metal-organic papers

[1,8-Bis(2-phenylethyl)-1,3,6,8,10,13-hexaazacyclotetradecane]nickel(II) bis(tetrafluoroborate)

Yan-Wu Li,[a]* Hua Xiang,[a] Tong-Bu Lu[a] and Seik Weng Ng[b]

[a]Instrument Analysis and Research Center, Sun Yat-Sen University, Guangzhou 510275, People's Republic of China, and [b]Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia

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

In the title complex, [Ni(C$_{24}$H$_{38}$N$_6$)](BF$_4$)$_2$, the 14-membered hexaazacyclotetradecane macrocycle chelates to the Ni atom through its four secondary N atoms. The tetrafluoroborate ion interacts with the Ni atom at a distance of about 3 Å, and the coordination geometry of the Ni atom is regarded as tetragonally distorted octahedral. The Ni atom lies on an inversion center.

Comment

The third of this series of nickel complexes of hexaazacyclotetradecane has a tetrafluoroborate ion as the counter-ion.


(I)
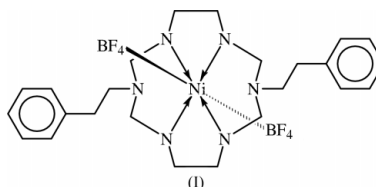
In Ni(C$_{24}$H$_{38}$N$_6$(BF$_4$)$_2$, (I) (Fig. 1), the Ni—F interactions are much longer than those found in formal tetrafluoroborate-coordinated Ni complexes (Tomlinson *et al.*, 1972). However, it has been pointed out that, although the tetrafluoroborate ion is generally non-coordinating, it can occupy the vacant coordination sites of ligand-deficient systems (Burch *et al.*, 1988), of which the square-planar Ni system is an example. As such, the coordination geometry of the Ni atom in (I) can also
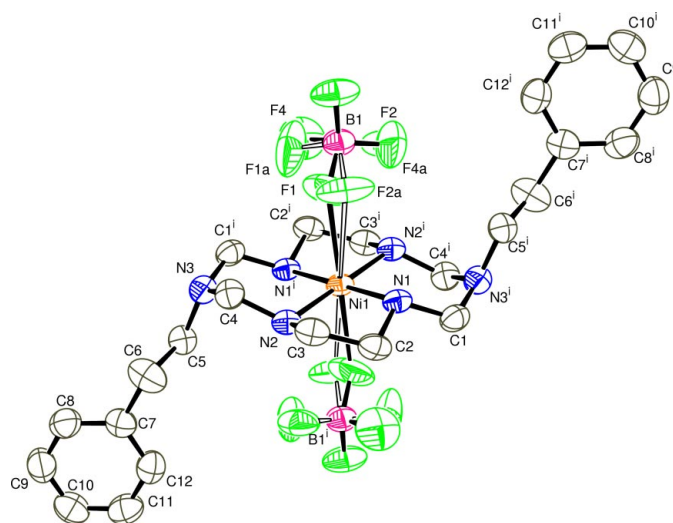
Figure 1
*ORTEP*III (Burnett & Johnson, 1996) plot of (I). Displacement ellipsoids are drawn at the 50% probability level. The disordered (primed) F atoms of one component are shown with open bonds. H atoms have been omitted for clarity. [Symmetry code (i): 1 −*x*, 1-*y*, 1-*z*.]
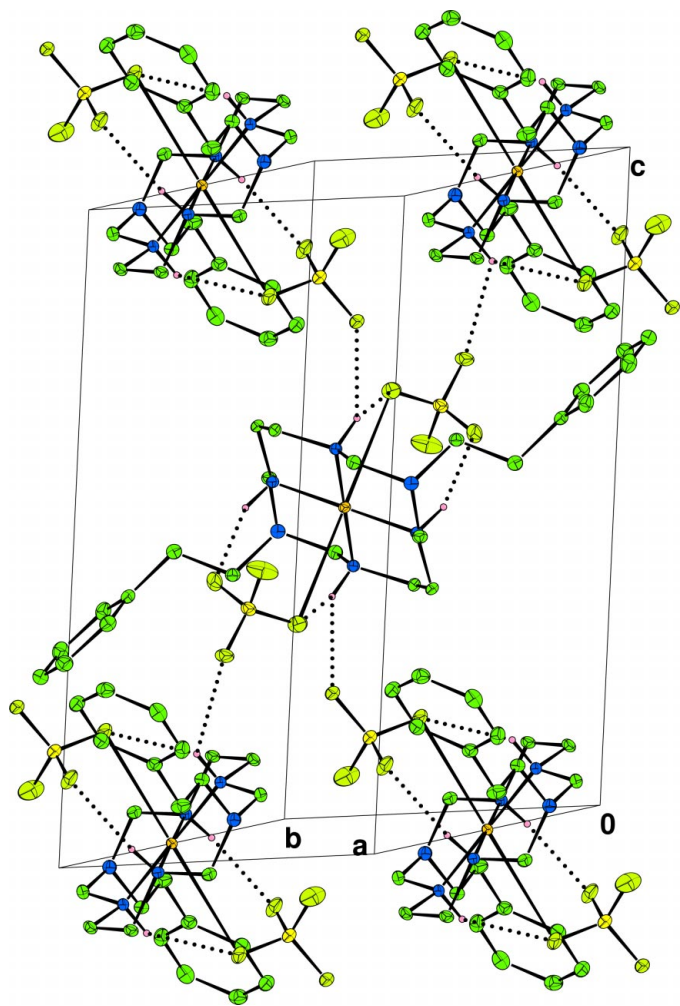
Figure 2
CAMERON (Watkin *et al.*, 1993) view showing the N—H···F hydrogen-bond interactions in the unit cell. Ellipsoids are drawn at the 10% probability level. For clarity, the second components of the disordered F atoms have been omitted and only the H atoms attached to nitrogen are shown.

be regarded as distorted octahedral, Ni lying on an inversion center. The packing is governed by N—H···F hydrogen bonds, as shown in Fig. 2.

Experimental

The title compound was similarly synthesized from 2-phenylethylamine (18.2 g, 0.15 mmol) and and sodium tetraborate along with the other reagents (Li *et al.*, 2004). CHN analysis for $C_{24}H_{38}BF_8N_6Ni$ found: C 44.67, H 6.23, N 12.91%; calculated: C 44.83, H 5.96, N 13.07%.

Crystal data

$[Ni(C_{24}H_{38}N_6)](BF_4)_2$	$D_x = 1.490$ Mg m^{-3}
$M_r = 642.93$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 831
$a = 11.427 (2)$ Å	reflections
$b = 8.329 (1)$ Å	$\theta = 2.4–24.2°$
$c = 15.622 (2)$ Å	$\mu = 0.76$ mm^{-1}
$\beta = 105.480 (3)°$	$T = 298 (2)$ K
$V = 1432.9 (4)$ Å^3	Plate, yellow
$Z = 2$	$0.39 \times 0.16 \times 0.04$ mm

Data collection

Bruker SMART 1K area-detector diffractometer	3246 independent reflections
φ and ω scans	2178 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$R_{int} = 0.043$
	$\theta_{max} = 27.5°$
$T_{min} = 0.757$, $T_{max} = 0.970$	$h = -9 \rightarrow 14$
8039 measured reflections	$k = -10 \rightarrow 10$
	$l = -20 \rightarrow 10$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.037$	$w = 1/[\sigma^2(F_o^2) + (0.0447P)^2]$
$wR(F^2) = 0.091$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.94$	$(\Delta/\sigma)_{max} < 0.001$
3246 reflections	$\Delta\rho_{max} = 0.29$ e Å^{-3}
216 parameters	$\Delta\rho_{min} = -0.23$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—N2	1.9205 (16)	Ni1—F1	3.056 (11)
Ni1—N1	1.9346 (16)	Ni1—F2A	3.084 (10)
N2^i—Ni1—N1	93.09 (7)	N1^i—Ni1—F1	105.9 (2)
N2—Ni1—N1	86.91 (7)	N2^i—Ni1—F2A	94.2 (2)
N2^i—Ni1—F1	98.41 (18)	N2—Ni1—F2A	85.8 (2)
N2—Ni1—F1	81.59 (17)	N1—Ni1—F2A	67.8 (2)
N1—Ni1—F1	74.1 (2)	N1^i—Ni1—F2A	112.2 (2)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···F2A	0.91	2.26	2.958 (11)	133
N1—H1···F3^{ii}	0.91	2.46	3.096 (2)	127
N1—H1···F1	0.91	2.52	3.137 (11)	126
N2—H2···F4A^i	0.91	2.18	3.029 (8)	154
N2—H2···F2^i	0.91	2.37	3.203 (9)	152

Symmetry codes: (ii) $1 - x, 1 - y, 1 - z$; (i) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$.

The nitrogen- and carbon-bound H atoms were placed at calculated positions and were refined in the riding-model approximation (N—H = 0.91 Å, methylene C—H = 0.97 and 0.96 Å, and phenyl C—H = 0.93 Å). The displacement parameters were set at 1.2 times U_{eq} of the parent atoms. The tetrafluoroborate group is disordered over two positions of nearly equal occupancy. The eight B—F distances were restrained to be approximately equal. In Table 1, as well as for the *ORTEP* plot (Fig. 1), the disordered F atoms are labeled with primes.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996), *ORTEP-3 for Windows* (Farrugia, 1997) and *CAMERON* (Watkin *et al.*, 1993); software used to prepare material for publication: *SHELXL*97.

metal-organic papers

References

Bruker (2001). *SAINT* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.

Burch, R. R., Calabrese, J. & Ittel, S. D. (1988). *Organometallics*, **7**, 1642–1648.

Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Li, Y.-W., Xiang, H., Lu, T.-B. & Ng, S. W. (2004). *Acta Cryst.* E**60**, m309–m311.

Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Tomlinson, A. A. G., Bonamico, M., Dessy, G., Fares, V. & Scaramuzza, L. (1972). *J. Chem. Soc. Dalton Trans.* pp. 1671–1674.

Watkin, D. M., Pearce, L. & Prout, C. K. (1993). *CAMERON* Chemical Crystallography Laboratory, University of Oxford, England.