Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Tetrakis(1,2-diaminobenzene)-$\kappa^2N;\kappa^4N,N'$-nickel(II) dichloride

W. G. Piyal Ariyananda and Richard E. Norman*

Chemistry Department, CNSB-210, University of Louisiana at Monroe, Monroe, LA 71209, USA

Correspondence e-mail: rnorman@ulm.edu

Received 19 November 2004
Accepted 17 December 2004
Online 24 December 2004

Key indicators

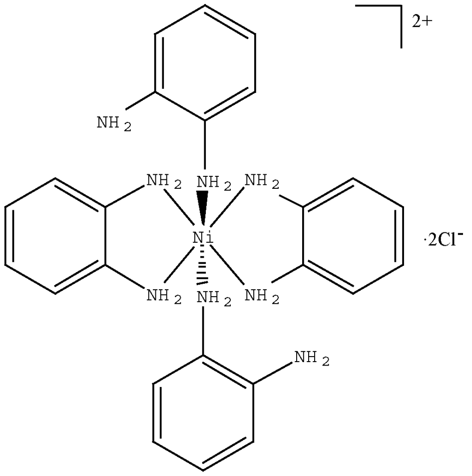
Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.004 Å
R factor = 0.062
wR factor = 0.110
Data-to-parameter ratio = 12.9

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

The title complex, $[\mathrm{Ni(C_6H_8N_2)_4}]\mathrm{Cl_2}$, consists of a centrosymmetric octahedral six-coordinate nickel(II) coordination complex cation and two chloride ions. The Ni atom sits on a crystallographic inversion center. Two of the 1,2-diaminobenzene ligands are chelating and the other two are monodentate. The chelating ligands define an equatorial plane and the monodentate ligands are axially *trans*. In addition to one hydrogen bond between the non-coordinated N atom of the monodentate ligand and an adjacent metal complex, there is extensive hydrogen bonding to the chloride ions.

Comment

We are currently investigating $\mathrm{Ni^{II}}$ complexes of the form $[\{\mathrm{Ni}L_4X\}_2]^{2+}$, where X is either $\mathrm{Cl^-}$ or $\mathrm{Br^-}$ and L_4 represents some combination of ligands to provide four N-atom donors. These dimeric complexes exhibit ferromagnetic coupling between the metal centers, with the coupling dependent upon the sum of the Ni—X bond lengths (Tong *et al.*, 1999, 2000). When we have attempted to make complexes using two bidentate ligands as L_4, we have often followed a modification of State's (1960) procedure in which a tris(bidentate chelate)nickel(II) complex is reacted with the appropriate $\mathrm{Ni}X_2$ hydrate (Xie, 2000; Ariyananda, 2003). During an attempted preparation of a crystalline form of a tris(1,2-diaminobenzene)nickel(II) complex, the title compound, (I), was obtained.



(I)

The title compound has been synthesized previously and some of its physical properties reported (Marks *et al.*, 1967); however, its structure was not reported. The cationic portion

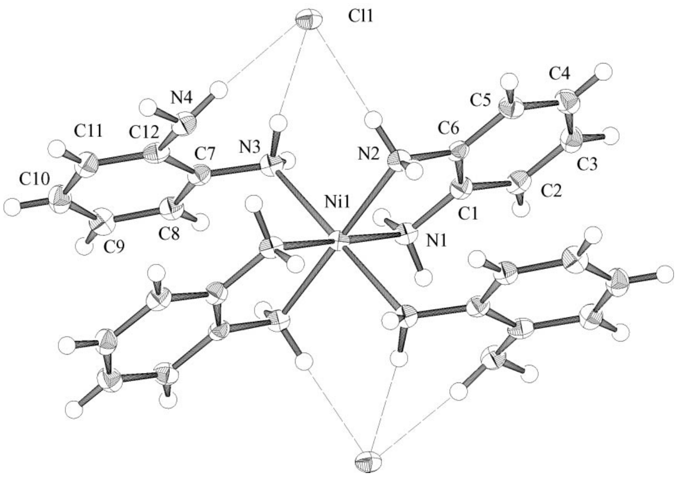


Figure 1
View of the symmetry-expanded molecule of (I), with displacement ellipsoids drawn at the 50% probability level.

along with chloride counter-ions and additional 1,2-diaminobenzene has been reported (Elder *et al.*, 1974) and the distances and angles within the cationic portion of the two structures agree within experimental error.

The structure consists of a centrosymmetric octahedral six-coordinate nickel(II) coordination complex cation and two chloride ions. The Ni atom sits on a crystallographic inversion center. Two of the 1,2-diaminobenzene ligands are chelating and the other two are monodentate. The chelating ligands define an equatorial plane and the monodentate ligands are axially *trans*. Seven of the eight NH groups donate an H atom for hydrogen bonding. With the exception of N1—H1, these hydrogen bonds are all to the chloride counter-ions. N1—H1 donates to N4 of an adjacent cation. The eighth group (N4—H15) does not participate in a hydrogen bond; H15 has its closest approach to C3 in an adjacent cation at $(-x, y-\frac{1}{2}, \frac{3}{2}-z)$.

Experimental

Nickel(II) chloride hexahydrate (0.2382 g, 1.002 mmol) was dissolved in 10 ml of 5% aqueous methanol, heated to 328 K and stirred for 10 min, producing a green solution. 1,2-Diaminobenzene (0.4320 g, 3.996 mmol) was added, giving a greenish purple solution. Purple 'flake-like' crystals appeared in a few minutes and were recrystallized from 5% aqueous methanol. Absorption spectrum (H_2O) λ_{max} (ε_M): 364.6 (12.3), 524 (5.0), 737 (*sh*), 971 (6.3). ^1H NMR (300 MHz, D_2O) 13, 14 and 16.5.

Crystal data

$[Ni(C_6H_8N_2)_4]Cl_2$
$M_r = 562.18$
Monoclinic, $P2_1/c$
$a = 12.8062\ (7)$ Å
$b = 8.1242\ (4)$ Å
$c = 12.4333\ (8)$ Å
$\beta = 100.610\ (2)^\circ$
$V = 1271.45\ (11)$ Å^3
$Z = 2$

$D_x = 1.468$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2903 reflections
$\theta = 2.5$–27.5°
$\mu = 1.00$ mm^{-1}
$T = 100$ K
Parallelepiped, violet
$0.15 \times 0.12 \times 0.10$ mm

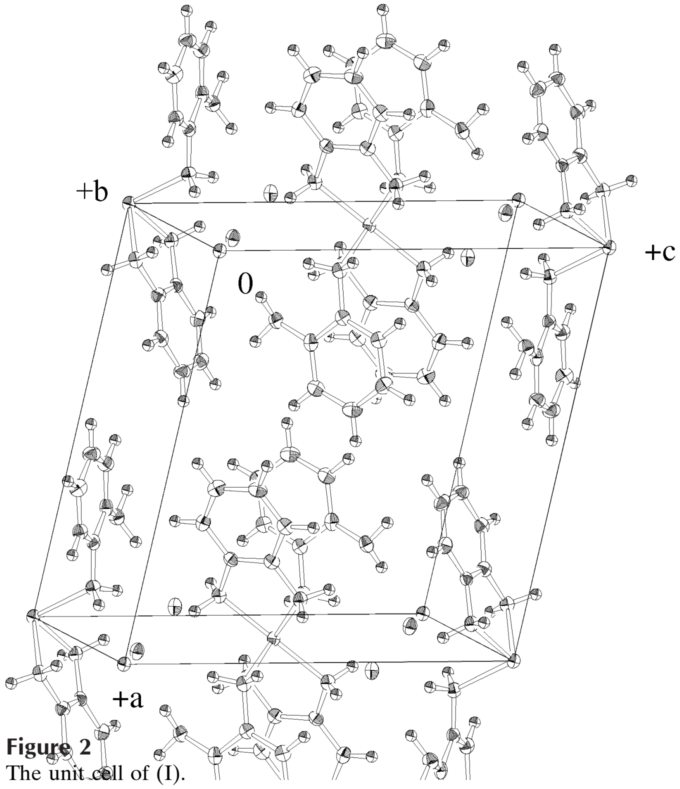


Figure 2
The unit cell of (I).

Data collection

Nonius KappaCCD diffractometer with an Oxford Cryosystems Cryostream cooler
ω scans with κ offsets
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)
$T_{min} = 0.854$, $T_{max} = 0.905$

12286 measured reflections
2919 independent reflections
2077 reflections with $I > 3\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 27.5^\circ$
$h = -16 \rightarrow 16$
$k = -10 \rightarrow 10$
$l = -16 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.110$
$S = 1.02$
2077 reflections
161 parameters
H atoms: see below

$w = 1/[\sigma^2(F_o) + 0.00140625|F_o|^2]$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.85$ e Å^{-3}
$\Delta\rho_{min} = -0.68$ e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: 0.69 (3)

Table 1
Selected geometric parameters (Å, °).

Ni1—N1	2.100 (2)	N3—C7	1.431 (4)
Ni1—N2	2.108 (2)	N4—C12	1.411 (4)
Ni1—N3	2.220 (2)	C1—C6	1.393 (4)
N1—C1	1.453 (4)	C7—C12	1.409 (4)
N2—C6	1.451 (4)		
N1—Ni1—N1^i	180	N3—Ni1—N3^i	180
N1—Ni1—N2	82.21 (9)	Ni1—N1—C1	110.2 (2)
N1—Ni1—N2^i	97.79 (9)	Ni1—N2—C6	110.1 (2)
N1—Ni1—N3	89.42 (8)	Ni1—N3—C7	121.1 (2)
N1—Ni1—N3^i	90.58 (8)	N1—C1—C6	118.3 (2)
N2—Ni1—N2^i	180	N2—C6—C1	118.2 (2)
N2—Ni1—N3	89.18 (8)	N3—C7—C12	121.3 (2)
N2—Ni1—N3^i	90.82 (8)		

Symmetry code: (i) $-x, -y, 2-z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···N4^{i}	0.95	2.19	3.021 (3)	145
N1—H2···Cl1^{ii}	0.95	2.69	3.313 (2)	124
N2—H7···Cl1^{iii}	0.95	2.62	3.414 (2)	141
N2—H8···Cl1	0.95	2.35	3.302 (2)	176
N3—H9···Cl1	0.95	2.41	3.351 (2)	174
N3—H10···Cl1^{iv}	0.95	2.39	3.306 (2)	161
N4—H16···Cl1	0.97	2.29	3.254 (3)	173

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

Atoms H15 and H16, the H atoms associated with N4 were found in difference maps but not refined (N—H = 0.972 and 0.967 Å). All other H atoms were placed in calculated positions (C—H = N—H = 0.95 Å). All of the H atoms are assigned $U_{\rm iso}$(H) values 1.2 times larger than $U_{\rm eq}$ of the atoms to which they are bound.

Data collection: *COLLECT* (Nonius 2000); cell refinement: *DENZO* and *SCALEPACK* (Version 1.96.2; Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *TEXSAN* for Windows (Version 1.06; MSC, 1999); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN* for Windows.

We thank Frank Fronczek for the data collection and the Louisiana Board of Regents Support Fund for financial support.

References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.

Ariyananda, W. G. P. (2003). MS thesis, University of Louisiana at Monroe, USA.

Elder, R. C., Koran, D. & Mark, H. B. Jr (1974). *Inorg. Chem.* **13**, 1644–1649.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Marks, D. R., Phillips, D. J. & Redfern, J. P. (1967). *J. Chem. Soc. A*, pp. 1464–1469.

Molecular Structure Corporation (1999). *TEXSAN for Windows*. Version 1.06. MSC, 9009 New Trails Drive, The Woodlands, TX 77381–5209, USA.

Nonius (2000). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr and R. M. Sweet, pp. 307–326. New York: Academic Press.

State, H. M. (1960). *Inorganic Synthesis*, Vol. 6, edited by E. G. Rochow, pp. 198–201. New York: McGraw-Hill.

Tong, B., Chang, S.-C. & Norman, R. E. (1999). *Acta Cryst.* C**55**, 1236–1238.

Tong, B., Chang, S.-C., Carpenter, E. E., O'Connor, C. J., Lay, J. O. Jr & Norman, R. E. (2000). *Inorg. Chim. Acta*, **300–302**, 855–861.

Xie, M. (2000). MS thesis, University of Louisiana at Monroe, USA.

Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.