

# Titanium<sup>3+</sup> Hexacyanometallates(II): Preparation and Porous Framework

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**Abstract.** The studied compounds were prepared by the precipitation method mixing  $\text{Ti}^{3+}$  in concentrated HCl with aqueous solution of  $[\text{M}(\text{CN})_6]^{4-}$  where  $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ . The formed solids,  $\text{Ti}_3\text{Cl}[\text{M}(\text{CN})_6]_2 \cdot 10\text{H}_2\text{O}$ , were characterized by IR spectroscopy, X-ray diffraction, thermogravimetry, Mössbauer spectroscopy, energy-disperse X-ray spectroscopy, UV/Vis spectroscopy, adsorption data, and chemical analyses. Their crystal structures were solved and refined from the recorded X-ray powder patterns in the  $Fm\bar{3}m$  space group. This series of compounds has a porous framework with a relatively

high free volume, which is occupied by coordinated and hydrogen bonded water molecules. The charge balancing  $\text{Cl}^-$  ion was found coordinated to titanium atoms. This series of porous solids was studied in order to explore the hydrogen interaction with the titanium atoms found at the surface of the cavities. On the water removal by moderate heating their porous framework collapses as reveal the nitrogen,  $\text{CO}_2$ , and hydrogen adsorption but without complex salt decomposition. On the solids rehydration the porous framework is partially restored.

## Introduction

Within titanium hexacyanometallates the most studied member is  $\text{Ti}^{4+}$  hexacyanoferrate(II) because of its ability for  $^{137}\text{Cs}$  sorption [1, 2]. This compound is usually prepared from solutions of  $\text{Ti}^{4+}$  chloride and  $\text{K}^+$  or  $\text{Na}^+$  hexacyanoferrate(II), where the mixed complex salt  $\text{Ti}_4[\text{Fe}(\text{CN})_6] \cdot x\text{H}_2\text{O}$  ( $A = \text{Na}, \text{K}$ ) precipitates. Its crystal structure is formed by a 3D framework of  $-\text{Ti}-\text{N}\equiv\text{C}-\text{Fe}-\text{C}\equiv\text{N}-\text{Ti}-$  chains with the alkali metal atoms occupying all the available interstitial spaces. Its ability for the cesium sorption is supported in the ionic exchange of these interstitial alkali metal atoms by cesium. Cesium is a big atom, which practically occupies all the available volume of the interstitial void and from this fact the ionic exchange is highly favorable [3]. For the  $^{137}\text{Cs}$  sorption other divalent transition metal ( $T$ ) mixed salts,  $\text{TA}_2[\text{Fe}(\text{CN})_6] \cdot x\text{H}_2\text{O}$  can also be used [4, 5]. In addition, metal hexacyanoferrates are relatively stable materials in acid media, which favors their application for the  $^{137}\text{Cs}$  recovery from nuclear waste plants [1–3]. The formed precipitate from solutions of  $\text{Ti}^{3+}$  chloride and  $\text{K}^+$  hexacyanoferrate(III) has also been studied, in which the solid precipitation is accompanied of an inner charge transfer to form

$\text{Ti}^{4+}$  hexacyanoferrate(II) [6]. From  $\text{Ti}^{3+}$  and ferrocyanic acid,  $\text{H}_4[\text{Fe}(\text{CN})_6]$ , the formation of a solid with formula unit  $\text{T}_4[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$  was reported [6]. The structure of these solids can be interpreted according to a structural model for Prussian blue (PB) analogues nowadays surpassed.

To the best of our knowledge, the preparations and characterizations of  $\text{Ti}^{3+}$  hexacyanometallates(II) with  $\text{Ru}^{\text{II}}$  and  $\text{Os}^{\text{II}}$  as inner metal atoms, have not been reported. In this contribution, the preparation of the  $\text{Ti}^{3+}$  hexacyanometallates(II) series and their characterization from energy-disperse X-ray spectroscopy (EDS), X-ray diffraction (XRD), infrared (IR) spectroscopy, Mössbauer spectroscopy, thermogravimetry (TG), UV/Vis spectroscopy, adsorption data and chemical analyses are discussed.

The interest for the  $\text{Ti}^{3+}$  hexacyanometallates(II) series was motivated by the possibility of obtaining porous solids of PB type,  $\text{Ti}_4[\text{M}(\text{CN})_6]_3$ , with  $\text{Ti}^{3+}$  atoms at the surface of the cavities with available coordination sites in the anhydrous material. Such a solid could be a prototype of porous material for molecular hydrogen storage through formation of a coordination bond between the metal and the hydrogen molecule [7]. The availability of open metal sites at the surface of cavities in PB analogues has stimulated their study for hydrogen storage [8–16]. For  $\text{Ti}^{3+}$  located at a silica surface hydrogen adsorption heats close to  $-22 \text{ kJ}\cdot\text{mol}^{-1}$  were reported [17]. That value is in the required ideal range of adsorption energy for technological applications of hydrogen storage in porous solids [18]. Titanium has extended 3d orbitals and this facilitates its coordination interaction with the hydrogen molecule. The obtained solids,  $\text{Ti}_3\text{Cl}[\text{M}(\text{CN})_6]_2 \cdot 10\text{H}_2\text{O}$  ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ) in the following  $\text{Ti}_3\text{ClM}_2$ , were found to be not appropriate for studies related to the hydrogen adsorption in porous materials because on the crystal water removal a partial collapse for the porous framework was observed; nevertheless, valuable information on the

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