

References

- ALLEN, F. H., KENNARD, O., WATSON, D. G., BRAMMER, L., ORPEN, A. G. & TAYLOR, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.
- BALES, J. R., MAZID, M. A., SADLER, P. J., AGGARWAL, A., KURODA, R., NEIDLE, S., GILMOUR, D. W., PEART, B. J. & RAMSDEN, C. A. (1985). *J. Chem. Soc. Dalton Trans.*, pp. 795–802.
- BLATON, N. M., PEETERS, O. M. & DE RANTER, C. J. (1979a). *Acta Cryst.* B35, 753–755.
- BLATON, N. M., PEETERS, O. M. & DE RANTER, C. J. (1979b). *Acta Cryst.* B35, 2465–2467.
- BLESSING, R. H. (1987). *Crystallogr. Rev.* 1, 3–58.
- CHASSEAUD, L. F., HENRICK, K., MATTHEWS, R. W., SCOTT, P. W. & WOOD, G. (1984). *J. Chem. Soc.* pp. 491–492.
- DE BONDT, H. L., BLATON, N. M., PEETERS, O. M., DE RANTER, C. J. & KJØLLER-LARSEN, I. (1991). *The Application of Charge Density Research to Chemistry and Drug Design*, edited by G. A. JEFFREY, pp. 341–349. New York: Plenum.
- DOMENICANO, A., MURRAY-RUST, P. & VACIAGO, A. (1983). *Acta Cryst.* B39, 457–468.
- EDWARDS, D. I. (1981). *Prog. Med. Chem.* 18, 87–116.
- FRENZ, B. A. (1985). *Enraf-Nonius Structure Determination Package*. College Station, Texas, USA, and Enraf-Nonius, Delft, The Netherlands.
- GERMAIN, G., DECLERCQ, J.-P. & VAN MEERSSCHE, M. (1977). *Acta Cryst.* B33, 2269–2270.
- IBERS, J. A. & HAMILTON, W. C. (1964). *Acta Cryst.* 17, 781–782.
- JOHNSON, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- McMULLAN, R. K., EPSTEIN, J., RUBLE, J. R. & CRAVEN, B. M. (1979). *Acta Cryst.* B35, 688–691.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
- NARDELLI, M. (1983). *Comput. Chem.* 7, 95–98.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.

SHORT-FORMAT PAPERS

Contributions intended for publication under this heading should follow the format given in the Checklist for Authors [*Acta Cryst.* (1985). C41, 1–4].

Acta Cryst. (1991). C47, 2433–2435

Structure of Gadolinium Hexacyanoferrate(III) Tetrahydrate

BY D. F. MULLICA AND E. L. SAPPENFIELD

Department of Chemistry, Baylor University, Waco, Texas 76798, USA

(Received 6 March 1991; accepted 30 May 1991)

Abstract. $\text{GdFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$, $M_r = 441.26$, orthorhombic, $Cmcm$, $a = 7.3964$ (3), $b = 12.8372$ (5), $c = 13.6726$ (4) Å, $V = 1298.21$ (8) Å³, $Z = 4$, $D_m = 2.23$ (2), $D_x = 2.26$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 6.223$ mm⁻¹, $F(000) = 832$, $T = 291$ K, final $R = 0.016$ for 1017 absorption-corrected unique reflections with $F_o \geq 6\sigma|F_o|$. The eight-coordinated Gd ion is bonded to six cyano N atoms and two water molecules in a square antiprism geometry (D_{4d}), the $\text{GdN}_6(\text{H}_2\text{O})_2$ group. The Fe ion is octahedrally coordinated to six cyano C atoms, the FeC_6 group. Cyanide bridging links these groups to build an infinite polymeric array. Cavities within the structure are occupied by uncoordinated zeolitic water molecules, O(1), which are within hydrogen-bonding distances (2.818 Å) to the coordinated water molecules, O(1). Important mean bond distances are: Gd—N

$= 2.489$ (14); Fe—C = 1.927 (4); and C≡N = 1.152 (1) Å.

Experimental. Crystals of $\text{GdFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ were synthesized by a procedure similar to that of Prandtl & Mohr (1938). An aqueous acidic solution (pH = 4.0) of 0.2M GdCl_3 was added to 15 ml of 0.1M $\text{K}_3\text{Fe}(\text{CN})_6$. The mixture was stirred, filtered and stored in the dark at room temperature. Clear dark-red crystals formed after three to five days. The metal constituents and their ratios were verified by X-ray fluorescence analysis on a Novascan 30 SEM. The water content was confirmed by thermal gravimetric analysis (TGA), 3.9 (1) H₂O molecules/formula unit. The flotation method (bromobenzene and 1,1,2,2-tetrabromoethane) was employed to determine the experimental density. Infrared spec-

Table 1. Atomic coordinates and isotropic equivalent thermal parameters ($\text{\AA}^2 \times 10^2$) with e.s.d.'s in parentheses

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Gd	0.0	0.32350 (1)	0.25	1.081 (4)
Fe	0.0	0.0	0.0	1.10 (1)
C(1)	0.3147 (3)	0.4526 (2)	0.0890 (2)	1.83 (4)
C(2)	0.0	0.1359 (2)	0.0593 (2)	1.81 (6)
N(1)	0.2025 (3)	0.4233 (2)	0.1505 (2)	2.26 (5)
N(2)	0.0	0.2161 (2)	0.0972 (2)	2.60 (7)
O(1)	0.2610 (4)	0.2164 (2)	0.25	3.41 (6)
O(2)	0.0	0.6567 (2)	0.0996 (3)	3.72 (8)

Table 2. Interatomic distances (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

Gd—N(1)	2.475 (2)	Fe—C(1)—N(1)	178.6 (2)
Gd—N(2)	2.503 (2)	Fe—C(2)—N(2)	178.3 (3)
Av.	2.489 (14)	Av.	178.4 (2)
Gd—O(1)	2.370 (2)	Gd—N(1)—C(1)	167.2 (2)
Fe—C(1)	1.931 (2)	Gd—N(2)—C(2)	150.1 (3)
Fe—C(2)	1.923 (3)	Av.	159 (9)
Av.	1.927 (4)	C(1)—Fe—C(1)'	89.6 (1)
C(1)—N(1)	1.152 (3)	C(1)—Fe—C(1)''	90.4 (1)
C(2)—N(2)	1.153 (4)	C(1)—Fe—C(2)	88.85 (8)
Av.	1.152 (1)	C(1)—Fe—C(2)	91.15 (8)
O(1)—O(2)	2.818 (3)	Av.	90.0 (9)
N(2)—O(2)	3.147 (4)		

trosopy (KBr pressed-pellet) provided relevant data: 3620 (ν , OH); 3415 (ν , broad OH, hydrogen bonding); 2130 (ν , $\text{C}\equiv\text{N}$); 1630 (δ , HOH); 550 (δ , Fe—CN) and 440 cm^{-1} (ν , Fe—C).

After verifying the biaxial nature and homogeneity of the system by a conoscopic examination, a single crystal ($0.13 \times 0.14 \times 0.26$ mm) was mounted on an Enraf-Nonius CAD-4F diffractometer equipped with graphite-monochromated $\text{Mo K}\alpha$ radiation, take-off angle 5.8° . The orientation matrix was obtained from 25 diffractometer-measured reflections ($5.0 < \theta < 18.0^\circ$). Final unit-cell parameters using 25 reflections were determined at high angles ($20 < \theta < 30^\circ$). 2190 reflections were collected using the ω - 2θ scan technique ($h, 0 \rightarrow 10; k, 0 \rightarrow 18; l, 0 \rightarrow 19$), variable scan rate of 0.37 – $2.75^\circ \text{min}^{-1}$, $3.0 < 2\theta < 60.0^\circ$; intensities of three check reflections ($400, \bar{1}, 11, \bar{2}, \bar{3}\bar{5}\bar{1}$) measured as a function of time (every 2 h) revealed only random deviations; Lorentz-polarization and empirical high- χ -angle absorption corrections, min. 0.9800–max. 1.0000 (North, Phillips & Mathews, 1968); after eliminating systematic absences, 1059 reflections were unique of which 1017 reflections ($F_o \geq 6\sigma|F_o|$) were used in the solution and refinement of the structure.

The structure was solved by isomorphic substitution (Mullica & Sappenfield, 1989) and refined using full-matrix least squares (SHELXTL-PC;

Sheldrick, 1989). Anisotropic refinement on F of 52 parameters yielded $R = 0.016$, $wR = 0.019$ with $w = [\sigma^2(|F_o|) + 0.0030(F_o)^2]^{-1}$, $S = 1.61$; $g = 8.0 (6) \times 10^{-7}$, in the form of $F_o = |F_c|/(1 + gI_c)$ (Stout & Jensen, 1989); shift/e.s.d. values $(\Delta/\sigma)_{\text{max}} = 1.06 \times 10^{-3}$ and $(\Delta/\sigma)_{\text{av}} = 3.9 \times 10^{-5}$; max. and min. heights in final difference Fourier synthesis $0.67 (3)$ and -0.31 e \AA^{-3} . Atomic scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Final positional parameters and the equivalent values of the anisotropic displacement parameters are given in Table 1.* Derived interatomic bond distances and angles are listed in Table 2. Fig. 1 presents a view of the coordination geometries about the metal ions whereas Fig. 2 is a stereodrawing of the contents of the unit cell.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54307 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

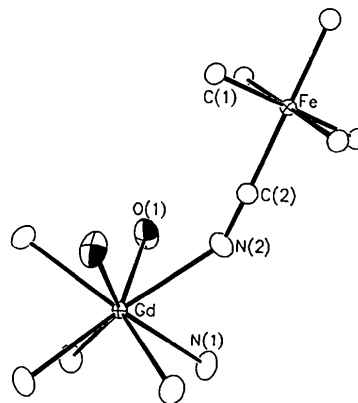


Fig. 1. A projected view of $\text{GdFe(CN)}_6 \cdot 4\text{H}_2\text{O}$ displaying 50% thermal probability and showing the eight-coordinated square antiprism geometry about the Gd ion (note parallelism between opposing faces) as well as the octahedral array about the Fe ion. The $\text{GdN}_6(\text{H}_2\text{O})_2$ and FeC_6 groups are connected by cyanide bridging.

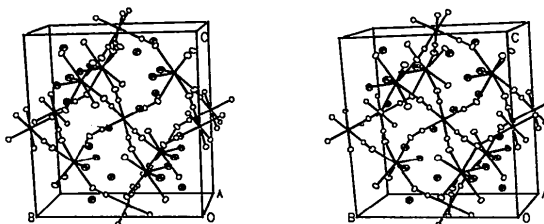


Fig. 2. A stereoscopic view of the contents of the unit cell. The metal ions (Gd, CN = 8; Fe, CN = 6) are shown fully coordinated. The uncoordinated zeolitic water molecules, O(2), occupy cavities within the structure.

Related literature. The reinvestigation of $\text{SmCo}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ and $\text{SmFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ (Mullica & Sappenfield, 1989), which were originally thought to be in the monoclinic system ($P2_1/m$), has shown that these analogous compounds belong in the higher symmetry orthorhombic system, space group $Cmcm$, even though both data sets solved equally well in $P2_1/m$. The reinvestigation was motivated due to a private communication (Marsh, 1989a) which was followed by a publication (Marsh, 1989b). The bond lengths and angles as well as the geometric structural arrangement were virtually the same in both $Cmcm$ and $P2_1/m$. For this reason, the title compound, which is situated where a detectable discontinuity among tripositive lanthanide ions in a particular series is usually observed (at the 'gadolinium break'), was investigated. The crystallographic results for $\text{GdFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ were equivalent in $Cmcm$ ($R = 0.016$, $wR = 0.019$, $S = 1.61$) and in $P2_1/m$ ($R = 0.019$, $wR = 0.023$, $S = 1.92$). Hulliger, Landolt & Vetsch (1973), using magnetic and structural powder data, have correctly described the pseudo-hexagonal $\text{LnT}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ series ($\text{Ln} = \text{Sm}, \dots, \text{Lu}$ and $T = \text{Fe}$ and Co) as having orthorhombic symmetry. Recently, Gramlich, Petter & Hulliger (1990) have also shown that $\text{ErFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ and its analogs

belong in an orthorhombic system rather than in a monoclinic system. The work and conclusions of Hulliger, Landolt & Vetsch (1973) and those in this laboratory (Mullica & Sappenfield, 1989, and this paper) are now in direct agreement.

The authors wish to acknowledge the financial support of the work by the Robert A. Welch Foundation (Grant No. AA-0668) and Baylor University.

References

- GRAMLICH, V., PETTER, W. & HULLIGER, F. (1990). *Acta Cryst.* **C46**, 724–726.
 HULLIGER, F., LANDOLT, M. & VETSCH, H. (1973). *Proc. Tenth Rare-Earth Res. Conf.* Carefree, Arizona. Vol. 80.
 MARSH, R. E. (1989a). Private communication, March 1989.
 MARSH, R. E. (1989b). *Acta Cryst.* **C45**, 127.
 MULLICA, D. F. & SAPPENFIELD, E. L. (1989). *J. Solid State Chem.* **82**, 168–171.
 NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
 PRANDTL, W. & MOHR, S. (1938). *Z. Anorg. Allg. Chem.* **236**, 243–251.
 SHELDRICK, G. M. (1989). *SHELXTL-PC*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 STOUT, G. H. & JENSEN, L. H. (1989). *X-ray Structure Determination*, 2nd ed., p. 393. New York: John Wiley.

Acta Cryst. (1991). **C47**, 2435–2437

Structure of the Second Polymorph of Niobium Pentachloride

BY F. ALBERT COTTON,* PIOTR A. KIBALA, MAREK MATUSZ AND ROBERT B. W. SANDOR

Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, TX 77843, USA

(Received 23 July 1990; accepted 2 January 1991)

Abstract. (1) NbCl_5 , $M_r = 270.17$, monoclinic, $P2_1/n$, $a = 7.785$ (2), $b = 10.201$ (2), $c = 8.074$ (2) Å, $\beta = 90.58$ (2)°, $V = 641.2$ (5) Å³, $Z = 4$, $D_x = 2.80$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 37.70$ cm⁻¹, $F(000) = 504$, $T = 294$ K, $R = 0.017$ for 1101 observed reflections. Two NbCl_5 units form an edge-sharing bioctahedron. The Nb atoms are separated by 3.9881 (3) Å. The mean Nb—Cl_{bridge} distance is 2.567 (1) Å and the mean non-bridging equatorial and axial Nb—Cl bond lengths are 2.246 (2) and 2.292 (1) Å, respectively. The Nb—Cl_{bridge}—Nb angle is 101.93 (2)° and the Cl_{bridge}—Nb—Cl_{bridge} angle is 78.07 (2)°.

* Author to whom correspondence should be addressed.

Experimental. A Pyrex tube evacuated to 2.67×10^{-2} Pa containing Nb (0.50 g, 5.4 mmol), S_2Cl_2 (0.43 mL, 5.4 mmol) and S (0.18 g, 5.4 mmol) was heated at 698 K for 48 h. Upon slow cooling several light yellow octahedral crystals of NbCl_5 formed on the walls of the tube. The quality of the crystals was confirmed by polarized light microscopy. An irregularly shaped crystal, $0.600 \times 0.40 \times 0.30$ mm, was sealed with epoxy cement in a glass capillary filled with degassed mineral oil under argon. Unit-cell dimensions were determined from least-squares analysis of 25 reflections with $20 < 2\theta < 30^\circ$. Laue class and unit-cell dimensions were confirmed with axial photographs. Intensity data were collected to $\sin\theta/\lambda = 0.596 \text{ \AA}^{-1}$ ($0 \leq h \leq 9$; $0 \leq k \leq 12$; $-9 \leq l \leq$