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Bis[bis(diethylenetriamine)zinc(II)] hexacyanoferrate tetrahydrate

Ibrahim Abdul Razak,[a] S. Shanmuga Sundara Raj,[a] Hoong-Kun Fun,[a]* Ye-Xiang Tong,[b] Zhong-Lin Lu[b] and Bei-Sheng Kang[b]

[a]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and [b]School of Chemistry and Chemical Engineering, Zhongshan University, Guangzhou 510275, People's Republic of China
Correspondence e-mail: hkfun@usm.my

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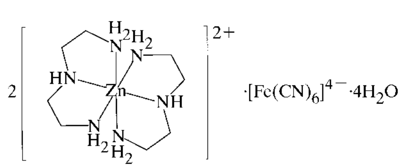
In the crystal structure of the title compound, $[Zn(C_4H_{13}N_3)_2]_2[Fe(CN)_6]\cdot 4H_2O$, the asymmetric unit is formed by a $[Zn(dien)_2]^{2+}$ cation (dien = diethylenetriamine, $NH_2CH_2CH_2NHCH_2CH_2NH_2$), water molecules and half of the $[Fe(CN)_6]^{4-}$ anion which is related by inversion symmetry through the Fe atom. The geometry around the Zn and Fe atoms is distorted octahedral and octahedral, respectively. Intramolecular O—H···O hydrogen bonds involving the water molecules, and intermolecular O—H···N hydrogen bonds involving the water molecules and the anions, result in an infinite chain. Intramolecular O—H···O and N—H···N, and intermolecular O—H···N, N—H···O and N—H···N hydrogen bonds form a three-dimensional framework.

Comment

Coordination polymers with supramolecular structures are one of the most interesting topics in current chemistry and crystal engineering, both for the theoretical aspects related to the topologies of novel frameworks with inner cavities and channels (Carlucci *et al.*, 1995; Yaghi & Li, 1995) and for their potential applications in catalysis (Fujita *et al.*, 1994), host–guest chemistry (Yaghi *et al.*, 1997; Kawata *et al.*, 1996; Zhang *et al.*, 1996) and molecular electronics (Fallah *et al.*, 1996; Miyasaka *et al.*, 1996). Cyanide is a versatile ligand capable of bridging different metal centres in an asymmetric mode. The most outstanding known example of such behaviour is represented by the mixed-valence polymeric structure of Prussian blue (Buser *et al.*, 1977), where cyanide is C-end attached to low-spin Fe^{II} and N-end attached to high-spin Fe^{III}. We have become interested in these types of complexes and now report the crystal structure of $[Zn(dien)_2]_2[Fe(CN)_6]\cdot 4H_2O$, (I).



(I)

The crystal structure of (I) is formed by $[Zn(dien)_2]^{2+}$ cations, water molecules and half of the $[Fe(CN)_6]^{4-}$ anions. The Fe atom lies on the inversion centre so that the $[Fe(CN)_6]^{4-}$ anion has an inversion symmetry. The bond lengths and angles of $[Zn(dien)_2]^{2+}$ are comparable with reported values (Hodgson & Penfold, 1974). The environment around the Zn atom formed by the N atoms of the diethylenetriamine moieties can be described as distorted octahedral [N—Zn—N 78.58 (4)–179.77 (4)°]. $[Fe(CN)_6]^{4-}$ assumes an octahedrally coordinated geometry with six CN^- groups. The bond lengths and angles observed show only small differences from the reported values, even in the presence of a different cation (Orpen *et al.*, 1989; Cauzzi *et al.*, 1993).

In the crystal, the water molecules are involved in O—H···O intramolecular hydrogen bonds (O1*W*—H1*W*1···O2*W*). Two of the N atoms from the $[Zn(dien)_2]^{2+}$ cations, N3 and N4, form N—H···N intramolecular hydrogen bonds with N8 from the $[Fe(CN)_6]^{4-}$ anions. In addition to the O—H···O intramolecular hydrogen bonds, both the water molecules are also involved in intermolecular O—H···N hydrogen bonds with N atoms from the $[Fe(CN)_6]^{4-}$ anions [O1*W*—H2*W*1···N9($1 - x, -y, 1 - z$), O2*W*—H1*W*2···N8($-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$) and O2*W*—H2*W*2···N7($\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$)]. These intramolecular O—H···O and intermolecular O—H···N hydrogen bonds involving water molecules and $[Fe(CN)_6]^{4-}$ anions form an infinite chain in the [101] direction where cyanide ligands are connected through the water molecules. The $[Zn(dien)_2]^{2+}$ cations are also involved in intermolecular N—H···O and N—H···N hydrogen bonds with the water molecules and the anions, respectively. These intramolecular O—H···O and N—H···N, and intermolecular O—H···N, N—H···O, N—H···N hydrogen bonds form a three-dimensional framework.

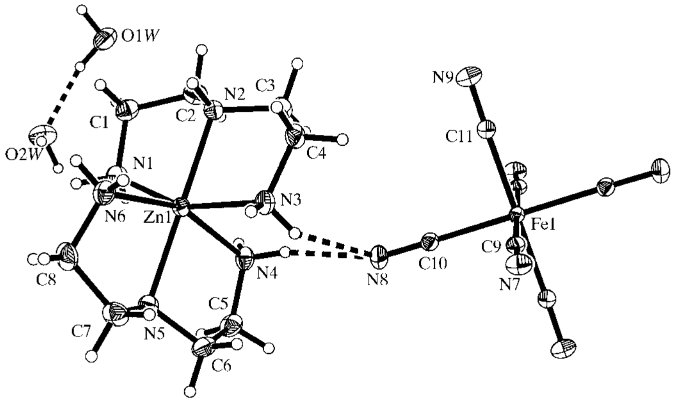


Figure 1
The structure of (I) showing 30% probability displacement ellipsoids and the atom-numbering scheme.

Experimental

$K_4Fe(CN)_6$ (184 mg, 0.5 mmol) in water (10 ml) was added to dien (0.30 ml, 4.0 mmol) in H_2O (20 ml) containing $Zn(NO_3)_2$ (188 mg, 1.0 mmol). The mixture was refluxed with stirring for 30 min and then allowed to stand in air at room temperature for 2 d. Colourless single crystals suitable for X-ray analysis were obtained and washed with ethanol.

Crystal data

$[Zn(C_4H_{13}N_3)_2]_2[Fe(CN)_6]\cdot 4H_2O$
$M_r = 827.47$
Monoclinic, $P2_1/n$
$a = 9.2597$ (2) Å
$b = 14.5473$ (3) Å
$c = 13.9263$ (2) Å
$\beta = 90.726$ (1)°
$V = 1875.77$ (6) Å^3
$Z = 2$
$D_x = 1.465$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5929 reflections
$\theta = 2.93$–33.17°
$\mu = 1.704$ mm^{-1}
$T = 293$ (2) K
Slab, colourless
0.48 × 0.32 × 0.18 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.495$, $T_{max} = 0.749$
17 004 measured reflections
6906 independent reflections
5745 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 33.11°$
$h = -14 \rightarrow 11$
$k = -22 \rightarrow 17$
$l = -21 \rightarrow 21$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.069$
$S = 1.07$
6906 reflections
230 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0304P)^2 + 0.3241P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.60$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—N5	2.155 (1)	Zn1—N4	2.245 (1)
Zn1—N2	2.163 (1)	Fe1—C9	1.922 (1)
Zn1—N6	2.204 (1)	Fe1—C10	1.924 (1)
Zn1—N1	2.219 (1)	Fe1—C11	1.930 (1)
Zn1—N3	2.230 (1)		
N5—Zn1—N2	179.77 (4)	N1—Zn1—N3	158.48 (5)
N5—Zn1—N6	79.68 (5)	N5—Zn1—N4	78.58 (4)
N2—Zn1—N6	100.55 (4)	N2—Zn1—N4	101.20 (4)
N5—Zn1—N1	100.07 (4)	N6—Zn1—N4	158.04 (5)
N2—Zn1—N1	79.91 (4)	N1—Zn1—N4	94.03 (5)
N6—Zn1—N1	92.75 (5)	N3—Zn1—N4	87.92 (4)
N5—Zn1—N3	101.32 (4)	C9—Fe1—C10	92.83 (5)
N2—Zn1—N3	78.70 (4)	C9—Fe1—C11	90.74 (5)
N6—Zn1—N3	93.36 (5)	C10—Fe1—C11	90.12 (5)

After checking their presence in the difference map, all H atoms were fixed geometrically and allowed to ride on their attached atoms, except for the H atoms of the water molecules which were refined isotropically.

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3D···N8	0.90	2.33	3.119 (2)	146
N4—H4D···N8	0.90	2.22	3.084 (2)	162
N4—H4C···N9^{i}	0.90	2.32	3.155 (2)	153
N1—H1D···O1W^{ii}	0.90	2.41	3.205 (2)	148
N5—H5C···N7^{iii}	0.91	2.15	3.054 (2)	172
N2—H2C···N7^{iv}	0.91	2.20	3.081 (2)	163
N3—H3C···N9^{iv}	0.90	2.40	3.283 (2)	167
N6—H6C···N9^{iv}	0.90	2.56	3.351 (2)	147
O1W—H1W1···O2W	0.91 (2)	1.95 (2)	2.814 (2)	157
O2W—H1W2···N8^{iii}	0.96 (2)	2.06 (2)	3.011 (2)	173
O1W—H2W1···N9^{v}	0.92 (2)	2.07 (2)	2.980 (2)	170
O2W—H2W2···N7^{i}	0.92 (2)	2.10 (2)	2.980 (2)	159

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

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1341). Services for accessing these data are described at the back of the journal.

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