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Key indicators

Single-crystal X-ray study
T = 273 K
Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
R factor = 0.023
wR factor = 0.061
Data-to-parameter ratio = 18.0

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

C-meso-(3,5,7,7,10,12,12,14-Octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)nickel(II) bis(thiocyanate)

The title complex, (1*RS*,3*SR*,8*SR*,10*RS*-3,5,7,7,10,12,12,14-octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene- $\kappa^4\text{N}^{1,4,8,11}$)-nickel(II) bis(thiocyanate), $[\text{Ni}(\text{C}_{18}\text{H}_{36}\text{N}_4)](\text{NCS})_2$, has a centrosymmetrical square-planar singlet ground state nickel(II) cation, with $\text{Ni}-\text{N}_{\text{amine}} = 1.940 (1) \text{ \AA}$ and $\text{Ni}-\text{N}_{\text{imine}} = 1.921 (1) \text{ \AA}$. The C-3 methyl substituent is axially oriented. The thiocyanate N atom is hydrogen bonded to the NH group.

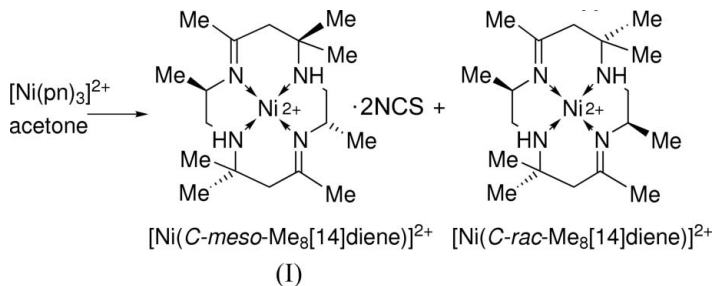
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Comment

The azamacrocyclic cations *C-meso*- and *C-rac*-($\text{Me}_8[14]$ -diene)nickel(II) ($\text{Me}_8[14]$ -diene = 3,5,7,7,10,12,12,14-octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene), formed by reaction of tris(*rac*-propane-1,2-diamine)nickel(II) complexes with acetone, were separated by fractional crystallization (see scheme; Blight & Curtis, 1962; Curtis, 1973). Compounds of the *C-meso* isomer can also be prepared from salts $[\text{H}_2(\text{C-meso-Me}_8[14]\text{diene})]\text{X}_2$, formed by reaction of mono-protonated salts $[\text{H}(\text{rac-propane-1,2-diamine})]\text{X}$, $\text{X}^- = \text{ClO}_4^-, \text{Br}^-, \text{NCS}^-$, etc, with acetone (Curtis, 1973).



The structure of yellow, singlet ground-state $[\text{Ni}(\text{C-meso-Me}_8[14]\text{diene})](\text{NCS})_2$ is reported here. It consists of a centrosymmetric square-planar cation $[\text{Ni}(\text{C-meso-Me}_8[14]\text{diene})]^{2+}$ with the thiocyanate ion located off the tetragonal axis [with closest approach $\text{Ni} \cdots \text{N}_{\text{NCS}} = 4.054 (1) \text{ \AA}$] and hydrogen bonded to the N-H group. The closest axial approach to the nickel is by the imine methyl group of another cation with $\text{Ni} \cdots \text{H51B} = 3.68 \text{ \AA}$.

The nickel(II) ion is coordinated by the four N-atoms of the macrocycle, with the $\text{Ni}-\text{N}$ distance 0.029 (2) \AA shorter for the imine than the secondary amine N atom (see Fig. 1 and Table 1). The propane-1,2-diamine residue methyl substituent is at ring position 3, adjacent to the imine N atom, axially oriented on the same side of the molecular plane as the N1-H atom, on the same side as the axial component of the *gem* dimethyl group, (C72). Displacements of atoms from the NiN_4 plane are: C2, -0.476 (2); C3, 0.1503 (2); C31, 1.627 (2); C5, -0.068 (2); C51, -0.109 (3); C6, -0.059 (3); C7, 0.703 (2); C71, 0.612 (3); C72, 2.167 (2) \AA .

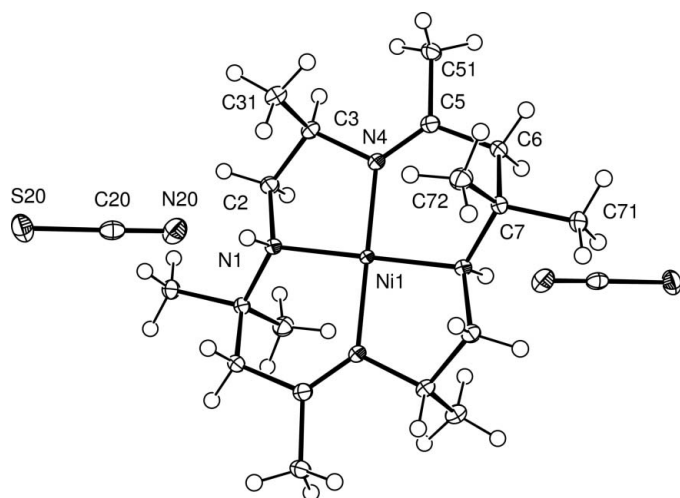


Figure 1

[Ni(*C-meso*-Me₈[14]diene)](NCS)₂ drawn with displacement ellipsoids at 50% probability level, with H atoms shown as circles of arbitrary radii. Unlabelled atom are related to labelled atoms by the symmetry operation (1 - x, 1 - y, 1 - z).

The structurally characterized compound of the *C-rac* isomeric cation, [Ni(*C-rac*-Me₈[14]diene)](ClO₄)₂, (Swann, *et al.*, 1972) has approximate twofold symmetry, with the C3 and C10 methyl substituents axially oriented on the same side of the molecular plane, and with the axially oriented components of the C7 and C14 gem-dimethyl groups oriented towards the other side of the plane, with mean distances Ni—N_{amine} = 1.93 (1) and Ni—N_{imine} = 1.89 (1) Å.

The compound [Cu(*C-meso*-Me₈[14]diene)](ClO₄)₂·2H₂O (Hazari *et al.*, 1999) has the same configuration and similar conformation of the macrocycle to the title compound, with Cu—N_{amine} = 2.010 (2), Cu—N_{imine} = 1.985 (3) Å, with perchlorate O atoms in approximate axial sites with Cu—O = 2.779 (3) Å.

The structures of thiocyanate complexes of (5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-5,11-diene)nickel(II), [Ni(Me₆[14]diene)]²⁺, (Curtis & Curtis, 1966) have been determined. The structure of *N-meso*-[Ni(Me₆[14]diene)](SCN)₂ (Hanic & Miklos, 1972) is similar to that of the title complex, with mean distances Ni—N_{amine} = 1.92 and Ni—N_{imine} = 1.88 Å, while *N-rac*-[Ni(Me₆[14]diene)](NCS)]ClO₄ (Shen *et al.*, 1999) has an unusual singlet ground-state five-coordinate structure with mean distances Ni—N_{amine} = 2.045 (8), Ni—N_{imine} = 2.015 (8) and Ni—N_{NCS} = 2.221 (5) Å.

The structure of *trans*-[Co(*C-meso*-Me₈[14]diene)Cl₂](ClO₄) (Lu *et al.*, 1992) and the space group and cell parameters of [Ni(*C-meso*-Me₈[14]diene)](ClO₄)₂ (Curtis *et al.*, 1969) have been reported.

Experimental

Excess of NaCNS was added to a hot saturated aqueous solution of orange [Ni(*C-meso*-Me₈[14]diene)](ClO₄)₂. The yellow thiocyanate salt was filtered off from the cold solution and recrystallized from methanol.

Crystal data

[Ni(C₁₈H₃₆N₄)](NCS)₂
*M*_r = 483.38
 Triclinic, *P* $\bar{1}$
a = 7.3383 (6) Å
b = 8.0955 (6) Å
c = 10.2042 (8) Å
 α = 69.917 (1)°
 β = 86.852 (1)°
 γ = 88.965 (1)°
V = 568.48 (8) Å³

Z = 1
*D*_x = 1.412 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 2683 reflections
 θ = 2.8–28.3°
 μ = 1.06 mm⁻¹
T = 273 (2) K
 Block, yellow
 0.40 × 0.20 × 0.18 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: none
 3335 measured reflections
 2472 independent reflections

2393 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.008
 θ _{max} = 28.4°
h = -9 → 9
k = -8 → 10
l = -13 → 13

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.023
 $wR(F^2)$ = 0.061
S = 1.06
 2472 reflections
 137 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0311P)^2 + 0.291P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.38 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.25 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Ni1—N4	1.921 (1)	N20—C20	1.167 (2)
Ni1—N1	1.940 (1)	C20—S20	1.644 (2)
N4—C5	1.289 (2)		
N4—Ni1—N1	86.05 (5)	N4—C5—C6	121.8 (1)
N4 ⁱ —Ni1—N1	93.95 (5)	N4—C5—C51	124.4 (1)
C5—N4—Ni1	129.2 (1)	N20—C20—S20	178.9 (1)

Symmetry code: (i) -x + 1, -y + 1, -z + 1.

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H1···N20	0.91	2.07	2.968 (2)	171

All H atoms were placed in calculated positions, with C—H = 0.96 Å, and were included in the least squares refinement as riding on their carrier atoms, with *U*_{iso}(H) = 1.2*U*_{eq} of the corresponding carrier atom.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINTE* (Siemens, 1995); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3.2* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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