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Co-Crystallized (Macrocyclic tetraamine)-bis(thiocyanato-*N*)nickel(II) Complexes

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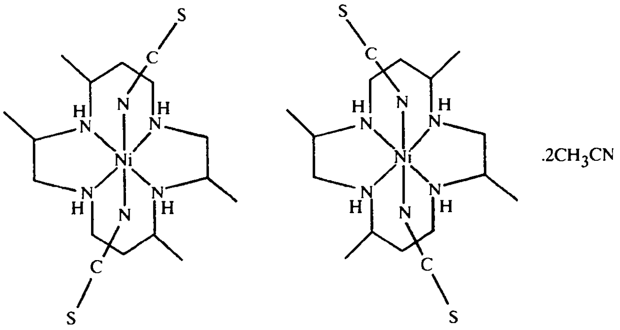
Abstract

In (2,7,9,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane-κ^4N)bis(thiocyanato-*N*)nickel(II) (2,5,9,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane-κ^4N)bis(thiocyanato-*N*)nickel(II) diacetonitrile solvate, $[NiL^1(NCS)_2][NiL^2(NCS)_2].2CH_3CN$, where L^1 and L^2 are isomeric tetraazacyclotetradecane ligands ($C_{14}H_{32}N_4$), each of the co-crystallized complex molecules has an NiN_4 square plane involving the four N atoms of the secondary amine. In each of the two isomeric complexes, the two thiocyanate ligands coordinate axially through their N atoms.

Comment

In the structure of $[NiL^1(NCS)_2][NiL^2(NCS)_2].2CH_3CN$, (I), shown in Fig. 1, the ligand skeleton of each complex contains two *gauche* five-membered chelate rings and two six-membered chelate rings in chair conformations.



(I)

The Ni^{II} ion in each complex occupies a crystallographic inversion centre and therefore the methyl

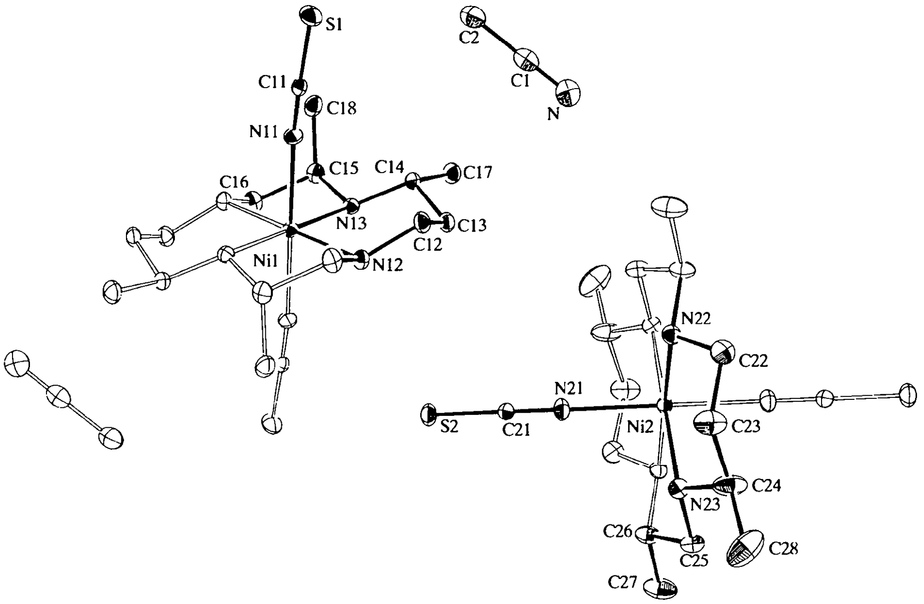


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title compound showing the atom-labelling scheme. The asymmetric unit is indicated by filled bonds. The displacement ellipsoids are drawn at the 40% probability level and H atoms have been omitted for clarity.

groups on the symmetry-related chelate rings are mutually *anti* with respect to the NiN_4 plane. The N—Ni—N angles of the six-membered chelate rings [96.03 (14) and 95.1 (2)°] are larger than those of the five-membered chelate rings [84.0 (1) and 84.9 (2)°]. Each centrosymmetric complex has an octahedrally coordinated Ni^{II} centre with Ni—N(secondary amine) distances of 2.051 (4)–2.103 (3) Å, which are significantly longer than in corresponding square-planar complexes, but normal for octahedral complexes of this type (Cramer *et al.*, 1976; Mochizuki & Kondo, 1995). The axial Ni—N(thiocyanato) distances, Ni1—N11 [2.108 (4) Å] and Ni2—N21 [2.109 (4) Å], are similar to each other. Each Ni—N(thiocyanato) linkage is bent slightly off the perpendicular to the NiN_4 plane, by 0.6 (2)–3.3 (2)° for Ni1—N11 and by 1.2 (2)–1.5 (2)° for Ni2—N21. The Ni—N—C(thiocyanato) angles are 171.8 (4) (Ni1—N11—C11) and 165.1 (4)° (Ni2—N21—C21).

Experimental

The isomeric ligands L^1 and L^2 were prepared by a slight modification of a known method (Hay & Jeragh, 1977). A methanol solution (20 ml) of the isomeric ligands (256 mg, 0.5 mmol) and $NiCl_2.6H_2O$ (119 mg, 0.5 mmol) was heated at reflux for 1 h. KSCN (97 mg, 1 mmol) was then added to the solution. The resulting solution was taken to dryness and the solid obtained dissolved in acetonitrile–water (1:1, 10 ml). When this mixture was allowed to stand at room temperature for a period of several days, violet crystals precipitated.

Compound (I)

Crystal data

$2[Ni(NCS)_2(C_{14}H_{32}N_4)].$-
$2C_2H_3N$
$M_r = 944.69$
Triclinic
$P\bar{1}$
$a = 9.999$ (1) Å
$b = 13.867$ (2) Å
$c = 8.911$ (4) Å
$\alpha = 90.81$ (2)°
$\beta = 91.18$ (2)°
$\gamma = 104.91$ (1)°
$V = 1193.5$ (6) Å^3
$Z = 1$
$D_x = 1.314$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25
reflections
$\theta = 11.35$–$14.10°$
$\mu = 1.005$ mm^{-1}
$T = 288$ (2) K
Block cut from a larger
crystal
0.36 × 0.20 × 0.20 mm
Violet

Data collection

Enraf–Nonius CAD-4
diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4374 measured reflections
4183 independent reflections
2576 reflections with
$I > 2\sigma(I)$

$R_{\rm int} = 0.046$
$\theta_{\rm max} = 24.97°$
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 16$
$l = -10 \rightarrow 10$
3 standard reflections
frequency: 240 min
intensity variation: 2.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.107$
$S = 1.270$
4183 reflections
257 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.02P)^2$
$+ 0.4P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.66$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.39$ e Å^{-3}
Extinction correction: none
Scattering factors from
International Tables for
Crystallography (Vol. C)

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

Ni1—N11	2.108 (4)	Ni2—N21	2.109 (4)
Ni1—N12	2.051 (4)	Ni2—N22	2.064 (4)
Ni1—N13	2.103 (3)	Ni2—N23	2.070 (4)
S1—C11	1.623 (5)	S2—C21	1.633 (5)
N11—C11	1.141 (5)	N21—C21	1.140 (5)
N12—Ni1—N13	96.03 (14)	N22—Ni2—N23	95.1 (2)
N12—Ni1—N11	89.4 (2)	N22—Ni2—N21	88.5 (2)
N13—Ni1—N11	93.32 (15)	N23—Ni2—N21	88.8 (2)
N11—C11—S1	177.8 (5)	N21—C21—S2	177.7 (5)

The crystal was a cylinder (0.36 × 0.20 × 0.20 mm) whose axis was mounted parallel to the diffractometer φ axis. As the possible variation as a function of φ is small (<7%), no corrections for absorption were applied. The acetonitrile H atoms were located from a circular difference Fourier synthesis, while others were included at calculated positions. H-atom positional and displacement parameters were allowed to ride on their parent atoms and fixed, except for the positional parameters of the H atoms of an acetonitrile solvent molecule, which were refined as part of a rigid group.

Data collection: *SDP* (Frenz, 1985). Cell refinement: *SDP*. Data reduction: *SDP*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976) in *NRCVAX* (Gabe *et al.*, 1989). Software used to prepare material for publication: *NRCVAX*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1168). Services for accessing these data are described at the back of the journal.

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