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A Cyano-Bridged Ionic Pair Complex: $[FeNd_2(CN)_6(C_{10}H_8N_2)_4(H_2O)_8][Fe(CN)_6].8H_2O$

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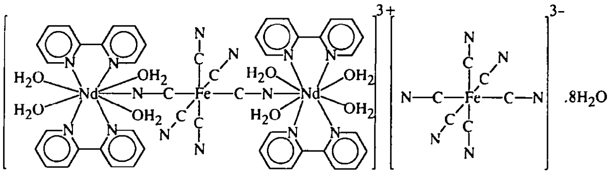
Abstract

The title compound, octaaqua-$2\kappa^4O,3\kappa^4O$-tetrakis(2,2′-bipyridyl)-$2\kappa^4N,N'$;$3\kappa^4N,N'$-di-μ-cyano-$1\kappa C$:$2\kappa N$;-$1\kappa C$:$3\kappa N$-tetracyano-$1\kappa^4C$-irondineodymium hexacyanoferrate octahydrate, is an ion-pair complex composed of an octahedral hexacyanoferrate(III) anion, a centrosymmetric cyano-linked [NdFeNd] trinuclear cation and eight solvate water molecules.

Comment

Two kinds of cyano-bridged bimetallic compounds, namely Prussian Blue-like phases and molecular species, have been reported. The former are three-dimensional-network solids and the latter are normally one- or two-dimensional compounds (Kahn, 1995). A few well characterized cyano-bridged molecular compounds have been reported recently (Mullica, Hayward & Sappenfield, 1996; Fu *et al.*, 1997). In the course of our work on 4*f*–3*d* heterometallic compounds, we obtained the title compound, (I), in which an isolated [NdFeNd] trinuclear cation is associated with an octahedral hexacyanoferrate(III) anion.



(I)

In the $[FeNd_2(CN)_6(dipy)_4(H_2O)_8]^{3+}$ (dipy is 2,2′-bipyridyl) trinuclear cation, six CN groups form an octahedral array around the Fe1 atom, which lies on a centre of symmetry. The average length of the Fe1—C distances is 1.937 (4) Å. Each Nd atom is nine-coordinate; the four N atoms of two dipy ligands [Nd—N 2.641 (3)–2.717 (3) Å], one N atom of the cyano group [Nd—N 2.550 (3) Å] and four O atoms of four water molecules [Nd—O 2.436 (3)–2.539 (3) Å] form an approximate tricapped trigonal prism. The three square faces of the prism are defined by the sets of atoms (O1*W*, O2*W*, O4*W*, N1), (O4*W*, N1, N4, N5) and (O1*W*, O2*W*, N4, N5), and the deviation of these atoms from the respective square faces is not larger than 0.08 Å. The three capping species are N2, N3 and O3*W*. The Fe1 atom is connected to two Nd atoms through two bridging cyano groups to form the centrosymmetric trinuclear cation. The bridging C—N bond length is 1.148 (4) Å, which is in the range of reported C—N distances (1.13–1.15 Å) of cyano bridges (Mullica, Hayward & Sappenfield, 1996; Fu *et al.*, 1997). The angles N5—C21—Fe1 and C21—N5—Nd1 are 173.9 (3) and 168.8 (3)°, respectively, deviating slightly from linearity. The distance between Fe1 and Nd1 is 5.583 (2) Å.

The $[Fe(CN)_6]^{3-}$ anion is octahedral with Fe2 lying on a centre of symmetry and with Fe2—C bond lengths in the range 1.936 (4)–1.949 (4) Å. The anion is connected to the trinuclear cation by O4*W*—H4*A*···N10 and O3*W*—H3*A*···N9 hydrogen bonds with O4*W*···N10 and O3*W*···N9 distances 2.912 (5) and 3.078 (5) Å, respectively. Compared with other bimetallic cyanide compounds, the most interesting feature of the structure is the discrete [NdFeNd] trinuclear unit, which is not the same as in the three-dimensional cubic Prussian Blue or other molecular cyanides.

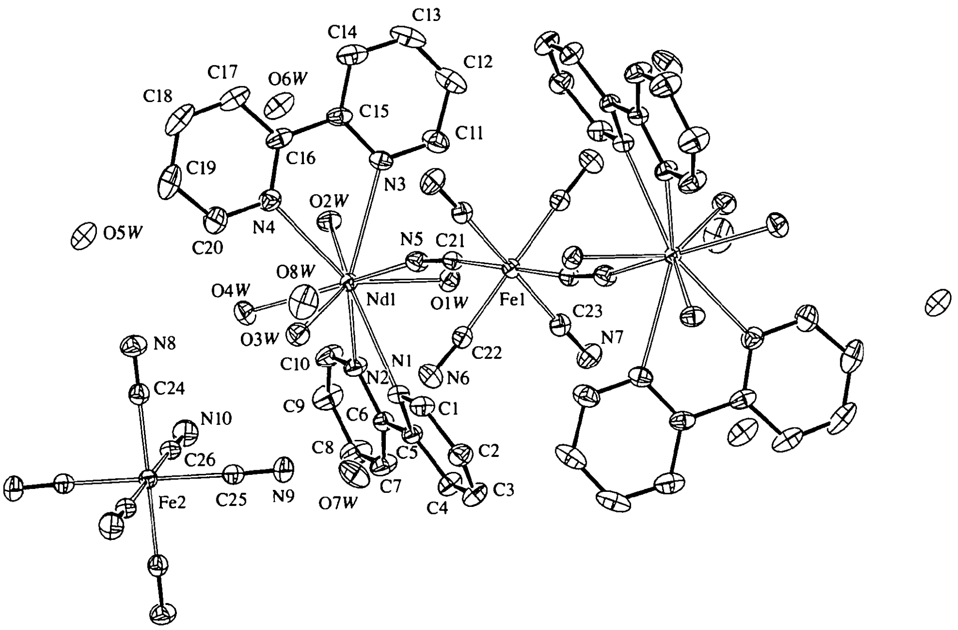


Fig. 1. The molecular structure of (I) showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

Experimental

The title complex was prepared by mixing 1 mmol of an aqueous solution of $K_3[Fe(CN)_6]$ and 3 mmol of an alcohol solution of dipy, followed by the slow addition of 1 mmol of an aqueous solution of $Nd(NO_3)_3$. Orange single crystals were obtained by slow evaporation of the solution at room temperature. The neodymium and iron proportions were determined by inductively coupled plasma (ICP): found Nd 16.41, Fe 5.16%; calculated Nd 17.75, Fe 6.87%. Elemental analysis (C, H, N) was performed using a Carlo Erba 1106: found C 38.30, H 3.82, N 17.62%; calculated C 38.40, H 3.98, N 17.23%.

Crystal data

$[FeNd_2(CN)_6(C_{10}H_8N_2)_4$-
$(H_2O)_8][Fe(CN)_6].8H_2O$
$M_r = 1625.42$
Triclinic
$P\overline{1}$
$a = 10.174\,(3)$ Å
$b = 11.482\,(3)$ Å
$c = 15.583\,(3)$ Å
$\alpha = 87.23\,(2)°$
$\beta = 87.63\,(2)°$
$\gamma = 66.21\,(2)°$
$V = 1663.4\,(8)$ Å^3
$Z = 1$
$D_x = 1.623$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 30 reflections
$\theta = 4.47$–$14.70°$
$\mu = 2.040$ mm^{-1}
$T = 293\,(2)$ K
Prism
0.6 × 0.5 × 0.3 mm
Orange

Data collection

Siemens *P*4 diffractometer
2θ scans
Absorption correction: ψ scan (Siemens, 1994*a*)
$T_{min} = 0.424$, $T_{max} = 0.542$
7151 measured reflections
5850 independent reflections
5169 reflections with $I > 2\sigma(I)$

$R_{int} = 0.017$
$\theta_{max} = 25.0°$
$h = -1 \rightarrow 11$
$k = -12 \rightarrow 13$
$l = -18 \rightarrow 18$
3 standard reflections every 97 reflections intensity decay: 3.59%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.070$
$S = 1.052$
5850 reflections
468 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0407P)^2 + 0.1104P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.026$
$\Delta\rho_{max} = 0.610$ e Å^{-3}
$\Delta\rho_{min} = -0.617$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU^{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Nd1	0.38043 (2)	0.72547 (2)	0.25695 (1)	0.02598 (7)
Fe1	0	1	0	0.02737 (15)
Fe2	0	1/2	1/2	0.02903 (16)
O1*W*	0.4178 (3)	0.9209 (2)	0.23060 (18)	0.0398 (6)
O2*W*	0.6435 (3)	0.6470 (3)	0.27943 (17)	0.0406 (6)
O3*W*	0.1748 (3)	0.6613 (3)	0.27219 (19)	0.0458 (7)
O4*W*	0.4456 (3)	0.5571 (3)	0.37796 (17)	0.0436 (6)
O5*W*	0.2265 (3)	0.1558 (3)	0.2114 (2)	0.0531 (8)
O6*W*	0.8905 (3)	0.4552 (3)	0.2118 (2)	0.0624 (9)
O7*W*	−0.3112 (3)	0.8733 (4)	0.2720 (2)	0.0612 (9)
O8*W*	0.0188 (4)	0.6309 (4)	0.1455 (3)	0.0766 (10)
N1	0.1487 (3)	0.9141 (3)	0.32495 (19)	0.0343 (7)
N2	0.4022 (3)	0.8213 (3)	0.40797 (19)	0.0399 (7)

N3	0.5395 (3)	0.6823 (3)	0.10836 (19)	0.0392 (7)
N4	0.4709 (4)	0.4994 (3)	0.1888 (2)	0.0423 (8)
N5	0.2270 (3)	0.8275 (3)	0.12648 (19)	0.0390 (7)
N6	−0.2092 (4)	0.9338 (4)	0.1201 (2)	0.0529 (9)
N7	−0.0302 (4)	1.2325 (3)	0.1041 (2)	0.0508 (9)
N8	0.1335 (4)	0.3511 (3)	0.3367 (2)	0.0517 (9)
N9	−0.0978 (4)	0.7463 (3)	0.3880 (2)	0.0537 (9)
N10	0.2739 (4)	0.5467 (3)	0.5300 (2)	0.0527 (9)
C1	0.0264 (4)	0.9628 (4)	0.2814 (2)	0.0419 (9)
C2	−0.0853 (4)	1.0769 (4)	0.2999 (3)	0.0473 (10)
C3	−0.0722 (5)	1.1435 (4)	0.3670 (3)	0.0524 (11)
C4	0.0501 (4)	1.0942 (4)	0.4140 (3)	0.0467 (10)
C5	0.1586 (4)	0.9797 (3)	0.3923 (2)	0.0334 (8)
C6	0.2930 (4)	0.9214 (3)	0.4423 (2)	0.0358 (8)
C7	0.3039 (5)	0.9643 (4)	0.5218 (3)	0.0514 (11)
C8	0.4272 (5)	0.9073 (5)	0.5667 (3)	0.0637 (13)
C9	0.5387 (5)	0.8062 (5)	0.5325 (3)	0.0604 (13)
C10	0.5222 (5)	0.7678 (4)	0.4533 (3)	0.0525 (11)
C11	0.5746 (5)	0.7721 (5)	0.0704 (3)	0.0543 (11)
C12	0.6789 (6)	0.7499 (6)	0.0071 (3)	0.0657 (14)
C13	0.7498 (5)	0.6296 (6)	−0.0193 (3)	0.0692 (15)
C14	0.7146 (5)	0.5356 (5)	0.0168 (3)	0.0598 (13)
C15	0.6081 (4)	0.5633 (4)	0.0804 (2)	0.0401 (9)
C16	0.5638 (4)	0.4646 (4)	0.1212 (2)	0.0414 (9)
C17	0.6131 (5)	0.3422 (4)	0.0913 (3)	0.0586 (13)
C18	0.5717 (5)	0.2545 (4)	0.1305 (4)	0.0688 (15)
C19	0.4780 (6)	0.2886 (4)	0.1991 (4)	0.0676 (14)
C20	0.4303 (5)	0.4106 (4)	0.2253 (3)	0.0562 (12)
C21	0.1482 (4)	0.8907 (3)	0.0759 (2)	0.0307 (8)
C22	−0.1343 (4)	0.9621 (3)	0.0745 (2)	0.0353 (8)
C23	−0.0205 (4)	1.1467 (4)	0.0666 (2)	0.0353 (8)
C24	0.0868 (4)	0.4054 (3)	0.3972 (2)	0.0366 (8)
C25	−0.0663 (4)	0.6557 (4)	0.4297 (2)	0.0354 (8)
C26	0.1730 (4)	0.5276 (3)	0.5198 (2)	0.0369 (8)

Table 2. *Selected geometric parameters (Å, °)*

Nd1—O1*W*	2.436 (3)	Fe1—C23	1.955 (4)
Nd1—O3*W*	2.483 (3)	Fe2—C25	1.936 (4)
Nd1—O2*W*	2.490 (3)	Fe2—C24	1.949 (4)
Nd1—O4*W*	2.539 (3)	Fe2—C26	1.949 (4)
Nd1—N5	2.550 (3)	N5—C21	1.148 (4)
Nd1—N4	2.641 (3)	N6—C22	1.150 (5)
Nd1—N1	2.696 (3)	N7—C23	1.138 (5)
Nd1—N2	2.699 (3)	N8—C24	1.135 (5)
Nd1—N3	2.717 (3)	N9—C25	1.136 (5)
Fe1—C22	1.925 (4)	N10—C26	1.151 (5)
Fe1—C21	1.930 (3)		
O1*W*—Nd1—O3*W*	137.71 (9)	O1*W*—Nd1—N3	76.57 (9)
O1*W*—Nd1—O2*W*	79.05 (9)	O3*W*—Nd1—N3	119.69 (10)
O3*W*—Nd1—O2*W*	142.66 (9)	O2*W*—Nd1—N3	66.44 (9)
O1*W*—Nd1—O4*W*	133.96 (9)	O4*W*—Nd1—N3	120.43 (10)
O3*W*—Nd1—O4*W*	74.62 (10)	N5—Nd1—N3	67.88 (10)
O2*W*—Nd1—O4*W*	72.00 (9)	N4—Nd1—N3	60.66 (10)
O1*W*—Nd1—N5	77.08 (10)	N1—Nd1—N3	137.85 (9)
O3*W*—Nd1—N5	74.97 (10)	N2—Nd1—N3	133.04 (10)
O2*W*—Nd1—N5	132.06 (9)	C22—Fe1—C22^{i}	180.0
O4*W*—Nd1—N5	147.90 (10)	C22—Fe1—C21^{i}	93.02 (15)
O1*W*—Nd1—N4	136.94 (10)	C22—Fe1—C21	86.98 (15)
O3*W*—Nd1—N4	74.41 (10)	C21^{i}—Fe1—C21	180.0
O2*W*—Nd1—N4	79.56 (10)	C22—Fe1—C23	91.98 (15)
O4*W*—Nd1—N4	71.59 (10)	C22^{i}—Fe1—C23	88.02 (15)
N5—Nd1—N4	90.54 (10)	C21^{i}—Fe1—C23	90.23 (14)
O1*W*—Nd1—N1	73.60 (9)	C21—Fe1—C23	89.77 (14)
O3*W*—Nd1—N1	69.59 (9)	C23—Fe1—C23^{i}	180.0
O2*W*—Nd1—N1	133.53 (9)	C25^{ii}—Fe2—C25	180.0
O4*W*—Nd1—N1	101.72 (9)	C25—Fe2—C24^{ii}	91.11 (15)
N5—Nd1—N1	76.85 (10)	C25—Fe2—C24	88.89 (15)
N4—Nd1—N1	143.80 (10)	C24^{ii}—Fe2—C24	180.0
O1*W*—Nd1—N2	70.25 (10)	C25—Fe2—C26^{ii}	92.20 (15)
O3*W*—Nd1—N2	107.21 (10)	C24—Fe2—C26^{ii}	88.68 (15)
O2*W*—Nd1—N2	75.24 (9)	C25—Fe2—C26	87.80 (15)
O4*W*—Nd1—N2	68.24 (10)	C24—Fe2—C26	91.32 (15)
N5—Nd1—N2	131.65 (10)	C26^{ii}—Fe2—C26	180.0
N4—Nd1—N2	137.41 (10)	C21—N5—Nd1	168.8 (3)
N1—Nd1—N2	60.50 (9)	N5—C21—Fe1	173.9 (3)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*A*···O5*W*^{i}	0.954 (19)	1.69 (2)	2.625 (4)	165 (6)
O1*W*—H1*B*···O7*W*^{ii}	0.916 (19)	1.81 (3)	2.686 (4)	158 (5)
O2*W*—H2*A*···O6*W*	0.958 (19)	1.95 (4)	2.796 (4)	146 (5)
O2*W*—H2*B*···O7*W*^{ii}	0.951 (19)	2.05 (4)	2.812 (5)	136 (4)
O3*W*—H3*A*···N9	0.922 (19)	2.21 (3)	3.078 (5)	158 (5)
O3*W*—H3*B*···O8*W*	0.985 (19)	1.78 (3)	2.704 (5)	155 (5)
O4*W*—H4*A*···N10	0.921 (19)	2.07 (3)	2.912 (5)	150 (5)
O4*W*—H4*B*···N10^{iii}	0.938 (19)	2.24 (4)	3.008 (5)	139 (5)
O5*W*—H5*A*···N8	0.910 (19)	2.00 (2)	2.879 (4)	161 (5)
O5*W*—H5*B*···N7^{iv}	0.956 (19)	2.08 (3)	2.960 (5)	152 (5)
O6*W*—H6*A*···N8^{ii}	0.978 (19)	2.56 (6)	3.019 (5)	109 (4)
O6*W*—H6*B*···N7^{v}	1.001 (19)	2.00 (3)	2.940 (5)	155 (4)
O7*W*—H7*A*···N6	0.984 (19)	1.75 (2)	2.717 (5)	169 (5)
O7*W*—H7*B*···N9	0.931 (19)	1.89 (2)	2.761 (5)	156 (5)
O8*W*—H8*A*···N6	0.943 (19)	2.53 (4)	3.327 (5)	143 (5)
O8*W*—H8*B*···O6*W*^{vi}	0.932 (19)	2.02 (2)	2.940 (5)	168 (5)

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

A graphite monochromator and a 1 mm diameter collimator were used during data collection. The structure was solved by direct methods and refined by full-matrix least-squares techniques. C and N atoms of bridging CN groups were assigned based on the starting material $K_3Fe(CN)_6$, and the coordination to Nd by the N atom of a bridging CN is chemically reasonable. All non-H atoms were refined anisotropically. The H atoms attached to C atoms were refined using a riding model. The H atoms of water molecules were located by difference Fourier synthesis and refined with distance restraints for O—H and H···H (0.96 and 1.52 Å, respectively) and one variable isotropic *U* for all. Extended displacement ellipsoids on some atoms probably reflect the amount of relatively free space around the dipy moieties.

Data collection: *XSCANS* (Siemens, 1994*a*). Cell refinement: *XSCANS*. Data reduction: *SHELXTL* (Siemens, 1994*b*). Program(s) used to solve structure: *SHELXTL*. Program(s) used to refine structure: *SHELXTL* and *SHELXL97* (Sheldrick, 1997). Molecular graphics: *XPMA* and *ZORTEP* (Zsolnai, 1997). Software used to prepare material for publication: *SHELXTL* and *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1180). Services for accessing these data are described at the back of the journal.

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