



# Tetrahedral coordination for Zn in hexacyanometallates: Structures of $Zn_3A_2[M(CN)_6]_2 \cdot xH_2O$ with $A = K, Rb, Cs$ and $M = Ru, Os$

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## ABSTRACT

Zinc hexacyanoruthenate (II) and hexacyanoosmate (II) were prepared and studied from X-ray diffraction (XRD), infrared (IR), and thermogravimetric (TG) data. These compounds were found to be isomorphous with the iron analogues, crystallizing with a rhombohedral unit cell (R-3c space group), where the zinc atom has tetrahedral coordination to N ends of CN groups. For Cs, compounds with formula unit  $ZnCs_2[M(CN)_6]$  and a cubic unit cell (Fm-3m) were also obtained. The crystal structures for the eight compositions were refined from the corresponding X-ray powder diffraction patterns using the Rietveld method. Related to the tetrahedral coordination for the Zn atom, the rhombohedral phase has a porous framework with ellipsoidal cavities of about  $12.5 \times 9 \times 8 \text{ \AA}$ , communicated by elliptical windows of  $\sim 5 \text{ \AA}$ . Within these cavities the exchangeable alkali metal ions are found. The filling of the cavity volume is completed with water molecules. IR spectrum senses certain charge delocalization from the inner metal, through the  $\pi$ -back donation mechanism. For Os compounds this effect is particularly pronounced, related to a more diffuse d orbitals for this metal.

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## 1. Introduction

The 3D structure of hexacyanometallates is formed by the assembling of the octahedral anionic building unit,  $[M^n(CN)_6]^{n-6}$ , through a second transition metal linked at the N ends. Usually that second metal (T) has also octahedral coordination and a solid with a cubic unit cell is obtained. When the CN group behaves as a single bridge between the two metal centers, to form -T-N-C-M-C-N-T- chains, the formed solids are known as Prussian blue (PB) analogues [1]. Deviations from such structural features are known. For hexacyanometallates (II) of Mn and Cd, the metals sequence is M-T...T-M, where two neighboring T metals remain bridged by two coordinated water molecules [2–4]. In their anhydrous phases the N end of the CN group behaves as a bifurcated ligand coordinating two neighboring T metals [5]. As a third example of such deviations, the tetrahedral coordination for the Zn atom in some hexacyanometallates can be considered [6]. In this contribution we are reporting the finding of this last atypical coordination for six new compositions, not previously studied.

Recently, hexacyanometallates of Zn with a tetrahedral coordination for the zinc atom have received certain attention,

due to their interesting porous framework, particularly in studies related to the hydrogen storage [7,8]. According to their framework, for these porous solids a zeolite-like behavior is expected. The alkali metal (A) is an exchangeable species found within the cavities. However, in zeolites the bridge group is the oxygen atom whose bonding properties are quite different from those known for the CN group, and quite different in the nature of the involved metals also. These features make Zn hexacyanometallates attractive porous materials, particularly related to the nature of possible interactions with guest species within the cavities, including molecular hydrogen.

## 2. Experimental

$Zn_3K_2[M(CN)_6]_2 \cdot xH_2O$  was prepared mixing hot aqueous solutions (0.01 M) of  $Zn^{2+}$  sulfate and  $K_4[M(CN)_6] \cdot 3H_2O$  where  $M = Ru, Os$ . The precipitate formed was aged at  $60^\circ C$  for 2 days within the mother liquor, then washed several times with distilled water in order to remove all the accompanying ions and finally dried in air until it had constant weight. Mixed compositions with  $A = Rb$  and  $Cs$  were prepared through ionic exchange at  $60^\circ C$  from  $Zn_3K_2[M(CN)_6]_2 \cdot xH_2O$  in hot aqueous solutions according to a reported procedure [9]. The potassium hexacyanoruthenate (II) and hexacyanoosmate (II) used were prepared from  $RuCl_2$  and  $OsO_4$  by alkaline fusion with KCN, and then re-crystallized several

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