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A dinuclear pyrazolato-*N*:*N*′-bridged dinickel(II) complex of 1,3-bis(5-chlorosalicylideneamino)propan-2-ol

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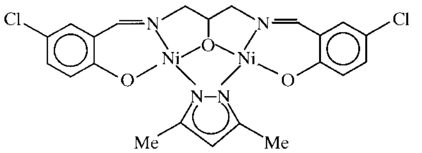
The title compound, μ-[1,3-bis(5-chloro-2-oxidobenzylideneamino)propan-2-olato(3−)]-*O*,*N*,*O*′:*O*′,*N*′,*O*″-μ-(3,5-dimethylpyrazolato)-*N*:*N*′-dinickel(II), $[Ni_2(C_{17}H_{13}Cl_2N_2O_3)(C_5H_7N_2)]$, has crystallographic mirror symmetry. The Ni atoms in the dinuclear structure are linked symmetrically by the N atoms of the 3,5-dimethylpyrazole group and by the alkoxo O atom. Each Ni^{II} ion is coordinated by two N atoms and two O atoms, forming a square plane with *trans*-N_2O_2 geometry.

Comment

The field of binucleating ligands and their metal complexes has developed considerably in recent years (Fenton & Okawa, 1993; Guerriero *et al.*, 1992; Bond *et al.*, 1989). Although a large number of unsymmetric doubly bridged dinuclear copper(II) complexes have been studied (Mazurek *et al.*, 1982, 1985; Nishida & Kida, 1988; Doman *et al.*, 1990; Tandon *et al.*, 1993; Chen *et al.*, 1996; Li *et al.*, 1997), relatively few structures of unsymmetric doubly bridged dinuclear nickel(II) complexes have been reported (Mikuriya *et al.*, 1992; Kruger *et al.*, 1994; Kondrad *et al.*, 1999). We have therefore made a detailed structural study of the title dinuclear pyrazolato-*N*:*N*′-bridged nickel(II) complex, (I), of 1,3-bis(5-chlorosalicylideneamino)propan-2-ol.



(I)

The crystal structure of (I) is illustrated in Fig. 1 and selected bond distances and angles are listed in Table 1. The Ni atoms in the dinuclear structure are linked symmetrically by the N atoms of the 3,5-dimethylpyrazole group and by the alkoxo O atom. Each Ni^{II} ion is coordinated by two N atoms and two O atoms, forming a square plane with *trans*-N_2O_2 geometry. The molecular structure of (I) has crystallographic mirror symmetry, so the asymmetric unit contains only half of the molecule.

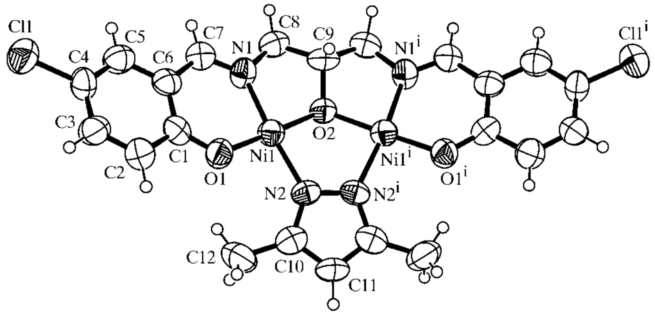


Figure 1
The molecular structure of (I), showing the atom-labelling scheme and 50% probability displacement ellipsoids. H atoms are drawn as small spheres of arbitrary radii [symmetry code: (i) *x*, $\frac{3}{2} - y$, *z*].

The Ni—O and Ni—N bond distances in (I) are in the ranges of those of conventional Schiff base and alkoxide-bridged nickel(II) complexes of square-planar coordination (Mikuriya *et al.*, 1992; Kruger *et al.*, 1994). The Ni···Ni separation [3.157 (3) Å] and the Ni—O—Ni angle [117.4 (2)°] are smaller than those reported for other unsymmetric doubly bridged dinuclear nickel(II) complexes (Mikuriya *et al.*, 1992; Kruger *et al.*, 1994). The dihedral angle between the coordinated planes is 33.52 (8)°, showing a considerable bending of the two coordination planes. Thus, the molecule of (I) has a bent structure. This bending of the molecule is caused by the twisting of the Schiff base backbone and leads to the smaller Ni···Ni separation and Ni—O—Ni angle.

The Ni^{II} ion is square planar, with the mean deviation from the least-squares plane defined by Ni1/O1/N1/O2/N2 being 0.03 Å and the mean deviation from the $Ni1/O2/Ni1^i/N2^i/N2$ plane being 0.17 Å [symmetry code: (i) *x*, $\frac{3}{2} - y$, *z*]. The remaining five-membered rings are not planar, as seen from the N1—C8—C9—O2 torsion angle of 49.7 (6)°. The six-membered rings are each planar to within 0.007 Å. Another important feature is the geometry of the bridging atom, O2: the bond angles around O2 of 108.8 (2), 117.4 (2) and 108.8 (2)° indicate a pyramidal stereochemistry at this atom.

Complex (I) is diamagnetic, which is consistent with the planar geometry around the Ni^{II} ions.

Experimental

Caution: perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small quantity of materials should be handled. The Schiff base ligand was prepared by the reaction of 1,3-diaminopropan-2-ol (0.1 mmol) with 5-chlorosalicylaldehyde (0.2 mmol) in methanol (100 ml). The yellow Schiff base precipitated from solution on cooling. The dinuclear complex, (I), was obtained when a sample of the Schiff base ligand (0.1 mmol) in methanol (50 ml) was added dropwise to a stirred mixture containing 3,5-dimethylpyrazole (0.1 mmol) and nickel(II) perchlorate hexahydrate

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(0.2 mmol) in methanol (25 ml). Triethylamine (0.3 mmol) was added to the solution. The mixture was stirred and thin brown crystals of (I) were collected and washed with methanol. Recrystallization from acetone afforded suitable single crystals.

Crystal data

$[Ni_2(C_{17}H_{13}Cl_2N_2O_3)(C_5H_7N_2)]$
$M_r = 576.70$
Orthorhombic, *Pnma*
$a = 7.492$ (3) Å
$b = 28.929$ (7) Å
$c = 10.334$ (5) Å
$V = 2239.8$ (15) Å^3
$Z = 4$
$D_x = 1.71$ Mg m^{-3}

Cu $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 12$–20°
$\mu = 4.57$ mm^{-1}
$T = 293$ (2) K
Plate, brown
0.19 × 0.15 × 0.09 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.482$, $T_{max} = 0.663$
2284 measured reflections
2284 independent reflections

1070 reflections with $I > 2\sigma(I)$
$\theta_{max} = 74.22°$
$h = 0 \rightarrow 9$
$k = -36 \rightarrow 0$
$l = 0 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity decay: 1.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.155$
$S = 1.041$
2284 reflections
154 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0672P)^2 + 2.4402P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—O1	1.807 (4)	Ni1—N2	1.912 (4)
Ni1—O2	1.847 (2)	N2—N2^i	1.358 (8)
Ni1—N1	1.869 (4)		
O1—Ni1—O2	176.66 (19)	O2—Ni1—N2	88.34 (17)
O1—Ni1—N1	94.60 (18)	N1—Ni1—N2	173.43 (17)
O2—Ni1—N1	85.14 (18)	Ni1^i—O2—Ni1	117.4 (2)
O1—Ni1—N2	91.96 (17)	N2^i—N2—Ni1	118.06 (12)

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

The positions of the H atoms bonded to C atoms were calculated (C—H 0.96 Å) and refined using a riding model, with H-atom displacement parameters constrained to be $1.2U_{eq}$ of the parent atom.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1993); cell refinement: *CAD*-4 *Software*; data reduction: *RC*93 (Watkin *et al.*, 1994); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1306). Services for accessing these data are described at the back of the journal.

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