# SHORT-FORMAT PAPERS

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## Structure of Monoclinic ErFe(CN)$_6$.4H$_2$O

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**Abstract.** $M_r = 451{\cdot}28$, monoclinic, $P2_1/m$, $a = 7{\cdot}431\,(1)$, $b = 13{\cdot}729\,(2)$, $c = 7{\cdot}435\,(2)$ Å, $\beta = 120{\cdot}02\,(2)°$, $V = 656{\cdot}76$ Å$^3$, $Z = 2$, $D_x = 2{\cdot}282$, $D_m = 2{\cdot}280\,(4)$ g cm$^{-3}$, $\lambda$(Mo $K\bar{\alpha}$) = 0·71073 Å, $\mu = 75{\cdot}7$ cm$^{-1}$, $F(000) = 424$, $T = 293$ K, final $R = 0{\cdot}024$ for 962 observed reflections. The structure is isotypic with BiFe(CN)$_6$.4H$_2$O. The Er atom is eight-coordinated to six cyano N atoms and two water molecules in a square antiprism geometry ($D_{4d}$), the ErN$_6$(H$_2$O)$_2$ group. The Fe atom is six-coordinated to cyano C atoms in an octahedral arrangement, the FeC$_6$ group. Cyanide bridging connects these groups forming an infinite polymeric array. Two uncoordinated water molecules occupy holes in the structure. Selective mean geometrical details are: Er—N = 2·513 (7); Er—O = 2·412 (4); Fe—C = 1·934 (4); and C≡N = 1·143 (2) Å.

**Experimental.** The synthesis of ErFe(CN)$_6$.4H$_2$O is reported elsewhere (Perkins, 1986). The metal constituents in the title compound were confirmed by X-ray fluorescence analysis using a Novascan 30 SEM. Thermal dehydration (TGA) results of 4·0 (1) water molecules formula unit$^{-1}$ were obtained. Density measured by flotation. Small red crystal, 0·063 × 0·063 × 0·250 mm, glass fiber mount, Enraf–Nonius CAD-4F diffractometer, Mo $K\alpha$ radiation, graphite monochromator; cell constants from least-squares fit of 25 reflections ($3{\cdot}5 \le \theta \le 18{\cdot}0°$); $\omega$–$2\theta$ scan technique, variable scan rate of 0·38 to 3·35° min$^{-1}$, intensities of two check reflections ($\bar{1}\bar{1}\bar{1}$, 080) measured every 2 h revealed only random deviations (< 1%) from mean intensities; 1208 reflections measured, range $3 \le 2\theta \le 50°$, $h$: −8/8, $k$: 0/17, $l$: 0/9, after averaging 962 reflections [$I \ge 3\sigma(I)$] used in solution and refinement of the structure (VAX*SDP*, Enraf–Nonius, 1982); corrections for Lorentz and polarization effects, empirical high-$\chi$-angle absorption (North, Phillips & Mathews, 1968), transmission range 0·0413 to 0·1427, secondary extinction ($g = 5{\cdot}14 \times 10^{-8}$); full-matrix least-squares refinement of 84 variables on $F$ yielded $R = 0{\cdot}0241$, $wR = 0{\cdot}0241$, $w = \sigma(F_o)^{-2}$ with $\sigma(F_o) = \{I_p + I_b + [0{\cdot}04(I_p - I_b)]^2\}^{1/2}$ where $I_p$ and $I_b$ were the peak and background counts, respectively; 'goodness of fit', $\sum_2 = 2{\cdot}02$; max. absolute value of convergence [$\Delta\xi/\sigma(\xi_i)$ where $\xi_i$ values are varied parameters] $1{\cdot}0 \times 10^{-4}$; final difference Fourier map, max. positive density 1·1 (2) e Å$^{-3}$ in the vicinity of the Er atom, min. negative density 0·8 (2) e Å$^{-3}$; scattering factors and anomalous-dispersion terms taken from *International Tables for X-ray Crystallography* (1974). The final atomic parameters are given in Table 1,† and interatomic distances and angles are presented in Table 2. Fig. 1 shows the fully coordinated Er$^{3+}$ (CN = 8) and Fe$^{3+}$ (CN = 6) ions. The two coordinated water molecules are located *trans* to one another on one of the square faces of the square antiprism polyhedron ($D_{4d}$). Both faces are planar to within 0·006 Å (least-squares-planes refinement) and the dihedral angle is 0·12°. Fig. 2 is a stereodrawing of the unit cell. The O(1) atom of the uncoordinated zeolitic water molecule is within hydrogen-bonding distance to the coordinated O(3) water molecule, 2·811 (5) Å.

Table 1. *Fractional atomic coordinates with equivalent isotropic thermal parameters* (*e.s.d.'s in parentheses*)

|  | $x$ | $y$ | $z$ | $U_{eq}$*(Å$^2$) |
|---|---|---|---|---|
| Er | 0·35294 (6) | 0·250 | 0·67642 (7) | 0·01104 (9) |
| Fe | 0·000 | 0·500 | 0·000 | 0·26 (2)† |
| C(1) | 1·0932 (9) | 0·4105 (5) | 1·2312 (9) | 0·009 (2) |
| C(2) | 0·7276 (9) | 0·4404 (5) | 0·8638 (9) | 0·013 (2) |
| C(3) | 0·0931 (9) | 0·4114 (5) | 0·8623 (9) | 0·012 (2) |
| N(1) | 0·1516 (8) | 0·3608 (5) | 0·3726 (8) | 0·018 (2) |
| N(2) | 0·5679 (8) | 0·4036 (4) | 0·7833 (9) | 0·016 (2) |
| N(3) | 0·1507 (8) | 0·3608 (5) | 0·7792 (8) | 0·017 (2) |
| O(1) | 0·3106 (8) | 0·5999 (4) | 0·6561 (9) | 0·027 (1) |
| O(2) | 0·569 (1) | 0·250 | 1·049 (1) | 0·026 (2) |
| O(3) | 0·570 (1) | 0·250 | 0·519 (1) | 0·025 (2) |

* Equivalent isotropic thermal parameters defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

† Refined isotropically.

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† Lists of structure-factor amplitudes, anisotropic thermal parameters and additional distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51436 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 2. *Interatomic distances* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

| | | | |
|---|---|---|---|
| Er–N(1) | 2·505 (4) | Er–N(1)–C(1) | 166·9 (4) |
| Er–N(2) | 2·522 (4) | Er–N(2)–C(2) | 149·4 (4) |
| Er–N(3) | 2·511 (4) | Er–N(3)–C(3) | 166·8 (4) |
| Av. | 2·513 (7) | Av. | 161 (8) |
| Er–O(2) | 2·408 (5) | | |
| Er–O(3) | 2·416 (5) | | |
| Av. | 2·412 (4) | | |
| Fe–C(1) | 1·938 (5) | Fe–C(1)–N(1) | 177·3 (4) |
| Fe–C(2) | 1·935 (5) | Fe–C(2)–N(2) | 178·8 (4) |
| Fe–C(3) | 1·928 (5) | Fe–C(3)–N(3) | 178·1 (4) |
| Av. | 1·934 (4) | Av. | 178·1 (6) |
| C(1)–N(1) | 1·141 (6) | C(1)–Fe–C(2) | 90·7 (2) |
| C(2)–N(2) | 1·144 (6) | C(1)–Fe–C(3) | 90·4 (2) |
| C(3)–N(3) | 1·145 (6) | C(2)–Fe–C(3) | 90·8 (2) |
| Av. | 1·143 (2) | Av. | 90·6 (2) |
| O(1)–O(3) | 2·811 (5) | | |

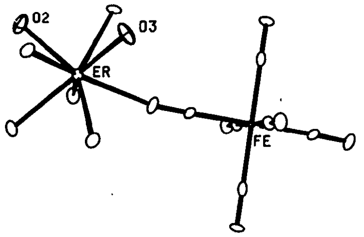

Fig. 1. $ErFe(CN)_6.4H_2O$. The square antiprism geometry about Er and the octahedrally arranged cyano groups about Fe. Cyanide bridging links the $ErN_6(H_2O)_2$ and $FeC_6$ groups.

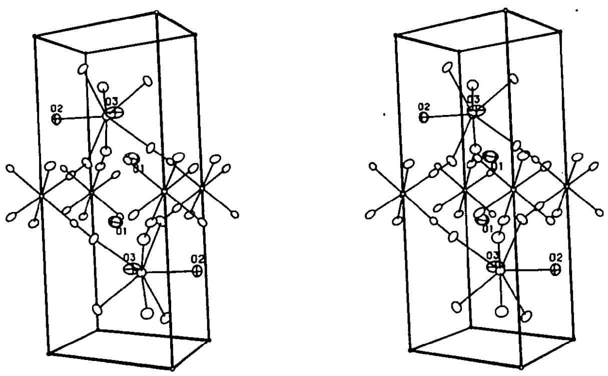

Fig. 2. A stereoscopic view of the contents of the unit cell (*a* axis horizontal, *b* axis vertical, *c* axis into plane of paper). The $Er^{3+}$ and $Fe^{3+}$ ions are shown fully coordinated. O(1) atoms associated with the zeolitic water molecules are seen within the Er—N≡C—Fe network.

**Related literature.** Bailey, Williams & Milligan (1973) reported the first single-crystal X-ray diffraction analysis [$LaFe(CN)_6.5H_2O$, hexagonal, $P6_3/m$] of the $LnFe(CN)_6.nH_2O$ series. In the same year, Hulliger, Landolt & Vetsch (1973) reported the $LnT(CN)_6.4H_2O$ series ($T$ = Fe, Co) to have orthorhombic symmetry (nearly pseudohexagonal) and Kietaible & Petter (1974), using single crystals from the Hulliger group, reported that $SmFe(CN)_6.4H_2O$ was orthorhombic (*Cmcm*). Hulliger *et al.* (1976) reported additional structural and magnetic data for $LnT(CN)_6.nH_2O$ ($T$ = Cr, Co, Fe; $n$ = 4, 5). The pentahydrate forms were classified as hexagonal and the tetrahydrate forms as orthorhombic. This work was based on powder work. Recent single-crystal structure analyses have revealed that Bi and $SmFe(CN)_6.4H_2O$ best fit a monoclinic system ($P2_1/m$) and not hexagonal or orthorhombic (Perkins, 1986; Mullica, Perkins & Sappenfield, 1988).

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# Structure of an Iridium-Containing Hydrogenation Catalyst

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**Abstract.** ($\eta^4$-1,5-Cyclooctadiene)(pyridine)(tricyclohexylphosphine)iridium(I) hexafluorophosphate, $[Ir(C_8H_{12})(C_5H_5N)\{P(C_6H_{11})_3\}][PF_6]$, $M_r = 804·9$, monoclinic, $P2_1$, $a = 9·625$ (6), $b = 16·440$ (8), $c = 10·383$ (5) Å, $\beta = 103·13$ (4)°, $V = 1600·1$ Å$^3$, $Z = 2$, $D_x = 1·67$ g cm$^{-3}$, $\lambda(Mo\ K\alpha) = 0·71069$ Å, $\mu =$

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