Table 9. *Hydrogen-bonding geometry (Å, °) for (III)*

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O4—H1$\cdots$O1$^{\text{i}}$	0.98	1.79	2.739 (6)	164
O4—H2$\cdots$O2$^{\text{ii}}$	0.91	1.83	2.732 (6)	175
O5—H3$\cdots$O1$^{\text{iii}}$	0.98	1.79	2.767 (6)	177
O5—H4$\cdots$O3$^{\text{iv}}$	1.03	1.80	2.799 (6)	161
O6—H5$\cdots$O2$^{\text{v}}$	0.95	1.82	2.771 (7)	174
O6—H6$\cdots$O3$^{\text{ii}}$	1.09	1.72	2.787 (6)	164

Symmetry codes: (i) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (iv) $x - 1, \frac{1}{2} - y, z - \frac{1}{2}$; (v) $-x, \frac{1}{2} + y, \frac{1}{2} - z$.

For the three title compounds, phenyl C—C distances were in the range 1.367 (7)–1.391 (7) Å, C4—C7 in the range 1.471 (8)–1.51 (1) Å, and C7—C8 in the range 1.24 (1)–1.28 (1) Å. The short double bond and the irregular displacement parameters are indicative of disorder involving C7 and C8, however, no additional peaks of electron density leading to such a model could be found. H atoms were either located on difference electron-density maps (O—H) or placed in calculated positions (C—H) with isotropic B values equal to 1.2 times those of the attached atoms at the time of their inclusion.

For all compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1991); program(s) used to solve structures: *MITHRIL* (Gilmore, 1983); program(s) used to refine structures: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

The Center for International Education and the College of Arts and Sciences at Central Michigan University provided funding to support SND's stay at CMU. The Herbert H. and Grace A. Dow Foundation and The Dow Chemical Company Foundation provided funding for the establishment of the CMU X-ray facility.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1487). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 39–41

[1,5-Bis(2-pyridylmethyl-*N*)-1,5-diazacyclooctane-*N*,*N*′]chloronickel(II) perchlorate

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(Received 21 April 1998; accepted 14 August 1998)

Abstract

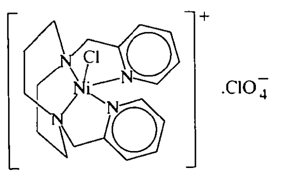
The structure of the title compound, $[NiCl(C_{18}H_{24}N_4)]ClO_4$, is comprised of discrete $[NiCl(C_{18}H_{24}N_4)]^+$ cations and perchlorate anions. The Ni$^{\text{II}}$ atom is five-coordinated by the four nitrogen donors of the new mini-ring macrocyclic ligand 1,5-bis(2-pyridylmethyl)-1,5-diazacyclooctane [Ni—N 2.074 (3)–2.108 (3) Å], and by a chloride anion in the apical site [Ni—Cl 2.302 (1) Å]. The coordination geometry of the complex could be considered as intermediate between square-pyramidal and trigonal-bipyramidal. The mini-ring macrocyclic ligand has a boat–chair conformation and the two pyridyl pendants are not coplanar.

Comment

The coordination properties toward metal ions of macrocycles bearing pendant donor groups have recently attracted much interest as models for protein–metal binding sites and multi-electron catalysis (Alexander, 1995; Norante *et al.*, 1990). Recently, we found that functionalized aza-macrocycles containing pendant pyridine groups can form stable complexes with transition metals and that these complexes exhibit interesting properties (Bu *et al.*, 1997). In order to extend our studies and to obtain some non-octahedral transition metal complexes possessing good catalytic functions, we synthesized a new mini-ring macrocyclic ligand, 1,5-

Acta Crystallographica Section C
ISSN 0108-2701 © 1999

bis(2-pyridylmethyl)-1,5-diazacyclooctane, and prepared its nickel(II) complex, $[NiCl(C_{18}H_{24}N_4)]ClO_4$, (I). We report herein the crystal structure of this new complex.



(I)

The structure of (I) consists of discrete $[NiCl(C_{18}H_{24}N_4)]^+$ cations (Fig. 1) and perchlorate anions. In the complex cation, the Ni^{II} atom is pentacoordinated (NiN_4Cl). The 1,5-bis(2-pyridylmethyl)-1,5-diazacyclooctane molecule acts as a tetradentate ligand, coordinating through the pair of nitrogen donors of the macrocyclic ring and the two N atoms of the pyridyl pendants. The coordination geometry about the Ni^{II} atom can be described as a distorted square pyramid with the four nitrogen donors of the tetradentate ligand occupying the equatorial positions and one chloride anion ligand occupying the apical site. The bond angles in the nickel coordination sphere reveal a slight trigonal distortion of the square pyramid, the τ value used to describe the degree of trigonal distortion being 0.38 (Addison *et al.*, 1984). The Ni^{II} atom is displaced from the mean plane formed by the four N atoms (N1–N4) by *ca* 0.3909 (5) Å towards the apical Cl1 atom.

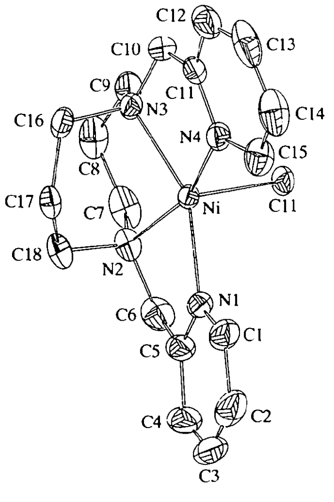


Fig. 1. *ORTEP*II view (Johnson, 1976) of the cation of the title complex with 30% probability ellipsoids. H atoms have been omitted for clarity.

The Ni—N2 and Ni—N3 bond distances of the macrocyclic ring and the Ni—N bond lengths of the pyridyl pendant N atoms are normal Ni—N bond lengths (Martin *et al.*, 1974). The apical Ni—Cl bond length is also normal. The mini-ring macrocyclic ligand has a boat–chair conformation and the distance between both N atoms (N2 and N3) of the macrocyclic ring is thereby restricted, so that the bond angle N2—Ni—N3 has a limited range and is smaller than the N1—Ni—N4 angle, where N1 and N4 are the donor atoms of the pendant groups.

Experimental

N,*N*′-Bis(pyridylmethyl)-1,5-diazacyclooctane dihydrochloride was prepared by the reaction of 1,5-diazacyclooctane hydrobromide and 2-(chloromethyl)pyridine hydrochloride in ethanol solution in the presence of KOH (Buhle *et al.*, 1943; Billman & Dorman, 1962); details will be published elsewhere. A mixture of $Ni(ClO_4)_2\cdot6H_2O$ (370 mg, 1 mmol) and *N*,*N*′-bis(pyridylmethyl)-1,5-diazacyclooctane hydrochloride (430 mg, 1 mmol) was dissolved in methanol (40 ml, room temperature). The ligand was neutralized by slow addition of an NaOH/methanol solution to the above mixture. The resulting solution was allowed to stand for *ca* 2 d, whereupon green block-shaped crystals were deposited slowly upon evaporation of the solvent. FT-IR data (KBr pellet, cm^{-1}): 3063 (*w*), 2912 (*w*), 1611 (*m*), 1571 (*w*), 1485 *m*), 1446 (*m*), 1093 (*s*), 773 (*m*), 624 (*m*).

Crystal data

$[NiCl(C_{18}H_{24}N_4)]ClO_4$
$M_r = 490.03$
Triclinic
$P\overline{1}$
$a = 7.3502 (13)$ Å
$b = 12.0783 (15)$ Å
$c = 12.476 (7)$ Å
$\alpha = 80.28 (3)^\circ$
$\beta = 79.53 (3)^\circ$
$\gamma = 72.713 (13)^\circ$
$V = 1032.1 (7)$ Å^3
$Z = 2$
$D_x = 1.58$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 23 reflections
$\theta = 14$–21°
$\mu = 1.24$ mm^{-1}
$T = 293$ K
Block
0.60 × 0.50 × 0.50 mm
Green

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scan (North *et al.*, 1968)
$T_{min} = 0.467$, $T_{max} = 0.538$
3640 measured reflections
3640 independent reflections

3154 reflections with $I > 3\sigma(I)$
$\theta_{max} = 25^\circ$
$h = 0 \rightarrow 8$
$k = -13 \rightarrow 14$
$l = -14 \rightarrow 14$
2 standard reflections every 250 reflections intensity decay: 1.7%

Refinement

Refinement on F
$R = 0.048$
$wR = 0.061$
$S = 1.21$

$(\Delta/\sigma)_{max} = 0.0095$
$\Delta\rho_{max} = 0.51$ e Å^{-3}
$\Delta\rho_{min} = -0.71$ e Å^{-3}
Extinction correction: none

3154 reflections
262 parameters
H atoms not refined
$w = 1/[\sigma^2(F) + (0.030F)^2 + 1.0] - F$

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

Ni—Cl1	2.302 (1)	N2—C7	1.498 (5)
Ni—N1	2.108 (3)	N2—C18	1.493 (6)
Ni—N2	2.081 (3)	N3—C9	1.487 (5)
Ni—N3	2.088 (3)	N3—C10	1.470 (5)
Ni—N4	2.074 (3)	N3—C16	1.492 (7)
N1—C1	1.338 (5)	N4—C11	1.334 (6)
N1—C5	1.335 (5)	N4—C15	1.343 (5)
N2—C6	1.464 (7)		
Cl1—Ni—N1	101.4 (2)	Ni—N1—C1	130.4 (3)
Cl1—Ni—N2	98.7 (2)	Ni—N1—C5	111.6 (3)
Cl1—Ni—N3	104.1 (1)	Ni—N2—C6	105.6 (4)
Cl1—Ni—N4	99.2 (2)	Ni—N2—C7	114.7 (3)
N1—Ni—N2	80.3 (1)	Ni—N2—C18	104.6 (2)
N1—Ni—N3	152.7 (1)	Ni—N3—C9	114.6 (4)
N1—Ni—N4	104.2 (1)	Ni—N3—C10	107.6 (3)
N2—Ni—N3	86.2 (1)	Ni—N3—C16	103.9 (3)
N2—Ni—N4	160.3 (2)	Ni—N4—C11	113.7 (2)
N3—Ni—N4	81.4 (1)	Ni—N4—C15	128.6 (3)

The title structure was solved by Patterson and difference Fourier methods and refined by full-matrix least-squares methods. H atoms were located and added to the structure-factor calculations, but their positions were not refined.

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD*-4 *Operations Manual.* Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN*. Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

We gratefully acknowledge financial support from the National Natural Science Foundation of China (No. 29771022) and Tianjin Natural Science Foundation. X-HB gratefully acknowledges a grant from the State Education Commission of China.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1060). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 41–43

[1,4,7-Tris(3-*tert*-butyl-5-methyl-2-hydroxybenzyl)-1,4,7-triazacyclononananato-*N*,*N*′,*N*″,*O*,*O*′,*O*″]chromium(III)†

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(*Received 1 June 1998; accepted 17 August 1998*)

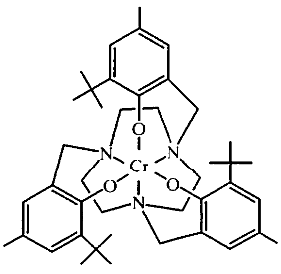
Abstract

The structure analysis of the title compound, $[Cr(C_{42}H_{60}N_3O_3)]$, shows the hexadentate ligand to be coordinated to Cr^{III} in a distorted octahedral arrangement, with the Cr atom situated on a crystallographic threefold axis. Cr—N distances are 2.109 (2) Å and Cr—O distances 1.919 (3) Å.

Comment

During a continuing investigation of the structure–mechanism–function relationship for a number of metalloenzymes, we have explored reactions involving coordinated phenolates. In particular, we are challenged by defining the role of molybdenum in the iron–molybdenum cofactor (FeMoco) in nitrogenase (Steifel *et al.*, 1993). The X-ray structural analysis of FeMoco (Kim & Rees, 1992) identifies the organic ligand, homocitrate, coordinated through two O atoms to the molybdenum. This ligand has been shown to be essential for enzyme function, however, its functional role remains elusive.

In order to define the relationship between the molybdenum centre, the homocitrate ligand and the nitrogenase function, we have prepared the title complex, (I), as a model system for FeMoco. Chromium has been selected as the 'electronic' mimic for molybdenum in these 'first-generation' model complexes and the donor atoms for the bio-mimetic model complex are N_3O_3.



(I)

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† Alternative name: [2,2′,2″-(1,4,7-triazacyclononane-1,4,7-triyl-κ^3N)-tris(6-*tert*-butyl-4-methylphenolato-*O*)]chromium(III).