

- Guseinov, G. A., Musaev, F. N., Amiraslanov, I. R., Usabaliev, B. T. & Mamedov, Kh. S. (1983). *Koord. Khim.* **9**, 1687–1694.
- Guseinov, G. A., Musaev, F. N., Usabaliev, B. T., Amiraslanov, I. R. & Mamedov, Kh. S. (1984). *Koord. Khim.* **10**, 117–122.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Nadzhafov, G. N., Shnulin, A. N. & Mamedov, Kh. S. (1981). *Zh. Strukt. Khim.* **22**, 124–128.
- Tahir, M. N., Ülkü, D. & Movsumov, E. M. (1996a). *Acta Cryst.* **C52**, 593–595.
- Tahir, M. N., Ülkü, D. & Movsumov, E. M. (1996b). *Acta Cryst.* **C52**, 1392–1394.
- Tahir, M. N., Ülkü, D. & Movsumov, E. M. (1996c). *Acta Cryst.* **C52**, 1449–1451.
- Tahir, M. N., Ülkü, D. & Movsumov, E. M. (1996d). *Acta Cryst.* **C52**, 2436–2439.

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Bis{2-[(2-hydroxybenzyl)iminomethyl]-phenolato(2-)-O:O,N,O'}dicopper(II)

DİNÇER ÜLKÜ,^{a*} FILİZ ERCAN,^a ORHAN ATAKOL,^b ISMAIL ERCAN^c AND ALI GENCER^d

^aDepartment of Engineering Physics, Hacettepe University, Beytepe 06532, Ankara, Turkey, ^bDepartment of Chemistry, Faculty of Science, Ankara University, Beşevler 06100, Ankara, Turkey, ^cAnkara Nuclear Research and Training Centre, Saray 06105, Ankara, Turkey, and ^dDepartment of Physics, Ankara University, Beşevler 06100, Ankara, Turkey. E-mail: dulku@eti.cc.hun.edu.tr

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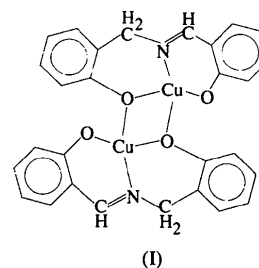
Abstract

The title compound, [Cu₂(C₁₄H₁₁NO₂)₂], consists of doubly oxygen-bridged centrosymmetric copper dimers. Each Cu atom has a distorted square-planar environment involving three O atoms and an N atom of the ligands. The Cu—O distances in the coordination plane vary from 1.881 (8) to 1.930 (10) Å and the Cu—N distance is 1.920 (10) Å. In the bridging plane, the Cu—O—Cu' and O—Cu—O' angles are 103.5 (4) and 76.5 (3)°, respectively. The Cu···Cu' distance is 3.073 (2) Å.

Comment

It is well known that dimeric copper(II) complexes with double oxygen bridges have subnormal magnetic moments due to the super-exchange mechanism over the O atoms (Kato, Jonassen & Fanning, 1964; Butcher & Sinn, 1975; Kato & Muto, 1988). The ligand stereochemistry around the Cu atom and the structure of the double bridge influences the magnetic properties. As an extension of our structural studies of the doubly oxygen-bridged dimeric copper complexes, of which

bis[4-[(5-chloro-2-hydroxyphenyl)imino]-2-penten-2-olato-O,O',N}copper(II)] (Tahir, Ülkü, Atakol & Akay, 1996) and bis[4-[(2-oxylbenzyl)imino]-2-penten-2-olato-O,O',N}copper(II)] (Ülkü, Tahir, Atakol & Tastekin, 1997) have been published, we report here the structure of the title compound, [Cu₂(C₁₄H₁₁NO₂)₂], (I). These structures have similarities with the structure of (acetylaceton)mono(*o*-hydroxyanil)copper(II) (Barclay & Hoskins, 1965).



The coordination around copper is distorted square planar, with bond angles ranging between 76.5 (3) and 98.0 (3)° (Fig. 1). The average Cu—O distance in the coordination square is 1.931 (9) Å and the Cu—N distance is 1.920 (10) Å. The Cu atom is located 0.021 (1) Å from the coordination best plane. Due to the centre of inversion at its centre, the Cu—O—Cu—O bridging plane moiety is planar, with Cu—O bond lengths of 1.930 (10) and 1.982 (9) Å. The bond angles within the bridging planes, Cu—O₂—Cuⁱ and O₂—Cu—O₂ⁱ, are 103.5 (4) and 76.5 (3)°, respectively [symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, -z$]. The bridging plane and the coordination square around copper have a dihedral angle of 11.3 (8)° between them. The Cu···Cuⁱ

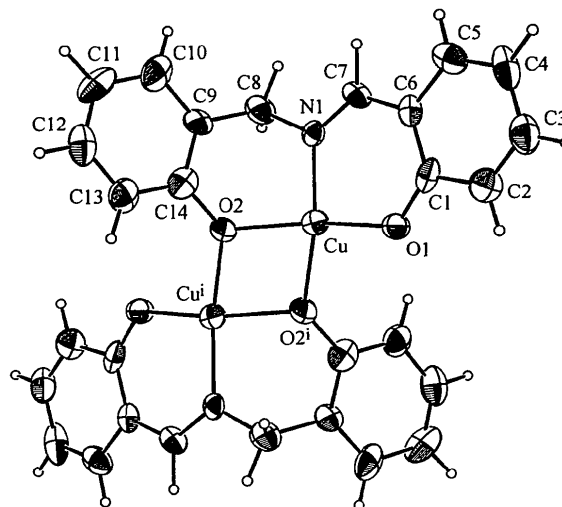


Fig. 1. ORTEPII (Johnson, 1976) drawing of [Cu₂(C₁₄H₁₁NO₂)₂] with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small circles of arbitrary radii.

distance [3.073 (2) Å] is long for a direct interaction. A comparison of the dihedral angle (τ) between the Cu—O—Cu—O bridging plane and the coordination plane around copper, along with the related distance ranges and bridging angle (φ), are given in Table 3 for the three dimeric copper complexes recently studied in this laboratory. The bond lengths and angles within the ligands show no unusual values.

AC susceptibility measurements were carried out in the temperature range 15–300 K using a commercial Lake Shore AC susceptometer 7130 model with a closed-cycle refrigerator. The sample, kept in helium exchange gas with a controllable temperature resolution better than 10 mK, was moved from the centre of one secondary coil to the other in order to eliminate unwanted signals and hence to maximize the signal from the sample itself. The magnetic anomaly was observed at 41.5 K. The value of μ_{eff} at this temperature was calculated to be $0.73\mu_{\text{B}}$.

Experimental

N-(2-Hydroxybenzyl)salicylaldehyde (0.227 g, 1 mmol) was dissolved in 70 ml hot methanol and the solution heated to boiling with the addition of 0.5 ml pure piperidine. To this mixture, a solution of [Cu(CH₃COO)₂].H₂O (0.199 g, 1 mmol) in 50 ml hot methanol was added and the resulting mixture set aside for 24 h. The precipitated dark green crystals were filtered and dried at 353 K.

Table 1. Selected geometric parameters (Å, °)

Cu...Cu ¹	3.073 (2)	C1—C2	1.42 (2)
Cu—O1	1.881 (8)	C1—C6	1.41 (2)
Cu—O2	1.982 (9)	C6—C7	1.42 (2)
Cu—N1	1.920 (10)	C7—N1	1.31 (2)
Cu—O2 ¹	1.934 (2)	N1—C8	1.45 (1)
O1—C1	1.29 (2)	C8—C9	1.49 (2)
O2—C14	1.35 (2)	C9—C14	1.38 (2)
O1—Cu—O2	164.0 (3)	C1—C6—C7	124 (1)
O1—Cu—N1	96.9 (4)	C5—C6—C7	117 (1)
O1—Cu—O2 ¹	98.0 (3)	C6—C7—N1	126 (1)
O2—Cu—N1	91.6 (4)	Cu—N1—C7	122.3 (8)
O2—Cu—O2 ¹	76.5 (3)	Cu—N1—C8	117.5 (8)
N1—Cu—O2 ¹	161.9 (3)	C7—N1—C8	120 (1)
Cu—O1—C1	124.0 (8)	N1—C8—C9	110.3 (8)
Cu—O2—C14	118.0 (8)	C8—C9—C10	121 (1)
Cu—O2—Cu ¹	103.5 (4)	C8—C9—C14	119 (1)
C14—O2—Cu ¹	132.7 (8)	C10—C9—C14	121 (1)
O1—C1—C2	118 (1)	O2—C14—C9	120 (1)
O1—C1—C6	126 (1)	O2—C14—C13	122 (1)
C2—C1—C6	116 (1)	C9—C14—C13	118 (1)
C1—C6—C5	120 (1)		
O1—Cu—O2 ¹ —Cu ¹	164.6 (3)		

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

Table 2. Dihedral angle τ , bridging angle φ , and magnetic and structural data for three Cu complexes

Complex	Cu—O bridge (Å)	Cu...Cu (Å)	τ (°)	φ (°)	T anomaly (K)	μ_{eff} (BM)	μ_{eff} (BM) (300 K)
[Cu ₂ (C ₁₁ H ₁₀ NO ₂ Cl) ₂] †	1.941 (5)–1.950 (4)	2.994 (2)	5 (1)	100.6 (2)	40.9	0.725	1.590
[Cu ₂ (C ₁₄ H ₁₁ NO ₂) ₂] ‡	1.930 (10)–1.982 (9)	3.073 (2)	11.3 (8)	103.5 (4)	41.5	0.730	1.565
[Cu ₂ (C ₁₂ H ₁₃ NO ₂) ₂] §	1.938 (3)–1.955 (3)	3.047 (6)	12.7 (2)	103.4 (1)	—	—	—

† Tahir *et al.* (1996). ‡ Title compound. § Ülkü, Tahir, Atakol & Tastekin (1997).

Crystal data

[Cu₂(C₁₄H₁₁NO₂)₂]

$M_r = 577.58$

Monoclinic

C2/c

$a = 16.903$ (2) Å

$b = 12.158$ (2) Å

$c = 12.342$ (2) Å

$\beta = 114.96$ (3)°

$V = 2299.5$ (8) Å³

$Z = 4$

$D_x = 1.668$ Mg m⁻³

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 25 reflections

$\theta = 10$ –18°

$\mu = 1.89$ mm⁻¹

$T = 295$ K

Prismatic

$0.56 \times 0.16 \times 0.06$ mm

Dark green

Data collection

Enraf–Nonius CAD-4 diffractometer

$\omega/2\theta$ scans

Absorption correction:

empirical via ψ scans

(*MolEN*; Fair, 1990)

$T_{\text{min}} = 0.828$, $T_{\text{max}} = 0.891$

3198 measured reflections

2930 independent reflections

1059 reflections with

$I > 2.3\sigma(I)$

$R_{\text{int}} = 0.027$

$\theta_{\text{max}} = 28.6^\circ$

$h = -22 \rightarrow 20$

$k = -16 \rightarrow 0$

$l = 0 \rightarrow 16$

3 standard reflections

frequency: 120 min

intensity decay: 1.1%

Refinement

Refinement on F

$R = 0.068$

$wR = 0.082$

$S = 0.94$

1059 reflections

163 parameters

H atoms: see below

$w = (47.59/F)^2$ if $F > 47.59$;

$w = 1.0$ if $F < 47.59$

$(\Delta/\sigma)_{\text{max}} = 0.002$

$\Delta\rho_{\text{max}} = 0.83$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.42$ e Å⁻³

Extinction correction: none

Scattering factors from *International Tables for X-ray*

Crystallography (Vol. IV)

All non-H atoms were refined with anisotropic displacement parameters. The H7, H81 and H82 atoms were taken from difference maps, while other H atoms were geometrically positioned 0.95 Å from their parent atom. For all H atoms, a riding model was used with $U_{\text{iso}}(\text{H}) = 1.3U_{\text{eq}}(\text{C})$.

Data collection: *CAD-4 Express* (Enraf–Nonius, 1993). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIMPEL* in *MolEN*. Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEPII* (Johnson, 1976) in *MolEN*. Software used to prepare material for publication: *MolEN*.

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

Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry have been deposited with the IUCr (Reference: FR1008). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Barclay, G. A. & Hoskins, B. F. (1965). *J. Chem. Soc.* pp. 1979–1991.
 Butcher, R. J. & Sinn, E. (1975). *Inorg. Chem.* **15**, 1604–1608.
 Enraf–Nonius (1993). *CAD-4 Express Software*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.
 Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
 Johnson, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 Kato, M., Jonassen, H. B. & Fanning, J. (1964). *Chem. Rev.* pp. 99–128.
 Kato, M. & Muto, Y. (1988). *Coord. Chem. Rev.* **92**, 45–83.
 Tahir, N., Ülkü, D., Atakol, O. & Akay, A. (1996). *Acta Cryst.* **C52**, 2676–2678.
 Ülkü, D., Tahir, N., Atakol, O. & Tastekin, M. (1997). *Acta Cryst.* In preparation.

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Bis{2-[(3-aminopropyl)iminomethyl]-4,6-dinitrophenolato-*O,N,N'*}nickel(II)

M. NAWAZ TAHIR,^a DINÇER ÜLKÜ,^{a*} HASAN NAZIR^b AND ORHAN ATAKOL^b

^aDepartment of Engineering Physics, Hacettepe University, Beytepe, 06532 Ankara, Turkey, and ^bDepartment of Chemistry, Faculty of Science, University of Ankara, Beşevler, 06100 Ankara, Turkey. E-mail: dulku@eti.cc.hun.edu.tr

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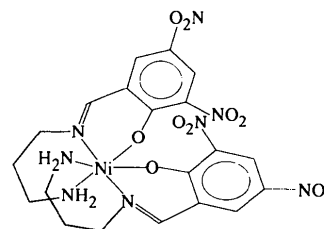
Abstract

The title compound, $[\text{Ni}(\text{C}_{10}\text{H}_{11}\text{N}_4\text{O}_5)_2]$, contains asymmetric Schiff base ligands. The coordination sphere around the Ni atom is a distorted octahedron, with an average Ni—O distance of 2.072 (2) Å and Ni—N distances ranging from 2.059 (2) to 2.084 (3) Å. Bond angles at the Ni atom have values between 83.80 (9) and 96.93 (9)°. The structure is stabilized through an intermolecular hydrogen-bonding network.

Comment

In general, the Schiff base reaction of aldehydes with symmetrical amino groups such as ethylenediamine, 1,3-

diaminopropane or 1,2-diaminobenzene involves both amino groups. Schiff bases prepared with this type of diamine are symmetrical. Nickel complexes of the diamine Schiff bases generally have square-planar coordination (Akhtar & Drew, 1982; Manfredotti & Guastini, 1983; Padha, Seshasayee, Ramalingam & Aravamudan, 1985; Drew, Prasad & Sharma, 1985; Elerman, Kabak & Atakol, 1993). To the best of our knowledge, the title compound, (I), is the first asymmetric Schiff base–nickel(II) complex obtained by a template reaction using 3,5-dinitrosalicylaldehyde and 1,3-diaminopropane.



(I)

The slightly distorted octahedral coordination around the Ni atom involves two nitrogen and one oxygen donor from each of the two ligands (Fig. 1), with imine and amine N atoms both taking part in coordination. The phenolic O atoms are mutually *cis*, with equal bond lengths [2.072 (1) and 2.072 (2) Å], with respect to the nickel centre. The apical Ni—N1 and Ni—N3 bond lengths of 2.059 (2) and 2.064 (2) Å are slightly shorter than the Ni—N2 and Ni—N4 bond lengths of 2.084 (3) and 2.077 (2) Å in the equatorial plane. Different Ni—N distances are expected, since these bonds are influenced by the nature of the N-donor atom and also by the chelate rings (Curtis, 1979). Unequal Ni—N distances

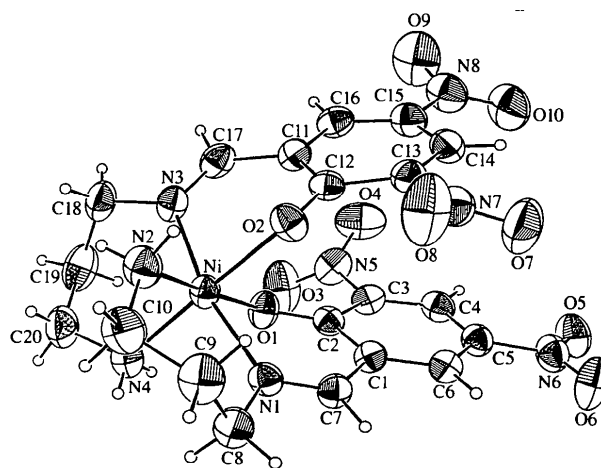


Fig. 1. ORTEP (Johnson, 1976) drawing of $[\text{Ni}(\text{C}_{10}\text{H}_{11}\text{N}_4\text{O}_5)_2]$ with the atomic numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small circles of arbitrary radii.