

Mössbauer spectra of ferrous salts of transition metal cyano complexes. A survey

Edilso Reguera* and Hernani Yee-Madeira

Depto. de Física, Esc. Sup. de Física y Matemáticas-IPN, Edif. 9 Unidad Prof. "ALM" 07738, México, D.F, México

José Fernández-Bertran

Centro de Química Farmacéutica, La Habana, Cuba

Lourdes Nuñez

Centro Nacional de Investigación Científica, La Habana, Cuba

Summary

Ferrous salts of ten hexacyanometallates and three tetracyanometallates were obtained and their Mössbauer spectra interpreted according to recent structural models for these families of compounds. Ferrous ferrocyanide (Williamson White) and its ruthenium and osmium analogs prepared mechanochemically are stable for hours, allowing their study by Mössbauer spectroscopy and other related techniques. For ferrous salts of trivalent hexacyanometallate anions, the random distribution of anion vacancies is discarded and a model of two well defined relative positions of CN and H₂O ligands around the Fe²⁺ is suggested. Iron was found octahedrally coordinated in tetracyanometallates.

Introduction

The Mössbauer study of cyano complexes of transition metals dates back to the early 1960's⁽¹⁾ when major attention was devoted to hexacyanoferrate salts. By contrast, tetracyanides have practically been ignored. Even in the case of hexacyanometallates, ferrous salts have been considered only occasionally^(2–6). In all the reports published in the 1960 decade on hexacyanides, spectra were interpreted on the basis of the Keggin and Miles structural model for Prussian Blue, with two different sites for the outer cations: one octahedrally coordinated to six nitrogens of the cyano ligands (structural sites) and one coordinated by water molecules and located in the cubic voids of the network (interstitial sites)⁽⁷⁾. That model has been superseded by the Ludi model with the outer cations always in structural sites⁽⁸⁾. In order to balance the stoichiometry, an equivalent number of hexacyanometallate anions are left vacant, creating a rather open structure. Even in relatively recent papers, dealing with hexacyanometallates, references to the old model or to incorrect interpretation of spectra are also found. In this paper we report a systematic Mössbauer study of ferrous salts of stable cyano complexes of transition and heavy metals, including some mixed potassium-ferrous salts. The Mössbauer spectra of some of these salts have not been previously reported.

Experimental

Ferrous salts of [Cr(CN)₆]^{3–}, [Mn(CN)₆]^{3–}, [Co(CN)₆]^{3–}, [Rn(CN)₆]^{3–}, [Ir(CN)₆]^{3–}, [Pd(CN)₆]^{2–}, [Pt(CN)₆]^{2–},

[Ni(CN)₄]^{2–}, [Pd(CN)₄]^{2–} and [Pt(CN)₄]^{2–} anions were prepared by mixing aqueous solutions of ferrous sulfate and potassium hexacyanometallate or tetracyanometallate. For [Fe(CN)₆]^{4–}, [Ru(CN)₆]^{4–}, and [Os(CN)₆]^{4–} anions, the synthesis was performed in the solid state, by milling the stoichiometric amount of ferrous sulfate heptahydrate and potassium hexacyanometallate trihydrate in an agate mortar⁽⁹⁾. Hydrazine hydrochloride was always added to the Fe²⁺ reactant to avoid the oxidation of iron during the reaction. All potassium hexacyanometallates were prepared and purified according to literature reports^(10–14), with the exception of K₄[Fe(CN)₆]·3H₂O, a commercial product (BDH). Potassium tetracyanides (K₂[M(CN)₄], M = Ni, Pd and Pt) were Aldrich products. All reagents used were analytical grade (BDH, Merck, Aldrich and Fluka).

The nature of the complexes was established through XRF (for inner-to-outer metal ratio), XRD (for those salts of well-known crystalline structure) and i.r. spectroscopy (for the nature of the complex anion). The i.r. spectra were run in Nujol mulls. The CN stretching frequency for ferrous hexacyanometallates must be ca. 12 cm^{–1} lower than the corresponding one for the ferric salts^(9,15,16). This characterization was also complemented with XRD and thermogravimetric measurements.

The Mössbauer spectra were recorded at room temperature with a ⁵⁷Co in Rh source (from Amersham), using a constant acceleration spectrometer (from Mosstech). All spectra were fitted through an iterative least squares minimization algorithm and pseudo-Lorentzian line shapes in order to obtain the values of isomer shift (δ), quadrupole splitting (Δ), linewidth (Γ) and relative area (A). The isomer shifts are reported relative to Fe-metal at 298 K.

Results and discussion

Ferrous salts of divalent hexacyanide complex anions

Two transition metal cations, palladium(IV) and platinum(IV), form stable divalent hexacyanide complex anions. Their ferrous salts, Fe[Pd(CN)₆] and Fe[Pt(CN)₆], crystallize with the fcc cell typical of Prussian Blue analogs⁽¹⁷⁾. Table 1 lists the cell edge (a₀) values. In this structure Fe²⁺ cations are always found octahedrally coordinated to six CN ligands at the N end. This highly symmetric environment of Fe²⁺ cations allows only a small splitting of their three t_{2g} levels (d_{xy}, d_{xz}, d_{yz}), which at room temperature can be equally populated by the valence electrons (see Figure 1a). Since in high spin ferrous cations the electric field gradient is

* Author to whom all correspondence should be directed.