

# Outer-sphere association of hexacyanoferrate and nitrogen betaine anions

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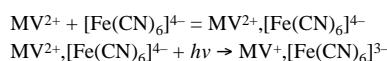
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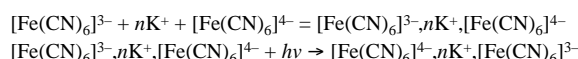
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The electronic spectrum of an aqueous solution of an equimolar mixture of nitrogen betaine ( $pK_1 = 1.72$ ,  $pK_2 = 3.62$ ) and hexacyanoferrate anions exhibited a charge-transfer band at  $26100\text{ cm}^{-1}$ , which is indicative of the outer-sphere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

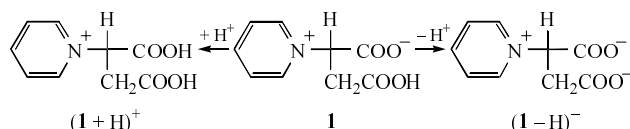
The cations of aromatic nitrogen-containing heterocycles [such as methyl viologen ( $MV^{2+}$ ) and pyridinium salts] are used as test materials in the studies of electron-transfer processes. Because the electron affinity of these cations is high, ion pairs with the participation of these cations exhibit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



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



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<sup>5</sup> by the reaction of pyridine with maleic acid in an aqueous solution (10 days at  $20^\circ\text{C}$ ).<sup>†</sup>



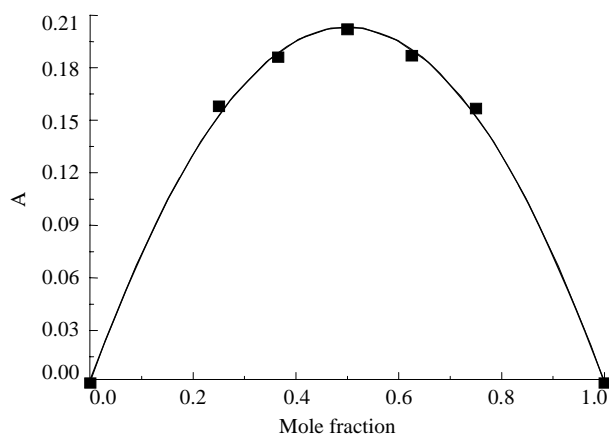
The dissociation constants of protonated  $(1 + H)^+$  and neutral **1** forms of the nitrogen betaine were found by potentiometric titration<sup>‡</sup> ( $pK_1 = 1.72 \pm 0.05$  and  $pK_2 = 3.62 \pm 0.05$ ). Betaine anion  $(1 - H)^-$  is resistant to an excess of an alkali (pH 11) at  $20^\circ\text{C}$ . This fact allowed us to examine its properties in aqueous solutions of compound **1** containing an excess of  $K_2CO_3$ . Note that the potassium salt is more readily soluble in water than compound **1**, as evidenced by the  $^1\text{H}$  NMR spectrum (in  $D_2O$ ) of the residue after evaporation of a solution of the potassium salt (*cf.* ref. 5). The electronic absorption spectrum<sup>§</sup> of  $(1 - H)^-$  exhibited a long-wavelength absorption band at  $38300\text{ cm}^{-1}$  ( $\epsilon = 3750\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ ) 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 measure-

<sup>†</sup> **1**: yield 85%, mp  $214^\circ\text{C}$ .  $^1\text{H}$  NMR ( $D_2O$ )  $\delta$ : 3.43 (m, 2H,  $CH_2$ , ABX<sub>3</sub> spectrum,  $\Delta\nu$  68.0 Hz,  $^3J_{AX}$  9.9 Hz,  $^3J_{BX}$  4.4 Hz,  $^2J_{AB}$  -18.0 Hz), 5.64 (dd, 1H, CH), 8.02 (dd, 2H, 2 $\beta$ -H,  $^3J$  6.1 Hz,  $^3J$  7.8 Hz), 8.52 (t, 1H,  $\gamma$ -H,  $^3J$  7.8 Hz) 8.88 (d, 2H, 2 $\alpha$ -H,  $^3J$  6.1 Hz). Found (%): N, 7.10, 7.20. Calc. for  $C_9H_9O_4N$  (%): N, 7.18.

The  $^1\text{H}$  NMR spectra were measured on a Bruker WM-400 spectrometer.  $K_4[Fe(CN)_6] \cdot 3H_2O$  and other chemicals were of reagent grade.

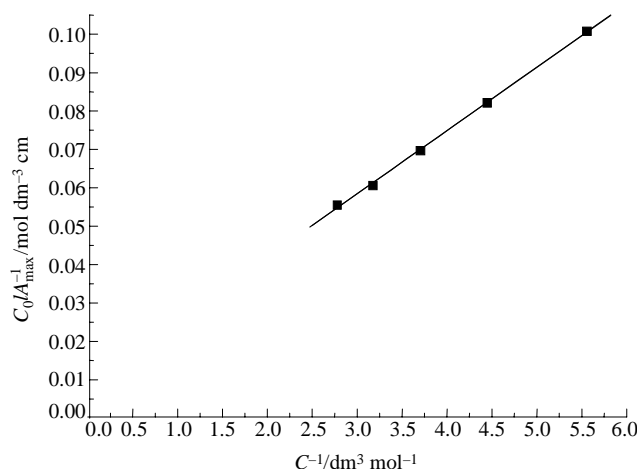
<sup>‡</sup> The potentiometric titration of a 0.1 M solution of compound **1** and its mixture with 0.1 M HCl was performed using a 0.1 M NaOH solution and a Mettler Delta 340 pH-meter with a combined pH electrode.

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



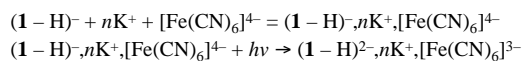
**Figure 1** Absorbance of the anion–anion complex  $(1 - H)^-,nK^+,[Fe(CN)_6]^{4-}$  at  $\nu = 25000\text{ cm}^{-1}$  as a function of the mole fraction of  $(1 - H)^-$ .  $C_{(1-H)} + C_{Fe(CN)_6} = 0.12\text{ mol dm}^{-3}$ ,  $C_K = 2\text{ mol dm}^{-3}$ .

ments. The electronic absorption spectrum of an aqueous solution containing compound **1**,  $K_4[Fe(CN)_6] \cdot 3H_2O$  ( $0.06\text{ mol dm}^{-3}$  each) and an excess of  $K_2CO_3$  ( $C_{K^+} = 2\text{ mol dm}^{-3}$ ) exhibited a broad band at  $26100 \pm 100\text{ cm}^{-1}$  ( $\nu_{1/2} = 4700 \pm 100\text{ cm}^{-1}$ ), 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 ( $0.54 \pm 0.06\text{ mol dm}^{-3}$  at  $C_{K^+} = 2.34\text{ mol dm}^{-3}$ ) and the molar extinction coefficient at a band maximum ( $115 \pm 15\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ ) were calculated by the Benesi–Hildebrand method<sup>6</sup> (Figure 2). The molar extinction coefficient is close to the typical values of  $150\text{--}200\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$  found for ion pairs of the hexacyanoferrate ion with N-heterocyclic cations.<sup>1</sup> The stability constant of the complex formed is close to  $0.05\text{--}0.3\text{ dm}^3\text{ mol}^{-1}$ , which is characteristic of outer-sphere anion–anion associates.<sup>3,4</sup> Thus, the



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

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



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  $(\mathbf{1}-\text{H})^-$  is lower than that of N-heterocyclic cations, which were studied previously.<sup>1</sup> The absorption bands of the ion pairs of these N-heterocyclic cations with  $[\text{Fe}(\text{CN})_6]^{4-}$  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  $(\mathbf{1}-\text{H})^-$ .

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