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Mixed valence properties of a new binuclear complex, [(edtaH)Ru^{III}NCRu^{II}(CN)$_5$]$^{4-}$ and kinetic studies of the aqua substitution reaction in Ru^{III}(edta)(H$_2$O)$^-$ by Ru(CN)$_6^{4-}$

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Abstract—A new asymmetric mixed valence complex, K$_4$[(edtaH)Ru^{III}NCRu^{II}(CN)$_5$] · 2H$_2$O, has been synthesized by aqua substitution reaction of [Ru(edtaH)H$_2$O] by K$_4$Ru(CN)$_6$. Kinetic studies revealed an associative mechanism for the substitution reaction with a second order rate constant 13.8 ± 0.6 M^{-1}s^{-1} at 25°C and pH = 5.0. This complex shows an MMCT maximum at 682 nm in water at 25°C. Thermochromism of the MMCT band has been discussed. On the basis of α^2 (ground state delocalisation) and H$_{AB}$ (coupling integral) values this complex can be categorized as a Robin–Day class-II type complex. © 1997 Elsevier Science Ltd

Keywords: synthesis; ruthenium; binuclear complexes; kinetics; mixed-valence; thermochromism.

The experimental and theoretical study of intervalence electron transfer is of great fundamental importance [1,2], especially in the domain of solid state chemistry [3], inorganic reaction mechanism [4] and the emerging field of molecular electronics [5]. Compounds exhibiting metal-to-metal charge transfer (MMCT) transitions have played a crucial role in the development and understanding of electron transfer reactions [1,6]. The ambient nature of the cyanide ligand has provided the synthetic flexibility to construct the stable group VIII homo/heterobinuclear mixed valence compounds by stabilizing the electron deficient metal (M^{III}, d^5) acceptor through σ-basicity and the electron rich metal (M^{II}, d^6) donor through π-acidity. To date a number of mixed valence binuclear complexes have been reported using cyanide as the bridging ligand [6].

In mixed valence binuclear complexes, which belong to the Robin–Day class-II, low energy absorption bands are frequently observed for MMCT or intervalence transition (IT) [7]. The perturbation theory of electronic approach of Hush Model [8] accounts for the degree of electronic coupling, extent of ground state delocalisation and the rate of electron transfer between donor and acceptor by using the information derived from MMCT oscillator strength. There are some specific advantages [9] of this theory over the more sophisticated method based on flash photolysis. These experiments are simple and more importantly, it is essentially insensitive to intermolecular electron transfer.

In our previous communication we have reported the effect of the length of the conjugated spaces on the degree of electronic coupling [10] and the thermochromic effect on the IT process of the heterobinuclear complexes [11,12] of Ru^{III}–CN–Fe^{II}. The present work was undertaken in order to study the electronic interaction between two ruthenium centers (Ru^{III}–Ru^{II}) and to search for the analogies and differences in the corresponding Ru^{III}–Fe^{II} system. In this paper we report the synthesis, kinetics of its formation, thermochromic effect of the MMCT band and studies of mixed valence properties of the binuclear complex K$_4$(edtaH)RuNCRu(CN)$_5$].

EXPERIMENTAL

Materials

K[Ru(edta)Cl] · 2H$_2$O was prepared using the published procedure [13]. K$_4$Ru(CN)$_6$ was used as

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received from Aldrich. [Bu$_4^i$N]ClO$_4$ was used as background electrolyte for electrochemical studies. All other chemicals used were of AR grade. Doubly distilled water was used through out the experiments.

Physical measurements

Microanalyses were carried out with a Perkin–Elmer elemental analyzer. Absorption spectra were recorded on a Shimadzu UV-3101 PC spectrophotometer equipped with a TCC-260 temperature controller. IR spectra were recorded on a Carl-Zeiss Specord M80 spectrometer as KBr pellets. ESR experiments were carried out by using a Bruker ESP 300X spectrometer either at room temperature or at 77K using a Dewar insert in the sample chamber. Electrochemical experiments were performed by using a PAR 273A instrument. A conventional three electrode cell assembly consisting of saturated calomel as reference and platinum as working electrode was used. Variable temperature electrochemical measurements were carried out by using a non-isothermal cell configuration [14] at which the reference electrode (SCE) was kept at constant temperature (room temperature). All potential quoted are vs. SCE as standard. pH measurements were carried out with a Digisun pH meter.

Synthesis of K$_4$[(edtaH)RuNCRu(CN)$_5$]·2H$_2$O ; (1)

K$_4$Ru(CN)$_6$ (0.083 gm, 0.2 mM) dissolved in minimum volume of water was added slowly to a stirred solution (10 cm^3) of K[Ru(edtaH)Cl]·2H$_2$O (0.1 gm, 0.2 mM) at room temperature. The color of the solution immediately changed to dark blue. The reaction mixture was stirred for 30 min at room temperature and then concentrated *in vacuo* to 2–3 cm^3. The desired blue complex was precipitated by the addition of cold acetone and was filtered off. The blue residue was further recrystallized twice from water–acetone mixture (3 : 7, v/v) and dried *in vacuo* (yield 80%). Found (Calc.) ; C 22.8 (22.9), H 2.1 (2.0), N 13.3 (13.3)%.

Kinetic studies

Kinetics of the aqua substitution reaction of [Ru(edta)H$_2$O)$^-$] by Ru(CN)$_6^{4-}$ was studied spectrophotometrically at 682 nm, the MMCT band (*vide infra*) for the mixed valence complex, using a High Tech SF-51 stopped flow spectrophotometer thermostated to ±0.2°C. In all instances pseudo-first order conditions were maintained (excess Ru(CN)$_6^{4-}$) and the corresponding first order plots were linear for at least 2–3 half lives of the reactions. Rate constants data represented as an average of triplicate runs and reproducible with in ±4%. pH was maintained with acetic acid–acetate buffer and ionic strength was maintained with KCl.

RESULTS AND DISCUSSION

K[Ru(edtaH)Cl] hydrolyses rapidly in aqueous solution to give Ru(edtaH)(H$_2$O) [15], which undergoes aqua substitution reaction in the presence of N-donor ligands within the stopped flow time scale [16]. Upon addition of K$_4$Ru(CN)$_6$ solution to the pale yellow aqueous solution of K[Ru(edtaH)Cl], the color changes to deep blue and the desired blue complex was isolated and characterized. Elemental analysis for this complex agrees well with the proposed formulation. The UV–vis spectrum for this complex shows an intervalence absorption band at 682 nm ($\varepsilon = 1900 \pm 50$ M^{-1} cm^{-1}) at room temperature (Fig. 1). An intervalence absorption band was reported for the analogous complex, [(NH$_3$)$_5$Ru^{III}NCRu^{II}(CN)$_5$]$^-$ at 685 nm ($\varepsilon = 2800$ M^{-1} cm^{-1}). The IR spectrum exhibited the usual band for metal coordinated —COO$^-$ and uncoordinated —COOH stretching frequencies at 1640 cm^{-1} (br) and 1725 cm^{-1}, respectively [10–12]. In addition a strong band appeared at 2055 cm^{-1}, which was assigned to cyanide stretching [11,12,17]. It may be noted here that the stretching frequencies for bridged and terminal cyanide groups are similar. A similar observation, only one stretching band at 2060 cm^{-1}, was reported earlier [17] for the complex [(NH$_3$)$_5$Ru^{III}NCRu^{II}(CN)$_5$]$^-$. The EPR spectra for complex **1**, both in powder form and frozen solution (77 K) showed a spectral pattern, which is almost identical to our previous observation for complex **2** ($g_1 = 2.39$, $g_2 = 2.34$ and $g_3 = 1.76$) and is characteristic for the Ru^{III}(edta)-unit. This is indicative of no apparent interaction (within the EPR time scale) between the two metal orbitals in **1** in the
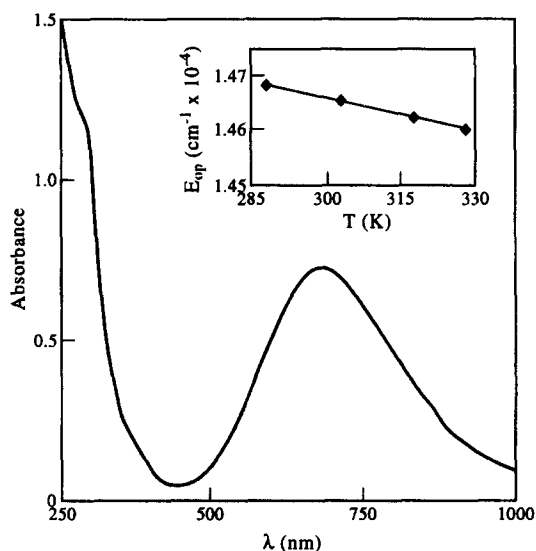

Fig. 1. Absorbance spectrum of K$_4$[(edtaH)RuNCRu(CN)$_5$] in water at room temperature ; [K$_4$[(edtaH) RuNCRu(CN)$_5$]] = 3.75 × 10^{-4} M. (Inset : Plot of E$_{op}$ versus temperature for the MMCT band of K$_4$[(edtaH) RuNCRu(CN)$_5$]).

ground state [11,12]. The cyclic voltammogram of **1** showed a quasi-reversible process at $E_{1/2} = -0.27$ V ($E_{pa} - E_{pc} = 150$ mV) and a reversible process at $E_{1/2} = 0.67$ V ($E_{pa} - E_{pc} = 80$ mV), which were assigned for the $Ru^{II/III}$ couple in Ru(edtaH) and $Ru^{II/III}$ couple in the $Ru(CN)_6$ components respectively. Little variation in the $E_{1/2}$ value for the two different ruthenium centers in complex **1** with that from their individual component [11,18] is due to a weak electrochemical interaction between the two metal centers in the ground state.

Kinetics of the formation of complex 1

The kinetics of the formation of **1** was monitored at 682 nm, (the λ_{max} of MMCT for the complex [(edta)RuNCRu(CN)$_5$]$^{5-}$) under pseudo order condition taking $Ru(CN)_6^{4-}$ in excess. The reaction was studied at pH 5.0 (acetic acid–acetate buffer). At this pH $Ru(edta)H_2O^-$ and $Ru(CN)_6^{4-}$ are the only reactive species [11,19,20]. Preliminary kinetic experiments showed that the aqua substitution reaction in [Ru(edta)H$_2$O]$^-$ by $Ru(CN)_6^{4-}$ was fast enough so that the buffer components and the chloride ions (used to maintain ionic strength) do not interfere with the formation kinetics. The rate of the reaction was found to be first order with respect to [Ru(edta)H$_2$O$^-$] and it increased linearly with the increase in [Ru(CN)$_6^{4-}$]. The plot of k_{obs} vs [Ru(CN)$_6^{4-}$] gave a straight line with negligible intercept (Fig. 2), which is indicative of the absence of reverse aquation reaction under the specified experimental conditions. Further the rate constant remain unchanged under the inert conditions. On the basis of above observations, the following mechanism (eq. 1) and rate expression (eq. 2) is proposed.
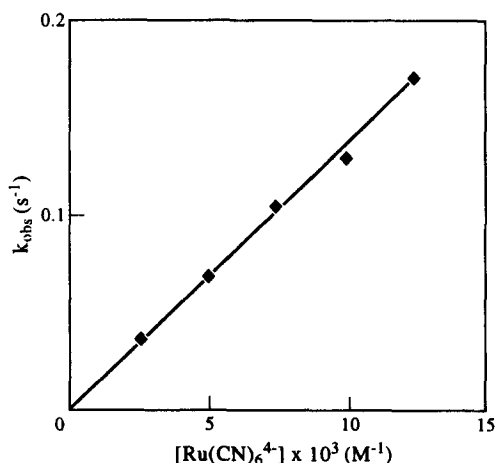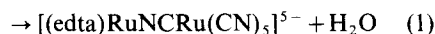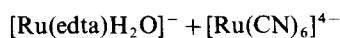

Fig. 2. Dependence of k_{obs} on [Ru(CN)$_6^{4-}$] for the reaction of Ru(edta)(H$_2$O)$^-$ with [Ru(CN)$_6^{4-}$]: [Ru(edta)(H$_2$O)$^-$]$_T$ = 2.00 × 10^{-4} M; pH = 5.0 (acetic acid/ acetate buffer, 0.2 M); μ = 0.5 M (KCl); T = 25 ± 0.2°C.

$[Ru(edta)H_2O]^- + [Ru(CN)_6]^{4-}$

$$\rightarrow [(edta)RuNCRu(CN)_5]^{5-} + H_2O \quad (1)$$

$$k_{obs} = k[Ru(CN)_6^{4-}] \quad (2)$$

Moreover dependence of ionic strength on the observed rate constant further consolidate our presumption. The plot of k_{obs} vs $\mu^{1/2}/(1 + \mu^{1/2})$, where μ is ionic strength (0.1–0.5 M, KCl) of the solution, resulted in a straight line with a slope equal to 3.95 ± 0.2. According to the Bronsted equation [21] the slope represents the product of the charges on the reactants. Thus the value obtained above is close to the value expected, 4 for the mechanism outlined in eq. 1. The substitution reaction was studied at four different temperatures; k at four different temperatures are 44.8 M^{-1} s^{-1} (45°C), 33.6 M^{-1} s^{-1} (40.7°C), 21.6 M^{-1} s^{-1} (35°C) and 14.4 M^{-1} s^{-1} (30°C). The activation parameters, calculated using the Eyring plot, are $\Delta H^{\ddagger} = 53 \pm 1$ kJmol^{-1} and $\Delta S^{\ddagger} = -31 \pm 3$ Jdeg^{-1} mol^{-1}. The negative $\Delta S^{\ddagger}$ value suggests an associative pathway for the substitution reaction [11].

Thermochromic effect

At room temperature aqueous solution of complex **1** shows the MMCT band at 682 nm (E_{op}) and the corresponding intervalence electron transfer reaction is represented in eq. 3. The charge transfer theories of Marcus [22] and Hush [23] correlate the optical charge transfer energy (E_{op}) and the redox potential in complex **1**. In this context, E_{op} can be equated with $\lambda + \Delta E$, where λ is the reorganization energy (expected to have a negligible contribution) and ΔE is the difference in redox potentials of the metal centers [11,12,24]. The more positive $E_{1/2}$ value of the $Ru^{II/III}$ couple (0.67V) for $Ru(CN)_6^{4-}$ in complex **1** compared to $Fe^{II/III}$ couple (0.23V) in $Fe(CN)_6^{4-}$ component in complex **2** gives a larger difference in redox potentials of the two ruthenium centers in **1** and thus a higher energy for the IT band is observed. Moreover the difference in energies of the IT bands (Table 1) for **1** and **2** is 0.49 V. This value compares favorably with the difference in redox potential (0.51V) of [M(CN)$_6$]$^{3-/4-}$ (M = Fe; $E_{1/2} = 0.19$ V [18b] and M = Ru; $E_{1/2} = 0.70$V vs SCE).

$[(edtaH)Ru^{III}NCRu^{II}(CN)_5]^{4-}$

$$\overset{E_{op}}{\underset{E_{th}}{\rightleftarrows}} [(edtaH)Ru^{II}NCRu^{III}(CN)_5]^{4-}. \quad (3)$$

The absorption maxima of the MMCT band for complex **1** changes with the change in temperature. The plot E_{op} vs temperature, (dE_{op}/dT), is shown in the Fig. 1 and the value estimated from the slope of the plot is -4.1 ± 0.5 cm^{-1} deg^{-1}. Hush's treatment for optically induced electron transfer energies [1,2,11,23] can be stated as

Table 1. Mixed-valence data for $K_4[(edtaH)Ru^{III}NCRu^{II}(CN)_5]$ **1** and $K_5[(edta)Ru^{III}NCFe^{II}(CN)_5]$ **2**

Complex/parameters	v_{max} (cm^{-1})	ε_{max} cm^{-1}	$\Delta v_{1/2}$ (cm^{-1}), calc. (expt)	α^2	H_{AB} (cm^{-1})
$[(edtaH)Ru^{III}NCRu^{II}(CN)_5]^{4-}$	14577	1900 ± 50	5802 (5950)	0.0118	1587
$[(edta)Ru^{III}NCFe^{II}(CN)_5]^{5-}$	10638	2700 ± 100	5312 (4950)	0.0197	1490

$$E_{op} = \lambda_{vib} + \lambda_s + \Delta E. \quad (4)$$

As described earlier [11,25,26] the temperature dependent term dE_{op}/dT, can be approximated to $\Delta S^o_{rxn} = \Delta S^o(Ru^{II}) - \Delta S^o(Ru^{III})$ [1,11,25]. We have determined the temperature dependence of $E_{1/2}$ for two ruthenium centers in **1** and found that $E_{1/2}$ for $Ru^{II/III}$ couple of the Ru(edtaH)—unit is practically immune to the temperature variation while that for $Ru(CN)_6$—center decreases with increase in temperature and is shown in Fig. 3. The value of $\Delta S^o(Ru^{II})$ (i.e. $\Delta E/dT$) obtained from slope of the plot, $E_{1/2}$ of $Ru^{II/III}$ couple (for $Ru(CN)_6^{4-}$ center) vs temperature [14,26,27] is equal to -3.45 ± 1.0. cm^{-1} deg^{-1}. Thus the $\Delta E/dT$ value obtained by CV studies under non-isothermal conditions is comparable to the dE_{op}/dT value obtained by spectral measurements. Despite asymmetry in complex **1**, the value for dE_{op}/dT observed is comparatively lower than that reported [25] for another asymmetric complex, $[(NH_3)_5Ru^{III}NCFe^{II}(CN)_5]^-$ ($dE_{op}/dT = -13.5$ cm^{-1} deg^{-1}). However this can be explained by considering the fact that the MMCT process involve another temperature dependent term (λ, reorganisation energy), a component of which seem to be very sensitive to a cationic environment but is unaffected by temperature in an anionic environment [28]. A recent report by Hupp and Dong [29] has further consolidated our presumption as they have observed a difference in dE_{op}/dT (-18 cm^{-1} deg^{-1}) and $d\Delta E/dT$ (-8 cm^{-1}
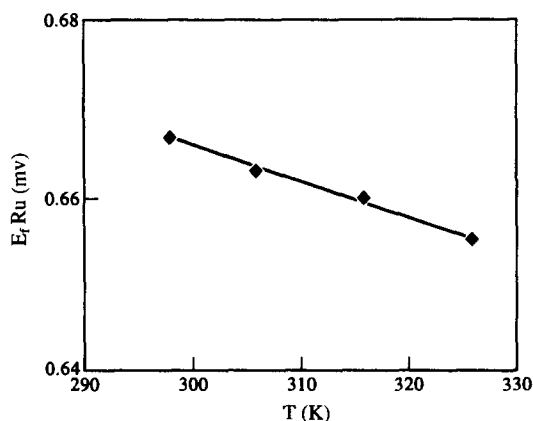
deg^{-1}) by a factor of two for the system Cl(2,2'-bipy)$Ru(pyz)Ru(NH_3)_5^{4+}$, where the charge type on both the metal centers is notably cationic.

Electronic coupling

Electrochemical studies as discussed above reveal only a weak electrochemical interaction in the ground state between the two metal centers for complex **1**. For weakly coupled mixed valence metal ions, the perturbation theory approach of the Hush model [1,8,30] accounts for the degree of electronic coupling between donor and acceptor wave function by using information derived from the MMCT oscillator strength. Assuming a Gaussian band shape, a lower limit for $\Delta v_{1/2}$ (band width in cm^{-1} at one-half ε_{max}, where ε_{max}, is molar absorptivity of the MMCT band) at room temperature can be obtained from the relation

$$\Delta v_{1/2}(calc) = (2304 \times v)^{1/2} \quad (5)$$

where v is the energy of the MMCT transition at ε_{max} in cm^{-1}. H_{AB}, the extent of electronic coupling arising from orbital mixing is given by:

$$H_{AB} = [(2.05 \times 10^{-2}/R)](\varepsilon_{max}\Delta v_{1/2}v)^{1/2}. \quad (6)$$

R is the separation between donor-acceptor wave function in eq. 6. Values for v and R for this complex are 14577 cm^{-1} and 5.2 Å respectively. The theoretically obtained value, calculated using eq. 5, for $\Delta v_{1/2}$ is 5802 cm^{-1}, which is lower than that observed experimentally [$\Delta v_{1/2}$ (exp.) = 5950 cm^{-1}]. This further indicates a weak interaction between the two metal orbitals [31]. The theoretical value for ground state delocalization in mixed valence complex can also be calculated from the relation

$$\alpha^2 = 4.24 \times 10^{-4}\varepsilon_{max}\Delta v_{1/2}/(vR^2). \quad (7)$$

The delocalisation parameter, α^2 is 0.0119, which corresponds to electron delocalisation of only 1.1%. While H_{AB} calculated on the basis of eq. 6 is 1.58×10^3 cm^{-1}. Comparison of the values of α^2 and H_{AB} with those of the other Robin–Day class-II type complexes reveals the valence localized [31] nature for the complex **1**. Further the α^2 value for complex **2** (0.019) is approximately double that for **1**. If there where significant interaction and metal-metal overlap, a more dramatic metal based dependence [32] of α^2 should have been observed.

Fig. 3. E_f versus temperature (non-isothermal cell configuration) for $Ru^{II/III}$ of $Ru(CN)_6$-unit in complex **1** in aqueous 0.1 M $[Bu^n_4N]ClO_4$.

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