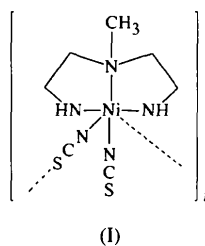Lorenz, I.-P., Walter, G. & Hiller, W. (1990). *Chem. Ber.* **123**, 979–982.

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(I)

Acta Cryst. (1998). C54, 208–210

A Polymeric Nickel(II) Thiocyanate Complex of N-(2-Aminoethyl)-N-methyl-1,2-ethanediamine†

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Abstract

The structure of [Ni(medien)(NCS)(μ-SCN)]$_n$ [medien is N-(2-aminoethyl)-N-methyl-1,2-ethanediamine, C$_5$H$_{15}$N$_3$] is a polymeric chain with each pair of neighbouring nickel(II) ions linked by one SCN⁻ bridging ligand. The coordination polyhedron about the Ni^{II} atom is a distorted octahedron consisting of three N atoms of the medien ligand coordinating facially, one N atom of the non-bridging thiocyanate ligand, and one N and one S atom of two bridging thiocyanate ligands. The five-membered chelate rings display envelope geometry.

Comment

The triamine complexes of nickel(II) thiocyanate exhibit a large variety of molecular structures. Depending on the coordination mode of the SCN⁻ anion and the chain length of the triamine, the resulting nickel(II) complexes are monomeric (Mukherjee *et al.*, 1994), dimeric (Mondal *et al.*, 1997) or polymeric (Vicente *et al.*, 1994). An X-ray structure analysis of the title complex, [Ni(medien)(NCS)$_2$] [medien is N-(2-amino-ethyl)-N-methyl-1,2-ethanediamine], (I), was motivated by our continued interest in establishing the coordination geometry around the metal centre and the effect of the substituent in the secondary amine on the conformation of the chelate rings.

The structure of the title complex, (I), is shown in Fig. 1. The structure consists of a polymeric chain of [Ni(medien)(NCS)$_2$] units in a *cis* configuration; each pair of neighbouring nickel(II) ions are linked by one SCN⁻ bridging ligand. Owing to the presence of one SCN⁻ terminal ligand on each Ni^{II} atom, the chains are neutral and linked by van der Waals forces in the crystal; there are no hydrogen bonds between the chains. The coordination polyhedron around the metal centre is best described as a distorted octahedron with an N$_5$S donor set. The two primary N atoms (N3 and N5) of the chelated triamine, the N atom of the non-bridging thiocyanate group (N1) and the symmetry-related S atom of the bridging thiocyanate moiety (S2^i; symmetry code as in Table 1) define an equatorial plane around the Ni atom; the remaining two N atoms, N2 and N4, are in *trans*-axial positions, with Ni displaced by 0.089 (1) Å towards N2. Consequently, the title complex has the same structural scheme, [Ni(medien)(NCS)(μ-SCN)]$_n$, as that reported for the μ-thiocyanatonickel(II) compounds (Mondal *et al.*, 1997; Vicente *et al.*, 1994), in which each Ni atom is bridged by only one thio-
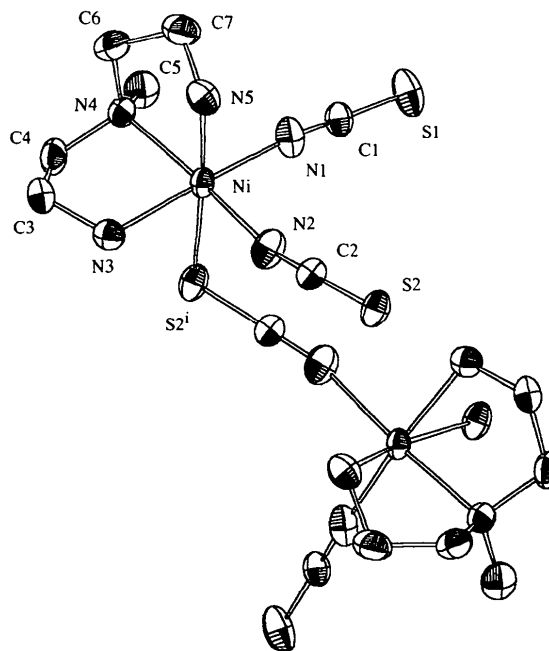

Fig. 1. A view of the title molecule with displacement ellipsoids shown at the 50% probability level.

cyanato ligand to its neighbour, with the other thio-cyanato ligand non-bridging.

The Ni—N distances are in the range 2.037 (2)–2.157 (2) Å and are consistent with corresponding values for the polymeric Ni^{II}–amine systems with octahedral metal coordination (Table 2). The observed lengthening of the Ni—N4 bond [2.156 (2) Å] compared with those of Ni—N3 [2.086 (3) Å] and Ni—N5 [2.078 (3) Å] is due to steric constraints introduced by the methyl substituent in the secondary amine. Table 2 reveals that the bridging Ni—S—C angle is practically constant [100.2 (1)–101.5 (1)°], but that the bridging Ni—N—C angle varies more widely [161.5 (6)–171.5 (3)°] in polymeric complexes of this kind. The two five-membered chelate rings associated with the metal centre display envelope conformations (C4 and C7 as flaps) and are approximately orthogonal to each other; the dihedral angle between the planar parts of the chelate rings (Ni, N3, N4, C3 and Ni, N4, N5, C6) is 84.4 (1)°.

Experimental

The title complex was synthesized by adding the medien ligand (1 mmol) dropwise with constant stirring to a methanolic solution (10 ml) of Ni(SCN)$_2$ (1 mmol). The resulting solution was kept in a desiccator for a few days and yielded blue crystals which were separated out, filtered and washed with methanol. Elemental analysis: calculated for C$_7$H$_{15}$N$_5$S$_2$Ni: C 28.7, H 5.1, N 23.9, Ni 20.1%; found: C 28.9, H 5.1, N 24.0, Ni 20.1%. Single crystals suitable for X-ray diffraction were obtained by recrystallization from acetonitrile–methanol.

Crystal data

[Ni(NCS)$_2$(C$_5$H$_{15}$N$_3$)]
M_r = 292.07
Monoclinic
$I2/a$
a = 15.476 (3) Å
b = 6.649 (1) Å
c = 24.080 (5) Å
β = 93.42 (2)°
V = 2473.4 (8) Å^3
Z = 8
D_x = 1.569 Mg m^{-3}
D_m = 1.573 Mg m^{-3}
D_m measured by flotation in benzene–bromoform mixture

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 8–16°
μ = 1.883 mm^{-1}
T = 293 (2) K
Prism
0.5 × 0.4 × 0.3 mm
Blue

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction:
ψ scans (North, Phillips & Mathews, 1968)
T_{min} = 0.504, T_{max} = 0.568
4283 measured reflections
2160 independent reflections

1944 reflections with $I > 2\sigma(I)$
R_{int} = 0.052
θ_{max} = 24.83°
h = $-18 \rightarrow 15$
k = $-7 \rightarrow 7$
l = $-15 \rightarrow 28$
3 standard reflections every 100 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.111
S = 1.081
2160 reflections
196 parameters
H atoms refined with individual U_{iso}

$w = 1/[\sigma^2(F_o^2) + (0.0806P)^2 + 0.2477P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.065
$\Delta\rho_{max}$ = 0.953 e Å^{-3}
$\Delta\rho_{min}$ = -0.735 e Å^{-3}
Extinction correction: none
Scattering factors from International Tables for Crystallography (Vol. C)

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

Ni—N1	2.037 (2)	Ni—S2^i	2.6621 (9)
Ni—N2	2.047 (3)	S1—C1	1.627 (3)
Ni—N5	2.078 (3)	S2—C2	1.652 (3)
Ni—N3	2.086 (3)	N1—C1	1.157 (4)
Ni—N4	2.156 (2)	N2—C2	1.146 (4)
N1—Ni—N2	91.85 (11)	N3—Ni—N4	82.21 (9)
N1—Ni—N5	90.93 (11)	N1—Ni—S2^i	88.06 (8)
N2—Ni—N5	92.86 (11)	N2—Ni—S2^i	93.19 (8)
N1—Ni—N3	171.90 (11)	N5—Ni—S2^i	173.90 (7)
N2—Ni—N3	91.33 (11)	N3—Ni—S2^i	84.32 (8)
N5—Ni—N3	96.36 (11)	N4—Ni—S2^i	91.69 (6)
N1—Ni—N4	95.29 (10)	C2—S2—Ni^{ii}	100.20 (10)
N2—Ni—N4	171.49 (10)	C1—N1—Ni	171.4 (3)
N5—Ni—N4	82.41 (10)	C2—N2—Ni	167.6 (3)
Ni—N3—C3—C4	29.6 (3)	Ni—N4—C6—C7	28.4 (3)
Ni—N4—C4—C3	43.5 (3)	Ni—N5—C7—C6	49.7 (3)
N3—C3—C4—N4	−49.9 (3)	N4—C6—C7—N5	−53.0 (3)

Symmetry codes: (i) $-\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$; (ii) $-\frac{1}{2} - x, y - \frac{1}{2}, 1 - z$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CAD-4 Software*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1995). Software used to prepare material for publication: *SHELXL93*.

Table 2. *A comparison of Ni—N(primary/secondary) and Ni—S(bridging) distances (Å), and Ni—S(bridging)—C(bridging) and Ni—N(bridging)—C(bridging) angles (°) in polynuclear octahedral nickel(II) thiocyanate complexes*

	[{Ni(medien)(NCS)$_2$}$_n$]^a	[{Ni(aepn)(NCS)$_2$}$_n$]^b	[{Ni(apmn)(NCS)$_2$}$_n$]^c	[{Ni(en)$_2$(NCS)}$_n$(PF$_6$)]^d
Ni—N(Pr)	2.078 (3)–2.086 (3)	2.081 (3)–2.104 (3)	2.084 (6)–2.088 (6)	2.072(6)–2.120 (5)
Ni—N(Sec)	2.156 (2)	2.101 (2)	2.176 (6)	
Ni—S(br)	2.662 (1)	2.632 (1)	2.553 (3)	2.621 (2)
Ni—S(br)—C(br)	100.2 (1)	101.5 (1)	100.5 (1)	100.8 (2)
Ni—N(br)—C(br)	167.6 (3)	170.8 (3)	161.5 (6)	171.5 (3)

Notes: (a) this work; (b) aepn is *N*-(2-aminoethyl)-1,3-propanediamine (Mondal *et al.*, 1997); (c) apmn is bis(3-aminopropyl)methylamine (Vicente *et al.*, 1994); (d) en is ethylenediamine (Monfort *et al.*, 1994).

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The Racemic C_3-Symmetrical Propeller Structure of Chlorotris(1,3-diphenyl-1,3-propanedionato-O,O')zirconium(IV)

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Abstract

The title compound, [ZrCl(C₁₅H₁₁O₂)₃], contains three 1,3-diphenyl-1,3-propanedionato (or dibenzoylmethanate) ligands arranged as propeller blades around the C_3 Zr—Cl axis to give a chiral molecule. The centrosymmetric space group contains a racemic mixture of left- and right-handed propellers. The coordination geometry around the seven-coordinate Zr metal atom is a capped octahedron.

Comment

Zirconium β-diketonate complexes have recently been described in combination with methylalumoxane as single-site catalysts for the polymerization of ethene (Janiak et al., 1994; Ueki et al., 1992) and styrene (Longo et al., 1994). The use of these chelate ligands or complexes in catalysis was based on the idea that bis- or tris-chelate complexes can assume chiral Δ and Λ forms. Chiral catalytic centres are a prerequisite for the tailored stereoregular coordination polymerization of prochiral α-olefins. To verify this formation of enantiomeric forms in the pre-catalytic chelate complexes, the molecular and crystal structures of the title compound, (I), were determined.

(I)
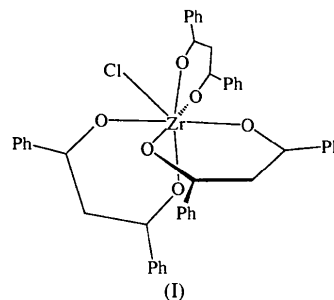
The molecular structure is shown in Fig. 1 and illustrates the C_3-symmetrical propeller arrangement of the diphenylpropanedionato ligands. A left- or right-handed position of the propeller 'blades' gives rise to the two enantiomeric forms. In the centrosymmetric space group $R\bar{3}$, the crystal comprises a racemic mixture. The crystal packing is based on the π-stacking of the phenyl groups. The parallel orientation of the phenyl π systems contrary to the geared or orthogonal stacking
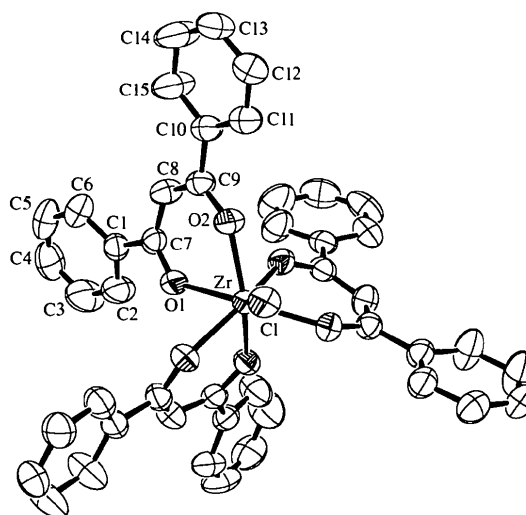

Fig. 1. The molecular structure of (1) viewed at an angle of 10° to the C_3 Cl—Zr axis; displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.