

Ion pairs in the crystal structure of potassium ethyl viologen hexacyanometallates(II)

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The isostructural potassium ethyl viologen hexacyanometallates $\text{EV}_{1.5}\text{K}[\text{M}(\text{CN})_6]\cdot 12.5\text{H}_2\text{O}$ (EV^{2+} is *N,N'*-diethyl-4,4'-bipyridinium, $\text{M} = \text{Fe}$ or Ru) were prepared and characterised.

The reactions between *N,N'*-dialkyl-4,4'-bipyridinium cations (alkyl viologens) and the hexacyanoferrate(II) ion in aqueous solutions result in the formation of ion pairs and are accompanied by the appearance of an absorption band at 18000–20000 cm^{-1} in the electronic absorption spectra.^{1–3} Meyer and co-authors² calculated the rate of the redox reaction between ions using the spectral characteristics of the absorption band and the electron-transfer distance estimated from the ionic radii. However, published data^{1–3} on the spectroscopic and geometric characteristics of ion pairs are inconsistent. The stability constants of ion pairs and structural data are commonly used for evaluating the electron-transfer distance in ion pairs. Contact distances between ions in the test systems are difficult to calculate from the stability constants and erroneous results can be obtained because the ions are non-spherical. The compound $\text{MV}_2[\text{Fe}(\text{CN})_6]\cdot 7\text{H}_2\text{O}$ (MV^{2+} is methyl viologen) was isolated;¹ however, its structure was not examined. In this work, we studied the structure and spectroscopic properties of nearest analogues of this compound.

Compounds $\text{EV}_{1.5}\text{K}[\text{Fe}(\text{CN})_6]\cdot 12.5\text{H}_2\text{O}$ **1** and $\text{EV}_{1.5}\text{K}[\text{Ru}(\text{CN})_6]\cdot 12.5\text{H}_2\text{O}$ **2** are intensely coloured compounds.[†] Their diffusion-reflectance spectra (Figure 1) exhibit charge-transfer bands at 18300 (**1**) and 22900 cm^{-1} (**2**). In the spectra of aqueous solutions containing viologen diiodide (0.01 mol dm^{-3}) and potassium hexacyanometallates (0.1 mol dm^{-3}), analogous band maxima are at 19200 (**1**) and 23500 cm^{-1} (**2**). This fact allowed us to conclude that the structures of ion pairs in solution and in crystals are similar.

In the crystal structures of **1**[‡] and **2**,[§] ethyl viologen cations form the walls of channels in which hydrogen-bonded water molecules and $\text{K}(\text{H}_2\text{O})_3[\text{M}(\text{CN})_6]$ units are arranged alternately (Figure 2). The shortest distances between *d*-metal atoms are

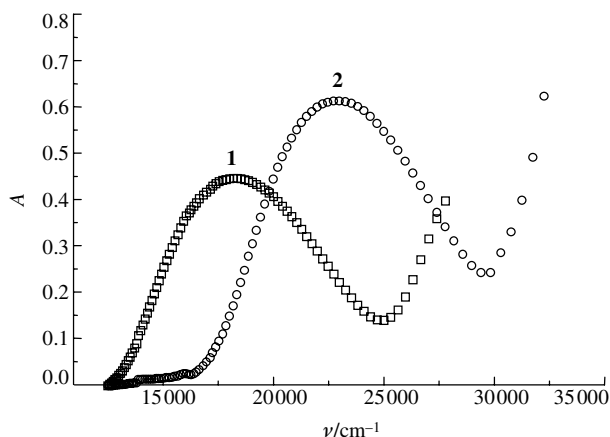


Figure 1 Diffuse-reflectance spectra of compounds **1** and **2**.

[†] The compounds $\text{EV}_{1.5}\text{K}[\text{M}(\text{CN})_6]\cdot 12.5\text{H}_2\text{O}$ ($\text{M} = \text{Fe}$ or Ru for **1** or **2**, respectively) were isolated by the isothermal ($T = 277$ K) evaporation of solutions of ethyl viologen diiodide (Aldrich) and potassium hexacyanoferrate (analytical grade) or potassium hexacyanoruthenate (Alfa) in the 1:1 molar ratio.

8.81 and 8.89 Å for **1** and **2**, respectively. The $[\text{M}(\text{CN})_6]^{4-}$ ion is surrounded with six ethyl viologen cations. The distances between *d*-metal atoms and nitrogen atoms of the pyridine rings of viologen are 5.05 (Å) and 5.40 Å (B) for **1** or 5.07 (Figure 3, A) and 5.45 Å (Figure 3, B) for **2**. The distances from metal atoms to the centres of pyridine rings are 5.96 (Figure 3, A) and 5.62 Å (Figure 3, B) for **1** or 5.99 (Figure 3, A) and 5.67 Å (Figure 3, B) for **2**. The above crystallographic distances are much shorter than the distances between ions in the ion pair $\text{MV}^{2+}[\text{Fe}(\text{CN})_6]^{4-}$ estimated at 6.3–8.1² or 10.4 Å,³ on the basis of the hexacyanoferrate ion radius 4.4–4.6 Å with respect to the fourfold axis of an octahedral complex.^{2,3} Previously,^{4,5} it was found that the effective radius of hexacyanoferrate ions with respect to the twofold axis of an octahedral complex, which is aligned with the direction of t_{2g} orbitals participating in electron

[‡] Crystallographic data for **1**: $\text{C}_{27}\text{H}_{52}\text{FeKN}_9\text{O}_{12.5}$, $M = 797.73$, trigonal, space group $P\bar{3}c1$ (no. 165), $a = 15.0433(14)$, $c = 20.853(5)$ Å, $V = 4086.8(11)$ Å³, $Z = 4$, $d_{\text{calc}} = 1.297$ g cm^{-3} , $F(000) = 1688$. Crystal size 0.20×0.20×0.10 mm. Experiments were performed on an Enraf Nonius CAD-4 diffractometer using $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å) and 294 K. The intensities of 3965 reflections were measured within the range $1.56 < \theta < 25.96^\circ$ ($\omega/2\theta$ scan); 2683 independent reflections were used in the calculations ($R_{\text{int}} = 0.0356$). The crystal was not decomposed in the course of experiments (the intensities of reference reflections decreased by 2.1%); absorption was not taken into account (minimum and maximum transmission was 0.90 and 0.95, respectively). The structure was solved by a direct method and refined by the least-squares technique in an anisotropic-isotropic approximation (H atoms). The maximum electron density peak in the zero Fourier synthesis was 0.481 e Å⁻³ (near a disordered water molecule). The final refinement parameters: $wR_2 = 0.1830$, $R_1 = 0.1587$ (all reflections), $wR_2 = 0.1418$, $R_1 = 0.0529$ [1270 reflections with $I > 2\sigma(I)$], $\text{GOF} = 1.013$ (193 refinement parameters). All calculations were performed using the SHELXS-97 and SHELXL-97 programs.^{7,8}

[§] Crystallographic data for **2**: $\text{C}_{27}\text{H}_{52}\text{RuKN}_9\text{O}_{12.5}$, $M = 842.95$, trigonal, space group $P\bar{3}c1$ (no. 165), $a = 15.1572(17)$, $c = 20.956(5)$ Å, $V = 4169.4(12)$ Å³, $Z = 4$, $d_{\text{calc}} = 1.343$ g cm^{-3} , $F(000) = 1760$. Crystal size 0.15×0.15×0.09 mm. Experiments were performed on an Enraf Nonius CAD-4 diffractometer using $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å) and 294 K. The intensities of 8227 reflections were measured within the range $1.55 < \theta < 28.01^\circ$ ($\omega/2\theta$ scan); 3356 independent reflections were used in the calculations ($R_{\text{int}} = 0.0911$). The crystal was not decomposed in the course of experiments (the intensities of reference reflections decreased by 3.1%); ψ -correction of the reflection array was performed (minimum and maximum transmission was 0.79 and 0.95, respectively). As a starting approximation in the refinement, the model of **1** was taken (without oxygen atoms of crystal water molecules). The refinement was performed by the least-squares technique in an anisotropic-isotropic approximation (H atoms). The maximum electron density peak in the zero Fourier synthesis was 1.004 e Å⁻³ (near a disordered water molecule). The final refinement parameters: $wR_2 = 0.1645$, $R_1 = 0.0990$ (all reflections), $wR_2 = 0.1438$, $R_1 = 0.0519$ [2035 reflections with $I > 2\sigma(I)$], $\text{GOF} = 1.058$ (185 refinement parameters). All calculations were performed using the SHELXL-97 program.⁸ Atomic coordinates, bond lengths, bond angles and thermal parameters for compounds **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2001. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/76.

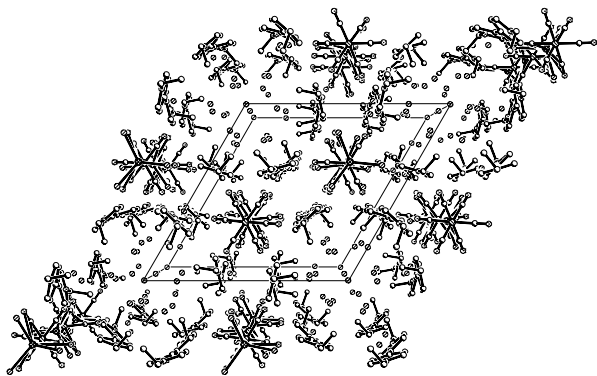


Figure 2 Projection of the structure of **1** along the z -axis.

transfer, is 3.4–3.7 Å. The effective radius of hexacyanoferrate ions with respect to the threefold axis of an octahedral complex can be estimated at 2.7 Å from the shortest distance between ions in the $\text{K}(\text{H}_2\text{O})_3[\text{Fe}(\text{CN})_6]$ unit taking the potassium ion radius to be equal to 1.38 Å (Figure 4). The above distances between EV^{2+} and $[\text{M}(\text{CN})_6]^{4-}$ ions lie between minimally and maximally possible values and are consistent with the fact that ethyl viologen ions are located in general positions.

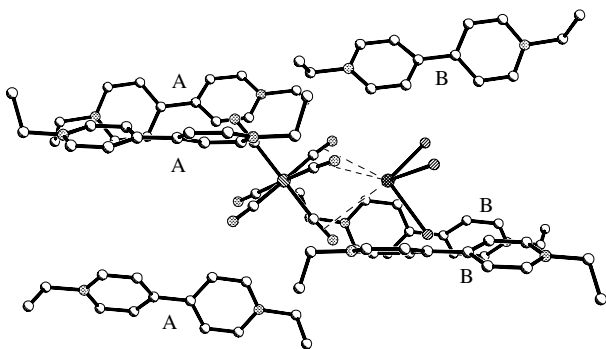


Figure 3 Structure fragment of **1**.

The structure of a $\text{K}(\text{H}_2\text{O})_3[\text{Fe}(\text{CN})_6]$ unit, in which potassium ions are coordinated to three cyanide ligands (Figure 4; $\text{N}(1)\text{--K}(1)$, 3.218(4) Å; $\text{C}(1)\text{--K}(1)$, 3.302(4) Å), is similar to the structure of the contact ion pair $\text{K}^+[\text{Fe}(\text{CN})_6]^{4-}$. This is supported by the similarity of the shortest distance 4.07 Å between ions with a value of 4.3 ± 0.1 Å derived from the thermodynamic stability constant of an ion pair.⁶ The structure of a doubled $\text{K}(\text{H}_2\text{O})_3[\text{Fe}(\text{CN})_6]$ unit makes it possible to estimate the distance between K^+ and $[\text{Fe}(\text{CN})_6]^{4-}$ ions in a solvent-separated ion pair at 6.35 Å. In this case, hexacyanoferrate ions are

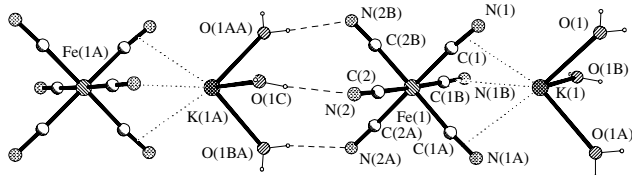


Figure 4 Chains of the $\text{K}(\text{H}_2\text{O})_3[\text{Fe}(\text{CN})_6]$ ion pairs in the structure of **1**.

hydrogen-bonded to water molecules of a hydrated potassium cation [Figure 4; $\text{O}(1\text{C})\cdots\text{N}(2)$, 2.895(6) Å]. Taking into account that the above value is close to 6.6 ± 0.2 Å found⁶ from the thermodynamic stability constant of the ion pair $\text{K}^+[\text{Fe}(\text{CN})_6]^{3-}$, we may believe that ions in this ion pair are separated by water molecules.

In the structures of **1** and **2**, $[\text{M}(\text{CN})_6]^{4-}$ ions exhibit C_3 symmetry. The geometry parameters of two crystallographically independent cyanide ligands differ from one another [$\text{C}(1)\text{--N}(1)$ 1.149(5) and 1.144(5) Å, $\text{M}(1)\text{--C}(1)$ 1.928(5) and 2.039(4) Å, $\text{M}(1)\text{--C}(1)\text{--N}(1)$ 174.6(4)° and 175.6(3)°; $\text{C}(2)\text{--N}(2)$ 1.171(5) and 1.152(5) Å, $\text{M}(1)\text{--C}(2)$ 1.910(5) and 2.030(4) Å, $\text{M}(1)\text{--C}(2)\text{--N}(2)$ 177.5(4)° and 177.9(3)° for **1** and **2**, respec-

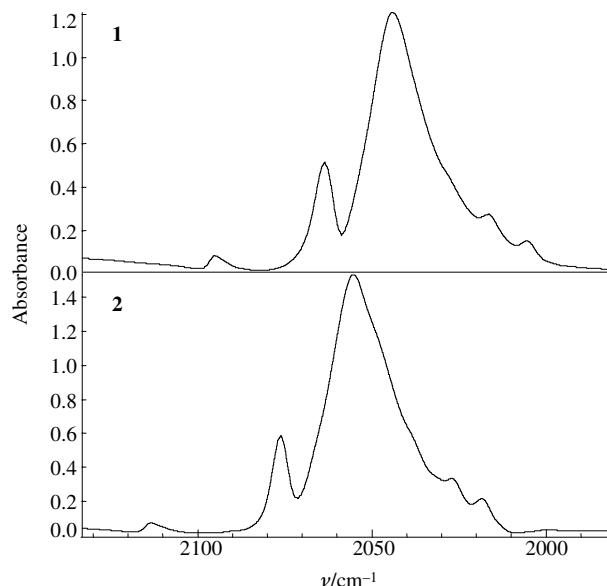


Figure 5 IR spectra of **1** and **2** in the region of ν_{CN} stretching vibrations.

tively]. The low symmetry of $[\text{M}(\text{CN})_6]^{4-}$ ions in crystals results in an increase in the number of active ν_{CN} vibrations in the IR spectra (Figure 5).[†] The free $[\text{M}(\text{CN})_6]^{4-}$ ion having O_h symmetry should exhibit only a single ν_{CN} band due to threefold degenerate F_{1u} vibrations. The correlation diagram that describes a change in the vibrational spectra in the ν_{CN} frequency region on going from an isolated ion to an ion in a crystal cell with C_3 site symmetry of anions for the D_{3d} group suggests that the spectra of a crystal should exhibit six ($2A_{2u} + 4E_u$) bands, and these bands were observed in the measured spectra.

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[†] The IR spectra of samples as Vaseline oil mulls were measured on a Nicolet Magna-750 Fourier spectrometer with a resolution of 2 cm^{-1} . The computer deconvolution of a spectrum on a mixed-contour (Gaussian + Lorentzian) basis revealed six components with frequencies of 2094, 2064, 2045, 2031, 2015 and 2005 cm^{-1} for **1** and 2113, 2076, 2055, 2040, 2027 and 2018 cm^{-1} for **2**.