inorganic compounds

Pseudo-merohedrally twinned praseodymium hexacyanoferrate(III) tetrahydrate

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Crystals of the title compound, diaquahexa-μ-cyano-ferrate(III)praseodymium(III) dihydrate, $Pr[Fe(CN)_6]\cdot4H_2O$ or $[PrFe(CN)_6(H_2O)_2]\cdot2H_2O$, are twinned with three components. The Pr atom is coordinated by eight atoms, *viz.* six N and two symmetry-related water O atoms. The Pr polyhedron (Pr has site symmetry $m2m$, Wyckoff position $4c$) is linked to an FeC_6 octahedron (Fe located on a site with imposed $2/m$ symmetry, Wyckoff position $4b$) through N atoms, forming an infinite array. The second (symmetry independent) water molecule lies on a mirror plane, is not included in coordination and is weakly hydrogen bonded to N atoms.

Comment

The crystal structures of $Pr[Fe(CN)_6]\cdot5H_2O$ and $Nd[Fe-(CN)_6]\cdot5H_2O$, solved in hexagonal cells ($P6_3/m$), have been reported (Wang *et al.*, 1999) to contain a water molecule with C_{2v} symmetry located on a threefold axis. Such an arrangement is rather unusual and implies a disorder of H atoms. A very similar hexagonal structure has been found for a related compound, $Pr[Co(CN)_6]\cdot5H_2O$, by Yukawa *et al.* (1996). For $Nd[Co(CN)_6]\cdot5H_2O$, however, the same authors reported the non-centrosymmetric orthorhombic space group $C222_1$, even though the structures were expected to be similar.

In contrast with these pentahydrates, the structures of the tetrahydrates have usually been described in the ortho-rhombic space group $Cmcm$, where no such possible conflict between molecular and crystal symmetry is possible. Such structures are $Er[Fe(CN)_6]\cdot4H_2O$ (Mullica *et al.*, 1989; Marsh, 1989; Gramlich *et al.*, 1990), $Gd[Fe(CN)_6]\cdot4H_2O$ (Mullica & Sappenfield, 1991), $Nd[Co(CN)_6]\cdot4H_2O$ (Mullica *et al.*, 1996), $Sm[Fe(CN)_6]\cdot4H_2O$ and $Sm[Co(CN)_6]\cdot4H_2O$ (Mullica & Sappenfield, 1989), and $Bi[Fe(CN)_6]\cdot4H_2O$ and $Bi[Co-(CN)_6]\cdot4H_2O$ (Petter & Gramlich, 1990). The only exception is the structure of $La[Fe(CN)_6]\cdot4H_2O$ (Mullica *et al.*, 1980),
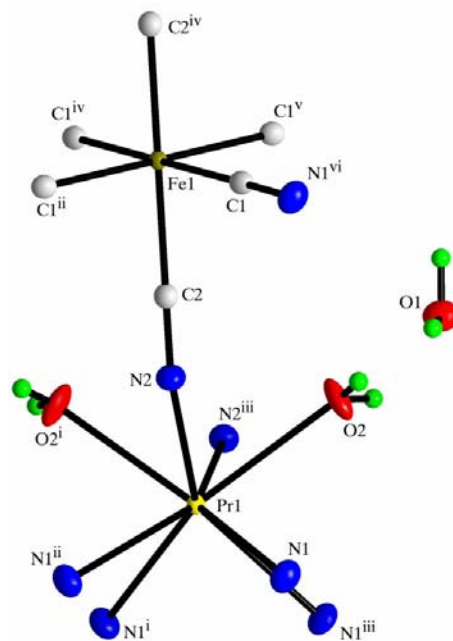

Figure 1
A view of the structure of $Pr[Fe(CN)_6]\cdot4H_2O$, with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $-x$, y, $\frac{1}{2}-z$; (ii) $-x$, y, z; (iii) x, y, $\frac{1}{2}-z$; (iv) $-x$, $1-y$, $1-z$; (v) x, $1-y$, $1-z$; (vi) $\frac{1}{2}-x$, $\frac{1}{2}-y$, $1-z$.]

which was reported, like $La[Fe(CN)_6]\cdot5H_2O$ (Bailey *et al.*, 1973), to be hexagonal (space group $P6_3/m$).

The diffraction data of the title compound were first processed as orthorhombic C-centred, with $R_{sym} = 0.076$ before an absorption correction, which is quite acceptable for a crystal containing a heavy atom. However, when evaluating the data, the mean value of $\Sigma(E^2 - 1)$ was observed to be rather low, at 0.539 [expected value 0.968 for centrosymmetric and 0.736 for non-centrosymmetric space groups (Wilson,
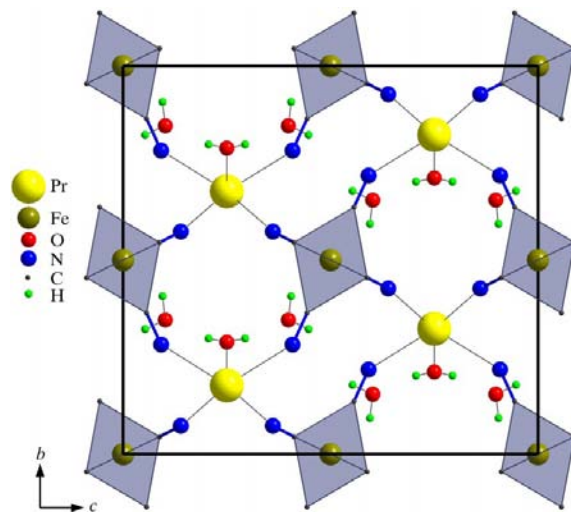

Figure 2
The structure of $Pr[Fe(CN)_6]\cdot4H_2O$ viewed along the *a* axis. Large spheres represent Pr atoms coordinated by N atoms and two molecules of water (O2). FeC_6 octahedra are shaded dark.
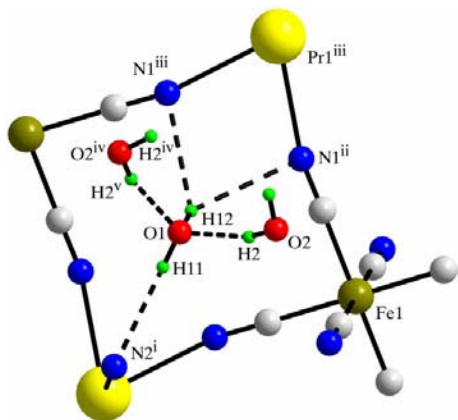
Figure 3
The hydrogen-bonding pattern in $Pr[Fe(CN)_6]\cdot4H_2O$ (dashed lines); details are given in Table 2. [Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, z$; (iii) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (iv) $1-x, y, \frac{1}{2}-z$; (v) $1-x, y, z$.]

1985)]. This is usually an indicator of twinned crystals (Herbst-Irmer & Sheldrick, 1998). In attempting to solve the structure in the orthorhombic system, the best result that could be achieved was in space group $Cmc2_1$ (No. 36), with $R = 0.151$ on observed data and large residuals in the difference Fourier synthesis (14 and -17 e Å^{-3}).

As the data indicated a pseudo-hexagonal symmetry with $R_{sym} = 0.164$, an attempt was made to solve the structure in space group $P6_3$ (No. 173). The best result achieved gave $R = 0.213$, and again large residuals were found in the difference Fourier synthesis (6 and -9 e Å^{-3}). Therefore, it was decided to use the hexagonal cell to solve the structure in the monoclinic system, space group $P2_1$ (No. 4). Even though the structure could be 'seen', the refinement was unsuccessful until the introduction of a twinning law (TWIN 0 0 1 0 1 0 $\bar{1}$ 0 $\bar{1}$ 3) for a twinned crystal with three components. The refinement was then satisfactory, with $R = 0.024$ and acceptable residuals in the difference Fourier synthesis (0.7 and -1.5 e Å^{-3}). At this stage, the analysis of the resulting structure by *PLATON* (Spek, 2001) clearly indicated the centrosymmetric space group $Cmcm$ (No. 63). To complete the refinement in the $Cmcm$ space group, the twinning law had to be reformulated as TWIN $-\frac{1}{2} \frac{1}{2} 0 -\frac{3}{2} -\frac{1}{2} 0 0 0 1$ 3. The volume fractions of the twin refined to 0.580 (2), 0.210 (1) and 0.210 (2).

The crystal structure of $Pr[Fe(CN)_6]\cdot4H_2O$ consists of $[Fe(CN)_6]$ octahedra, the N atoms of which also coordinate Pr atoms (Fig. 1). The polyhedron around the Pr atoms is completed by two water molecules (O2). The N atoms formally provide links between these two polyhedra, forming an infinite array (Fig. 2). The second water molecule (O1), as well as bonding to O2, also bonds weakly to three N atoms through hydrogen bonds, with atom H12 forming a symmetrical bifurcated bridge (Fig. 3).

The discrepancy between the expected and observed chemical composition can best be explained by the fact that at least some crystals of the batch dehydrated by losing a water molecule, and thus a more stable tetrahydrate was formed.

Such a process has also been reported previously for metastable $Nd[Co(CN)_6]\cdot5H_2O$ and $Pr[Co(CN)_6]\cdot5H_2O$ (Yukawa *et al.*, 1996).

Experimental

Potassium hexacyanoferrate(III), $K_3[Fe(CN)_6]$, was purchased from Waco Pure Chemical Ltd, and praseodymium nitrate hexahydrate, $Pr(NO_3)_3\cdot6H_2O$, was purchased from the Shin-etu Chemical Co. The complex praseodymium hexacyanoferrate(III) pentahydrate, $Pr[Fe(CN)_6]\cdot5H_2O$, was prepared by adding equimolar quantities of an aqueous solution of $K_3[Fe(CN)_6]$ (0.25 M) to a solution of $Pr(NO_3)_3\cdot6H_2O$ (0.25 M). Single crystals of $Pr[Fe(CN)_6]\cdot4H_2O$ were obtained from the mixture by keeping it at room temperature for several days. Although the synthesis was conducted to provide the pentahydrate, the analysed crystal turned out to be the tetrahydrate.

Crystal data

$[PrFe(CN)_6(H_2O)_2]\cdot2H_2O$	Mo $K\alpha$ radiation
$M_r = 424.94$	Cell parameters from 8192
Orthorhombic, $Cmcm$	reflections
$a = 7.4920$ (1) Å	$\theta = 1.5–33.1°$
$b = 12.9293$ (1) Å	$\mu = 4.71$ mm^{-1}
$c = 13.7904$ (1) Å	$T = 173$ (2) K
$V = 1335.83$ (2) Å^3	Irregular plate, dark red
$Z = 4$	$0.05 \times 0.04 \times 0.02$ mm
$D_x = 2.113$ Mg m^{-3}	

Data collection

Siemens SMART 1K CCD area-detector diffractometer	1408 independent reflections
	1388 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.062$
Absorption correction: multi-scan	$\theta_{max} = 33.1°$
(*SADABS*; Sheldrick, 2002)	$h = -11 \rightarrow 11$
$T_{min} = 0.816$, $T_{max} = 0.929$	$k = -19 \rightarrow 19$
12 392 measured reflections	$l = -20 \rightarrow 20$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.017$	$w = 1/[\sigma^2(F_o^2) + (0.0233P)^2]$
$wR(F^2) = 0.039$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.001$
1408 reflections	$\Delta\rho_{max} = 0.52$ e Å^{-3}
61 parameters	$\Delta\rho_{min} = -1.30$ e Å^{-3}

Table 1
Selected interatomic distances (Å).

Pr1—O2^i	2.439 (2)	Fe1—C2	1.928 (3)
Pr1—O2	2.439 (2)	Fe1—C1	1.928 (2)
Pr1—N1^i	2.5438 (18)	Fe1—C1^{iv}	1.928 (2)
Pr1—N1^{ii}	2.5438 (18)	Fe1—C1^v	1.928 (2)
Pr1—N1^{iii}	2.5438 (18)	Fe1—C1^{ii}	1.928 (2)
Pr1—N1	2.5438 (18)	N1—C1^{vi}	1.156 (3)
Pr1—N2^{iii}	2.572 (3)	N2—C2	1.159 (4)
Pr1—N2	2.572 (3)	C1—N1^{vi}	1.156 (3)
Fe1—C2^{iv}	1.928 (3)		

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

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

D—H$\cdots$A	D—H	H$\cdots$A	$D\cdots$A	D—H$\cdots$A
O1—H11$\cdots$N2^i	0.83 (3)	2.31 (2)	3.137 (4)	173 (5)
O1—H12$\cdots$N1^{ii}	0.83 (3)	2.69 (2)	3.351 (3)	138 (2)
O2—H2$\cdots$O1	0.82 (3)	2.01 (2)	2.809 (2)	166 (4)

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

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H atoms were refined isotropically, with a common atomic displacement parameter of 0.059 (9) Å and with O—H distances restrained to 0.82 (2) Å.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *SADABS* (Sheldrick, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXTL* (Bruker, 2001); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1764). Services for accessing these data are described at the back of the journal.

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