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

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Mixed potassium-ferrous ferrocyanide and its Ru\textsuperscript{II} and Os\textsuperscript{II} analogs have been synthesized tribochemically by grinding Fe(SO\textsubscript{4})\textsubscript{2} \cdot 7H\textsubscript{2}O with the equivalent amount of K\textsubscript{4}(Fe(CN)\textsubscript{6})\textsubscript{3} \cdot 3H\textsubscript{2}O and the Ru\textsuperscript{II} and Os\textsuperscript{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 Fe\textsuperscript{2+} cation and [Fe(CN)\textsubscript{6}]\textsuperscript{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(SO\textsubscript{4})\textsubscript{2} \cdot 7H\textsubscript{2}O is milled with the potassium hexacyanometallates of Fe\textsuperscript{II}, Ru\textsuperscript{II} and Os\textsuperscript{II}, relatively stable products are obtained which contain the Fe\textsuperscript{2+} 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(SO\textsubscript{4})\textsubscript{2} \cdot 7H\textsubscript{2}O and K\textsubscript{4}(Fe(CN)\textsubscript{6})\textsubscript{3} \cdot 3H\textsubscript{2}O, K\textsubscript{4}(Ru(CN)\textsubscript{6})\textsubscript{3} \cdot 3H\textsubscript{2}O and K\textsubscript{4}(Os(CN)\textsubscript{6})\textsubscript{3} \cdot 3H\textsubscript{2}O, 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 CaF\textsubscript{2} 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\textalpha radiation. Thermogravimetric analyses (TGA) were carried out using a MOM Q-1500 equipment.

Mössbauer spectra were recorded at room temperature with a \textsuperscript{57}Co 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 (\textbf{\alpha}), quadrupole splitting (\textbf{\Delta}), linewidth (\textbf{\Gamma}) and relative area (\textbf{A}). Isomer shift values are reported relative to sodium nitroprusside.

Results and Discussion

When stoichiometric amounts (1:1 molar ratio) of Fe(SO\textsubscript{4})\textsubscript{2} \cdot 7H\textsubscript{2}O and K\textsubscript{4}(Fe(CN)\textsubscript{6})\textsubscript{3} \cdot 3H\textsubscript{2}O 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
observed in the final product indicating that some water evaporates off on grinding. IR spectra of the reacted mixture show the presence of a ferrous ferrocyanide and potassium sulfate (K$_2$SO$_4$), which is also confirmed by XRD powder pattern. Its Mössbauer spectrum reveals an approximate 1:1 area ratio for Fe$^{2+}$ (high-spin) to Fe$^{11+}$ (low-spin) (see Fig. 1 and Table I), corresponding to a mixed potassium-ferrous ferrocyanide, FeK$_2$[Fe$^{11+}$(CN)$_6$]$_x$·xH$_2$O. The area ratio is equivalent to Fe$^{2+}$ to the Fe$^{11+}$ population ratio since in ferrocyanides inner and outer cations have approximately the same probability of Mössbauer absorption [2]. TGA reveals that the tribochemically synthesized product dehydrates endothermically around 100 °C with a loss of weight of about 17%. Since potassium sulfate is anhydrous we have taken $x = 6$ in the formula of potassium-ferrous ferrocyanide. We attempted to prepare a Fe$_2$[Fe(CN)$_6$]·xH$_2$O by milling together appropriate amounts (2:1 molar ratio) of ferrous sulfate heptahydrate and potassium ferrocyanide trihydrate without success. Always the mixed salt is obtained. Similar results were reached using the K salts of the Ru$^{11+}$ and Os$^{11+}$ complexes. The mixed ferrocyanide is white, but the Ru$^{11+}$ and Os$^{11+}$ analogs are pale-violet. They are stable for days when kept in dry air, but in a humid atmosphere they slowly oxidize to give potassium-ferric ferrocyanide (Soluble Prussian Blue) and its analogs.

When anhydrous ferrous sulfate, Fe(SO$_4$)$_2$, is used instead of Fe(SO$_4$)$_2$·7H$_2$O, the tribochemical reaction does not take place, even after long milling times. Apparently, the water of crystallization of the heptahydrate is necessary for the reaction, or the structure of the anhydrous salt is too strong to be broken tribochemically in an agate mortar. A similar effect of the water of crystallization has been observed by Güttlich et al. when a solid mixture of ferrous sulfate and potassium cyanide reacts in pressed disks to give potassium ferrocyanide [6].

IR spectra of the complexes show a very intense singlet in the 2060 cm$^{-1}$ region corresponding to bridging CN group (see Table I). The $v_{CN}$ frequencies are 12 cm$^{-1}$ lower than those of the corresponding Fe$^{3+}$ compounds to which they oxidize on aging. This is the expected shift for the increase in charge of the outer Fe cation [7, 8].

<table>
<thead>
<tr>
<th>Compound</th>
<th>$a_0$ [Å]</th>
<th>$v_{CN}$ [cm$^{-1}$]</th>
<th>$\delta$ [mm/s]</th>
<th>$\Delta$ [mm/s]</th>
<th>$\Gamma$ [mm/s]</th>
<th>$\alpha$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeK$_2$[Fe(CN)$_6$]·6H$_2$O</td>
<td>10.28(1)</td>
<td>2068</td>
<td>1.33</td>
<td>0.45</td>
<td>0.59</td>
<td>49</td>
</tr>
<tr>
<td>FeK$_2$[Ru(CN)$_6$]·6H$_2$O</td>
<td>10.39(1)</td>
<td>2057</td>
<td>1.33</td>
<td>0.46</td>
<td>0.55</td>
<td>100</td>
</tr>
<tr>
<td>FeK$_2$[Os(CN)$_6$]·6H$_2$O</td>
<td>10.44(1)</td>
<td>2062</td>
<td>1.31</td>
<td>0.51</td>
<td>0.60</td>
<td>100</td>
</tr>
</tbody>
</table>

Errors in $\delta$, $\Delta$ and $\Gamma$ are no higher than 0.01 mm/s. Isomer shift values are reported relative to sodium nitroprusside.

Table I. Cell edge $a_0$, $v_{CN}$ stretching and Mössbauer parameters at room temperature of mixed potassium-ferrous ferrocyanide, ruthenocyanide and osmo-cyanide.

Fig. 1. Mössbauer spectra of: (a) ferrous sulfate heptahydrate, (b) potassium ferrocyanide trihydrate, and (c) potassium-ferrous ferrocyanide, FeK$_2$[Fe(CN)$_6$]·6H$_2$O, obtained by grinding stoichiometric amounts (1:1 molar ratio) of ferrous sulfate heptahydrate and potassium ferrocyanide trihydrate.
Mössbauer spectra of the tribochemically synthesized potassium-ferrous hexacyanometallates are very simple (see Fig. 1 and 2). A doublet due to high-spin ferrous cation plus a singlet of low-spin iron(II) in the case of ferrocyanide salt are observed. The isomer shift (relative to sodium nitroprusside) of these high-spin ferrous cations is in the range \(1.32 \pm 0.01\) mm/s (see Table I), about 0.20 mm/s lower than the corresponding value of the starting reagent (ferrous sulfate). The previously reported Mössbauer spectrum for Williamson White [3] is just the spectrum of the unreacted mixture of anhydrous ferrous sulfate and potassium ferrocyanide where the left component of the Fe\(^{2+}\) doublet coincides in position with the singlet of Fe\(^{2+}\) in potassium ferrocyanide.

The XRD powder patterns of potassium-ferrous hexacyanometallates obtained by the tribochemical reactions belong to the fcc crystal cell typical of Prussian Blue analogs [9]. The measured cell edge values \((a_0)\) (see Table I) are consistent with a cubic framework of Fe\(^{2+}\)-N-C-M\(^{II}\) chains (M = Fe, Ru and Os) with the potassium cations occupying all small cubic voids in the network [9]. The unsplit \(\nu_{CN}\) stretching data (see Table I) are in accordance with that arrangement of cations and ligands. The monotonic increase in \(a_0\) is due to the increasing radius of the inner cation (Fe\(^{II}\), Ru\(^{II}\) and Os\(^{II}\)). The presence of potassium cations in the cubic voids of the network of these salts causes certain asymmetry in the electric field gradient around Fe\(^{2+}\) cations which is observed as a \(\Delta\) value in the range 0.45–0.51 mm/s. Ferrous hexacyanometallates with the same network but where potassium cations are excluded (e.g. Fe[M(CN)\(_6\)]; M = Pd or Pt) have \(\Delta = 0\) [10].

**Conclusions**

Mixed potassium-ferrous ferrocyanide, ruthenocyanide and osmocyanide were tribochemically synthesized by milling together ferrous sulfate heptahydrate and the corresponding potassium hexacyanometallate trihydrate. Always the mixed salts are obtained in this way. The reactions do not proceed when anhydrous sulfate is used instead the heptahydrated salt. The complexes crystallize with the fcc cell typical of Prussian Blue analogs, with potassium cations occupying all small cubic voids in that structure. The Mössbauer parameters \((\delta\) and \(\Delta\)) for Fe\(^{2+}\) cations in these complexes are very different from the corresponding values in ferrous sulfate, allowing the tribochemical reactions to be followed through their Mössbauer spectra.

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