

Tribochemical Synthesis and Study of Mixed Potassium-Ferrous Ferrocyanide and its Ru^{II} and Os^{II} Analogs

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Mixed potassium-ferrous ferrocyanide and its Ru^{II} and Os^{II} analogs have been synthesized tribochemically by grinding Fe(SO₄)·7H₂O with the equivalent amount of K₄[Fe(CN)₆]·3H₂O and the Ru^{II} and Os^{II} compounds. Their XRD powder patterns and Mössbauer and IR spectra were recorded and interpreted. The role of hydration water on the feasibility of the tribochemical synthesis is discussed.

Introduction

When aqueous solutions containing Fe²⁺ cation and [Fe(CN)₆]⁴⁻ anion are mixed, a white precipitate of ferrous ferrocyanide is produced (Williamson White) [1, 2]. The white precipitate turns bluish rapidly, and in a short time the ferrous cation has been oxidized in the air, transforming into the stable ferric ferrocyanide (Soluble Prussian Blue) [2]. For this reason, erroneous reports on Mössbauer spectra of Williamson White have appeared in the literature [3]. We are not aware of similar reports on the study of the ferrous salts of ruthenocyanide and osmocyanide, most probably due to the instability of these compounds which oxidize to ferric salt rapidly. However, we have observed that when Fe(SO₄)·7H₂O is milled with the potassium hexacyanometallates of Fe^{II}, Ru^{II} and Os^{II}, relatively stable products are obtained which contain the Fe²⁺ cation. In this paper we report details of their tribochemical synthesis and their characterization through XRD, Mössbauer and IR techniques.

Experimental

The studied compounds were prepared by milling stoichiometric amounts of Fe(SO₄)·7H₂O and K₄[Fe(CN)₆]·3H₂O, K₄[Ru(CN)₆]·3H₂O and K₄[Os(CN)₆]·3H₂O, respectively, in an agate mortar to obtain the ferrous salts. The reactants were first powdered separately and mixed before grinding them together. Ferrous sulfate and potassium ferrocyanide were analytical grade reagents

(BDH). Potassium ruthenocyanide and osmocyanide were prepared according to classical procedures [4, 5]. Solid hydrazine hydrochloride was added to the mixture of reactants to prevent the oxidation of the ferrous cation during the milling process.

The course of the tribochemical reaction was monitored through IR spectra recorded in Nujol mulls between CaF₂ windows with a Philips 9512 spectrometer. XRD powder patterns were obtained of the final products using an HZG-4 diffractometer (Carl Zeiss) and monochromatic CuK α radiation. Thermogravimetric analyses (TGA) were carried out using a MOM Q-1500 equipment.

Mössbauer spectra were recorded at room temperature with a ⁵⁷Co in Rh source, using a constant acceleration spectrometer in the transmission mode. Samples were sealed in the sample holder to prevent their oxidation. All Mössbauer spectra were fitted with an iterative least-squares minimization algorithm using Lorentzian line shapes to obtain the values of the isomer shift (δ), quadrupole splitting (Δ), linewidth (Γ) and relative area (A). Isomer shift values are reported relative to sodium nitroprusside.

Results and Discussion

When stoichiometric amounts (1:1 molar ratio) of Fe(SO₄)·7H₂O and K₄[Fe(CN)₆]·3H₂O are milled together, the mixture becomes pasty and then dry again with further milling. Obviously, the water of crystallization of the starting compounds is liberated during the tribochemical reaction and later partially used as water of crystallization of the final compound. A certain loss of weight is

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