

Structure of $\{N-[2-(2\text{-Aminoethylamino})ethyl]salicylideneaminato-O,N,N',N''\}$ nickel(II) Rhodanide

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Abstract. $[\text{Ni}(\text{C}_{11}\text{H}_{16}\text{N}_3\text{O})]\text{NCS}$, $M_r = 323.1$, monoclinic, $P2_1/c$, $a = 13.121(3)$, $b = 12.439(5)$, $c = 17.366(5)$ Å, $\beta = 96.52(2)^\circ$, $V = 2816(2)$ Å³, $Z = 8$, $D_m = 1.51(2)$, $D_x = 1.524(1)$ Mg m⁻³, $\lambda(\text{Mo K}\alpha) = 0.70926$ Å, $\mu = 1.47$ mm⁻¹, $F(000) = 1344$, $T = 295$ K, $R = 0.070$ for 3941 observed reflections. There are two independent but almost identical $\text{Ni}(\text{saden})\text{NCS}$ ($\text{saden} = \text{C}_{11}\text{H}_{16}\text{N}_3\text{O}^-$) molecules with $[\text{Ni}(\text{saden})]^+$ complex cations and rhodanide anions. The coordination polyhedron around Ni is a distorted square with the tetradentate saden ligand bonded to the metal through one O and three N atoms.

Introduction. The study of the title compound is a continuation of the investigation of complexes with unsymmetrical tetradentate Schiff bases (Haber, Loub, Podlahová, Kopf & Weiss, 1988). The aim is to obtain further information about the structure of the saden ligand and to solve the problem of the coordination of the rhodanide groups, which could not be determined from IR spectra and magnetic susceptibility measurement (Haber & Holý, 1988).

Experimental. The crystals were prepared by Haber (1986) in the form of reddish-orange intergrowths, stable in air and to X-rays. The density was measured by flotation in a $\text{CHCl}_3/\text{CH}_2\text{I}_2$ mixture. A spherical crystal of $r = 0.10$ mm was used for the measurements. Hilger & Watts diffractometer, graphite monochromator, 20 reflections with 2θ from 13 to 20° for refinement of lattice parameters; θ - 2θ scan; absorption ignored; max. $(\sin\theta)/\lambda = 0.60$ Å⁻¹; h 0–15, k 0–14, l –20–20; three standard reflections measured after 97 reflections with variation < 1.5%; 5647 measured reflections, 4978 unique reflections, 3941 observed reflections with $I \geq 1.96\sigma(I)$; heavy-atom method; F magnitudes in full-matrix least-squares refinement in two blocks; H atoms localized in

calculated positions; all positional parameters were refined with the exception of those of H atoms; anisotropic thermal parameters of Ni, O, N and C atoms and isotropic thermal parameters of H atoms [one for H bonded to N and C(1)–C(4), one for phenyl C] were refined; $R = 0.070$, $wR = 0.075$, $w = 1/[\sigma^2(F) + 0.0009F^2]$; $(\Delta/\sigma)_{\text{max}} = -0.561$ for U_{11} of C(1); max. and min. heights in final $\Delta\rho$ map 1.03 and -1.18 e Å⁻³; atomic scattering factors and corrections for anomalous dispersion from *International Tables for X-ray Crystallography* (1974); ICL 4-72 computer; programs *SHELXS86* (Sheldrick, 1986), *SHELX76* (Sheldrick, 1976) and *SCHAKAL86* (Keller, 1986).†

Discussion. The final atomic parameters are given in Table 1. Selected intramolecular bond distances and angles are given in Table 2. The complex cation of molecule (1) is depicted in Fig. 1. There are two independent molecules (1) and (2). Statistically significant differences are found only in the Ni–O(1) and Ni–N(1) distances and in the N–C–S angles. The complex cations of molecules (1) and (2) are nearly perpendicular, the angle between the NiN_3O best planes being 96°. In the cation, the coordination polyhedron around Ni approximates to a square formed by three N and one O of the saden ligand. The deviations of the NiN_3O core from the best plane are in the range $-0.024(5)$ to $0.0305(7)$ Å for molecule (1) and $-0.065(5)$ to $0.049(5)$ Å for molecule (2). The deviations of the C atoms in the five-membered chelate rings from the Ni(1)–N(11)–N(21) and Ni(1)–N(21)–N(31) planes for molecule (1) are $0.023(8)$ and $-0.620(8)$ Å for C(11) and C(21) and $-0.577(7)$ and

† Lists of atomic coordinates and isotropic thermal parameters for the H 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 51479 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters U_{eq} ($\times 10^3$) with e.s.d.'s in parentheses
$$U_{eq} = [U_{22} + (U_{11} + U_{33} + 2U_{13}\cos\beta)/\sin^2\beta]/3.$$

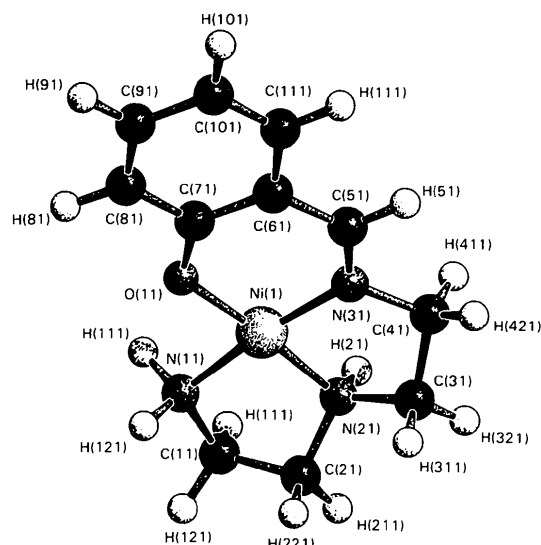
	x	y	z	$U_{eq}(\text{\AA}^2)$
Ni(1)	5602.2 (6)	4208.9 (6)	3467.2 (4)	45.2 (3)
O(11)	5748 (3)	5571 (3)	3892 (2)	47 (1)
N(11)	6986 (4)	4246 (4)	3222 (3)	54 (2)
N(21)	5514 (4)	2862 (4)	2965 (3)	56 (2)
N(31)	4246 (4)	4011 (4)	3620 (3)	50 (2)
C(11)	7234 (6)	3249 (6)	2807 (5)	68 (3)
C(21)	6256 (6)	2843 (6)	2393 (5)	71 (3)
C(31)	4435 (5)	2658 (6)	2676 (4)	67 (3)
C(41)	3812 (6)	2984 (6)	3319 (4)	64 (3)
C(51)	3675 (5)	4665 (6)	3957 (4)	54 (2)
C(61)	4029 (5)	5683 (5)	4268 (3)	45 (2)
C(71)	5023 (4)	6094 (5)	4204 (3)	44 (2)
C(81)	5256 (5)	7144 (5)	4498 (4)	52 (2)
C(91)	4534 (6)	7735 (6)	4847 (4)	62 (2)
C(101)	3568 (6)	7302 (7)	4927 (4)	66 (3)
C(111)	3327 (5)	6298 (6)	4644 (4)	58 (2)
S(1)	7534 (3)	-331 (3)	3143 (2)	133 (2)
N(1)	5602 (4)	273 (5)	3524 (3)	47 (2)
C(1)	6396 (12)	221 (9)	3400 (5)	116 (5)
Ni(2)	1230.3 (5)	1453.4 (6)	1776.4 (4)	43.6 (3)
O(12)	2195 (3)	1066 (4)	2565 (2)	51 (1)
N(12)	2300 (4)	1981 (5)	1192 (3)	54 (2)
N(22)	287 (4)	1864 (4)	926 (3)	52 (2)
N(32)	104 (4)	1152 (4)	2268 (3)	49 (2)
C(12)	1835 (5)	2230 (6)	377 (4)	64 (3)
C(22)	791 (5)	2668 (6)	460 (4)	62 (2)
C(32)	-663 (5)	2219 (6)	1230 (4)	65 (3)
C(42)	-886 (5)	1349 (6)	1805 (4)	63 (3)
C(52)	104 (5)	792 (5)	2962 (4)	53 (3)
C(62)	1016 (5)	536 (5)	3466 (3)	46 (2)
C(72)	2014 (5)	679 (5)	3255 (3)	45 (2)
C(82)	2848 (5)	423 (5)	3793 (4)	53 (2)
C(92)	2701 (6)	27 (6)	4512 (4)	66 (3)
C(102)	1734 (7)	-138 (6)	4728 (4)	67 (3)
C(112)	917 (6)	143 (5)	4206 (4)	60 (2)
S(2)	321 (3)	3492 (3)	3450 (2)	140 (2)
N(2)	-1058 (5)	4298 (6)	4429 (4)	65 (3)
C(2)	-556 (9)	3995 (7)	4049 (6)	96 (4)

0.028 (7) Å for C(31) and C(41). Both rings have the envelope conformation. The deviations of the C atoms in the analogous rings of molecule (2) are 0.235 (7) and -0.489 (7) Å for C(12) and C(22) and -0.642 (7) and 0.010 (7) Å for C(32) and C(42). The first ring has the half-chair conformation and the second ring the envelope conformation. The deviations of the atoms in the six-membered chelate rings Ni-N(3)-C(5)-C(6)-C(7)-O(1) from the best plane are in the ranges -0.016 (5) [N(31)] to 0.026 (5) Å [C(61)] and -0.010 (6) [C(52)] to 0.006 (5) Å [N(32)], respectively. The torsion angles N(1)-C(1)-C(2)-N(2) and N(2)-C(3)-C(4)-N(3) are -48 and 44° (molecule 1) and -53 and 46° (molecule 2), respectively.

The rhodanide anions have the expected bond lengths and angles. The bonding of the complex cations and the rhodanide atoms is predominantly ionic. The shortest distance between Ni atoms and rhodanide groups is Ni(2)-N(2ⁱ) = 3.393 (7) Å ($i = -x, y-0.5, 0.5-z$). The other distances are greater than 4 Å. The shortest intermolecular contacts are N(11)⋯O(12ⁱⁱ) = 2.912 (7), O(11)⋯N(12ⁱⁱ) = 3.121 (6) and N(11)⋯N(2ⁱⁱⁱ) = 3.125 (9) Å ($ii = 1-x, 0.5+y, 0.5-z$; $iii = 1+x, y, z$).

Table 2. Interatomic distances (Å) and angles (°)

	Molecule (1)	Molecule (2)
Ni-O(1)	1.849 (4)	1.821 (4)
Ni-N(1)	1.912 (5)	1.937 (5)
Ni-N(2)	1.886 (5)	1.887 (5)
Ni-N(3)	1.845 (5)	1.828 (5)
N(1)-C(1)	1.489 (9)	1.510 (8)
C(1)-C(2)	1.485 (10)	1.496 (10)
C(2)-N(2)	1.467 (10)	1.487 (9)
N(2)-C(3)	1.470 (9)	1.476 (9)
C(3)-C(4)	1.511 (11)	1.523 (11)
C(4)-N(3)	1.471 (9)	1.468 (8)
N(3)-C(5)	1.290 (9)	1.287 (9)
C(5)-C(6)	1.432 (9)	1.436 (9)
C(6)-C(7)	1.418 (9)	1.411 (9)
C(7)-O(1)	1.319 (7)	1.336 (7)
C(7)-C(8)	1.423 (9)	1.393 (8)
C(8)-C(9)	1.391 (10)	1.377 (10)
C(9)-C(10)	1.399 (11)	1.378 (12)
C(10)-C(11)	1.365 (11)	1.370 (11)
C(11)-C(6)	1.413 (10)	1.395 (9)
S-C	1.748 (15)	1.752 (12)
C-N	1.090 (16)	1.054 (14)
O(1)-Ni-N(1)	90.5 (2)	90.0 (2)
N(1)-Ni-N(2)	85.9 (2)	87.0 (2)
N(2)-Ni-N(3)	86.5 (2)	85.9 (2)
N(3)-Ni-O(1)	97.1 (2)	97.2 (2)
N-C-S	160 (1)	177 (1)

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

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