Dissolution of water-insoluble [Co(en)$_3$]$_2$I$_2$[Fe(CN)$_6$]·4.6H$_2$O in a saturated K$_4$[Fe(CN)$_6$] solution

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It has been shown for [Co(en)$_3$]$_2$I$_2$[Fe(CN)$_6$]·4.6H$_2$O as an example that a water-insoluble compound can be dissolved in an electrolyte solution containing ions common to both salts.

The precipitate formed upon mixing 0.1 M solutions of [Co(en)$_3$]I$_3$ (en = 1,2-diaminoethane) and K$_4$[Fe(CN)$_6$] is insoluble in water. However, it dissolves if an excess of solid K$_4$[Fe(CN)$_6$]·3H$_2$O is added to the system. Evaporation of this solution at 25 °C gives a crystalline mixture of K$_4$[Fe(CN)$_6$]·3H$_2$O and water-insoluble dark-orange [Co(en)$_3$]$_2$I$_2$[Fe(CN)$_6$]·4.6H$_2$O **1**. It was unexpected that the compound isolated was soluble in a potassium hexacyanoferrate solution, as, according to the law of mass action, the solubility of ionic compounds decreases in electrolyte solutions containing ions common to both salts. As an example, Figure 1 shows the calculated dependence of the solubility of poorly soluble compounds (in comparison with their solubility in 0.1 mol dm^{-3} KCl) on the concentration of KCl. However, it turned out that, as the charges of the ions contained in the reference electrolyte increase, significant changes in the activity factors[1] with an increase in the reference electrolyte concen-
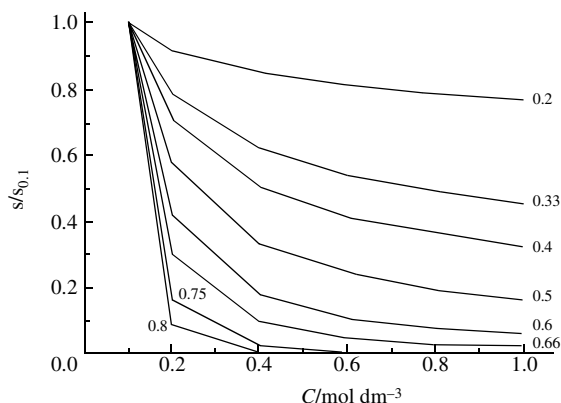
Figure 1 Dependence of the relative solubility of poorly soluble compounds on KCl concentration. The solubility of salts in 0.1 mol dm^{-3} KCl is taken as a measurement unit. The numbers at the curves indicate the molar fractions of the ions common to both salts.
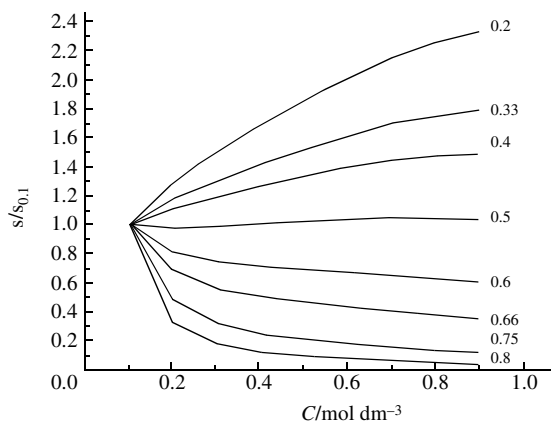
Figure 2 Dependence of the relative solubility of poorly soluble compounds on K$_4$[Fe(CN)$_6$] concentration. The solubility of salts in 0.1 mol dm^{-3} K$_4$[Fe(CN)$_6$] is taken as a measurement unit. The numbers at the curves indicate the molar fractions of the ions common to both salts.
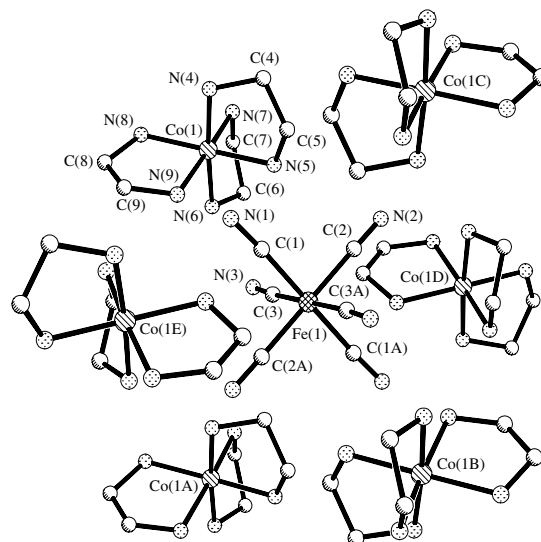
Figure 3 A fragment of the structure of compound **1**.

tration enable dissolution of weakly soluble compounds in solutions of reference electrolytes containing ions common to both salts. In fact, Figure 2 shows that the solubility of compounds in which the total molar fraction of K$^+$ and [Fe(CN)$_6$]$^{4-}$ ions (in the anhydrous compound) is less than 0.5 is higher in concentrated K$_4$[Fe(CN)$_6$] solutions than in dilute solutions. The fraction of these ions in compound **1** is as small as 0.2, which predefines its considerable solubility in saturated K$_4$[Fe(CN)$_6$] solutions.

The structure† of compound **1** is formed from [Fe(CN)$_6$]$^{4-}$ and [Co(en)$_3$]$^{3+}$ complex ions, iodide ions, and crystallisation

water molecules. The iodide ions and two of the three crystallo-graphically independent water molecules are disordered. The centrosymmetrical $[Fe(CN)_6]^{4-}$ complex is surrounded by six $[Co(en)_3]^{3+}$ complexes (Figure 3). The Fe–Co distances are 5.66–6.94 Å; the Co–Fe–Co angles range from 86.3 to 93.7°. All the eight compounds containing hexacyanometallate ions and octahedral complexes with polyamine ligands that we were able to find in the literature (only compounds with five-membered ethylenediamine bridges were considered) incorporated similar associates.[2–9] Because the $[M(CN)_6][M'(NR)_6]_6$ associate is present in crystal structures irrespective of the composition and stoichiometry of compounds, it should be regarded as a structure-forming unit in compounds of this type.

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