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Outer-sphere association of hexacyanoferrate and nitrogen betaine anions

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The electronic spectrum of an aqueous solution of an equimolar mixture of nitrogen betaine (pK_1 = 1.72, pK_2 = 3.62) and hexacyanoferrate anions exhibited a charge-transfer band at 26100 cm^{-1}, which is indicative of the outer-sphere association of these ions.

The cations of aromatic nitrogen-containing heterocycles [such as methyl viologen (MV^{2+}) and pyridinium salts] are used as test materials in the studies of electron-transfer processes. Because the electron affinity of these cations is high, ion pairs with the participation of these cations exhibit absorption in the visible region of the electronic spectrum:[1,2]

$$\mathrm{MV^{2+} + [Fe(CN)_6]^{4-} = MV^{2+},[Fe(CN)_6]^{4-}}$$

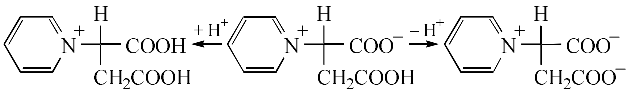
$$\mathrm{MV^{2+},[Fe(CN)_6]^{4-}} + h\nu \rightarrow \mathrm{MV^{+},[Fe(CN)_6]^{3-}}$$

It is well known that charge-transfer bands are characteristic of not only cation–anion associates but also anion–anion systems.[3,4] In these latter, the complex ions $[\mathrm{Fe(CN)_6}]^{3-}$, $[\mathrm{FeNO(CN)_5}]^{2-}$ or $[\mathrm{Co(edta)}]^{-}$ serve as electron acceptors. The contact between anions in these systems takes place by the cooperative interaction:

$$\mathrm{[Fe(CN)_6]^{3-}} + n\mathrm{K^+} + \mathrm{[Fe(CN)_6]^{4-}} = \mathrm{[Fe(CN)_6]^{3-}},n\mathrm{K^+},\mathrm{[Fe(CN)_6]^{4-}}$$

$$\mathrm{[Fe(CN)_6]^{3-}},n\mathrm{K^+},\mathrm{[Fe(CN)_6]^{4-}} + h\nu \rightarrow \mathrm{[Fe(CN)_6]^{4-}},n\mathrm{K^+},\mathrm{[Fe(CN)_6]^{3-}}$$

We examined the association of hexacyanoferrate(II) ions and the anions of a nitrogen betaine, 2-*N*-pyridiniumhydrosuccinate-1 **1**. Compound **1** was prepared according to the published procedure[5] by the reaction of pyridine with maleic acid in an aqueous solution (10 days at 20 °C).[†]



(**1** + H)$^+$ **1** (**1** – H)$^-$

The dissociation constants of protonated (**1** + H)$^+$ and neutral **1** forms of the nitrogen betaine were found by potentiometric titration[‡] (pK_1 = 1.72±0.05 and pK_2 = 3.62±0.05). Betaine anion (**1** – H)$^-$ is resistant to an excess of an alkali (pH 11) at 20 °C. This fact allowed us to examine its properties in aqueous solutions of compound **1** containing an excess of $\mathrm{K_2CO_3}$. Note that the potassium salt is more readily soluble in water than compound **1**, as evidenced by the ^{1}H NMR spectrum (in $\mathrm{D_2O}$) of the residue after evaporation of a solution of the potassium salt (*cf.* ref. 5). The electronic absorption spectrum[§] of (**1** – H)$^-$ exhibited a long-wavelength absorption band at 38300 cm^{-1} (ε = 3750 dm^3 mol^{-1} cm^{-1}) and no absorption in the visible and UV regions of the spectrum. Thus, the concentration can be varied over a wide range in the course of spectrophotometric measurements. The electronic absorption spectrum of an aqueous solution containing compound **1**, $\mathrm{K_4[Fe(CN)_6]\cdot 3H_2O}$ (0.06 mol dm^{-3} each) and an excess of $\mathrm{K_2CO_3}$ ($C_{\mathrm{K^+}}$ = 2 mol dm^{-3}) exhibited a broad band at 26100±100 cm^{-1} ($\nu_{1/2}$ = 4700±100 cm^{-1}), which was absent from the spectra of the initial components of the mixture. The 1:1 composition of the resulting complex was determined by the isomolar series method (Figure 1). The stability constant (0.54±0.06 mol dm^{-3} at $C_{\mathrm{K^+}}$ = 2.34 mol dm^{-3}) and the molar extinction coefficient at a band maximum (115±15 dm^3 mol^{-1} cm^{-1}) were calculated by the Benesi–Hildebrand method[6] (Figure 2). The molar extinction coefficient is close to the typical values of 150–200 dm^3 mol^{-1} cm^{-1} found for ion pairs of the hexacyanoferrate ion with N-heterocyclic cations.[1] The stability constant of the complex formed is close to 0.05–0.3 dm^3 mol^{-1}, which is characteristic of outer-sphere anion–anion associates.[3,4] Thus, the

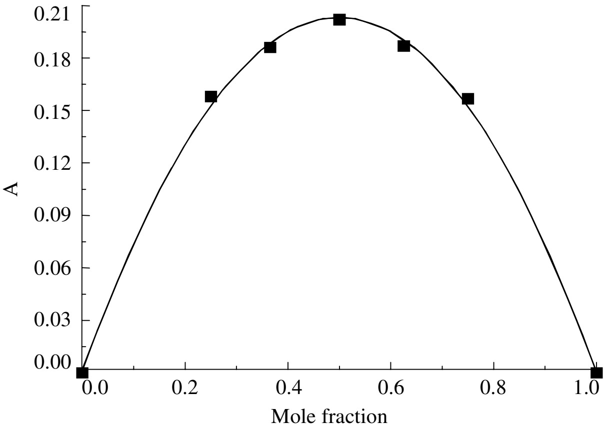


Figure 1 Absorbance of the anion–anion complex (**1** – H)$^-$,$n\mathrm{K^+}$,$\mathrm{[Fe(CN)_6]^{4-}}$ at ν = 25000 cm^{-1} as a function of the mole fraction of (**1** – H)$^-$. $C_{(1\text{-H})}$ + + $C_{\mathrm{Fe(CN)_6}}$ = 0.12 mol dm^{-3}, C_{K} = 2 mol dm^{-3}.

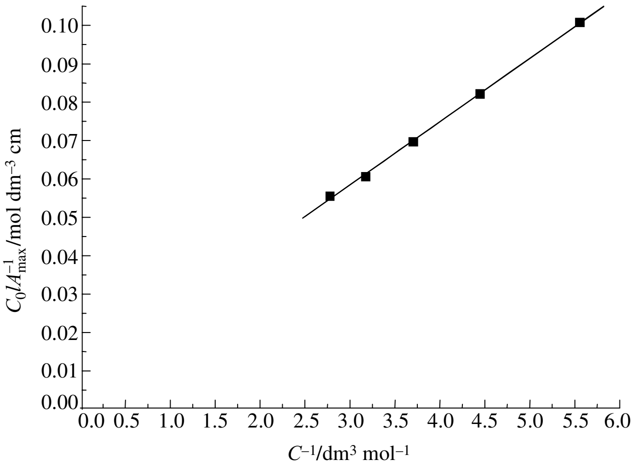


Figure 2 Absorbance of the anion–anion complex (**1** – H)$^-$,$n\mathrm{K^+}$,$\mathrm{[Fe(CN)_6]^{4-}}$ as a function of the concentration of (**1** – H)$^-$ in the Benesi–Hildebrand equation coordinates. $C_{\mathrm{Fe(CN)_6}}$ = 0.12 mol dm^{-3}, C_{K} = 2.34 mol dm^{-3}.

[†] **1**: yield 85%, mp 214 °C. ^{1}H NMR ($\mathrm{D_2O}$) δ: 3.43 (m, 2H, $\mathrm{CH_2}$, $\mathrm{ABX_3}$ spectrum, $\Delta\nu$ 68.0 Hz, $^3J_{\mathrm{AX}}$ 9.9 Hz, $^3J_{\mathrm{BX}}$ 4.4 Hz, $^2J_{\mathrm{AB}}$ –18.0 Hz), 5.64 (dd, 1H, CH), 8.02 (dd, 2H, 2β-H, ^3J 6.1 Hz, ^3J 7.8 Hz), 8.52 (t, 1H, γ-H, ^3J 7.8 Hz) 8.88 (d, 2H, 2α-H, ^3J 6.1 Hz). Found (%): N, 7.10, 7.20. Calc. for $\mathrm{C_9H_9O_4N}$ (%): N, 7.18.
The ^{1}H NMR spectra were measured on a Bruker WM-400 spectrometer. $\mathrm{K_4[Fe(CN)_6]\cdot 3H_2O}$ and other chemicals were of reagent grade.

[‡] The potentiometric titration of a 0.1 M solution of compound **1** and its mixture with 0.1 M HCl was performed using a 0.1 M NaOH solution and a Mettler Delta 340 pH-meter with a combined pH electrode.

[§] The electronic absorption spectra were measured on a Cary 100 spectrophotometer (Varian) in the frequency range 20000–50000 cm^{-1} at 25 °C using quartz cuvettes with an optical path length of 1 cm. The absorption bands were approximated by Gaussian functions.

observed absorption band can be reliably attributed to the outer-sphere charge transfer between the anions:

$$(\mathbf{1} - \mathrm{H})^- + n\mathrm{K}^+ + [\mathrm{Fe(CN)}_6]^{4-} = (\mathbf{1} - \mathrm{H})^-,n\mathrm{K}^+,[\mathrm{Fe(CN)}_6]^{4-}$$
$$(\mathbf{1} - \mathrm{H})^-,n\mathrm{K}^+,[\mathrm{Fe(CN)}_6]^{4-} + h\nu \rightarrow (\mathbf{1} - \mathrm{H})^{2-},n\mathrm{K}^+,[\mathrm{Fe(CN)}_6]^{3-}$$

The position of the charge-transfer band maximum in the test associate at the boundary between the visible and UV regions of the spectrum indicates that the electron affinity of nitrogen betaine anion $(\mathbf{1} - \mathrm{H})^-$ is lower than that of N-heterocyclic cations, which were studied previously.[1] The absorption bands of the ion pairs of these N-heterocyclic cations with $[\mathrm{Fe(CN)}_6]^{4-}$ lie in the visible region of the spectrum, and the electron affinity is 2.8–3.5 eV, as estimated according to ref. 7. An analogous estimation gave a value of 2.5 eV for $(\mathbf{1} - \mathrm{H})^-$.

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