

VII. As discussed previously,<sup>4a</sup> the fact that canonical form VII contributes more to the resonance stabilization of the terminal thioxanthate ligand than to the bridging one facilitates the assignment of the molecule's pmr spectrum. Since the terminal thioxanthate is involved in the formation of a four-membered ring with the iron atom (Fe-S-C angle, 86.9°), it is reasonable that resonance form VII would contribute more to its electronic structure than to that of the bridging thioxanthate group (Fe-S-C angle, 111.5°).

A final point worthy of mention is that, although the CS<sub>3</sub> atom groupings are calculated to be strictly coplanar, the two S=C=S angles within each ethyl thioxanthate are unexpectedly nonequivalent (Table V). One possible explanation is that intramolecular

packing forces distort the angles at C1 and C4 in order to accommodate the stereochemical requirements of the ethyl groups. Consistent with this suggestion is the fact that, for both thioxanthate ligands, the larger S=C=S angle occurs on the side of the ligand occupied by the ethyl group (Table V and Figure 1). Similar results have been obtained for the S=C=O angles of the ethyl xanthate ligands in their M(S<sub>2</sub>-COC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> complexes, where M is iron<sup>39</sup> and cobalt.<sup>44</sup>

**Acknowledgments.**—We are grateful to the National Institutes of Health for its generous support of this research under Grant No. GM 16449 and to Dr. S. J. LaPlaca for assistance in preparing the figures for this paper.

## Notes

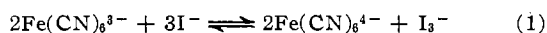
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### Specific Interaction between Tetraalkylammonium and Hexacyanoferrate(III) Ions

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In a previous communication,<sup>1</sup> it has been reported that tetramethylammonium chloride exerts a negative salt effect on the equilibrium



whereas alkali metal salts exhibit the normal positive effect. To obtain detailed information about such an abnormal salt effect exerted by tetraalkylammonium salts, investigations have been carried out on the specific cation effects on the activity coefficients of Fe(CN)<sub>6</sub><sup>3-</sup> and Fe(CN)<sub>6</sub><sup>4-</sup> ions by emf and solubility measurements.

#### Experimental Section

**Materials.**—K<sub>3</sub>Fe(CN)<sub>6</sub> (E. Merck, *pro analysi*) was dried in an electric oven at 110° and standard solutions were prepared by accurate weighing. K<sub>4</sub>Fe(CN)<sub>6</sub> (E. Merck, *pro analysi*) was recrystallized and dried. Standard solutions were prepared by weighing and used on the same day.

The halide salts used were of reagent quality (Merck) and solutions were standardized against silver nitrate solution. Potassium nitrate, lithium nitrate, and tetramethylammonium nitrate were prepared by mixing equivalent amounts of the corresponding hydroxides and nitric acid.

Potassium barium hexacyanoferrate(II), K<sub>2</sub>BaFe(CN)<sub>6</sub>, was prepared by adding BaCl<sub>2</sub> solution to a saturated solution of K<sub>4</sub>Fe(CN)<sub>6</sub>. The pale yellow precipitate was kept overnight and then filtered under suction, with thorough washing with

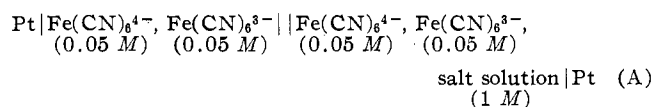
water and alcohol. The purity of the sample was checked by estimating the barium content as sulfate.

Tl<sub>4</sub>Fe(CN)<sub>6</sub> was prepared by mixing equivalent amounts of TlNO<sub>3</sub> and K<sub>4</sub>Fe(CN)<sub>6</sub> and keeping the precipitate overnight, filtering under suction, and thoroughly washing with water and alcohol.

Hexaamminecobalt(III) hexacyanoferrate(III) was prepared by mixing equivalent amounts of K<sub>3</sub>Fe(CN)<sub>6</sub> and Co(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> which was prepared and purified by the usual method.<sup>2</sup> All the samples were stored in a vacuum desiccator.

Twice distilled water was used for solubility measurements, and triple distilled de-oxygenated water for electrometric measurements.

**Electrometric Measurements.**—Emf measurements at 35° were carried out on the concentration cell



Potassium chloride (saturated) in agar was used in the salt bridge.

The measurements were carried out with a specially designed cell, made of Pyrex glass, having two compartments 7 cm high and 2.5 cm in diameter, and each of them was fitted with two standard joints (B7). Through the two extreme joints the platinum electrodes were fitted, and the joints at the inner side were used for inserting the salt bridge. The electrodes and the salt bridge were also provided with standard joints (B7).

After placing the solutions in the cell compartments, pure and dry nitrogen gas was passed through the extreme joints of both the compartments for about 10 min. Then the platinum electrodes (after cleaning with aqua regia and washing thoroughly with distilled water and burning over alcohol flame) were quickly inserted through the extreme joints of both the compartments. The salt bridge (agar + KCl) was then introduced through the inner joints. The nitrogen atmosphere was maintained within the cell compartments. The cell was placed in a thermostat (35 ± 0.01°). The asymmetry potentials of the electrodes were tested before use and the best pairs were selected for experimental observations. Readings were taken at intervals of 10 min and found to remain constant for 1 hr or more. The emf measurements were made with a potentiometer (Rubicon Co., Philadelphia, Pa.) and a moving coil galvanometer until the values were constant within ±0.1 mV.

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(1) M. K. Basu and M. N. Das, *Indian J. Chem.*, **7**, 358 (1969).

(2) J. Bjerrum and J. P. McReynolds, *Inorg. Syn.*, **2**, 217 (1963).

**Solubility Measurements.**—Solubility measurements at 25° were carried out on the sparingly soluble salts  $Tl_4Fe(CN)_6$ ,  $K_2BaFe(CN)_6$ , and  $Co(NH_3)_6Fe(CN)_6$  in the presence of added salts. With the thallium(I) salt,  $KNO_3$ ,  $LiNO_3$ , and  $((CH_3)_4N)NO_3$  were used as the added salts. For the other two substances, the added salts were  $KCl$ ,  $NaCl$ ,  $LiCl$ ,  $(CH_3)_4NCl$ , and  $(C_2H_5)_4NCl$ .

The respective salts were shaken with water or the desired salt solutions at a temperature slightly higher than 25°, in a shaker for 2 hr, and then placed in a thermostat ( $25 \pm 0.01^\circ$ ) for 1 hr with intermittent shaking. The solutions were then quickly filtered under suction, aliquots were suitably diluted, and the optical densities were measured at suitable wavelengths with the help of a Beckman DU spectrophotometer.

The optical densities of  $K_2BaFe(CN)_6$  and  $Tl_4Fe(CN)_6$  solutions were examined at 325 and 322  $m\mu$ , the extinction coefficients being 314 and 323, respectively. The optical densities of the solutions of hexaamminecobalt(III) hexacyanoferrate(III) were examined at 420  $m\mu$ . The extinction coefficient of  $Fe(CN)_6^{3-}$  is 1060 at this wavelength. The  $Co(NH_3)_6^{3+}$  ion is itself a colored species, and its extinction coefficient ( $\sim 17$ ) was determined at this wavelength by using a solution of hexaamminecobalt(III) chloride. The sum of the two extinction coefficient values (1077) was used for obtaining the concentrations of  $Co(NH_3)_6Fe(CN)_6$  solutions from the observed optical densities.

### Results and Discussion

**Salt Effects on Emf of the  $Fe(CN)_6^{4-}-Fe(CN)_6^{3-}$  System.**—The emf (volts) of cell A is given by

$$E = \frac{2.303RT}{F} \log \frac{a_{III}a_{IV}^0}{a_{IV}a_{III}^0} \quad (2)$$

where  $a_{III}$  and  $a_{IV}$ , respectively, denote the activities of  $Fe(CN)_6^{3-}$  and  $Fe(CN)_6^{4-}$  ions in the salt solution (at the right) and  $a_{III}^0$  and  $a_{IV}^0$  in water (at the left). Since the concentrations of the two ions are identical on the two sides and since the same solution has always been used for the reference electrode (left), the variation in the observed emf of the cell should be a direct measure of the variation in the activity coefficient ratio  $f_{III}/f_{IV}$ . The observed emf may be expressed as

$$E = \frac{-2.303RT}{F} \log \frac{f_{III}^0}{f_{IV}^0} + \frac{2.303RT}{F} \log \frac{f_{III}}{f_{IV}} \quad (3)$$

The liquid junction potential in the cell may not be negligible, but in any way it should not show a pronounced change with varying salt concentrations in the solution shown at the right.

The emf values of the cell have been plotted against the concentrations of the added salts and the results are shown in Figure 1. As indicated by eq 2, the usual convention regarding the sign of the emf of the cell has been used, namely, that the sign has been taken to be positive when the left-hand electrode serves as the source of electrons. Figure 1 shows that, in the presence of added  $KCl$  and  $LiCl$  at all the concentrations used, the emf of the cell is positive, the magnitude increasing with increasing salt concentration. It follows, therefore, from eq 3, that the ratio  $f_{III}/f_{IV}$  is higher than  $f_{III}^0/f_{IV}^0$  and increases regularly with increasing ionic strength. This is just what is to be expected from our general ideas regarding interionic forces. Increasing ionic strength should decrease the activity coefficient of the quadruply charged hexacyanoferrate(II) ion by a

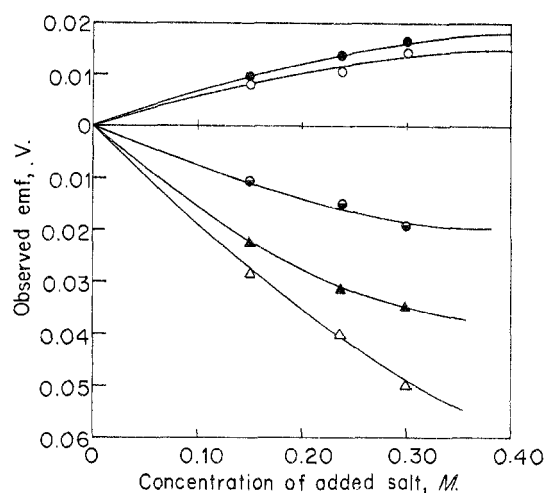


Figure 1.—Plot of emf of cell A against concentration of added salt: ●,  $KCl$ ; ○,  $LiCl$ ; ⊙,  $(CH_3)_4NCl$ ; ▲,  $(C_2H_5)_4NCl$ ; △,  $(C_4H_9)_4NCl$ .

larger extent than that of the triply charged hexacyanoferrate(III) ion, so that  $f_{IV}$  decreases more rapidly with increasing ionic strength than  $f_{III}$ , resulting in an increase in the ratio  $f_{III}/f_{IV}$ .

On the other hand, the emf of the cell in the presence of tetraalkylammonium chlorides is negative, the negative value increasing with increasing concentration of the added salts (Figure 1). The magnitude of the negative values lies in the order butyl > ethyl > methyl for the three tetraalkylammonium chlorides used. Similar results were obtained by Hanania, Irvine, Eaton, and George,<sup>3</sup> from emf measurements of a cell, using the  $Fe(CN)_6^{4-}-Fe(CN)_6^{3-}$  electrode in conjunction with a calomel electrode.

The results show that added quaternary salts cause an abnormal change in the overall activity coefficient ratio of the  $Fe(CN)_6^{3-}$  and  $Fe(CN)_6^{4-}$  ions. Which of the two ions is responsible for this abnormal behavior is yet to be determined.

**Specific Cation Effects on Solubility.**—To study the variation of the activity coefficients of the individual ions in the presence of added salts, solubility measurements were carried out on  $Tl_4Fe(CN)_6$ ,  $K_2BaFe(CN)_6$ , and  $Co(NH_3)_6Fe(CN)_6$ . The results are shown in Figures 2–4. The solubility of  $Tl_4Fe(CN)_6$  increases regularly with the concentration of the added salts. The effects of the cations, which are of a similar order of magnitude, lie in the order  $(CH_3)_4N^+ > K^+ > Li^+$ .

Tetramethylammonium ion does not seem to produce any abnormal effect on the activity coefficient of  $Fe(CN)_6^{4-}$  ion, as otherwise this would have been reflected in an abnormal behavior regarding solubility. This point seems to be further substantiated from the solubility data of  $K_2BaFe(CN)_6$  in the presence of  $NaCl$ ,  $LiCl$ , and  $(CH_3)_4NCl$ . The addition of tetraethylammonium chloride, however, produces relatively little changes in the solubility. Potassium chloride exerts a negative effect which obviously arises from the

(3) G. Hanania, D. Irvine, W. Eaton, and P. George, *J. Phys. Chem.*, **71**, 2022 (1967).

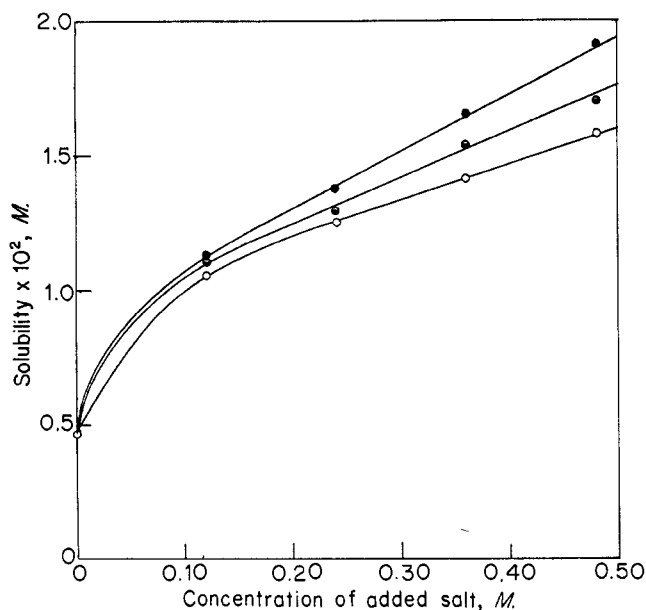


Figure 2.—Plot of solubility ( $M$ ) of  $Tl_4Fe(CN)_6$  against concentration of added salt: ●,  $(CH_3)_4NO_3$ ; ○,  $KNO_3$ ; □,  $LiNO_3$ .

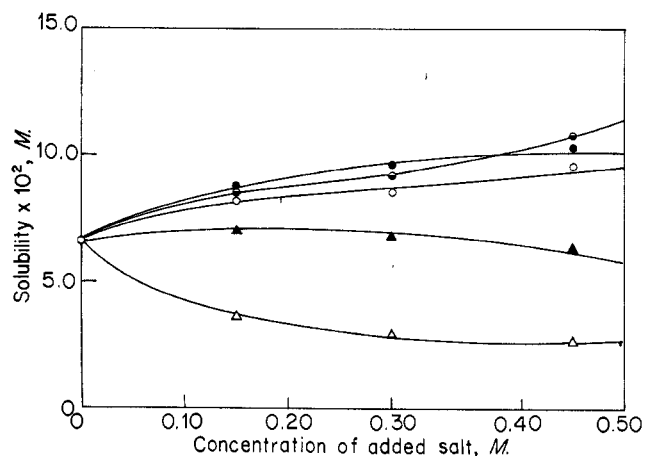


Figure 3.—Plot of solubility ( $M$ ) of  $K_2BaFe(CN)_6$  against concentration of added salt: ●,  $NaCl$ ; ○,  $LiCl$ ; ◐,  $(CH_3)_4NCl$ ; ▲,  $(C_2H_5)_4NCl$ ; △,  $KCl$ .

“common ion effect,” since the saturating salt,  $K_2BaFe(CN)_6$ , itself gives rise to  $K^+$  ions in solution.

Figure 4 shows that the increase in solubility of  $Co(NH_3)_6Fe(CN)_6$  in the presence of  $(CH_3)_4NCl$  and  $(C_2H_5)_4NCl$  is much higher than in the presence of  $KCl$ ,  $NaCl$ , and  $LiCl$ . In fact, two families of curves are obtained, one for the alkali metal chlorides and the other for the quaternary salts. The rather abnormally large effect of the tetraalkylammonium salts on the solubility may reasonably be attributed to an abnormally large decrease in the activity coefficient of the  $Fe(CN)_6^{3-}$  ion in the presence of the quaternary ions.

#### Conclusion

From the results, it seems reasonable to conclude that at the same ionic strength, the tetramethylammonium ion decreases the activity coefficient of the triply charged  $Fe(CN)_6^{3-}$  ion ( $f_{III}$ ) by a larger extent than that of the quadruply charged  $Fe(CN)_6^{4-}$  ion ( $f_{IV}$ ), and that  $f_{III}$  decreases more rapidly with increasing ionic

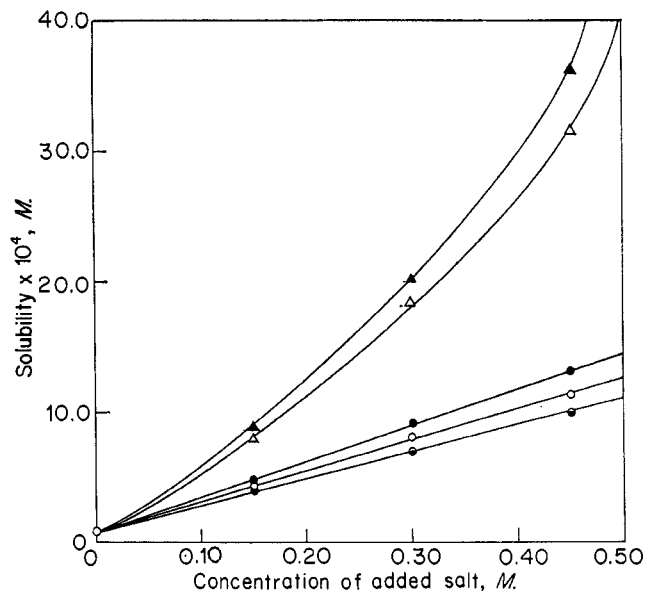


Figure 4.—Plot of solubility ( $M$ ) of  $Co(NH_3)_6Fe(CN)_6$  against concentration of added salt: ▲,  $(C_2H_5)_4NCl$ ; △,  $(CH_3)_4NCl$ ; ●,  $KCl$ ; ○,  $NaCl$ ; ◐,  $LiCl$ .

strength than  $f_{IV}$ , although the opposite might be expected from a simple consideration of interionic forces.

Rather high salt concentrations have been used in the present work, and under these conditions specific interaction between ions, arising out of short-range forces, is likely to preponderate over normal electrostatic factors. It appears that specific interaction between a tetraalkylammonium ion and the  $Fe(CN)_6^{3-}$  ion is stronger than that between this cation and  $Fe(CN)_6^{4-}$  ion and also stronger than that between an alkali metal ion and the  $Fe(CN)_6^{3-}$  ion. However, no quantitative treatment can be attempted at this stage.

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### Synthesis and Some Properties of Yttrium and Lanthanide Isopropoxides<sup>1</sup>

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Transition metal alkoxides have been studied extensively in the past two decades by a number of investigators. This work has been reviewed by Bradley<sup>2,3</sup>

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(1) Presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 7-12, 1969.

(2) D. C. Bradley, *Advan. Chem. Ser.*, No. 23, 10 (1959).

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