

Crystal structure of the coordination polymer $[\text{Fe}^{\text{III}}_2\{\text{Pt}^{\text{II}}(\text{CN})_4\}_3]$

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The title complex, poly[dodeca- μ -cyanido-diiron(III)triplatinum(II)], $[\text{Fe}^{\text{III}}_2\{\text{Pt}^{\text{II}}(\text{CN})_4\}_3]$, has a three-dimensional polymeric structure. It is built-up from square-planar $[\text{Pt}^{\text{II}}(\text{CN})_4]^{2-}$ anions (point group symmetry $2/m$) bridging cationic $[\text{Fe}^{\text{III}}\text{Pt}^{\text{II}}(\text{CN})_4]_{\infty}^{+}$ layers extending in the bc plane. The Fe^{III} atoms of the layers are located on inversion centres and exhibit an octahedral coordination sphere defined by six N atoms of cyanide ligands, while the Pt^{II} atoms are located on twofold rotation axes and are surrounded by four C atoms of the cyanide ligands in a square-planar coordination. The geometrical preferences of the two cations for octahedral and square-planar coordination, respectively, lead to a corrugated organisation of the layers. The distance between neighbouring $[\text{Fe}^{\text{III}}\text{Pt}^{\text{II}}(\text{CN})_4]_{\infty}^{+}$ layers corresponds to the length $a/2 = 8.0070(3)$ Å, and the separation between two neighbouring Pt^{II} atoms of the bridging $[\text{Pt}^{\text{II}}(\text{CN})_4]^{2-}$ groups corresponds to the length of the c axis [$7.5720(2)$ Å]. The structure is porous with accessible voids of 390 Å³ per unit cell.

Keywords: crystal structure; polycyanidometalate; spin-crossover.

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1. Related literature

Coordination compounds have interesting properties in catalysis (Kanderal *et al.*, 2005; Penkova *et al.*, 2009) or as photoactive materials (Yan *et al.*, 2012). Magnetically active polycyanidometalate network complexes of Fe^{II} $[\text{Fe}^{\text{II}}L_2\{M^{\text{I}}(\text{CN})_2\}_2]$ or $[\text{Fe}^{\text{II}}L_2\{M^{\text{II}}(\text{CN})_4\}]$ ($M^{\text{I}} = \text{Ag}, \text{Au}$; $M^{\text{II}} = \text{Ni}, \text{Pd}, \text{Pt}$; $L = N$ -heterocyclic ligand) have been studied because they show versatile polymeric structures (Piñeiro-López *et al.* 2014;

Seredyuk *et al.*, 2007, 2009), spin transition (Muñoz & Real, 2013) and functionalities such as sorption–desorption of organic and inorganic molecules (Muñoz & Real, 2013) or reversible chemisorption (Arcís-Castillo *et al.*, 2013).

2. Experimental

2.1. Crystal data

$[\text{Fe}_2\text{Pt}_3(\text{CN})_{12}]$	$V = 1633.78(9)$ Å ³
$M_r = 1009.18$	$Z = 2$
Monoclinic, $C2/m$	Mo $K\alpha$ radiation
$a = 16.0140(5)$ Å	$\mu = 13.68$ mm ⁻¹
$b = 13.8250(5)$ Å	$T = 293$ K
$c = 7.5720(2)$ Å	$0.04 \times 0.04 \times 0.02$ mm
$\beta = 102.946(2)^\circ$	

2.2. Data collection

Oxford Diffraction Gemini S Ultra diffractometer	3358 measured reflections
Absorption correction: multi-scan (Blessing, 1995)	1909 independent reflections
$T_{\text{min}} = 0.611$, $T_{\text{max}} = 0.772$	1568 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.038$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	71 parameters
$wR(F^2) = 0.106$	$\Delta\rho_{\text{max}} = 1.25$ e Å ⁻³
$S = 0.97$	$\Delta\rho_{\text{min}} = -1.33$ e Å ⁻³
1909 reflections	

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

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Supporting information for this paper is available from the IUCr electronic archives (Reference: WM5094).

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supporting information

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Crystal structure of the coordination polymer $[\text{Fe}^{\text{III}}_2\{\text{Pt}^{\text{II}}(\text{CN})_4\}_3]$

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S1. Synthesis and crystallization

Single crystals of the title compound were grown using a slow diffusion technique. During the reaction time a side product had formed serendipitously due to oxidation of the initial Fe^{II} salt. One side of a multi-arm shaped vessel contained $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (20 mg, 51 mmol) dissolved in water (0.5 mL). The second arm contained $\text{K}_2[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$ (22 mg, 51 mmol) in water (0.5 ml). The vessel was filled with a water/methanol (1:1) solution. Square shaped orange crystals suitable for single crystal X-ray analysis were obtained after several weeks.

S2. Refinement

The highest and lowest remaining electron density are located 3.66 and 0.83 Å, respectively, from the Pt atom. The highest electron densities are connected with positions in the voids of the framework. However, modelling of the electron density *e.g.* under consideration of disordered (partially occupied) water molecules lead to implausible models.

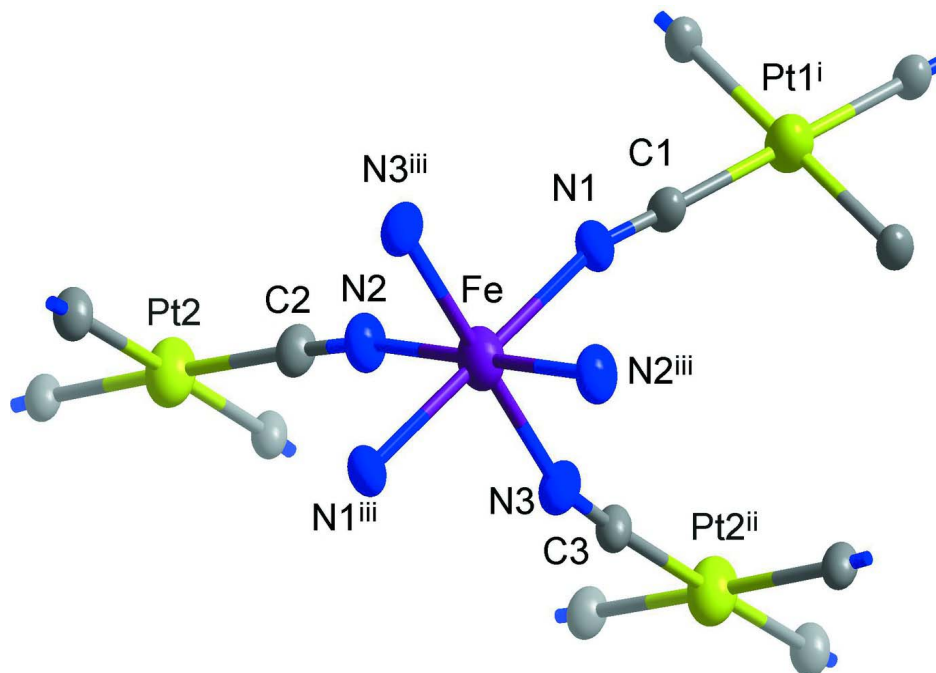
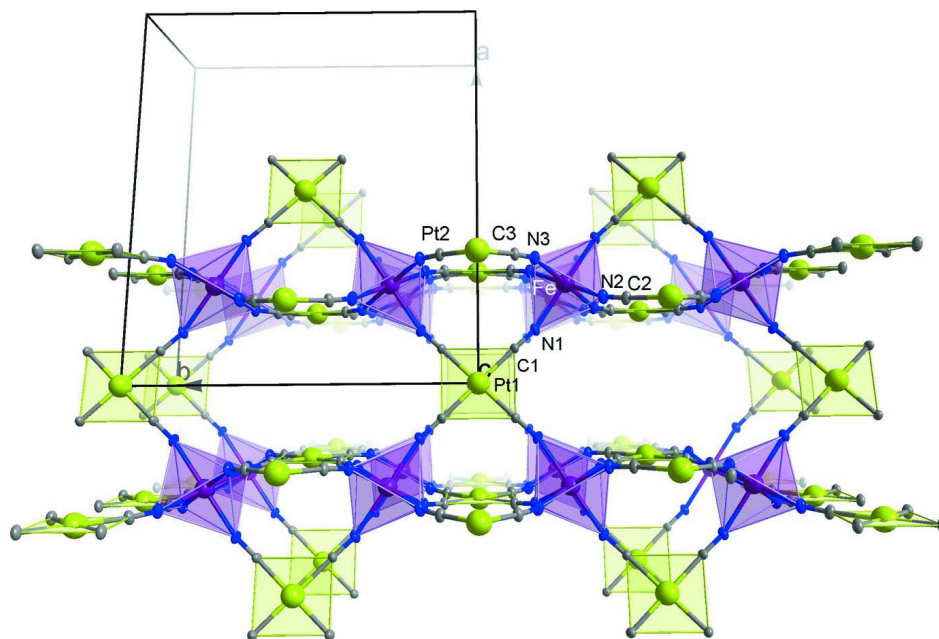


Figure 1

Displacement ellipsoid plot (30% probability level) of the principal building units of the structure of the title compound.

[Symmetry codes: (i) $1/2 + x, 1/2 + y, 1 + z$; (ii) $0.5 - x, 1/2 + y, 1 - z$, (iii) $x, 1 - y, 1 + z$.]

**Figure 2**

A fragment of three-dimensional coordination polymer of the title compound in a perspective view along *c*. Polyhedra correspond to FeN₆ and PtC₄ chromophores.

Poly[dodeca- μ -cyanido-diiron(III)triplatinum(II)]

Crystal data

[Fe₂Pt₃(CN)₁₂]

$M_r = 1009.18$

Monoclinic, *C2/m*

Hall symbol: -C 2y

$a = 16.0140 (5) \text{ \AA}$

$b = 13.8250 (5) \text{ \AA}$

$c = 7.5720 (2) \text{ \AA}$

$\beta = 102.946 (2)^\circ$

$V = 1633.78 (9) \text{ \AA}^3$

$Z = 2$

$F(000) = 884$

$D_x = 2.051 \text{ Mg m}^{-3}$

Mo *K* α radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 200 reflections

$\theta = 12\text{--}20^\circ$

$\mu = 13.68 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Prismatic, orange

$0.04 \times 0.04 \times 0.02 \text{ mm}$

Data collection

Oxford Diffraction Gemini S Ultra diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan (Blessing, 1995)

$T_{\min} = 0.611$, $T_{\max} = 0.772$

3358 measured reflections

1909 independent reflections

1568 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.038$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.0^\circ$

$h = -20 \rightarrow 20$

$k = -17 \rightarrow 16$

$l = -9 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.038$

$wR(F^2) = 0.106$

$S = 0.97$

1909 reflections

71 parameters

0 restraints

0 constraints
 Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map

$$w = 1/[\sigma^2(F_o^2) + (0.0615P)^2 + 15.455P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.25 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -1.33 \text{ e } \text{Å}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Pt1	0.0000	0.0000	0.0000	0.02376 (17)
Pt2	0.19452 (3)	0.5000	0.47749 (5)	0.02524 (16)
Fe	0.2500	0.2500	0.0000	0.0215 (3)
N1	0.1335 (5)	0.1622 (5)	-0.0284 (10)	0.0368 (17)
N2	0.2081 (6)	0.3449 (5)	0.1843 (10)	0.0400 (18)
N3	0.3039 (6)	0.1577 (5)	0.2273 (10)	0.0385 (17)
C1	0.0859 (5)	0.1023 (6)	-0.0190 (12)	0.0310 (17)
C2	0.2001 (6)	0.4002 (6)	0.2915 (11)	0.0335 (19)
C3	0.3072 (6)	0.1012 (6)	0.3373 (10)	0.0312 (18)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pt1	0.0208 (3)	0.0167 (3)	0.0343 (3)	0.000	0.0073 (2)	0.000
Pt2	0.0389 (3)	0.0182 (2)	0.0195 (2)	0.000	0.00824 (18)	0.000
Fe	0.0294 (8)	0.0165 (7)	0.0199 (7)	-0.0040 (6)	0.0083 (6)	-0.0004 (5)
N1	0.041 (4)	0.026 (4)	0.042 (4)	-0.009 (3)	0.008 (4)	-0.002 (3)
N2	0.056 (5)	0.030 (4)	0.038 (4)	-0.004 (4)	0.017 (4)	-0.006 (3)
N3	0.053 (5)	0.026 (4)	0.037 (4)	0.002 (4)	0.011 (4)	0.006 (3)
C1	0.028 (4)	0.023 (4)	0.043 (4)	0.000 (3)	0.011 (4)	0.004 (3)
C2	0.050 (6)	0.026 (4)	0.026 (4)	0.003 (4)	0.012 (4)	-0.001 (3)
C3	0.045 (5)	0.021 (4)	0.025 (4)	-0.001 (4)	0.004 (4)	0.000 (3)

Geometric parameters (Å , $^\circ$)

Pt1—C1	2.000 (8)	Fe—N2	2.130 (7)
Pt1—C1 ⁱ	2.000 (8)	Fe—N3 ^{vii}	2.161 (7)
Pt1—C1 ⁱⁱ	2.000 (8)	Fe—N3	2.161 (7)
Pt1—C1 ⁱⁱⁱ	2.000 (8)	Fe—N1 ^{vii}	2.195 (7)
Pt2—C3 ^{iv}	1.986 (8)	Fe—N1	2.195 (7)
Pt2—C3 ^v	1.986 (8)	N1—C1	1.139 (10)

Pt2—C2	1.988 (8)	N2—C2	1.143 (11)
Pt2—C2 ^{vi}	1.988 (8)	N3—C3	1.134 (10)
Fe—N2 ^{vii}	2.130 (7)	C3—Pt2 ^v	1.986 (8)
C1—Pt1—C1 ⁱ	90.0 (5)	N3 ^{vii} —Fe—N3	180.0 (3)
C1—Pt1—C1 ⁱⁱ	180.0 (6)	N2 ^{vii} —Fe—N1 ^{vii}	91.1 (3)
C1 ⁱ —Pt1—C1 ⁱⁱ	90.0 (5)	N2—Fe—N1 ^{vii}	88.9 (3)
C1—Pt1—C1 ⁱⁱⁱ	90.0 (5)	N3 ^{vii} —Fe—N1 ^{vii}	86.0 (3)
C1 ⁱ —Pt1—C1 ⁱⁱⁱ	180.0 (6)	N3—Fe—N1 ^{vii}	94.0 (3)
C1 ⁱⁱ —Pt1—C1 ⁱⁱⁱ	90.0 (5)	N2 ^{vii} —Fe—N1	88.9 (3)
C3 ^{iv} —Pt2—C3 ^v	89.6 (4)	N2—Fe—N1	91.1 (3)
C3 ^{iv} —Pt2—C2	178.1 (4)	N3 ^{vii} —Fe—N1	94.0 (3)
C3 ^v —Pt2—C2	91.2 (3)	N3—Fe—N1	86.0 (3)
C3 ^{iv} —Pt2—C2 ^{vi}	91.2 (3)	N1 ^{vii} —Fe—N1	180.0 (2)
C3 ^v —Pt2—C2 ^{vi}	178.1 (4)	C1—N1—Fe	164.2 (7)
C2—Pt2—C2 ^{vi}	87.9 (5)	C2—N2—Fe	168.3 (8)
N2 ^{vii} —Fe—N2	180.0 (5)	C3—N3—Fe	159.4 (8)
N2 ^{vii} —Fe—N3 ^{vii}	88.3 (3)	N1—C1—Pt1	178.3 (7)
N2—Fe—N3 ^{vii}	91.7 (3)	N2—C2—Pt2	175.9 (9)
N2 ^{vii} —Fe—N3	91.7 (3)	N3—C3—Pt2 ^v	176.4 (8)
N2—Fe—N3	88.3 (3)		

Symmetry codes: (i) $x, -y, z$; (ii) $-x, -y, -z$; (iii) $-x, y, -z$; (iv) $-x+1/2, y+1/2, -z+1$; (v) $-x+1/2, -y+1/2, -z+1$; (vi) $x, -y+1, z$; (vii) $-x+1/2, -y+1/2, -z$.