

Note

Charge type effects on the temperature dependence of intervalence transfer in ferrocyanide substituted ruthenium(III) amine and aminopolycarboxylate compounds

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Abstract

The $K_4[Ru^{III}(hedtra)NCFe^{II}(CN)_5]$ (**3**) (hedtra = *N*-hydroxyethylethylenediaminetriacetate) complex has been synthesised and characterised by physicochemical analysis. The temperature dependence of intervalence transfer in **3** has been studied and compared with that observed in $[Ru^{III}(edta)NCFe^{II}(CN)_5]^{5-}$ (**1**) and $[Ru^{III}(NH_3)_5NCFe^{II}(CN)_5]^-$ (**2**), complexes. The charge type on the ruthenium centre of the binuclear complexes has been found to effect the intervalence thermochromism. This has been discussed in terms of a charge type effect on the temperature dependency of ΔE (vibrationally relaxed initial state/final state separation energy) and the χ (reorganisation energy) component of E^{IVCT} (intervalence charge transfer energy).

Keywords: Intervalence transfer; Ruthenium complexes; Amine complexes; Aminopolycarboxylate complexes

1. Introduction

In an earlier communication [1] we reported the synthesis and physicochemical properties of a new mixed-valence binuclear complex, $(Ru^{III}(edta)NCFe^{II}(CN)_5]^{5-}$ (**1**) (edta = ethylenediaminetetraacetate). Complex **1** exhibited an intervalence absorption maximum (E_{op}) at 940 nm (at room temperature), the position of which was found to change with temperature. The value of dE_{op}/dT estimated for complex **1** ($-5 \text{ cm}^{-1} \text{ deg}^{-1}$) is lower than that ($-13.5 \text{ cm}^{-1} \text{ deg}^{-1}$) reported for $[Ru^{III}(NH_3)_5NCFe^{II}(CN)_5]^-$ (**2**) [2]. On the basis of electrochemical thermodynamics [3], we explained the lower dE_{op}/dT value observed in our case [1] by correlating dE_{op}/dT with the reaction entropy (ΔS_{rc}) [3] which is largely dependent on the nature of the coordinating ligands and the charge type of redox couples [4]. Coordination of anionic ligands changes the cationic environment of the metal fragments and generally yields substantially smaller values [4] of ΔS_{rc} . Although, it is obvious that the charge type on the ruthenium centre in complex **1** is more anionic ($-1/-2$) than that in complex **2** ($+3/+2$), the nature of the coordinating ligands is also different in complexes

1 and **2**. So, in order to examine the consequences of the earlier interpretation we have prepared another edta type binuclear complex, $[Ru^{III}(hedtra)NCFe^{II}(CN)_5]^{4-}$ (**3**) (hedtra = *N*-hydroxyethylethylenediaminetriacetate) (in which the charge type on the ruthenium centre is less anionic ($0/-1$) than that ($-1/-2$) of complex **1**, but the ligand environment in complex **3** is almost identical to that in complex **1**), and studied the intervalence thermochromism in aqueous solution. In this paper we describe the synthesis and characterisation of complex **3** and compare the effect of charge type on the observed thermochromism of IT in complexes **1**, **2** and **3**.

2. Experimental

2.1. Materials

$K[Ru^{III}(hedtra)Cl]$ was prepared by following the published procedure [5] and characterised. On dissolution the $K[Ru^{III}(hedtra)Cl]$ complex is rapidly aquated [6] to give a neutral $[Ru^{III}(hedtra)(H_2O)]$ species at low pH (<5). All other chemicals used were of A.R. grade. Double-distilled water was used throughout the experiments.

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2.2. Synthesis of $K_4[Ru^{III}(hedtra)NCFe^{II}(CN)_5]H_2O$ (3)

To a stirred solution (10 ml) of $K[Ru^{III}(hedtra)Cl]$ (1 mmol) was slowly added $K_4[Fe^{II}(CN)_6]$ (1.1 mmol) dissolved in the minimum volume of water. The reaction mixture was allowed to stir under Ar for 30 min at room temperature and then concentrated at room temperature under vacuum to 2–3 ml. On addition of acetone a green crystalline compound separated which was filtered off and washed with acetone–water (9:1). *Anal.* Found: C, 25.76; H, 2.11; N, 15.11. Calc.: C, 25.79; H, 2.01; N, 15.05%.

2.3. Instrumentation and techniques

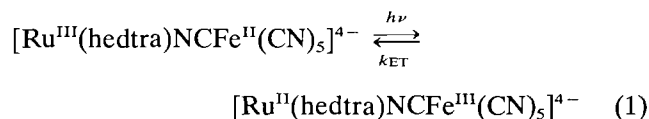
Elemental (C, H, N) analyses were carried out with a Carlo Erba elemental analyser. Spectral measurements (UV–Vis) were performed on a Shimadzu UV–Vis(160) spectrophotometer coupled with a temperature controller (TCC 240A). IR spectra (as KBr pellets) were recorded using a Carl Zeiss Specord M80 spectrometer. The EPR spectra of complex **2** were recorded in both powdered form (at r.t.) and frozen solution (at 77 K). A Bruker ESP 300 X-band spectrometer (100 kHz field modulation) with a built-in ERO 35 NMR gaussmeter (for magnetic field calibrations) was used for this purpose. Cyclic voltammetric measurements were carried out with Princeton Applied Research electrochemical instruments; a glassy carbon working electrode and saturated calomel electrode (as reference) were used for this purpose. KCl (0.1 M) was used as the supporting electrolyte for all electrochemical measurements. Variable temperature cyclic voltammetric studies were performed by adapting a non-isothermal cell configuration [3] of which the reference electrode (SCE) was kept at constant temperature (r.t.). Kinetic measurements were performed spectrophotometrically using a HI-TECH stopped-flow spectrophotometer coupled with an Apple IIe data analyser. The pH measurements were carried out with a Digisun pH meter.

3. Results and discussion

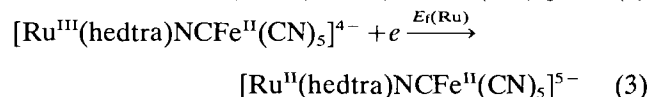
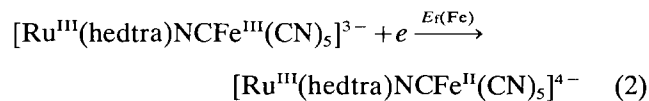
Upon addition of $K_4[Fe(CN)_6]$ the pale yellow solution of the $[Ru^{III}(hedtra)(H_2O)]$ complex changed immediately to green. This green product was isolated (see Section 2) and characterised. Elemental analysis of the green product confirmed the formula as $K_4[Ru^{III}(hedtra)NCFe^{II}(CN)_5]$ (3). The spectrum of complex **3** shows an intervalence absorption band at 945 nm ($\epsilon_{max}=2680$) at room temperature. The IR spectrum of **3** exhibited the usual ligand band of coordinated hedtra [5], and a broad band at 1620 cm^{-1} of the coordinated COO^- group [7]. Another broad

unsplit [1] band at 2062 cm^{-1} , was assigned to cyanide stretching. The EPR spectra of complex **3** both in powder form and frozen solution (77 K) consist of two well resolved g features ($g=2.323$ and 1.783) corresponding to the axial g tensor. The nature of the EPR spectrum of complex **3** and its component complex $[Ru^{III}(hedtra)(H_2O)]$ is almost identical and consistent with the fact that there is no apparent interaction between the two metal orbitals of complex **3** in the ground state. The cyclic voltammogram of complex **3** at room temperature showed two pairs of reversible waves associated with the $Ru^{III}-Fe^{III}/Ru^{III}-Fe^{II}$ (at $E_{1/2}=0.71\text{ V}$ versus NHE) and $Ru^{III}-Fe^{II}/Ru^{II}-Fe^{II}$ (at $E_{1/2}=0.01\text{ V}$ versus NHE) redox couples. The peak currents were found to be linearly dependent on the square root of the potential scan rate. The rate of formation of complex **3** was found to be dependent on the concentrations of $Ru^{III}(hedtra)(H_2O)$ and $Fe(CN)_6^{4-}$. The value of the second-order rate constant ($k=2.6\text{ M}^{-1}\text{ s}^{-1}$ at $25\text{ }^\circ\text{C}$) obtained in this case is smaller (as expected [6]) than that reported ($99\text{ M}^{-1}\text{ s}^{-1}$ at $25\text{ }^\circ\text{C}$) for the formation of complex **1**.

At room temperature complex **3** (in H_2O) shows the intervalence charge transfer (IVCT) maximum (E_{op}) at 945 nm. The corresponding optical electron transfer can be represented as follows



The position of E_{op} changes with a change in temperature (Fig. 1); the temperature dependence (dE_{op}/dT) of this thermal effect is shown in the inset of Fig. 1. The value of dE_{op}/dT estimated from the slope of the plot (inset of Fig. 1) is $-6.8 \pm 0.5\text{ cm}^{-1}\text{ deg}^{-1}$. As described earlier [1, 2] this temperature dependence term, dE_{op}/dT , can be approximated to $\Delta S_{rc}^\circ(Fe) - \Delta S_{rc}^\circ(Ru)$ for the following electrochemical processes



where E_r is the formal potential for the $M(III) \rightarrow M(II)$ electrochemical process. The temperature coefficient (dE_r/dT) of the individual E_r gives the corresponding ΔS_{rc}° value. The temperature dependences of E_r for the above described electrochemical processes (2) and (3) were estimated using non-isothermal cell configuration [3a] as described earlier and it was again found that there is a negligible temperature dependence of E_r for the Ru centre. The E_r for the Fe centre was

Table 1
Temperature dependence of E_{op} , ΔE and E_t ($M^{III} \rightarrow M^{II}$) of individual redox centres in complexes 1, 2 and 3

Complex	E_{op} (cm^{-1})	dE_{op}/dT^a (cm^{-1} deg^{-1})	Charge type on Ru fragments	Charge type on Fe fragments	$d\Delta E/dT^b$ (cm^{-1} deg^{-1})	$dE_t(Ru)/dT^c$ ($cm^{-1} deg^{-1}$)	$dE_t(Fe)/dT^d$ ($cm^{-1} deg^{-1}$)	Ref.
$[Ru^{III}(edta)NCFe^{II}(CN)_5]^{5-}$ (1)	10638	-5 ± 0.4	$-1/-2^e$	$-3/-4$	-6 ± 1		-6 ± 1	[1]
$[Ru^{III}(NH_3)_5NCFe^{II}(CN)_5]^-$ (2)	10360	-13.5 ± 1	$+3/+2$	$-3/-4$	-9.2 ± 1.5	1 ± 1	-8 ± 0.5	[2]
$[Ru^{III}(hedtra)NCFe^{II}(CN)_5]^{4-}$ (3)	10582	-6.8 ± 0.5	$0/-1$	$-3/-4$	-6.2 ± 1.1		-6.2 ± 1	this work

^aEstimated by spectral measurements.

^bEstimated by cyclic voltammetry using non-isothermal cell configuration; $d\Delta E/dT = \Delta S_{rc}^\circ$ (see Refs. [1] and [2]).

^c $dE_t(Ru)/dT = \Delta S_{rc}^\circ(Ru)$.

^d $dE_t(Fe)/dT = \Delta S_{rc}^\circ(Fe)$.

^eIn fact the charge type on the Ru redox site in 1 is $0/-1$, but the negative charge on the deprotonated and uncoordinated carboxylate arm of the edta ligand in 1 accounts for the overall charge type $-1/-2$ on the ruthenium fragment in complex 1.

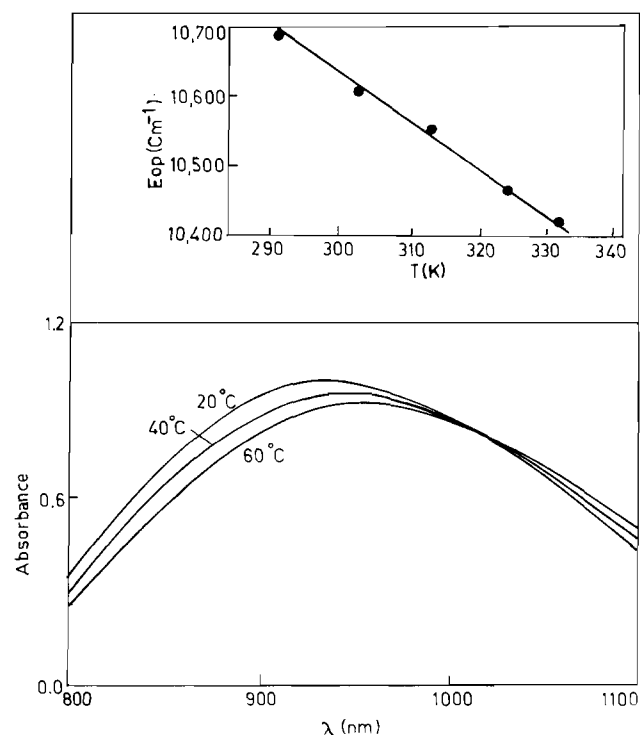


Fig. 1. Intervalence absorption spectra for complex 3 in water at 20, 40 and 60 °C. Inset: E_{op} (cm^{-1}) vs. temperature (K).

found to be temperature sensitive and the value of $dE_t(Fe)/dT$ (i.e. $\Delta S_{rc}^\circ(Fe)$) is estimated as -6.2 ± 1 $cm^{-1} deg^{-1}$ (units volt deg^{-1} converted to $cm^{-1} deg^{-1}$). The electrochemical quantity value (-6.2 ± 1 $cm^{-1} deg^{-1}$) compares reasonably well with that (-6.8 $cm^{-1} deg^{-1}$) obtained from intervalence absorption measurements. The values of dE_{op}/dT , $d\Delta E/dT$ and other relevant thermodynamic data obtained for the three complexes 1, 2 and 3 are summarised in Table 1. The order of decrease in magnitude of the temperature coefficient terms ($2 > 3 > 1$) for the different ferrocyanide substituted binuclear ruthenium(III) complexes can be understood qualitatively, by reference to earlier reports, as being due to a decrease in the cationic environment

on the ruthenium fragments (Table 1) of the binuclear compounds. However, a careful analysis of the data obtained from electrochemical experiments suggests that the values of $d\Delta E/dT$ (i.e. ΔS_{rc}°) are due mainly to $\Delta S_{rc}^\circ(Fe)$ as the $E_t(Ru)$ values in all three complexes are seemingly temperature independent (Table 1). Further, it also appears that the binding of the Ru(III)/Ru(II) redox sites does not influence the $\Delta S_{rc}^\circ(Fe)$ values as they are almost unchanged in the above three complexes (Table 1). Recognising that the ΔS_{rc}° value for cyano Fe(III)/Fe(II) systems is extremely sensitive to the cationic environment [8], the values of $\Delta S_{rc}^\circ(Fe)$ obtained here for complexes 1 and 3 should have been very different to that reported for complex 2 (Table 1). This apparent contradiction may be due to the fact that in a valence-localised¹ system, binding of Ru(III)/Ru(II) sites, cationic or anionic, does not change the solvation around the Fe(III)/Fe(II) redox site as much as it occurs between cyano-ferrate and its conjugated acid systems [8]. Concerning the values of $d\Delta E/dT$ for complexes 1, 2 and 3 (Table 1) (which are not very different when considering the error limits), one may think that the difference in the values of dE_{op}/dT (-13.5 $cm^{-1} deg^{-1}$) and $d\Delta E/dT$ (-9.2 $cm^{-1} deg^{-1}$) is not fortuitous and can be accounted for by some other components of E_{op} which are not considered by Dong and Hupp in their earlier report [2]. In a very recent report for a somewhat different [9] system ($[2,2'-bipy]_2Cl$ Ru-pyrazine-Ru(NH_3) $_3$) $^{4+}$) they explained the difference between dE_{op}/dT and $d\Delta E/dT$ by considering E_{op} as composed of two factors namely ΔE (vibrationally relaxed initial state/final state separation energy) and χ (reorganisation energy) for a valence localised system, then a decrease in temperature would make the system more localised which would cause the increase in the solvent polarisation component of χ . In this situation

¹For a valence localised asymmetric system $\chi + \Delta E \gg 2H_{if}$, where H_{if} = initial state/final state coupling energy. In this situation $E^{IVCT} = \chi + \Delta E$.

more charge will probably be transferred upon absorption to E_{op} . However, our experimental results suggest that this temperature effect of χ would be small in an anionic environment. Although, our systems (complexes **1** and **3**) are valence localised, the negligible difference between the two estimates dE_{op}/dT and $d\Delta E/dT$ obtained for complexes **1** and **3** strengthens our view.

4. Conclusions

We conclude from this work that the charge type on the ruthenium fragment influences the temperature dependence of the IVCT process rather than ΔE of the binuclear systems described earlier [3,4]. This occurs because the former process involves another temperature dependent term namely reorganisation energy (χ), a component (solvent polarisation component) of which seems to be very sensitive to a cationic environment but is unaffected by temperature in an anionic environment. A very recent observation by Hupp and Dong [9] reinforces our arguments as they report the difference between dE_{op}/dT ($-18 \text{ cm}^{-1} \text{ deg}^{-1}$) and $d\Delta E/dT$ ($-8 \text{ cm}^{-1} \text{ deg}^{-1}$) as more than a factor of two for the system $[(2,2\text{-bipy})_2\text{Cl Ru-pyrazine-}$

$\text{Ru}(\text{NH}_3)_5]^{4+}$ in which the charge type on both the metal centres is notably cationic. Although, our observation is restricted to only three different ferrocyanide substituted Ru(III)–amine and –aminopolycarboxylate complexes, we believe that the above described effect may operate in other asymmetric mixed-valence (and of course valence localised) binuclear system. Work pertinent to this matter is in progress.

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