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[2,3-Bis(salicylideneamino-*O*,*N*)pyridinato]-nickel(II)

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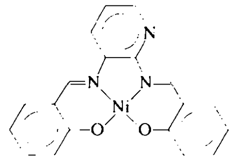
Abstract

The coordination around the Ni atom in the title compound, {2,2′-[2,3-pyridinediylbis(iminomethyl-*N*)]diphenolato-*O*,*O*′}nickel(II), [Ni($C_{19}H_{13}N_3O_2$)], is slightly distorted from square planar. Within the coordination square, the bond angles are in the range 83.8 (1)–94.8 (2)°. The Ni—N and Ni—O distances are equal within experimental error, with average values of 1.854 (2) and 1.835 (2) Å, respectively. Comparison of bond lengths in free and nickel-coordinated ligands indicates a shortening of the C—O bonds due to packing effects. On complex formation, the whole molecule assumes a more planar form, which brings the Ni atoms of neighbouring molecules as close as 3.1908 (10) Å to each other.

Comment

Schiff bases derived from salicylaldehyde and aminopyridines are of interest because of their metal-complexing behaviour. The structure of the Schiff base 2,3-bis(salicylideneamino)pyridine (bimorphous) has been determined previously (Cimerman *et al.*, 1992). Both forms of the molecule have the imine structure and there was no evidence of tautomerism with the ketamine isomer. 2-Salicylideneaminopyridine has potential use as an anti-inflammatory agent and the corresponding complex with Co^{II} has been reported (Parashar *et al.*, 1988). The thermochromic and photochromic properties of a series of 2-, 3- and 4-salicylideneaminopyridines have been observed and reported by Hadjoudis (1981).

The structure of the title compound, (I), was determined to find out whether it has the imine or the ketamine tautomeric form. As can be seen from Fig. 1, the Ni^{II} ion has slightly distorted square-planar coordination. The displacement of the Ni^{II} ion from the best plane through the donor atoms O1, O2, N1 and N3 is 0.0081 (6) Å. The coordination bond angles have values between 83.8 (1) (O1—Ni—O2) and 94.8 (2)° (O1—Ni—N1), their sum being 360.0 (1)°. The Ni—O distances [1.834 (3) and 1.837 (3) Å], as well as the Ni—N distances [1.853 (4) and 1.856 (4) Å], are equal within experimental error. The free ligand molecule, 2,3-bis(salicylideneamino)pyridine, which is not planar (Cimerman *et al.*, 1992), seems to assume a more planar form on coordination to nickel. For instance, the dihedral angles between the pyridine and two benzene rings in the free ligand are 5.7 (4) and 51.1 (4)°, while the corresponding angles in the title complex are equal within experimental error, with a mean value of 5 (1)°. The molecule as a whole is practically planar. The planarity of the molecule permits parallel packing in the unit cell so that the closest intermolecular Ni···Ni distance is 3.1908 (10) Å.



(I)

A comparison of the bond lengths reported for the free Schiff base with those observed here indicates that on complex formation the C—O bond lengths are shortened [average value 1.35 (1) *versus* 1.293 (4) Å],

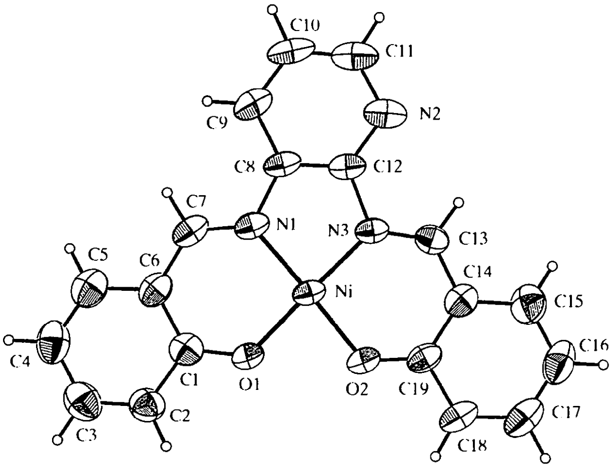


Fig. 1. The title compound with the atomic numbering scheme and displacement ellipsoids at the 50% probability level. H atoms are shown as small circles of arbitrary radii.

most likely as a result of the chelation of the ligand around nickel. The changes in the C—C bonds relevant to the tautomerism are equal within experimental error. The expected C—N(imine) bond lengthening for a ketamine structure was not observed.

A comparison with the analogous nickel complexes with salphen (*N*,*N'*-*o*-phenylenedisalicylideneamine) (Radha *et al.*, 1985) and salen [bis(salicylidene)ethylenediamine] (Manfredotti & Guastini, 1983) indicates that, in the present compound, the Ni—O distances are equal within experimental error to the corresponding bond lengths observed in the Ni-salphen complex [1.838 (7) Å], but shorter than those in the Ni-salen complex [average 1.853 (2) Å]. The Ni—N and C—O bond lengths of all three compounds have comparable values. The title compound is isostructural with the copper complex of 2,3-bis(salicylideneamino)pyridine (Atakol *et al.*, 1997).

Experimental

2,3-Bis(salicylideneamino)pyridine was prepared by the condensation of salicylaldehyde with 2,3-diaminopyridine in ethanol. Solutions of the Schiff base (0.189 g, 0.5 mmol) in 100 ml of CH_3CN and $Ni(CH_3COO)_2.4H_2O$ (0.125 g, 0.5 mmol) in 10 ml of methanol were prepared. These two solutions were mixed and the resulting mixture kept for 5 min at *ca* 333 K and then left aside overnight. The crystals which formed were filtered, washed with cold methanol, dried and used for X-ray data collection. ^1H NMR [δ (p.p.m.), reference TMS in DMSO-d_6, 400 MHz]: HC=N 9.34 (*s*) and 9.04 (*s*); ring C—H 8.56–6.63 (four doublets and three multiplets, 11 protons altogether). NMR data indicate that the composition of the solution is the same as that of the single crystal.

Crystal data

[Ni($C_{19}H_{13}N_3O_2$)]
M_r = 374.044
Monoclinic
$P2_1/n$
a = 10.9539 (12) Å
b = 8.1317 (11) Å
c = 17.9391 (14) Å
β = 105.566 (4)°
V = 1539.3 (3) Å^3
Z = 4
D_x = 1.614 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 11.69–20.73°
μ = 1.281 mm^{-1}
T = 295 K
Needle
0.40 × 0.10 × 0.10 mm
Red

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (Fair, 1990)
$T_{\min}$ = 0.646, $T_{\max}$ = 0.878
3759 measured reflections
3613 independent reflections

2368 reflections with $I > \sigma(I)$
$R_{\rm int}$ = 0.037
$\theta_{\max}$ = 27.41°
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 10$
$l = -23 \rightarrow 22$
3 standard reflections
frequency: 120 min
intensity decay: 0.16%

Refinement

Refinement on F
R = 0.052
wR = 0.056
S = 0.88
2368 reflections
226 parameters
H atoms riding (see below)
$w = 1/[\sigma^2(F) + (0.02F)^2 + 1.0]$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.60 e Å^{-3}
$\Delta\rho_{\min}$ = −0.22 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Ni···Ni^{i}	3.1908 (10)	N1—C8	1.424 (6)
Ni—O1	1.834 (3)	N3—C12	1.429 (6)
Ni—O2	1.837 (3)	N3—C13	1.290 (6)
Ni—N1	1.853 (4)	C1—C2	1.414 (7)
Ni—N3	1.856 (4)	C2—C3	1.360 (8)
O1—C1	1.297 (6)	C17—C18	1.347 (8)
O2—C19	1.290 (6)	C18—C19	1.422 (6)
N1—C7	1.292 (6)		
O1—Ni—O2	83.8 (1)	Ni—O1—C1	127.7 (3)
O1—Ni—N1	94.8 (2)	Ni—O2—C19	127.6 (3)
O1—Ni—N3	178.3 (2)	Ni—N1—C7	126.8 (3)
O2—Ni—N1	178.4 (2)	Ni—N1—C8	112.2 (3)
O2—Ni—N3	94.5 (2)	Ni—N3—C12	112.2 (3)
N1—Ni—N3	86.9 (2)	Ni—N3—C13	127.2 (3)

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

To identify atoms N2 and C9, a difference map was calculated to see the trace of H-atom density in the neighbourhood of C9. After that, H atoms were placed geometrically 0.95 Å from their parent C atoms and a riding model was used with $U_{\rm iso}(H) = 1.3U_{\rm eq}(C)$.

Data collection and cell parameters: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1993). Data reduction, program used to solve structure, program used to refine structure, molecular graphics and software used to prepare material for publication: *MolEN* (Fair, 1990). Other programs used include *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1106). Services for accessing these data are described at the back of the journal.

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