C7	−0.1600 (6)	−0.4251 (4)	−0.5297 (4)	0.054 (3)
C8	−0.0781 (5)	−0.3560 (4)	−0.5293 (4)	0.039 (1)
C9	−0.1136 (6)	−0.3142 (4)	−0.6227 (4)	0.052 (3)
C10	−0.0289 (6)	−0.2493 (4)	−0.6143 (4)	0.047 (3)
C11	0.0911 (6)	−0.2245 (4)	−0.5114 (4)	0.039 (1)
C12	0.0486 (5)	−0.3274 (3)	−0.4297 (4)	0.032 (1)
C13	0.0935 (5)	−0.3669 (3)	−0.3302 (4)	0.032 (1)
C14	0.5635 (5)	−0.2169 (4)	−0.0262 (4)	0.042 (2)
C15	0.6988 (6)	−0.2295 (4)	0.0755 (4)	0.049 (3)
C16	0.7962 (6)	−0.2875 (4)	0.0863 (4)	0.046 (3)
C17	0.7597 (5)	−0.3326 (3)	−0.0039 (4)	0.033 (1)
C18	0.8554 (6)	−0.3953 (4)	−0.0002 (4)	0.048 (3)
C19	0.8171 (6)	−0.4367 (4)	−0.0891 (4)	0.049 (3)
C20	0.6771 (5)	−0.4218 (3)	−0.1941 (4)	0.038 (1)
C21	0.6282 (5)	−0.4640 (4)	−0.2902 (4)	0.047 (1)
C22	0.4967 (6)	−0.4452 (4)	−0.3831 (4)	0.052 (3)
C23	0.4087 (6)	−0.3825 (4)	−0.3852 (4)	0.043 (2)
C24	0.5794 (5)	−0.3617 (3)	−0.2025 (4)	0.032 (1)
C25	0.6210 (5)	−0.3157 (3)	−0.1041 (4)	0.030 (1)

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

Cu—Cl	2.679 (2)	C5—C13	1.389 (8)
Cu—N1	1.960 (6)	C6—C7	1.33 (1)
Cu—N2	2.043 (5)	C7—C8	1.434 (9)
Cu—N3	2.060 (4)	C8—C9	1.399 (9)
Cu—N4	2.064 (4)	C8—C12	1.399 (8)
Cu—N5	2.370 (5)	C9—C10	1.36 (1)
S—C1	1.633 (7)	C10—C11	1.382 (9)
N1—C1	1.137 (7)	C12—C13	1.430 (8)
N2—C2	1.326 (8)	C14—C15	1.388 (9)
N2—C13	1.360 (7)	C15—C16	1.36 (1)
N3—C11	1.308 (8)	C16—C17	1.384 (9)
N3—C12	1.353 (7)	C17—C18	1.435 (9)
N4—C14	1.319 (8)	C17—C25	1.405 (8)
N4—C25	1.349 (7)	C18—C19	1.33 (1)
N5—C23	1.315 (8)	C19—C20	1.438 (9)
N5—C24	1.352 (7)	C20—C21	1.40 (1)
C2—C3	1.383 (9)	C20—C24	1.396 (8)
C3—C4	1.353 (9)	C21—C22	1.33 (1)
C4—C5	1.392 (9)	C22—C23	1.39 (1)
C5—C6	1.448 (9)	C24—C25	1.476 (8)
Cl—Cu—N1	94.9 (2)	C19—C20—C24	118.6 (7)
Cl—Cu—N2	86.3 (1)	C21—C20—C24	116.2 (6)
Cl—Cu—N3	99.0 (1)	C20—C21—C22	120.3 (7)
Cl—Cu—N4	96.8 (1)	C21—C22—C23	119.9 (8)
Cl—Cu—N5	169.9 (1)	C4—C5—C13	117.9 (6)
N1—Cu—N2	174.5 (2)	C6—C5—C13	118.0 (6)
N1—Cu—N3	93.9 (2)	C5—C6—C7	121.8 (7)
N1—Cu—N4	92.8 (2)	C6—C7—C8	120.7 (7)
N2—Cu—N3	80.6 (2)	C7—C8—C9	124.8 (7)
N2—Cu—N4	92.4 (2)	C7—C8—C12	119.1 (6)
N3—Cu—N4	162.2 (2)	C9—C8—C12	116.1 (6)
N1—Cu—N5	92.1 (2)	C8—C9—C10	120.6 (7)
N2—Cu—N5	87.4 (2)	C9—C10—C11	118.6 (7)
N3—Cu—N5	87.7 (2)	N3—C11—C10	123.5 (7)
N4—Cu—N5	75.6 (2)	N3—C12—C8	123.1 (6)
Cu—N1—C1	165.2 (5)	N3—C12—C13	117.1 (5)
Cu—N2—C2	129.4 (4)	C8—C12—C13	119.8 (6)
Cu—N2—C13	113.1 (4)	N2—C13—C5	122.8 (6)
C2—N2—C13	117.5 (5)	N2—C13—C12	116.5 (5)
Cu—N3—C11	129.3 (4)	C5—C13—C12	120.6 (6)
Cu—N3—C12	112.4 (4)	N4—C14—C15	123.4 (6)
C11—N3—C12	118.0 (5)	C14—C15—C16	119.1 (7)
Cu—N4—C14	123.1 (4)	C15—C16—C17	119.7 (6)
Cu—N4—C25	119.2 (4)	C16—C17—C18	123.6 (6)
C14—N4—C25	117.7 (5)	C16—C17—C25	117.8 (6)
C23—N5—C24	117.3 (6)	C18—C17—C25	118.6 (6)
S—C1—N1	178.6 (6)	N5—C23—C22	122.8 (7)
N2—C2—C3	122.4 (7)	N5—C24—C20	123.5 (6)
C2—C3—C4	120.5 (7)	N5—C24—C25	116.9 (5)
C3—C4—C5	118.8 (7)	C20—C24—C25	119.6 (6)
C4—C5—C6	124.0 (6)	N4—C25—C17	122.4 (6)
C17—C18—C19	121.8 (7)	N4—C25—C24	118.3 (5)
C18—C19—C20	122.1 (7)	C17—C25—C24	119.3 (5)
C19—C20—C21	125.2 (7)		

Data collection and cell refinement: Enraf–Nonius CAD-4 software. Data reduction, structure solution, structure refinement, molecular graphics and software used to prepare material for publication: *MolEN* (Fair, 1990).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: HR1027). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(Ethylenediamine-*N*,*N*′)(1,4,7,11-tetraazacyclotetradecane-*N*,*N*′,*N*″,*N*‴)nickel(II) Diperchlorate

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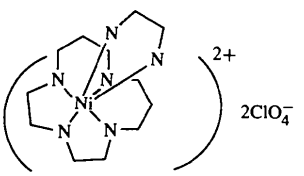
Abstract

Two slightly different complex ions, related by a pseudo-twofold axis, exist in the asymmetric unit of the title compound, $[Ni(C_2H_8N_2)(C_{10}H_{24}N_4)](ClO_4)_2$. There is a mirror plane passing through the Ni and four ligand N atoms in each complex ion. The Ni^{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 envelope conformations and the two six-membered rings are in chair conformations. The complex has 1*SR* and 7*RS* configurations at the two chiral N-atom centres and the C atoms of the ethylenediamine ligands are disordered.

Comment

Although the thermodynamics and kinetics of mixed-ligand complexes have been studied extensively (Banerjea, 1993), relatively few crystal structures of these complexes have been reported. In order to expand the knowledge in this area, we have studied the crystal structure of the title mixed-ligand complex, (I).



(I)

Two slightly different ethylenediamine(1,4,7,11-tetraazacyclotetradecane)nickel(II) complex ions exist in the asymmetric unit, are related by a pseudo-twofold axis. Each complex ion has mirror symmetry with the Ni and four ligand N atoms on the mirror plane. In [Cu(1,4,7,11-tetraazacyclotetradecane)(NCS)$_2$] (Tahirov, Lu, Lan & Chung, 1993), the tetradentate macrocyclic ligand has planar coordination. The title complex has 1*SR* and 7*RS* configurations at the two chiral N-atom centres. The two five-membered rings are in envelope conformations and the two six-membered rings have chair forms. The C atoms of the ethylenediamine ligand are disordered. The Ni—N distances span a range between 2.10 (1) and 2.23 (1) Å. The average Ni—N distance of this complex is slightly longer than that of the six-coordinate Ni^{II} complex of a related macrocyclic ligand (Lu, Chung & Ashida, 1991). Three weak hydrogen bonds exist between the ligand amine groups and the perchlorate ions.

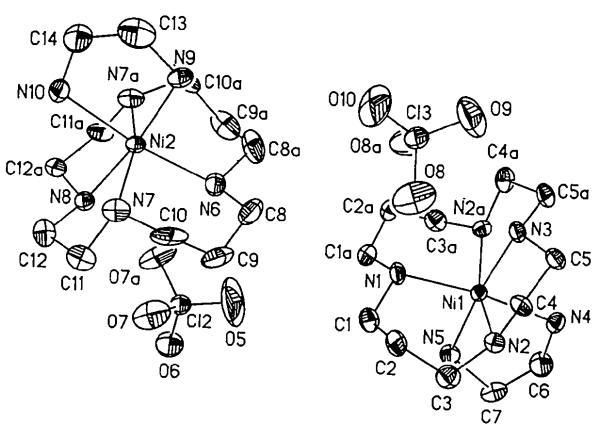


Fig. 1. A perspective view of the title complex excluding the H atoms and the perchlorate ion of Cl1. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

The complex [Ni(1,4,7,11-tetraazacyclotetradecane)](ClO$_4$)$_2$ was prepared using literature methods (Richman & Atkins, 1974; Sabatini & Fabbrizzi, 1979). 1 g of this material was dissolved in distilled water (100 ml). A solution of excess ethylenediamine was added dropwise with stirring and the solution was heated on a steam bath to approximately 333 K for several hours. The resulting blue–violet solution was allowed to stand at room temperature for a few days. Crystals of [Ni(ethylenediamine)(1,4,7,11-tetraazacyclotetradecane)](ClO$_4$)$_2$ were filtered off and recrystallized from water.

Crystal data

$[Ni(C_2H_8N_2)(C_{10}H_{24}N_4)](ClO_4)_2$	Mo $K\alpha$ radiation
M_r = 518.038	λ = 0.71073 Å
Orthorhombic	Cell parameters from 25 reflections
$Ccm2_1$	θ = 7.95–16.65°
a = 13.3863 (9) Å	μ = 1.18 mm^{-1}
b = 13.5141 (7) Å	T = 298 (3) K
c = 24.227 (2) Å	Parallelepiped
V = 4382.7 (5) Å^3	0.38 × 0.28 × 0.25 mm
Z = 8	Blue
D_x = 1.57 Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 diffractometer	1706 observed reflections [$I > \sigma(I)$]
$\theta/2\theta$ scans	R_{int} = 0.021
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)	θ_{max} = 24.9°
	$h = 0 \rightarrow 15$
	$k = 0 \rightarrow 16$
T_{min} = 0.9529, T_{max} = 0.9996	$l = 0 \rightarrow 28$
4021 measured reflections	3 standard reflections
2065 independent reflections	frequency: 60 min
	intensity decay: 1%

Refinement

Refinement on F	$(\Delta/\sigma)_{max}$ = 0.033
R = 0.045	$\Delta\rho_{max}$ = 0.57 (7) e Å^{-3}
wR = 0.064	$\Delta\rho_{min}$ = −0.42 (7) e Å^{-3}
S = 1.40	Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)
1706 reflections	
294 parameters	
$w = 1/[\sigma^2(F) + 0.0016F^2]$	

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

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Ni1	0.99479 (10)	0	0.39500	3.04 (7)
Ni2	0.50511 (9)	0	0.11644 (6)	3.11 (7)

Cl1	0.21192 (16)	0.25102 (16)	0.50436 (16)	5.21 (9)
Cl2	0.4529 (3)	0	0.31900 (19)	4.78 (15)
Cl3	0.9740 (3)	0	0.18939 (17)	5.18 (16)
O1	0.2603 (8)	0.3416 (5)	0.5096 (6)	9.9 (5)
O2	0.1057 (6)	0.2675 (7)	0.5069 (7)	10.7 (6)
O3	0.2267 (12)	0.1897 (8)	0.5469 (6)	13.4 (9)
O4	0.2295 (9)	0.2030 (8)	0.4532 (4)	10.5 (6)
O5	0.5489 (11)	0	0.3319 (4)	21.7 (27)
O6	0.3978 (10)	0	0.3672 (6)	8.4 (7)
O7	0.4229 (10)	0.0806 (7)	0.2866 (4)	11.3 (7)
O8	0.9492 (12)	0.0788 (7)	0.2232 (5)	12.1 (9)
O9	1.0755 (10)	0	0.1819 (11)	13.4 (14)
O10	0.9223 (16)	0	0.1429 (7)	17.4 (19)
N1	0.8616 (7)	0	0.3450 (5)	5.0 (6)
N2	1.0165 (5)	0.1576 (5)	0.3855 (4)	4.1 (3)
N3	1.0952 (7)	0	0.3286 (5)	4.3 (5)
N4	1.1158 (9)	0	0.4581 (5)	4.7 (5)
N5	0.9052 (9)	0	0.4690 (5)	5.0 (5)
N6	0.6091 (8)	0	0.1839 (5)	5.3 (6)
N7	0.4795 (6)	0.1572 (6)	0.1216 (5)	5.3 (4)
N8	0.3748 (7)	0	0.1645 (5)	3.7 (4)
N9	0.6258 (10)	0	0.0593 (5)	4.8 (5)
N10	0.4224 (9)	0	0.0394 (5)	4.4 (5)
C1	0.7999 (7)	0.0896 (8)	0.3531 (5)	5.5 (4)
C2	0.8533 (7)	0.1854 (8)	0.3435 (5)	5.7 (4)
C3	0.9272 (8)	0.2159 (7)	0.3856 (5)	6.0 (5)
C4	1.0830 (7)	0.1754 (7)	0.3374 (5)	5.3 (4)
C5	1.1541 (5)	0.0895 (6)	0.3314 (4)	4.8 (4)
C6	1.0664 (14)	0	0.5113 (7)	7.5 (10)
C7†	0.9695 (18)	0.0420 (14)	0.5130 (7)	4.9 (8)
C8	0.6753 (9)	0.0913 (13)	0.1876 (6)	9.1 (8)
C9	0.6163 (11)	0.1856 (11)	0.1907 (6)	8.3 (7)
C10	0.5663 (10)	0.2218 (8)	0.1383 (6)	7.9 (7)
C11	0.3924 (8)	0.1765 (6)	0.1575 (5)	5.7 (4)
C12	0.3183 (6)	0.0920 (8)	0.1534 (5)	5.6 (4)
C13	0.5865 (20)	0	0.0033 (10)	12.2 (17)
C14	0.4915 (14)	0	−0.0072 (9)	9.2 (16)

† Occupancy 0.5.

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

Ni1—N1	2.16 (1)	Ni2—N10	2.17 (1)
Ni1—N2	2.162 (7)	N1—C1	1.48 (1)
Ni1—N3	2.10 (1)	N2—C3	1.43 (1)
Ni1—N4	2.23 (1)	N2—C4	1.49 (1)
Ni1—N5	2.16 (1)	N3—C5	1.445 (9)
Ni2—N6	2.15 (1)	N6—C8	1.52 (2)
Ni2—N7	2.156 (7)	N7—C10	1.51 (1)
Ni2—N8	2.10 (1)	N7—C11	1.48 (1)
Ni2—N9	2.13 (1)	N8—C12	1.48 (1)
N1—Ni1—N2	92.9 (2)	N7—Ni2—N10	88.2 (3)
N1—Ni1—N3	95.7 (4)	N8—Ni2—N9	173.1 (4)
N1—Ni1—N4	170.9 (4)	N8—Ni2—N10	93.0 (4)
N1—Ni1—N5	90.4 (4)	N9—Ni2—N10	80.1 (5)
N2—Ni1—N2^{i}	160.2 (3)	Ni1—N1—C1	112.8 (6)
N2—Ni1—N3	80.3 (2)	C1—N1—C1^{i}	109.9 (8)
N2—Ni1—N4	88.6 (2)	Ni1—N2—C3	115.4 (6)
N2—Ni1—N5	99.4 (2)	Ni1—N2—C4	108.9 (6)
N3—Ni1—N4	93.5 (4)	C3—N2—C4	114.4 (8)
N3—Ni1—N5	173.9 (4)	Ni1—N3—C5	108.3 (6)
N4—Ni1—N5	80.4 (4)	C5—N3—C5^{i}	113.6 (8)
N6—Ni2—N7	93.3 (3)	Ni2—N6—C8^{i}	115.0 (7)
N6—Ni2—N8	96.7 (4)	C8—N6—C8^{i}	108 (1)
N6—Ni2—N9	90.2 (4)	Ni2—N7—C10	117.6 (7)
N6—Ni2—N10	170.3 (4)	Ni2—N7—C11	109.5 (6)
N7—Ni2—N7^{i}	160.5 (3)	C10—N7—C11	110.4 (9)
N7—Ni2—N8	80.5 (2)	Ni2—N8—C12	108.9 (6)
N7—Ni2—N9	99.1 (3)	C12—N8—C12^{i}	114.4 (8)
C1—N1—C1—C2	−178 (1)	C12—N8—C12—C11	−171 (1)
C4—N2—C3—C2	71.8 (8)	N1—C1—C2—C3	−72.4 (8)
C3—N2—C4—C5	−161 (1)	C1—C2—C3—N2	71.4 (9)
C5—N3—C5—C4	−171 (1)	N2—C4—C5—N3	54.2 (6)
C8—N6—C8—C9	−174 (1)	N6—C8—C9—C10	−74 (1)
C11—N7—C10—C9	76 (1)	C8—C9—C10—N7	70 (1)
C10—N7—C11—C12	−162 (1)	N7—C11—C12—N8	52.8 (7)

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

Data reduction, structure solution and structure refinement were carried out using *NRCVAX* (Gabe, Le Page, White & Lee, 1987). H atoms were located by theoretical calculation. H atoms attached to N5, C6 and C7 were not calculated. Atom C7 had a site occupation factor of 0.5.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1130). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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trans,trans-$[Ni_2(CN)_4(Me_2PCH_2PMe_2)_2]$

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Abstract

The molecular structure of *trans,trans*-bis[μ-bis(dimethylphosphino)methane-*P*:*P*′]bis(dicyanonickel), $[Ni_2(CN)_4(C_5H_{14}P_2)_2]$, is of the face-to-face type. It contains an eight-membered $Ni_2P_4C_2$ ring with an elongated chair conformation and a transannular Ni···Ni separation of 3.2085 (6) Å. The coordination geometry around the Ni atoms is square planar.

Comment

Binuclear transition metal complexes with bridging diphosphinomethane ligands, $R_2PCH_2PR_2$, interact with