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Acetonitrile{*N*-[2-(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)ethyl]-*N*-[(1-methylbenzimidazol-2-yl)methyl]-methylamine}nickel(II) bis(perchlorate) acetonitrile solvate

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In the title compound, $[Ni(C_2H_3N)(C_{20}H_{34}N_6)](ClO_4)_2\cdot CH_3CN$, Ni^{II} has approximately octahedral coordination geometry. The ligand donor atoms are five N atoms from the pendant-arm macrocyclic ligand (three from the macrocycle and two from the pendant arm) and one N atom from a coordinated acetonitrile molecule.

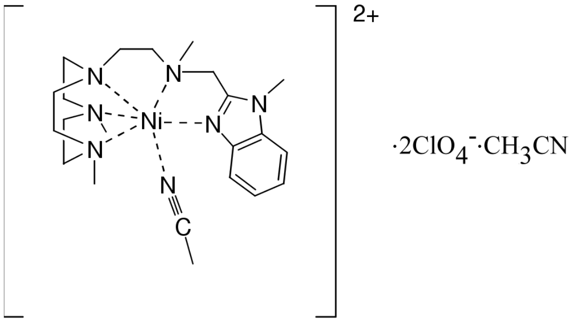
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
Disorder in solvent or counterion
R factor = 0.053
wR factor = 0.118
Data-to-parameter ratio = 11.7

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

Comment

Complexes that model structural aspects of the active sites of metalloproteins and enzymes have been valuable tools for the interpretation of enzyme mechanism and function at the molecular level (Kaim & Schwederski, 1994). For binuclear metalloenzymes, a large number of ligands with symmetric coordination environments have been prepared and their metal complexes investigated (Du Bois *et al.*, 2000). However, to date, there has been a paucity of ligands that model asymmetric coordination environments in metalloenzymes. The *de novo* design of a new family of ligands that offer potentially binuclear asymmetric coordination environments for metal ions has now been achieved and will be reported elsewhere (Daly & Martin, 2001). These ligands offer potentially binuclear asymmetric coordination donor atoms that can result in selectivity in coordination to metal ions. Some examples of metalloenzymes that contain asymmetry as described include Cu/Zn superoxide dismutase (Holm *et al.*, 1996), ribonucleotide reductase (Stubbe & Riggs-Gelasco, 1998), purple acid phosphatases (Barford *et al.*, 1998) and haemerythrin (Liang *et al.*, 1999).



(I)

The title compound, (I), was prepared to structurally characterize the pentadentate ligand, *N*-[2-(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)ethyl]-*N*-[(1-methylbenzimidazol-2-yl)methyl]methylamine. The nickel ion in the complex has approximately octahedral geometry, with a coordinated acetonitrile (N7) molecule in a *trans* position with respect to

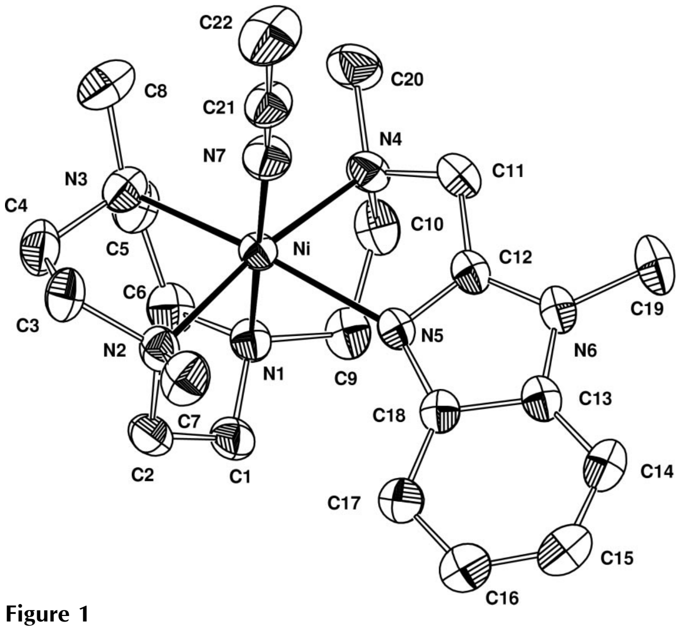


Figure 1
The cation of the title compound with displacement ellipsoids at the 40% probability level.

N1; the Ni—N7 bond length is 2.040 (3) Å. The pendant aminomethylbenzimidazole is bound so that its donor atoms, N4 and N5, are in *trans* positions with respect to atoms N2 and N3 of the macrocycle, respectively. Distortions from regular octahedral geometry about the metal ion are evident from the bond angles N1—Ni—N7, N2—Ni—N4 and N3—Ni—N5 of 177.39 (12), 169.99 (11) and 172.90 (11)°, respectively. The Ni—N(macrocycle) bond lengths are in the range 2.051 (3)–2.176 (3) Å. The uncoordinated acetonitrile molecule appears to have only a space-filling role in the crystal.

Experimental

To a refluxing solution of $[Ni(H_2O)_6](ClO_4)_2$ (0.15 g, 0.559 mmol) in methanol (1 ml) was added a solution of the ligand, *N*-[2-(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)ethyl]-*N*-[(1-methylbenzimidazol-2-yl)methyl]methylamine (*L*; 0.20 g, 0.559 mmol) in methanol (1 ml) and the heating continued for 1 h. The resultant gum was stirred with ether to give a pink solid that was collected by filtration. This compound was recrystallized by ether diffusion into an acetonitrile solution to give pink plates. Yield: 0.202 g (55%). Microanalysis for $C_{22}H_{37}Cl_2N_7NiO_8$, calculated: C 40.21, H 5.67, N 14.92%; found: C 39.85, H 5.60, N 14.92%. λ_{max} (CH_3CN): 550 nm, ε: 8.628 M^{-1} cm^{-1}, 924 nm; ε: 14.050 M^{-1} cm^{-1}; μ: 3.88 BM. Crystals, grown by vapour diffusion of diethyl ether into an acetonitrile solution of the pink plates, formed in two habits. The majority of the complex crystallized as very thin plates with microanalysis of this compound suggesting the formula $[NiL(CH_3CN)](ClO_4)_2$. However, a small amount of complex crystallized as larger prisms that were suitable for X-ray structure determination. The IR spectra for both compounds over the range 2200–2360 cm^{-1} displayed the CN stretch of a coordinated acetonitrile molecule. The main product showed one weak absorbance at ~2245 cm^{-1}, whereas the prisms of (I) showed an additional two CN bands at 2315 and 2286 cm^{-1}, attributable to a free acetonitrile molecule in the lattice, as they are equivalent to those bands arising from pure acetonitrile. The crystal used for data collection was cut from a 0.2 mm thick prism of the minor component.

Crystal data

$[Ni(C_2H_3N)(C_{20}H_{34}N_6)]$-$(ClO_4)_2 \cdot C_2H_3N$
$M_r = 698.23$
Monoclinic, $P2_1/c$
$a = 10.474$ (1) Å
$b = 30.475$ (2) Å
$c = 10.572$ (1) Å
$\beta = 111.54$ (1)°
$V = 3138.9$ (5) Å^3
$Z = 4$
$D_x = 1.477$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 18.1$–21.8°
$\mu = 0.85$ mm^{-1}
$T = 293$ (2) K
Prism, pink
0.50 × 0.44 × 0.20 mm

Data collection

Enraf–Nonius CAD-4/PC diffractometer
$\theta/2\theta$ scans
Absorption correction: Gaussian (*ABSORB*; Hall *et al.*, 1995)
$T_{min} = 0.657$, $T_{max} = 0.851$
9685 measured reflections
7088 independent reflections
5189 reflections with $F^2 > 2\sigma(F^2)$
$R_{int} = 0.021$
$\theta_{max} = 27.5$°
$h = -13 \rightarrow 12$
$k = 0 \rightarrow 39$
$l = -13 \rightarrow 13$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.118$
$S = 1.63$
5177 reflections
444 parameters
H-atom parameters not refined
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.60$ e Å^{-3}
$\Delta\rho_{min} = -0.48$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni—N1	2.051 (3)	Ni—N4	2.190 (3)
Ni—N2	2.101 (3)	Ni—N5	2.260 (3)
Ni—N3	2.176 (3)	Ni—N7	2.040 (3)
N1—Ni—N2	86.34 (11)	N2—Ni—N7	95.97 (12)
N1—Ni—N3	83.38 (12)	N3—Ni—N4	100.52 (11)
N1—Ni—N4	84.61 (11)	N3—Ni—N5	172.90 (11)
N1—Ni—N5	89.51 (11)	N3—Ni—N7	95.69 (13)
N1—Ni—N7	177.39 (12)	N4—Ni—N5	78.95 (10)
N2—Ni—N3	82.64 (12)	N4—Ni—N7	93.17 (12)
N2—Ni—N4	169.99 (11)	N5—Ni—N7	91.42 (12)
N2—Ni—N5	96.72 (10)		

Many reflections had streaks that extended into the scan range of neighbouring reflections causing background imbalance and large net negative intensity, particularly for low order weak reflections. The original diffractometer output file was edited to remove severely affected reflections. This reduced the measured data from 10116 to 9685 reflections. H atoms were placed at calculated positions and not refined although their coordinates were recalculated several times during the refinement. Both perchlorate groups are severely disordered. They have been modelled by using two rigid groups each, with refined population parameters [Cl1/Cl1′ 0.624/0.376(8); Cl2/Cl2′ 0.51/0.49(1)]. This has satisfactorily accounted for the electron density in the regions of these groups.

Data collection: *CAD*-4/*PC* (Enraf–Nonius, 1992); cell refinement: *CAD*-4/*PC*; data reduction: *Xtal*3.4 *DIFDAT ABSORB SORTRF ADDREF* (Hall *et al.*, 1995); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *Xtal*3.4 *CRYLSQ*; molecular graphics: *Xtal*3.4 *PIG ORTEP*; software used to prepare material for publication: *Xtal*3.4 *BONDLA CIFIO*.

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