

## Reactions of co-ordinated ligands : Kinetics and mechanisms in the charge transfer interaction between dichloro or diaquo triethylene tetramine Co(III) and ferrocyanide

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**Abstract.** The cherry red-coloured solid state product obtained by the reaction of *cis-a* diaquo Co(III) triethylene tetramine with ferrocyanide was examined by thermogravimetric, infrared and Mössbauer techniques. Its electronic spectrum in aqueous medium was interpreted to consist of charge transfer IT transition at 440 nm and a ligand field transition around 330 nm. The kinetics of formation of this 1 : 1 product in solution was also studied.

**Keywords.** *Cis-a* diaquo Co(III) triethylene tetramine ; charge transfer IT transition ; kinetics of formation.

### 1. Introduction

In recent years there has been increasing interest in intranuclear electron transfer processes especially for identifying and isolating long-lived dinuclear intermediates. The studies by Jwo and Haim (1976) and those of Haim and Sutin (1976) are typical examples wherein complex ferrocyanides were employed. If the dinuclear complex is to be long-lived, the thermal electron transfer reaction should be preferably absent or be very slow. This paper presents the isolation of a cherry red dinuclear complex formed in the reaction between *cis-a* diaquo Co(III) triethylene tetramine and ferrocyanide, and a study of its behaviour.

### 2. Experimental

#### 2.1. Preparation

The cherry red complex was prepared as follows : The *cis-a* dichloro Co(III) triethylenetetramine complex was prepared and purified according to the method suggested by Sargeson and Searle 1967. The *cis-a* diaquo complex was prepared by dissolving the

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dichloro complex in water and allowing it to stand for 24 hr for aquation. When the aquo complex was mixed with aqueous solution of  $K_4Fe(CN)_6$  a cherry red colour was immediately formed. This solution showed an electronic absorption at 440 nm and a pH between 7 and 8. Equal volumes of equimolar solution of the two reactants were mixed and allowed to stand for an hour at room temperature with occasional stirring. On adding ethanol and keeping under refrigeration, bright cherry red solid separated out. After filtering, the solid was repeatedly washed with ice-cold ethanol and dried under vacuum in a desiccator.

### 2.2. Chemical analysis

The solid was dissolved by heating first with nitric acid, then with perchloric acid and finally with sulphuric acid. The K, Co and Fe content was determined by standard analytical techniques. K was determined by flame photometric method. Fe and Co were estimated spectrophotometrically by ortho phenanthroline (Vogel 1961) and nitroso-R-salt (Sandell 1959) methods respectively.

### 2.3. Instrumental

A Perkin-Elmer IR spectrophotometer was employed for recording the IR spectra of the sample using hexachloro butadiene as the mulling agent. A Stanton TG balance with a sample size of 400 mg and a heating rate of 6 K min<sup>-1</sup> in static air was employed. Electronic spectra were recorded with a Hitachi Model spectrophotometer. A home-made constant acceleration Mössbauer spectrometer using 3 mci Co-57 (pd) in conjunction with an MCA was used to record the <sup>57</sup>Fe Mössbauer spectra of the solid.

## 3. Results and discussion

The results of chemical analysis of the cherry red solid for Fe, Co and K content (table 1) show a reasonable fit for the molecular formula  $KCo(trien)Fe(CN)_6 \cdot 4H_2O$  consistent with the expectation from the route followed for its synthesis.

The cherry red complex on dissolution in water satisfies Beer's law. The molar extinction coefficient is 1000 litre mole<sup>-1</sup> cm<sup>-1</sup> and its stoichiometry is found to

Table 1. Results of chemical analysis of cherry red solid.

Element	Weight (%)	
	Observed	Calculated
K	7.4	7.4
Fe	10.5	10.6
Co	11.0	11.1

be 1:1 by Job's method of continuous variation and molar ratio method. These results support the above-mentioned molecular formula for the complex arrived at from chemical analysis. Its stability constant was found to be  $4.5 \times 10^5$  litre mole<sup>-1</sup>. To ascertain whether the colour of the complex is vested in the cationic or anionic moiety of the solid, its solution was passed through the Na form of a cationic exchanger, which did not retain the colour. The moiety can either be neutral or anionic in nature. A similar treatment with the chloride form of an anionic exchanger resulted in the retention of the colour on the exchanger proving that the moiety responsible for the colour is anionic in nature.

The TG analysis of the cherry red complex was performed with the object of probing the thermal stability of the solid complex as well as to determine if all the four molecules of water are bound equally strongly from its dehydration behaviour. The observed TG run is given in figure 1. The thermogram shows a very slow and gradual loss in weight in the temperature interval 313–873 K with a superposed very sharp loss in weight around 480 K. The overall loss in weight between 313–873 K accounts for loss of one molecule of trien and four molecules of H<sub>2</sub>O. However, if one calculates the loss in weight represented by the steep loss alone,

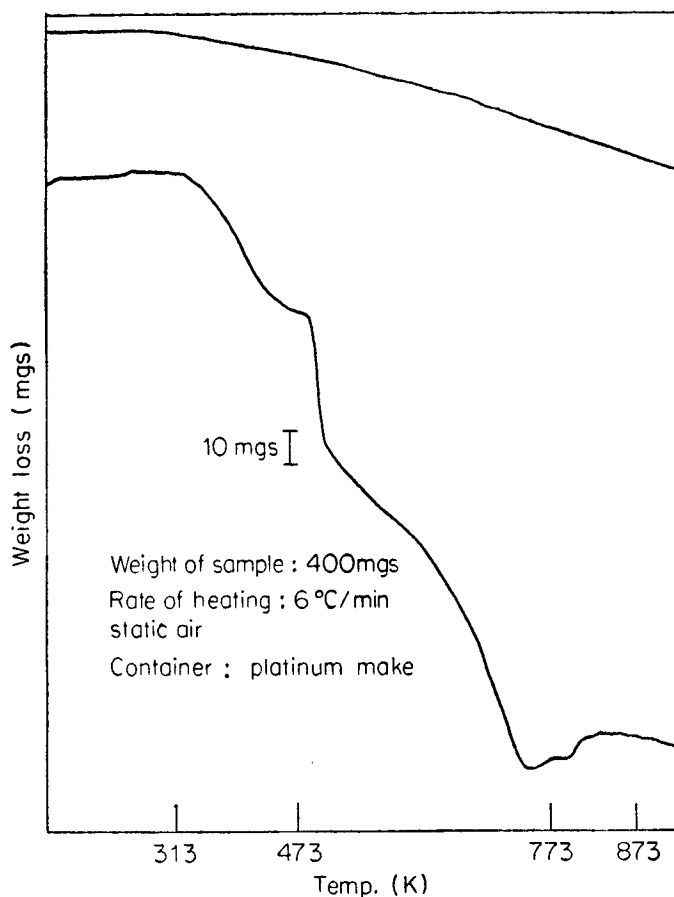
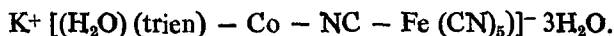


Figure 1. Thermogram of cherry red solid.

it accounts for only three molecules of water. Thus it is clear that of the four molecules of water in the cherry red complex, three are bound differently as compared to the fourth in the solid state, i.e., structurally there are two kinds of water molecules in 3 to 1 ratio. Considering that ferrocyanide was used as the starting material and in the light of the TG and ion exchange results mentioned above, the following structural units are proposed for the cherry red complex.

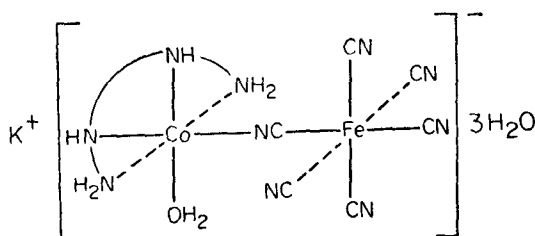


This does not disturb the ferrocyanide unit and involves a single linear CN bridge, which is well documented as far as cyanides are concerned.

This type of structural unit gets independent support from IR results. The IR spectrum shows an absorption at  $2040\text{ cm}^{-1}$  with a clear shoulder at  $2100\text{ cm}^{-1}$ . The former is attributed to stretching of terminal CN groups whereas the latter comes from that of bridging  $\text{C}\equiv\text{N}$  groups (Nakamoto 1963). A band at  $585\text{ cm}^{-1}$  attributable to Fe-C stretching in ferrocyanide was also observed in the IR spectrum of the cherry red solid.

It is reported (Nakamoto 1963) that in solids both co-ordinated as well as lattice water molecules give characteristic IR absorption in the range  $3550\text{--}3200\text{ cm}^{-1}$  (due to antisymmetric and symmetric O-H stretching) and also in the range  $1630\text{--}1600\text{ cm}^{-1}$  (due to H-O-H bending). On the other hand, the co-ordinated  $\text{H}_2\text{O}$  molecules give an additional absorption in the region  $880\text{--}650\text{ cm}^{-1}$  due to rocking mode of the water molecule. In the IR spectrum of our complex at room temperature, there are absorptions in the neighbourhood of  $3000\text{ cm}^{-1}$  and  $1600\text{ cm}^{-1}$  in addition to several sharp ones in the range  $600\text{--}850\text{ cm}^{-1}$ . It is difficult to unequivocally discern the absorption arising out of rocking modes of  $\text{H}_2\text{O}$  in this group of peaks. The spectrum in this  $600\text{--}850\text{ cm}^{-1}$  region remains unaffected after heating the sample at  $473\text{ K}$ , i.e., after the steep loss of  $3\text{H}_2\text{O}$  molecules, as indicated by the TG scan. It implies that the lone co-ordinated water molecule is lost after  $473\text{ K}$ .

The foregoing results enable us to propose the following structure for the cherry red complex.



In order to investigate the origin of colour of this cherry red complex, the electronic spectra of solution of the complex in water with different concentrations were taken. The spectra are shown in figure 2. Two well-defined maxima at  $330$  and  $440\text{ nm}$  were observed. Vogler and Kunkely (1975) have reported the electronic spectra of dinuclear complex  $[(\text{CN})_5\text{Co(III)NCFe(II)(CN)}_5]^{4-}$  as having two maxima at  $326$  and  $385\text{ nm}$ . They assigned the  $326\text{ nm}$  band to Co(III) ligand field separation, and the  $385\text{ nm}$  band to intervalence charge transfer process involving the two cations. On the same lines, in our case, the  $440\text{ nm}$

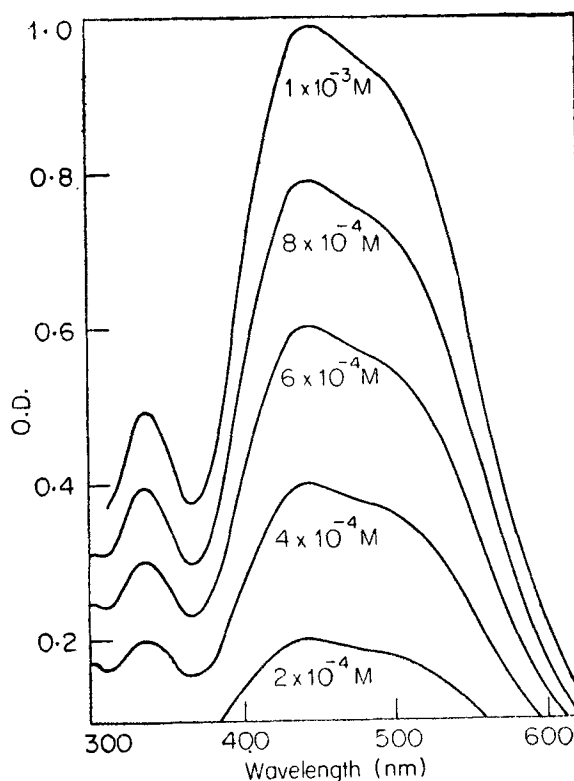


Figure 2. Absorption spectra of solutions obtained by the dissolution of different amounts of cherry red solid in water.

band is assigned to charge transfer involving the interaction of the two metals of the anionic species. The 330 nm band is assigned to the Co(III) ligand field. According to the qualitative potential energy diagram constructed by Vogler and Kunkely (1975), the 440 nm band observed here represents a spin allowed intervalence transition.

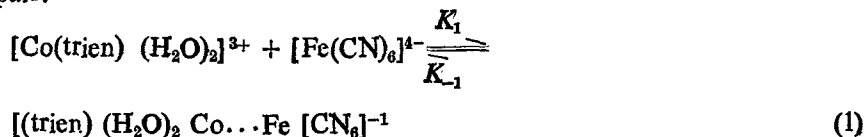
It would be worthwhile and interesting to probe the extent of electron transfer in these charge transfer complexes. A bulk magnetic susceptibility measurement would not be a very sensitive tool to do this since such a transfer is very small in practice and the macroscopic measurement could not detect it. A microscopic technique which looks more closely at either cobalt(III) or iron (II) site is desirable. At least for iron site, it was felt that Mössbauer might throw some light on the situation.

It is well-known that the two extreme situations in which the 6th *d* electron of Fe either stays on it or goes over to Co completely far away from it can be easily distinguished by Mössbauer spectroscopy from different isomer shifts observed for Fe(II) and Fe(III) cases. With this in mind, we recorded the  $^{57}\text{Fe}$  Mössbauer spectra of the cherry red complex and to our surprise observed that its isomer shift is identical to that in  $[\text{Fe}(\text{CN})_6]^{4-}$  proving beyond doubt that the 6th *d*-electron stays almost on the Fe-site. Only a negligible amount of the

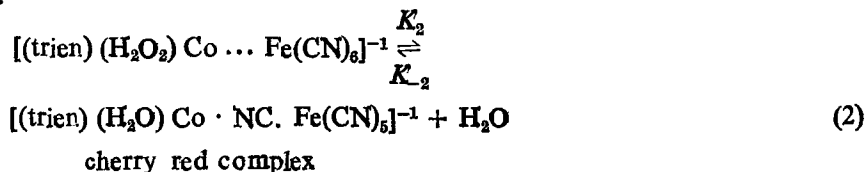
charge density is transferred to the cobalt site *via* the intervening bridging CN group.

#### 4. Kinetics of interaction

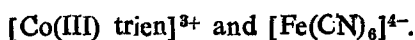
The first step in the formation of the cherry red complex is the constitution of an ion-pair.



The rate of formation of this ion-pair is very fast, so that  $K_{-1}$  compared to  $K_1$  can be neglected in practice. If this ion-pair gives the final cherry red product through a unimolecular reaction, the next step can be logically visualised as follows:



The slowest step in this process is the removal of water molecule and hence it is the rate-determining step. The overall reaction rate depends on the concentration of the ion-pair, which in turn depends on the concentration of the starting ions, viz.,



The rate expression may then be written as

$$dc/dt = K [\text{Co} (\text{trien}) (\text{H}_2\text{O})_2]^{3+} [\text{Fe} (\text{CN})_6]^{4-} \quad (3)$$

where  $K = K_1 K_2 / (K_1 + K_2)$ .

Data pertaining to kinetic studies namely values for OD at 440 nm *vs* time plots presented in figure 3 show that in diaquo complex, it is difficult to resolve the semilog plots. In order to investigate if the two  $t_{1/2}$ 's can be resolved, the starting diaquo complex of cobalt was replaced by the corresponding dichloro complex of cobalt. The resulting kinetic data plotted in figure 3 also show that for dichloro Co (III) trien complex the semilog plots are resolvable into two linear components having distinct  $t_{1/2}$  values. This clearly shows that in dichloro complex its aquation takes place prior to the interaction with ferrocyanide.

A linear plot of  $dc/dt$  (figure 4) against the product of concentrations of the reactants indicates an overall second order kinetics. The reaction rate and  $t_{1/2}$  for the system [ $9 \times 10^{-4}$  M Co(III) trien complex and  $9 \times 10^{-4}$  M ferrocyanide] were measured at temperatures 301, 308, 318 and 333 K to estimate  $E_a$ , the activation energy of the reaction. A linear plot of  $\log K$  *vs*  $1/T$  was obtained. The activation energy for the interaction of *cis-a* diaquo Co(III) trien complex with ferrocyanide was found to be 28.8 kJ.

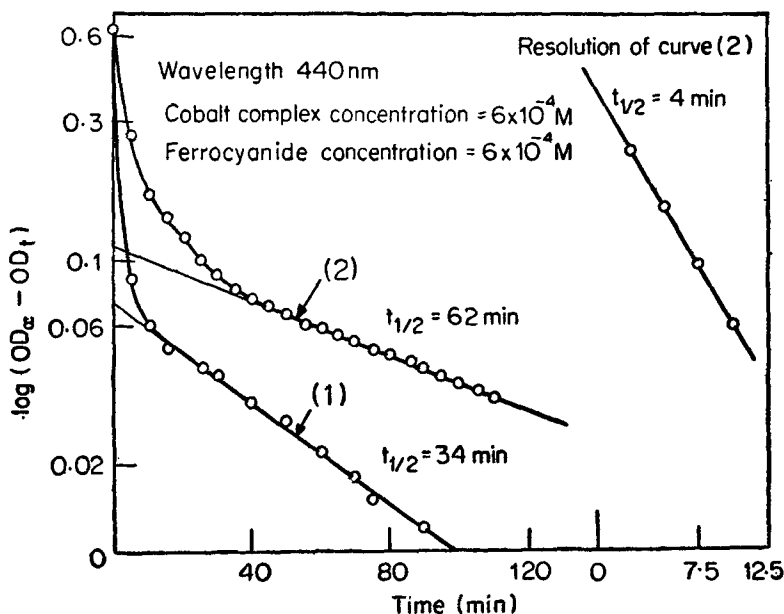


Figure 3. Plot of  $\log(OD_{\infty} - OD_t)$  vs. time for *cis-a* diaquo/dichloro cobalt(III) trien complex and ferrocyanide system. Curve (1) diaquo cobalt(III) complex and ferrocyanide system. Curve (2) dichloro cobalt(III) complex and ferrocyanide system.

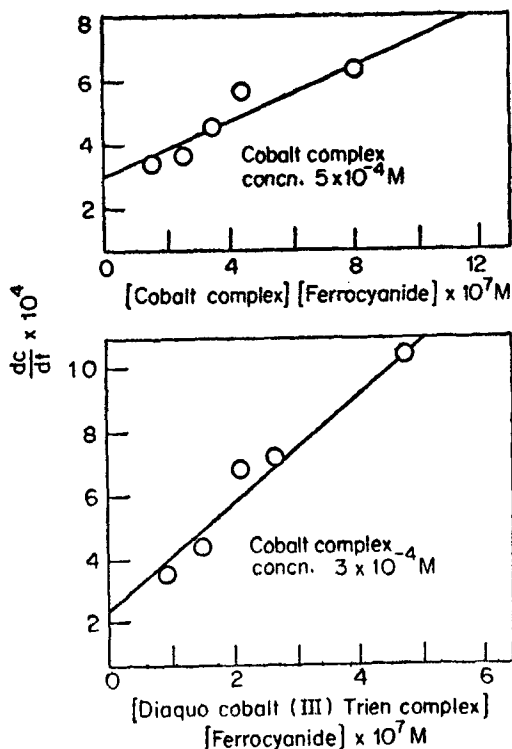


Figure 4. Plot of  $dc/dt$  vs. [Diaquo Co(III) trien complex] [Ferrocyanide].

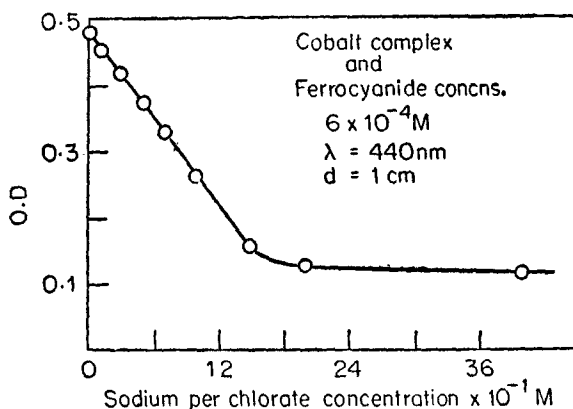
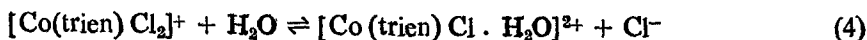


Figure 5. Effect of sodium perchlorate on the optical density of the system under study.

The ion-pair formation being the primary step leading to the formation of the cherry red complex, it is essential that the effect of ionic strength be investigated. Optical density measured after 5 min of addition of all reagents showed a marked decrease with increase in sodium perchlorate concentration (figure 5). The maximum and minimum concentration of sodium perchlorate that would interfere in the rate of cherry red complex formation was found to be 2 M and 0.1 M respectively.

It was shown by Satyal *et al* (1977) that the dichloro complex aquates in two steps:



In both the aquation steps, one of the products is naturally a chloride ion. Since this is an equilibrium process, it will be interesting to study the effect of chloride ions. Optical density at 440 nm characteristic of cherry red complex decreased with increase in sodium chloride concentration. The minimum and maximum concentrations of sodium chloride which would interfere with the rate of ion-pair formation of *cis-α* diaquo complex and ferrocyanide were found to be 0.1 M and 2 M respectively. The half-time of interaction for diaquo Co(III) trien complex and ferrocyanide equiconcentration ( $6 \times 10^{-4}$  M) mixture was determined at different concentrations of sodium chloride. The  $\log(OD_\infty - OD_t)$  vs time plot of diaquo Co(III) trien complex and ferrocyanide could be resolvable into two components with the increase in the addition of sodium chloride.

## 5. Conclusion

The results presented in this paper clearly indicated that the dinuclear precursor formed in the charge transfer interaction between *cis-α* diaquo Co(III) trien complex and ferrocyanide can be isolated in the solid state. Selected physico-chemical data on the complex are presented. The kinetic studies for the formation of the



cherry red complex indicated an overall second order process and both perchlorate and chloride ions were shown to affect the course of the reaction, though through different mechanisms.

### **Acknowledgements**

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