Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DE1023). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Cabbiness, D. K. & Margerum, D. W. (1969). *J. Am. Chem. Soc.* **91**, 6540–6541.

Curtis, N. F. (1964). *J. Chem. Soc.* pp. 2644–2650.

Curtis, N. F. (1972). *J. Chem. Soc. Dalton Trans.* pp. 1357–1362.

Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Lee, C.-S, Wu, S. Y. & Chung, C.-S. (1984). *Inorg. Chem.* **23**, 1298–1303.

Lee, T.-J., Lee, T.-Y., Juang, W.-B. & Chung, C.-S. (1985). *Acta Cryst.* C**41**, 1745–1748.

Lee, T.-J., Lu, T.-H., Chung, C.-S. & Lee, T. Y. (1984). *Acta Cryst.* C**40**, 70–72.

Liang, B.-F. & Chung, C.-S. (1980). *Inorg. Chem.* **19**, 1867–1871.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (1990). *SHELXTL-Plus*. PC Version 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1996). C**52**, 3035–3037

[1,8-Bis(2-hydroxyethyl)-1,3,6,8,10,13-hexaazacyclotetradecane]nickel(II) Bis(maleonitriledithiolato)nickelate(II)

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Abstract

In the solid state, the title compound, [1,3,6,8,10,13-hexaazacyclotetradecane-1,8-diylbis(2-ethanol)-N^3,N^6,-N^{10},N^{13}]nickel(II) bis(maleonitriledithiolato-S,S')nickelate(II), $[Ni(C_{12}H_{30}N_6O_2)][Ni(C_4N_2S_2)_2]$, forms two-dimensional layers parallel to the (201) plane and its crystal structure is stabilized by N—H···O, N—H···S, C—H···N and O—H···S hydrogen bonds. The short S···Ni anion-to-cation contact of 3.5516 (8) Å is interpreted as a weak interaction between these atoms.

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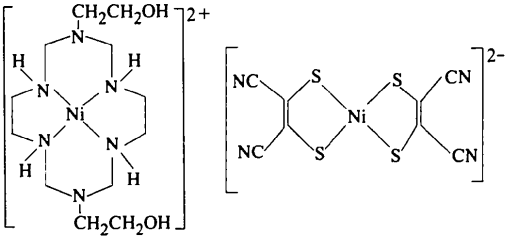
Comment

Salts of the metal dithiolate complex anions $[M(mnt)_2]^{n-}$ [M = Ni, Zn; mnt = maleonitriledithiolato(2−)], with a variety of cations, are found to possess interesting magnetic, electric and optical properties (Manoharan, Noordik, de Boer & Keijzers, 1981; Clemenson, 1990). As part of our work on the synthesis and characterization of such complexes (Shan, Zhang, You, Fun & Sivakumar, 1996), we report the structure determination of the title compound, [1,8-bis(2-hydroxyethyl)-1,3,6,8,10,13-hexaazacyclotetradecane]nickel(II) bis(maleonitriledithiolato)nickelate(II), (I).



(I)

In the macrocyclic nickel cation, the Ni atom, which is located at a centre of inversion, is coordinated to four N atoms of the macrocyclic ligand (Fig. 1). The Ni—N distances of 1.919 (2) and 1.929 (2) Å are similar to those found in other nickel(II) tetraaza macrocycles (Thom, Fox & Boeyens, 1984). The Ni atom in the anion also lies on an inversion centre and is surrounded by a square plane of four S atoms.

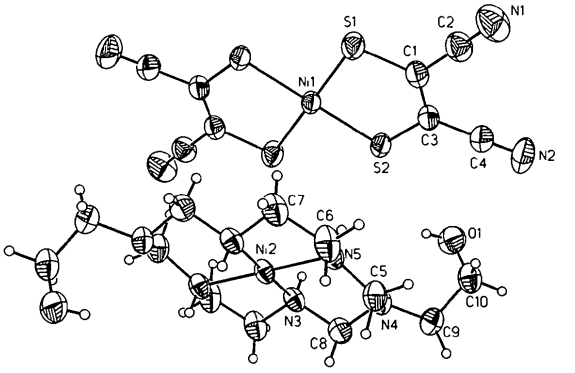


Fig. 1. An ellipsoid plot of the cation and anion of (I) showing the atom-numbering scheme and ellipsoids at the 50% probability level.

A projected view of the packing of the molecules in a unit cell down the b axis is shown in Fig. 2. The molecules are connected through hydrogen bonds forming two-dimensional layers (sheets) parallel to the (201) plane; C—H···N hydrogen bonds link the molecules into chains [C5···N2^{i} 3.377 (4) Å and C5—H5A···N2 162 (3)°; symmetry code: (i) $-x$, y, $\frac{3}{2}-z$]. The N—H···S, N—H···O and O—H···S hydrogen bonds cross-link these chains into sheets and also establish

the interlayer connections [N5···S2 3.468 (2) Å and N5—H5N···S2 174 (4)°; N3···O1^{ii} 2.871 (3) Å and N3—H3N···O1 155 (3)°; O1···S2 3.455 (2) Å and O1—H1O···S2 136 (4)°; symmetry code: (ii) $-x, 2-y, 1-z$]. There is a short contact between the anion and cation of 3.5516 (8) Å (Ni2···S1) which may be interpreted as a weak interaction between the atoms involved.

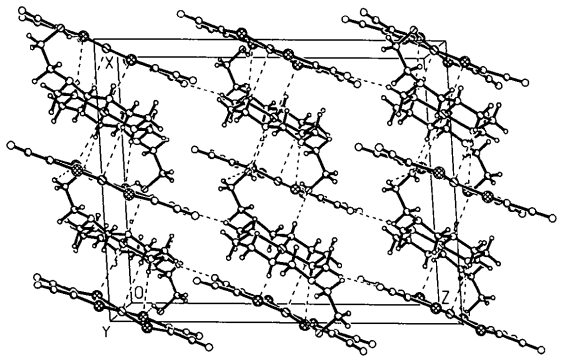


Fig. 2. The unit-cell contents viewed down the *b* axis.

Experimental

The title compound was synthesized by adding an aqueous solution of the macrocyclic cation (as its chloride salt), obtained according to the method of Hay, Armstrong & Hassan (1992), to a solution containing the anionic dithiolene complex $[Ni(mnt)_2]^{2-}$ (as its NBu_4^+ salt). Single crystals of (I) were obtained by recrystallization from dimethylformamide.

Crystal data

$[Ni(C_{12}H_{30}N_6O_2)][Ni(C_4N_2S_2)_2]$
M_r = 688.20
Monoclinic
$C2/c$
a = 15.181 (2) Å
b = 9.911 (1) Å
c = 19.114 (4) Å
β = 93.64 (1)°
V = 2870.1 (8) Å^3
Z = 4
D_x = 1.593 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 49 reflections
θ = 5.0–12.5°
μ = 1.641 mm^{-1}
T = 293 (2) K
Rectangular
0.60 × 0.52 × 0.44 mm
Dark red

Data collection

Siemens *P4* diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical *via* ψ scans (*XSCANS*; Siemens, 1994)
T_{min} = 0.764, T_{max} = 0.911
4076 measured reflections
3284 independent reflections
2793 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.0283
θ_{max} = 27.5°
$h = -1 \rightarrow 19$
$k = -1 \rightarrow 12$
$l = -24 \rightarrow 24$
3 standard reflections monitored every 97 reflections
intensity decay: <2%

Refinement

Refinement on F^2
$R(F)$ = 0.0330
$wR(F^2)$ = 0.0993
S = 1.059
3284 reflections
235 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0607P)^2 + 0.8743P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Ni1	0	1/2	1/2	0.0330 (1)
Ni2	1/4	3/4	1/2	0.0321 (1)
S1	−0.05061 (5)	0.37688 (6)	0.58230 (3)	0.0463 (2)
S2	−0.03251 (4)	0.68526 (6)	0.55338 (3)	0.0412 (2)
O1	−0.03472 (14)	1.0265 (2)	0.59016 (14)	0.0603 (6)
N1	−0.1240 (2)	0.4007 (4)	0.76208 (13)	0.0703 (8)
N2	−0.1153 (3)	0.8070 (4)	0.7199 (2)	0.0881 (11)
N3	0.20973 (13)	0.9272 (2)	0.47100 (10)	0.0360 (4)
N4	0.14825 (13)	0.9895 (2)	0.57807 (10)	0.0392 (4)
N5	0.19005 (14)	0.7568 (2)	0.58535 (10)	0.0370 (4)
C1	−0.0737 (2)	0.4946 (3)	0.64587 (12)	0.0393 (5)
C2	−0.1018 (2)	0.4429 (3)	0.71123 (13)	0.0484 (6)
C3	−0.0674 (2)	0.6276 (3)	0.63334 (12)	0.0395 (5)
C4	−0.0935 (2)	0.7272 (3)	0.6827 (2)	0.0543 (7)
C5	0.1898 (2)	0.8875 (3)	0.62266 (13)	0.0445 (6)
C6	0.2252 (2)	0.6479 (3)	0.63307 (14)	0.0519 (7)
C7	0.2385 (2)	0.5268 (3)	0.5882 (2)	0.0490 (6)
C8	0.2052 (2)	1.0334 (3)	0.52451 (14)	0.0433 (5)
C9	0.1138 (2)	1.1020 (3)	0.61911 (15)	0.0472 (6)
C10	0.0261 (2)	1.0637 (3)	0.64625 (15)	0.0496 (6)

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

Ni1—S1	2.1697 (7)	N4—C5	1.442 (3)
Ni1—S2	2.1725 (6)	N4—C8	1.448 (3)
Ni2—N5	1.919 (2)	N4—C9	1.477 (3)
Ni2—N3	1.929 (2)	N5—C5	1.479 (3)
S1—C1	1.736 (2)	N5—C6	1.490 (3)
S2—C3	1.746 (2)	C1—C3	1.344 (4)
O1—C10	1.419 (4)	C1—C2	1.439 (3)
N1—C2	1.129 (4)	C3—C4	1.438 (4)
N2—C4	1.128 (4)	C6—C7	1.497 (4)
N3—C8	1.472 (3)	C9—C10	1.508 (4)
N3—C7^i	1.490 (3)		
S1—Ni1—S2	91.91 (2)	C8—N3—Ni2	118.6 (2)
N5—Ni2—N3	93.07 (8)	C7^i—N3—Ni2	108.92 (15)
C1—S1—Ni1	103.08 (9)	C5—N5—Ni2	117.2 (2)
C3—S2—Ni1	103.00 (9)	C6—N5—Ni2	108.92 (15)

Symmetry code: (i) $\frac{1}{2}-x, \frac{3}{2}-y, 1-z$.

The title structure was solved by direct methods and refined by full-matrix least-squares techniques. H atoms were located from difference maps and refined isotropically.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Molecular geometry: *PARST* (Nardelli, 1983). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1259). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Clemenson, P. I. (1990). *Coord. Chem. Rev.* **106**, 171–203.
Hay, R. W., Armstrong, J. M. & Hassan, M. M. (1992). *Transition Met. Chem.* **17**, 270–272.
Manoharan, P. T., Noordik, J. H., de Boer, E. & Keijzers, C. P. (1981). *J. Chem. Phys.* **74**, 1980–1989.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
Shan, B.-Z., Zhang, X.-M., You, X.-Z., Fun, H.-K. & Sivakumar, K. (1996). *Acta Cryst.* C**52**, 1148–1150.
Sheldrick, G. M. (1990). *SHELXTL/PC Users Manual.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Siemens (1994). *XSCANS Users Manual.* Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Thom, V. J., Fox, C. C. & Boeyens, J. C. A. (1984). *J. Am. Chem. Soc.* **106**, 5947–5951.

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Trichloro[η^5-(trimethylstannyl)cyclopentadienyl]titanium

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Abstract

The title compound, $[TiCl_3\{(CH_3)_3Sn(C_5H_4)\}]$, is the first structurally characterized complex of an early transition metal with a cyclopentadienyl ligand-bearing stannyl moiety. The Ti—*Cp* distance of 1.986 (4) Å [where *Cp* is the centroid of the cyclopentadienyl (Cp) ring] is the shortest among the complexes containing the $CpTiCl_3$ moiety.

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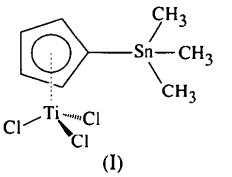
Comment

The structure of the title compound, (I), has been established as part of a study on ring-substituted monocyclopentadienyl complexes of titanium (Churakov, Lemenovskii & Kuz'mina, 1995; Rufanov, Churakov, Kazennova, Brusova, Lemenovskii & Kuz'mina, 1995).



(I)

The molecular structure of (I) is shown in Fig. 1. The Ti—C distances are quite regular [2.299 (7)–2.337 (8) Å], the shortest being to the C(1) atom which is bonded to Sn. The displacement of the Ti atom from the least-squares plane of the cyclopentadienyl ring is 1.986 (4) Å. A search of the Cambridge Structural Database (Version 5.10 of October 1995; Allen *et al.*, 1991) shows that this is the shortest reported value among ring-substituted complexes containing the $CpTiCl_3$ moiety (2.003–2.022 Å).

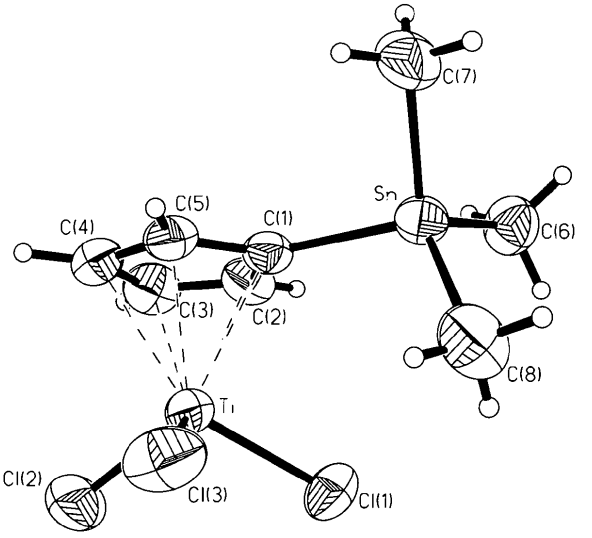


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids.

The coordination at the Sn atom is tetrahedral, with C—Sn—C angles ranging from 103.3 (4) to 113.5 (4)°. The deviation of the Sn atom from the Cp ring plane is 0.093 (13) Å. The Sn—C_{Cp} bond distance [2.169 (8) Å] is significantly longer than those found in ferrocenyls [2.146 (3) and 2.125 (4) Å (Clearfield, Simmons, Withers & Seyferth, 1983), and 2.103 (5) Å (Dong, Hwang, Wen & Hwang, 1990)] and cemantrenylstannanes [2.109 (4) Å (Bokii & Struchkov, 1978)].