

Cs sorption by “soluble” and “insoluble” iron hexacyanocobaltates probed by Mössbauer spectroscopy

A. I. Rykov · J. Wang · T. Zhang · K. Nomura

Published online: 29 January 2013
© Springer Science+Business Media Dordrecht 2013

Abstract Efficient sorbents of radiocesium are essential for purifying the radioactive contaminated wastewaters and soils. Cyanometallates analogous of Prussian Blue possess a very high sorption capacity and selectivity for Cs. Aiming to explore the mechanisms of Cs fixation in cobaltcyanides our study focuses on the Mössbauer spectra in cesium-embedding ferrous hexacyanocobaltates prepared by three different routes: the precipitation of $\text{CsFe}[\text{Co}(\text{CN})_6]$, ion exchange of K for Cs in “soluble” $\text{KFe}[\text{Cs}(\text{CN})_6]$ and Cs intercalation into “insoluble” porous $\text{Fe}[\text{Cs}(\text{CN})_6]_{2/3}$. The Cs capture is accompanied by removal of anionic vacancies and densifying the porous framework that is seen in Mössbauer spectra through increasing the population of the Fe^{2+} species enclosed into FeN_6 octahedra. The number of water molecules coordinating to iron, on average, decreases. This leads to reduction of the asymmetry in distribution of the Fe^{2+} valence electron over *d*-orbitals and reduces also the valence term of electric field gradient. An exception to this rule applies where recrystallization is prevented during the Cs intrusion into existing dense phase at low temperature.

Keywords Prussian Blue · Hexacyanocobaltate · Mössbauer · Cesium sorption

A. I. Rykov · J. Wang (✉) · T. Zhang
Mössbauer Effect Data Center, Dalian Institute of Chemical Physics,
Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China
e-mail: wangjh@dicp.ac.cn

K. Nomura
Graduate School of Engineering, The University of Tokyo,
Hongo 7-3-1, Bunkyo-ku, Tokyo 113-8656, Japan

1 Introduction

So-called “soluble” and “insoluble” Prussian Blues are the alkali-free and alkali-filled hexacyanometallate metal-organic polymer frameworks, described by structure models of Keggin [1] and Ludi [2], respectively. Both of them are insoluble, whereas naming them “soluble” and “insoluble” refers to a difference of their peptization property rather than solubility. In hexacyanocobaltate (III) family, Mössbauer spectra of the “insoluble” PB analogues $\text{Fe}[\text{Co}(\text{CN})_6]_{2/3} \cdot x\text{H}_2\text{O}$ are well documented [3, 4]. However, no ferrous hexacyanocobaltates(III), enclosing alkaline ions, were characterized so far. We report the synthesis and Mössbauer spectra in the “soluble” PB analogues, containing K, Rb and Cs ions. Valence electron distribution and valence term of electric field gradient (EFG) reveal the multiple orbital ground states of Fe^{2+} ions which compete with each other bringing into being the interplay of multiple quadrupole doublets susceptible to insertion and withdrawal of alkali ions. Cs insertion normally reduces the asymmetry of the valence electron distribution, except when recrystallization is prevented. We compare this complex behaviour with the sorption response of ferric hexacyanoferrate where the valence term of EFG is absent.

2 Experimental

The “soluble” hexacyanocobaltates were prepared from the solutions of ferrous chloride tetrahydrate and $\text{K}_3[\text{Co}(\text{CN})_6]$ in excess of the latter. Oppositely, when the excess of FeCl_2 was allowed the precipitation of the potassium-free “insoluble” phase was observed.

In the X-ray diffraction patterns (Fig. 1) the intensity ratio of the reflections 200 and 220 changes when K, Rb or Cs ions enter into the structure. For Cs ion this ratio changes more than 10 times.

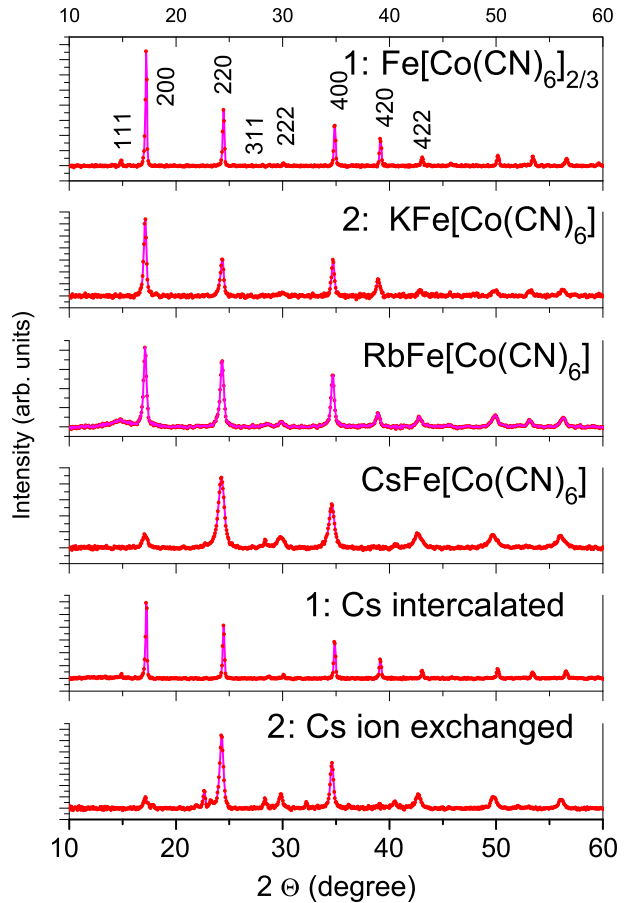
The X-ray patterns showed no significant changes for the “insoluble” phase stirred in 0.1 M solution of CsCl for 24 h. In contrast, in the “soluble” phase, the Rietveld analysis suggests that the K^+ ions were replaced with Cs^+ .

Mössbauer spectra were measured with a Topologic 500A spectrometer. Isomer shifts are reported relative to $\alpha\text{-Fe}$ at room temperature.

3 Results and discussion

The archetypal “insoluble” Prussian Blue $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot 14\text{H}_2\text{O}$ shows a drop of quadrupole splitting upon the insertion of an alkali ion (Fig. 2). Here, the Mössbauer spectra are sensitive to the changes in the environment of ferric ions outside the complex anion $[\text{Fe}(\text{CN})_6]^{3-}$. Note that the valence term of EFG is non-existing for the high-spin Fe^{3+} species located in these sites. The octahedral environment of high-spin Fe^{3+} in $\text{CsFe}[\text{Fe}(\text{CN})_6] \cdot \text{H}_2\text{O}$ is more symmetric than that in $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot 14\text{H}_2\text{O}$. The reduction the lattice term of EFG upon insertion of Cs is consistent with a better symmetry of the FeN_6 octahedral environment in $\text{CsFe}[\text{Fe}(\text{CN})_6] \cdot \text{H}_2\text{O}$. The “soluble” $\text{CsFe}[\text{Fe}(\text{CN})_6] \cdot \text{H}_2\text{O}$ contains only zeolitic water that occupies the same interstitials as Cs does. On the other hand, the

Fig. 1 Cu $K\alpha$ X-ray diffraction patterns of the as-prepared and ion-exchanged ferrous hexacyanocobaltates (III)



“insoluble” $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot 14\text{H}_2\text{O}$ contains also the crystallization water [5] that molecules enter the first coordination sphere of Fe^{3+} and reduce the symmetry of the Fe^{3+} environment.

More complicated situation arises when the cations occupying the cationic nodes of the PB framework are not ferric but ferrous. In high-spin Fe^{2+} , the valence contribution of the EFG is predominant and exceeds the lattice EFG term by an order of magnitude [6].

In Fig. 3, we compare the Mössbauer spectra of the Cs-containing products synthesized by three different routes, which can be conventionally named as insertion, exchange and precipitation. In the insertion and exchange routes, the hexacyanocobaltates $\text{Fe}[\text{Co}(\text{CN})_6]_{2/3} \cdot x\text{H}_2\text{O}$ and $\text{KFe}[\text{Co}(\text{CN})_6] \cdot x\text{H}_2\text{O}$ were stirred in a 0.1 M solution of CsCl for 24 h at room temperature. The insertion process has resulted in composition of $\text{Cs}_{0.1}\text{Fe}[\text{Co}(\text{CN})_6]_{0.7} \cdot x\text{H}_2\text{O}$. Accordingly, the Mössbauer spectra are almost unchanged. On the other hand, the ion exchange of K for Cs in $\text{KFe}[\text{Co}(\text{CN})_6] \cdot x\text{H}_2\text{O}$ carried out in the same conditions has showed much higher rate and resulted in composition $\text{CsFe}[\text{Co}(\text{CN})_6] \cdot x\text{H}_2\text{O}$. Similar compound was obtained by the precipitation method, Fig. 3 (4). Despite of similarity of the

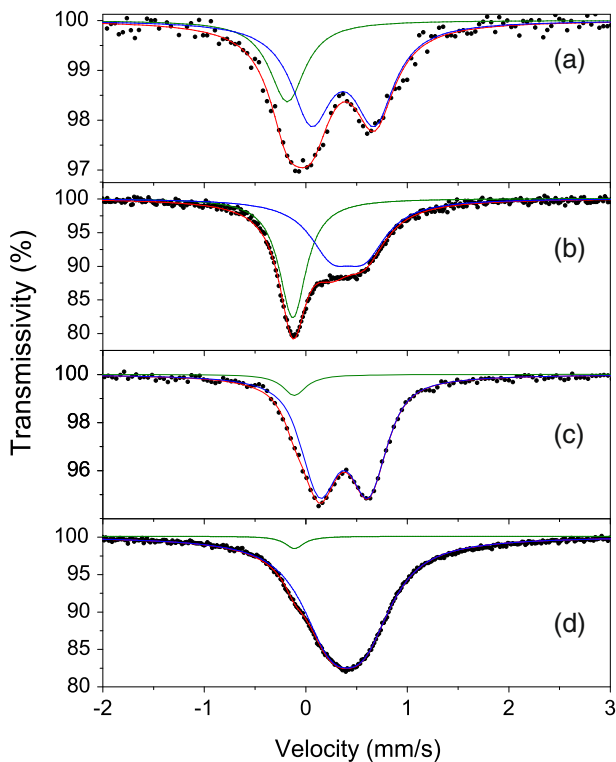


Fig. 2 Mössbauer spectra in precipitated (**a**, **b**, **c**) and Cs-intercalated (**d**) hexacyanoferrates. The archetypal “insoluble” Prussian Blues $\text{Fe}[\text{Fe}(\text{CN})_6]_{3/4} \cdot 14/4\text{H}_2\text{O}$ (**a**), $\text{CsFe}[\text{Fe}(\text{CN})_6]$ (**b**) and ^{57}Fe enriched $^{57}\text{Fe}[\text{Fe}(\text{CN})_6]_{3/4} \cdot 14/4\text{H}_2\text{O}$ (**c**) were precipitated from solutions. The Cs-intercalated $\text{Cs}^{57}\text{Fe}[\text{Fe}(\text{CN})_6]$ (**d**) was obtained from 8 mg of the precursor shown in (**c**) stirred with 20 mL of 0.1 M solution of CsCl overnight (16 h) at 20 °C. The experimental spectra are fitted with a singlet with isomer shift of -0.1 mm/s (low spin Fe^{2+} in FeC_6 coordination) and a doublet with isomer shift of 0.39 mm/s (high-spin Fe^{3+} in FeN_6 (**b**, **d**) and $\text{FeN}_{6-n}\text{O}_n$ (**a**, **c**) coordinations, with n in the range $0 < n < 6$). Note that the doublet quadrupole splitting decreases from 0.6 to 0.2 mm/s as water molecules leave the first coordination sphere of Fe^{3+} upon Cs intercalation

X-ray patterns, different quadrupole splitting of the ion-exchanged and precipitated samples of $\text{CsFe}[\text{Co}(\text{CN})_6] \cdot x\text{H}_2\text{O}$ indicates the difference of distributions of the valent electrons over the orbitals of t_{2g} group.

The as-precipitated samples of $\text{RbFe}[\text{Co}(\text{CN})_6] \cdot x\text{H}_2\text{O}$ and $\text{CsFe}[\text{Co}(\text{CN})_6] \cdot x\text{H}_2\text{O}$ show only one Mössbauer doublet. This means that the sixth d -electron of Fe^{2+} is found in a singular ground state. Asymmetric localization of the valent electron is associated with one or another distortion of the octahedral environment of Fe^{2+} [7]. We observe that only one type of the octahedron distortion is preferred when the Rb and Cs occupy the interstitials. On the other hand, in the case of $A = \text{K}$ or in alkali-free $\text{Fe}[\text{Co}(\text{CN})_6]_{2/3} \cdot x\text{H}_2\text{O}$ (Samples 2 and 1 of Fig. 3) the appearance of the second doublet indicate the coexistence and competition of multiple orbital ground states. A variety of different local configurations of the Fe^{2+} ligands, N and H_2O , is responsible for multiplicity of the local ground states of Fe^{2+} . In addition, the Prussian Blues,

Fig. 3 Mössbauer spectra of the ferrous hexacyanocobaltates (from top to bottom in order according to Fig. 1 and Table 1). The samples were obtained in three different procedures: precipitation (1–4), insertion of Cs into alkali-free “insoluble” $\text{Fe}[\text{Co}(\text{CN})_6]_{2/3}$ (5) and ionic-exchange with “soluble” $\text{KFe}[\text{Co}(\text{CN})_6]$ (6). Note that for the sake of clarity the minor Fe^{3+} subspectra (less than 6 % in Table 1) are not drawn. All the Fe^{2+} spectral contributions are represented by two (1,2,5), one (3 and 4) and three (6) quadrupole doublets

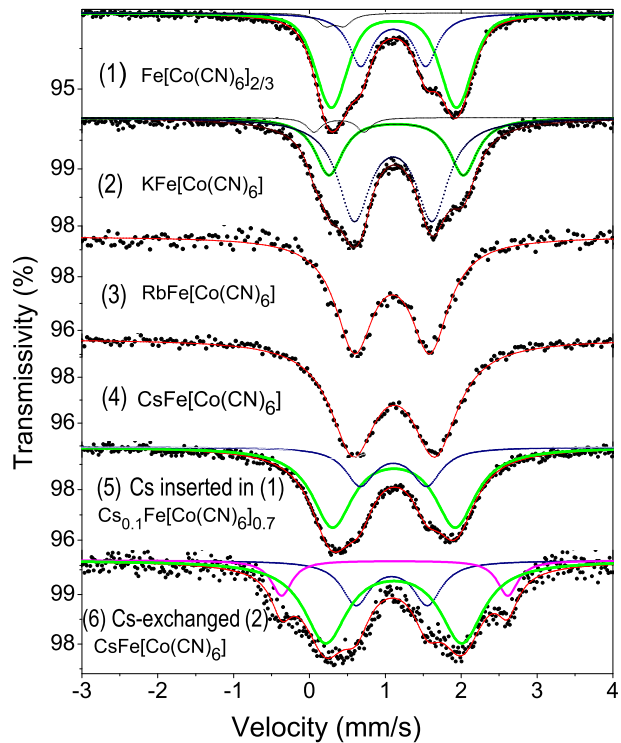


Table 1 Parameters of Mössbauer spectra in the hexacyanocobaltates

Compound	δ (mm/s)	Δ (mm/s)	Γ (mm/s)	%	Assignment
“insoluble” (1) $\text{Fe}[\text{Co}(\text{CN})_6]_{0.67}$	1.114(2)	1.65(1)	0.45(1)	64	Fe^{2+} : OS ^a
	1.104(2)	0.86(1)	0.38(1)	31	Fe^{2+} : OD ^b
	0.33(1)	0.23(2)	0.26(3)	5	Fe^{3+}
“soluble” (2) $\text{KFe}[\text{Co}(\text{CN})_6]$	1.144(3)	1.77(1)	0.44(2)	32	Fe^{2+} : OS
	1.104(2)	1.03(1)	0.52(2)	64	Fe^{2+} : OD
	0.39(1)	0.66(2)	0.23(3)	4	Fe^{3+}
Precipitated (3) $\text{RbFe}[\text{Co}(\text{CN})_6]$	1.091(5)	0.992(8)	0.60(1)	100	Fe^{2+} : OD
Precipitated (4) $\text{CsFe}[\text{Co}(\text{CN})_6]$	1.116(3)	1.077(4)	0.71(1)	100	Fe^{2+} : OD
Ion-exchanged (1) $\text{Cs}_{0.1}\text{Fe}[\text{Co}(\text{CN})_6]_{0.7}$	1.113(4)	1.62(2)	0.65(2)	70	Fe^{2+} : OS
	1.106(7)	0.88(3)	0.46(3)	24	Fe^{2+} : OD
	0.35(6)	0.36(6)	0.5(2)	6	Fe^{3+}
Ion-exchanged (2) $\text{CsFe}[\text{Co}(\text{CN})_6]$	1.111(5)	1.80(3)	0.69(4)	64	Fe^{2+} : OS
	1.084(9)	0.94(3)	0.45(4)	23	Fe^{2+} : OD
	1.123(8)	2.98(2)	0.33(4)	13	Fe^{2+} : OS

^aOS orbital singlet ground state

^bOD orbital doublet ground state

containing small alkali ions, could be susceptible to distortion isomerism [7], because potassium and sodium were reported to be eccentrically located in their cavities [8].

The ionic exchange of K for Cs in the Sample 2 results in strong enhancement of the outer quadrupole subspectrum with $\Delta E_Q = 1.8$ mm/s, from 32 to 64 %. The inner and outer subspectra are assigned to the orbital doublet and singlet ground states, respectively. In addition, there appears a component (13 %) with extremely large ΔE_Q of 3 mm/s. It is assigned to another orbital singlet state with larger energy splitting within the t_{2g} group. In the X-ray patterns, the intensity ratio I_{200}/I_{220} decreased more than 10 times during the Cs ion exchange and reached the ratio I_{200}/I_{220} of the precipitated $\text{CsFe}[\text{Co}(\text{CN})_6] \cdot x\text{H}_2\text{O}$. But the latter shows much broader XRD line-widths, suggesting the smallness of the crystal size. This unusual quadrupole splitting may suggest that the larger ion-exchanged crystals are in a strained metastable state. The excess of free energy can be created in the course of ionic exchange, however, such large Cs-rich crystals cannot be normally obtained by standard precipitation technique.

Acknowledgements This work was partly supported by the Chinese Academy of Sciences Visiting Professorships for Senior International Scientists. Grant No. 2011T1G15. Financial support obtained from the Chinese Academy of Sciences for “100 Talents” Project, the National Natural Science Foundation of China (No. 11079036) and the Natural Science Foundation of Liaoning Province (No. 20092173) is also greatly acknowledged.

References

1. Keggin, J.F., Miles, F.D.: *Nature (London)* **137**, 577–578 (1936)
2. Ludi, A., Güdel, H.U.: *Struct. Bonding* **14**, 1–21 (1973)
3. Rasmussen, P.G., Meyers, E.A.: *Polyhedron*, **3**, 183–190 (1984)
4. Reguera, E., Yee-Madeira, H., Demeshko, S., Eckold, G., Jimenez-Gallegos, J.: *Z. Phys. Chem.* **223**, 701–711 (2009)
5. Herren, F., Fischer, P., Ludi, A., Hälgl, W.: *Inorg. Chem.* **19**, 956–959 (1980)
6. Evans, R.J., Rancourt, D.G., Grodzicki, M.: *Am. Mineral.* **90**, 187–198 (2005)
7. Latorre, R., Abeledo, C.R., Frankel, R.B., Costamagna, J.A., Reiff, W.M., Frank, E.: *J. Chem. Phys.* **59**, 2580–2585 (1973)
8. Widmann, A., Kahlert, H., Petrovic-Prelevic, I., Wulff, H., Yakhmi, J. V., Bagkar, N., Scholz, F.: *Inorg. Chem.* **41**, 5706–5715 (2002)