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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1385). Services for accessing these data are described at the back of the journal.

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cis-(Nitrato-*O*,*O*′)[(1*RS*,4*SR*,5*SR*,8*RS*,11*SR*,12*SR*)-*C*-*rac*-1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane-κ^4N]nickel(II) nitrate

Kaliyamoorthy Panneerselvam,[a] Tian-Huey Lu,[a] Ta-Yung Chi,[b] Fen-Ling Liao[b] and Chung-Sun Chung[b]

[a]*Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 300, Republic of China, and* [b]*Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 300, Republic of China. E-mail: thlu@phys.nthu.edu.tw*

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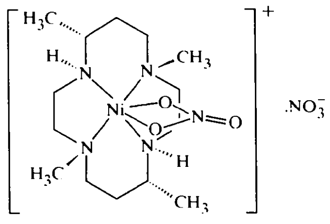
Abstract

The crystal structure of the title compound, [Ni(NO$_3$)(C$_{14}$H$_{32}$N$_4$)]NO$_3$, was determined by X-ray diffraction. The Ni$^{\rm II}$ ion is six-coordinate in a distorted octahedral arrangement, with the tetradentate macrocyclic ligand in a folded conformation. The two five-membered rings of the macrocyclic ligand have skew conformations, while the two six-membered rings adopt chair conformations. The four chiral N-atom centers are 1*RS*, 4*SR*, 8*RS* and 11*SR*, and the chiral C-atom centers are 5*SR* and 12*SR*.

Comment

The macrocyclic ligand 1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane exists as two isomers, *i.e.* *C*-*meso* and *C*-*rac* (Miyamura *et al.*, 1987). The crystal structure of the nickel(II) complex of the *C*-*meso* isomer has been reported previously (Miyamura *et al.*, 1987). This paper reports the crystal structure of the nickel(II) complex, (I), of the *C*-*rac* isomer.



(I)

The title complex cation has a distorted octahedral geometry, with the coordination formed by the tetradentate macrocyclic ligand in a folded conformation and the two O atoms of the bidentate nitrato group. The Ni1, N3 and O2 atoms lie on a crystallographic twofold axis. The four Ni—N bonds can be classified into two groups, *i.e.* the Ni1—N2 secondary amine bonds and the Ni1—N1 tertiary amine bonds. The Ni—N bond lengths are similar to those of the six-coordinate Ni$^{\rm II}$ complexes in related macrocyclic ligands (Lu *et al.*, 1991). The Ni—O bond is 2.154 (2) Å, which is longer than those found in *cis*-diaqua(1,4,8,11-tetraazacyclotetradecane)nickel(II) (2.140 and 2.130 Å; Barefield *et al.*, 1986), but shorter

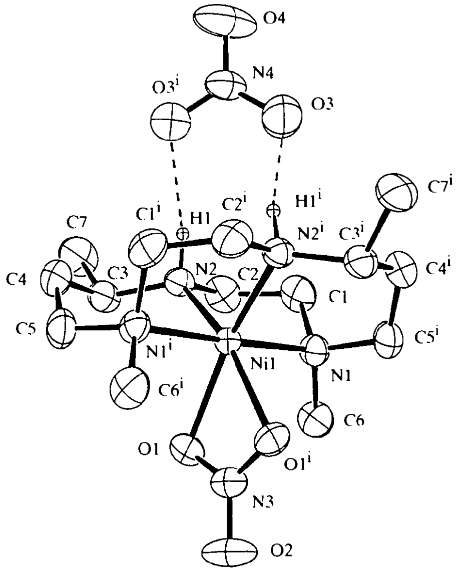


Fig. 1. The structure of the title compound showing 30% probability displacement ellipsoids. H atoms have been excluded, except for that on N2. The dotted lines represent N—H···O hydrogen bonds [symmetry code: (i) $1-x, y, \frac{1}{2}-z$].

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than those found in *cis*-diaqua(1,4,7,11-tetraazacyclotetradecane)nickel(II) (2.176 and 2.161 Å; Satake *et al.*, 1992).

The four chiral N-atom centers are 1*RS*, 4*SR*, 8*RS* and 11*SR*, and the chiral C-atom centers are 5*SR* and 12*SR*. The configuration of the four chiral N atoms in the complex cation corresponds to that of the *trans*-V diastereomer of planar [Ni(1,4,8,11-tetraazacyclotetradecane)]$^{2+}$ (Bosnich *et al.*, 1965). Such a configuration is also observed in the related macrocyclic cations *cis*-dichloro(*C-rac*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane)cobalt(III) (Tahirov *et al.*, 1994) and *cis*-diaqua(1,4,8,11-tetraazacyclotetradecane)nickel(II) (Barefield *et al.*, 1986). All bond lengths and angles in the ligand moiety are normal. An intermolecular N—H···O hydrogen bond between the NH group and the NO_3^- anion stabilizes the crystal structure [N2···O3$^{\rm i}$ 2.997 (4), H1···O3$^{\rm i}$ 2.097 Å and N2—H1···O3$^{\rm i}$ 169.6°; symmetry code: (i) $1-x, y, \frac{1}{2}-z$].

Experimental

C-rac-1,5,8,12-Tetramethyl-1,4,8,11-tetraazacyclotetradecane was prepared according to literature methods (Tahirov *et al.*, 1996). Nickel(II) nitrate hexahydrate (0.6 g) and *C-meso*-1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane (0.5 g) were dissolved in water (50 ml) and stirred for 4 h at 353 K. The solvent was removed from the resulting solution by rotatory evaporation. The residue was redissolved in a 1:1 water–methanol mixture. Crystals suitable for X-ray analysis were obtained by slow evaporation at room temperature over a period of several days.

Crystal data

$[Ni(NO_3)(C_{14}H_{32}N_4)]NO_3$
$M_r = 439.17$
Monoclinic
$C2/c$
$a = 10.399\ (3)$ Å
$b = 14.467\ (5)$ Å
$c = 14.216\ (6)$ Å
$\beta = 104.27\ (3)°$
$V = 2072.7\ (13)$ Å^3
$Z = 4$
$D_x = 1.407$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 6.12–14.52°$
$\mu = 0.977$ mm^{-1}
$T = 293\ (2)$ K
Columnar
0.552 × 0.287 × 0.253 mm
Blue

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.743$, $T_{\max} = 0.781$
1960 measured reflections
1853 independent reflections
1650 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.049$
$\theta_{\max} = 25.05°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 17$
$l = -16 \rightarrow 16$
3 standard reflections every 50 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.104$
$S = 1.075$
1853 reflections
127 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0621P)^2 + 1.2395P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.370$ e Å^{-3}
$\Delta\rho_{\min} = -0.480$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^ia^j\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Ni1	1/2	0.69783 (3)	1/4	0.03931 (18)
O1	0.5931 (2)	0.82665 (14)	0.30438 (16)	0.0600 (5)
O2	1/2	0.9574 (2)	1/4	0.0996 (14)
O3	0.4563 (4)	0.4149 (2)	0.1752 (2)	0.1246 (12)
O4	1/2	0.2880 (3)	1/4	0.152 (3)
N1	0.5858 (2)	0.69500 (16)	0.12827 (18)	0.0545 (6)
N2	0.6504 (2)	0.60586 (16)	0.31336 (17)	0.0531 (6)
N3	1/2	0.8729 (2)	1/4	0.0591 (9)
N4	1/2	0.3709 (3)	1/4	0.0751 (12)
C1	0.6693 (4)	0.6114 (3)	0.1453 (3)	0.0763 (10)
C2	0.7466 (3)	0.6063 (3)	0.2506 (3)	0.0771 (10)
C3	0.7164 (3)	0.6211 (2)	0.4169 (2)	0.0662 (8)
C4	0.6164 (4)	0.6136 (3)	0.4778 (2)	0.0763 (10)
C5	0.5137 (4)	0.6894 (3)	0.4668 (2)	0.0734 (9)
C6	0.6682 (4)	0.7772 (3)	0.1229 (3)	0.0758 (10)
C7	0.8314 (4)	0.5534 (3)	0.4549 (3)	0.0948 (13)

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

Ni1—N2	2.081 (2)	Ni1—N1	2.134 (2)
Ni1—N2$^{\rm i}$	2.082 (2)	Ni1—O1	2.154 (2)
Ni1—N1$^{\rm i}$	2.134 (2)	Ni1—O1$^{\rm i}$	2.154 (2)
N2$^{\rm i}$—Ni1—N2	100.54 (13)	N2$^{\rm i}$—Ni1—O1	158.71 (9)
N2—Ni1—N1	85.34 (10)	N1$^{\rm i}$—Ni1—O1	88.08 (9)
N2$^{\rm i}$—Ni1—N1	93.25 (10)	N1—Ni1—O1	93.82 (9)
N1$^{\rm i}$—Ni1—N1	177.80 (13)	O1$^{\rm i}$—Ni1—O1	60.19 (12)
N2—Ni1—O1	100.04 (9)		

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

Data collection: *P*4 (Siemens, 1994*a*). Cell refinement: *XSCANS* (Siemens, 1994*b*). Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *NRCVAX* (Gabe *et al.*, 1989). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1219). Services for accessing these data are described at the back of the journal.

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A W–Ag–Se cluster compound: (μ_3-bromo)(μ_3-tetraselenidotungstide)tris(triphenylphosphinesilver) ethanol solvate, $[(\mu_3\text{-Br})(\mu_3\text{-WSe}_4)(\text{AgPPh}_3)_3]\cdot\text{EtOH}$

QIANFENG ZHANG,[a] XINQUAN XIN,[a] MAOCHUN HONG,[b] RONG CAO,[b] S. SHANMUGA SUNDARA RAJ[c] AND HOONG-KUN FUN[c]

[a]State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, Nanjing University, Nanjing 210093, People's Republic of China, [b]State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Fuzhou, Fujian 350002, People's Republic of China, and [c]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia. E-mail: hkfun@usm.my

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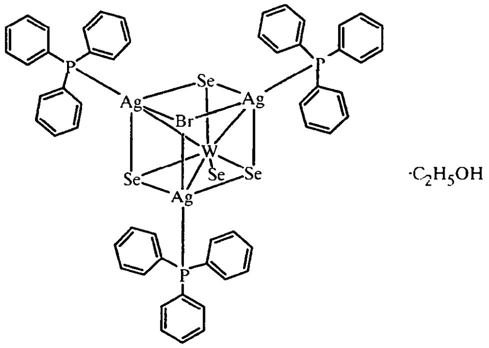
Abstract

The title compound, μ_3-bromo-2:3:4κ^3*Br*-tri-μ_3-selenido-1:2:3κ^3*Se*;1:2:4κ^3*Se*;1:3:4κ^3*Se*-selenido-1κ*Se*-tris(triphenylphosphine)-2κ*P*,3κ*P*,4κ*P*-trisilvertungsten ethanol solvate, $[Ag_3WBrSe_4(C_{18}H_{15}P)_3]\cdot C_2H_5OH$, is composed of discrete $[(\mu_3\text{-Br})(\mu_3\text{-WSe}_4)(\text{AgPPh}_3)_3]$ neutral clusters and EtOH molecules. The structure can be described either as (i) a cubane-like $[WAg_3Se_3Br]^{2+}$ cluster core with another Se^{2-} ligand bound to the W atom and three PPh_3 ligands attached to the three Ag atoms, or as (ii) three $Ag(PPh_3)^+$ fragments linked by one μ_3-WSe_4^{2-} and one μ_3-Br ligand. The average W—Ag bond distance is 3.01 (1) Å, which is too long to be considered a metal–metal interaction.

Comment

The coordination chemistry of MS_4^{2-} (M = Mo, W) has been widely investigated, primarily because of its relevance in modeling certain molybdo-enzymes (Holm & Berg, 1986; Coucouvanis, 1991) and hydrodesulfurization catalysts (Harris & Chianelli, 1984; Müller, 1986), especially certain Mo(W)–Cu(Ag)–S clusters, which have been found to have non-linear optical properties (Shi *et al.*, 1994). However, research on the corresponding chemistry of MSe_4^{2-} (M = Mo, W) has only been carried out recently (Ansari & Ibers, 1990; Roof & Kolis, 1993). Up to now, only a few mixed-metal selenide compounds containing MSe_4^{2-} (M = Mo, W) units have been structurally characterized; examples include $[(\mu_3\text{-Cl})(\mu_3\text{-WSe}_4)(\text{CuPPh}_3)_3]$ (Christuk *et al.*, 1992), $[(NC)Cu(\mu\text{-Se})_2M\text{Se}_2\text{Cu(CN)}]^{2-}$ and $[(Me_2PhP)Au(\mu\text{-Se})_2M(\mu\text{-Se})_2]^{2-}$ (M = Mo, W; Salm & Ibers, 1994; Salm *et al.*, 1995), $[(\mu_3\text{-I})(\mu_3\text{-}M\text{Se}_4)(\text{Ag}L)_3]$ (M = Mo, W; L = PMe_2Ph, PPh_3; Ansari *et al.*, 1994; Du *et al.*, 1994; Zhang *et al.*, 1997) and $[MoSe_4(CuR_2NCS_2)_x]^{2-}$ (R = Et, Me; x = 3, 4; Hong *et al.*, 1997). We report herein the crystal structure of $[(\mu_3\text{-Br})(\mu_3\text{-WSe}_4)(\text{AgPPh}_3)_3]\cdot\text{EtOH}$, (I).



(I)

The crystal structure of (I) consists of two neutral molecules. The structure is similar to the Mo–Ag–S cubane $[(\mu_3\text{-Cl})(\mu_3\text{-MoS}_4)(\text{AgPPh}_3)_3]$ (Zhu *et al.*, 1992) and the W–Cu–Se cubane $[(\mu_3\text{-Cl})(\mu_3\text{-WSe}_4)(\text{CuPPh}_3)_3]$ (Christuk *et al.*, 1992). The $[WAg_3Se_3Br]^{2+}$ cluster core is cubane-like and is completed by three Ag atoms, one Br atom and a tridentate WSe_4^{2-} ligand. One PPh_3 ligand is also attached to each of the three Ag atoms. The coordination geometry of the W atom is a distorted tricapped tetrahedron. The W—Se_t (t = terminal) bond length is 0.10–0.12 Å shorter than the W—Se_b (b = bridging) bond lengths. However, the angles between the terminal and bridging Se atoms are less obtuse than those between the bridging Se atoms themselves, and this is probably caused by some hindrance exerted by

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