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.

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

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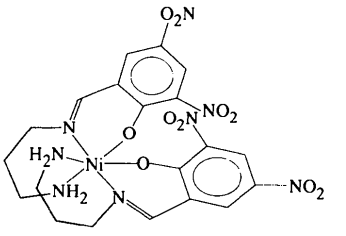
Abstract

The title compound, $[Ni(C_{10}H_{11}N_4O_5)_2]$, 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

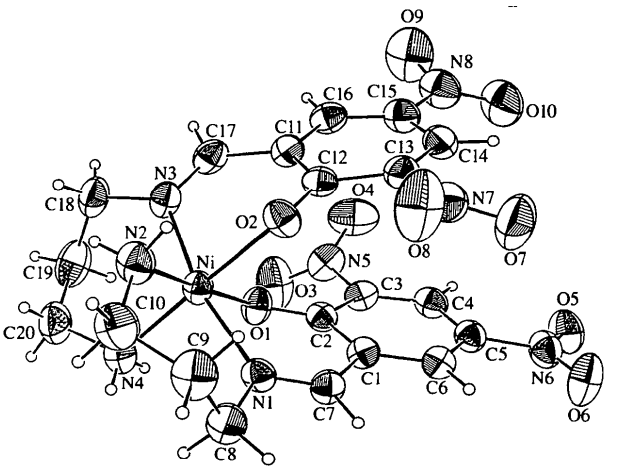


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of $[Ni(C_{10}H_{11}N_4O_5)_2]$ with the atomic numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small circles of arbitrary radii.

were also observed in our previously reported square-planar coordinated Schiff base–nickel(II) complexes (Ülkü, Tahir, Uçar & Atakol, 1996; Tahir, Ülkü, Atakol & Kenar, 1996). Within the coordination octahedron, the maximum deviation of the bond angles from 90° is 6.93 (9)°. The maximum displacement of the Ni atom from the centre of the octahedron is 0.1120 (4) Å in the direction of the O2 atom. Each ligand provides two chelating rings to the coordination sphere. The two benzene rings make a dihedral angle of 15.2 (3)° with one another. Details of the hydrogen-bonding geometry are given in Table 3: although numerous intermolecular hydrogen bonds appear to stabilize the asymmetric molecule, it seems likely that the shortest of these are the most significant and the other interactions are a consequence of these. The IR spectrum of the complex is in agreement with the molecular structure; observed stretching frequencies (cm^{-1}) are C=N 1646, N—H 3361 and 3310, and N—O 1335 and 1300.

Experimental

1,3-Diaminopropane (0.074 g, 1 mmol) was added to a solution of 3,5-dinitrosalicylaldehyde (0.212 g, 1 mmol) in hot MeCN (50 ml) and the mixture heated to boiling point. A solution of $[Ni(CH_3COO)_2].4H_2O$ (2.490 g, 1 mmol) in hot methanol (30 ml) was added and the mixture was set aside for a week at room temperature. The precipitated crystals were filtered off and found to be suitable for X-ray data collection.

Crystal data

$[Ni(C_{10}H_{11}N_4O_5)_2]$
M_r = 593.156
Triclinic
$P\overline{1}$
a = 9.144 (1) Å
b = 11.087 (2) Å
c = 13.241 (1) Å
α = 91.64 (2)°
β = 102.62 (1)°
γ = 112.09 (2)°
V = 1204.6 (4) Å^3
Z = 2
D_x = 1.635 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 8.45–18.08°
μ = 0.877 mm^{-1}
T = 295 K
Prism
0.25 × 0.20 × 0.15 mm
Dark red

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (*MolEN*; Fair, 1990)
T_{min} = 0.844, T_{max} = 0.877
4229 measured reflections
4027 independent reflections

2980 reflections with $I > 3\sigma(I)$
R_{int} = 0.015
θ_{max} = 25.01°
$h = -10 \rightarrow 10$
$k = -13 \rightarrow 13$
$l = 0 \rightarrow 15$
3 standard reflections
frequency: 120 min
intensity decay: −0.9%

Refinement

Refinement on F
R = 0.031
wR = 0.038
S = 1.22
2916 reflections
352 parameters
H atoms: see below
Weighting scheme: see below

$(\Delta/\sigma)_{max}$ = 0.0003
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.10 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

Ni—O1	2.072 (2)	Ni—N2	2.084 (3)
Ni—O2	2.072 (1)	Ni—N3	2.064 (2)
Ni—N1	2.059 (2)	Ni—N4	2.077 (2)
O1—Ni—O2	92.99 (7)	O2—Ni—N4	178.56 (9)
O1—Ni—N1	85.74 (9)	N1—Ni—N2	94.0 (1)
O1—Ni—N2	177.03 (7)	N1—Ni—N3	166.0 (1)
O1—Ni—N3	83.80 (9)	N1—Ni—N4	93.20 (8)
O1—Ni—N4	86.04 (9)	N2—Ni—N3	96.0 (1)
O2—Ni—N1	85.66 (7)	N2—Ni—N4	96.93 (9)
O2—Ni—N2	84.04 (8)	N3—Ni—N4	95.33 (9)
O2—Ni—N3	85.62 (7)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H21···O10^{i}	0.820	2.65 (3)	3.451 (3)	164 (3)
N4—H41···O5^{i}	0.813	2.35 (3)	3.088 (4)	151 (2)
N4—H42···O6^{ii}	0.877	2.54 (3)	3.296 (4)	144 (2)
C8—H81···O7^{iii}	0.950	2.77	3.453 (4)	129
C8—H82···O5^{ii}	0.950	2.73	3.326 (3)	121
C9—H92···O6^{iii}	0.950	2.59	3.418 (5)	144
C18—H182···O10^{i}	0.950	2.60	3.479 (5)	154
C19—H191···O9^{iv}	0.950	2.59	3.166 (5)	119
C20—H201···O10^{i}	0.950	2.58	3.475 (5)	157

Symmetry codes: (i) $x, y-1, z$; (ii) $-x, 1-y, -z$; (iii) $1-x, 1-y, -z$; (iv) $-x, 1-y, 1-z$.

The weighting scheme used was $w = 4F^2/[\sigma(I)^2 + (pF^2)^2]$, if $F^2 <$ cutoff × $[\sigma(I)^2 + (pF^2)^2]^{1/2}$, then the reflection is omitted (p = 0.04 and cutoff = 3.0). All non-H atoms were refined with anisotropic displacement parameters. H atoms on C atoms were placed geometrically 0.95 Å from their parent atoms and the H atoms of N2 and N4 were refined for a few cycles. For all H atoms, a riding model was used with $B_{eq}(H) = 1.3B_{eq}(C,N)$.

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: *ORTEP*II (Johnson, 1976) in *MolEN*. Software used to prepare material for publication: *MolEN*.

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Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry have been deposited with the IUCr (Reference: BM1107). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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{2-[(2,3-Dimethylphenyl)amino]benzoato-*O*:*O*′}trimethyltin(IV)

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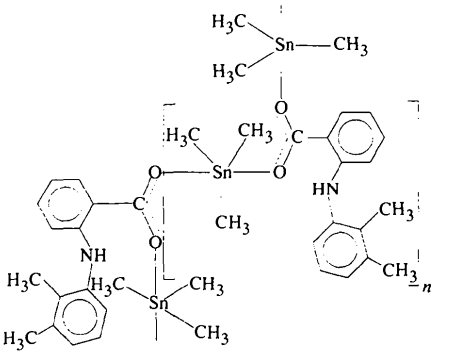
Abstract

In the title compound, $[Sn(C_{15}H_{14}NO_2)(CH_3)_3]$, the Sn atom has a distorted trigonal bipyramidal coordination. The three bonds to methyl groups in the equatorial plane have almost the same values [Sn—C range 2.106 (3)–2.113 (4) Å], but the Sn—O bonds in the axial positions involving one carboxyl O atom [Sn1—O1 2.153 (2) Å] and another symmetry-related carboxyl O atom in the *trans* position [Sn1—O2 2.495 (2) Å] have quite different values. The O1—Sn1—O2 angle is 173.60 (8)°. Each trimethyltin group bridges two neighbouring 2-[(2,3-dimethylphenyl)amino]benzoate ligands *via* carboxyl moieties to form polymeric chains.

Comment

Organotin carboxylates containing a six-membered ring with a heteroatom either as part of the ring skeleton or as an additional functional group, have various structural possibilities. Such variations depend on the nature of the heteroatom. If the heteroatom is a potential donor ligand, like N, O or S, it increases the coordination number of the Sn atom, either intramolecularly or by forming an intermolecular interaction with the Sn atom of a symmetry-related molecule. The known examples with nitrogen as the heteroatom are: dimethylchlorotin 2-pyridinecarboxylate (Nowell, Brooks, Beech & Hill, 1983), dicarboxylatotetraorganodistannoxane $\{[^nBu_2Sn(O_2CC_5H_4N)]_2O\}_2$ (Parulekar *et al.*, 1989) and three $Me_2Sn(chelate)_2$ compounds bearing five-membered chelate rings (Lockhart & Davison, 1987). In the last case, when the heteroatom is away from the CO_2 group (either included or attached to the ring), the intermolecular interactions result in the formation of an infinite polymeric chain, at least in the solid state, *e.g.* trimethylstannyl 2-furancarboxylate (Tiekink, Sandhu & Verma, 1989). In the present case, however, the heteroatom (in the form of an amino group) connects two six-membered rings, namely the benzoate and xylyl groups, but is itself located on the C atom adjacent to the CO_2 group. The structure of the title compound, (I), was determined in order to study the influence of the N atom on the coordination number of the Sn atom.



(I)

As can be seen from Fig. 1, the central five-coordinated Sn atom has a distorted trigonal bipyramidal environment. The three methyl groups are located in the basal plane and the more electronegative O atoms from symmetry-related carboxylate ligands occupy the axial positions. The Sn atom is 0.153 (2) Å out of the equatorial plane towards the more strongly bound O1 atom. The three Sn—C distances are equal within experimental error [2.106 (3), 2.113 (4) and 2.109 (3) Å] and are also in agreement with the values reported for related compounds. The Sn—O bond lengths are significantly different [Sn1—O1 2.153 (2) and Sn1—O2 2.495 (2) Å]. The C—O bonds within the carboxyl group also have different lengths. The longer C4—O1 bond [1.292 (4) Å] and the shorter Sn—O1 bond [2.153 (2) Å] share the same O atom and *vice versa*.