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Infrared Spectroscopic Study on Ion Association of Hexacyanoferrate(III) and Hexacyanoferrate(II) Ions

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The ion association of hexacyanoferrate(III) and hexacyanoferrate(II) anions with univalent or bivalent cations in aqueous solutions has been studied by the measurement of the infrared absorption band due to the C≡N stretching vibrations. All the solutions measured in which ion-pairs with hexacyanoferrates(III) predominated gave an absorption maximum at 2121 cm^{-1}, and those in which ion-pairs with hexacyanoferrates(II) predominated, at 2020 cm^{-1}, although hexacyanoferrates(III) and hexacyanoferrates(II) of potassium and alkaline earth metals gave different spectra from each other in solid state. No difference in absorption band obtained with different solutions was supported by the distance between two ions in ion-pair, which was estimated from the structures of hexacyanoferrate(III) and hexacyanoferrate(II) ions and the closest approach of the ion-pair; this indicates that there is no direct interaction between the complex anion and the cation, but one or more water molecules interpose between the two ions.

A number of investigations on ion-pair formation in solutions have been made by the conductometric method, but only a few, by the measurements of Raman and infrared spectra. Hester and Plane(1) measured Raman spectra of aqueous solutions of some metal nitrates, sulfates and perchlorates and discussed on the interionic (inner-sphere) association of metal ions with these anions from the change in the symmetry and the force constant estimated from the Raman spectra. Fronaeus and Larsson(2,3) obtained infrared spectra of some metal thiocyanato complexes both in solution and in solid state and correlated the changes in absorption frequency and intensity with the structure and the bonding characteristics of the complexes. Larsson studied(4) also on the infrared spectra of hexamminecobalt(III) ions in aqueous solutions of some electrolytes in order to know of the kind of the bonding forces of the outer-sphere complexes.

This investigation was undertaken for the purpose of obtaining some information of the bonding character of the outer-sphere ion association of hexacyanoferrate(III) and hexacyanoferrate-(II) ions with univalent and bivalent cations.

Experimental

Materials.—Magnesium, calcium and barium hexacyanoferrates(III) were prepared from potassium hexacyanoferrate(III) by the following procedure. More than three equivalents of perchloric acid was

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1) R. E. Hester and R. A. Plane, *Inorg. Chem.*, **3**, 769 (1964).

2) S. Fronaeus and R. Larsson, *Acta Chem. Scand.*, **16**, 1433 (1962).

3) S. Fronaeus and R. Larsson, ibid., **16**, 1447 (1962).

4) R. Larsson, ibid., **16**, 2460 (1962).

TABLE I. WAVE NUMBERS OF ABSORPTION BAND DUE TO THE C≡N STRETCHING VIBRATION OF AQUEOUS SOLUTIONS OF POTASSIUM HEXACYANOFERRATE(III) OF VARIOUS CONCENTRATIONS

Concn. of $K_3[Fe(CN)_6]$ added, mol./l.	K_c	Concn. of $K^+[Fe(CN)_6]^{3-}$, mol./l.	Degree of ion-pair formation, %	Wave number of $\nu_{C≡N}$, cm^{-1}
0.02	7.0	0.006	30	2121
0.05	5.1	0.02	43	2121
0.10	4.5	0.06	57	2121
0.25	4.5	0.19	78	2121
1.00	4.5	0.93	93	2121

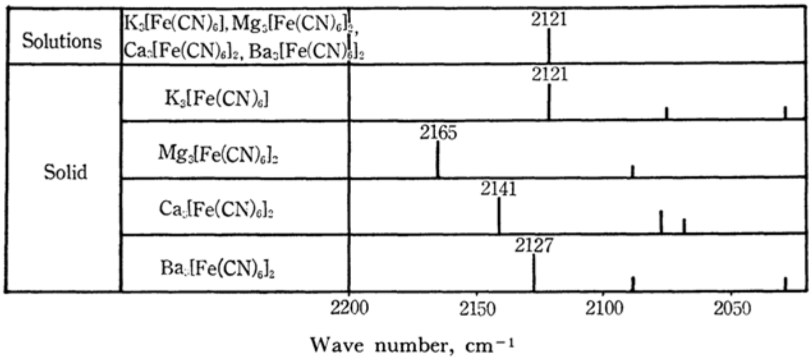

Fig. 1. Wave numbers of the absorption bands of hexacyanoferrates(III) in aqueous solution and in solid state. Solutions contain each complex by 0.02 M up to saturation. For solid state, crystalline water is not described.

added to one equivalent of potassium hexacyanoferrate(III) to precipitate potassium perchlorate. The solution of hydrogen hexacyanoferrate(III) thus obtained was neutralized with magnesium hydroxide, and then magnesium hexacyanoferrate(III) was precipitated by the addition of magnesium chloride in excess. Calcium and barium hexacyanoferrates(III) were prepared in the same way. All the materials obtained were recrystallized three times from water and washed by water, ethanol and ether. Calcium hexacyanoferrate(II) was obtained from potassium hexacyanoferrate(II) in a similar way.

Measurements of Infrared Spectra.—Infrared spectra were measured by using a Hitachi EPI-2G infrared spectrophotometer equipped with a potassium bromide foreprism and a grating double monochrometer. Cells with windows of sodium chloride and those of calcium fluoride were used. In the former case, polyethylene pouch was used to prevent the dissolution of the window material. Platinum foil of 0.05 mm. thick was used for a spacer. Infrared spectra of solid samples were measured by the potassium bromide disk method and the Nujol mull method. The spectra were precisely recorded in the region of 1900 to 2300 cm^{-1}. The internal standard method was adopted when the accurate determination of relative wave numbers was required.

Results

Infrared absorption due to the C≡N stretching vibration was measured with the solutions of potassium hexacyanoferrate(III) of various concentrations. The concentration of ion-pair $K^+[Fe(CN)_6]^{3-}$ present in the solution was calculated in the following way. The concentration association constant of potassium hexacyanoferrate(III), K_c, was calculated from the reported value of the thermodynamic association constant ($\log K_a = 1.3$[5]), using activity coefficients which were obtained from the diagram given by Ringbom.[6] In order to increase the accuracy in the measurements of wave numbers, an absorption band due to the C N stretching vibration of potassium hexacyanoferrate(II) at 2047 cm^{-1} was used as the internal standard, to which the C≡N stretching bands of all hexacyanoferrates(III) were referred. The results obtained with aqueous solutions of potassium hexacyanoferrate(III) are shown in Table I. Absorptions due to the C≡N stretching vibration gave maxima at 2121 cm^{-1} in all cases.

The solutions which contained 0.04 M potassium hexacyanoferrate(III) and 0.2 M magnesium, calcium or barium chloride, and the saturated solutions of magnesium, calcium and barium hexacyanoferrates(III) gave also the absorption due to the C≡N stretching vibration at 2121 cm^{-1}. In the former solutions 70—80% of hexacyanoferrate(III) ions present in the solutions existed in the form of ion-pairs $M^{2+}[Fe(CN)_6]^{3-}$. The calculation was made with the same procedure as in the case of ion-pairs $K^+[Fe(CN)_6]^{3-}$, using the

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[5] J. C. James and C. B. Monk, *Trans. Faraday Soc.*, **46**, 1041 (1950).

[6] A. Ringbom, "Complexation in Analytical Chemistry," Interscience, New York (1964), p. 24.

TABLE II. CLOSEST APPROACH AND DISTANCE FOR HYDRATED METAL IONS WITH HEXACYANOFERRATES(III) AND HEXACYANOFERRATES(II)

Ion-pair	log K_a	Closest approach (a), Å	Available distance for hydrated metal ions (l),* Å	Hydrated metal ion radius, Å
$K^+[Fe(CN)_6]^{3-}$	1.3	7.7	5.3	2.18
$Mg^{2+}[Fe(CN)_6]^{3-}$	2.79	7.1	4.7	1.50
$Ca^{2+}[Fe(CN)_6]^{3-}$	2.83	6.8	4.4	1.84
$Ba^{2+}[Fe(CN)_6]^{3-}$	2.88	6.4	4.0	2.20
$K^+[Fe(CN)_6]^{4-}$	2.3^10)	4.5	2.4	2.18
$Ca^{2+}[Fe(CN)_6]^{4-}$	3.77^11)	5.8	3.7	1.84

* See Fig. 3 for l.

concentration association constants of $M^{2+}[Fe(CN)_6]^{3-}$ which were converted from the thermodynamic association constants[7] of $10^{2.79}$ for Mg^{2+}-$[Fe(CN)_6]^{3-}$, $10^{2.83}$ for $Ca^{2+}[Fe(CN)_6]^{3-}$ and $10^{2.88}$ for $Ba^{2+}[Fe(CN)_6]^{3-}$. The absorption spectra of potassium, magnesium, calcium and barium hexacyanoferrates(III) in solid state were measured and compared with the spectra of the solutions of those compounds. They are shown in Fig. 1.

The solutions of hexacyanoferrate(II) salts were also subjected to the measurements of absorption spectra, and compared with each other. The absorption spectra of these solutions were also compared with those of the solids. In this measurement the absorption at 2349 cm^{-1} of carbon dioxide was taken as the internal standard. In the case of the solutions only one absorption band was observed at 2020 cm^{-1} with all the solutions of various concentrations both for potassium and calcium hexacyanoferrates(II). In solid state, however, the spectra of the calcium salt differed from those of the potassium salt. The results are shown in Fig. 2.

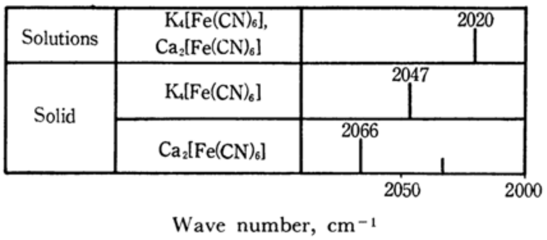

Fig. 2. Wave numbers of the absorption bands of hexacyanoferrates(II) in aqueous solution and in solid state. Solutions contain each complex by 0.02 M up to saturation. For solid state, crystalline water is not described.

Discussion

The solutions of various hexacyanoferrates(III) gave the same frequency and shape of absorption band due to the C≡N stretching vibration under widely different conditions, although these compounds gave different absorption spectra from each other in solid state. The same was found with hexacyanoferrates(II). The absoprtion bands due to the C≡N stretching vibration observed in solid state were at higher frequencies than those observed with the solutions in all cases except potassium hexacyanoferrate(III). One of the explanations of the phenomena is that the complex anion has no direct interaction with a metal cation but it forms an ion-pair with a hydrated metal cation.

Fronaeus and Larsson state[8] in their report that, because a sulfate ion bonds to a metal ion in the form of outer-sphere complex, the disturbance of the symmetry may be so small that its spectra will be identical with those of the free sulfate ion. Since no non-aqueous solvent in which hexacyanoferrates(II) and hexacyanoferrates(III) are soluble in required concentrations was found, an experimental approach to the examination of direct interaction of a complex anion and a metal cation was not successful. Alternatively, the possibility of existence of one or more water molecules between the complex anion and the metal cation was examined by the calculation of the distance of these two ions in ion-pair.

The relation between the closest approach of two ions in ion-pair, a, and the association constant, K, is given by the equations,[9]

$$K = \frac{4\pi N}{1000}\left(\frac{|z_i z_j| e^2}{\varepsilon \boldsymbol{k} T}\right)^3 Q(b) \tag{1}$$

$$Q(b) = \int_2^b x^{-4} \exp(x)\, \mathrm{d}x \tag{2}$$

where

$$x = \frac{|z_i z_j| e^2}{r \varepsilon \boldsymbol{k} T} \tag{3}$$

and

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[7] C. W. Gibby and C. B. Monk, *Trans. Faraday Soc.*, **48**, 632 (1952).

[8] S. Fronaeus and R. Larsson, *Proc. 8 ICCC (1964)*, p. 383.

[9] C. W. Davies, "Ion Association," Butterworths, London (1962), p. 164.

[10] C. W. Davies, *J. Am. Chem. Soc.*, **59**, 1760 (1937).

[11] C. W. Davies, *J. Chem. Soc.*, **1945**, 460.

$$b = \frac{|z_i z_j| e^2}{a \varepsilon \boldsymbol{k} T} \tag{4}$$

N represents the Avogadro number, ε dielectric constant, z the charge of ion, $\boldsymbol{k}$ the Boltzmann's constant and r the distance between two ions in ion-pair. For infinitely dilute aqueous solutions at 25°C, Eqs. 1. and 4 are written as,

$$\log K = 0.4386 + 3 \log |z_i z_j| + \log Q(b) \tag{5}$$

$$\log a = \log |z_i z_j| - 7.1468 - \log b \tag{6}$$

The values of a for various ion-pairs of hexacyanoferrate(III) and hexacyanoferrate(II) ions with the metal cations were calculated with Eqs. 5 and 6, and given in Table II.

The positions of water molecule interposing between a complex anion and a metal cation is assumed to be located on the face of the octahedron of a hexacyanoferrate ion as shown in Fig. 3.[12)]

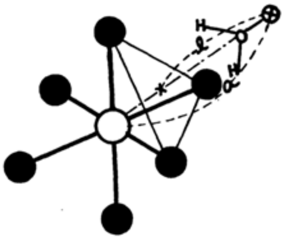

Fig. 3. The possible position of a hydrated metal ion forming an ion-pair with a hexacyanoferrate ion. ○ indicates Fe atom, ● C≡N group and ⊗ a center of a hydrated metal cation.

From the crystal structure of potassium hexacyanocobaltate(III)[13)] similar to hexacyanoferrate(III), the Fe-C distance is estimated to be about 2.5 Å and the C-N distance about 1.15 Å. In the case of hexacyanoferrates(II), Marcus[14)] reported that the Fe-C distance in the iron cyanide ions may be assumed to be 1.85 Å, which equals the Fe-C bond distance in $Fe(CNCH_3)_6{}^{2+}$. This value agrees with the Fe-C distance calculated from the crystal structure of potassium hexacyanoferrate(II)[15)]; the Fe-C and the C-N distance were calculated to be about 1.9 Å and 1.18 Å, respectively. Using these distances and the values for the closest approach the available distance for the hydrated metal ion, l, was calculated for the univalent and bivalent cations, which are given in Table II. The ionic radii of hydrated metal ions were considered to be the ionic radii of the metal ions plus 0.85 Å.[16)] From these values and the available distance for the hydrated metal ions given in Table II, it may be concluded that a water molecule or molecules interpose between the metal cation and the complex anion when they are in the state of ion-pair. This, in turn, suggests that there is no direct interaction between univalent and bivalent cations and hexacyanoferrate(III) and hexacyanoferrate(II) ions.

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[12)] B. E. Conway and J. O'M. Bockris, *Electrochim. Acta*, **3**, 340 (1961).

[13)] H. Kuroya and Y. Saito, "Mukikagakuzensho, Sakuen," Ed. by K. Yamasaki and T. Inoue, Maruzen, Tokyo (1959), p. 220.

[14)] R. A. Marcus, *J. Chem. Phys.*, **26**, 867 (1957).

[15)] V. A. Pospelov and G. S. Zdanov, *Z. Fiz. Khim. SSSR*, **21**, 405, 521, 879 (1947).

[16)] W. M. Latimer, K. S. Pitzer and G. M. Slansky, *J. Chem. Phys.*, **7**, 108 (1939).