metal-organic papers

Tris[bis(diethylenetriamine)nickel(II)] bis[hexacyanoferrate(III)] decahydrate

Iñaki Muga, Pablo Vitoria, Juan M. Gutiérrez-Zorrilla,* Antonio Luque and Pascual Román

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

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

Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean σ(C–C) = 0.007 Å
H-atom completeness 80%
Disorder in solvent or counterion
R factor = 0.051
wR factor = 0.177
Data-to-parameter ratio = 24.3

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, tris[bis-(diethylenetriamine)nickel(II)] bis[hexacyanoferrate(III)] decahydrate, [Ni(C$_4$H$_{13}$N$_3$)$_2$]$_3$[Fe(CN)$_6$]$_2 \cdot$10H$_2$O, reveals the presence of complex cations [Ni(dien)$_2$]$^{2+}$ and complex anions [Fe(CN)$_6$]$^{3-}$. In the cationic unit, the ligand geometry around nickel(II) is nearly octahedral, with two tridentate dien molecules coordinated in *mer* fashion. The complex anion also shows a distorted octahedral environment. The cations and anions are linked by N—H···O and N—H···N hydrogen bonds to form a three-dimensional network.

Comment

Cyano-complexes attract the interest of both chemists and physicists, due to their remarkable magnetic properties (Verdaguer *et al.*, 1999; Ohba & Okawa, 2000; Kitazawa *et al.*, 1996; Cernak *et al.*, 2001). During our research on low-dimensional molecular magnetic materials based on cyano-complexes, the title compound [Ni(dien)$_2$]$_3$[Fe(CN)$_6$]$_2 \cdot$10H$_2$O, (I), was synthesized. It was obtained from NiCl$_2$, diethyl-enetriamine and K$_3$Fe(CN)$_6$. In this work we report the preparation and structure of (I).

(I)
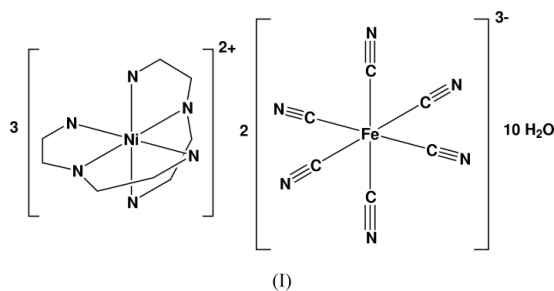
The asymmetric unit consists of a hexacyanoferrate(III) complex anion, one bis(diethylenetriamine)nickel(II) complex cation, one-half of the bis(diethylenetriamine)-nickel(II) complex cation (the other half is related by a crystallographic twofold axis) and five water molecules. The complex anion has a distorted octahedral geometry. The coordination geometry around each nickel atom is NiN$_6$ distorted octahedral, where the two tridentate dien molecules are coordinated in *mer* fashion (Fig. 1).

In the crystal, the cations and anions are alternately arranged to form layers approximately parallel to ($\bar{4}$02). The layers, which are stacked along the *a* axis, are linked by hydrogen bonds involving the water molecules (short contact distances are given in Table 2) and also by N—H···O and N—H···N hydrogen bonds (Table 3). A view of the molecular packing down the *b* axis is shown in Fig. 2.
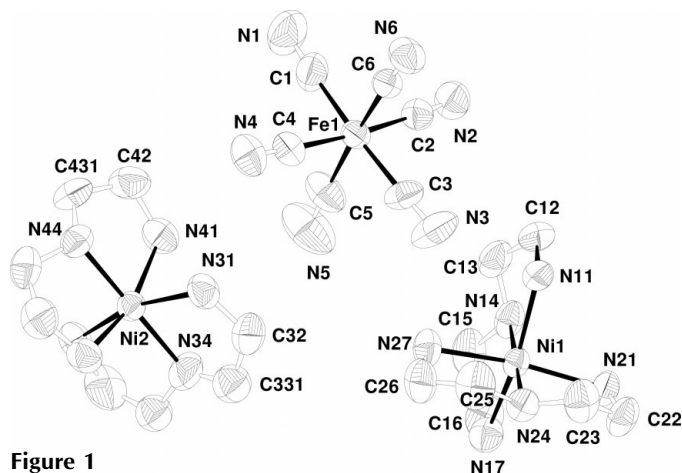
Figure 1
The molecular structure of (I), showing the atom-numbering scheme, with 50% probability displacement ellipsoids. Water O atoms have been omitted and only one conformation of each disordered dien ligand (bonded to Ni2) is shown for clarity.

Experimental

All operations for the synthesis were carried out in darkness to avoid decomposition of the hexacyanoferrate complex. Nickel chloride (0.07 g, 0.29 mmol) and diethylenetriamine (0,06 g, 0.595 mmol) were mixed in aqueous solution (50 ml). The resulting purple solution and $K_3Fe(CN)_6$ (0.098 g, 0.29 mmol) in DMF were mixed by slow diffusion. A light brown solid was filtered off and the resulting solution was allowed to stand. Black crystals suitable for X-ray analysis were obtained by slow evaporation after seven months. CHN analysis, found: C 30.50, H 6.84, N 29.70%; calculated for $C_{36}H_{98}Fe_2N_{30}Ni_3O_{10}$: C 30.90, H 7.06, N 30.03%. IR(KBr plate): $\nu_{as}(CN)$ 2118(s), 2007(w); $\delta(CH_2)$ 1462(w), 1439(m) cm^{-1}.

Crystal data

$[Ni(C_4H_{13}N_3)_2]_3[Fe(CN)_6]_2 \cdot 10H_2O$
$M_r = 1399.27$
Monoclinic, $C2/c$
$a = 27.195 (3)$ Å
$b = 12.602 (1)$ Å
$c = 19.747 (2)$ Å
$\beta = 104.51 (1)°$
$V = 6551.7 (11)$ Å^3
$Z = 4$
$D_x = 1.419$ Mg m^{-3}
$D_m = 1.42$ Mg m^{-3}

D_m measured by flotation in a mixture of CCl_4 and $CHBr_3$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 11.6$–$14.2°$
$\mu = 1.35$ mm^{-1}
$T = 293 (2)$ K
Prism, black
$0.51 \times 0.40 \times 0.22$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.520$, $T_{max} = 0.704$
9775 measured reflections
9512 independent reflections
6070 reflections with $I > 2\sigma(I)$

$R_{int} = 0.020$
$\theta_{max} = 30.0°$
$h = -38 \rightarrow 36$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 27$
2 standard reflections every 90 reflections intensity decay: 4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.178$
$S = 1.04$
9512 reflections
391 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1005P)^2 + 3.0322P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.79$ e Å^{-3}
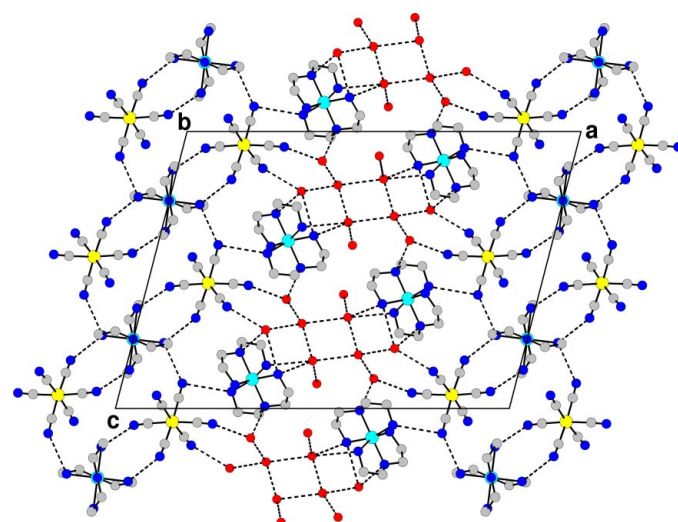$\Delta\rho_{min} = -0.57$ e Å^{-3}

Figure 2
View of the packing, projected on the (101) plane. H atoms have been omitted for clarity.

Table 1
Selected geometric parameters (Å).

Fe1—C1	1.915 (4)	Ni1—N17	2.146 (3)
Fe1—C2	1.940 (4)	Ni1—N21	2.129 (3)
Fe1—C3	1.928 (4)	Ni1—N24	2.062 (3)
Fe1—C4	1.945 (4)	Ni1—N27	2.176 (3)
Fe1—C5	1.924 (4)	Ni2—N31	2.157 (3)
Fe1—C6	1.919 (4)	Ni2—N34	2.060 (5)
Ni1—N11	2.162 (3)	Ni2—N41	2.171 (3)
Ni1—N14	2.062 (3)	Ni2—N44	2.056 (4)

Table 2
Contact distances (Å).

O1···N6^i	2.806 (6)	O3···O6	3.101 (15)
O1···N1^{ii}	2.841 (7)	O3···O5	3.243 (13)
O1···O3^i	2.727 (11)	O3···O4^v	3.305 (12)
O2···N5	2.762 (8)	O5···N3	3.106 (9)
O2···O4	2.694 (8)	O5···N4^i	2.998 (8)
O2···N1^{iii}	2.865 (7)	O6···N2^{vi}	2.973 (10)
O3···O4^{iv}	2.808 (11)	O6···N4^i	2.916 (10)

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

Table 3
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N11—H11A···N3	0.90	2.24	3.122 (5)	168
N11—H11B···N2^i	0.90	2.64	3.455 (5)	158
N14—H14···O1^{ii}	0.91	2.22	3.121 (5)	168
N17—H17A···N4^{iii}	0.90	2.60	3.498 (6)	172
N17—H17B···O4	0.90	2.29	3.075 (6)	146
N21—H21B···N6^i	0.90	2.23	3.101 (5)	164
N24—H24···O5^{iv}	0.91	2.27	3.182 (8)	178
N27—H27A···N3	0.90	2.43	3.214 (6)	145
N27—H27B···O4	0.90	2.59	3.421 (7)	153
N31—H31A···N4	0.90	2.51	3.342 (5)	154
N31—H31B···N2^v	0.90	2.37	3.264 (5)	170
N41—H41A···N5	0.90	2.55	3.417 (7)	161
N44—H44···O6^{vi}	0.91	2.38	3.276 (11)	169

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

Both diethylenetriamine ligands of the cation located on a C_2 axis show a disordered arrangement for the atoms C33 (C331 and C332) and C43 (C431 and C432), respectively, over two positions. Refinement of the site-occupation factors revealed a partial occupation of nearly 0.50 for each position, and this value was fixed in the final stages of the refinement. During the refinement steps, soft restraints were imposed on C431 and C432 so that the components of the anisotropic displacement parameters of both atoms were similar. Distance restraints were used for the ligand arm defined by N31, C32, C331/C332 and N34 in order to get a sensible geometry. Both atoms C331 and C332 were refined isotropically. There is a water molecule disordered over two positions O5 and O6, separated by a distance of just 1.648 (12) Å. Their site-occupation factors, with the sum constrained to be unity, refined to values of 0.629 (8) and 0.371 (8) for O5 and O6, respectively.

The H atoms of the water molecules were neither located nor positioned geometrically. The positions of all remaining H atoms were calculated geometrically and were treated as riding, with isotropic displacement parameters fixed at 1.2 times the equivalent isotropic displacement parameters of their parent atoms (C or N), except H34 and H44 whose coordinates were kept fixed at the calculated positions.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *DIRDIF*99 (Beurskens *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 for Windows (Farrugia, 1997); *PLATON* (Spek, 1990); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

References

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

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

Enraf–Nonius (1994). *CAD-4 EXPRESS*. Enraf–Nonius, Delft, The Netherlands.

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

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

Harms, K. & Wocadlo, S. (1995). *XCAD*4. University of Marburg, Germany.

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

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

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

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

Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.

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*a*). *Coord. Chem. Rev.* **190–192**, 1023–1047.