Outer-sphere anion–anion charge transfer in a solid hexacyanoferrate

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A solid solution based on $Cs_2Mg[Fe(CN)_6]$ containing both $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ ions exhibits a green colour associated with electronic absorption spectra bands due to the outer-sphere charge transfer between complex anions.

Aqueous solutions simultaneously containing the hexacyanoferrate ions $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ can exhibit a green colour, which was never observed in systems with only one of the ions. The electronic absorption spectra demonstrate[1] outer-sphere charge-transfer bands in the region 12000–12500 cm^{-1}. Inasmuch as the position and intensity of these bands depend on the type and concentration of alkali metal cations,[2] we can suggest that association of the anions results from cooperative interactions. Similar interactions were also observed in other anion–anion systems.[3–6] A comparative analysis of spectral and kinetic parameters of electron transfer for ionic associates in solutions containing K^+, $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ ions revealed[7] that the best results can be obtained at a contact distance between ions taken to be 6.9 Å. This value is close to the distance between iron atoms in the crystalline hexacyanoferrates $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]\cdot 3H_2O$.[8,9] This fact allowed us to expect that spectra of solid solutions containing hexacyanoferrate ions will also exhibit outer-sphere charge-transfer bands. We studied solid solutions based on caesium and magnesium hexacyanoferrates and related systems in order to find outer-sphere charge-transfer bands. We decided on these test materials because isostructural analogues of these compounds are known, for which the charges of complex ions differ by unity, for example, $Cs_2Mg[Fe(CN)_6]$–$Cs_2Li[Fe(CN)_6]$ and $KLa[Fe(CN)_6]\cdot 4H_2O$–$La[Fe(CN)_6]\cdot 5H_2O$.[10–13]

We obtained three compounds in the $Cs_2Mg[Fe(CN)_6]$–$Cs_2Li[Fe(CN)_6]$ system. By adding caesium chloride to a concentrated aqueous solution simultaneously containing lithium chloride and $K_3[Fe(CN)_6]$, a well crystallised orange precipitate was obtained. X-Ray diffraction data (Guignet monochromator; CuKα radiation, Ge standard) indicate that this compound is crystallised in the space group *Fm*3*m* with the lattice parameter a = 10.561(6) Å, which is consistent with the published data[11] for $Cs_2Li[Fe(CN)_6]$.

Upon the addition of a caesium chloride solution (0.1 mol dm^{-3}) to a solution containing $K_4[Fe(CN)_6]$ and $MgSO_4$ (0.1 mol dm^{-3} each), a poorly crystalline white precipitate was formed. After washing with water and acetone and drying in air, the precipitate became pale green. The compound crystallised in the space group *Fm*3*m*. The lattice parameter a = 10.396(3) Å was substantially lower than the published[12] value a = 10.446 Å for $Cs_2Mg[Fe(CN)_6]$. The IR spectrum (Nicolet-Magna 750, Nujol) of the compound in the region of 400–4000 cm^{-1} exhibited bands due to water molecules and sulfate anions in addition to the valence bands and bands of deformation vibrations for $Cs_2Mg[Fe(CN)_6]$[14] [Figure 1(*a*)]. According to the thermogravimetry data (TGD-7000, Ulvac Sinku-Riko), approximately 1.4 water molecules accounts for the formula unit $Cs_2Mg[Fe(CN)_6]$. The presence of water and sulfate ions in the isolated compound suggests that this compound is a solid solution in which a part of $[Fe(CN)_6]^{4-}$ ions in the $Cs_2Mg[Fe(CN)_6]$ matrix is displaced by sulfate ions. Moreover, the charge is compensated by the displacement of caesium ions in the tetrahedral lattice interstitials by water molecules. Additional water molecules enter the lattice ligand positions and saturate the coordination positions of magnesium ions.

Upon the addition of a caesium chloride (0.1 mol dm^{-3}) solution to a solution simultaneously containing lithium chloride (0.1 mol dm^{-3}), magnesium sulfate (0.1 mol dm^{-3}), $K_3[Fe(CN)_6]$ (0.05 mol dm^{-3}) and $K_4[Fe(CN)_6]$ (0.05 mol dm^{-3}), a lettuce-green precipitate was isolated. The colour of the precipitate remained unchanged after the addition of an alkali solution to the initial solution (alkalies usually destroy coloured bridge cyanide complexes). The compound crystallises in the space group *Fm*3*m*. The cubic lattice parameter a = 10.370(5) Å is substantially lower than that in two samples isolated earlier. Such a deviation from the Vegard law allowed us to assume that, during the formation of this compound, the substitution of $[Fe(CN)_6]^{3-}$ for $[Fe(CN)_6]^{4-}$

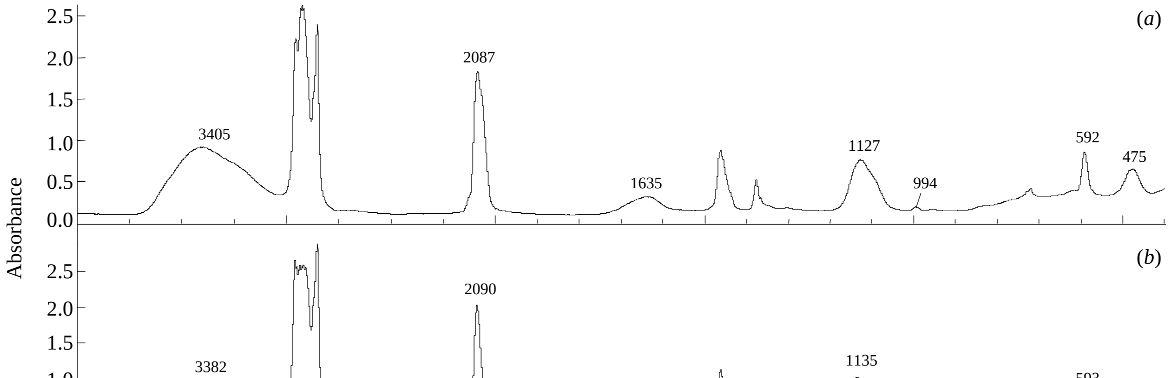

Figure 1 IR spectra of solid solutions based on $Cs_2Mg[Fe(CN)_6]$: (*a*) without $[Fe(CN)_6]^{3-}$ and (*b*) with $[Fe(CN)_6]^{3-}$.

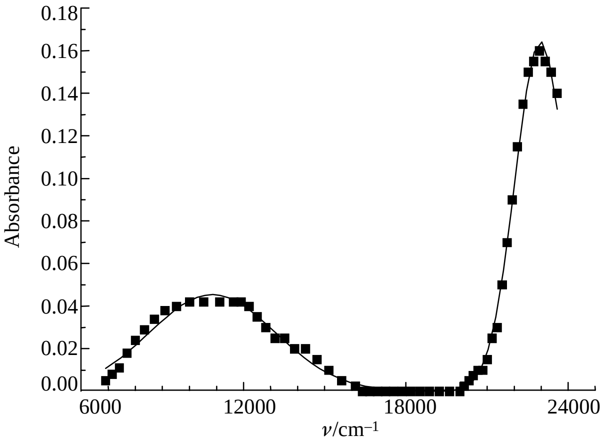

Figure 2 Difference electronic absorption spectrum of a solid solution based on $Cs_2Mg[Fe(CN)_6]$ with $[Fe(CN)_6]^{3-}$, as measured with reference to a sample without $[Fe(CN)_6]^{3-}$.

ions was accompanied by the displacement of caesium ions with water molecules rather than by the displacement of magnesium ions with lithium ions. Indeed, the removal of lithium ions from the initial solution had no effect on the colour and lattice parameters of the precipitate. The peak positions and intensities in the IR spectra of the isolated substance [Figure 1(*b*)] were consistent with the parameters of similar peaks for samples obtained in the absence of $[Fe(CN)_6]^{3-}$ ions. In accordance with the thermogravimetry data, approximately 1.5 water molecules account for the formula unit $Cs_2Mg[Fe(CN)_6]$. The diffuse reflection (Hitachi M 340) and electronic absorption spectra (Hitachi EPS 3T, Nujol, quartz substrate) of the solid solution exhibited additional bands in comparison with the spectrum of a Fe^{III}-free sample (Figure 2). The absorption band at 23000 cm^{-1} is associated with the $[Fe(CN)_6]^{3-}$ ion. The absorption at 11000 (absorption spectrum) or 10000 cm^{-1} (reflection spectrum) can be attributed to the outer-sphere charge transfer between the ions $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$. Note that the intensity ratio between the above bands in the difference spectrum is about 4, whereas the ratio between the molar absorption coefficients of $[Fe(CN)_6]^{3-}$ and the associate $[Fe(CN)_6]^{4-}$, nK^+, $[Fe(CN)_6]^{3-}$ is about 37 in aqueous solutions.[4] Probably, this is due to specific effects of the cationic composition and different Fe^{II}:Fe^{III} ratios in an aqueous solution (1:1)[4] and in a solid. The relative $[Fe(CN)_6]^{3-}$ content of the solid solution was estimated as 4–6% by comparing the absorbance of $[Fe(CN)_6]^{3-}$ under similar conditions. Hence, a $[Fe(CN)_6]^{3-}$ ion can be surrounded by up to eight $[Fe(CN)_6]^{4-}$ ions (the closest distance 7.33 Å). The conclusion concerning the predominance of Fe^{II} is consistent with the Mössbauer data for isolated compounds at 293 K (a ‘Perseus’ spectrometer with laser stabilization, control and calibration of the velocity; ^{57}Co source in chromium). The isomeric shift with reference to sodium nitroprusside and the width at half-height of the singlet signal for green samples are 0.175(2) and 0.285(3) mm s^{-1}, respectively. The analogous values for $Cs_2Li[Fe(CN)_6]$ are 0.120(2) and 0.257(3) mm s^{-1} and for a solid solution based on $Cs_2Mg[Fe(CN)_6]$ containing no $[Fe(CN)_6]^{3-}$, 0.179(2) and 0.321(7) mm s^{-1}, respectively.

The low concentration of $[Fe(CN)_6]^{3-}$ ions in the green solid solution is explained by a much lower solubility of Fe^{II} compounds as compared with Fe^{III} compounds. Indeed, an aqueous solution containing potassium hexacyanoferrate(III), magnesium sulfate and sodium chloride (0.1 mol dm^{-3} each) is stable in storage. A cyclic voltammogram [glassy carbon electrode, PI-50-1.1 potentiostat, cycling in the range $0 < E < 1.2$ V (SCE), scan rate 50 mV s^{-1}] exhibits a peak that corresponds to the reduction of complex ions in solution at $E = 0.2$ V. The peak corresponding to the oxidation of complex ions is shifted to $E = 0.7$ V (in the absence of magnesium and caesium salts, the corresponding current peak is observed at $E = 0.34$ V). In the first approximation, the voltammograms are reproducible in the first 10–12 cycles; this fact is probably associated with quasi-reversibility of the formation of insoluble films on the electrode during the reduction of the complex and the oxidative dissolution. However, the latter process is incomplete because, in the course of further cycling, the nonconductive film becomes thicker and can cause a substantial potential drop, which leads to a gradual smoothing and, ultimately, the complete disapperance of peaks. The lower the potential of the anodic cycling limit, the quicker the increase in the potential difference between the peaks and the greater their distortion.

The results obtained allowed us to expect the appearance of outer-sphere charge-transfer bands in the spectra of other systems similar in composition, for instance, in the $KLa[Fe(CN)_6]\cdot 4H_2O$–$La[Fe(CN)_6]\cdot 5H_2O$ system. However, upon the addition of lanthanum nitrate to solutions with the $K_3[Fe(CN)_6]$: $K_4[Fe(CN)_6]$ ratios 1:1 and 10:1, colourless precipitates were formed. According to the X-ray diffraction data, the unit-cell parameters of these compounds coincide with those of $KLa[Fe(CN)_6]\cdot 4H_2O$. The replacement of potassium by caesium in this system or of magnesium by calcium in the system studied earlier did not result in the formation of coloured precipitates. Taking into account similar contact distances between hexacyanoferrate ions in all of the isolated systems, we can conclude that two factors are responsible for the formation of coloured precipitates. The first factor is associated with different mutual solubilities of hexacyanoferrates. The second is determined by the arrangement of ions in solid solutions. Hexacyanoferrate ions are localised on the second-order axes with respect to one another only for the magnesium system in solid solutions with relatively high contents of different-valence ions. In such a mutual arrangement of complex ions, the overlap between the t_{2g} orbitals responsible for the electron transfer between ions was found to be maximum, and this is favourable for an increase in the intensity of charge-transfer bands.

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