C1—C2—C3	126.6 (4)	C22—Sn—C1	112.74 (14)
C1—S—C9	105.1 (2)	C10—Sn—C1	107.9 (2)
C16—Sn—C22	111.57 (14)		

Compound (II) - *E* isomer

Crystal data

$[Sn(C_6H_5)_3(C_9H_9S)]$
$M_r = 499.21$
Triclinic
$P\bar{1}$
$a = 9.5512$ (8) Å
$b = 11.0433$ (8) Å
$c = 12.3793$ (10) Å
$\alpha = 83.380$ (8)°
$\beta = 81.737$ (8)°
$\gamma = 67.018$ (7)°
$V = 1187.1$ (2) Å^3
$Z = 2$
$D_x = 1.397$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 32 reflections
$\theta = 10.0$–$13.5°$
$\mu = 1.174$ mm^{-1}
$T = 293$ (2) K
Prism
0.4 × 0.3 × 0.2 mm
Colourless

Data collection

Stoe Stadi-4 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: semi-empirical *via* ψ scan (North *et al.*, 1968)
$T_{\min} = 0.62$, $T_{\max} = 0.79$
3732 measured reflections
3732 independent reflections

3070 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 25°$
$h = -11 \rightarrow 8$
$k = -12 \rightarrow 13$
$l = 0 \rightarrow 14$
1 standard reflection frequency: 60 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.189$
$S = 1.239$
3721 reflections
287 parameters
Only H-atom *U*'s refined
$w = 1/[\sigma^2(F_o^2) + (0.1046P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.766$ e Å^{-3}
$\Delta\rho_{\min} = -0.841$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.030 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Selected geometric parameters (Å, °) for (II)*

C1—C2	1.345 (11)	C10—Sn	2.162 (8)
C1—S	1.761 (7)	C16—Sn	2.135 (8)
C1—Sn	2.148 (7)	C22—Sn	2.141 (7)
C9—S	1.769 (10)		
C2—C1—S	120.7 (6)	C16—Sn—C1	108.1 (3)
C2—C1—Sn	117.6 (5)	C22—Sn—C1	110.6 (3)
S—C1—Sn	121.6 (4)	C16—Sn—C10	105.6 (3)
C1—C2—C3	130.0 (7)	C22—Sn—C10	110.9 (3)
C1—S—C9	105.1 (5)	C1—Sn—C10	111.6 (3)
C16—Sn—C22	110.0 (3)		

For both compounds, data collection: *STADI*4 (Stoe & Cie, 1996*a*); cell refinement: *STADI*4; data reduction: *X-RED* (Stoe & Cie, 1996*b*); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1382). Services for accessing these data are described at the back of the journal.

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A dimeric form of the nickel(II) thiocyanate complex of bis(3-aminopropyl)methylamine

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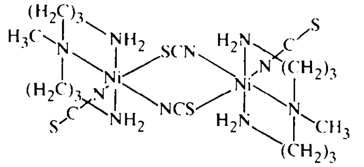
Abstract

The structure of bis[*N*,*N*-bis(3-aminopropyl)methylamine]-1κ^3N,2κ^3N-di-μ-thiocyanato-1:2κ^2N:*S*;1:2κ^2S:*N*-dithiocyanato-1κN,2κN-dinickel(II), $[Ni_2(NCS)_4(C_7H_{19}N_3)_2]$ or $[Ni_2(\mu\text{-}SCN)_2(medpt)_2(NCS)_2]$, where medpt is bis(3-aminopropyl)methylamine, consists of two crystallographically independent dimer types differing in their orientations. In each dimer, the two Ni^{II} ions are bridged by two SCN$^-$ ligands in an end-to-end fashion. The coordination polyhedra about the Ni^{II} atoms are distorted octahedra consisting of three N atoms of the medpt lig-

and coordinating meridionally, one N atom of the non-bridging thiocyanate ligand, and one N and one S atom of two bridging thiocyanate ligands. The six-membered chelate rings display chair conformations.

Comment

Diamine or triamine complexes of nickel(II) thiocyanate isomerize into different forms depending on the method of preparation. In a continuation to our studies on the synthesis and characterization of triamine complexes of nickel(II) thiocyanate, we have recently reported the structures of $[Ni(aepn)(NCS)_2]$ [Mondal *et al.*, 1997; aepn is *N*-(2-aminoethyl)-1,3-propanediamine] and $[Ni(medien)(NCS)_2]$ [Nayak *et al.*, 1998; medien is *N*-(2-aminoethyl)-*N*-methyl-1,2-ethanediamine], where different synthetic routes following Ghosh *et al.* (1997) and Escuer *et al.* (1994) resulted in the same polymeric forms of the complexes. In the case of $[Ni(medpt)(NCS)_2]$ [medpt is bis(3-aminopropyl)methylamine], (1), variation of the preparative technique as described above led to two isomeric forms, and the structure of the polymeric form of (1) has been reported previously (Vicente *et al.*, 1994). The present paper reports the synthesis and crystal structure of a new dimeric isomer of (1), $[Ni(medpt)(NCS)_2]_2$.



(1)

The structure consists of two types of crystallographically independent dinuclear $[Ni_2(medpt)_2(NCS)_4]$ units. The two Ni^{II} atoms in the dimers are bridged by two thiocyanate ions in an end-to-end fashion, with the other two thiocyanate groups acting as terminal ligands. The asymmetric unit comprises two half dimers. Apart from small changes in the crystallographically equivalent bond lengths and angles (Table 1), the two dimer types differ significantly in the orientation of the thiocyanate ligands. The secondary amine N atom in dimer *A* (N2) is *trans* to the bridging thiocyanate N atom (N4), whereas in dimer *B*, the secondary amine N atom (N7) is *trans* to the bridging thiocyanate S atom [$S3^{ii}$; symmetry code: (ii) $1-x$, $-y$, $-z$]. The bridging thiocyanate moiety (N4—C8—S1) in *A* is inclined at 86.5 (1)° to the terminal NCS group (N5—C9—S2), while the corresponding angle in *B* is 44.9 (1)°. In each dimer, the two bridging thiocyanate ligands are coplanar, being related by an inversion centre; the two Ni^{II} ions in *A* and *B* lie 0.125 (1) and 0.546 (1) Å, respectively, above and below the corresponding least-squares plane. The geometry of the $Ni(NCS)_2Ni$ units in the dimers is similar to that found in other dithiocyanato-bridged Ni^{II} complexes (Table 2), *i.e.* with approximately linear Ni—N—C angles and strongly bent Ni—S—C angles. Consequently, the structural scheme of the title complex is $[Ni_2(\mu\text{-}SCN)_2(medpt)_2(NCS)_2]$, whereas that reported for the polymeric form of (1), $[\{Ni(medpt)(NCS)(\mu\text{-}SCN)\}_n]$ (Vicente *et al.*, 1994), had neighbouring Ni atoms bridged by only one thiocyanato ligand. The coordination polyhedra around the metal centres in the title complex are best described as distorted octahedra with N_5S donor sets. The two N atoms of the bridging and the terminal NCS groups (N4 and N5 in *A*, and N9 and N10 in *B*), the secondary N atom of the chelated triamine (N2 in *A* and N7 in *B*) and the S atom of the second NCS bridging moiety [$S1^{i}$ in *A* and $S3^{ii}$ in *B*;

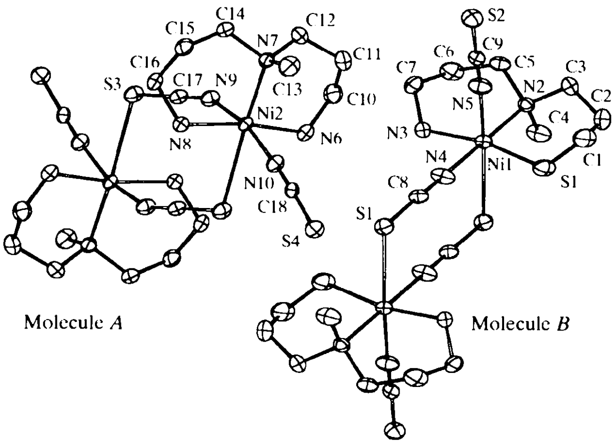


Fig. 1. A view of the title dimer, with displacement ellipsoids shown at the 50% probability level.

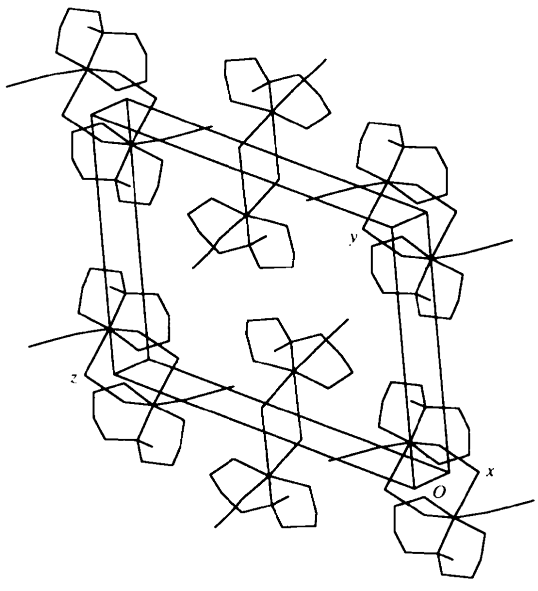


Fig. 2. Packing diagram of the title dimer.

symmetry code: (i) $1-x$, $-y$, $1-z$] define the equatorial planes around the Ni atoms, with the remaining two N atoms (N1 and N3 in *A*, and N6 and N8 in *B*) in *trans*-axial positions; the metal ions are practically on the equatorial planes [maximum deviation for Ni2 is 0.01 (1) Å]. The dihedral angle between the two equatorial planes around Ni1 and Ni2 is 61.9 (1)°.

The Ni—N bond lengths [2.027 (3)–2.184 (3) Å] and the bridging Ni—S distances [2.832 (1)–2.835 (2) Å] are consistent with corresponding values for the octahedral Ni^{II} systems (Table 2). The observed lengthening of the Ni1—N2 [2.184 (3) Å] and Ni2—N7 [2.151 (3) Å] bonds compared with other Ni—N distances (Table 2) is due to steric constraints introduced by the methyl substituent in the secondary amine. The six-membered chelate rings associated with the metal centres display chair conformations; the dihedral angles between the planar parts of the chelate rings in *A* (N1, N2, C1, C3 and N2, N3, C5, C7) and *B* (N6, N7, C10, C12 and N7, N8, C14, C16) are 41.1 (2) and 43.2 (2)°, respectively.

Experimental

The title complex was synthesized by adding the medpt ligand (2 mmol) dropwise with constant stirring to a methanolic solution (10 ml) of Ni(SCN)$_2$ (2 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 $C_9H_{19}N_5NiS_2$ C 33.8, H 6.0, N 21.9%; found C 33.6, H 5.9, N 21.8%. Single crystals suitable for X-ray diffraction were obtained by recrystallization from methanol.

Crystal data

$[Ni_2(NCS)_4(C_7H_{19}N_3)_2]$
$M_r = 640.24$
Triclinic
$P\overline{1}$
$a = 7.720\,(6)$ Å
$b = 13.720\,(1)$ Å
$c = 15.161\,(3)$ Å
$\alpha = 63.30\,(1)°$
$\beta = 88.10\,(5)°$
$\gamma = 86.56\,(5)°$
$V = 1432.0\,(12)$ Å^3
$Z = 2$
$D_x = 1.485$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8$–$16°$
$\mu = 1.633$ mm^{-1}
$T = 293\,(2)$ K
Prism
0.42 × 0.34 × 0.20 mm
Blue

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: empirical (North *et al.*, 1968)
$T_{min} = 0.582$, $T_{max} = 0.721$
6177 measured reflections
5678 independent reflections

4778 reflections with $I > 2\sigma(I)$
$R_{int} = 0.015$
$\theta_{max} = 26.90°$
$h = 0 \rightarrow 9$
$k = -17 \rightarrow 16$
$l = -19 \rightarrow 19$
3 standard reflections every 100 reflections intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.095$
$S = 1.277$
5678 reflections
307 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0378P)^2 + 1.1178P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.005$
$\Delta\rho_{max} = 0.507$ e Å^{-3}
$\Delta\rho_{min} = -0.592$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Ni1—N5	2.027 (3)	Ni2—N9	2.053 (3)
Ni1—N3	2.048 (3)	Ni2—N6	2.061 (3)
Ni1—N1	2.072 (4)	Ni2—N10	2.064 (3)
Ni1—N4	2.079 (3)	Ni2—N8	2.070 (3)
Ni1—N2	2.184 (3)	Ni2—N7	2.151 (3)
Ni1—S1^{i}	2.835 (2)	Ni2—S3^{ii}	2.832 (1)
N5—Ni1—N3	97.06 (14)	N9—Ni2—N8	87.18 (12)
N5—Ni1—N1	95.95 (15)	N10—Ni2—N8	91.12 (12)
N5—Ni1—N4	89.46 (13)	N9—Ni2—N7	97.03 (12)
N3—Ni1—N4	88.67 (14)	N6—Ni2—N7	95.80 (12)
N1—Ni1—N4	89.0 (2)	N10—Ni2—N7	96.32 (12)
N5—Ni1—N2	89.79 (12)	N8—Ni2—N7	93.57 (11)
N3—Ni1—N2	91.65 (12)	N5—Ni1—S1^{i}	175.49 (11)
N1—Ni1—N2	90.86 (14)	N7—Ni2—S3^{ii}	174.2 (1)
N4—Ni1—N2	179.21 (11)	C8—N4—Ni1	174.0 (3)
N9—Ni2—N6	90.40 (13)	C9—N5—Ni1	171.9 (3)
N9—Ni2—N10	166.62 (12)	C17—N9—Ni2	153.3 (3)
N6—Ni2—N10	89.14 (12)	C18—N10—Ni2	169.5 (3)

Symmetry codes: (i) $1-x$, $-y$, $1-z$; (ii) $1-x$, $-y$, $-z$.

Table 2. *Structure parameters (Å, °) for dinuclear nickel(II) complexes with end-to-end NCS$^-$ bridging ligands*

Complex	Ni—N—C	Ni—S—C	Ni—N	Ni—S	*D*
[Ni$_2$(2-methyl)-(μ-NCS)$_2$]^a	142.4 (3) 165.2 (3)	100.7 (1) 105.8 (1)	2.056 (3) 2.103 (3)	2.546 (1) 2.636 (1)	0.84 0.42
[Ni$_2$(2-methyl)(μ-NCS)$_2$](PF$_6$)$_2$^{a}	166.7 (4)	96.2 (2)	1.93 (7)	2.83 (3)	0.16
[Ni$_2$(terpy)$_2$(NCS)$_2$-(μ-NCS)$_2$]^b	159 (2)	100.0 (8)	1.99 (2)	2.625 (5)	0.56
[Ni$_2$(bza)$_6$(NCS)$_2$-(μ-NCS)$_2$]^c	164.9 (6)	102.2 (3)	2.050 (6)	2.639 (3)	0.02
[Ni$_2$(medpt)$_2$(NCS)$_2$-(μ-NCS)$_2$]^d	174.0 (3) 153.3 (3)	98.4 (1) 109.8 (1)	2.079 (3) 2.053 (3)	2.835 (2) 2.832 (1)	0.12 0.55

Notes: *D* = deviation of Ni from the plane of the bridging ligands. References: (*a*) Monfort *et al.* (1994), 2-methyl = 1,2-diamino-2-methylpropane; (*b*) Rojo *et al.* (1991), terpy = 2,2′:6′,2″-terpyridine; (*c*) Taniguchi & Ouchi (1986), bza = benzylamine; (*d*) this work.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1995). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1416). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 368–370

Triaquabis(nitrato-*O*,*O*′)(2,2′:6′,2″-terpyridine-κ^3*N*)gadolinium(III) nitrate

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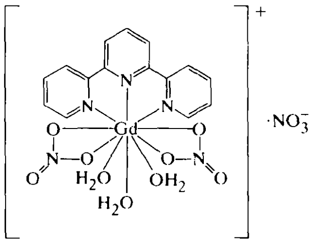
Abstract

Gadolinium nitrate forms a complex with terpyridine at the interface between an aqueous solution of the metal cation and a chloroform solution of the organic ligand. The title complex, $[Gd(terpy)(NO_3)_2(H_2O)_3]NO_3$ (terpy = terpyridine, $C_{15}H_{11}N_3$), is ten-coordinate and its coordination polyhedron can be described as a distorted bicapped square antiprism. The coordinated nitrates are bidentate. The three water ligands form hydrogen bonds in the lattice.

Comment

Lanthanide cations are present, along with the actinides, in radioactive waste solutions produced by the nuclear industry. Their separation in aqueous nitric acid solutions using selective extractants is an important goal for the management and recycling of nuclear fuels. In this respect, the comparative study of the coordination of various classes of complexing agents, in particular the terpyridine family, with lanthanide nitrates has been undertaken. Characterization of the complexes thus obtained is of particular importance for the understanding of extraction processes. Crystal structures of lanthanide salts coordinated with terpyridine derivatives were reported as early as 1969 (Frost *et al.*, 1969; Radonovitch & Glick, 1971; Holtz & Thompson, 1988; Mallet *et al.*, 1993; Kepert *et al.*, 1994), but to our knowledge only two structures of nitrate compounds have been published, namely, $[Eu(spy)(NO_3)_2]NO_3$ (spy = hexapyridine; Constable *et al.*, 1992) and $[La(terpy)_2(NO_3)_2][La(terpy)(NO_3)_4]$ (terpy = terpyridine; Fréchette & Bensimon, 1995). Both were synthesized in organic media. We present herein the crystal structure of the title compound, $[Gd(terpy)(NO_3)_2(H_2O)_3]NO_3$, (I).



(I)

In (I) (Fig. 1), the Gd cation is ten-coordinate, with three N donors from the terpyridine ligand, and seven O atoms from the three molecules of water and the two bidentate NO_3^- ligands. The coordination polyhedron can best be described as a distorted bicapped square antiprism, with O1*A* and O2*B* occupying the capping sites and N5/N6/O6/O2*A* and O4/O5/O1*B*/N4 defining the faces. Averaged Gd—N, Gd—O_{NO_3} and Gd—O_{H_2O} distances are 2.553 (3), 2.582 (3) and 2.433 (3) Å, respectively. These are slightly longer than those reported previously for the related complexes [Gd(terpy)$Cl_3(H_2O)_{7.1}$] [Gd—N 2.537 (5) and Gd—O_{H_2O} 2.45 (4) Å; Kepert *et al.*, 1994], $[Gd(H_2O)_9]^{3+}$ [Gd—O_{H_2O} 2.474 (2) Å; Harrowfield *et al.*, 1983] or [Gd-