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(1,4-Dioxane-O){3,3',5,5'-tetrachloro-2,2'-[4-methyl-4-azaheptane-1,7-diyl-bis(nitrilomethylidene-N)]diphenolato-O,O'}nickel(II), [Ni(3,5-Cl₄salMetrien)]

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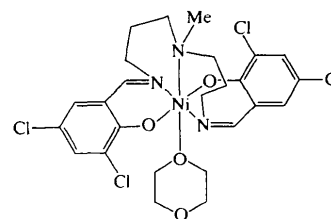
Abstract

In the title compound, [Ni(C₂₁H₂₁Cl₄N₃O₂)(C₄H₈O₂)], the Ni atom has a distorted octahedral coordination geometry in which the pentadentate Schiff base ligand acts as an N₃O₂ donor and a molecule of 1,4-dioxane occupies the remaining coordination position. The N atoms adopt a meridional arrangement, coplanar with the O-donor atom of the dioxane molecule, and the ligand O atoms are *trans*-related. This conformation results in an approximate square-pyramidal coordination for the pentadentate ligand, with the dioxane molecule *trans* to the amine N atom.

Comment

We are currently interested in the redox properties of nickel(II) complexes with mixed-donor polydentate Schiff base ligands (Freire & de Castro, 1998; Azevedo *et al.*, 1994; Carrondo *et al.*, 1993; de Castro & Freire, 1990) due to their potential use as synthetic catalysts and as models for metalloenzymes. We reported previously that nickel(II) complexes with N₂O₂-tetradentate Schiff base ligands derived from salicylaldehyde and diamines are oxidized to nickel(III) only in the presence of strong donating solvents (Freire & de Castro, 1998; Vilas-Boas *et al.*, 1997; Azevedo *et al.*, 1994; Carrondo *et al.*, 1993; de Castro & Freire, 1990). In order to

overcome the strong solvent effect on the oxidative properties of the latter complexes, we have prepared a group of pentadentate Schiff base ligands using the same aldehyde derivatives but condensed with triamines, and have studied the feasibility of their nickel(II) complexes being oxidized to nickel(III). Due to the variability of coordination modes of these pentadentate ligands (Freyberg *et al.*, 1979; Healey *et al.*, 1975), we found it necessary to determine the structure of the title complex, [Ni(3,5-Cl₄salMetrien)], to ascertain the coordination mode of the Schiff base ligand.



[Ni(3,5-Cl₄salMetrien)]

The structure consists of discrete molecules in which the Ni atom has a distorted octahedral coordination geometry, with the pentadentate ligand acting as an N₃O₂ donor and a molecule of 1,4-dioxane occupying the remaining coordination site (Fig. 1). The N atoms adopt a *mer* arrangement, coplanar with the O-donor atom of the dioxane molecule, and consequently the Schiff base ligand O atoms are *trans*-related. In the observed conformation, the pentadentate ligand coordination is approximately square pyramidal, leaving the other axial position *trans* to the amine N atom free to bind a dioxane molecule. The equatorial bond distances are similar, but the Ni—N(amine) axial bond distance is much longer than any of the equatorial ones. All bond distances are longer than those observed in the homologous complexes with the Schiff base ligand derived from the non-substituted aldehyde, which exhibit a distorted trigonal-bipyramidal structure (Di Vaira *et al.*, 1971). The longest bond is that of Ni—O(dioxane), as expected for a weakly coordinated monodentate ligand. The angular distortion from normal octahedral geometry is in the range 3–11°, and the maximum deviation of the Ni atom from the least-squares equatorial plane of coordination (N1A/O1A/N1/O1) is 0.093(1) Å. However, the ligand chelate-ring atoms (N1A/C7A/C6A/C1A/O1A and N1/C7/C6/C1/O1) define planes that make angles of 34.2(1) and 31.6(1)°, respectively, with the plane of coordination, and each is almost coplanar with the plane defined by the atoms of the corresponding benzene ring; the angle between the two salicyl moieties is 71.2(1)°. The umbrella shape of the molecule may be a consequence of steric constraints imposed by the long flexible —(CH₂)₃—N(CH₃)—(CH₂)₃— imine bridge, which exhibits disorder in some of the C atoms; this dis-

order affects the orientation of the methyl group bound to the amine N2 atom and has prevented the location of the methyl H atoms.

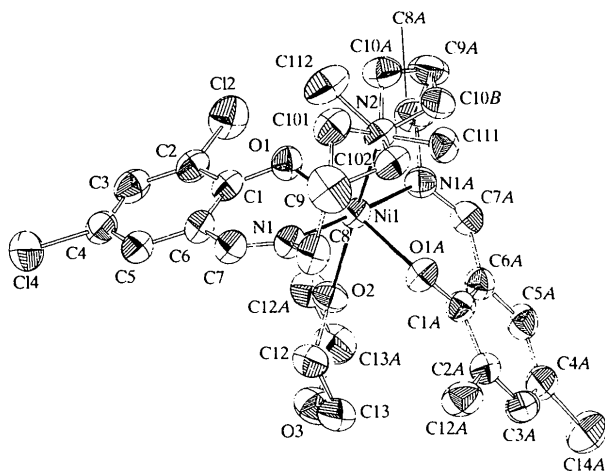


Fig. 1. The molecular structure of [Ni(3,5-Cl₄salMetrien)] with the atom-labelling scheme and 50% probability displacement ellipsoids. H atoms have been omitted for clarity. Both positions of the disordered atoms are shown.

Nickel(II) complexes with structurally related pentadentate ligands usually exhibit a distorted trigonal-bipyramidal structure or one that is intermediate between the latter and a square pyramid (Di Vaira *et al.*, 1971; Seleborg *et al.*, 1971), although octahedral complexes have also been observed, with the remaining coordination site usually occupied by a molecule of the crystallization solvent (Cameron & McCullough, 1990; Freyberg *et al.*, 1979). In these latter complexes, the pentadentate ligand usually adopts a conformation in which the N atoms have a *mer* arrangement, but leaving the phenolic O atoms in a *cis* position and the solvent molecule *cis* to the amine N atom.

Experimental

The title nickel(II) complex was prepared by addition of an ethanolic solution of nickel acetate monohydrate to a stoichiometric amount of the ligand in ethanol. The resulting solution was refluxed for 1 h and upon cooling, a green solid was obtained and recrystallized from acetonitrile. Crystals of diffractometric quality were obtained by slow evaporation of *N,N'*-dimethylformamide/1,4-dioxane solutions.

Crystal data

[Ni(C₂₁H₂₁Cl₄N₃O₂)-
(C₄H₈O₂)]
M_r = 636.01
Monoclinic
C2/c

Mo K α radiation
 λ = 0.71069 Å
Cell parameters from 458
reflections
 θ = 4.8–28.2°

a = 28.308 (3) Å
b = 11.306 (3) Å
c = 20.622 (3) Å
 β = 123.50 (2)°
V = 5503.7 (18) Å³
Z = 8
D_x = 1.535 Mg m⁻³
D_m not measured

μ = 1.130 mm⁻¹
T = 298 (2) K
Block
0.4 × 0.3 × 0.3 mm
Red

Data collection

Stoe Image Plate Detector
System (IPDS) diffractometer
Area-detector scans
Absorption correction: none
28 622 measured reflections
6208 independent reflections
4420 reflections with
I > 2 σ (*I*)

*R*_{int} = 0.054
 θ_{\max} = 28.17°
h = -36 → 37
k = -14 → 14
l = -24 → 24
3 standard reflections
frequency: 90 min
intensity decay: none

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.046
wR(*F*²) = 0.091
S = 1.346
5656 reflections
434 parameters
Only coordinates of H atoms
refined
 $w = 1/[\sigma^2(F_o^2) + (0.0220P)^2 + 7.2932P]$
where $P = (F_o^2 + 2F_c^2)/3$

(Δ/σ)_{max} = 0.008
 $\Delta\rho_{\max}$ = 0.378 e Å⁻³
 $\Delta\rho_{\min}$ = -0.482 e Å⁻³
Extinction correction:
SHELXL93
Extinction coefficient:
0.00054 (15)
Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Ni1—O1	2.006 (2)	Ni1—N1A	2.028 (2)
Ni1—N1	2.019 (3)	Ni1—N2	2.147 (3)
Ni1—O1A	2.021 (2)	Ni1—O2	2.260 (2)
O1—Ni1—N1	87.61 (9)	O1A—Ni1—N2	94.83 (9)
O1—Ni1—O1A	169.97 (9)	N1A—Ni1—N2	90.08 (10)
N1—Ni1—O1A	93.97 (9)	O1—Ni1—O2	86.04 (8)
O1—Ni1—N1A	91.75 (9)	N1—Ni1—O2	90.29 (9)
N1—Ni1—N1A	179.25 (10)	O1A—Ni1—O2	84.05 (8)
O1A—Ni1—N1A	86.72 (9)	N1A—Ni1—O2	90.07 (9)
O1—Ni1—N2	95.08 (9)	N2—Ni1—O2	178.86 (9)
N1—Ni1—N2	89.58 (10)		

Data collection: *IPDS* (Stoe, 1996a). Cell refinement: *CELL* (Stoe, 1996b). Data reduction: *INTEGRATE* (Stoe, 1996c). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1403). Services for accessing these data are described at the back of the journal.

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Tri-*n*-butyl(*N*-maleoyl- β -alaninato)tin†

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Abstract

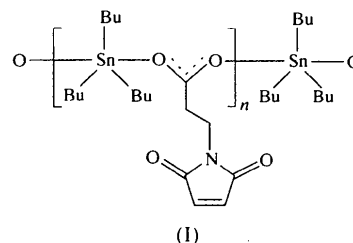
The Sn atom in [Sn(C₄H₉)₃(C₇H₆NO₄)]_n adopts a distorted trigonal-bipyramidal geometry, with three *n*-butyl groups defining the trigonal plane [mean Sn—C dis-

† Alternative name: *catena*-poly[[trimethyltin(IV)]- μ -[3-(2,5-dioxo-3-pyrazolin-1-yl)propionoato-*O*:*O'*]].

tance 2.145 (1) Å] and the axial positions occupied by the O atoms of different carboxylate groups having significantly different Sn—O bond lengths [2.215 (5) and 2.424 (5) Å]. The structure forms a polymeric chain of complex molecules linked *via* carboxylate moieties.

Comment

The structural chemistry of triorganotin complexes of amino acids and protected amino acids has revealed a wide variety of features and a rich diversity of structural motifs. For example, in the crystal structures of aquatributyltin (*N*-phthaloylglycinate) (Ho *et al.*, 1980), tricyclohexyl(*N*-phthaloylglycinate)tin (Ng & Kumar Das, 1997*a*), tricyclohexyl[*(N,N*-diethylthiocarbamoylthio)acetato-*O*]tin (Ng & Kumar Das, 1997*b*) and aquatrimethyltin 4-(4-chlorophenyl)-2-phenyl-5-thiazoleacetate (Parvez, Ali, Mazhar, Bhatti & Khokhar, 1999), Sn atoms show distorted bipyramidal geometry. On the other hand, the Sn atom adopts a tetrahedral geometry in the structure of *N*-phthaloylleucinate triphenyltin (Ng *et al.*, 1990). In a continuation of our work on the structural chemistry of organotin complexes of carboxylate-protected amino acids (Bhatti *et al.*, 1999; Parvez, Ali, Mazhar, Bhatti & Khokhar, 1999; Parvez, Ali, Mazhar, Bhatti & Choudhary, 1999), we now report the crystal structure of tri-*n*-butyl(*N*-maleoyl- β -alaninato)tin, (I).



The structure of (I) is presented in Fig. 1. The Sn atom has three *n*-butyl groups bonded in equatorial positions, with Sn—C distances [mean 2.145 (8) Å] equal within experimental error and in agreement with the values reported for related structures (Allen *et al.*, 1983). The axial positions are occupied by O atoms of carboxylate residues, with a linear O—Sn—O angle of 171.88 (17)°. The intramolecular Sn1—O1 separation of 2.215 (5) Å is significantly shorter than the intermolecular Sn1—O2' distance of 2.424 (5) Å [symmetry code: (i) $\frac{1}{2} + x, \frac{1}{2} - y, z$], indicating that the former is a covalent bond and the latter is a coordinate bond. The Sn atom has a distorted trigonal-bipyramidal geometry, with the Sn atom 0.149 (5) Å out of the equatorial plane formed by the three methyl C atoms towards the more strongly bound O1 atom.

The structure is composed of infinite chains of (I) running parallel to the *a* axis. The molecular dimensions in the *N*-maleoyl- β -alaninate ligand are normal.