

# Dissolution of water-insoluble $[\text{Co}(\text{en})_3]_2\text{I}_2[\text{Fe}(\text{CN})_6]\cdot 4.6\text{H}_2\text{O}$ in a saturated $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution

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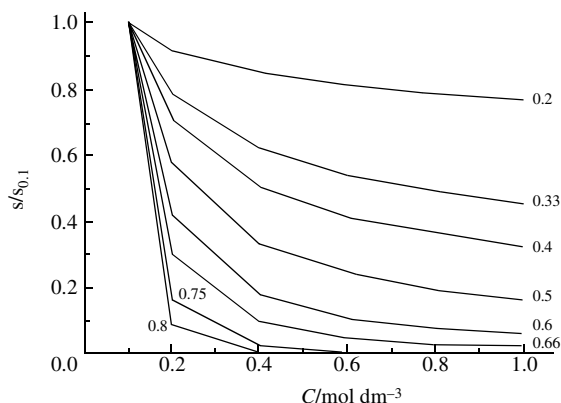
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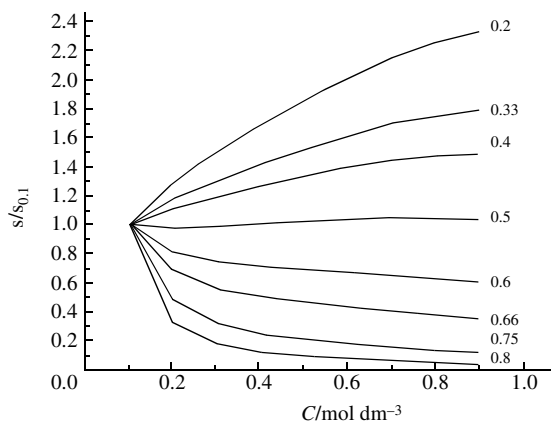
10.1070/MC2003v013n04ABEH001725

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

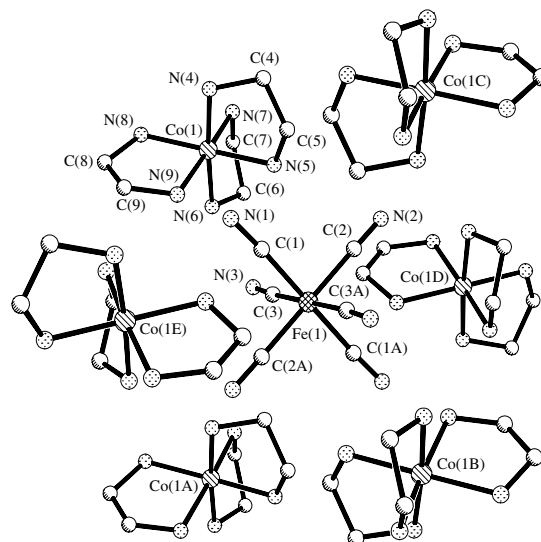
The precipitate formed upon mixing 0.1 M solutions of  $[\text{Co}(\text{en})_3]\text{I}_3$  ( $\text{en} = 1,2\text{-diaminoethane}$ ) and  $\text{K}_4[\text{Fe}(\text{CN})_6]$  is insoluble in water. However, it dissolves if an excess of solid  $\text{K}_4[\text{Fe}(\text{CN})_6]\cdot 3\text{H}_2\text{O}$  is added to the system. Evaporation of this solution at 25 °C gives a crystalline mixture of  $\text{K}_4[\text{Fe}(\text{CN})_6]\cdot 3\text{H}_2\text{O}$  and water-insoluble dark-orange  $[\text{Co}(\text{en})_3]_2\text{I}_2[\text{Fe}(\text{CN})_6]\cdot 4.6\text{H}_2\text{O}$  **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<sup>-3</sup> 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<sup>1</sup> 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<sup>-3</sup> 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  $\text{K}_4[\text{Fe}(\text{CN})_6]$  concentration. The solubility of salts in 0.1 mol dm<sup>-3</sup>  $\text{K}_4[\text{Fe}(\text{CN})_6]$  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  $\text{K}^+$  and  $[\text{Fe}(\text{CN})_6]^{4-}$  ions (in the anhydrous compound) is less than 0.5 is higher in concentrated  $\text{K}_4[\text{Fe}(\text{CN})_6]$  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  $\text{K}_4[\text{Fe}(\text{CN})_6]$  solutions.

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

<sup>†</sup> Crystal data for **1**.  $\text{C}_{18}\text{H}_{57.2}\text{Co}_2\text{FeI}_2\text{N}_{18}\text{O}_{4.6}$ ,  $M_r$  1027.13, monoclinic, space group  $P2_1/n$  (no. 14),  $a = 8.9293(17)$ ,  $b = 14.1970(18)$  and  $c = 15.016(2)$  Å,  $\beta = 98.26(2)^\circ$ ,  $V = 1883.8(5)$  Å<sup>3</sup>,  $Z = 2$ ,  $d_{\text{calc}} = 1.811$  g cm<sup>-3</sup>,  $F(000) = 1028$ . Crystal dimensions 0.3×0.3×0.3 mm. Data were recorded at 295 K on an Enraf Nonius CAD-4 diffractometer, MoK $\alpha$  radiation,  $\lambda = 0.71073$  Å. The intensities of 5005 reflections in the range  $1.98 < \theta < 25.98^\circ$  were measured ( $\omega/2\theta$  scan technique); 3687 unique reflections ( $R_{\text{int}} = 0.0342$ ) were used for the structure analysis. Empirical absorption correction via  $\psi$  scans was applied. The structure was solved by direct methods and refined by a least-squares method with anisotropic-isotropic (H atoms) approximation. Highest peak in final difference Fourier 1.308 eÅ<sup>-3</sup> (near water molecule). The final discrepancy factors were  $wR_2 = 0.1520$ ,  $R_1 = 0.1347$  (all data),  $wR_2 = 0.1242$ ,  $R_1 = 0.0478$  [2001 reflections with  $I > 2\sigma(I)$ ], GOF = 1.013 (227 parameters refined). All calculations were carried out using the SHELXS-97 and SHELXL-97 programs.<sup>10,11</sup>

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 217804. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2003.

water molecules. The iodide ions and two of the three crystallographically independent water molecules are disordered. The centrosymmetrical  $[\text{Fe}(\text{CN})_6]^{4-}$  complex is surrounded by six  $[\text{Co}(\text{en})_3]^{3+}$  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.<sup>2–9</sup> Because the  $[\text{M}(\text{CN})_6][\text{M}'(\text{NR})_6]_6$  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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