

[1,8-Bis(2-benzyl)-1,3,6,8,10,13-hexaazacyclotetradecane]nickel(II) diperchlorateYan-Wu Li,^a Hua Xiang,^a
Tong-Bu Lu^a and Seik Weng Ng^{b*}^aInstrument Analysis and Research Center, Sun Yat-Sen University, Guangzhou 510275, People's Republic of China, and ^bDepartment of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia

Correspondence e-mail: seikweng@um.edu.my

Key indicatorsSingle-crystal X-ray study
T = 298 K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
R factor = 0.036
wR factor = 0.105
Data-to-parameter ratio = 17.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

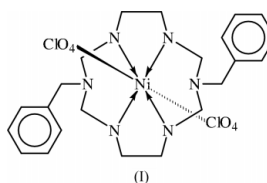
In the title compound, $[\text{Ni}(\text{C}_{22}\text{H}_{34}\text{N}_6)](\text{ClO}_4)_2$, the 14-membered hexaazacyclotetradecane macrocycle chelates to the Ni atom through its four secondary N atoms. The asymmetric unit contains two independent half-molecules, with the Ni atoms located on inversion centers. The Ni atoms have a distorted octahedral geometry, with long Ni—O(perchlorate) bonds. The occurrence of hydrogen-bonding interactions results in a linear chain structure.

Received 13 January 2004
Accepted 30 January 2004
Online 20 February 2004

Nickel complexes of 1,8-diorganyl-1,3,6,8,10,13-hexaazacyclotetradecane. Part I.

Comment

Nickel complexes of the 14-membered hexaaza macrocycle 1,8-diorganyl-1,3,6,8,10,13-hexaazacyclotetradecane are readily synthesized in a one-pot reaction involving nickel chloride, ethylenediamine, formaldehyde and a primary amine (Suh *et al.*, 1994); the reaction affords a compound whose chloride ion can then be exchanged by other counter-ions. Before the macrocyclic chemistry of nickel was reviewed (Suh, 1997), there were few crystallographic studies (Ballester *et al.*, 1994; Shan *et al.*, 1996; Suh *et al.*, 1994), but, since then, a large number of structural reports have been published. They all contain a similar framework with only a change of the organic group *R* attached to the non-bonded N atoms. Examples include *R* = CH₃ (Choi *et al.*, 2001; Kou *et al.*, 1999, 2001; Kou, Bu *et al.*, 2000), *R* = CH₂CH₃ (Kou, Gao *et al.*, 2000*b*; Kou *et al.*, 2001; Kou, Si *et al.*, 2002; Lu *et al.*, 2002), *R* = CH₂CH₂CN (Liu *et al.*, 2002), *R* = CH₂CH₂OH (Ballester *et al.*, 1994; Choi & Suh, 1998, 1999; Cho *et al.*, 2002; Kim & Lee, 1999; Kim *et al.*, 2000, 2002; Kou, Bu *et al.*, 2000; Lu, Xiang, Su *et al.*, 2001; Shan *et al.*, 1996; Xiang, Gao *et al.*, 2001; Xiang, Lu *et al.*, 2001), *R* = CH₂CH₂NH₂ (Kou, Zhou *et al.*, 2002), *R* = CH₂CH₂NH₃⁺ (Kang *et al.*, 1999), *R* = CH₂CH₂CH₂OH (Suh *et al.*, 1994), *R* = CH₂-4-C₃H₄N (Min & Suh, 2001*a,b*) and *R* = CH₂CH₂C₆H₅ (Lu *et al.*, 2000; Lu, Xiang, Luck *et al.*, 2001) groups. Some of the anions are capable of direct interaction with the Ni center,



such as, for example, the N₃⁻ (Kim & Lee, 1999) and C₂N₃⁻ (Cho & Suh, 2000) ions, as well as mono- (Min & Suh, 1999*b*), di- (Choi & Suh, 1999; Kim *et al.*, 2002; Min & Suh, 2001*b*; Xiang, Lu *et al.*, 2001) and tricarboxylate (Choi *et al.*, 2001; Min & Suh, 2001*a*; Lu, Xiang, Su *et al.*, 2001; Lu *et al.*, 2002) groups. In the crystal structure of the —CH₂CH₂C₆H₅ derivative, the perchlorate anion is more than 3 Å from the Ni

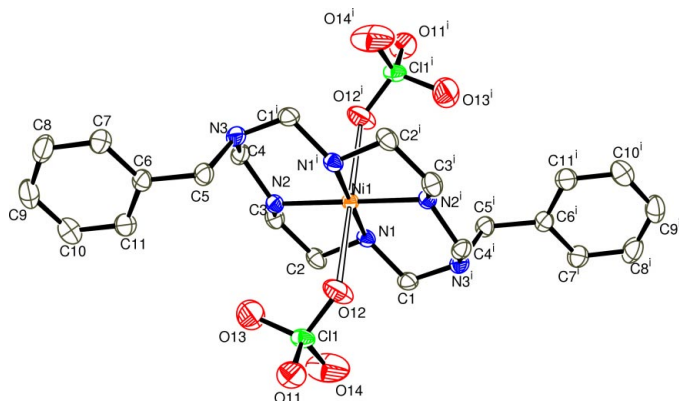


Figure 1
ORTEP (Burnett & Johnson, 1996) plot of the first $\text{Ni}(\text{C}_{22}\text{H}_{34}\text{N}_6)(\text{ClO}_4)_2$ molecule of the asymmetric unit of (I). Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

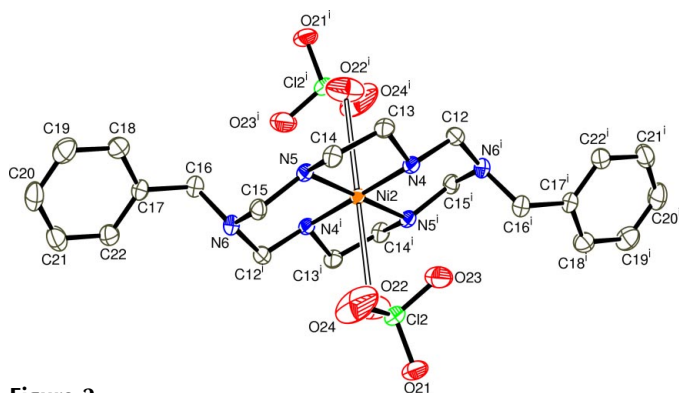


Figure 2
ORTEP (Burnett & Johnson, 1996) plot of the second $\text{Ni}(\text{C}_{22}\text{H}_{34}\text{N}_6)(\text{ClO}_4)_2$ molecule of the asymmetric unit of (I). Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry code: (ii) $1 - x, -y, -z$.]

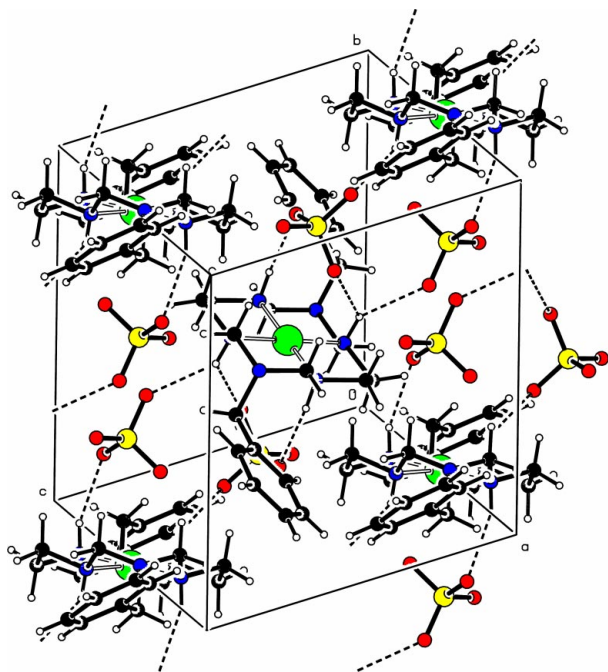


Figure 3
Packing diagram showing the $\text{N}-\text{H}\cdots\text{O}$ interactions in (I) (Spek, 1990).

atom and the geometry of the Ni atom is described as square planar, the long $\text{Ni}\cdots\text{O}$ distance being attributed to the packing of the pendent groups (Lu *et al.*, 2000).

In the title compound, (I), in which $R = \text{CH}_2\text{C}_6\text{H}_5$, the 14-membered hexaazacyclotetradecane macrocycle chelates to the Ni atom through its four secondary N atoms (see scheme). The two independent molecules in the asymmetric unit show slightly different $\text{Ni}-\text{O}(\text{perchlorate})$ interactions [2.730 (2) and 2.916 (2) Å]; the geometry is better interpreted in terms of a tetragonally distorted octahedron (Figs. 1 and 2). The packing is slightly more compact than that of the $-\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$ analog, as noted from the higher density (1.552 Mg m^{-3} , compared with 1.506 Mg m^{-3} for the $-\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$ complex). The complex is not, however, isostructural with the isoelectronic $-\text{CH}_2\text{C}_5\text{H}_4\text{N}$ complex, which crystallizes as a dihydrate and whose perchlorate group is involved in hydrogen bonding with the lattice water molecules; the pyridyl rings are not involved in any interaction either (Min & Suh, 2001*b*). The occurrence of $\text{N}-\text{H}\cdots\text{O}$ hydrogen-bonding interactions (Table 1) results in a two-dimensional hydrogen-bond network (Fig. 3).

Experimental

A methanol solution (50 ml) of nickel chloride hexahydrate (11.5 g, 0.05 mol) and ethylenediamine (6.0 g, 0.10 mol) was added dropwise to a methanol solution (70 ml) of a mixture of formaldehyde (24 ml, 0.30 mol) and benzylamine (16.1 g, 0.15 mol). The mixture was heated under reflux for 24 h. The solvent was removed and the product treated with a saturated aqueous solution of sodium perchlorate. The yellow product was purified by recrystallation from a mixture of acetone and saturated sodium perchlorate in 30% yield. CHN analysis for $\text{C}_{22}\text{H}_{34}\text{Cl}_2\text{N}_6\text{O}_8\text{Ni}$, found: C 40.95, H 5.58, N 13.07%; calculated: C 41.27, H 5.35, N 13.13%.

Crystal data

$[\text{Ni}(\text{C}_{22}\text{H}_{34}\text{N}_6)](\text{ClO}_4)_2$
 $M_r = 640.16$
 Triclinic, $P\bar{1}$
 $a = 10.209$ (1) Å
 $b = 11.617$ (1) Å
 $c = 11.916$ (1) Å
 $\alpha = 87.633$ (2)°
 $\beta = 75.940$ (2)°
 $\gamma = 88.501$ (2)°
 $V = 1369.5$ (2) Å³

$Z = 2$
 $D_x = 1.552 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 855 reflections
 $\theta = 4.0\text{--}29.8^\circ$
 $\mu = 0.96 \text{ mm}^{-1}$
 $T = 298$ (2) K
 Prism, yellow
 $0.23 \times 0.22 \times 0.12 \text{ mm}$

Data collection

Bruker SMART 1 K area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.809, T_{\text{max}} = 0.893$
 8366 measured reflections

6134 independent reflections
 5089 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.011$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -13 \rightarrow 9$
 $k = -15 \rightarrow 12$
 $l = -15 \rightarrow 12$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.105$
 $S = 1.05$
 6134 reflections
 357 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0591P)^2 + 0.4245P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.66 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.51 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Ni1—Ni1	1.9340 (17)	Ni2—N4	1.9314 (17)
Ni1—N2	1.9372 (17)	Ni2—N5	1.9318 (16)
Ni1—O12	2.730 (2)	Ni2—O22	2.916 (2)
N1—Ni1—N2	86.66 (7)	N4—Ni2—N5	86.70 (7)
N1 ⁱ —Ni1—N2	93.34 (7)	N4 ⁱⁱ —Ni2—N5	93.30 (7)
N1—Ni1—O12	100.60 (8)	N4—Ni2—O22	97.51 (7)
N1 ⁱ —Ni1—O12	79.40 (8)	N4 ⁱⁱ —Ni2—O22	82.49 (7)
N2—Ni1—O12	93.11 (7)	N5—Ni2—O22	99.83 (9)
N2 ⁱ —Ni1—O12	86.89 (7)	N5 ⁱⁱ —Ni2—O22	80.17 (9)

Symmetry codes: (i) 1 - x, 1 - y, 1 - z; (ii) 1 - x, -y, -z.

Table 2

Hydrogen-bonding geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1...O21 ⁱⁱⁱ	0.91	2.25	3.024 (3)	142
N1—H1...O12 ^{iv}	0.91	2.50	3.042 (3)	118
N2—H2...O13	0.91	2.23	3.094 (3)	158
N4—H4...O23	0.91	2.17	3.020 (3)	155
N5—H5...O11 ^v	0.91	2.18	2.947 (3)	142

Symmetry codes: (iii) x, y, 1 + z; (iv) 1 - x, 1 - y, 1 - z; (v) x, y - 1, z.

H atoms attached to C and N atoms were located in a difference Fourier map but were introduced in the refinement in calculated positions and treated with a riding model (N—H = 0.91 Å, methylene C—H = 0.97 Å and phenyl C—H = 0.93 Å). The displacement parameters were set at 1.2U_{eq}(CH, CH₂, N). Although the O atoms of the perchlorate anions have large ellipsoids, no reasonable disorder models were obtained.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996), *ORTEP-3 for Windows* (Farrugia, 1997) and *PLUTON* (Spek, 1990); software used to prepare material for publication: *SHELXL97*.

The authors thank the National Science Foundation of China (grant No. 20371051), the Ministry of Education of China and the University of Malaya for supporting this work.

References

- Ballester, L., Barral, M. C., Gutierrez, A., Monge, A., Perpignan, M. F., Ruiz-Valero, C. & Sanchez-Pelaez, A. E. (1994). *Inorg. Chem.* **33**, 2142–2146.
- Bruker (2001). *SAINT* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
- Cho, J., Lee, U. & Kim, J. C. (2002). *Transition Met. Chem.* **27**, 429–432.
- Choi, H. J. & Suh, M. P. (1998). (1998). *J. Am. Chem. Soc.* **120**, 10622–10628.
- Choi, H. J. & Suh, M. P. (2000). *Inorg. Chem.* **38**, 6309–6312.
- Choi, H. J., Lee, T. S. & Suh, M. P. (2001). *J. Inclusion Phenom. Macrocycl. Chem.* **41**, 155–162.
- Choi, H. J. & Suh, M. P. (1999). *Inorg. Chem.* **38**, 6309–6312.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Kang, S.-G., Ryu, K., Jung, S.-K. & Kim, J. (1999). *Inorg. Chem. Acta*, **293**, 140–146.
- Kim, J. C. & Lee, B. M. (1999). *J. Korean Chem. Soc.* **43**, 231–236.
- Kim, J. C., Lough, A. J., Fettingner, J. C., Choi, K.-Y., Kim, D., Pyun, S.-Y. & Cho, J. (2000). *Inorg. Chem. Acta*, **303**, 163–167.
- Kim, J. C., Lough, A. J. & Kim, H. (2002). *Inorg. Chem. Commun.* **5**, 771–776.
- Kou, H.-Z., Bu, W.-M., Gao, S., Liao, D.-Z., Jiang, Z.-H., Yan, S.-P., Gan, Y.-G. & Wang, G.-L. (2000). *J. Chem. Soc. Dalton Trans.* pp. 2996–3000.
- Kou, H.-Z., Gao, S., Bai, U. & Wang, Z.-M. (2001). *Inorg. Chem.* **40**, 6287–6294.
- Kou, H.-Z., Gao, S., Bu, W.-M., Liao, D.-Z., Ma, B.-Q., Jiang, Z.-H., Yan, S.-P., Fan, Y.-G. & Wang, G.-L. (1999). *J. Chem. Soc. Dalton Trans.* pp. 2477–2480.
- Kou, H.-Z., Gao, S., Ma, B.-Q. & Liao, D.-Z. (2000a). *J. Chem. Soc. Chem. Commun.* pp. 713–714.
- Kou, H.-Z., Gao, S., Ma, B.-Q. & Liao, D.-Z. (2000b). *J. Chem. Soc. Chem. Commun.* pp. 1309–1310.
- Kou, H.-Z., Si, S. F., Gao, S., Liao, D.-Z., Jiang, Z.-H., Yan, S. P., Fan, Y. G. & Wang, G. L. (2002). *Eur. J. Inorg. Chem.* pp. 699–702.
- Kou, H.-Z., Zhou, B.-C., Liao, D.-Z., Wang, R.-J. & Li, Y. D. (2002). *Inorg. Chem.* **41**, 6887–6891.
- Liu, J., Lu, T.-B., Xiang, H., Mao, Z.-W. & Ji, L.-N. (2002). *CrystEngComm*, **4**, 64–71.
- Lu, T.-B., Xiang, H., Li, X. Y., Mao, Z. W. & Ji, L. N. (2000). *Inorg. Chem. Commun.* **3**, 597–599.
- Lu, T.-B., Xiang, H., Luck, R. L., Jiang, L., Mao, Z.-W. & Ji, J.-N. (2002). *New J. Chem.* **26**, 969–971.
- Lu, T.-B., Xiang, H., Luck, R. L., Mao, Z.-W., Wang, D., Chen, C. & Ji, L.-N. (2001). *CrystEngComm*, article No. 41, 1–2.
- Lu, T.-B., Xiang, H., Su, C.-Y., Chen, P., Mao, Z.-W. & Ji, L.-N. (2001). *New J. Chem.* **25**, 216–217.
- Min, K. S. & Suh, M. P. (2001a). *Chem. Eur. J.* **7**, 303–313.
- Min, K. S. & Suh, M. P. (2001b). *Eur. J. Inorg. Chem.* pp. 449–455.
- Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.
- Shan, B.-Z., You, X.-Z., Fun, H.-K. & Sivakumar, K. (1996). *Acta Cryst.* **C52**, 3035–3057.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Suh, M. P. (1997). *Adv. Inorg. Chem.* **44**, 93–146.
- Suh, M. P., Shim, B. Y. & Yoon, T.-S. (1994). *Inorg. Chem.* **33**, 5509–5514.
- Xiang, H., Gao, S., Lu, T.-B., Luck, R. L., Mao, Z.-W., Chen, X.-M. & Ji, L. N. (2001). *New J. Chem.* **25**, 875–878.
- Xiang, H., Lu, T.-B., Chen, S.-Y., Mao, Z.-W., Feng, X.-L. & Yu, K.-B. (2001). *Polyhedron*, **20**, 313–319.