Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Bis(diethylenetriamine)nickel(II) tetracyanonickelate(II)

Iñaki Muga, Pablo Vitoria, Santiago Reinoso and Juan M. Gutiérrez-Zorrilla*

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad del País Vasco, Apdo. 644, E-48080 Bilbao, Spain

Correspondence e-mail: qipguloj@lg.ehu.es

Received 26 June 2003
Accepted 2 July 2003
Online 17 July 2003

Key indicators

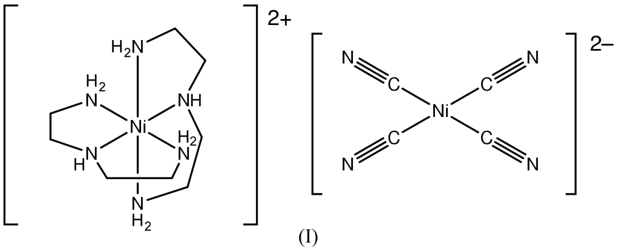
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.012 Å
R factor = 0.042
wR factor = 0.078
Data-to-parameter ratio = 15.6

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

The structure determination of the title compound, $[Ni(C_4H_{13}N_3)_2][Ni(CN)_4]$, reveals the presence of a complex $[Ni(dien)_2]^{2+}$ cation (dien is diethylenetriamine) and a pair of crystallographically independent half-complex $[Ni(CN)_4]^{2-}$ anions in the asymmetric unit. The Ni atoms of the anions lie on crystallographic inversion centres. In the cationic unit, the ligand geometry around the nickel(II) is distorted octahedral, with the two dien ligands coordinated in *mer* fashion, whereas in the anionic unit, the geometry of the nickel(II) atom is square planar. The crystal structure shows a three-dimensional hydrogen-bonding network involving alternating anionic and cationic rows placed in the $(1\bar{1}1)$ plane.

Comment

Cyano complexes attract the interest of both chemists and physicists due to their remarkable magnetic properties (Kitazawa *et al.*, 1996; Verdaguer *et al.*, 1999; Ohba & Okawa, 2000; Cernak *et al.*, 2001). In the course of our investigations on low-dimensional molecular magnetic materials based on transition metal–oxalate dimers and cyano–metallates (Vitoria *et al.*, 2003; Muga *et al.*, 2002), the title compound, (I), was synthesized from the dissociation of $[\{Ni(dien)(H_2O)\}_2(ox)]^{2+}$ by a cyanide source. The structures of the dihydrated compound (Rodríguez *et al.*, 1999) and the $[Pd(CN)_4]^{2-}$ analogue (Cernak *et al.*, 2002) have been previously reported.



(I)

The asymmetric unit in (I) consists of one $[Ni(dien)_2]^{2+}$ complex cation and two independent half $[Ni(CN)_4]^{2-}$ complex anions on inversion centres. The coordination geometry around the Ni^{II} atom in the complex $[Ni(dien)_2]^{2+}$ cation is distorted octahedral, where the two dien ligands are coordinated in *mer* fashion. $[Ni(CN)_4]^{2-}$ shows the well known square planar geometry of the group 10 cyano–metallates (Fig. 1). Both the complex cations and the complex anions are arranged in alternating cationic and anionic rows placed in the $(1\bar{1}1)$ plane. These layers are linked by an extended and intricate three-dimensional hydrogen bonding network which involves all the N atoms, with the exception of N24 (Fig. 2).

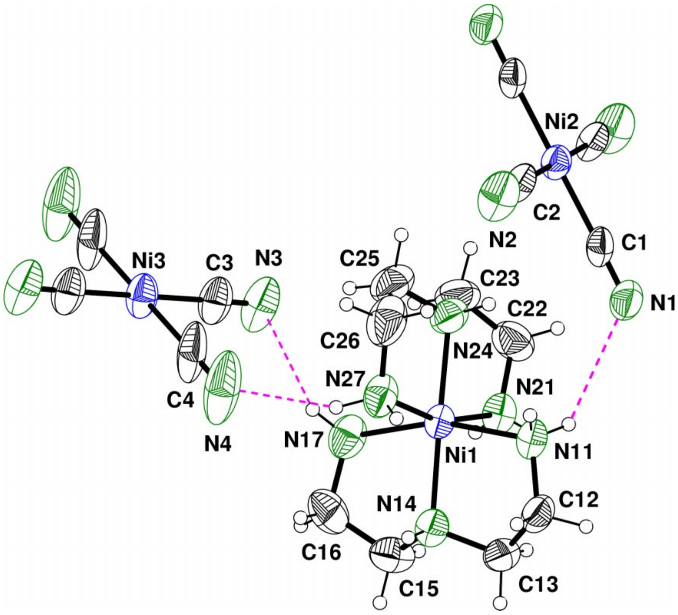


Figure 1
View of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme for the contents of the asymmetric unit.

Experimental

A solution containing 12 mg of CuCN and 42 mg of KCN in 50 ml of water was added to a solution of 100 mg of [{Ni(dien)-(H_2O)}$_2$(ox)](PF_6)$_2$ in 50 ml of water. After filtering off a violet precipitate, the resulting solution was allowed to stand at room temperature, to obtain pale-violet needle-shaped crystals of the title compound. Elemental analysis (%) found (C, H, N): 33.50, 6.32, 32.90; calculated for $C_{12}H_{26}N_{10}Ni_2$: 33.69, 6.13, 32.74. IR (cm^{-1}): 3329, 3205, 2117, 1081, 978.

Crystal data

$[Ni(C_4H_{13}N_3)_2][Ni(CN)_4]$
$M_r = 427.85$
Monoclinic, $P2_1/c$
$a = 15.138\ (2)$ Å
$b = 9.458\ (1)$ Å
$c = 15.248\ (2)$ Å
$\beta = 111.884\ (16)^\circ$
$V = 2025.8\ (5)$ Å^3
$Z = 4$
$D_x = 1.403$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4000 reflections
$\theta = 2.7$–30°
$\mu = 1.87$ mm^{-1}
$T = 293\ (2)$ K
Needle, pale violet
0.51 × 0.11 × 0.09 mm

Data collection

Stoe IPDS area-detector diffractometer
φ scans
Absorption correction: analytical (*X-RED*; Stoe & Cie, 1996)
$T_{\min} = 0.744$, $T_{\max} = 0.897$
11 730 measured reflections
3410 independent reflections
1449 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.121$
$\theta_{\max} = 25^\circ$
$h = -18 \rightarrow 18$
$k = -11 \rightarrow 11$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.078$
$S = 0.70$
3410 reflections
218 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.013P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.26$ e Å^{-3}
$\Delta\rho_{\min} = -0.47$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00329 (18)

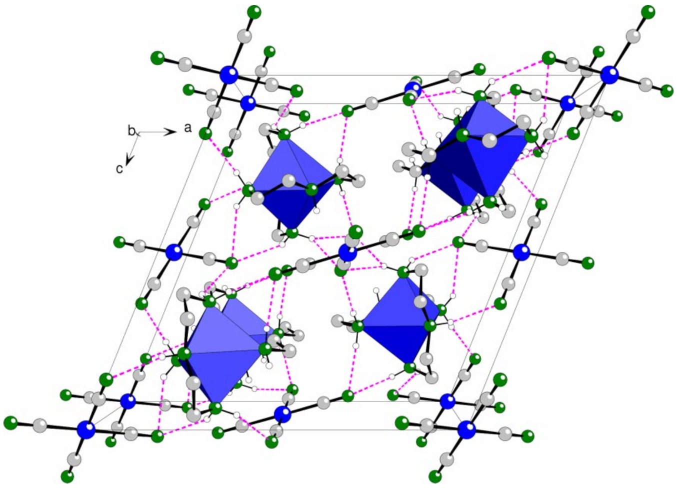


Figure 2
View of the crystal packing along the *b* axis.

Table 1
Selected geometric parameters (Å, °).

Ni1—N24	2.063 (5)	Ni2—C2	1.887 (8)
Ni1—N14	2.072 (5)	Ni3—C4	1.851 (9)
Ni1—N27	2.120 (5)	Ni3—C3	1.862 (8)
Ni1—N11	2.136 (4)	C1—N1	1.157 (7)
Ni1—N17	2.179 (5)	C2—N2	1.124 (8)
Ni1—N21	2.185 (5)	C3—N3	1.139 (8)
Ni2—C1	1.843 (7)	C4—N4	1.133 (9)
N24—Ni1—N27	81.6 (3)	C1—Ni2—C2$^{\rm i}$	88.8 (3)
N14—Ni1—N11	81.9 (2)	C1—Ni2—C2	91.2 (3)
N14—Ni1—N17	81.5 (2)	C4—Ni3—C3$^{\rm ii}$	91.9 (3)
N24—Ni1—N21	81.0 (2)	C4—Ni3—C3	88.1 (3)

Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $2-x, 1-y, 1-z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H11*A*···N1$^{\rm iii}$	0.90	2.57	3.288 (8)	138
N11—H11*A*···N1	0.90	2.69	3.258 (8)	122
N11—H11*B*···N3$^{\rm iv}$	0.90	2.39	3.161 (9)	144
N14—H14···N4$^{\rm v}$	0.91	2.31	3.128 (10)	150
N17—H17*A*···N3	0.90	2.54	3.183 (9)	129
N17—H17*B*···N2$^{\rm vi}$	0.90	2.29	3.143 (9)	159
N21—H21*A*···N1$^{\rm iii}$	0.90	2.25	3.127 (7)	165
N21—H21*B*···N2$^{\rm vi}$	0.90	2.19	3.046 (8)	158
N27—H27*A*···N4	0.90	2.24	3.067 (8)	153

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

The H atoms were placed geometrically and were treated as riding on their parent atoms (C or N), with C—H = 0.97 Å, N—H = 0.90 or 0.91 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(C or N). The high $R_{\rm int}$, low *S* value and low ratio of observed to unique reflections (0.42) are due to the poor quality of the crystal. The experiment was repeated with several crystals (even from different syntheses) and all of them diffracted quite poorly.

Data collection: *IPDS* (Stoe & Cie, 1996); cell refinement: *IPDS*; data reduction: *X-RED* (Stoe & Cie, 1996); program(s) used to solve structure: *DIRDIF*99.2 (Beurskens *et al.*, 1999); program(s) used to

Acta Cryst. (2003). E**59**, m576–m578 Iñaki Muga *et al.* • $[Ni(C_4H_{13}N_3)_2][Ni(CN)_4]$ **m577**

refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2002); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

This work was supported by MCT (MAT2002–03166). SR thanks Gobierno Vasco for a Doctoral Fellowship.

References

Beurskens, P. T., Beurskens, G., de Gelder, R., García-Granda, S., Gould, R. O., Israel, R. & Smits, J. M. M. (1999). *The DIRDIF*99 *Program System.* Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

Brandenburg, K. (2002). DIAMOND. Version 2.1e. Crystal Impact GbR, Bonn, Germany.

Cernak, J., Orendac, M., Potocnak, I., Chomic, J., Orendacova, A., Skorsepa, J. & Feher, A. (2001). *Coord. Chem. Rev.* **224**, 51–66.

Cernak, J., Paharova, J., Skorsepa, J. & Massa, W. (2002). *Z. Anorg. Allg. Chem.* **628**, 344–348.

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

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Kitazawa, T., Gomi, Y., Takahashi, M., Tadeka, M., Enomoto, A., Miyazaki, A. & Enoki, T. (1996). *J. Mater. Chem.* **6**, 119–121.

Muga, I., Gutiérrez-Zorrilla, J. M., Vitoria, P., Román, P. & Lloret, F. (2002). *Polyhedron*, **21**, 2631–2638.

Ohba, M. & Okawa, H. (2000). *Coord. Chem. Rev.* **198**, 313–328.

Rodríguez, V., Gutiérrez-Zorrilla, J. M., Vitoria, P., Luque, A., Román, P. & Martínez-Ripoll, M. (1999). *Inorg. Chim. Acta*, **290**, 57–63.

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

Stoe & Cie (1996). *IPDS* (Version 2.75) and *X-RED* (Version 1.08). Stoe & Cie, Darmstadt, Germany.

Verdaguer, M., Bleuzen, A., Marvaud, V., Vaisserman, J., Seuleiman, M., Desplanches, C., Scuiller, A., Train, A., Garde, R., Gelly, G., Lomenech, C., Roseman, I., Veillet, P., Cartier, C. & Villain, F. (1999). *Coord. Chem. Rev.* **190**/**192**, 1023–1047.

Vitoria, P., Muga, I., Gutiérrez-Zorrilla, J. M., Luque, A., Román, P., Lezama, L., Zuñiga, F. J. & Beitia, J. I. (2003). *Inorg. Chem.* **42**, 960–969.

m578 Iñaki Muga *et al.* • $[Ni(C_4H_{13}N_3)_2][Ni(CN)_4]$ *Acta Cryst.* (2003). E**59**, m576–m578