The Structure Model of an Inorganic Ion Exchanger
Cobalt(II)-hexacyanoferrate(II)

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Cobalt(II)-hexacyanoferrates(II) with incorporated monovalent Na+, K+, NH4+ and Cs+ ions have been synthesized. Chemical composition and structure of the unit cell of the crystallites have been determined by X-ray and IR analysis. It has been found that all crystallites containing the monovalent cations are isomorphous having an FCC structure, whereas the cobalt(II)-hexacyanoferrate(II) crystallites tetragonally. In order to explain the properties of these crystallites (which are similar to zeolites) causing their selectivity to monovalent cations, a structure model has been proposed. The values of effective radii of the “cages” and their entrances have been calculated.

1. Introduction

Although there is a number of inorganic ion-exchangers which have been studied so far (silica gel, natural and synthetic zeolites etc.), there is a doubtless interest for the insoluble hexacyanoferrates(II) of transition metal ions (Cu, Ni, Co, Zn) with ion exchange properties showing a selectivity in separations of monovalent cations (Na, K, NH4, Cs).

The present investigations are related to cobalt(II)-hexacyanoferrate(II) used for extensive separations of trace amounts of cesium from urine [1] and of 137Cs from nuclear waste solutions [2]. Most of the results of X-ray analyses point out these crystallites have a FCC structure [3–6], although there are some claims that their structure is tetragonal [7]. Hexacyanoferrates(II) of divalent transition metal ions Cu, Ni, Co, Zn and Fe are isostructural compounds which do not change their structure if K+ and Cs+ ions are incorporated in them [4–6, 8].

All investigations of the structure dealt so far mainly with the influence of transition metal ions, sited in the lattice, on the properties of the formed crystallites [9–11], whereas little attention has been paid to the interstitial ions from the internal part of the unit cell (u.c.). The mobile interstitial ions can have part in the ion exchange reaction which is essential for the explanations of the observed selectivity of these inorganic ion exchangers for the monovalent cations. In the present work an attempt is made to postulate a structural model by which the ion exchange properties of cobalt(II)-hexacyanoferrate(II) can be explained.

2. Experimental

Synthesis

The synthesis has been performed by precipitation with H4[Fe(CN)6] of cobalt(II) alone or cobalt(II) in the presence of monovalent cations from aqueous solutions of their chloride salts. The acid H4[Fe(CN)6] is obtained by passing a 0.05 mol l–1 solution of K4[Fe(CN)6] through a column of Dowex 50X8 cation exchanger in its H+ form. The molar ratio of components in the reacting solution where cobalt(II)-hexacyanoferrate(II), (CoFC)Co, was synthetized amounted to Co2+: [Fe(CN)6]3– = 2:1, whereas for synthetising the cobalt(II)-M-hexacyanoferrate(II), (CoFC)M, the ratio was Co2+: M2+: [Fe(CN)6]3– = 2:10:1, where M2+ = Na, K, NH4 and Cs. In order to facilitate filtering, the precipitates were left for 48 h, after that they were filtered off and rinsed with doubly distilled water until the Cl– reaction disappeared. Then they were dried in air at ambient temperature until constant weight had been attained.

Chemical analyses

The synthetized crystalline samples were decomposed by concentrated H2SO4, the reaction mixture evaporated to dryness and then repeatedly heated with concentrated HCl in order to obtain the soluble forms of cobalt, iron and monovalent cations. The total amounts of cobalt and iron were determined by spectrophotometry [12], sodium and potassium by flame photometry; cesium, after separating cobalt and iron by ion exchange (Dowex 1X8 in Cl– form), was determined by isotope dilution with 137Cs. The NH4+ concentration was determined by the method of Kjeldahl.

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Table I. Chemical composition of synthetized crystallites.

<table>
<thead>
<tr>
<th>Crystallite</th>
<th>Fe²⁺ (Wt.%)</th>
<th>Co²⁺ (Wt.%)</th>
<th>M⁺ (Wt.%)</th>
<th>CN⁶ (Wt.%)</th>
<th>TG (Wt.%)</th>
<th>H₂O (Wt.%)</th>
<th>DSC (Wt.%)</th>
<th>Sum (Wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CoFC)Co</td>
<td>12.84</td>
<td>26.64</td>
<td></td>
<td>35.88</td>
<td>23.94</td>
<td>6.12</td>
<td>99.30</td>
<td></td>
</tr>
<tr>
<td>(CoFC)Na</td>
<td>12.30</td>
<td>19.45</td>
<td>5.29</td>
<td>34.32</td>
<td>26.50</td>
<td>20.52</td>
<td>97.86</td>
<td></td>
</tr>
<tr>
<td>(CoFC)K</td>
<td>13.96</td>
<td>15.32</td>
<td>19.59</td>
<td>39.00</td>
<td>11.52</td>
<td>7.02</td>
<td>99.39</td>
<td></td>
</tr>
<tr>
<td>(CoFC)NH₄</td>
<td>15.63</td>
<td>16.20</td>
<td>10.08</td>
<td>43.60</td>
<td>12.96</td>
<td>7.92</td>
<td>98.47</td>
<td></td>
</tr>
<tr>
<td>(CoFC)Cs</td>
<td>8.94</td>
<td>10.02</td>
<td>43.89</td>
<td>24.96</td>
<td>13.02</td>
<td>4.32</td>
<td>100.83</td>
<td></td>
</tr>
</tbody>
</table>

* Abbreviated formulae of the synthetized crystallites; b cyanide content as calculated from the content of iron; c in the summation the water content as determined by TG analysis has been taken.

The total water content was determined by TG analysis performed with a Stanton model Standanta 6-25 instrument at a constant heating rate of 7.5 K min⁻¹. The water content in the crystallites themselves was determined by using the Perkin-Elmer DSC-13 device having an effluent analysis attachment. The water adsorbed on the surface has not been recorded since the device starts to operate at 303 K where the loosely bound water is leaving the system carried by the stream of argon. The results of chemical analyses are presented in Table I.

X-ray analyses

A Siemens-Kristalloflex 4 diffractometer with GM counter and CuKα (λ = 0.54178 nm) anticathode was used for the powder diffraction analyses. The results for the hydrated crystallites and calculated lattice parameters are listed in Table II.

IR analyses

IR spectra of synthetized crystallites were recorded on a Perkin-Elmer Model 457 instrument by using Nujol for sample preparation. Characteristic bands of asymmetric vibrations of the CN group for all types of synthetized crystallites are presented in Fig. 1.

Density of the crystallites

The samples are dehydrated in vacuum (pressure of 1 mPa) at 373 K. The density ρexp was determined by the picnometer method with benzene as the picnometer liquid. From the X-ray data the volume of u.c., V_u.c., and from chemical analysis the stoichiometric molecular weight, M, were derived. Taking the number n of molecules per u.c. as 4 it was possible to calculate the density ρcal of the crystallite as:

\[ \rho_{\text{cal}} = \frac{n M}{V_{\text{u.c.}} N_A} \]  

where \( N_A \) is the Avogadro number. The experimental and calculated values of density, as well as the number of molecules per u.c. calculated from ρexp are given in Table III.

3. Results and Discussion

Derived from the results (Table I to III) the compositions of the u.c. are as follows:

- (CoFC)Co : \( ([\text{Fe(CN)}_6\text{Co}]_4\text{Co}_4, 5.93 \text{ H}_2\text{O} \)
- (CoFC)Na : \( ([\text{Fe(CN)}_6\text{Co}]_4\text{Co}_4\text{Na}_4, 6.17 \text{ H}_2\text{O} \)
- (CoFC)K : \( ([\text{Fe(CN)}_6\text{Co}]_4\text{K}_8, 6.24 \text{ H}_2\text{O} \)
Fig. 1. IR absorption bands of asymmetric CN stretching vibrations for the synthetized crystallites: a) hydrated; b) dehydrated at 423 K. 1) (CoFC)Co; 2) (CoFC)Na; 3) (CoFC)K; 4) (CoFC)NH₄ and 5) (CoFC)Cs.

Table III. Densities of synthetized crystallites and number of stoichiometric molecules per unit cell (eq. (1)).

<table>
<thead>
<tr>
<th>Crystallite</th>
<th>( \rho_{\text{the}} ) g/cm³</th>
<th>( \rho_{\text{exp}} ) g/cm³</th>
<th>( V_{\text{u.c.}} \times 10^{-21} ) cm³</th>
<th>( n_{\text{exp}} ) per u.c.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CoFC)Co</td>
<td>1.71</td>
<td>1.69</td>
<td>1.280</td>
<td>3.95</td>
</tr>
<tr>
<td>(CoFC)Na</td>
<td>1.75</td>
<td>1.88</td>
<td>1.074</td>
<td>4.29</td>
</tr>
<tr>
<td>(CoFC)K</td>
<td>2.28</td>
<td>2.22</td>
<td>1.018</td>
<td>3.90</td>
</tr>
<tr>
<td>(CoFC)NH₄</td>
<td>1.86</td>
<td>1.83</td>
<td>1.030</td>
<td>3.83</td>
</tr>
<tr>
<td>(CoFC)Cs</td>
<td>3.24</td>
<td>3.03</td>
<td>1.099</td>
<td>3.73</td>
</tr>
</tbody>
</table>

a Calculated with lattice parameter for FCC structure (Table II).

\[
\text{(CoFC)NH₄} : \{[\text{Fe(CN)}₆\text{Co}_4]_8(\text{NH}_4)_8, 6.29 \text{ H}_2\text{O}
\]
\[
\text{(CoFC)Cs} : \{[\text{Fe(CN)}₆\text{Co}_4]_8\text{Cs}_8, 6.00 \text{ H}_2\text{O}
\]

if the results of DSC analysis are taken for the water content. A schematic diagram of u.c. of (CoFC)Co and (CoFC)M, where M = K, NH₄ and Cs is presented in Fig. 2.

Iron and cobalt, bound via a CN group, are located in the corners of the u.c. Iron is located in the octahedral cavity of carbon, whereas cobalt is located in that of nitrogen \([4, 11]\). Since the formal charge of iron amounts to \(-2\) and of the CN group to \(-1\) the internal space of the u.c. is negatively charged, which is compensated by the \(\text{Co}^{2+}\) or \(\text{K}^+\), \(\text{NH}_4^+\) and \(\text{Cs}^+\) ions. The cations situated in the channels of the u.c. (Fig. 2) are mobile and they are the only ones which take part in the ion exchange reactions. The water molecules occupy the rest of the crystal lattice and their number is about the same in all crystallites, i.e. 6 molecules per u.c.

The results of X-ray analyses (Table II) show that the crystallites of (CoFC)K, (CoFC)NH₄ and (CoFC)Cs have FCC structure, which agrees with the results of some other authors \([4, 5, 8]\). The lattice parameters of those crystallites increase with the increasing crystal radius of the monovalent cations. The crystallinity, however, decreases causing a decreasing number of lines in the diffractograms (Table II). This is due to the steric limitations of the crystal lattice, thus \(e.g., \text{Cs}^+\) ion, having a radius of 169 pm, probably leads to the collapse of the framework.

A number of authors \([3, 5, 6, 9, 13]\) found that the crystallites of the same chemical composition as (CoFC)Co have FCC structure, whereas the results in Table II point to a structure with a lower symmetry, \(e.g., \) a tetragonal lattice. The disagreement is most probably due to the different procedure of the synthesis of the crystallites. The authors mentioned above used \(\text{K}_4[\text{Fe(CN)}_6]\) or \(\text{Na}_4[\text{Fe(CN)}_6]\) for the precipitation of cobalt, whereas in the
present work $\text{H}_4[\text{Fe(CN)}_6]$ has been applied. From some of our earlier results [14] it follows that if $\text{K}_4[\text{Fe(CN)}_6]$ is used for precipitation of cobalt, the $\text{K}^+$ ions take place in the composition of crystallites, which even in the lowest concentration caused a transition from tetragonal into FCC structure. In the present experiments it has been shown that the presence of $\text{Na}^+$ together with $\text{Co}^{2+}$ in the reaction solution, during the precipitation procedure with $\text{H}_4[\text{Fe(CN)}_6]$, yields crystallites of a complex structure in which cobalt is partially replaced by $\text{Na}^+$ (Table II). In the diffractogram of these crystallites two types of lines are identified: the ones corresponding to the FCC and the others to the tetragonal structure. It appears therefore as most probable that the analyzed crystallites are a kind of a mixture of the FCC form having a composition of $[[\text{Fe(CN)}_6]\text{Co}]_4\text{Na}_8$ (the highest intensity lines in diffractogram) and the tetragonal $[[\text{Fe(CN)}_6]\text{Co}]_4\text{Co}_4$.

The IR absorption bands assigned to the asymmetric stretching vibrations of the CN group (Fig. 1 a, b) confirmed the results of X-ray analysis. The $\nu_{\text{CN}}$ bands of the (CoFC)M crystallites (M-monovalent cation) are almost symmetric and sharp whereas the (CoFC)Co band is complex and its splitting is even more visible after the dehydration of crystallites (Fig. 1 b). A similar behaviour is shown by $\text{K}_4[\text{Fe(CN)}_6]$ which has tetragonal structure [13]. Splitting of the $\nu_{\text{CN}}$ band is probably due to the lower symmetry of the unit cell caused by the localized influence of $\text{Co}^{2+}$ ions, which becomes more evident if the water has been removed from the crystallites (Fig. 2 a).

The distortion of FCC lattice into the tetragonal form of the (CoFC)Co crystallites can be explained by the Jahn-Teller steric effect. Ions $\text{Co}^{2+}$ which compensate the charge of the lattice are surrounded by water molecules as ligands with a weak interaction, thus their probable configuration of d-orbitals is $t_2^g e_g^2$, which is typical for tetrahedral fields. The octahedral field interaction from the CN ligand as well as the tetrahedral field from the water ligand most probably leads to the observed distortion of the lattice.

The structure of these crystallites has some similarities with zeolites; the selectivity for monovalent cations could therefore be explained by the “sieve” effect. It was therefore necessary to determine the effective radii of the “cages” (8 cages per u.c.) and also of their entrances.

In the hexacyanoferrate(II) complexes the CN group is ellipsoidal in form with an equatorial radius $r_{e,\text{CN}}$ of 178 pm [15] and polar radii $r_{p,\text{CN}}$ of 115 pm [6, 9]. It is also assumed in this consideration that the bond length of $\text{C}=\text{N}$ does not change considerably with changing the type of the ion to which it is bound. The equatorial radii $r_{e,\text{CN}}$ also represent the sphere of the CN group interaction out of the direction of the bond, thus forming a kind of window at the entrance to each “cage” (Fig. 3a).

The effective radii of those windows, $r_w$, are calculated according to

$$r_w = (a/2) - 2r_{e,\text{CN}}$$

where $a$ is the lattice parameter (Table II).

For the estimation of the effective radii of the “cage”, $r_{\text{ef}}$, the radii of partially hydrated mobile cations, $\bar{r}$, were taken into account, since their degree of hydration depends on the water content in the crystallites. To calculate the $\bar{r}$-values the Nightingale [16] equation has been used:

$$\bar{r} = r_e + (W/100)^{1/3}(r_h - r_e)$$

where $W$ is the water content in % as determined by the DSC analysis (Table I), $r_e$ the Pauling radii of the cation in the “cage” and $r_h$ the radii of the totally hydrated cations in the “cages”. The ef-
fective radii of the cages, \( r_{cg} \), are now calculated from

\[
    r_{cg} = 2 \bar{r}
\]

(4)

The calculated values for radii of partially hydrated ions, \( \bar{r} \), for effective radii of "cages" and for the ones of the windows are given in Table IV. The schematic diagram of one cage and its cross section is presented in Fig. 3a and b.

The crystallites (CoFC)Na due to their complex and scarcely defined structure were not considered in the present paper.

The structure model postulated has enabled us to explain the mechanism of ion exchange reactions as well as the selectivity of these inorganic ion-exchangers to monovalent cations, which is to be published soon.

Table IV. Effective radii of cages and windows in the hydrated crystallites.

<table>
<thead>
<tr>
<th>Crystallite</th>
<th>( r_a ) pm</th>
<th>( r_b ) pm</th>
<th>( \bar{r} ) pm</th>
<th>( r_{cg} ) pm</th>
<th>( r_w ) pm</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CoFC)Co</td>
<td>72</td>
<td>423</td>
<td>210</td>
<td>420</td>
<td>155 (257)c</td>
</tr>
<tr>
<td>(CoFC)K</td>
<td>133</td>
<td>331</td>
<td>215</td>
<td>430</td>
<td>147</td>
</tr>
<tr>
<td>(CoFC)NH₄</td>
<td>148</td>
<td>331</td>
<td>226</td>
<td>450</td>
<td>149</td>
</tr>
<tr>
<td>(CoFC)Cs</td>
<td>169</td>
<td>329</td>
<td>225</td>
<td>450</td>
<td>160</td>
</tr>
</tbody>
</table>

\( a \) Pauling radius; \( b \) ref. 17; \( c \) tetragonal structure causes two radii of the window as calculated from lattice parameters \( a \) and \( c \).