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CRYSTAL STRUCTURE AND SPECTROSCOPIC STUDY OF THE MIXED HEXACYANOMETALLATE $Cs(N(CH_3)_4?_2Fe(CN)_6$

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ABSTRACT. The structure of the cubic compound hexacyano ferrate III of cesium and tetramethylammonium, has been determined by single crystal x-ray diffraction: a = 12,610(3) Å, space group Fm3m, Z = 4, R = 0,0621 for 109 independent reflections. The structure, which is supported by IR and Mössbauer data, has a perfect ordering of the tetramethylammonium cations in the cubic voids of the Fe CN Cs NC Fe framework.

RESUMEN. Fue determinada la estructura del compuesto cúbico: hexamino ferrato (III) de cesio y tetratilamonio mediante difracción de rayos X simple: a = 12,610(3) Å, grupo espacial Fm3m, Z = 4, R = 0,0621 para 109 reflexiones independientes. Esta estructura, corroborada por los datos suministrados por las espectroscopías IR y Mössbauer, presenta un ordenamiento perfecto de los cationes del tetrametilamonio en las cavidades de la red Fe CN Cs NC Fe.

INTRODUCTION

Hexacyanometallates form double salts with alkali cations (M^I, M^{II}) of the form $M^I M^{II}_2$ [$M^{III}(CN)_6$] where M^{III} is a transition metal cation (Cr, Mn, Fe, Co).(1-3)

Particularly interesting are the structures where tetramethylammonium cations (TMA) are present.(4,5) The cubic compound $Cs(TMA)_2Co(CN)_6$, Fm3m, Z = 4, a = 12,610(3) Å, crystallizes with elpasolite type structure and has perfectly ordered (TMA) cations.(6) The $Cs(TMA)_2Fe(CN)_6$ analog has been refined by Babel (7) in the Fd3c group, Z = 32 with a double value of the cell parameter a = 25,274 Å. This assignment was adopted since in the single crystal data were observed weak (odd) type reflections and all strong reflections were of g g g type (g even), which is common in cases of superstructure. Furthermore the compound was reported with a partially disordered structure.

In this communication we present our results of XRD studies of single crystals of $Cs(TMA)_2Fe(CN)_6$ which reveal a perfectly ordered network, isostructural to the Co derivative.(6)

EXPERIMENTAL

Preparation of complexes

The crystals of $Cs(TMA)_2Fe(CN)_6$ were grown by slow evaporation of solutions of $Cs_3Fe(CN)_6$ and (TMA)Cl in 1 to 3 molar ratios. These crystals were orange, transparent and of octahedral form. Atomic absorption analysis of Cs and Fe carried out in a Phllips PU-9000, confirmed the proposed stechiometry. The absence of water of crystallization was confirmed from IR spectra and d.t.a. analysis.

Physical measurements

The IR spectra of the crystalline samples were run in a UR-20 Carl Zeiss spectrometer using KBr disk and Nujol mull techniques. Precision of the bands is $1 cm^{-1}$ and the resolution is $3 cm^{-1}$. The Mössbauer spectra were obtained in a Wissell spectrometer in constant acceleration mode with a ^{57}Co source at room temperature. The REM computer program was used for numerical fitting of spectra and hyperfine parameter determination (isomer shift δ, quadrupole splitting and line width γ).(8) Sodium nitroprusside was used as reference.

Crystal data

$Cs(TMA)_2Fe(CN)_6$, Fw = 493,159 g/mol. Cubic, a = 12,610(3) Å, V = 2005,1(8) $Å^3$. Space group Fm3m, Z = 4 , D_c = 1,63, D_x = 1,62 g/cm^3.

Crystal dimensions (0,5 x 0,3 x 0,3) mm.

Data collection and processing

The intensities were measured in a URS-50 diffractometer using use of monochromatized Mo-$K\alpha$ radiation. The w scan mode with a speed of 2°/min was employed with rotating crystal and fixed detector configuration.

A total of 119 independent reflections were made in the range up to $(\sin \sigma / \lambda)_{max}$ = 0,70 Å-1. 109 of these reflections with I > 11,96 σ(I) were considered. The intensities were corrected for Lorentz and polarization factors.

Structure analysis and refinement

The structure was solved by using metal-atom coordinates derived from the structure of $Cs(TMA)_2Co(CN)_6$ as starting parameters for least squares refinement. Later on, from successive Fourier synthesis, the carbons and nitrogens of the cyano groups and (TMA) cation were located. The coordinates of non-hydrogen atoms were refined using isotropic and anisotropic approximations to a factor R = 0,062. The temperature factors were refined with the following constraints: Fe, Cs, and N(2) (TMA) atoms isotropic; C(1) and N(1) (CN group) atoms with $U_{11} = U_{22} = U_{33}$, $U_{12} = U_{13} = U_{23} = 0$ and C(2) atom with $U_{11} = U_{22} = U_{33}$, $U_{12} = U_{13} = U_{23}$.(9)

The positions of the H atoms were determined from difference synthesis and were refined with a fixed isotropic temperature parameter U_{11} = 0,08 $Å^2$.

The Program SHELX-76 was used for the calculations. No absorption correction was applied.

RESULTS & DISCUSSIONS

In Table 1 are reported the positions that occupy the different atoms of the compound for both spatial groups in which refinements have been carried out; in the Fm3m group, according to the elpasolite type and in the Fd3c group, according to the disordered structure reported by Babel.(7)

TABLE 1
Comparison of the positions assigned to each atom in the selected spatial group

Elpasolite type structure						Disorder structure			
Group Fm3m. Z = 4						Group Fd3c. Z = 32			
a_o = 12,592 (A)						a_o = 25,274 (Å)			
Cs	b	1/2	1/2	1/2		32b	1/4	1/4	1/4
Fe	a	0	0	0		32c	0	0	0
C(1)N(1)	4e	x	0	0		192h	x	y	z
N(2)*	8c	1/4	1/4	1/4	N(2)*	16a	1/8	1/8	1/8
N(3)*	248d	7/8	1/8	1/8					
C(2)*	232f	x	x	x	C(2)*	192h/2	x	y	z
C(3)*	192h	x	v	z					

* Of the tetramethvlammonium

In our case, nitrogen and carbon atoms of the (TMA), occupy particular positions in Fm3m. These positions are equivalent between themselves from a crystallographic point of view. On the other hand, in Babel's assignment, there are two kinds of (TMA) cations due to the different crystallographic positions of nitrogen (N(2), N(3)). Furthermore, the carbon atom C(2), associated to the N(2) atom of the (TMA), is distributed in statistical form in a general position (192 h/2) implicating the disorder of the (TMA) cations.

In Table 2 and Table 3 are summarized the atomic fractional coordinates, thermal parameters, bond distances and angles of the $Cs(TMA)_2Fe(CN)_6$, refined in the cubic Fm3m group which is isostructural to its analog $Cs(TMA)_2Co(CN)_6$.(6)

TABLE 2
Fractional coordinates (Å) and anisotropic parameters (Å^2).
$T = \exp -2\pi^3 [U_{ij}\ \ H_i\ \ A_i^*\ \ A_j^*]$

	x/a	y/b	z/c	U_{11}	U22	U_{33}	U_{23}	U_{13}	U_{12}
Fe	0	0	0	0,015(2)	U_{11}	$=U_{11}$	0	0	0
Cs	1/2	1/2	1/2	0,030(2)	U_{11}	=U11	0	0	0
C(1)	0,152(2)	0	0	0,05(2)	0,023(8)	$=U_{22}$	0	0	0
N(1)	0,246(2)	0	0	0,02(1)	0,11(2)	$=U_{22}$	0	0	0
N(2)	1/4	1/4	1/4	0,028(4)	U_{11}	=U11	0	0	0
C(2)	0,310(4)	0,310(4)	0,310(4)	0,23(3)	U_{11}	=U11	-0,06(2)	$=U_{23}$	$=U_{23}$
H	0,31	0,031	0,038	0,08					

TABLE 3
Principal bond lengths (Å) and angles (°) in $Cs(TMA)_2Fe(CN)_6$

Bond lengths			Angles
Fe----------C(1)	1,92(2)	N(1)-----C(1)-----Fe	180°
Cs----------N(1)	3,20(2)	C(1)-----Fe-------C(1)	90°
C(1)-------N(1)	1,19(3)	C(2)----N(2)-----C(2)	109,5°
N(2)-------C(2)	1,32(5)		

The larger values of a_o, M-C and C-N (cyano group) distances in the compound (12,610, 1,92, 1,19 Å respectively) with respect to the cobalt analog (12,592, 1,87, 1,18 Å) are logical due to the greater polarizing power Z/r^2 of Co^{III} than Fe^{III}.(10) Both structures (Fe^{III}, Co^{III}) are characterized by the following features:

The CN ligands are located along the crystallographic axes and are collinear with the cesium atoms, forming perfect octahedrons $M(CN)_6$, M = Co, Fe and $Cs(NC)_6$. All (TMA) tetrahedrons are completely ordered in the two complexes and the methyl groups are directed towards the cesium atoms (Figure 1). These groups also have restricted rotation, the CH bonds pointing towards the faces of the cubic network. This position allows the maximum distance between the CH bond protons and the CN ligands.

All these points are novel with respect to the previously reported results, in which there exists a distorted arrangement of the $Fe(CN)_6$ octahedrons which are rotated 7,4° from their crystallographic axis, three quarters of the (TMA) cations are well oriented occupying fixed positions, while the remaining quarter shows orientation disorder.(7)

IR and Mössbauer spectra

The frequencies of the absorption bands of the IR spectra of the crystalline solid are collected in Table 4. The sharpness and symmetry of the degenerate modes of vibration of the CH_3, CN and NC_4 structures are proof of the great symmetry of the crystal. Also, the high value of $\nu\alpha$ of the CH_3 group at 3141 cm^{-1} is strong evidence that there is no attractive (Hydrogen bond type) interaction between these protons and the basic N end of the ligand.(11,12)

In Table 4 are also given the analogous vibrations of $Cs(TMA)_2Co(CN)_6$. The slightly lower value of ν_{CN} in the iron compound is in accordance with the larger CN distance, compared to the cobalt analog.

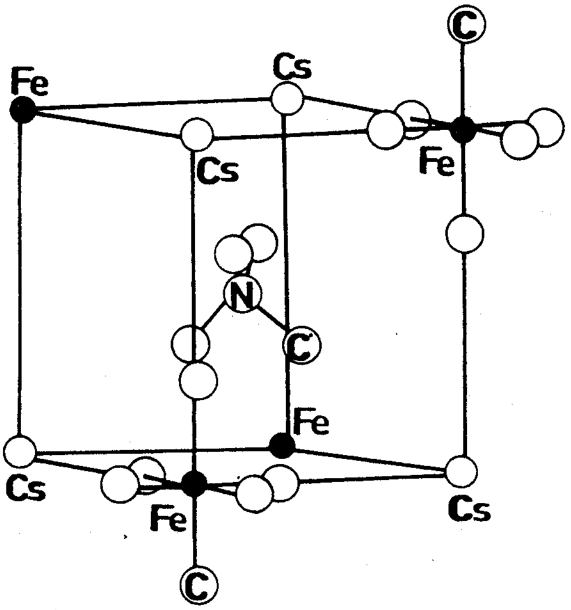

FIGURE 1. An octant of the unit cell of the complexes $Cs(TMA)_2M^{III}(CN)_6$, M^{III} = Co, Fe. The methyl groups are directed towards the cesium atoms.

TABLE 4
IR vibrations of $Cs(TMA)_2Fe(CN)_6$ and $Cs(TMA)_2Co(CN)_6$*
(in cm^{-1})

Vibrational Assignment(**)		Fe^{III}	Co^{III}
ν_{14} (F_2)	NC_4 ass. stretch	956	954
ν_{15} (F_2)	CH_3 rock	1 293	1 293
ν_{16} (F_2)	NCH ass. def.	1 419	1 420
ν_7 (E)	NCH ass. def.	1 448	1 448
ν_{17} (F_2)	NCH ass. def.	1 485	1 486
$F_{1\mu}$	CN ass. stretch	2 104	2 113
ν_8 (E); ν_{19} (E_2)	CN ass. stretch	3 041	3 041

* Data from reference (5)

** Assignment of TMA vibrations according to Kabisch (13)

The vibration of the (TMA) cations are equal in the iron and cobalt complexes due to the similar environment of the CH_3 groups near the cesium cation.(13,14)

In Table 5 we collected the Mössbauer parameters of $Cs(TMA)_2Fe(CN)_6$. The spectra is fitted perfectly to a doublet with narrow line characteristic of ferricyanides with all the anions in equivalent positions. If there were two types of (TMA) cations, the iron signal would present itself as two doublets or at least as a broad doublet.(12) The Mössbauer evidence is therefore in favor of the structure obtained by x-ray diffraction analysis.

TABLE 5
Mössbauer parameters of $Cs(TMA)_2Fe(CN)_6$ Internal reference: Sodium nitroprusside

Isomer shift cm/s	Quadrupole splitting mm/s	Line width mm/s
0,126 ± 10,001	0,241 ± 10,002	0,306 ± 10,005

CONCLUSIONS

IR, Mössbauer and XRD studies are in favor of a completely ordered cubic framework for $Cs(TMA)_2Fe(CN)_6$, isostructural to that of the cobalt analog.

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