, N1 and N2 atoms, consists of two N and two bridging O atoms from a SALPD²⁻ ligand. The axial position of the square pyramid is occupied by an O atom of the bridging NO₃ group. The two Cu—O bond lengths [1.945 (2) and 1.941 (2) Å], as well as the two Cu—N distances [1.964 (3) and 1.959 (3) Å] in the basal plane, are equal among themselves within experimental error. The Cu—O4 distance along the pyramidal axis is considerably longer [2.355 (3) Å] than those observed in the basal plane. The bond angles in the five coordinated polyhedra have values between 81.5 (1) (O1—Cu—O2)

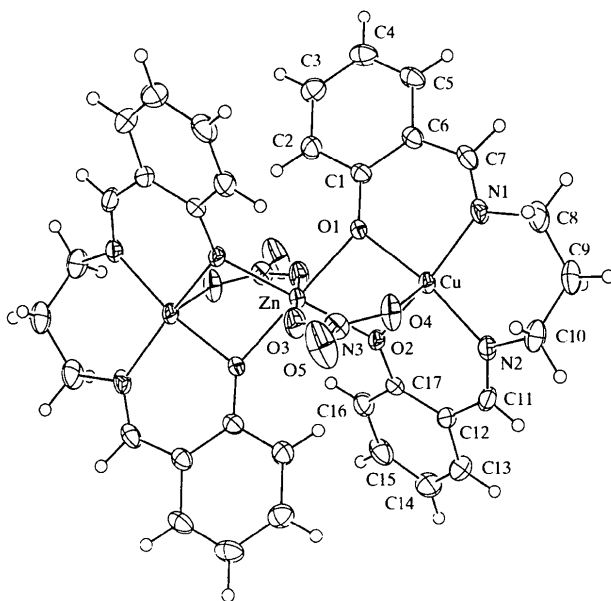


Fig. 1. ORTEP-3 (Farrugia, 1997) drawing of (I). Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small circles of arbitrary radii.

and $97.0(1)^\circ$ (N1—Cu—N2). The Cu^{2+} ion is located $0.0997(4) \text{ \AA}$ from the basal plane.

The dihedral angle between the equatorial plane around the Zn^{2+} ion and the basal plane around the Cu^{2+} ion is $25.4(1)^\circ$. The bridging plane is not flat. The planes through atoms O1—Zn—O2 and O1—Cu—O2 have a dihedral angle of $28.1(2)^\circ$ between them. Atoms Cu, N1, C8, C9, C10 and N2 form a chelate ring with a chair conformation. The diagonally positioned Cu and C9 atoms are at distances of $-0.4946(4)$ and $0.705(4) \text{ \AA}$, respectively, from the least-squares plane through the remaining four atoms of the ring.

There is a C7—H7...O5 intermolecular hydrogen bond (details given in Table 1). The Zn...Cu distance is $3.0017(6) \text{ \AA}$. The coordination in this trinuclear complex is very similar to that of the trinuclear complexes cited in the literature, although different types of metal ions and coordinating groups were employed. The choice of ligand is decisive.

Experimental

An ammonia solution (20%, 10 ml) was added to a solution of *N,N'*-bis(salicylidene)-1,3-propanediamine (2.82 g, 0.01 mol) in hot ethanol (50 ml) and the mixture was heated to boiling. A solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.510 g, 3 mmol) in hot water (20 ml) was added and the resulting mixture was set aside for 2 h. The precipitated complex (0.343 g, 1.00 mmol) was then dissolved in hot dioxane (50 ml) and the temperature of the solution increased to boiling. A solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.150 g, 0.5 mmol) in hot methanol (20 ml) was added to the solution. The resulting mixture was set aside for 2–3 d, after which time the crystals which formed were filtered off and dried in air.

Crystal data

$[\text{ZnCu}_2(\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2)_2(\text{NO}_3)_2]$
 $M_r = 877.14$
 Monoclinic
 $P2_1/c$
 $a = 9.0652(10) \text{ \AA}$
 $b = 11.5566(11) \text{ \AA}$
 $c = 16.2857(16) \text{ \AA}$
 $\beta = 100.558(8)^\circ$
 $V = 1677.3(3) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.737 \text{ Mg m}^{-3}$
 D_m not measured

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: empirical via ψ scans (Fair, 1990)
 $T_{\min} = 0.786$, $T_{\max} = 0.857$
 3673 measured reflections
 3274 independent reflections

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 10.51\text{--}18.11^\circ$
 $\mu = 2.04 \text{ mm}^{-1}$
 $T = 295 \text{ K}$
 Prismatic
 $0.300 \times 0.100 \times 0.075 \text{ mm}$
 Green

2529 reflections with

$I > \sigma(I)$
 $R_{\text{int}} = 0.015$
 $\theta_{\max} = 26.2^\circ$
 $h = -11 \rightarrow 0$
 $k = 0 \rightarrow 14$
 $l = -19 \rightarrow 20$
 3 standard reflections
 frequency: 120 min
 intensity decay: 0.023%

Refinement

Refinement on F
 $R = 0.036$
 $wR = 0.040$
 $S = 1.01$
 2529 reflections
 241 parameters
 H-atom parameters constrained

$w = 1/[\sigma F^2 + (0.02F)^2 + 0.10]$, except $w = 0$ if $F^2 < \sigma F^2$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.366 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.205 \text{ e \AA}^{-3}$
 Extinction correction: none
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters and hydrogen-bonding geometry (\AA , $^\circ$)

Zn...Cu	3.0017 (6)	Cu—O4	2.355 (3)	
Zn—O1	2.063 (2)	Cu—N1	1.964 (3)	
Zn—O2	2.055 (2)	Cu—N2	1.959 (3)	
Zn—O3	2.188 (2)	O3—N3	1.261 (4)	
Cu—O1	1.945 (2)	O4—N3	1.233 (4)	
Cu—O2	1.941 (2)	O5—N3	1.240 (4)	
O1—Zn—O2	76.04 (9)	O4—Cu—N1	102.1 (1)	
O1—Zn—O3	91.5 (1)	O4—Cu—N2	84.0 (1)	
O2—Zn—O3	93.74 (9)	N1—Cu—N2	97.0 (1)	
O1—Cu—O2	81.5 (1)	Zn—O1—Cu	96.9 (1)	
O1—Cu—O4	91.2 (1)	Zn—O2—Cu	97.3 (1)	
O1—Cu—N1	91.8 (1)	Zn—O3—N3	133.2 (2)	
O1—Cu—N2	170.7 (1)	Cu—O4—N3	126.7 (2)	
O2—Cu—O4	94.3 (1)	O3—N3—O4	121.2 (3)	
O2—Cu—N1	162.4 (1)	O3—N3—O5	118.5 (3)	
O2—Cu—N2	90.9 (1)	O4—N3—O5	120.4 (3)	
D—H...A	D—H	H...A	D...A	D—H...A
C7—H7...O5'	0.95	2.50	3.441 (5)	171

Symmetry code: (i) $1 + x, y, z$.

All H atoms were placed geometrically 0.95 \AA from their parent atoms. H-atom displacement parameters were fixed at $U_{\text{eq}}(\text{H}) = 1.3U_{\text{eq}}(\text{C})$ and a riding model was used. Hydrogen bonds were calculated with *PLATON* (Spek, 1990).

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1993). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN*. Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP-3* (Farrugia, 1997). Software used to prepare material for publication: *MolEN*.

The authors acknowledge the purchase of the CAD-4 diffractometer under grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1295). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). **C55**, 1654–1655

Aqua[*N,N'*-bis(salicylidene)-1,3-propanediaminato]copper(II)†

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(Received 19 April 1999; accepted 30 June 1999)

Abstract

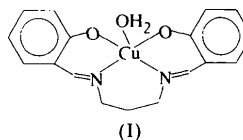
The title compound, [Cu(C₁₇H₁₆N₂O₂)(H₂O)], has *m* symmetry. The Cu atom has an approximately square-pyramidal environment involving the two O atoms and two N atoms of the *N,N'*-bis(salicylidene)-1,3-propane-

† Systematic name: aqua- μ -{2,2'-[1,3-propanediylbis(nitrilomethylidene)]diphenolato}-1- κ^4 -O,*N,N',O'*-copper(II).

diaminate ligand and one O atom of the water molecule in the apical position. In the coordination sphere, the O—Cu—N and N—Cu—O(water) angles are 89.6(1) and 96.7(1)°, respectively.

Comment

The Schiff base reactions of aldehydes with a symmetrical amino group such as 1,3-propanediamine or ethylenediamine are of interest because of their metal-complexing behaviour. The structure of the Schiff base complex aqua[*N,N'*-bis(salicylidene)-1,3-propanediamine]nickel(II) has been determined previously (Elerman *et al.*, 1993). Nickel complexes of the diamine Schiff bases generally have square-planar coordination (Akhtar & Drew, 1982; Manfredotti & Guastini, 1983; Radha *et al.*, 1985; Drew *et al.*, 1985). The title copper complex, aqua[*N,N'*-bis(salicylidene)-1,3-propanediaminato]copper(II), (I), has the same environ-



The coordination sphere around the Cu atom in (I) is a square pyramid (Fig. 1). The copper ion is coordinated with the four equatorial positions occupied by the two N and two O atoms of the *N,N'*-bis(salicylidene)-1,3-propanediaminate ligand (SALPD²⁻). The Cu atom is located 0.157(1) Å from the coordination best plane (N1, N1', O1 and O1'). The axial position of the square-pyramidal polyhedron is occupied by the O atom of the water molecule. The displacement of the O2 atom from the basal coordination plane is 2.472(1) Å.

The metal complex has *m* symmetry. The SALPD²⁻ ligand is not planar. The chelate ring composed of atoms Cu1, N1, C8, C9, C8' and N1' has a chair conformation. The distances of the two *para*-positioned

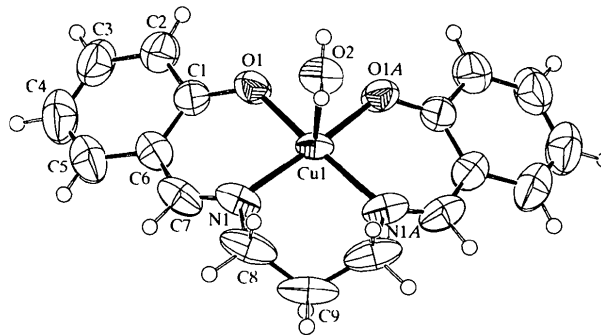


Fig. 1. PLATON99 (Spek, 1999) drawing of (I) with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small circles of arbitrary radii.