

A New Polymeric Barium-Iron (III) Complex with Chain and Large Ring Structure

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The compound $\{[\text{Ba}_6(\text{Phen})_{12}(\text{CF}_3\text{COO})_6\{\text{Fe}(\text{CN})_6\}_2(\text{H}_2\text{O})_8] \cdot 6 \text{H}_2\text{O}\}_n$ (**1**) (Phen = 1,10-phenanthroline) has been synthesized and structurally characterized. In the crystal structure, the two consecutive Ba centres are bridged through trifluoroacetate groups and also *via* cyano groups of $[\text{Fe}(\text{CN})_6]^{3-}$ and form the zigzag chain resulting the formation of 24-membered ring structure. The Ba-centres are 8-fold coordinated with distorted cubic geometry. Six H_2O molecules per asymmetric unit remain in the structure without any direct interaction with the metal atoms but they act in hydrogen bond formation.

Key words: Barium-Iron Complex, Cyano and Trifluoroacetate Bridge, Chain and Large Ring, Crystal Structure

Introduction

In the past decade, there has been an impressive surge of the chemistry of alkaline earth cations [1–3]. The coordination chemistry of alkaline earth metal cations has received a strong impetus from the view of bioinorganic chemistry [4]. This is due to the search for suitable precursors, high temperature conducting ceramics or materials with valuable electronic properties [5, 6]. With neutral ligands such as NH_3 [7], 2,2'-bipyridyl [8], 1,10-phenanthroline [8], diglyme [9] and methanol [10], barium forms either mononuclear or dinuclear species with anionic polydentate ligands. A number of oligomeric barium complexes have been reported [11–14], but barium complexes of infinite polymeric chains are still very few [14–16]. Recently, there has been growing interest in the formation of polymers using $[\text{Fe}(\text{CN})_6]^{n-}$ and the carboxylate ion, and several complexes have been reported involving transitional metal ions [17–20]. We have already reported some trimeric and polymeric cyano-bridged transition [21–23] and alkaline earth metal [24–26] complexes as well as some carboxylate bridged transition metal complexes [27, 28].

Simultaneous cyano- and carboxylato-bridged heterometallic complexes have not been well documented so far. In this contribution we report the synthesis, IR

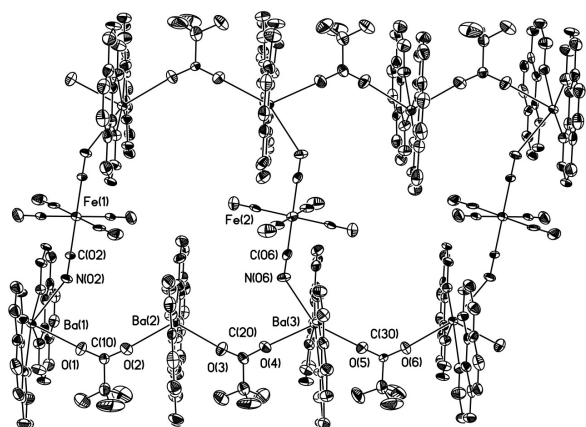
spectrum, thermal analysis and X-ray crystal structure of a chain and 24-membered ring polymeric barium-iron complex $\{[\text{Ba}_6(\text{Phen})_{12}(\text{CF}_3\text{COO})_6\{\text{Fe}(\text{CN})_6\}_2(\text{H}_2\text{O})_8] \cdot 6\text{H}_2\text{O}\}_n$ (**1**) (Phen = 1,10-phenanthroline) containing simultaneously cyano and trifluoroacetate bridges.

Results and Discussion

Complex **1** was synthesised by addition of an aqueous solution of potassium hexacyanoferrate(III) to an aqueous-methanolic solution of barium trifluoroacetate and 1,10-phenanthroline.

IR spectrum

In the IR spectrum of the complex **1**, the $\nu(\text{O-H})$ and $\nu(\text{N-H})$ absorption bands appear at 3050–3420 cm^{-1} [32]. A sharp band at 1622 cm^{-1} is assigned to the $\delta(\text{H-OH})$ mode. Again a band at 413 cm^{-1} may be assigned to $\rho_w(\text{H}_2\text{O})$ and the bands at 844 and 859 cm^{-1} to $\rho_r(\text{H}_2\text{O})$, showing the presence of both coordinated and crystal water molecules [26]. For the $\nu(\text{C}\equiv\text{N})$ mode of $[\text{Fe}(\text{CN})_6]^{3-}$, two bands appear at 2109 and 2022 cm^{-1} for the inter-metallic $\text{C}\equiv\text{N}$ and the terminal $\text{C}\equiv\text{N}$ groups, respectively. The bands at 1520, 1219, 1137, 710, 412 cm^{-1} may be attributed to 1,10-phenanthroline. The IR spectrum con-



tains $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$ bands at 1699 and 1393 cm^{-1} respectively, giving a frequency difference of $(\Delta \nu)$ 306 cm^{-1} , which reflects the bridging nature of the carboxylate group [29].

The thermal study shows that the complex is stable up to $\sim 60^\circ\text{C}$. Beyond this temperature, the compound decomposes and corresponds exactly to the loss of both six uncoordinated and eight coordinated water molecules without any distinguishable step in the temperature range $60\text{--}142^\circ\text{C}$. The mass loss in the temperature range $150\text{--}212^\circ\text{C}$ corresponds to the release of six trifluoroacetate groups followed by the loss of twelve 1,10-phenanthroline molecules in the temperature range $220\text{--}371^\circ\text{C}$. The presence and absence of the ligands are confirmed by recording the IR spectra [32] of the intermediate by isolating them at suitable temperature.

The molecular structure of **1** is illustrated in Fig. 1 and selected structural parameters are collected in Table 1. Crystallographic studies show that the complex has a polymeric large ring structure with a repeating unit $[\text{Ba}_6(\text{Phen})_{12}(\text{CF}_3\text{COO})_6\{\text{Fe}(\text{CN})_6\}_2(\text{H}_2\text{O})_8]$. The Ba centres are bridged by a single trifluoroacetate group and form infinite zig-zag chains extending along the crystallographic *c*-axis. The two zig-zag chains are cross-linked by *trans* CN-groups of the $[\text{Fe}(\text{CN})_6]^{3-}$ ion, which results in the formation of a 24-membered ring structure. The Ba...Ba distances (through a tri-

Empirical formula	C ₁₆₈ H ₁₂₄ Ba ₆ F ₁₈ Fe ₂ N ₃₆ O ₂₆
Formula weight	4340.77
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	<i>P</i> 1
Unit cell dimensions	
<i>a</i> [Å]	14.12(2)
<i>b</i> [Å]	14.47(2)
<i>c</i> [Å]	20.76(2)
α [°]	85.14(10)
β [°]	89.63(9)
γ [°]	85.25(10)
<i>V</i> [Å ³]	4212(9)
<i>Z</i>	1
Density (calculated)	1.711 g/cm ³
Absorption coefficient	1.647 mm ⁻¹
<i>F</i> (000)	2142
Crystal size [mm ³]	0.06 × 0.04 × 0.03
θ Range for data collection	0.98 to 20.68°
Index ranges	−14 ≤ <i>h</i> ≤ 14, −14 ≤ <i>k</i> ≤ 14, 0 ≤ <i>l</i> ≤ 20
Reflections collected	8634
Independent reflections	8634 [<i>R</i> (int) = 0.0000]
Absorption correction	Integration
Max. and min. transmission	0.696 and 0.527
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/ parameters	8634/ 710/ 1284
Goodness-of-fit on <i>F</i> ²	1.076
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0521, <i>wR</i> 2 = 0.1190
<i>R</i> Indices (all data)	<i>R</i> 1 = 0.0786, <i>wR</i> 2 = 0.1317
Largest diff. peak and hole [e.Å ⁻³]	0.873 and −0.490

fluoroacetate link) are almost similar: Ba(1)-Ba(2) = 6.93, Ba(1)-Ba(3) = 6.92, Ba(2)-Ba(3) = 6.95 Å. The Fe-Ba distances are Ba(1)-Fe(1) = 5.77 and Ba(3)-Fe(2) = 5.61 Å linked *via* the -CN- ligands of iron. Both ions are at special positions, inversion centres, so that these distances occur twice at each Fe centre. The standard deviation of all these long distances is about 0.02 Å.

Each of the Ba(1) and Ba(3) centres is coordinated to two Phen ligands, one N from the CN group of the $[\text{Fe}(\text{CN})_6]^{3-}$ anion, two oxygen atoms of two bridging trifluoroacetates and one water molecule. Each Ba centre thus achieves an 8-fold coordination with distorted cubic geometry. This coordination is rather uncommon for Ba-complexes [30]. The Ba(2) centre bears also the same geometry defined by a N_4O_4 donor set *i.e.* the Ba(2) atom is chelated by two Phen ligands, directly bonded to two water molecules and two oxygen atoms of two bridging trifluoroacetates. The $[\text{Fe}(\text{CN})_6]^{3-}$ anion is, as expected, octahedral with only minor deviations from the ideal geometry [31]. The Fe-C and C-N distances lie in the ranges, 1.924(13)–1.965(12) and

The Ba-N(Phen) bond lengths are very close [2.921(9)–2.968(9) Å] and are slightly longer than the Ba-N (CN), Ba-O(bridging) and Ba-O(terminal) bond lengths. In the chain packing feature, due to the marked pseudotranslational symmetry, there are nearly equidistant (6.92 Å) and parallel phenanthroline molecules. In between, *i.e.* at 3.46 Å there is a nearly ideal void for phenanthrolines of a neighboring chain and there is a remarkable overlap of the π -systems as is visible from a projection along the crystallographic c-axis. Correspondingly there is an enormous number of intermolecular C-C and C-N contacts in the range between 3.4 and 3.5 Å (C and N from phenanthrolines). The six additional water molecules per asymmetric unit in the structure remain in the structure without any direct interaction with the metal atoms taking

Synthesis of the complex $\{[Ba_6(Phen)_{12}(CF_3COO)_6\cdot\{Fe(CN)_6\}_2(H_2O)_8]\cdot 6H_2O\}_n$ (**1**)

An aqueous solution (15 ml) of $K_3[Fe(CN)_6]$ (330 mg, 1 mmol) was added to a stirred mixture of 20 ml aqueous solution of $Ba(CF_3COO)_2$ (1090 mg, 3 mmol) and 10 ml ethanolic solution of 1,10-phenanthroline (1180 mg, 4 mmol). On slow evaporation of the solution at room temperature, light yellow crystals of **1** appeared after 3–4 days. Yield: 65%.

Analysis for $C_{168}H_{124}Ba_6F_{18}Fe_2N_{36}O_{26}$ (4340.7): calcd. C 46.44, H 2.85, N 11.60; found C 46.10, H 2.87, N 11.29.

X-ray crystallography

A light yellow air stable crystal of **1** was mounted on a glass fibre. Crystallographic data are given in Table 1. Selected bond lengths and bond angles are listed in Table 2. Intensity data were measured at 293(2) K on a Syntex P2₁ four-circle diffractometer. No significant loss of intensity

was noted for the crystal. Data were corrected for absorption by psi-scans. The structure was solved by direct methods using SHELXTL-PLUS [33] and refined by a full-matrix least-squares procedure based on F^2 using SHELXL-93 [34]. The positions of hydrogen atoms were calculated and constrained such that their coordinates and isotropic displacement parameters were treated as riding on the bound atom.

Supplementary material

Crystallographic data has been deposited at the Cambridge Crystallographic Data Centre with deposition Number 242136. Copies of the information may be obtained free of charge from The director, CCDC, 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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