

0.016 (7) Å at C(23) of (I)]. The Cu—O—C—C—N(amino acid) five-membered chelate rings have an envelope conformation with N(4) 0.326 (7) Å out of plane in (I) and C(3) 0.256 (9) Å out of plane in (II). These variations in conformation are assigned to packing forces. In compound (I) O(2) and N(4) are hydrogen bonded to the hydrate water molecule [lengths: OW...O(2ⁱ) 2.805 (8) and OW...N(4ⁱⁱ) 3.15 (2) Å; symmetry code: (i) $x-\frac{1}{2}, \frac{1}{2}-y, 1-z$; (ii) $\frac{3}{2}-x, 1-y, \frac{1}{2}+z$], while in (II) only O(W1) (apical position) is strongly hydrogen bonded to O(W2) [O(W2)...O(W1ⁱ) 2.69 (1) Å; (i) x, y, z].

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Structure of {N-[2-(2-Aminoethylamino)ethyl]salicylideneaminato-O,N,N',N''}nickel(II) Perchlorate

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Abstract. [Ni(C₁₁H₁₆N₃O)]ClO₄, $M_r = 364.43$, monoclinic, $P2_1/c$, $a = 8.930$ (4), $b = 13.391$ (5), $c = 11.902$ (6) Å, $\beta = 98.34$ (4)°, $V = 1408$ (1) Å³, $Z = 4$, $D_m = 1.74$ (2), $D_x = 1.718$ (1) Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 1.59$ mm⁻¹, $F(000) = 752$, $T = 295$ K, $R = 0.078$ for 2498 unique observed reflections. The structure consists of [Ni(C₁₁H₁₆N₃O)]⁺ complex cations and perchlorate anions. The coordination polyhedron around Ni is a distorted square with the tetradentate C₁₁H₁₆N₃O⁻ ligand (saden) bonded to the metal through one O and three N atoms. The perchlorate anion is disordered.

Introduction. The study of the title compound was undertaken as part of an investigation of complexes with unsymmetrical tetradentate Schiff bases (Haber, 1986).

Experimental. The crystals were prepared by crystallization from a mixture of nickel(II) perchlorate, salicylaldehyde and diethylenetriamine from aqueous ethanol (Haber, 1986). Orange crystals were obtained, stable in air and to X-rays. Density determined pycnometrically. A sphere-shaped crystal of $r = 0.15$ mm was used for the measurements. Syntex P2₁ diffractometer, graphite monochromator, 20 reflections with 2θ from 8.86 to 20.66° for measuring lattice

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Table 1. Atomic coordinates [$\times 10^4$, for O(3)–O(5) $\times 10^3$] and equivalent isotropic thermal parameters U_{eq} [for O(3)–O(5) U_{iso} $\times 10^3$] with e.s.d.'s in parentheses

$$U_{eq} = (U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta)/3.$$

	x	y	z	$U_{eq}/U_{iso}(\text{\AA}^2)$
Ni	941 (1)	4436 (1)	6730 (1)	35.4 (3)
Cl	2861 (2)	1528 (2)	6552 (2)	58.7 (7)
O(1)	-945 (5)	3886 (3)	6330 (4)	39 (1)
N(1)	462 (8)	4758 (5)	8224 (6)	48 (2)
N(2)	2863 (7)	5038 (5)	7218 (6)	49 (2)
N(3)	1701 (6)	4073 (4)	5433 (5)	38 (2)
C(1)	1663 (10)	5401 (7)	8828 (7)	62 (3)
C(2)	3105 (10)	5069 (8)	8462 (7)	64 (3)
C(3)	4008 (8)	4504 (6)	6634 (7)	57 (3)
C(4)	3309 (8)	4373 (6)	5428 (7)	51 (2)
C(5)	1031 (7)	3557 (5)	4598 (5)	39 (2)
C(6)	-497 (7)	3202 (5)	4538 (5)	35 (2)
C(7)	-1391 (7)	3367 (5)	5419 (5)	35 (2)
C(8)	-2866 (8)	2939 (5)	5277 (6)	43 (2)
C(9)	-3400 (9)	2387 (6)	4336 (6)	51 (3)
C(10)	-2514 (9)	2205 (6)	3493 (6)	51 (3)
C(11)	-1108 (9)	2606 (5)	3589 (6)	45 (2)
O(2)	2924 (10)	503 (6)	6817 (8)	119 (3)
O(31)	350 (1)	183 (1)	564 (1)	75 (3)
O(41)	379 (2)	196 (1)	756 (1)	187 (10)
O(51)	140 (1)	182 (1)	660 (1)	89 (4)
O(32)	225 (2)	223 (1)	722 (1)	96 (4)
O(42)	439 (1)	187 (1)	655 (2)	128 (6)
O(52)	217 (2)	160 (1)	538 (1)	160 (8)

Table 2. Bond distances (\AA) and angles ($^\circ$)

Ni–O(1)	1.837 (4)	O(1)–Ni–N(1)	90.7 (2)
Ni–N(1)	1.936 (7)	O(1)–Ni–N(3)	96.4 (2)
Ni–N(2)	1.909 (6)	N(1)–Ni–N(2)	86.3 (3)
Ni–N(3)	1.839 (6)	N(2)–Ni–N(3)	86.7 (3)
N(1)–C(1)	1.48 (1)	N(1)–C(1)–C(2)	106.4 (7)
C(1)–C(2)	1.49 (1)	C(1)–C(2)–N(2)	107.3 (7)
C(2)–N(2)	1.47 (1)	C(2)–N(2)–C(3)	118.1 (7)
N(2)–C(3)	1.50 (1)	N(2)–C(3)–C(4)	106.5 (6)
C(3)–C(4)	1.49 (1)	C(3)–C(4)–N(3)	107.3 (6)
C(4)–N(3)	1.492 (8)	C(4)–N(3)–C(5)	118.8 (6)
N(3)–C(5)	1.285 (9)	N(3)–C(5)–C(6)	123.2 (6)
C(5)–C(6)	1.437 (9)	C(5)–C(6)–C(7)	122.8 (6)
C(6)–C(7)	1.424 (9)	C(6)–C(7)–O(1)	124.1 (6)
C(7)–O(1)	1.300 (7)	C(6)–C(7)–C(8)	117.2 (6)
C(7)–C(8)	1.424 (9)	C(7)–C(8)–C(9)	121.4 (6)
C(8)–C(9)	1.368 (10)	C(8)–C(9)–C(10)	121.2 (7)
C(9)–C(10)	1.386 (10)	C(9)–C(10)–C(11)	119.3 (6)
C(10)–C(11)	1.354 (10)	C(10)–C(11)–C(6)	122.2 (6)
C(11)–C(6)	1.425 (9)	C(11)–C(6)–C(7)	118.6 (6)
Cl–O(2)	1.407 (8)	O(2)–Cl–O(31)	117.5 (7)
Cl–O(31)	1.36 (1)	O(2)–Cl–O(41)	101.6 (8)
Cl–O(41)	1.48 (1)	O(2)–Cl–O(51)	106.3 (7)
Cl–O(51)	1.37 (1)	O(2)–Cl–O(32)	122.2 (7)
Cl–O(32)	1.39 (1)	O(2)–Cl–O(42)	107.5 (7)
Cl–O(42)	1.44 (1)	O(2)–Cl–O(52)	106.1 (8)
Cl–O(52)	1.44 (1)		

parameters; ω - 2θ scan; absorption ignored; max. $(\sin\theta)/\lambda = 0.681 \text{ \AA}^{-1}$; h -12–12, k 0–18, l 0–16; three standard reflections measured after 33 reflections with no significant variation; 4157 measured reflections, 3765 unique reflections, 1267 unobserved reflections with $I < 1.96\sigma(I)$; heavy-atom method; F magnitudes in full-matrix least-squares refinement; H(N) atoms localized from a $\Delta\rho$ map, H(C) atoms localized in theoretical positions; all positional parameters were

refined with the exception of those of H(C) atoms; anisotropic thermal parameters of Ni, Cl, O(1), N, C and isotropic thermal parameters of O(Cl) and H atoms were refined; $R = 0.078$, $wR = 0.082$, $w = 2.29/[\sigma^2(F) + 0.0009F^2]$; the ratio of max. least-squares shift to e.s.d. in the last refinement cycle -0.935 for O(51); max. and min. heights in a final $\Delta\rho$ map 1.74 [0.85 \AA from O(51)] and -0.82 e \AA^{-3} ; atomic scattering factors and corrections for anomalous dispersion from *International Tables for X-ray Crystallography* (1974); ICL 4-72 computer; program *SHELX76* (Sheldrick, 1976).*

Discussion. The final atomic parameters are given in Table 1. The selected intramolecular bond distances and angles are given in Table 2. The complex cation with omitted H atoms is depicted in Fig. 1.

In the cation, the coordination polyhedron around Ni approximates to the square formed by three N and one O of the saden ligand. The deviations of the NiN₃O core from the best plane are in the range of -0.048 (7) to 0.064 (5) \AA . The deviations of the atoms in the five-membered chelate rings Ni–N(1)–C(1)–C(2)–N(2) and Ni–N(2)–C(3)–C(4)–N(3) from the best planes are in the range of -0.245 (9) [C(1)] to 0.29 (1) [C(2)] and -0.224 (7) [N(2)] to 0.280 (8) \AA [C(3)] respectively. The conformations of the first and second chelate rings correspond to skew and envelope respectively. The deviations of the atoms in the six-membered chelate ring Ni–N(3)–C(5)–C(6)–C(7)–O(1) from

* Lists of atomic coordinates and isotropic thermal parameters for H atoms, bond distances and angles for the H(N) atoms, anisotropic thermal parameters for the non-H atoms and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44664 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

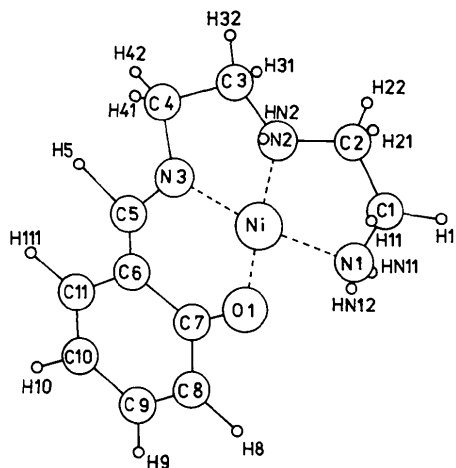


Fig. 1. A view of the $[\text{Ni}(\text{C}_{11}\text{H}_{16}\text{N}_3\text{O})]^+$ complex cation along b.

the best plane are in the range of -0.022 (4) [O(1)] to 0.016 (1) Å (Ni). The phenyl ring is planar with the value of χ^2 (0.05, 3) = 6.6. The torsion angles N(1)–C(1)–C(2)–N(2) and N(2)–C(3)–C(4)–N(3) are 50 and -42° respectively. From the above planes, the largest dihedral angle of 12.9° is between the phenyl and the Ni–N(2)–C(3)–C(4)–N(3) planes.

The perchlorate anion is disordered. The maxima of the electron density related to the O atoms of the perchlorate anion were interpreted as two perchlorate anions with one shared Cl–O(2) bond and with occupancy factors of 0.5 for the O atoms O(31), O(32), O(41), O(42), and O(51), O(52) respectively. From a number of perchlorate locations tried, this model led to the best *R*-factor value. The large thermal parameters of O(Cl) atoms and the allocation of the maxima and minima in the $\Delta\rho$ map to these atoms shows that the perchlorate anion may rotate along the Cl–O(2) bond. This is in accordance with the fact that the ν_3 and ν_4

bands (1085 and 620 cm^{-1} respectively) in the infrared spectrum are not split.

An inspection of the crystal packing shows that the bonding of the complex cations and the perchlorate anions is predominantly ionic. The shortest intermolecular contacts are Ni \cdots O(32) = 3.20 (1), N(1) \cdots O(2ⁱ) = 3.18 (1) and N(1) \cdots O(51ⁱ) = 3.25 (2) Å ($i = -x, 0.5+y, 1.5-z$).

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Dibutyldichlorotin(IV)

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Abstract. [SnCl₂(C₄H₉)₂], $M_r = 303.8$, monoclinic, *C2/c*, $a = 14.071$ (6), $b = 9.418$ (8), $c = 19.836$ (11) Å, $\beta = 103.78$ (4) $^\circ$, $V = 2553$ (5) Å³, $Z = 8$, $D_x = 1.58\text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 23.9\text{ cm}^{-1}$, $F(000) = 1200$, $T = 298\text{ K}$, $R = 0.070$ for 1163 reflections with $I \geq 3\sigma(I)$. In the lattice, molecules of Bu₂SnCl₂ form polymeric chains *via* asymmetric Sn–Cl \cdots Sn bridges which are bent at Cl [Sn–Cl \cdots Sn = 104.3 (1), 104.8 (1) $^\circ$] and nearly linear at Sn [Cl \cdots Sn–Cl = 172.3 (1), 173.1 (1) $^\circ$]. Overall the geometry at Sn is distorted octahedral with C–Sn–C, Cl–Sn–Cl and $\langle\text{Cl–Sn–C}\rangle$ angles of 132.1 (7), 97.2 (2) and 105.6 (4) $^\circ$, respectively. The primary Sn–Cl and secondary Sn \cdots Cl distances are 2.372 (5) and 2.388 (5) Å and 3.544 (5) and 3.514 (5) Å, respectively. The observed CSnC angle is significantly larger than that predicted by NMR data for Bu₂SnCl₂ in solution but is comparable to that observed in Et₂SnCl₂ and related molecules.

Introduction. The discussion concerning the degree of association, the nature of the intra- or intermolecular interactions or secondary bonding and the influence of

these interactions on the primary geometry of the Sn^{IV} atoms in the crystal structures of several diorgano- or triorganotin(IV) halides, R₂SnX₂ or R₃SnX continues unabated (see, for example, Alcock & Sawyer, 1977; Amini, Holt & Zuckerman, 1987; Baxter, Holt & Zuckerman, 1985; Ganis, Valle, Furlani & Tagliavini, 1986; Lefferts, Molloy, Hossain, van der Helm & Zuckerman, 1982; Molloy, Quill & Nowell, 1985). Moreover, some correlations between intramolecular and intermolecular parameters by the use of the structure correlation method on data for Sn^{IV} compounds in the Cambridge Structural Database have been reported (Britton & Dunitz, 1981) and recently some evidence for molecular association in Me₂SnCl₂ has been presented using IR-band frequency shifts as a function of temperature (Herber, 1985). Similarly a very recent comparison of the solid-state and solution NMR structures of Me₂SnCl₂ (Lockhart & Farlee, 1987) has indicated that there is a small but significant change in the structure arising from solid-state effects (most notably in a change in the Me–Sn–Me angle of $ca\ 6^\circ$). The present structure was determined in order to provide further data for these discussions, par-