

Synthesis, Characterisation and Crystal Structure of a Cyano-Bridged Polymeric Yttrium-Iron Complex $\{[Y(\text{phen})_2(\text{H}_2\text{O})_2\text{Fe}(\text{CN})_6] \cdot 8\text{H}_2\text{O}\}_n$

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Yttrium-Iron Complex, Cyano-Bridge, Thermal Analysis

A new cyano-bridged 1D polymeric linear chain complex $\{[Y(\text{phen})_2(\text{H}_2\text{O})_2\text{Fe}(\text{CN})_6] \cdot 8\text{H}_2\text{O}\}_n$ (where phen = 1,10-phenanthroline) has been synthesised and its crystal structure determined. The yttrium(III) and iron(III) centres achieve distorted square antiprismatic and slightly distorted octahedral geometry, respectively. Presence of an extensive network of hydrogen bonds present in the complex impart the overall stability to the system. The presence of ten water molecules per molecular unit has been confirmed by thermogravimetric analysis.

Introduction

It is well known that the cyanide ion can connect two metal ions as a bridging ligand. The cyano-bridged lanthanide-transition-metal complexes have great importance because of their applications as precursors in the preparation of oxide fuel cells [1], electroceramic [2], chemical sensor [3], and zeolite type materials [3, 4], in the medical treatment of heavy-metal poisoning, in the environmental cleanup of radioactive materials and heavy metals [2], and in ion-exchange columns for selective metal separation [5].

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 [6]. Mullica *et al.* [7, 8] and others [9 - 12] reported a series of cyano-bridged lanthanide-transition-metal hydrates. The water-free cyano-bridged lanthanide-transition metal complexes have also been reported [13, 14]. The trinuclear cyano-bridged complex $[\text{Nd}(2,2'\text{-bipy})_2(\text{H}_2\text{O})_4\text{Fe}(\text{CN})_6\text{-Nd}(2,2'\text{-bipy})_2(\text{H}_2\text{O})_4][\text{Fe}(\text{CN})_6] \cdot 8\text{H}_2\text{O}$ is also known [15]. Recently, we have reported two cyano-bridged bimetallic complexes, $[\text{Cu}(\text{dmen})]_2\text{-}[\text{Fe}(\text{CN})_6]$ [16] and $\{[\text{Ba}_2(\text{phen})_4(\text{H}_2\text{O})_6\text{Fe}(\text{CN})_6] \cdot \text{Cl} \cdot 2(\text{phen}) \cdot 3\text{H}_2\text{O}\}_n$ [17], both of which utilise the $[\text{Fe}(\text{CN})_6]^{3-}$ ion as the bridging unit. It was shown

by crystal structure analysis that the Cu_2Fe complex forms a two-dimensional sheet structure, whilst the Ba_2Fe complex forms a zig-zig polymer chain. The latter complex contains alternating single cyano and double aquo bridges [17].

The yttrium atom has a larger size, a higher coordination number and shows similarity in chemical behaviour with the heavy lanthanide(III) ions. The structural chemistry is also similar in many ways. Cyano-bridged heterometallic Fe-Y complexes are not well documented. We have been able to obtain a new polymeric yttrium-iron complex $\{[Y(\text{phen})_2(\text{H}_2\text{O})_2\text{Fe}(\text{CN})_6] \cdot 8\text{H}_2\text{O}\}_n$ using $[\text{Fe}(\text{CN})_6]^{3-}$ ion. To the best of our knowledge this compound represents the first example of a chained yttrium-iron cyano-bridged complex. The synthesis, properties and X-ray structure of this complex are reported in the present paper.

Experimental Part

Materials

All chemicals and solvents used for synthesis were of reagent grade. $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich), 1,10-phenanthroline monohydrate and $\text{K}_3[\text{Fe}(\text{CN})_6]$ (Loba Chemie, India) were used as received.

Physical techniques

Elemental analyses were carried out using a Perkin-Elmer 2400 II elemental analyser. Infrared spectra were

Table 1. Selected bond lengths (Å) and angles (°) for the title complex.

Y(1)-O(1)	2.311(2)	Y(1)-N(3)	2.414(3)
Y(1)-N(4)	2.545(3)	Y(1)-N(5)	2.499(2)
Fe(1)-C(1)	1.938(3)	Fe(1)-C(2)	1.918(4)
Fe(1)-C(3)	1.923(3)	N(1)-C(1)	1.151(4)
N(2)-C(2)	1.166(4)	N(3)-C(3)	1.155(4)
O(1)-Y(1)-O(1) ^a	80.2(1)	O(1)-Y(1)-N(3) ^a	76.47(8)
O(1)-Y(1)-N(3)	81.27(8)	N(3)-Y(1)-N(3) ^a	150.8(1)
O(1)-Y(1)-N(5)	77.36(8)	N(3)-Y(1)-N(5) ^a	112.96(8)
N(3)-Y(1)-N(5)	79.69(8)	O(1)-Y(1)-N(5) ^a	149.31(8)
N(5)-Y(1)-N(5) ^a	130.5(1)	O(1)-Y(1)-N(4) ^a	145.22(7)
N(3)-Y(1)-N(4) ^a	73.66(9)	N(5)-Y(1)-N(4) ^a	74.78(8)
O(1)-Y(1)-N(4)	115.78(8)	N(3)-Y(1)-N(4)	134.05(9)
N(5)-Y(1)-N(4)	64.84(8)	N(4)-Y(1)-N(4) ^a	69.6(1)
C(1)-Fe(1)-C(1) ^b	180.0	C(2)-Fe(1)-C(2) ^b	180.0
C(3)-Fe(1)-C(3) ^b	180.0	C(2)-Fe(1)-C(3) ^b	91.8(1)
C(2)-Fe(1)-C(3)	88.2(1)	C(2)-Fe(1)-C(1) ^b	87.7(1)
C(3)-Fe(1)-C(1) ^b	92.1(1)	C(2)-Fe(1)-C(1)	92.3(1)
C(3)-Fe(1)-C(1)	87.9(1)	C(3)-N(3)-Y(1)	170.5(3)
N(1)-C(1)-Fe(1)	179.2(3)	N(2)-C(2)-Fe(1)	176.8(3)
N(3)-C(3)-Fe(1)	177.9(3)		

Symmetry transformations used to generate equivalent atoms: ^a $-x, y, -0.5 + z$; ^b $0.5 - x, 0.5 - y, 1 - z$.

recorded on a Perkin-Elmer 883-Infrared spectrophotometer in the range 4000 - 200 cm^{-1} as KBr pellets. Thermal investigation was carried out on a Shimadzu TGA-50 thermal analyser under a dynamic nitrogen environment.

X-ray crystallography

Crystal data: Formula $[\text{C}_{30}\text{H}_{20}\text{FeN}_{10}\text{O}_2\text{Y}] \cdot 8 \text{H}_2\text{O}$, FW = 841.45, monoclinic, space group C2/c, $a = 23.546(5)$, $b = 11.957(2)$, $c = 14.693(3)$ Å, $\beta = 116.01(3)^\circ$, $V = 3717.3(13)$ Å³, $T = 150$ K, $Z = 4$, $D_c = 1.504$ g cm^{-3} , $\mu(\text{Mo-K}\alpha) = 2.010$ mm⁻¹, no. of measured reflections = 13158, no. of independent reflections = 4450 ($R_{\text{int}} = 0.0484$). The unit cell dimensions and intensity data were obtained by using an Enraf-Nonius Kappa CCD area detector diffractometer [18] mounted at the window of a FR590 X-ray generator (molybdenum, $\lambda = 0.71073$ Å) operating at 55 kV and 30 mA at the temperature 150(2) K. The stability of the crystal was checked by measuring standard reflections at fixed intervals during the data collection. However, no significant loss of intensity was noted for the crystal. The data were corrected for absorption effects by using the program SORTAV [19]. The structure was solved by direct method (SHELXS-96) [20] and refined on F^2 by full-matrix least squares (SHELXL-96) [21] using all unique 4450 data and 277 parameters to final wR_2 (on F^2 , all data) = 0.1187 and R_1 (on F , 6973 data with $[I > 2\sigma(I)]$) = 0.0481. All non-hydrogen atoms

Table 2. Dimensions of the possible hydrogen bonds (D = donor, A = acceptor). The distances are in Å and angles in deg.

D-H...A	D-H	H...A	D...A	\angle D-H...A
O(1)-(H1A)...O(5) ⁱ	0.95	1.77	2.711	173
O(1)-(H1B)...O(3) ⁱ	0.95	1.80	2.720	163
O(2)-(H2A)...N(1) ⁱ	0.95	2.01	2.872	150
O(3)-(H3A)...O(2) ⁱ	0.95	1.80	2.741	171
O(3)-(H3B)...O(4) ⁱ	0.95	1.79	2.716	164
O(4)-(H4B)...N(2) ⁱ	0.95	2.01	2.942	166
O(5)-(H5B)...N(2) ⁱⁱ	0.95	2.52	3.372	149
O(2)-(H2B)...N(2) ⁱⁱⁱ	0.95	2.03	2.970	170
O(5)-(H5A)...O(3) ^{iv}	0.95	1.88	2.822	169
O(4)-(H4A)...N(1) ^v	0.95	1.98	2.932	175

Equivalent positions: ⁱ x, y, z ; ⁱⁱ $-x, y, 1/2 - z$; ⁱⁱⁱ $x, -y, -1/2 + z$; ^{iv} $-x, -y, -z$; ^v $1/2 - x, -1/2 + y, 1/2 - z$.

were treated anisotropically. The ring hydrogen atoms were included in calculated positions (riding model), and those on the water molecules were located from difference maps and refined with the constraints O-H = 0.95 and H...H = 1.52 Å. Selected distances and inter-bond angles are given in Table 1. The dimensions of the hydrogen bonds are listed in Table 2.

Synthesis of $\{[Y(\text{phen})_2(\text{H}_2\text{O})_2\text{Fe}(\text{CN})_6] \cdot 8\text{H}_2\text{O}\}_n$

An aqueous solution (10 ml) of $\text{K}_3[\text{Fe}(\text{CN})_6]$ (0.33 g, 1 mmol) was added to a stirred mixture of 15 ml of an aqueous solution of $\text{Y}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$ (0.38 g, 1 mmol) and 10 ml of an ethanolic solution of 1,10-phenanthroline monohydrate (0.395 g, 2 mmol). On slow evaporation of the solvents, at room temperature, light orange coloured crystals appeared after 4-5 days. The crystals were washed with water and dried in air and used for X-ray analysis. Analysis for $\text{C}_{30}\text{H}_{36}\text{FeN}_{10}\text{O}_{10}\text{Y}$: calcd. C 42.78, H 4.27, N 16.64; found C 42.61, H 4.14, N 16.47.

Results and Discussion

IR spectra

In the IR spectrum of the title compound the broad absorption bands at 3412 and 3040 cm^{-1} indicate the presence of $\nu(\text{O-H})$ and $\nu(\text{N-H})$ [22, 23]. A sharp band at 1649 cm^{-1} is due to the H-OH bending. The band at 422 cm^{-1} may be assigned to $\rho_w(\text{H}_2\text{O})$ and those at 850 and 865 cm^{-1} to $\rho_r(\text{H}_2\text{O})$ vibrations. These results suggest the presence of both coordinated and crystal water in the complex [24]. For the $\nu(\text{C}\equiv\text{N})$ modes of $[\text{Fe}(\text{CN})_6]^{3-}$ two bands of comparable intensity are observed. The band at

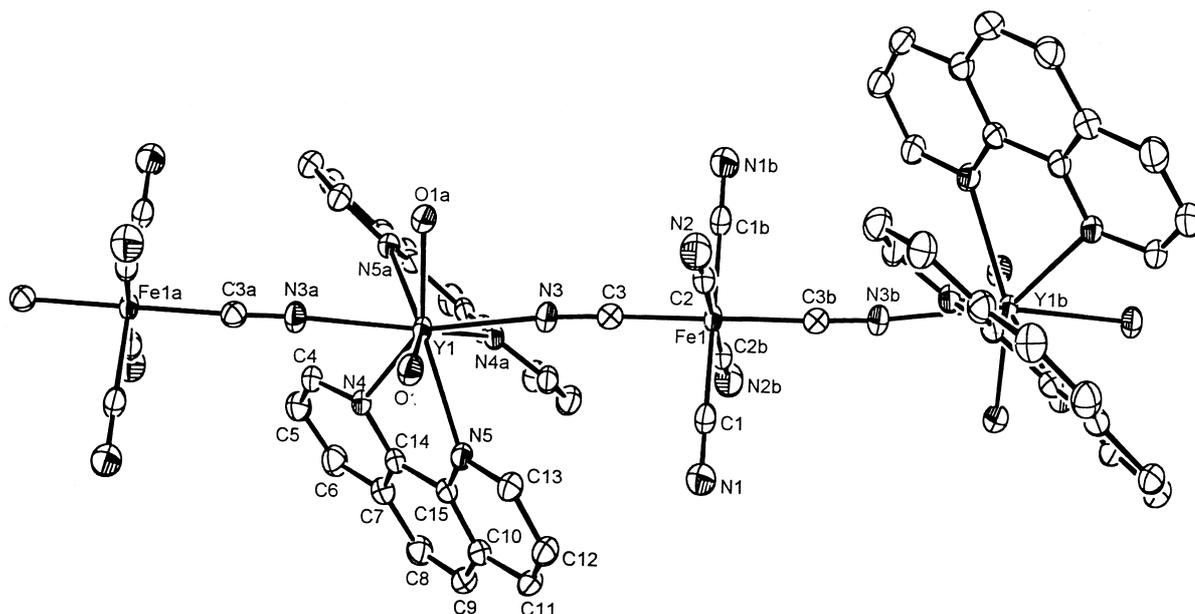


Fig. 1. Atom labeling in part of the polymer chain. The unique Y(1) and Fe(1) atoms are located on a two fold axis at $(0, y, 1/4)$ and a center of inversion at $(1/4, 1/4, 1/2)$, respectively. Atoms designated with a and b are generated by the symmetry operations $(-x, y, -1/2 + z)$ and $(1/2 - x, 1/2 - y, 1 - z)$ respectively.

2120 cm^{-1} is assigned to the intermetallic $\text{C}\equiv\text{N}$ stretching and that at 2051 cm^{-1} to the terminal $\text{C}\equiv\text{N}$ stretching mode. The characteristic absorptions of 1,10-phenanthroline appear at 1893, 1521, 1143, 1105 and 730 cm^{-1} .

Thermal analysis

The thermogravimetric study shows that the mass loss of the title complex occurs in two steps: In the temperature range $45 - 105\text{ }^\circ\text{C}$ it corresponds exactly to the release of ten water molecules. The mass loss in the second process, in the temperature range $105 - 370\text{ }^\circ\text{C}$, is consistent with the loss of two 1,10-phenanthroline molecules from the anhydrous complex. The presence or absence of the ligands in the intermediates are confirmed by IR spectra [23, 24].

Description of the structure

The X-ray study shows that the complex $\{[\text{Y}(\text{phen})_2(\text{H}_2\text{O})_2\text{Fe}(\text{CN})_6] \cdot 8\text{H}_2\text{O}\}_n$ has a polymeric chain structure as shown in Fig. 1. The chain is formed by alternating groups of $[\text{Y}(\text{phen})_2(\text{H}_2\text{O})_2]^{3+}$ cations and $[\text{Fe}(\text{CN})_6]^{3-}$ anions that are

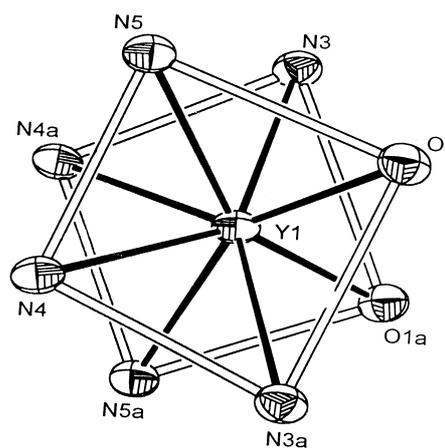


Fig. 2. Coordination polyhedron of the yttrium atom.

linked by bridges involving two mutually trans CN groups of the $[\text{Fe}(\text{CN})_6]$ moiety. The chain extends to infinity along the $[-1\ 0\ 1]$ direction. A small part of the chain with relevant crystallographic atom numbering is illustrated in Fig. 1. The Fe atom resides on a crystallographic centre of inversion $(1/4, 1/4, 1/2)$ and the Y atom on a two-fold axis $(0, y, 1/4)$. The yttrium-iron separation in the chain is 5.471 \AA . The four additional water molecules per

asymmetric unit in the structure remain in the lattice without any direct interaction with the metal atoms.

The yttrium(III) ion is chelated to two phen ligands and directly bonded to two water molecules and two bridging NC groups of the $[\text{Fe}(\text{CN})_6]^{3-}$ anion. Thus the yttrium(III) centre is eight coordinated in a distorted square antiprismatic geometry as shown in Fig. 2. This type of geometry is very common for many yttrium and lanthanide complexes [25 - 29]. The $[\text{Fe}(\text{CN})_6]^{3-}$ anion is, as expected, octahedral with only minor deviations from the ideal geometry. The Fe-C and C-N distances lie in the narrow ranges, 1.918(4) - 1.938(3) and 1.151(4) - 1.166(4) Å, respectively; the C-Fe-C angles for the cis positions vary from 87.7(1) to 92.3(1)°. The CN groups are bonded linearly to Fe as shown by the values 176.8(3) - 179.2(3)° for the Fe-C-N angles. Similarly, the Y-N-C bridge angles, 170.5(3)°, are also close to linear suggesting a very favourable position for relatively strong Y-NC-Fe bonding. The Y-O distance 2.311(2) Å in the present compound is comparable with those in related complexes, *e. g.* Y-O (water) 2.386 Å for $[\text{CuY}(\text{Ala})_4(\text{H}_2\text{O})_5](\text{ClO}_4)_5 \cdot 3\text{H}_2\text{O}$ [30], 2.36 Å for $[\text{Y}(\text{H}_2\text{O})_6(\text{OSMe}_2)_2]\text{Cl}_3$ [30] and 2.37 Å for $[\text{Y}(\text{H}_2\text{O})_8]\text{Cl}_3 \cdot 15\text{-crown-5}$ [31]. The Y-N(4) and Y-N(5) distances of the phen ligand in the present complex, 2.545(3) and 2.499(2) Å respectively, are significantly different. These distances are also considerably longer than both the Y-N(3) (NC) [2.414(3) Å] and Y-O(1) bonds. Comparable Y-N(phen) distances in the range 2.587 - 2.543 Å were found in other complexes [32]. It may be pointed out that the asymmetry in the two Y-N (phen) chelate bonds is most probably due to severe steric crowding around the Y atom. The non-bonded short contacts involving N(4) and N(5) of phen [N(4)...N(3a) 2.974(5), N(4)...N(4a) 2.906(5), N(4)...N(5a) 3.063(5), and N(5)...O(1) 3.010(5), N(5)...N(4a) 3.063(5), N(5)...N(3) 3.149(5) Å] indicate that those involving N(4) are slightly shorter than those involving N(5), even after the Y(1)-N(4)

bond has been lengthened. It is also observed that although the bond lengths and angles within the phen ligand are as expected, the ligand as a whole suffers considerable distortions from planarity as indicated by atomic deviations from -0.078(2) to +0.088(2) Å from the mean plane of the ring. Further, the Y atom does not lie in the mean plane of the phen ring, and the latter shows a dihedral angle of 21.3(1)° with the YN_4N_5 plane. These deviations and distortions from expected geometry may be again attributed at least in part to steric crowding.

An important aspect of the present crystal structure is an extensive network of O-H...O/N hydrogen bonds (Table 2). The H...O/N distances lie in the range 1.767 - 2.519 Å and fall within acceptable limits of hydrogen bond interactions [33]. All the water molecules act as donors and those uncoordinated in the lattice all act also as acceptors. In addition, the nitrogen atoms of the cyano groups (on $[\text{Fe}(\text{CN})_6]^{3-}$) that are not bonded to Y are also involved in hydrogen bonding as acceptors. The effect of this extensive hydrogen bonding is to hold the parallel chains of the polymer in the crystal and impart overall stability to the system. Thus the water molecules play crucial roles not only by satisfying the coordination requirements of the Y atom but also by crosslinking the polymer chains.

Supplementary data

Supplementary data have been deposited with the Cambridge Crystallographic Data Center, CCDC reference number 170488. Copies of this information are available free of charge from: The Director, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44- 1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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