

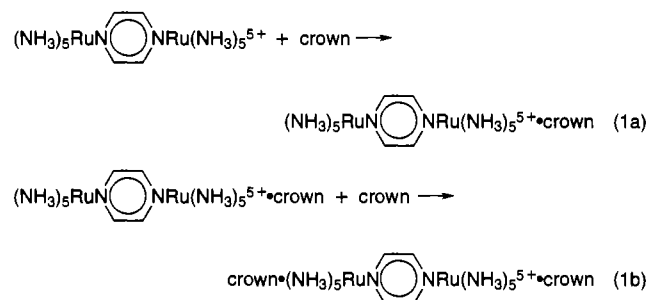
# Intervallence Energy Effects Accompanying Double Crown Encapsulation of the Creutz–Taube Ion: An Interpretation Based on Three-Site Mixing

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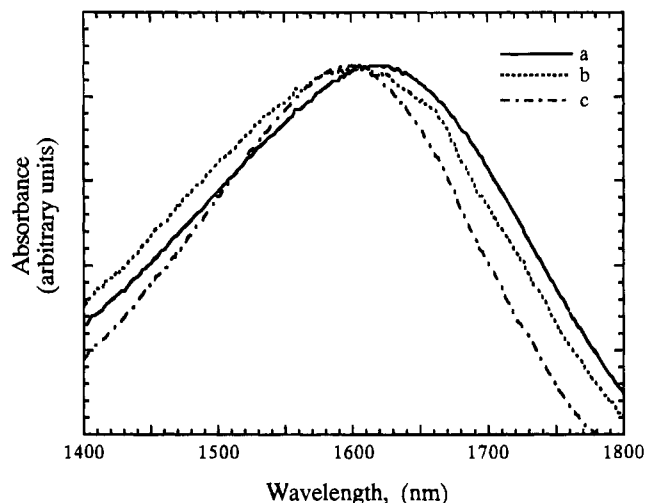
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Recently we reported the profound effects of second-sphere crown ether binding upon the redox energetics and intervalence spectroscopy of selected mixed-valence species.<sup>1–4</sup> (Crown/metal complex associatio is driven primarily by ether oxygen/amine hydrogen interactions, where the H-bond-donating capability of NH<sub>3</sub> is greatly enhanced by coordination to a transition-metal cation.) For delocalized species such as the Creutz–Taube ion and its derivatives,<sup>5</sup> asymmetric binding of a single crown (eq 1a) can significantly perturb the basic



electronic structure of the system, resulting in striking shifts in intervalence absorption energies,<sup>4</sup> substantial changes in intervalence line shapes,<sup>4</sup> and drastic redistributions of intervalence-related Franck–Condon activity.<sup>6</sup> Collectively these effects have been attributed to the possible onset of asymmetry-induced valence localization or partial localization.<sup>4</sup> Consistent with that interpretation, binding of a second crown ether (eq 1b) largely restores the original spectra (and, of course, the overall supramolecular symmetry). Nevertheless, closer examination of the available data for doubly bound or encapsulated complexes<sup>4</sup> shows that modest spectral changes (in comparison to the case of free species) do accompany the binding. Most notably, intervalence spectra become somewhat narrower and are shifted detectably in energy. These effects, while small, are difficult to understand within the context of standard two-site models<sup>7</sup> for valence delocalization. We show here that related effects occur in the visible portion of the electronic spectrum, that the effects in both spectral regions increase with increasing macrocycle size, and that the effects can be correlated with previously observed,<sup>3</sup> crown-induced electrochemical effects. We additionally show that the multiplicity of spectral effects can be explained—at least qualitatively—on the basis of a three-site description<sup>8</sup> of electronic delocalization.

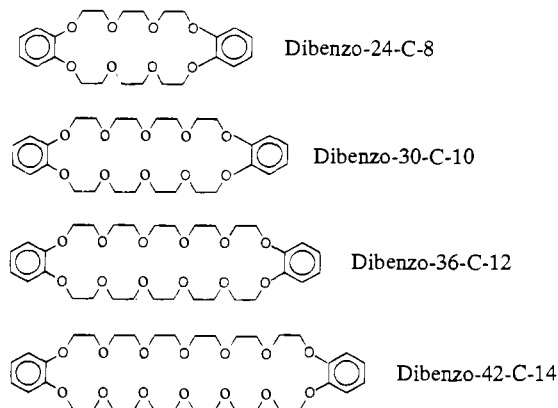
- (1) Todd, M. D.; Dong, Y.; Hupp, J. T. *Inorg. Chem.* **1991**, *30*, 4685.
- (2) Curtis, J. C.; Roberts, J. A.; Blackburn, R. L.; Dong, Y.; Massum, M.; Johnson, C. S.; Hupp, J. T. *Inorg. Chem.* **1991**, *30*, 3856.
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- (4) Dong, Y.; Yoon, D.; Hupp, J. T. *J. Am. Chem. Soc.* **1993**, *115*, 4379.
- (5) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 3988; **1973**, *95*, 1086.
- (6) Petrov, V. I.; Hupp, J. T. Unpublished studies of intervalence enhanced Raman scattering.



**Figure 1.** Intervalence absorption spectra for the Creutz–Taube ion in nitromethane as solvent, with no crown (a) and with double encapsulation by dibenzo-24-crown-8 (b) and dibenzo-42-crown-14 (c).

Shown in Figure 1 are intervalence absorption spectra for the Creutz–Taube ion<sup>9</sup> without crown encapsulation (curve a) and with double encapsulation (curves b and c) by dibenzo-24-crown-8 and dibenzo-42-crown-14.<sup>10,11</sup> (For clarity, additional spectra for dibenzo-30-crown-10 and dibenzo-36-crown-12 have been omitted.) (Crown structures are shown in Figure 2.) Table 1 summarizes the crown-induced energy shifts ( $\Delta E^{\text{IT}}$ ) for the entire series, together with intervalence absorption bandwidths ( $\Delta \bar{\nu}_{1/2}$ ) and extinction coefficients ( $\epsilon$ ). Perhaps the most important observation is that the spectrum shifts to higher energy following encapsulation. Related data are presented in Table 2 for the visible-region absorption band. The spectra themselves (usually described as metal-to-pyrazine charge

- (7) Two-site models: (a) Piepho, S. B.; Krausz, E. R.; Schatz, P. N. *J. Am. Chem. Soc.* **1978**, *100*, 6319. (b) Wong, K. Y.; Schatz, P. N. In *Mechanistic Aspects of Inorganic Reactions*; Rorabacher, D. B., Endicott, J. F., Eds.; ACS Symposium Series 198; American Chemical Society: Washington, DC, 1982; pp 281–296, 330. (c) Neuen-schwander, K.; Piepho, S. B.; Schatz, P. N. *J. Am. Chem. Soc.* **1985**, *107*, 7862. (d) Wong, K. Y.; Schatz, P. N. *Prog. Inorg. Chem.* **1981**, *23*, 369. (e) Prassides, K.; Schatz, P. N. *J. Phys. Chem.* **1989**, *93*, 83. (f) Ratner, M. A. *Int. J. Quantum Chem.* **1978**, *14*, 675. (g) Dubicki, L.; Ferguson, J.; Krausz, E. R. *J. Am. Chem. Soc.* **1985**, *107*, 179.
- (8) Three-site models: (a) Root, L. J.; Ondrechen, M. *Chem. Phys. Lett.* **1982**, *93*, 421. (b) Ondrechen, M. J.; Ko, J.; Root, L. J. *J. Phys. Chem.* **1984**, *88*, 5919. (c) Ko, J.; Ondrechen, M. *Chem. Phys. Lett.* **1984**, *112*, 507. (d) Ko, J.; Ondrechen, M. *J. Am. Chem. Soc.* **1985**, *107*, 6161. (e) Ondrechen, M. J.; Ko, J.; Zhang, L. T. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1986**, *19*, 393. (f) Ondrechen, M. J.; Ellis, D. E.; Ratner, M. A. *Chem. Phys. Lett.* **1984**, *109*, 50. (g) Zhang, L. T.; Ko, J.; Ondrechen, M. J. *J. Am. Chem. Soc.* **1987**, *109*, 1666. (h) Ondrechen, M. J.; Ko, J.; Zhang, L. T. *J. Am. Chem. Soc.* **1987**, *109*, 1672. (i) Ondrechen, M. J.; Gozashiti, S.; Zhang, L.-T.; Zhou, F. *Adv. Chem. Ser.* **1990**, *226*, 225. (j) Zhang, L.-T.; Ko, J.; Ondrechen, M. J. *J. Phys. Chem.* **1989**, *93*, 3030. (k) Piepho, S. B. *J. Am. Chem. Soc.* **1988**, *110*, 6319. (l) Piepho, S. B. *J. Am. Chem. Soc.* **1990**, *112*, 4197.
- (9)  $(\text{NH}_3)_5\text{Ru}(\text{pyrazine})\text{Ru}(\text{NH}_3)_5(\text{PF}_6)_4$  was prepared analogously to a published method for the 4,4'-bipyridine analog (Blackbourn, R. L.; Hupp, J. T. *J. Phys. Chem.* **1988**, *92*, 2817). The mixed-valence form was prepared *in situ* by using Br<sub>2</sub> vapor as oxidant. Br<sub>2</sub> was chosen because Br is transparent in both the near-IR and the visible regions. Selected comparisons (necessarily in the near-IR only) revealed no dependence of absorption energy on oxidant identity (Br<sub>2</sub> vs [Fe(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>3</sub>).
- (10) Dibenzo-42-crown-14 was prepared as described in ref 3. Dibenzo-36-crown-12 was prepared as described by Colquhoun et al. (*J. Chem. Soc., Perkin Trans. 2* **1985**, 607). The remaining macrocycles were purchased from Aldrich. Nitromethane-d<sub>3</sub> was used as received from Aldrich.
- (11) Absorption measurements were made on a Cary 14 spectrophotometer that had been rebuilt by OLIS.

**Figure 2.** Crown ethers used for double encapsulation.**Table 1.** Near-Infrared Absorption Energy Shifts, Bandwidths, and Extinction Coefficients for the Creutz-Taube ion, following Double Crown Encapsulation

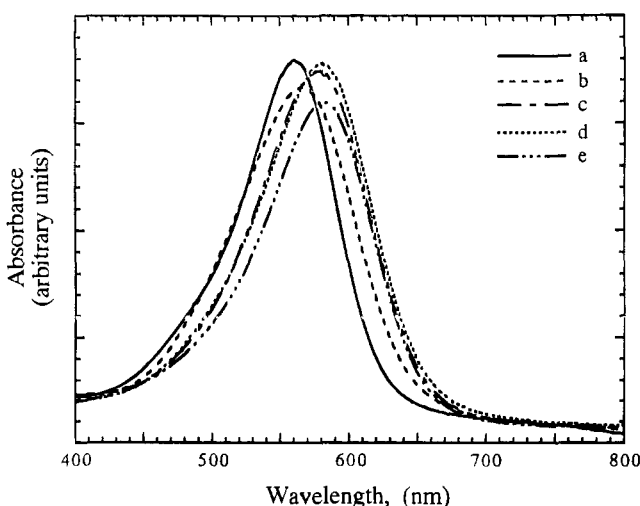
crown	$\Delta E^{\text{IT}}$ , $\text{cm}^{-1}$	$\Delta \bar{\nu}_{1/2}$ , $\text{cm}^{-1}$	$\epsilon$ , $\text{M}^{-1} \text{cm}^{-1}$
none <sup>a</sup>		$1540 \pm 20$	$5500 \pm 200$
dibenzo-24-C-8	60	$1530 \pm 20$	$3400 \pm 200$
dibenzo-30-C-10	70	$1280 \pm 20$	$4300 \pm 200$
dibenzo-36-C-12	70	$1350 \pm 20$	$4200 \pm 200$
dibenzo-42-C-14	80	$1270 \pm 20$	$4100 \pm 200$

<sup>a</sup> The absolute  $E^{\text{IT}}$  value in the absence of crown is  $6170 \text{ cm}^{-1}$  (nitromethane as solvent).

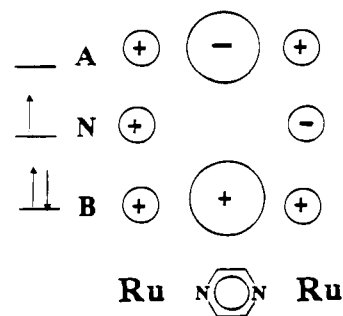
**Table 2.** Visible-Region Absorption Energy Shifts, Bandwidths, and Extinction Coefficients for the Creutz-Taube Ion, following Double Crown Encapsulation

crown	$\Delta E^{\text{MLCT}}$ , $\text{cm}^{-1}$	$\Delta \bar{\nu}_{1/2}$ , $\text{cm}^{-1}$	$\epsilon$ , $\text{M}^{-1} \text{cm}^{-1}$
none <sup>a</sup>		$3000 \pm 60$	$14\,800 \pm 500$
dibenzo-24-C-8	$-130 \pm 60$	$3700 \pm 100$	$13\,900 \pm 500$
dibenzo-30-C-10	$-560 \pm 60$	$3260 \pm 50$	$15\,020 \pm 500$
dibenzo-36-C-12	$-620 \pm 30$	$3210 \pm 30$	$14\,900 \pm 400$
dibenzo-42-C-14	$-660 \pm 20$	$3200 \pm 80$	$13\,500 \pm 300$

<sup>a</sup> The absolute  $E^{\text{MLCT}}$  value in the absence of crown is  $17\,850 \text{ cm}^{-1}$  (nitromethane as solvent).

**Figure 3.** Visible-region absorption spectra for the Creutz-Taube ion in nitromethane as solvent, with no crown (a) and with double encapsulation by dibenzo-24-crown-8 (b), dibenzo-30-crown-10 (c), dibenzo-36-crown-12 (d), and dibenzo-42-crown-14 (e).

transfer) are shown in Figure 3. Note that the energy shifts here are opposite in sign to the intervalence shifts and somewhat larger. Systematic variations of absorption properties with encapsulating crown size, however, are clearly evident in both sets of data. (The crown size dependence of the spectral shifts

**Scheme 1**

is not unexpected: solvatochromic studies<sup>3b</sup> of a related mixed-valence system clearly show that the absolute degree of encapsulation of  $-\text{Ru}(\text{NH}_3)_5$  increases systematically with increasing crown size. Presumably the number of crown/complex hydrogen bonds formed (per assembly) similarly increases.)

To interpret the results we first make use of a primitive model of electronic delocalization developed primarily by Ondrechen and co-workers.<sup>8</sup> This model differs from standard models in that it recognizes explicitly the role of strong ruthenium-to-pyrazine backbonding interactions in promoting delocalization. As suggested by the simplified diagram in Scheme 1, mixing of a pair of filled or half-filled Ru ( $d_{xz}$ ) orbitals with an empty pyrazine ( $\pi^*$ ) bridge orbital leads to three new molecular orbitals. The lowest of these is doubly occupied and formally bonding; the next is half-occupied and nonbonding; the highest is antibonding and empty. The intervalence transition is then one which promotes an electron from the three-center bonding orbital to the nonbonding orbital, while the visible-region transition is viewed as a nonbonding-to-antibonding transition. (The bonding-to-antibonding transition is symmetry forbidden.) Importantly, when three-site mixing is strong, the "intervalence" transition more closely resembles a ligand-to-double metal charge transfer than a conventional metal-to-metal charge transfer transition. We note that the model has significant theoretical support<sup>8</sup> and that some of its more important features were recently verified experimentally via intervalence-enhanced Raman scattering.<sup>12</sup>

If Franck-Condon effects are neglected, then the energies of the intervalence ( $E^{\text{IT}}$ ) and visible-region ( $E^{\text{MLCT}}$ ) transitions in the three-site model can be written approximately as<sup>8i</sup>

$$E^{\text{IT}} = E_{\text{N}} - E_{\text{B}} = (U - \alpha)/2 \quad (2)$$

$$E^{\text{MLCT}} = E_{\text{A}} - E_{\text{N}} = (U + \alpha)/2 \quad (3)$$

where  $E_{\text{B}}$ ,  $E_{\text{N}}$ , and  $E_{\text{A}}$  are relative bonding, nonbonding, and antibonding orbital energies and  $\alpha$  is the zeroth-order  $\pi^*(\text{pyz})-\text{d}\tau(\text{Ru})$  separation energy. The parameter  $U$  is defined as

$$U = (\alpha^2 + 8J^2)^{1/2} \quad (4)$$

where  $J$  is the ruthenium-pyrazine coupling energy.

For the Creutz-Taube ion,  $J$  has been estimated previously as ca.  $-6500 \text{ cm}^{-1}$ ,<sup>8</sup> we assume, to first order, that it is solvent (or crown) invariant. The parameter  $\alpha$ , on the other hand, is very clearly sensitive to local environmental effects—and in particular, crown binding. The environmental sensitivity has its origin in the metal-ammine localized nature of the crown

(12) Petrov, V. I.; Hupp, J. T.; Mottley, C. S.; Mann, L. *J. Am. Chem. Soc.* **1994**, *116*, 2171.

**Table 3.** Electronic Spectral Parameters for the Creutz–Taube Ion and Electrochemical Parameters for a Model complex in the Absence and Presence of Double Crown Encapsulation

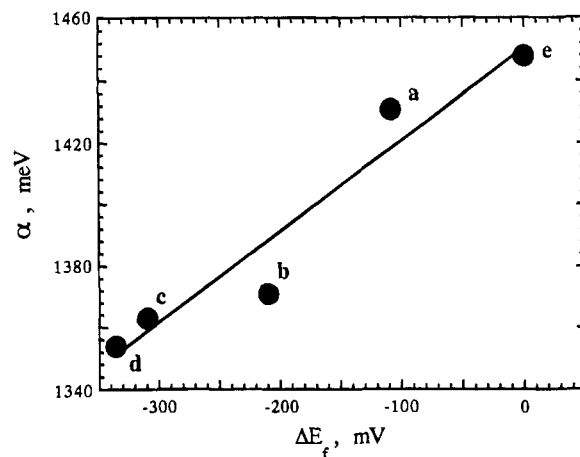
crown	$\alpha,^a \text{ cm}^{-1}$	$J,^b \text{ cm}^{-1}$	$\Delta E_f,^c \text{ mV}$
none	11 680	7420	0
dibenzo-24-C-8	11 490	7430	$-110 \pm 10^d$
dibenzo-30-C-10	11 060	7340	$-210 \pm 10$
dibenzo-36-C-12	10 990	7330	$-310 \pm 10$
dibenzo-42-C-14	10 940	7330	$-338 \pm 6$

<sup>a</sup> Calculated from eqs 2 and 3 by using experimental values of  $E^{\text{MLCT}}$  and  $E^{\text{IT}}$ . <sup>b</sup> Calculated from eq 4 by using the accompanying experimental estimates for  $\alpha$ . <sup>c</sup> Data for  $\text{Ru}(\text{NH}_3)_5(\text{pyridine})^{3+/2+}$  taken from ref 3a. <sup>d</sup> Calculated from oxidation-state-dependent crown binding constants reported in ref 3a.

binding;<sup>1–4,13</sup> direct binding interactions with pyridyl or pyrazyl ligands appear to be relatively unimportant.<sup>14</sup> (More specifically, a dependence of  $\alpha$  on extent of crown encapsulation is expected on the basis of ammine ligand mediated stabilization of  $d\pi(\text{Ru})$  levels. The relative energies of pyrazine  $\pi$  and  $\pi^*$  levels, on the other hand, should be unaffected (to zeroth order) by crown binding.) An approximate measure of  $\alpha$  is, in principle, provided by the difference in electrochemical potentials for metal oxidation versus ligand reduction. Alternatively, the change in  $\alpha$  in response to an environmental perturbation can be estimated from the change in the metal-based formal potential ( $E_f$ ) in response to the same perturbation (i.e., a one to one correspondence between  $\Delta\alpha$  and  $\Delta E_f$  is expected). For the Creutz–Taube ion,<sup>4</sup> as well as a model system ( $\text{Ru}(\text{NH}_3)_5(\text{pyridine})^{3+/2+}$ ),<sup>3</sup> we have observed significant negative shifts in  $E_f$ —and therefore, negative shifts in relative  $\alpha$  values—in response to crown encapsulation. In the context of eqs 2–4, the electrochemical experiments would suggest a decrease in  $E^{\text{MLCT}}$ , and a smaller increase in  $E^{\text{IT}}$ , with crown binding—in qualitative agreement with the available spectral results (Figures 1 and 3 and Tables 1 and 2).

A more quantitative evaluation based on direct application of the energy equations to the spectral experiments is possible. We observe that absolute values of  $\alpha$  can be obtained simply from the difference between  $E^{\text{MLCT}}$  and  $E^{\text{IT}}$  (eqs 3 and 2). Estimates for  $J$  can then be obtained from eq 4. Table 3 lists the  $\alpha$  and  $J$  values derived in this way for the free Creutz–Taube ion and for each of the double-crown assemblies. The apparent  $J$  values (ca.  $-7400 \text{ cm}^{-1}$ ) are slightly larger than Ondrechen's estimate and slightly dependent on environment. The unexpected environmental dependence, however, may well reflect the extreme simplicity of the model, rather than a genuine chemical effect. In any case, the more interesting parameter,  $\alpha$ , is somewhat larger than  $J$  and considerably more responsive to crown encapsulation:  $\alpha$  varies from  $\sim 11\,700 \text{ cm}^{-1}$  for the free C–T ion to  $\sim 10\,900 \text{ cm}^{-1}$  for the dibenzo-42-crown-14-encapsulated ion. The corresponding change in  $\alpha$  based on electrochemical measurements with the model compound is  $-2700 \text{ cm}^{-1}$ —or about 3–4 times the spectral estimate (see Table 3). Nevertheless, for the series of crown experiments, a correlation clearly does exist (Figure 4) between  $\alpha(\text{spectral})$  and  $\Delta E_f$ .<sup>15</sup>

If  $J$  is arbitrarily held constant (such that the crown-based energy shifts are attributed entirely to variations in separation

**Figure 4.** Spectral separation energy,  $\alpha$  (eqs 2 and 3), for the Creutz–Taube ion versus crown-induced electrochemical energy shifts,  $\Delta E_f$ , for a model complex,  $\text{Ru}(\text{NH}_3)_5\text{py}^{3+/2+}$ . Key to crowns: (a) dibenzo-24-crown-8; (b) dibenzo-30-crown-10; (c) dibenzo-36-crown-12; (d) dibenzo-42-crown-14. Point e is without added crown.

energy; see eqs 2–4),  $\alpha(\text{spectral})$  remains well correlated with  $\Delta E_f$ ,<sup>16</sup> but the (unitless) slope of the correlation plot increases from 0.3 (see Figure 4) to 0.5. Since the “expected” value is 1, additional or alternative factors clearly must be involved. One of these factors may be the neglect of Franck–Condon effects. That these are also environment dependent is clearly shown by the systematic decrease in intervalence absorption bandwidth with increasing crown size. Correction for these effects would tend to increase the apparent dependence of  $E_N - E_B$  on crown size. To the extent that the corrections are not offset by corresponding corrections to the visible-region absorption energies,  $\alpha(\text{spectral})$  will tend to show greater variability with crown encapsulation than indicated in Table 3. A third factor may be neglect of ruthenium  $d\pi/\text{pyrazine } \pi$  interactions, as discussed by Lauher<sup>17</sup> and by Creutz and Chou.<sup>18</sup> The relevant separation energies for these interactions should vary in precisely the opposite sense, with metal–ammine environment, as the  $d\pi(\text{Ru})-\pi^*(\text{pyrazine})$  separation energy (leading to a loss of sensitivity of  $E^{\text{IT}}$  to  $d\pi(\text{Ru})$  energy perturbations). Piepho has additionally argued that significant  $d\pi(\text{Ru})-\pi^*(\text{pyrazine})$  (back-bonding) interactions may exist in the molecular orbital labeled as “nonbonding” in Scheme 1—and indeed, recent calculations from her laboratory are supportive of this more complex description. Presumably, further parametrization of our results in terms of the  $\alpha$ ,  $\alpha^*$ , and various  $\epsilon$  quantities (i.e., relative state energies) described by Piepho<sup>8k,l</sup> would lead to better agreement between predicted and observed crown effects upon MLCT and intervalence absorption energies.

- (15) A reviewer has pointed out that our analysis of crown effects is essentially identical to Creutz and Chou's analysis<sup>18</sup> of solvent effects (where their parameters  $\beta$  and  $\delta_{\pi^*}$  correspond to our parameters  $-J$  and  $\alpha$ ). For nitromethane as solvent, they find (reassuringly)  $J = -7500 \text{ cm}^{-1}$ . They also find  $\alpha = 11\,800 \text{ cm}^{-1}$ . They additionally observe that  $\alpha$  decreases systematically with increasing solvent basicity, as expected from the known preferential stabilization of  $d\pi$  metal orbitals by ligand/solvent hydrogen bonding in am(m)ine-containing complexes. Interestingly, the extent of decrease in  $\alpha$  is substantially less than anticipated from independent electrochemical measurements of relative  $d\pi(\text{Ru})$  stabilization by high Lewis basicity (i.e., good hydrogen bond accepting) solvents. The close similarities in the analyses—as well as the findings—suggest that double crown encapsulation could reasonably be viewed as a special case of mixed solvation, within the context of the broader study of C–T ion solvation by Creutz and Chou.<sup>18</sup>
- (16) The correlation coefficient,  $r$ , decreases from 0.96 (Figure 4) to 0.93.
- (17) Lauher, J. W. *Inorg. Chim. Acta* **1980**, *39*, 119.
- (18) Creutz, C.; Chou, M. H. *Inorg. Chem.* **1987**, *26*, 2995.

(13) For reviews, see: (a) Colquhoun, H. M.; Stoddart, J. F.; Williams, D. *J. Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 487. (b) Stoddart, J. F.; Zarzycki, R. In *Cation Binding by Macrocycles*; Inoue, Y., Gokel, G. W., Eds.; Marcel Dekker: New York, 1990; pp 631–700.

(14) Exceptions exist for planar (bipyridyl)platinum(II) ammine/dibenzo crown adducts, for which  $\pi \rightarrow \pi$  charge-transfer interactions appear to be important (Colquhoun, H. M.; et al. *Isr. J. Chem.* **1985**, *25*, 15 and ref 15a).

Finally, if intervalence excitation entails any net metal-to-metal charge transfer (MMCT), then the electronic description underlying eqs 2–4 will be incomplete and other sources of spectral perturbation would need to be considered. Most notably, Marcus–Hush solvent reorganizational effects<sup>19</sup> would need to be evaluated—with crowns playing the role of local solvent.<sup>1</sup> For the Creutz–Taube ion, the available evidence indicates that even residual MMCT effects can be neglected.<sup>20</sup> These effects conceivably could play a role, however, for trans-substituted analogs.

To summarize, double crown encapsulation induces small

energy shifts in both the visible and near-infrared portions of the electronic spectrum of the Creutz–Taube ion. The energy effects are difficult to understand within the context of standard two-site treatments of valence delocalization, but they are readily interpreted on the basis of three-site (metal–bridge–metal) descriptions.

**Acknowledgment.** We thank the reviewers for helpful comments, Dr. Dong Yoon for preparing the samples of dibenzo-36-crown and dibenzo-42-crown-14, and the Basic Energy Sciences Office of the U.S. Department of Energy (Grant No. DE-FG02ER-13808) for support of this research. J.T.H. additionally acknowledges support from the Camille and Henry Dreyfus Foundation (Teacher-Scholar Award, 1991–6).

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(19) (a) Marcus, R. A. *J. Chem. Phys.* **1965**, *45*, 679. (b) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391.

(20) See, for example: Oh, D. H.; Boxer, S. G. *J. Am. Chem. Soc.* **1990**, *112*, 8161; **1991**, *113*, 6880.