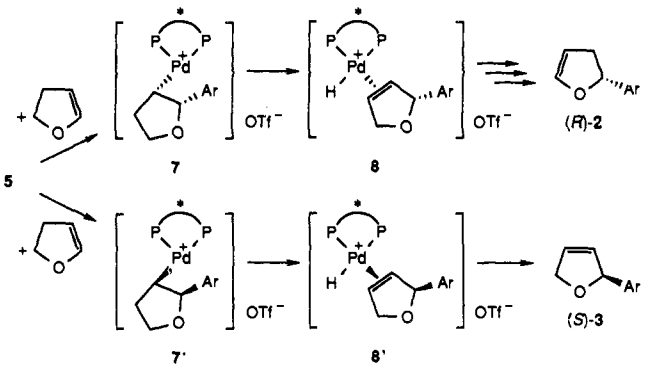

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Supplementary Material Available: Experimental details and spectroscopic data for **2a–g**, **3a–f**, **9a**, and **10a** (4 pages). Ordering information is given on any current masthead page.

Control of Back Electron Transfer from Charge-Transfer Ion Pairs by Zeolite Supercages

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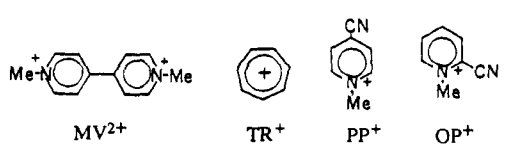
Charge-transfer activation of the precursor complexes[1] from nucleophiles (D) and electrophiles (A) is a viable formulation for a variety of organic and organometallic reactions, i.e.,

$$D + A \rightleftharpoons [D,A] \underset{k_{-1}}{\overset{CT}{\rightleftharpoons}} [D^{\bullet+},A^{\bullet-}] \xrightarrow{k_2} \text{etc.} \qquad (1)$$

where CT includes both photochemical ($h\nu_{CT}$) and thermal (adiabatic) processes.[2] The critical assessment of charge-transfer efficiency depends largely on the rate of back electron transfer (k_{-1}) relative to that of the followup reaction (k_2), especially as evaluated in photoactivated systems.[3] Since the available methodology for the general control of back electron transfer is limited,[4] we describe in this report how the zeolite supercage can be used to strongly modulate the magnitude of k_{-1}.

The stepwise assembly of various charge-transfer complexes directly within the zeolite (Y) supercage has recently been achieved by the prior ion exchange of NaY with the different cationic electrophiles (A^+) MV^{2+}, TR^+, PP^+, and OP^+ followed by exposure of the doped zeolite to arene donors (D = Ar) dissolved in organic solvents.[5] Importantly the correlation of the



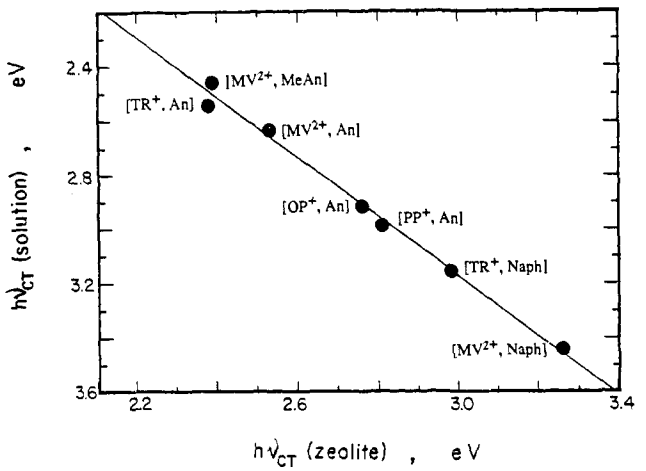


Figure 1. Charge-transfer spectra ($h\nu_{CT}$) of various charge-transfer complexes (as indicated) in zeolite-Y supercages by diffuse reflectance relative to the absorption spectra of the same complexes in acetonitrile solution.

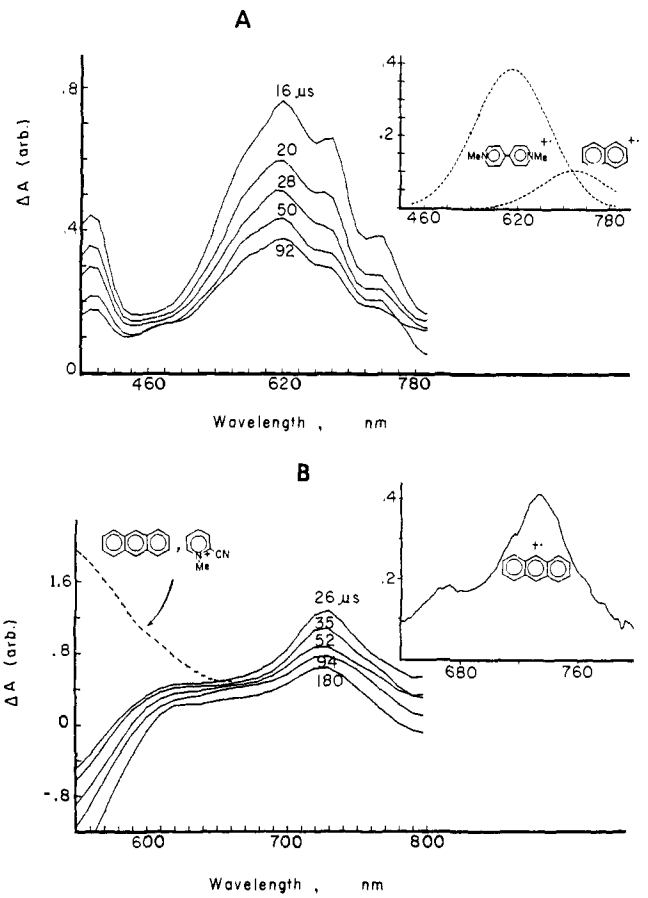


Figure 2. Time-resolved diffuse reflectance spectra obtained at microsecond intervals following the 10-ns laser pulse at (A) 355 nm of [MV^{2+},Naph] and (B) 532 nm of [OP^+,An] immobilized in zeolite-Y. The insets show the transient spectra of the ion-radicals $MV^{\bullet+}$ (smoothed), $Naph^{\bullet+}$, and $An^{\bullet+}$ in acetonitrile solutions.

charge-transfer bands in Figure 1 establishes the intermolecular complexes [A^+,Ar] that are formed within the zeolite-Y supercage to be the same as those produced in solution.[6] Indeed the latter relate to the cofacial pairs of A^+ and Ar in the π-complexes (established by X-ray crystallography[7]) that can be accommodated

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Table I. Spectral Decay of Charge-Transfer Ion Pairs in Zeolite-Y Supercages and in Acetonitrile Solution

		zeolite		acetonitrile	
Ar ($E°_{ox}$)[a]	A^+ ($E°_{red}$)[b]	λ_{CT}[c]	τ,[d] μs	λ_{CT}[c]	τ,[d] ps
Naph (1.62)	MV^{2+} (−0.43)	380	6.8	~360	30
	$C_7H_7^+$ (−0.18)	415	3.3	393	25[f]
	OP^+ (−0.62)	–	6.2	~330[e]	–
	PP^+ (−0.64)	–	0.11	~330[e]	25
An (1.41)	MV^{2+}	490	64	472	19
	$C_7H_7^+$	520	4.2	488	25[f]
	OP^+	449	9.2	425	–
	PP^+	441	3.9	415	–
9-$MeC_{14}H_9$ (1.23)	MV^{2+}	518	5.6	504	28
	PP^+	–	–	439	27
9,10-$Me_2C_{14}H_8$ (1.09)	MV^{2+}	–	–	526	21
	PP^+	–	–	474	22

[a] Naph = naphthalene, An = anthracene, $C_{14}H_9$ = anthracenyl, and $C_{14}H_8$ = anthracenediyl; oxidation potential in MeCN (V vs SCE). [b] MV^{2+} = methylviologen, $C_7H_7^+$ = tropylium, OP^+ = *N*-methyl-2-cyanopyridinium, and PP^+ = *N*-methyl-4-cyanopyridinium; reduction potential in MeCN (V vs SCE). [c] Charge-transfer band maximum (nm). [d] Lifetime as first-order decay. [e] Unresolved band. [f] From ref 16b.

within the zeolite-Y supercage.[5]

The deliberate photoexcitation of such immobilized CT complexes was initially carried out with a 10-ns (fwhm) pulse at 355 or 532 nm from a Nd^{3+}:YAG laser, and the spectral transients were detected by the diffuse reflectance method of Kessler and Wilkinson.[8] The typical time-resolved (difference) spectra in Figure 2 show (A) the simultaneous formation of the CT ion pair [$MV^{•+}$,$Naph^{•+}$] from the naphthalene (Naph) complex with methylviologen (MV^{2+}) and (B) the bleaching (negative ΔA) of the charge-transfer band (λ_{max} 490 nm) accompanying the production of the anthracene cation radical ($An^{•+}$, λ_{max} 725 nm) from the CT excitation of the *N*-methyl-2-cyanopyridinium complex with anthracene (An).[9] In each case, the charge-transfer transients produced in zeolite-Y were identified by direct comparison of their spectra with the transient spectra of the same ion radicals previously produced in acetonitrile solution by either spectroelectrochemical or flash photolytic techniques.[10,11] The gradual diminution of the transient spectrum shown in Figure 2 over a period of several microseconds corresponded to the mutual annihilation of the CT ion pairs by back electron transfer (k_{-1}), e.g.,

$$[MV^{2+},Ar] \underset{k_{-1}}{\overset{h\nu_{CT}}{\rightleftharpoons}} [MV^{•+},Ar^{•+}] \qquad (2)$$

[Note that the control experiments established that the (CT) colored zeolites remained intact despite the steady-state irradiation of the charge-transfer bands for prolonged periods with monochromatic light.] For example, the kinetics analysis of the transient spectrum in Figure 2A, consisting of the simple superposition of the spectral bands of $MV^{•+}$ and $Naph^{•+}$ by Gaussian deconvolution, showed a homogeneous decay profile over the entire envelope from 540 to 740 nm. The lifetimes (τ) of the CT ion pairs thus produced within the zeolite supercage varied by roughly an order of magnitude between 0.11 and 9.2 μs among the various complexes listed in Table I.[12] The transient absorbance did not return completely to the base line,[13] somewhat reminiscent of the decay previously observed from arene and carbonyl triplet states in zeolites.[14]

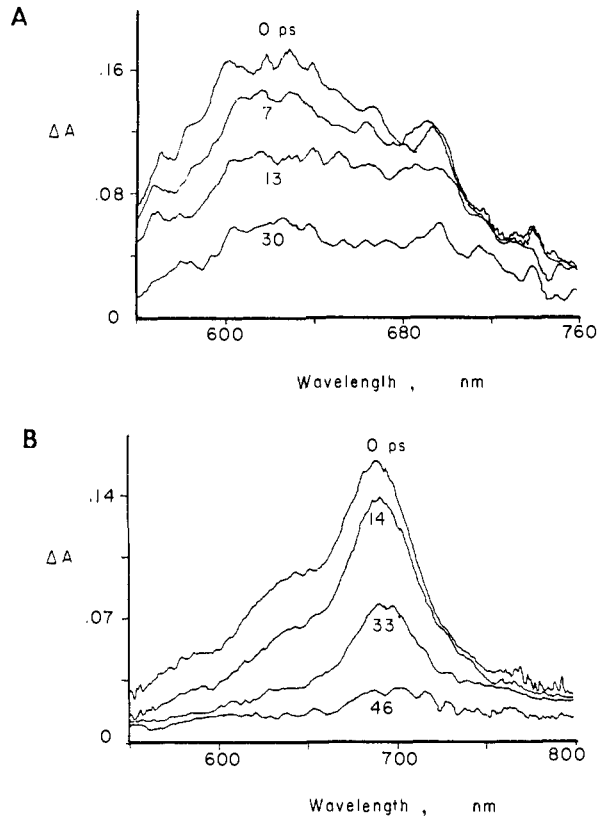

Figure 3. Time-resolved picosecond absorption spectra following the excitation of the CT complexes (A) [MV^{2+},Naph] and (B) [PP^+,-$MeC_{14}H_9$] in acetonitrile solutions with a 20-ps (fwhm) laser pulse.

In strong contrast to the rather prolonged (microsecond) lifetimes of CT ion pairs produced within zeolite supercages, the laser flash photolysis of the same complexes generated in solution yielded spectral transients that could be detected only on the picosecond time scale. Thus Figure 3 shows the time-resolved picosecond spectra in the spectral region between 550 and 750 nm of (A) the CT ion pair [$MV^{•+}$,$Naph^{•+}$] from the naphthalene complex with methylviologen and (B) the 9-methylanthracene cation radical from the corresponding complex with the *N*-methyl-4-cyanopyridinium acceptor following the application of the 20-ps (fwhm) pulse from a Nd^{3+}:YAG laser. In all cases, the time-resolved picosecond spectrum in solution was the same as that observed in the zeolite supercage (vide supra). Most importantly, the short lifetimes of the CT ion pairs in solution, as given in Table I,[12] lie close to the temporal resolution of the laser-flash spectrometer, and they are in the range of those previously measured in solution for other systems[15,16] with similar driving forces for back electron transfer. As such, the factor of 10^5–10^6 that prolongs the lifetimes of the CT ion pairs in the zeolite supercage (column 4) is sufficient to distinguish the strong environmental influences that modulate

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(12) The absorbance decrease was treated as a first-order decay.
(13) For example, the minor residual absorbance (after ~100 μs) did not arise from a photoproduct since the intensity of the CT band in the zeolite was unchanged after irradiation (vide supra).
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the rate of back electron transfer relative to that in solution (column 6). Adsorption effects of ionic species at the polar aluminosilicate surface and/or the electrostatic field within the zeolite supercage[17,18] could be the contributory factors in the marked retardation of the electron-transfer rate. Indeed from the magnitude of the latter, we estimate the CT ion pair to be stabilized within the zeolite supercage over that in solution by roughly 8 kcal mol^{-1}.[19,20] The chemical consequences accompanying the dramatically prolonged lifetimes of CT ion pairs enabled by zeolite supercages will be reported at a later time.

Acknowledgment. We thank the National Science Foundation, Robert A. Welch Foundation, and Texas Advanced Research Program for financial support.

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(18) The same experiment on a wet zeolite afforded a transient spectrum that consisted only of that derived from $MV^{\bullet+}$ owing to the rapid hydration of $Naph^{\bullet+}$ (compare Steenken, S., et al. in ref 10b) at the wall. Furthermore, note the poor correlation between the driving force for back electron transfer $\mathcal{F}$ ($E^{\circ}_{red} + E^{\circ}_{ox}$) and the lifetime ($-\log \tau$) of the CT ion pairs.

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Applications of the N_2S_2 Ligand, *N,N'*-Bis(mercaptoethyl)-1,5-diazacyclooctane, toward the Formation of Bi- and Heterometallics: $[(BME\text{-}DACO)Fe]_2$ and $[(BME\text{-}DACO)NiFeCl_2]_2$

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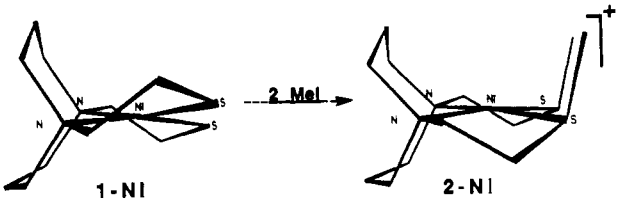
Recently we reported the synthesis of a new macrocyclic ligand based on a derivative of diazacyclooctane, *N,N'*-bis(mercaptoethyl)-1,5-diazacyclooctane, $H_2BME\text{-}DACO$.[1] The X-ray crystal structures of the complexes $(BME\text{-}DACO)Ni^{II}$ (**1**-Ni) and $[(Me_2BME\text{-}DACO)Ni^{II}][I]_2$ (**2**-Ni) were the first determined for



the N_2S_2 Busch-type[2] complexes as monomers, a success presumably due to the control of aggregation provided by steric bulk

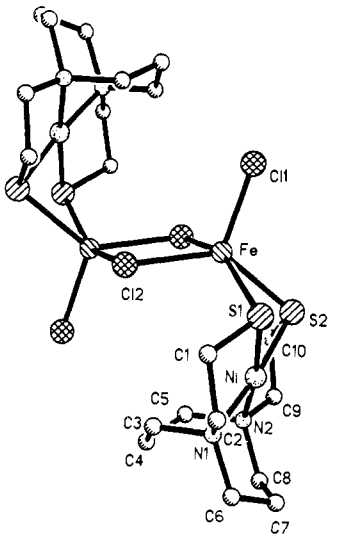


Figure 1. Molecular structure of $[(BME\text{-}DACO)NiFeCl_2]_2$ (**1**-Ni_2Fe_2). Selected bond lengths (Å): Fe-Cl(1), 2.286 (3); Fe-Cl(2), 2.422 (3); Fe-Cl(2A), 2.547 (3); Fe-S(1), 2.552 (3); Fe-S(2), 2.462 (3); Ni-S(1), 2.172 (3); Ni-S(2), 2.165 (3); Ni-N(1), 1.974 (8); Ni-N(2), 1.966 (9). Selected bond angles (deg): S(1)-Fe-Cl(2A), 153.6 (1); Cl(2)-Fe-S(2), 134.3 (1); Cl(1)-Fe-Cl(2A), 99.4 (1); Cl(1)-Fe-Cl(2), 111.9 (1); Cl(1)-Fe-S(1), 106.2 (1); Cl(1)-Fe-S(2), 113.7 (1); S(1)-Fe-S(2), 72.2 (1); Cl(2)-Fe-S(1), 93.1 (1); Cl(2)-Fe-Cl(2A), 82.9 (1); S(2)-Fe-Cl(2A), 91.9 (1); S(1)-Ni-S(2), 85.9 (1); N(1)-Ni-N(2), 91.0 (3); S(2)-Ni-N(2), 91.0 (2); S(1)-Ni-N(1), 91.3 (3); Ni-S(1)-Fe, 81.6 (1); Ni-S(2)-Fe, 83.9 (1); Fe-Cl(2)-Fe(A), 97.1 (1).

of the ligand. The structures evidenced the well-known conformational requirements of the DACO ring,[3] resulting in a sterically protected hydrophobic pocket, especially for the **2**-Ni complex, where dialkylation occurred on the same side of the square plane.[1] This methylated derivative (and others alkylated with C_2H_5I, $C_6H_5CH_2Br$, $i\text{-}C_3H_7I$, and $BrCH_2CH_2CH_2Br$)[4] results from the reactivity of the metal-bound thiolate sulfur atoms of **1**-Ni analogous to that of the Busch-type $(H_2NCH_2CH_2S)_2Ni^{II}$ complexes.[5] In fact, the sulfurs in such complexes are potential binding sites for an additional metal as illustrated by $[(H_2NCH_2CH_2S)_4Ni_3](I)_2$.[2] Structural studies by Dahl and Wei showed the trimetallic to consist of three linked square planes: two NiN_2S_2 planes separated by a NiS_4 plane at torsional angles of 109°.[6]

We are applying the ability of **1**-Ni to serve as a complex ligand toward the preparation of Ni and Fe heterometallics in biological-type ligation settings appropriate to provide redox and magnetic behavior for comparison to nickel-containing hydrogenases.[7] To our knowledge $[(BME\text{-}DACO)Ni(\mu\text{-}Cl)FeCl]_2$ (**1**-Ni_2Fe_2) is the first Ni/Fe heterometallic complex with classical (as opposed to organometallic) donor atoms and represents a new type of heterotetrametallic, containing two square-planar nickel(II) and two pseudo-square-pyramidal iron(II) ions. Square-pyramidal iron is also seen in $[(BME\text{-}DACO)Fe]_2$ (**1**-Fe_2) in which the iron(II) centers are simultaneously bound to two BME-DACO ligands, resulting in a 2Fe-2S core, analogous to the dimeric iron complex of dimethyl-*N,N'*-bis(2-mercaptoethyl)-1,3-propanediamine, $BME\text{-}Me_2PDA$.[8]

Reaction of **1**-Ni in CH_3CN with anhydrous $FeCl_2$ in either 2:1 or 1:1 molar equivalents results in formation of a thermally

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