

Structural Characterization of Cadmium Hexacyanometallates(II) and Related Complexes

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Cadmium hexacyanometallates (II) crystallize in the same monoclinic cell (space group $C_{2h}^5 - P2_{1/n}$) reported for the analogs of manganous complexes. In that monoclinic framework, two outer cations ($M = Mn^{2+}$ or Cd^{2+}) of neighboring structural units $M_2[L^{II}(CN)_6]$, ($L = Fe^{II}$, Ru^{II} , Os^{II}), are linked by two common water molecules. On heating above $100^\circ C$, these water bridges are removed. In dehydrated complexes, the outer cation (M) remains linked to only three CN ligands. The loss of aquo-ligands induces a remarkable π -back donation from the inner cation (L) to CN ligands, which was studied using IR, Raman, and Mössbauer spectroscopies.

KEY WORDS: Hexacyanometallate; IR spectra; Raman spectra; Mössbauer spectra; X-ray diffraction.

INTRODUCTION

Hexacyanometallates (II) are a well-studied family of metal complexes which show properties as molecular sieves, cation exchangers and radionuclide sorbents [1, 2], and are used to recover valuable metals [3], and to carry out some catalytic reactions [4]. Many of these properties are related to their features as microporous materials. In a previous study on dehydration and rehydration of hexacyanides, we observed an anomalous behavior, in the case of manganous ferrocyanide. When manganous ferrocyanide is dehydrated, its $\nu_{(CN)}$ absorption band shifts from 2066 to 2032 cm^{-1} , preserving its nature as a metal hexacyanometallate(II) [5]. This was an unexpected result, since CN stretching absorption in hexacyanides falls at well defined values of frequency for the different compounds [6–9]. A similar result was observed when cadmium ferricyanide was

reduced by heating or milling. The resulting cadmium ferrocyanide absorbs at 2030 cm^{-1} , about 34 cm^{-1} below the normal $\nu_{(CN)}$ absorption for this compound [10]. Mössbauer spectra of these two low-frequency species of manganous and cadmium ferrocyanides are quadrupole doublets, differing from normal ferrocyanides whose Mössbauer spectra are single absorption lines corresponding to iron coordinated to six CN ligands at the C end and a low-spin electronic configuration [11–14]. In both cases, when the dehydrated samples are rehydrated in air, their original characteristics are restored.

An answer to the mentioned characteristics in the IR and Mössbauer spectra of dehydrated manganous and cadmium ferrocyanides must be found in their crystalline structures. However, the crystalline structure has been reported for manganous ferrocyanide and its Ru^{II} and Os^{II} analogs [15], but not for the cadmium complexes. Manganous hexacyanometallates(II) crystallize in the monoclinic space group $C_{2h}^5 - P2_{1/n}$, with two formula units, $Mn_2[L^{II}(CN)_6] \cdot 8\text{ H}_2\text{O}$, ($L^{II} = Fe^{II}$, Ru^{II} and Os^{II}), per cell ($Z = 2$) [15, 16]. The L^{II} cation is octahedrally coordinated-forming $[L^{II}C_6]$ unit, while the Mn^{2+} cation has a mixed coordination sphere with three N and three O atoms from CN ligands and coordinated water. Two such $[Mn^{2+}N_3(H_2O)_3]$ octahedra are linked by two bridging water molecules, giving a di-

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