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Key indicators

Single-crystal X-ray study

T = 301 K

Mean $\sigma(C-C)$ = 0.008 Å

R factor = 0.038

wR factor = 0.095

Data-to-parameter ratio = 17.1

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

{[μ -*N,N'*-Bis(salicylidene)-2,2'-dimethyl-1,3-propanediamine](piperidine)copper(II)]dibromozinc(II)}

In the crystal structure of the dinuclear title compound, [CuZnBr₂(C₁₉H₂₂N₂O₂)(C₅H₁₁N)], the Cu^{II} ion has a distorted square-pyramidal coordination involving two iminic N and two phenolic O atoms of the *N,N'*-bis(salicylidene)-2,2'-dimethyl-1,3-propanediamine (SALPD²⁻ or C₁₇H₁₆N₂O₂²⁻) ligand and one N atom of the piperidine group. The coordination around the Zn^{II} ion is distorted tetrahedral, with two O atoms of the SALPD²⁻ ligand and two bromide ions. The Zn—Br bond lengths are 2.3309 (9) and 2.3508 (10) Å. The Cu···Zn distance is 3.0800 (9) Å.

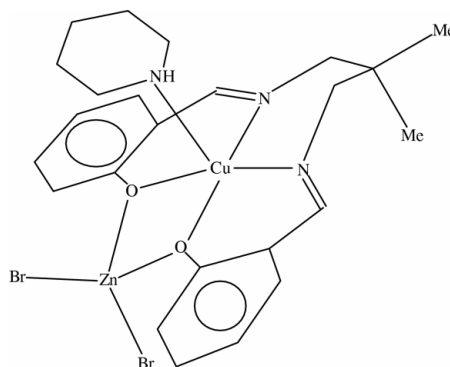
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Comment

Copper and zinc are essential elements for all living beings. While copper plays an important role in crucial activities, such as electron transfer and respiration, zinc is involved in more than enzymatic reactions (Bertini *et al.*, 1994; Lippard & Berg, 1994). Some of the Cu^{II} complexes have been widely used in pharmacology (Blower, 1998; Yao *et al.*, 1997); therefore complexes containing both metals have gained increasing attention in bio-inorganic chemistry.



(I)

Dinuclear metal complexes based on Schiff base ligands are of interest because of the magnetic superexchange interactions between the bridged metal ions. These dinuclear complexes have been the subject of considerable interest in our laboratory. In these complexes, instead of a piperidine group, pyridine and dimethylformamide groups are used for Cu²⁺ and Ni²⁺ ions, and the Zn ion is coordinated by I and Cl atoms (Ercan *et al.*, 1999; Arici *et al.*, 1999; Atakol *et al.*, 1999). We report here a new member of the heterometallic dinuclear compound family, the title compound, (I), which contains four equivalent molecules in the monoclinic unit cell.

The Cu^{II} ion has a distorted square-pyramidal environment. The five nearest neighbours around Cu^{II} atom are the two O

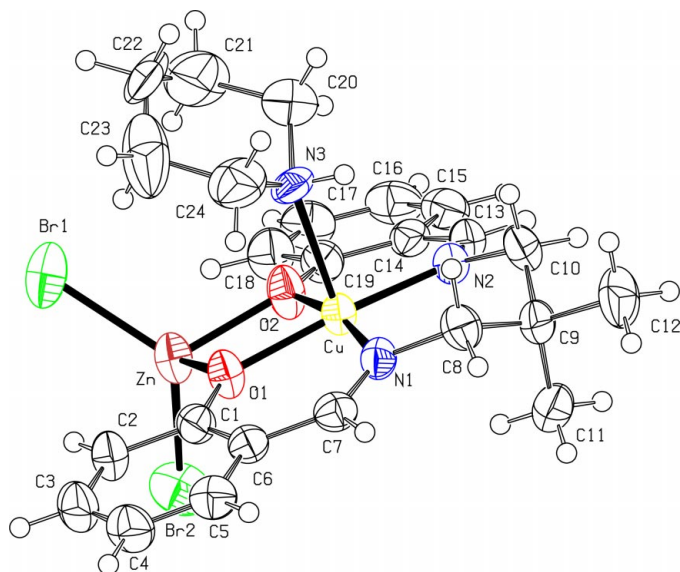


Figure 1

View of the title compound with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small circles with arbitrary radii.

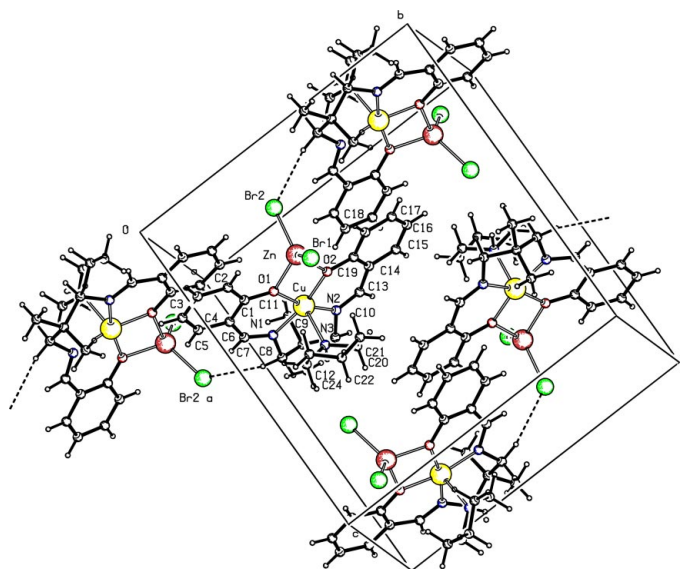


Figure 2

View of the hydrogen-bonding geometry. Colour coding: Cu yellow, Zn orange, Br green, O red, N blue, C black and H black.

and two N atoms of a SALPD²⁻ ligand and one N atom from a piperidine group (Fig. 1). The Cu atom is displaced by 0.1278 (1) Å towards N3 from the mean coordination plane (N1/N2/O1/O2), and the dihedral angle between the two Cu/N/O planes is 10.67 (1)°. The distorted tetrahedral coordination of the Zn^{II} ion is provided by two O atoms from SALPD²⁻ ligand and two bromide ions.

The distortion of the regular pyramids is revealed by the bond angles [O2—Cu—N1 and O1—Cu—N2 are 168.33 (15) and 167.54 (15)°, respectively] between the donor atoms (Table 1). The value of this distortion (represented by τ) is 0.0132 for the Cu^{II} ion. $\tau = [(\alpha - \beta)/60]$ where α and β are the two

largest angles around the central atom] is equal to 0 in a regular square pyramid (Addison *et al.*, 1984).

An inspection of the possible hydrogen bonds indicates a weak intermolecular C8—H8A...Br2ⁱ hydrogen bond, as can be seen from Table 2 and Fig. 2.

Experimental

The ligand *N,N'*-bis(salicylidene)-2,2'-dimethyl-1,3-propanediamine (1.410 g, 0.005 mol) was dissolved in hot EtOH (1:1, 70 ml). To this solution were added 20% concentrated ammonia (10 ml) and a solution of CuCl₂·2H₂O (0.850 g, 0.005 mol) in 50 ml hot water for the preparation of the Cu complex. The mixture was set aside for 2–3 h and the green crystals which formed were filtered and dried in an oven at 373 K. The complex (0.373 g, 0.001 mol) was dissolved by heating in 60 ml dioxane by heating. To this solution, 0.7 ml piperidine and a solution of 0.225 g anhydrous ZnBr₂ in 20 ml hot MeOH were added. The mixture was set aside for 3–4 d and after this period, the light-green crystals which formed were filtered and dried in air.

Crystal data

[CuZnBr₂(C₁₉H₂₂N₂O₂)(C₅H₁₁N)]
M_r = 682.25
 Monoclinic, *P*₂₁/*n*
a = 10.659 (2) Å
b = 14.550 (1) Å
c = 16.992 (3) Å
 β = 97.91 (2)°
V = 2610.2 (7) Å³
Z = 4

D_x = 1.736 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 1.9–26.0°
 μ = 4.82 mm⁻¹
T = 301 (2) K
 Prism, light green
 0.35 × 0.30 × 0.25 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: empirical via ψ scans (Fair, 1990)
 $T_{\min} = 0.202$, $T_{\max} = 0.300$
 8583 measured reflections
 5111 independent reflections
 3403 reflections with $I > 2\sigma(I)$

*R*_{int} = 0.041
 θ_{\max} = 26.0°
 $h = -13 \rightarrow 6$
 $k = -17 \rightarrow 0$
 $l = -20 \rightarrow 20$
 3 standard reflections
 frequency: 120 min
 intensity decay: 1.2%

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.095$
 $S = 1.10$
 5111 reflections
 299 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0506P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.82 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.50 \text{ e } \text{Å}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0028 (3)

Table 1

Selected geometric parameters (Å, °).

Cu—Zn	3.0800 (9)	Cu—N3	2.312 (4)
Cu—O1	1.969 (3)	Zn—Br1	2.3309 (9)
Cu—O2	1.948 (3)	Zn—Br2	2.3508 (10)
Cu—N1	1.972 (3)	Zn—O1	2.003 (3)
Cu—N2	1.975 (3)	Zn—O2	2.001 (3)
O2—Cu—O1	78.84 (12)	N1—Cu—N3	91.07 (15)
O2—Cu—N1	168.33 (15)	N2—Cu—N3	93.34 (15)
O1—Cu—N1	91.17 (13)	O2—Cu—Zn	39.37 (9)
O2—Cu—N2	91.32 (14)	O1—Cu—Zn	39.55 (9)
O1—Cu—N2	167.54 (15)	N1—Cu—Zn	130.12 (10)
N1—Cu—N2	97.70 (15)	N2—Cu—Zn	129.85 (11)
O2—Cu—N3	95.80 (15)	Cu—O2—Zn	102.50 (13)
O1—Cu—N3	95.22 (14)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C8-H8A \cdots Br2^i$	0.99	2.86	3.837 (5)	168

Symmetry code: (i) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

H atoms bonded to C atoms were positioned geometrically. All H atoms were refined as riding with $U_{eq}(H) = 1.2U_{eq}(C \text{ or } N)$.

Data collection: *CAD-4 EXPRESS* (Enraf-Nonius, 1993); cell refinement: *CAD-4 EXPRESS* (Sheldrick, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *SHELXL97*.

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References

- Addison, A. W., Nageswara, R. T., Reedijk, J., Rijn, J. V. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.
- Arici, C., Ercan, F., Atakol, O., Akay, A. & Ülkü, D. (1999). *Acta Cryst. C55*, 928–930.
- Atakol, O., Ercan, F., Arıcı, C., Fuess, H. & Svoboda, I. (1999). *Acta Cryst. C55*, 2023–2026.
- Bertini, I., Gray, H. B., Lippard, S. J. & Valentine, J. S. (1994). *Bioinorganic Chemistry*, pp. 37–102. Mill Valley: University Science Books.
- Blower, P. J. (1998). *Transition Met. Chem.* **23**, 109–112.
- Enraf-Nonius (1993). *CAD-4 EXPRESS*. Version 1.1. Enraf-Nonius, Delft, The Netherlands.
- Ercan, F., Arıcı, C., Ülkü, D., Atakol, O. & Aksu, M. (1999). *Acta Cryst. C55*, 930–932.
- Fair, C. K. (1990). *MolEN*. Enraf-Nonius, Delft, The Netherlands.
- Lippard, S. J. & Berg, J. M. (1994). *Principles of Bioinorganic Chemistry*, pp. 3–19. Mill Valley: University Science Books.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2000). *PLATON*. Utrecht University, The Netherlands.
- Yao, H.-H., Lo, J.-M., Chen, B.-H. & Lu, T.-H. (1997). *Acta Cryst. C53*, 1012–1013.