β-Cyclodextrin-Assisted Intervalence Charge Transfer in Mixed-Valent [2]Rotaxane Complexes Having Metal Centers Linked by an Interrupted π-Electron System**

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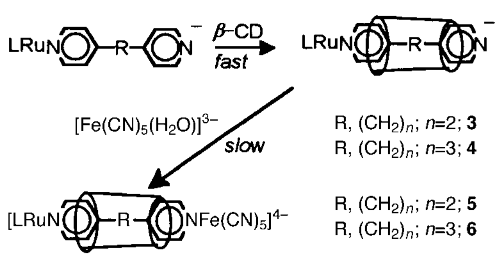
The study of intramolecular electron transfer in redox active dinuclear transition metal complexes, where redox active metal centers are linked by a hydrocarbon bridge is of fundamental importance and an area of contemporary research.[1] Though there are many reports on the role of the bridging ligand (BL) in tuning metal–metal interactions in di/polynuclear metal complexes,[2] to date very little is known about the role of the BL when it is trapped in hydrophobic cyclodextrin (CD) cavity.[3] Spectroscopic and kinetic studies on supramolecular self assembly of [2]rotaxanes with symmetric/asymmetric threads, that is, hydrocarbon chains with identical bulky metal units as stoppers or cationic species as electric traps have been reported.[4] These studies exploit the phenomenon of non-covalent bonding interaction between α- or β-CD and hydrocarbon spacers. However, no such supramolecular assembly using metal units in different oxidation states as stoppers has been reported. This approach can enable us to investigate the effect that inclusion of BLs in the CD cavity has and thus the effect of nonbonding interactions on intervalence charge transfer (IVCT) and metal–metal interactions. We report herein the syntheses of [2]rotaxane complexes having transition metal units with different oxidation states as stoppers, β-CD as a cyclic molecular head, and 4,4-bipyridyl derivatives as the BL. Also, the effect of the inclusion of the BL in the hydrophobic CD cavity is discussed.

The complexes [RuL(H$_2$O)] (L is Hedta^{3-}; H$_4$edta is ethylenediaminetetraacetic acid) and Na$_3$[Fe(CN)$_5$(H$_2$O)] produced by the rapid aquation of K[RuLCl]$\cdot$2H$_2$O and Na$_3$[Fe(CN)$_5$(NH$_3$)]$\cdot$3H$_2$O, respectively, react with N-donor heterocycles through a facile aqua-substitution pathway on the stopped-flow time scale to form the corresponding metal complex in near quantitative yield.[4–6] We have taken advantage of the aqua-substitution reaction of these two complexes, along with the great tendency of β-CD to bind 1,2-bis(4-pyridyl)ethane (bpe) and 1,3-bis(4-pyridyl)propane (bpp),[6] to synthesize [2]rotaxane complexes, **5** and **6**, respectively by treating the semirotaxane complexes **3** and **4** with [Fe(CN)$_5$(H$_2$O)]$^{3-}$ (Scheme 1). In the UV/Vis spectra complexes **5** and **6** show a characteristic broad absorbance at $\approx$1000 nm both in aqueous solution and the solid state, this absorbance is not seen for the complexes **1**–**4**. Proposed formulations for the isolated inclusion complexes **3**–**6** match nicely with the analytical data.[7] The formation in solution of semirotaxane complexes of bpe and bpp with β-CD, **3**, and **4**, can also be demonstrated in the ^{1}H NMR spectra by inspection of the complexation-induced shift of the resonance signals for the guest molecule (Figure 1). The [2]rotaxane species **5** and **6** also form in solution by self-assembly through the reverse aquation reaction of the pre-synthesized dinuclear complexes **1** and **2** (Scheme 2), respectively, in the presence of excess β-CD (Figure 2). On addition of excess DMSO[8] to aqueous solutions of complexes **5** and **6** a decrease in the



Scheme 1.

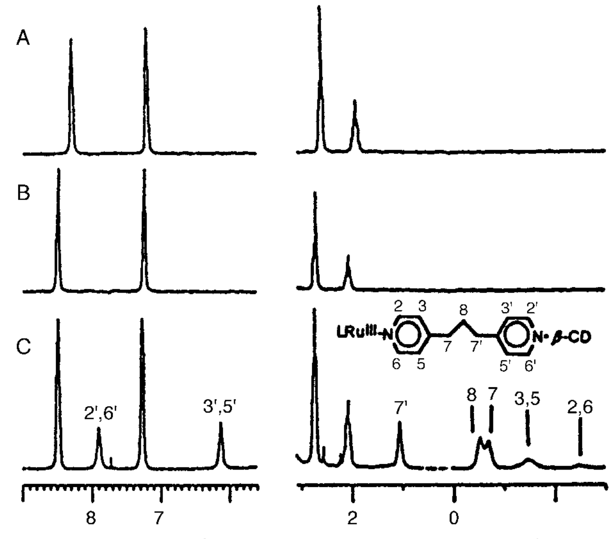
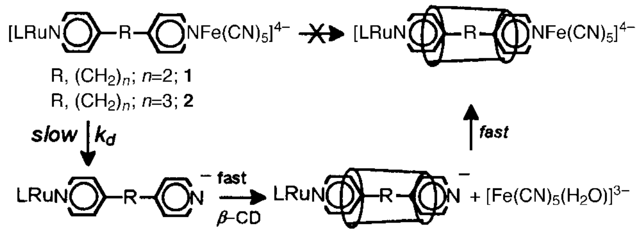


Figure 1. ^{1}H NMR spectra (200 MHz) of A) bpp in D$_2$O; B) (bpp$\cdot\beta$-CD) and excess β-CD in D$_2$O; C) (LRubpp$\cdot\beta$-CD, bpp$\cdot\beta$-CD) and excess β-CD in D$_2$O. [bpp] = 2.0×10^{-3} M, [β-CD] = 1.6×10^{-2} M, and [RuL(H$_2$O)] = 6.66×10^{-4} M. Spectral features arising from β-CD protons are excluded for clarity. The pH of the resulting mixture was maintained at $\approx$5.0 using Na$_2$HPO$_4$.



Scheme 2.

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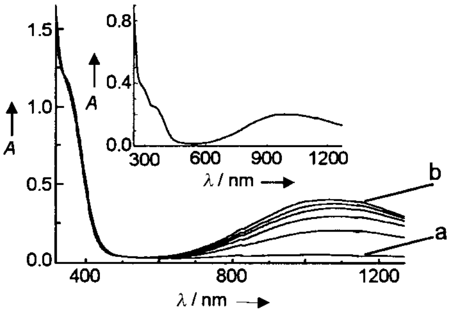

Figure 2. UV/Vis/NIR absorption spectra of aqueous solutions of: [(edta)Ru(bpp)] (1 mL; 3.5×10^{-3} M), $[Fe(CN)_5(H_2O)]^{3-}$ (0.1 mL; 3.5×10^{-4} M), $\mu = 0.1$ M (KCl) which were kept in dark of 15 min after mixing at pH 5.0. To this solution β-CD (1.2 mL; 1.6×10^{-2} M) was added and electronic spectra were recorded at different time intervals, keeping reaction temperature at 35 °C. The time interval between the initial (a) and final (b) spectra was 90 min; inset: absorption spectra of isolated complex **6** (1.5×10^{-4} M) in water.

absorbance at $\approx$1000 nm was registered with time. DMSO reacts with the $[Fe(CN)_5(H_2O)]$ species, produced by dissociation of complex **5** or **6**, to form an inert complex $[Fe(CN)_5(DMSO)]^{3-}$ and thereby prevents further dinuclear complex formation [Eq. (1)]. This result also confirms that the synthesis of [2]rotaxane complexes, **5** and **6** is through a self-assembly route. Further, almost identical spectral features are observed for the complexes **5** and **6** in both the solid state and in freshly prepared aqueous solutions, which suggests that these complexes remain unchanged in solution.

$$[(L)RuBL \cdot \beta\text{-CD-}Fe(CN)_5]^{4-} \xrightarrow[\text{DMSO}]{\beta\text{-CD}} [(L)RuBL \cdot \beta\text{-CD}]^{-} + [Fe(CN)_5(DMSO)]^{3-} \quad (1)$$

The UV/Vis/NIR spectra of aqueous solutions of complexes **5** and **6** show a broad absorption band centered around 1000 nm in addition to the bands expected for LMCT (ligand to metal charge transfer) transitions (310 nm) for the (edta)-Ru-py chromophore (py = pyridine) and the MLCT (metal to ligand charge transfer) band (360 nm) for the $(CN)_5Fe^{II}$-py chromophore.[7] The band at 1000 nm disappears when the Ru^{III} center of complex **5** or **6** is reduced by bulk electrolysis (at −0.3 V, vs. SCE). This observation indicates that the band around 1000 nm arises from an optical electron transfer from Fe^{II} to Ru^{III}.[5, 9] No such IVCT band is either expected or observed for complex **1** or **2**, where the Fe^{II} and Ru^{III} centers are separated by the interrupted π-electron system of the BL.[9, 10] The inclusion into the CD cavity also prevents folding of the bpe or bpp units as well as a closed conformation for **5** and **6**, as was proposed for $[(CN)_5Fe(bpe)Co(NH_3)_5]$.[11] This excludes any probability of electron transfer "through space" because in the absence of folding the two metal centers cannot come closer than 11 Å which is too large a distance for direct electron transfer through space. Moreover, cyclodextrin is made of carbohydrates and is not expected to mediate electron transfer.

Upon inclusion of the coordinated N-heterocyclic ligand into the β-CD cavity the MLCT band ($d_{Fe} \rightarrow \pi^*_{Py}$; 380 nm for complex **5** and 378 nm for complex **6**) for the $(CN)_5Fe$-py center shows a red shift of about 22 nm—indicating a lowering of the LUMO energy of the BL as a result of inclusion—while a small blue shift ($\approx$10 nm) is observed for the LMCT band ($d_{Ru} \leftarrow \pi_{Py}$) at 300 nm for the (edta)Ru-py center. Careful analysis of the results of cyclic and differential pulse voltammetric experiments for **5** and **6** show that the $E_{1/2}$ for the $Fe^{II/III}$ couple in both complexes has shifted to the anodic side (< 20 mV) on the inclusion of the BL into the β-CD cavity, while $E_{1/2}$ for the Ru^{II}/Ru^{III} couple remains almost unchanged. The ΔE ($E_{1/2}(Ru^{III}/Ru^{II}) - E_{1/2}(Fe^{III}/Fe^{II})$) value decreases by only $\sim$15 mV on the inclusion of the BL in the β-CD cavity. Thus, there is no appreciable change in the potential energy barrier for electron transfer even after the inclusion of the BL in the β-CD cavity. Other noticeable changes in the cyclic voltammogram include an appreciable decrease in the current intensity and broadening of the redox waves ($E_p - E_a \geq 180$ mV for both Fe^{II}/Fe^{III} and Ru^{II}/Ru^{III} couples) for complexes **3**–**6**. This is expected considering the anticipated decrease in the values for the diffusion coefficient of the respective complexes compared to the non-inclusion complexes at the same concentration. These results reveal that inclusion of the BL in the β-CD cavity does not alter the ground state energy of the metal centers. Thus it is reasonable to presume that hydrogen bonding and other non-covalent interactions, which account for the stability of the inclusion complex of the bpe or bpp groups in the β-CD cavity,[3, 12] play a role in lowering the energy of the LUMO of the BL without affecting the energy of the d-orbitals of the Fe^{II} and Ru^{III} centers. Thus, it seems plausible that for **5** and **6**, inclusion of the BL in the β-CD cavity lowers the energy of the LUMO so that the energy of the respective metal orbital and the LUMO of the BL are similar, which allows the electron transfer to occur. A similar explanation was also offered for a series of donor–acceptor type molecules containing rigid saturated hydrocarbon bridges (dimethoxy napthyl donor and dicyanovinyl acceptor separated by norbornyl group or $Ru^{II}(NH_3)$ and $Ru^{III}(NH_3)$ separated by dithiospiro rings).[13] It was proposed that for the dithiospiro spacer group, electron transfer between the ends was possible because of the energetic proximity of the donor and acceptor centers and the LUMO of the BL. Further, the apolar interior of β-CD requires less reorganization to accompany the optical electron transfer in **5** and **6**, than the solvent water surrounding a non-inclusion complex (**1** and **2**) would.[14] Although small, this may have some contribution in lowering the energy of activation for optical electron transfer. Following the Hush theory for weakly interacting mixed-valence species, ground state electronic delocalisation[15] (α^2; 1.6×10^{-3} for **5** and 1.06×10^{-3} for **6**) and the extent of ground state electronic coupling arising for orbital mixing (H_{AB}, 400 for **5** and 330 for **6**) reveal that metal–metal coupling is much weaker than in the related mixed valence complex separated by a conjugated spacer.[9] Electron transfer through space between donor and acceptor sites linked by a proline oligomer was explained by the participation of solvent water molecules bound to the helical bridging peptide which connect different peptide residues in the helicate through nonbonding interactions and short circuit the long "through bond" electron-transfer pathway across the peptide covalent bonds.[16] A similar possibility for electron transfer in the present system involving the OH functionality and the high electron density inside the β-CD cavity also cannot be ruled out. However, the absence of charge transfer between aromatic donors and acceptors,[17] separated by a saturated hydrocarbon bridge in the β-CD inclusion complex does not favor this proposition. Further, Kaim and co-workers have demonstrated[18] that a low lying π^* LUMO of BLs with higher molecular orbital (MO) coefficient at the coordinating center is crucial in effecting stronger metal–metal coupling in dinuclear complexes.

In conclusion, we have synthesized two mixed valent [2]rotaxane complexes with Ru^{III} and Fe^{II} units as the two molecular heads. Inclusion of a saturated bridging ligand (bpe or bpp for complex **5** and **6**, respectively) into the β-CD cavity has initiated optical electron transfer from the Fe^{II} to the Ru^{III} center, which is not observed in the absence of inclusion.

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[7] Formation of 1:1 inclusion complex, as proposed for complexes **3**–**6** was ascertained by FAB and ES mass spectrometry and analytical data. Complex **3**: FAB m/z: 1710 [M^+]; elemental analysis: calcd with $2H_2O$ (%): C 44.9, H 5.55, N 3.28; found C 44.1, H 5.7, N 3.2; UV/Vis (H_2O): 269 nm (sh); Complex **4**: FAB m/z: 1722 [M^+]; elemental analysis: calcd with $2H_2O$ (%): C 44.7, H 5.6, N 3.28; found: C 43.6, H 5.6, N 3.2; UV/Vis (H_2O): 270 nm (sh); Complex **5**: ES-MS m/z: 1963 [M^+], elemental analysis: calcd with $2H_2O$ (%): C 41.7, H 4.8, N 6.34; found: C 41.0, H 4.9, N 6.2; UV/Vis/NIR (ε, H_2O): 296 (7.3×10^3), 352 (5.3×10^3), 998 nm (1.46×10^3); diffused reflectance spectra ($BaSO_4$ matrix): 376, 1042 nm (br); Complex **6**: ES-MS m/z: 1977 [M^+], elemental analysis: calcd with 0.07β-CD and $2H_2O$ (%): C 42.0, H 4.85, N 6.3 (0.07 mole β-CD, in addition to the included one, is trapped with Complex **6**); found: C 41.6, H 4.9, N 6.2; UV/Vis/NIR (ε, H_2O): 300 (2.4×10^3), 356 (1.6×10^3), 985 nm (1.36×10^3), diffused reflectance spectra ($BaSO_4$ matrix): 380, 1050 nm (br) (for detailed synthetic procedure see the Supporting Information).

[8] Complex **5** or **6** was dissolved in a 1.0 mM aqueous solution of β-CD (0.1 mM) to which DMSO was added to give a final DMSO concentration of 0.2 M.

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Synthesis and Self-Assembly of Monodisperse Indium Nanoparticles Prepared from the Organometallic Precursor [In(η^5-C_5H_5)]**

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The current interest in studying elements of nanometer size[1] stems from the structural changes that can arise from size reduction, from the physical properties which can be modified (melting point, band gap of semiconductors, magnetism), from the expected enhanced chemical properties, and from the possibility to use organized nanoparticles for various applications, for example, in microelectronic devices.[2] Hence, much attention has been devoted during the past few years to precise spatial arrangement in two- and three-dimensional superlattice structures[3] of metals (Au, Ag, Cu, Pt, Pd, Co),[4] semiconductors (CdSe, CdS, CdTe),[5] sulfides (Ag_2S)[6] and oxides (CoO, Fe_2O_3, $BaCrO_4$).[7] However, ordering and exploitation of the nanomaterials necessitates the synthesis of monodisperse individual particles, for which no general method is presently available. Low-temperature decomposition of organometallic precursors produces monodisperse nanoparticles of noble or magnetic metals.[8] This method was recently extended to the synthesis of alloys and of semiconducting oxides for gas sensors.[8b, 9]

To prove the generality of the method and its potential use for preparing particles that can be organized in superlattices, we considered indium, for which to our knowledge no organized nanoparticles have been reported. Indium, a low-melting metal, is a likely candidate for such studies; it adopts a tetragonal structure which may or may not be affected by size reduction[10] and can be of various practical interests. It is easily alloyed and converted, for example, to InP[11] and InAs,[12] which are III–V semiconductors that display interesting optoelectronic properties. Indium is easily oxidized to In_2O_3, a transparent semiconducting material (band gap: 3.6 eV), which forms with SnO_2 the mixed indium tin oxide (ITO), a conducting glass.[13] However, studies on indium nanoparticles are very rare. Indium particles 8–15 nm in size were prepared by metal vapor deposition.[10] In addition, indium nanoparticles were prepared, among other colloidal metals, by evaporation of metal into a polymerizable monomer in order to study the thermal stability of the resulting composite material.[14] Indium particles displaying an oxidized surface were synthesized by reduction of $InCl_3$ by alkalides or

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