

Perturbation of the Electronic Structure of the Creutz-Taube Ion via Asymmetric Encapsulation with Macrocyclic Ether Species

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Ligand-bridged mixed-valence ions can exist in either valence-localized (double-minimum ground potential energy surface) or valence-delocalized (single-minimum ground PE surface) form.¹ The determining factor is the balance between twice the initial-state/final-state electronic coupling energy (H_{if}) and the sum of the zeroth-order reorganization or trapping energy (χ) and any redox asymmetry (ΔE).^{1,2} For the Creutz-Taube ion ($(\text{NH}_3)_5\text{Ru}^{\text{II}1/2}\text{-pyrazine-Ru}^{\text{II}1/2}(\text{NH}_3)_5^{5+}$, **1**), redox asymmetry is absent, the valencies are completely delocalized, and $2H_{if}$ evidently exceeds χ .³⁻⁵ We reasoned, however, that "electronic isomerization" to a valence-localized form might be possible if significant redox asymmetry could be introduced. We report here the introduction of the desired asymmetry in an unusual way: via binding of a macrocyclic ether to just one of the two available ruthenium ammine sites. We also report optical evidence for the onset of valence localization in both **1** and a trans pyridine (py) substituted analog (**2**), in the presence of either dibenzo-36-crown-12 (DB-36-C-12) or dibenzo-30-crown-10 (DB-30-C-10) species.

The primary evidence for partial electronic localization (or at least diminished delocalization) comes from optical intervalence charge transfer (IT) absorption spectra. Figure 1, curve a, shows the IT spectrum of **2** in nitromethane as solvent. Notable features are the narrow bandwidth, low energy, asymmetric line shape, and high extinction coefficient, all of which typify valence-delocalized systems.¹ Curve b shows that in the presence of 1 equiv of DB-36-C-12 the absorption shifts to higher energy, nearly doubles in width, and suffers a loss of peak intensity. All three features are characteristic of the onset of valence localization and the induction of charge-transfer character in the intervalence transition.¹ Curve c shows that, with a larger amount of crown, the initial spectrum is essentially recovered.⁶ Plots of intervalence bandwidth versus crown:complex ratio (Figures 2 and 3) additionally show that (a) the maximum effects occur with 1:1 stoichiometry,^{7,8} (b) the effects are larger with the larger crown, and (c) similar (but smaller) effects exist for **1**.

Previous studies have amply demonstrated the affinity of ether oxygens for metal-ammine hydrogens;⁹ additional studies specifically with a valence-localized dimeric complex have shown that

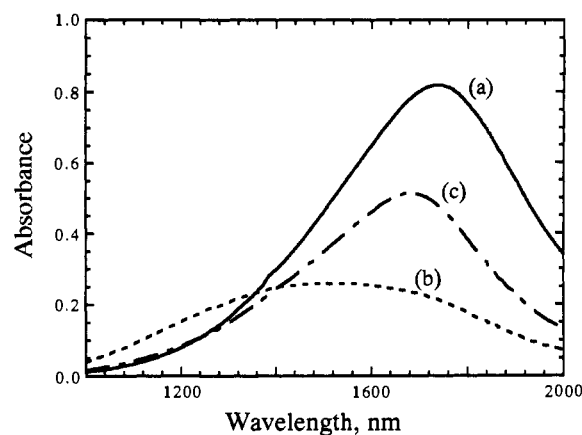
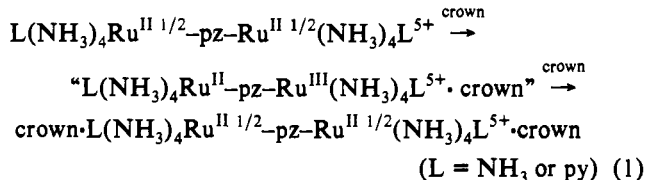


Figure 1. Intervalence absorption spectra for 8.6 mM **2** in nitromethane- d_3 ($b = 0.01$ cm) with (a) no added crown, (b) 1 equiv of DB-36-C-12, and (c) 16 equiv of DB-36-C-12.¹⁷

substantial IT energy shifts accompany asymmetric crown binding.¹⁰ On this basis, we interpret the current experiments as follows:¹¹



In the reaction, the driving force for localization is the redox asymmetry energy provided by asymmetric binding (and the quotation marks are meant to signify the possibility of only partial localization). Addition of a second crown restores the symmetry (both structural and energetic) and, therefore, the delocalization. Electrochemical studies of the monomeric complex, $\text{Ru}(\text{NH}_3)_5\text{py}^{3+/2+}$ (a model for zeroth-order dimer behavior), indicate that the magnitude of the redox asymmetry is ca. 1700 cm^{-1} with DB-30-C-10 and ca. 2600 cm^{-1} with DB-36-C-12.¹² Energy contributions of this size evidently are sufficient to offset, at least partially, the strong tendency toward delocalization provided by

(8) The equilibrium



could lead to absorption contributions from other species, even when formally at 1:1 stoichiometry. For the crown-transfer reaction, K equals $K(2)/K(1)$, where $K(2)$ and $K(1)$ are stepwise binding constants. For **2** with DB-36-crown-12 in CH_3NO_2 , $K(1) \approx 40\,000 \text{ M}^{-1}$, $K(2) \approx 40 \text{ M}^{-1}$, and $K \approx 0.001$. For nominally 1:1 stoichiometry, this suggests ca. 94% crown·Ru-L-Ru and ca. 3% (each) crown·Ru-L-Ru·crown and Ru-L-Ru. The spectroscopic consequences should be (1) a slight broadening of the apparent IT band for crown·Ru-L-Ru in comparison to its true width and (2) a slight decrease in the IT band energy in comparison to its true value.

(9) Representative references: (a) Colquhoun, H. M.; Stoddart, J. F.; Williams, D. J.; Wolstenholme, J. B.; Zarzycki, R. *Angew. Chem.* **1981**, *93*, 1093. (b) Colquhoun, H. M.; Doughty, S. M.; Maud, J. M.; Stoddart, J. F.; Williams, D. J.; Wolstenholme, J. H. B. *Isr. J. Chem.* **1985**, *25*, 15. (c) Ando, I.; Fujimoto, H.; Nakayama, K.; Ujimoto, K.; Kurihara, H. *Polyhedron* **1991**, *10*, 1139. (d) Curtis, J. C.; Roberts, J. A.; Blackburn, R. L.; Dong, Y.; Massum, M.; Johnson, C. S.; Hupp, J. T. *Inorg. Chem.* **1991**, *30*, 3856.

(10) Todd, M. D.; Dong, Y.; Hupp, J. T. *Inorg. Chem.* **1991**, *30*, 4687. (11) Related evidence for stepwise binding comes from MLCT studies. Addition of DB-30-crown-10 to a 7 mM solution of **1** (0.01 cm path length cell) leads to a red shift (-200 cm^{-1}) and then a blue shift (up to $+620 \text{ cm}^{-1}$) at higher crown concentrations.

(12) Representative electrochemical data (differential pulse voltammetry) for **1** (7.0 mM) with added DB-30-crown-10 in CH_3NO_2 , expressed as shifts in formal potentials: 1.2 mM crown, $\Delta E(5+/4+) = -78 \text{ mV}$, $\Delta E(6+/5+) = -4 \text{ mV}$; 3.5 mM crown, $\Delta E(5+/4+) = -128 \text{ mV}$, $\Delta E(6+/5+) = -25 \text{ mV}$; 7.0 mM crown, $\Delta E(5+/4+) = -150 \text{ mV}$, $\Delta E(6+/5+) = -58 \text{ mV}$; 14 mM crown, $\Delta E(5+/4+) = -200 \text{ mV}$, $\Delta E(6+/5+) = -115 \text{ mV}$; 33 mM crown, $\Delta E(5+/4+) = -222 \text{ mV}$, $\Delta E(6+/5+) = -146 \text{ mV}$; 47 mM crown, $\Delta E(5+/4+) = -225 \text{ mV}$, $\Delta E(6+/5+) = -148 \text{ mV}$.

(1) For a review, see: Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1-74.

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(6) Spectrum c (crown·2·crown) is slightly blue shifted from spectrum a. The shift appears to be real, but could be exaggerated by absorption contributions (to c) from residual 2·crown.

(7) Larger ratios (crown:complex) were observed with dibenzo-30-crown-10 and **2**. Furthermore, the optimal ratio proved to be dependent on **2** concentration, implying that its magnitude is determined not only by the overall binding stoichiometry but also by the sizes of binding constants.

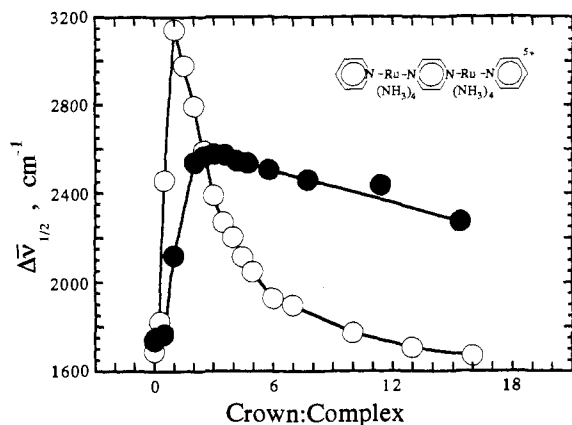


Figure 2. Intervalence absorption bandwidths at half-height, as a function of crown:complex ratio, for 8.6 mM **2** with (○) DB-36-C-12 and (●) DB-30-C-10. (Maximum shifts in the IT energy peak are 880 and 360 cm^{-1} , respectively.)⁸

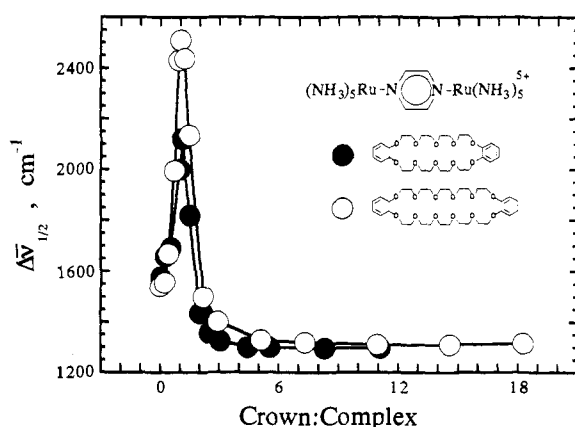


Figure 3. Intervalence absorption bandwidths at half-height, as a function of crown:complex ratio, for 5.3–7.5 mM **1** with (○) DB-36-C-12 and (●) DB-30-C-10. (Maximum shifts in the IT energy peak are 500 and 200 cm^{-1} , respectively.)⁸

the electronic coupling energy in the symmetrical systems. Notably the shift toward localization is greater (as expected) when the binding-induced asymmetry is greater. It is also greater (as expected) when H_{if} is smaller (note **2** vs **1**, where coupling in the former has been diminished by trans pyridine competition for $d\pi$ electron density).

An additional comparison of interest is with systems in which redox asymmetry has been introduced by asymmetric substitution

within the primary ligand sphere.¹³ A remarkable similarity exists between t -(3-Cl-pyridine)(NH_3)₄Ru-pz-Ru(NH_3)₅⁵⁺ and (NH_3)₅-Ru-pz-Ru(NH_3)₅⁵⁺-DB-36-crown-12, both in terms of intervalence energy shifts and broadening effects. A zeroth-order assessment¹⁰ (based on formal potentials for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ versus $\text{Ru}(\text{NH}_3)_5(3\text{-Cl-py})^{3+/2+}$)¹⁴ yields $\Delta E = 2500 \text{ cm}^{-1}$ for the substituted mixed-valence complex, i.e. essentially identical to that for the **1**-crown assembly.

Finally, it is possible that the binding-induced broadening and energy effects represent only a shift toward less strongly delocalized valencies, rather than true conversion to a localized (or partially localized) form (i.e. $2H_{if}$ may still exceed $\chi + \Delta E$). Attempts to resolve the issue via IR measurements¹⁵ yielded ambiguous results, in part because of solvent interferences. We are optimistic, however, that the issue can be clarified via electronic Stark effect studies (assessment of ground-state/excited-state dipole moment differences)¹⁶ and by appropriate theoretical simulation of absorption line shape effects.⁵ We are also hopeful, on the basis of studies with other macrocycles, that even larger effects can be uncovered.

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Supplementary Material Available: A figure showing intervalence absorption spectra for **1** in the absence and presence of dibenzo-36-crown-12 (1 page). Ordering information is given on any current masthead page.

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(15) The goal was to observe a centrosymmetric pyrazine stretch near 1595 cm^{-1} . This vibration should become IR allowed when the bridge experiences an asymmetric metal charge environment (see: Callahan, R. W.; Meyer, T. J. *Chem. Phys. Lett.* **1976**, *39*, 82).

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(17) A reviewer has commented on the decrease in IT oscillator strength accompanying double crown encapsulation (both **1** and **2**) and has suggested, therefore, that electronic coupling is diminished by encapsulation. It is not obvious to us, however, that interpretation of the oscillator strength in this fashion is fully appropriate for class III systems. An alternative criterion—decrease in absorption bandwidth (see Figure 3)—would, in fact, suggest *greater* electronic coupling following double encapsulation.