

Spectroscopic evidence for Metal-Metal electronic coupling of suspected $L_5Ru^{III}CNFe^{II}(CN)_5$ System

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Abstract

Inorganic donor-acceptor complexes containing inter-valence (IT) or metal-to-metal charge transfer bands have received significant attention in the last few decades due to their potential applications to solar energy conversions, photocatalysis and/or electrochromic materials. For this purpose, $L_5Ru^{III}CNFe^{II}(CN)_5$ complex (where $L = H_2O, Cl$), similar to Prussian blue, has been synthesized. By mixing aqueous solutions of brown-coloured $RuCl_3$ and light yellow $K_4[Fe(CN)_6]$, the colour of the resultant solution suddenly changed to dark green. The electronic spectrum of the solution mixture showed an intense inter-valence (IT) charge transfer absorption with an extinction of $362 M^{-1}cm^{-1}$ at approximately 742 nm. The absorption spectrum is totally different from that of the relevant monomers. Dark green solids were isolated after leaving the solution for few hours at room temperature. The solid is very insoluble in many common solvents. The estimated Ru/Fe ratio of the new polymetallic system, using the Job's method, was found to be 1:1.

Introduction

The electronic coupling between an electron transfer donor and acceptor is a fundamental aspect of electron transfer reactivity.^{1,2} There have been many studies of electronic coupling in simple donor(D)-acceptor (A) complex systems.³⁻⁵ The understanding of the metal-metal coupling (D/A coupling) of bimetallic complexes has important implication for a range of chemical and biochemical areas. A major thrust of many of these studies has been to investigate the unusual properties associated with multimetallic systems compared to those of the relevant monomers since the metal properties can be affected by the metal-metal interaction of the multimetallic system in contrast to the monometallic systems. Therefore the investigation of spectroscopic, electrochemical (oxidation-reduction), structural, photochemical, photophysical, kinetic and thermodynamic as well as catalytic properties of these complexes have received considerable attention.⁶

On the other hand, the importance of such systems, for example to apply in various industrial processes⁷ such as the synthesis of various kinds of paints and electrochromic materials (for making, smart windows used in cars and buildings, protective eye wears, sunglasses, antiglare car rear-view mirrors, controllable light reflective devices, etc) has provided the motivation for investigation of the metal ion chemistry of many multimetallic systems in general. The well-known Prussian blue^{8,9,10,12}, which is a cyanide bridged homobimetallic system made by mixing the monometallic complexes of the first transition series, is a very good example of this kind of electrochromic material. We were interested to see the possibility of making Prussian blue type heterobimetallic systems by mixing monometallic systems of the first transition series with the monometallic systems of second and/or third transition series. The novel bimetallic system that we report here shows new spectroscopic properties compared to the relevant monomers indicating a significant metal-metal electronic interaction (coupling) like in the case of Prussian blue and may be important for making materials with novel physical properties.

Experimental

A. Materials. Potassium ferrocyanide ($K_4[Fe(CN)_6].3H_2O$), Sulphuric acid, Hydrochloric acid, Ruthenium trichloride, Dimethyl sulphoxide, Dimethyl formamide, Acetonitrile, Acetic acid, Oxalic acid, Methanol, Acetone were obtained from BDH and FLUCKA and were used without further purification.

B. Instrumentation: SHIMADZU UV-1601 spectrophotometer was used to record the UV-Visible absorption spectra.

C. Method: Aqueous solutions (at pH = 3) of 0.1 M $RuCl_3$ (brown coloured) and 0.1 M $K_4[Fe(CN)_6].3H_2O$ (light yellow) were mixed in dark. The UV-Visible absorption spectrum of the resultant dark green solution was recorded. Dark green solids were isolated after leaving the green

solution for few hours at room temperature. Many attempts were made to recrystallize the solid in several solvents such as water, Methanol, Acetic acid, DMF, DMSO; Oxalic acid, Acetonitrile, etc. Prussian blue was also synthesized by following the literature procedures.^{8,14}

The stoichiometry of the reactants was determined by the Job method¹¹ in which the optical absorbance at 740 nm was monitored as a function of the ratio of potassium ferrocyanide to ruthenium trichloride.

Results

A. Synthesis: A Ru/Fe complex, $L_5Ru^{III}CNFe^{II}(CN)_5$, of which the behavior is similar to Prussian blue, has been prepared by mixing equimolar aqueous solutions of brown $RuCl_3$ and yellow $K_4[Fe(CN)_6]$. The colour of the solution suddenly changed to green. The solid obtained after leaving the solution sometime at room temperature was not soluble in any of the common solvents.

B. Spectroscopy and stoichiometry: The UV-Visible spectral data of the complexes are given in table 1 and the absorption spectrum of the new complex/ion pair is given in Figure 1. A broad low energy band around 742 nm with an extinction of $362 M^{-1}cm^{-1}$ can be seen in the UV-Visible spectrum of the product and there is no such a low energy intense band in any of the relevant monomers. For Prussian blue a broad band around 690 nm with a considerably large extinction is observed.

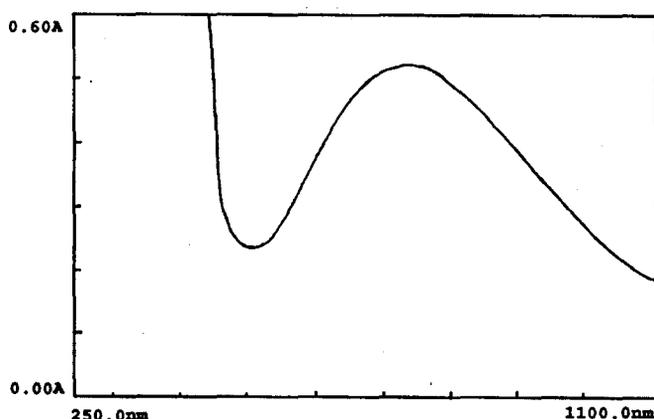


Figure 1. The UV-Visible spectrum of the new bimetallic system in H_2O at $pH = 3$

Data for the Job Plot is given in Table 2. The maximum absorbance at 740 nm is observed when the mole fraction of Ru(III) solution is around 0.5 according to the Job plot shown in Figure 2.

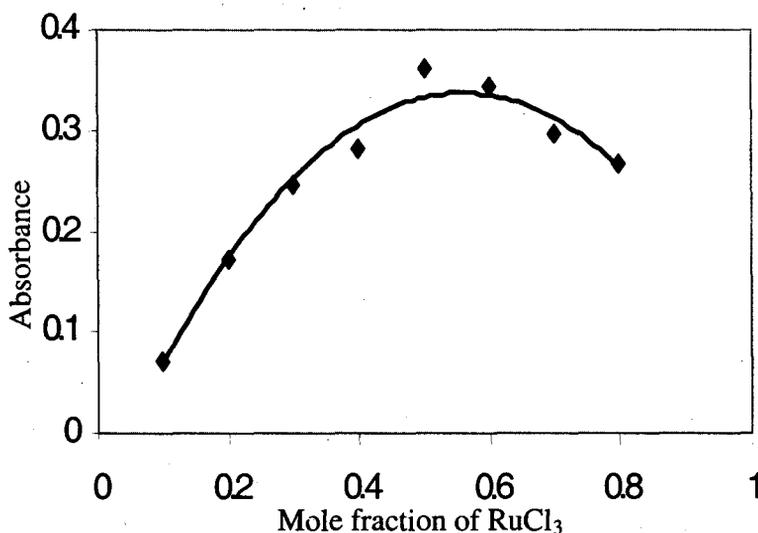


Figure 2. Job plot depicting the 1:1 ratio for the new complex in solution with the absorbance monitored at 742 nm.

Table 1. UV-Visible spectral data of the complexes in water at pH = 3.

Complex	λ_{\max} , nm	Absorptivity (ϵ_{\max}), $M^{-1}cm^{-1}$
$K_4[Fe(CN)_6]$	374	28
$RuCl_3$	~300, a shoulder	-
Prussian Blue	690	6030
$L_5Ru^{III}CNFe^{II}(CN)_5$ bimetallic system	742	362

Table 2. Absorbance at $\lambda_{\max} = 742$ nm with different mole fraction of $RuCl_3$.

Mole fraction of $RuCl_3$	Absorbance
0.1	0.072
0.2	0.173
0.3	0.247
0.4	0.280
0.5	0.362
0.6	0.344
0.7	0.295
0.8	0.268
0.9	0.286

Discussion

According to the job plot, the complex formed is a 1:1 dimer (i.e. Ru/Fe ratio of the new complex is 1:1). The high insolubility of the complex indicates that it's a highly charged species. The shoulder around 300 nm in the UV-Visible spectrum of the Ru^{III} monomer may be the ligand- (Cl)- to- metal (Ru^{III}) charge transfer band and the absorption around 374 nm of $K_4[Fe(CN)_6]$ may be due to the d-d or metal-to-ligand charge transfer transition. The UV-Visible spectrum of the dimer (Ru/Fe complex) is totally different from the relevant monomers and gives evidence for electronic coupling. The broad intense low energy band around 742 nm may be due to a charge transfer transition. Since it is novel to the product only, the observed band may be the metal- to- metal charge transfer (MMCT) band due to the electron transfer from Fe^{II} center to Ru^{III} center. This electron transfer can be taken place either coupling through the bridging ligand as in the case of usual inner sphere complexes such as Prussian blue or interacting two monometallic systems as ion pairs (or outer sphere complexes). However, the MMCT band of the novel complex is red sifted compared to that of Prussian blue implying low energy electron transfer process.

In aqueous solutions, $RuCl_3$ may exist as $Ru(H_2O)_6^{3+}$. But in a medium containing Cl^- ions (since dilute HCl has been added to the aqueous solution to adjust the pH of the medium) an aquo-chloro series of Ru^{III} complexes (of the type $[RuCl_n(H_2O)_{6-n}]^{(n-3)+}$ from $n = 6$ to $n = 0$)¹² can be present. The first quantitative problem is that the coordination sphere stoichiometry is not easy to define. The ratio of chloride to water will affect the Ru^{III}/Ru^{II} potential and the energy of the absorption maximum. If we assume only water is the ligand in the coordination sphere, then the $\{(H_2O)_6Ru^{III}, Fe^{II}(CN)_6\}$ ion pair would have an absorption maximum at about 505 nm with the absorptivity of $30-50 M^{-1}cm^{-1}$ ¹³.

However, aquo-ruthenium species are generally labile and we would expect some Ru-CN-Fe species (inner-sphere complex) to be formed since Ru^{III} complexes are amenable to coordinate with N-donor ligands. Then the inner-sphere complex such as Ru-CN-Fe should have an extinction of at least $1000 M^{-1}cm^{-1}$. The observed extinction of $362 M^{-1}cm^{-1}$ may be due to the reorganizational barrier for the electron transfer of the novel complex. Further, the smaller extinction of the observed inter-valence band of novel Ru/Fe complex compared to that of Prussian blue may be indicative of the less efficient electron transfer through CN bridge from Fe^{II} center to Ru^{III} center. On the other hand, the same argument and correlations observed for inner sphere complexes suggest that our observation might be consistent with a complex or ion pair containing monochloro- tetra- aquo-ruthenium center, too. The energy of the new absorption band (inter-valence band) of the novel Ru/Fe complex is both consistent with that of similar systems (table 3) and lower than that of Prussian blue. However, significantly high absorptivity with a low energy absorbance may be indicative of the formation of an inner sphere complex of the type Ru-CN-Fe or Ru-Cl-Fe and bridged mediated feasible electronic coupling. X-ray crystallographic analysis of the solid is expected to be carried out in order to determine the real structure and coordination stoichiometry of the new system.

Table 3. Ion-pair charge transfer spectral data: $\{M^{III}L_6^{m+}, X^n\} \rightarrow \{M^{II}L_6^{(m-1)+}, X^{(n-1)-}\}$

Acceptor	Donor	λ_{max} , nm	ϵ_{max} , $M^{-1}cm^{-1}$	Reference
$Ru(NH_3)_5Cl_2^{2+}$	$Fe(CN)_6^{4-}$	649	30	11
$Ru(NH_3)_5^{3+}$	$Fe(CN)_6^{4-}$	763	34	11
$Ru(H_2O)_{6-n}Cl_n^{(n-3)-}$ Where n = 6,5,4,3,2,1,0	$Fe(CN)_6^{4-}$	742	362	Current study

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