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Y[Fe_{1-x}Co_x(CN)₆]·4H₂O ($0 \le x \le 1$) solid solutions: Synthesis, crystal structure, thermal decomposition and spectroscopic and magnetic properties

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ABSTRACT

The series of solid solutions $Y[Fe_{1-x}Co_x(CN)_6]$ - $4H_2O$ ($0 \le x \le 1$) were prepared and characterized by means of powder X-ray diffraction (PXRD), Infrared and Mössbauer spectroscopy and magnetic measurements. The thermal decomposition process has been followed by thermogravimetric and differential thermal analysis (TGA-DTA). The crystal structure of the complexes was refined by means of Rietveld analysis. The $Y[Fe_{1-x}Co_x(CN)_6]$ - $4H_2O$ complexes crystallize in the orthorhombic crystal system, space group *Cmcm*. The Y^{3+} ion is eight-coordinated forming a bicapped distorted trigonal prism YN_6O_2 . The Fe³⁺ and Co³⁺ ions are six-coordinated in the form of an irregular octahedra (Fe,Co)C₆ group and cyanide linkages between YN_6O_2 and (Fe,Co)C₆ groups build an infinite polymeric array.

The Mössbauer spectra of all solid solutions $Y[Fe_{1-x}Co_x(CN)_6]$ - $4H_2O$ present quadrupolar splittings with negative isomer shifts values due to the existence of a strong π back-bonding effect from the Fe³⁺ ion towards the CN ligands.

All compounds follow the Curie–Weiss law showing anti-ferromagnetic interactions at very low temperatures.

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1. Introduction

The rare-earth hexacyanometalates (III) hydrates, $Ln[M(CN)_6]$ - nH_2O (Ln = lanthanide; M = transition metal; n = 4, 5) are precursors for the synthesis of perovskite-type oxides which have a variety of applications such as chemical sensors, catalysts [1–4], colossal magnetoresistant materials [5] and multiferroism [6]. Traditionally, the ceramic method has been employed to synthesize mixed oxides. However, this method usually needs very high temperatures to reach chemical homogeneity, producing very low surface areas and oxygen deficient materials. The thermal decomposition of heteronuclear complexes was proposed by Gallaguer in 1968 to prepare LaFeO₃ and LaCoO₃ from hexacyanometal-lates as precursors [7]. The oxides obtained by this method were formed at shorter annealing times and lower temperatures than ceramic methods. In addition, the use of soft chemical routes can yield homogeneous phases with small grain size [7–15].

The crystal structure of hexacyanometallates consists of alternating cyanide-bridged MC_6 and LnN_6O_y (y = 2, 3) polyhedra in an orthorhombic or hexagonal lattice, depending on the degree of hydration at the lanthanide centers [8,16]. The CN ligand has the ability to serve as bridge group between neighboring metal centers, removing electron density from the metal linked at its C end, through a π back-bonding interaction, to increase the charge density on the N end that is the coordination site for the other metal. This leads to the overlapping between the electron clouds of neighboring metal centers and to their spin coupling and, thereby, a magnetic ordering is established. This supports the role of hexacyanometallates as prototype of molecular magnets [17].

In the present article we report the synthesis, structural, spectroscopic and magnetic characterization of solid solutions $Y[Fe_{1-x}Co_x(CN)_6]\cdot 4H_2O$. The crystal structure refinement of $Y[Fe_{1-x}Co_x(CN)_6]\cdot 4H_2O$ complexes were performed by means of Rietveld analysis using standard powder X-ray diffraction (PXRD). These measurements were complemented by thermogravimetric and differential thermal analysis, Infrared (IR) and Mössbauer spectroscopy. The magnetic properties of $Y[Fe_{1-x}Co_x(CN)_6]\cdot 4H_2O$ have also been investigated.

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2. Experimental

2.1. Synthesis

The polycrystalline samples of the series $Y[Fe_{1-x}Co_x(CN)_6] \cdot nH_2O$ were prepared by the co-precipitation method, mixing aqueous solutions of equimolar amounts of $K_3[Fe(CN)_6]$, $K_3[Co(CN)_6]$ and $Y(NO_3)_3 \cdot 6H_2O$ under continuous stirring at 60 °C for 2 h. $Y(NO_3)_3 \cdot 6H_2O$ was prepared from the evaporation of a solution of concentrated HNO₃ and Y₂O₃. The color of the precipitates changes from orange to white as we move from Y[Fe(CN)₆]·4H₂O to $Y[Co(CN)_6]$ ·4H₂O in the series. The resulting precipitates were filtered, washed many times with distilled water and ethanol, and finally stored in the dark in a dry box with silica gel.

2.2. Characterization

Thermogravimetry (TGA) and differential thermal analysis (DTA) measurements were performed in a Shimadzu TGA/DTA-50 in the temperature range from 20 to 800 °C at a heating rate of 5°/min under flowing air.

Infrared spectra (in the region of $4000-400 \text{ cm}^{-1}$) were recorded at room temperature (RT) on a FTIR Perkin Elmer 1600 spectrophotometer in the transmission mode using KBr pellets.

Mössbauer spectroscopy (MS) characterizations were performed at room temperature (RT) in transmission geometry using a conventional Mössbauer spectrometer in constant acceleration mode. γ -Rays were provided by a ⁵⁷Co (Rh) source with an initial activity of 50 mCi. The velocity scale was calibrated by using a standard iron foil absorber. The Mössbauer spectra were analyzed with a non-linear least-square routine with Lorentzian line shapes. Hyperfine magnetic field distributions were occasionally traced by means of histograms with a fixed linewidth (Γ). All isomer shift (IS) data given in this paper are relative to α -Fe.

PXRD patterns were obtained at RT in a PANalyticals X'Pert Pro diffractometer with Cu K α radiation λ = 1.5418 Å, between 5° and 120° in 2θ , in steps of 0.02° and step time of 10 s. The crystal structure refinements were performed by means of the Rietveld method [18] using the FULLPROF program [19] in the space group Cmcm using as initial model the structure of Er[Fe(CN)₆]·4H₂O [20]. A pseudo-Voigt function convoluted with an axial divergence asymmetry function [21] was chosen to generate the peak shapes. The following parameters were refined: zero-point, scale factor, pseudo-Voigt parameters of the peak shape full-width at half-maximum, atomic positions and cell parameters.

The magnetic measurements in the temperature range 5–300 K were performed with a Quantum Design MPMS-5S superconducting quantum interference device (SQUID). The Magnetization values were measured under zero field-cooled (ZFC) and field-cooled (FC) conditions at an applied magnetic field of 5 T.

The size and morphology of the particles were determined by scanning electron microscopy (SEM) in a ZEIS SUPRA-55 VP microscope and the chemical composition of the powder was determined by Energy dispersive spectroscopy (EDS) with an Oxford INCA PentaFet X3 energy dispersive X-ray analyzer.

3. Results and discussion

3.1. Crystal structures refinement

The PXRD patterns of all the complexes are very similar (Fig. 1a), as expected for isostructural compounds. Fig. 1b shows the refined PXRD pattern for one representative of the series, Y[Fe_{0.5}Co_{0.5}-(CN)₆]·4H₂O. The refined PXRD patterns of the other complexes are shown in Supplementary information. Crystallographic



parameters and discrepancy factors for Y[Fe_{0.5}Co_{0.5}(CN)₆]·4H₂O after Rietveld refinement are summarized in Table 1. The series of complexes $Y[Fe_{1-x}Cox(CN)_6] \cdot 4H_2O$ crystallizes in the orthorhombic crystal system, space group Cmcm. The cell parameters obtained after the refinement process are summarized in Table 2.

The variation of the cell volume and one of lattice parameter (a) with x in the complexes is shown in Fig. 1b (inset). The lattice parameters and cell volume decreases linearly with the Co3+ doping, following the Vegard's law for ideal solid solutions as shown in Table 2. These results are in agreement with Traversa et al. who have prepared and studied the solid solutions series $La[Fe_{1-x}Co_{x}(CN)_{6}] \cdot nH_{2}O$ [22].

Fig. 2 shows the coordination environment for Y and Fe atoms. In the crystal structure of tetrahydrate complexes Y[Fe_{1-x-}

Table 1

Crystallographic parameters and discrepancy factors for Y[Fe_{0.5}Co_{0.5}(CN)₆]·4H₂O after Rietveld refinement with PXRD data obtained at RT.

Atom	Wyckoff site	x	У	Ζ
Y	4c	0	0.3249(1)	0.25
Fe (Co)	4a	0	0	0
C1	16h	0.3185(9)	0.4541(7)	0.0940(5)
C2	8f	0	0.1294(9)	0.0675(1)
N1	16h	0.2041(7)	0.4324(5)	0.1323(5)
N2	8f	0	0.2105(7)	0.0806(7)
01	8g	0.2911(8)	0.2088(5)	0.25
02	8f	0	0.6578(6)	0.1022(4)

Discrepancy factors: $R_{wp} = 20.8$, $R_{exp} = 5.05$, $R_p = 16.6$, $R_{Bragg} = 11.4$.

(a)



Table 2

Cell parameters of the series of complexes $Y[Fe_{1-x}Co_x(CN)_6]\cdot 4H_2O$ obtained after Rietveld refinement.

Compounds	a (Å)	b (Å)	c (Å)	$V(Å^3)$
Y[Fe(CN) ₆]·4H ₂ O	7.3421(1)	12.7886(1)	13.6033(1)	1277.28(2)
Y[Fe _{0.7} Co _{0.3} (CN) ₆]·4H ₂ O	7.3265(1)	12.7469(2)	13.5771(2)	1267.97(3)
Y[Fe _{0.5} Co _{0.5} (CN) ₆]·4H ₂ O	7.3172(1)	12.7231(2)	13.5620(2)	1262.58(3)
$Y[Fe_{0.3}Co_{0.7}(CN)_6] \cdot 4H_2O$	7.3048(1)	12.6941(2)	13.5406(1)	1255.59(3)
Y[Co(CN) ₆]·4H ₂ O	7.2947(1)	12.6654(2)	13.5224(2)	1249.34(3)



Fig. 2. Coordination environment for Y³⁺ and Fe³⁺ or Co³⁺ ions in Y[Fe_{1-x-}Co_x(CN)₆].4H₂O complexes. Y³⁺ ions are eight-coordinated to six N atoms from CN ligands and two O from coordinated water molecules.

 $Co_x(CN)_6$]·4H₂O, Y³⁺ ions are eight coordinated to four N(1), two N(2) and two O(1) forming a bicapped distorted trigonal prism (YN₆O₂). This type of geometry is very common for many complexes with Y³⁺ or Ln³⁺ as counter-ions. Y³⁺ is located in the Wyck-off site 4c of the space group *Cmcm* with a site symmetry *m2m*, consistent with the square antiprism 8-fold coordination. Fe³⁺ and Co³⁺ are coordinated to four C(1) and two C(2) with the usual irregular octahedral coordination (Fe,CoC₆). Bicapped trigonal prisms YN₆O₂ and irregular octahedra (Fe,Co)C₆ are bridged through cyano groups. There are two uncoordinated water molecules occupying zeolitic holes in the structure. The two O(2) are hydrogen bonded to the coordinated water molecules.

In pentahydrate complexes of the type $Ln[M(CN)_6]$ ·5H₂O, Ln = Nd, Pr or La), Ln^{3+} ion is nine-coordinated in the form of LnN_6O_3 group forming a tricapped trigonal prism. M³⁺ is six-coordinated in the form of an octahedral MC₆ group and cyanide linkages between LnN₆O₃ and MC₆ groups build an infinite polymeric array. Pentahydrate complexes formed by La³⁺ and Nd³⁺ are very unstable and convert to the stable tetrahydrate by losing one water molecule [23,24]. It is easy to understand the change from pentahydrates to tetrahydrates. As the ionic radii of Ln³⁺ decrease, one of the coordinated water molecules is lost to form the bicapped distorted trigonal prism, since it gets more stable to accommodate eight ligands instead of 9 in the smaller lanthanides. This bicapped trigonal prism is distorted as a consequence of the imbalance in repulsions produced by the absence of one of the oxygens. In the samples of our series we have not observed the formation of pentahydrate $Y[Fe_{1-y_2}]$ $Co_x(CN)_6$]·5H₂O indicating that the tetrahydrate is very stable due to the fact that Y^{3+} has the correct size for an 8-fold coordination.

3.2. IR spectroscopy

IR spectra of the five studied complexes Y[Fe_{1-x}Co_x(CN)₆]·4H₂O are very similar, with a well-defined set of v_{CN} , δ_{MCN} and v_{MC}

absorption bands characteristic of hexacyanometallate complexes. Fig. 3 shows the IR spectra of the series of solid solutions $Y[Fe_{1-x-Co_x}(CN)_6]$ -4H₂O in KBr pellets.

3.2.1. C≡N stretching bands

The IR spectra of the complexes $Y[Fe_{1-x}Co_x(CN)_6]\cdot 4H_2O$ show two strong bands, in the frequency range of 2154–2138 cm⁻¹, due to ${}^{12}C^{14}N$ stretching of the bridged $Y-N\equiv C-(Fe,Co)$ system and corresponds to the antisymmetric and symmetric v(CN)stretching vibrations. These bands are accompanied by four weak isotopic bands at lower frequencies due to the presence of ${}^{13}C$ and ${}^{15}N$ in their relative natural abundance [25,26]. The bands corresponding to the stretching of the group ${}^{13}C^{15}N$ are not observed because the relative natural abundance of the ${}^{13}C^{15}N$ group is 0.004%.

3.2.2. Water bands

The O—H stretching absorption bands (symmetrical and asymmetrical vibrations) of coordinated water are observed as two narrow bands in the frequency range of 3600–3500 cm⁻¹. The vibrations of uncoordinated water are very broad and are located at lower frequency, at about 3400–3200 cm⁻¹.

The bending mode of water molecules appears as a doublet $(1690-1600 \text{ cm}^{-1})$ due to the presence of different types of water molecules. The band located at higher frequencies is attributed to water molecules with a strong interaction with the Y³⁺ (coordinated water) and the band at lower frequencies corresponds to the weakly bonded water (uncoordinated water).

The librational modes of coordinated water, which usually present low intensity and are overlapped with other modes, are difficult to identify. The rocking and wagging vibration modes appear in the region 900–700 cm⁻¹. These bands are characteristic of coordinated water molecules [26].

3.2.3. $M-C \equiv N$ and M-C bands

The $\delta(M-C=N)$ and $\nu(M-C)$ vibrations are observed in the range 600–400 cm⁻¹, in the expected frequency values for hexacy-anometallates (III) [27].

3.3. Mössbauer spectra

In order to study the spin states of Fe ions in these compounds, Mössbauer spectra at RT were recorded (see Fig. 4). The values of isomer shift (IS), quadrupole splitting (QS), linewidth (Γ) and relative area are listed in Table 3. The values of IS correspond to the



Fig. 3. IR spectra for the series of complexes $Y[Fe_{1-x}Co_x(CN)_6] \cdot 4H_2O$.



Fig. 4. Mössbauer spectra at room temperature of $Y[Fe_{1-x}Co_x(CN)_6] \cdot 4H_2O$ for x = 0, 0.3, 0.5 and 0.7.

Table 3Mössbauer parameters for $Y[Fe_{1-x}Co_x(CN)_6] \cdot 4H_2O$.

Compounds	Doublet			
	IS (mm/s)*	QS (mm/s)	Γ (mm/s)	Área (%)
Y[Fe(CN) ₆]·4H ₂ O	-0.17	0.82	0.28	100
Y[Fe _{0.7} Co _{0.3} (CN) ₆]·4H ₂ O	-0.17	0.80	0.28	100
Y[Fe _{0.5} Co _{0.5} (CN) ₆]·4H ₂ O	-0.18	0.81	0.29	100
Y[Fe _{0.3} Co _{0.7} (CN) ₆]·4H ₂ O	-0.18	0.82	0.27	100

 * The isomer shift (IS) values are relative to $\alpha\text{-Fe}$ at room temperature. QS, quadrupole splitting.

low-spin state of Fe^{3+} ions (*S* = 1/2). Similar values were found for $Fe[Fe(CN)_6] \cdot 4H_2O$ and $Cu_{1.5}[Fe(CN)_6] \cdot 6H_2O$ [28,29].

In hexacyanoferrates, the Fe atom coordinated to the C ends of the CN groups is always found in a low-spin configuration, and their Mössbauer spectra are single lines for ferrocyanides and a quadrupole splitting doublet for ferricyanides as shown in Fig. 4. The quadrupole splittings observed in the Mössbauer spectra of solid solutions $Y[Fe_{1-x}Co_x(CN)_6]$ - $4H_2O$ have low isomer shift values (Table 3) due to the existence of a strong π back-bonding effect from the iron atom toward the CN ligands. This effect reduces the number of 3d electrons on the metal and their shielding of the *s* electron density at the iron nucleus. The π back-bonding effect is more pronounced in ferrocyanides than in ferricyanides due to the higher 3d electrons availability in ferrocyanides. From this fact, the isomer shift values in ferricyanides are very low (in some cases negative). The quadrupole splitting in these ferricyanides is mainly related to the existence of an unpaired electron in their t_{2g} orbitals, which creates an electric field gradient around the iron nucleus. This unpaired electron is also responsible for the magnetic order at low temperature in ferricyanides (see below) [30–32].

3.4. Magnetic properties

We know that the magnetic interactions in hexacyanometallates are due to superexchange interactions via CN bridges. These interactions may be positive (ferromagnetic) or negative (anti-ferromagnetic) depending upon the symmetries of the magnetic orbitals involved. Superexchange interactions between orthogonal orbitals (for example, t_{2g} and e_g) favor a ferromagnetic ordering whereas superexchange interactions between orbitals of the same symmetry, like t_{2g} and t_{2g} , or e_g and e_g , are anti-ferromagnetic [29,30]. Yttrium ferricyanide tetrahydrate is an example of antiferromagnetic behavior because in this complex, the superexchange is established through the overlapping of identical t_{2g}^5 orbitals from iron atoms, and its anti-ferromagnetic nature is a result of the Pauli Exclusion Principle [26,31].

Fig. 5 shows the temperature dependence of the magnetization under both ZFC (zero field cooling) and FC (field cooling) conditions for $Y[Fe_{1-x}Co_x(CN)_6]$ ·4H₂O complexes. No difference between both curves is observed, indicating the absence of any long range magnetic ordering.



Fig. 5. Temperature dependence of magnetization for $Y[Fe_{1-x}Co_x(CN)_6]$ - $4H_2O$. Inset: temperature dependence of the inverse magnetic susceptibility for $Y[Fe_{0.5}Co_{0.5}(CN)_6]$ - $4H_2O$.

Table 4Values of Curie constants, Curie-Weiss temperatures and effective magneticmoments for $Y[Fe_{1-x}Co_x(CN)_6]$ -4H2O.

Compounds	C (emu K/g Oe)	θ (K)	$\mu_{\mathrm{eff}}\left(\mu_{\mathrm{B}} ight)$
Y[Fe(CN) ₆]·4H ₂ O Y[Fe _{0.7} Co _{0.3} (CN) ₆]·4H ₂ O	$\begin{array}{c} 1.649 \times 10^{-3} \\ 1.019 \times 10^{-3} \end{array}$	-14.65 -15.45	2.217 2.087
Y[Fe _{0.5} Co _{0.5} (CN) ₆]·4H ₂ O Y[Fe _{0.3} Co _{0.7} (CN) ₆]·4H ₂ O	$\begin{array}{l} 6.270 \times 10^{-4} \\ 2.950 \times 10^{-4} \end{array}$	$-8.750 \\ -1.074$	1.939 1.717

From a Curie–Weiss law, $\chi^{-1} = (T - \theta)/C$, fitting (in the temperature range of 5–300 K) of the reciprocal mass susceptibility versus temperature curve (inset Fig. 5), the values for the Curie constant (*C*) and for Curie–Weiss temperature (θ) in Y[Fe_{1–x}Co_x(CN)₆]·4H₂O complexes were estimated. Table 4 shows the Curie constant, Curie–Weiss temperature and effective magnetic moment (μ_{eff}) for all the compounds of the series. For x = 0-0.7 the negative values of θ indicate anti-ferromagnetic interactions in these compounds at very low temperatures. The relatively strong magnetic interaction between distant Fe³⁺ ions in Y[Fe_{1–x}Co_x(CN)₆]·4H₂O solid solutions is possible due to the charge delocalization through the CN bridges in the –Fe–C \equiv N–Y–N \equiv C–Fe– path. The obtained effective magnetic moments for the complexes with x = 0, 0.3, 0.5 are a little higher than the spin only value $\mu_{eff} = 1.73 \ \mu_B$ expected for Fe³⁺ in the low-spin state. It is attributed to a small orbital contribution to the magnetic moment due to the low-spin configuration (t_{2g}^5) , S = 1/2 of Fe³⁺ [33]. The effective magnetic moment and the Curie–Weiss temperature of the series of complexes decrease with the increasing of Co³⁺ content due to the dilution of a paramagnetic ion (Fe³⁺, low spin) with a diamagnetic one (Co³⁺, low spin).

3.5. Thermal decomposition

The thermal behavior of the series of solid solutions was studied by TG and DT analysis. Fig. 6 shows TGA and DTA curves for the thermal decomposition of Y[Fe_{0.5}Co_{0.5}(CN)₆]·4H₂O in air. The first step ends at 180 °C with a mass loss of 14.58% and it corresponds to the loss of three water molecules. The second step ends at 265 °C with a mass loss of 4.86% and it is attributed to the loss of one water molecule. These processes suggest that there are two different kinds of water molecules, as was deduced from the crystal structure and FTIR analysis. The third decomposition step occurs in the temperature range 265-650 °C and is attributed to the elimination and oxidation (exothermic combustion) of the CN groups with the simultaneous formation of mixed oxide $YFe_0 = Co_0 = O_3$ with perovskite-type structure. The mass losses expected in each of the decomposition steps are in good agreement with those calculated from TG curve. These results are summarized in Table 5. The total mass loss from RT to 650 °C is 48.33%. It is in agreement with the theoretical mass loss (48.08%) for the formation of YFe_{0.5}Co_{0.5}O₃ from the complex.

The sequence of decomposition steps could be expressed as:

$$Y[Fe_{0.5}Co_{0.5}(CN)_6] \cdot 4H_2O_{(s)} \rightarrow Y[Fe_{0.5}Co_{0.5}(CN)_6] \cdot H_2O_{(s)} + 3H_2O_{(g)}$$
(1)

$$Y[Fe_{0.5}Co_{0.5}(CN)_6] \cdot H_2O_{(s)} \to Y[Fe_{0.5}Co_{0.5}(CN)_6]_{(s)} + H_2O_{(g)} \eqno(2)$$

$$Y[Fe_{0.5}Co_{0.5}(CN)_6]_{(s)} + \frac{27}{2}O_{2(g)} \rightarrow YFe_{0.5}Co_{0.5}O_{3(s)} + 6CO_{2(g)} + 6NO_{2(g)}$$
(3)

The mechanisms of the thermal decomposition of the $Y[Fe_{1-x}-Co_x(CN)_6]\cdot 4H_2O$ solid solutions are very similar and no difference were observed with the variation of the Co³⁺ content in the complexes.



Fig. 6. TGA and DTA curves for Y[Fe_{0.5}Co_{0.5}(CN)₆]·4H₂O in air.

Table 5 Steps for the thermal decomposition of Y[Fe_{0.5}Co_{0.5}(CN)₆]·4H₂O and % of mass loss.

Steps	Temperature range (°C)	Observed mass loss (%)	Theoretical mass loss (%)
1	25-180	14.58	14.42
2	180-265	4.86	4.81
3	265-650	28.89	28.85
Total mass	s loss (%)	48.33	48.08



Fig. 7. SEM photograph of $Y[Fe_{0.5}Co_{0.5}(CN)_6] \cdot 4H_2O$.

The DTA curve shows two endothermic peaks, at 141 and 185 °C, both due to dehydration process. The third exothermic peak located at 377 °C corresponds to the elimination and oxidation (combustion) of the cyanide groups.

3.6. Scanning electron microscopy (SEM)

Fig. 7 shows the SEM photograph of the complex $Y[Fe_{0.5}]$ Co_{0.5}(CN)₆]·4H₂O. This powder consists of large well-defined crystals with different shapes and sharp edges up to 3 µm in size.

4. Conclusions

The series of solid solutions $Y[Fe_{1-x}Co_x(CN)_6] \cdot 4H_2O$ was synthesized for the first time and their crystal structures were refined with the Rietveld method from PXRD data. All the complexes crystallize in the orthorhombic crystal system, space group Cmcm. In these structures, Fe³⁺ and Co³⁺ ions are octahedrally coordinated to six cyano groups and the Y³⁺ ion is eight-coordinated to six N atoms from CN ligands and two O from coordinated water molecules. Cell parameters and cell volume change linearly with x in $Y[Fe_{1-x}Co_x(CN)_6] \cdot 4H_2O.$

The Mössbauer spectra of the series of complexes are quadrupole doublets corresponding to low-spin Fe^{3+} (S = 1/2). Negative isomer shifts are observed as a consequence of a strong π backbonding effect from the iron atom toward the CN ligands that reduces the number of 3d electrons on the metal and their shielding of the *s* electron density at the iron nucleus.

According to the magnetic measurements, complexes with x = 0, 0.3, 0.5 and 0.7 show anti-ferromagnetic interactions ($\theta < 0$) at low temperatures. The values of effective magnetic moment are a little higher than the spin only value μ_{eff} = 1.73 μ_{B} expected for Fe³⁺ in the LS state. This is attributed to a small orbital contribution to the magnetic moment due to the LS configuration $(t_{2\alpha}^5)$, S = 1/2 of Fe³⁺. Weiss temperatures and μ_{eff} decrease with increasing Co³⁺ content in the complexes due to the dilution of a paramagnetic ion (Fe^{3+} , LS) with a diamagnetic one (Co^{3+} , LS).

 $Y[Fe_{1-x}Co_x(CN)_6]$ ·4H₂O decompose in three steps. The first one corresponds to the elimination of three water molecules (noncoordinated water), the second one to the loss of the remaining water molecule strongly bounded (coordinated water), the third one to the cyanide elimination and oxidation to give $YFe_{1-x}Co_xO_3$ oxides with perovskite structure as final products.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2012.02.023.

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