Self-Organization of Highly Stable Electron Donor−Acceptor Complexes via Host−Guest Interactions[†]

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Biscrown stilbene **S** forms complexes of 1:1 and 2:1 composition with bisammonium viologen salt $\mathbf{V}^{4+}$ in acetonitrile solution. Both of the complexes exhibit spectroscopic behavior typical of molecular electron donor−acceptor complexes. The 1:1 complex $[\mathbf{S{\cdot}V}]^{4+}$ has a very high thermodynamic stability ($\log K = 9.08$), which is due to simultaneous interaction of the two ammonium groups of $\mathbf{V}^{4+}$ with the two 18-crown-6-ether units of **S**. The 2:1 complex ($\log K = 12.28$) $[\mathbf{S{\cdot}V{\cdot}S}]^{4+}$ likely has a sandwich-type layered structure in which the acceptor salt is located between two complexed molecules of the biscrown stilbene.

Introduction

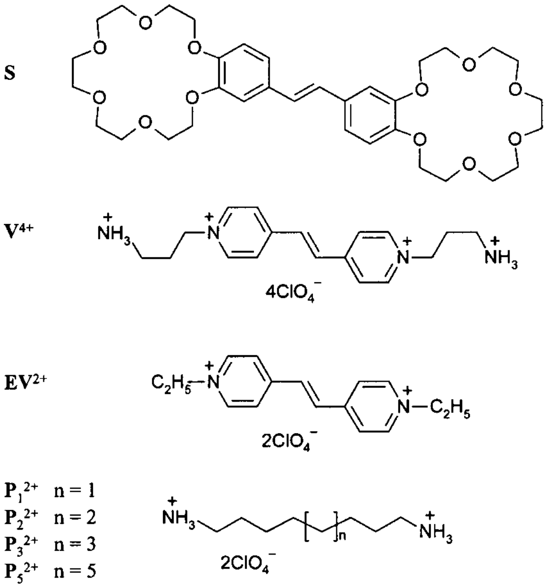
Molecular electron donor−acceptor complexes, i.e., ground-state charge-transfer (CT) complexes, play an important role in chemical and photochemical reactions,[1] in molecular self-assembly,[2] and in biological systems.[3] In addition, they have potential for use as organic conductors[4] and photoconductors,[5] and as second-order nonlinear optical materials.[6] Recently, ground-state CT complexation has been employed for the development of optical sensors for ions.[7] It was shown that in acetonitrile complexation of biscrown stilbene **S** (Chart 1) with bisammonium viologen salt $\mathbf{V}^{4+}$ takes place through two-center host−guest bonding. This complexation results in total luminescence quenching from both components and in the appearance of a new absorption band in the visible region. Metal ions are able to displace the bisammonium salt complexed with the biscrown stilbene, leading to disruption of the CT complex and to the appearance of intense fluorescence from the metal-complexed biscrown stilbene.[7]

In this communication, we report evidence for the formation of a termolecular CT complex, $[\mathbf{S{\cdot}V{\cdot}S}]^{4+}$, between **S** and $\mathbf{V}^{4+}$ in acetonitrile and describe the results of spectroscopic measurements of stability constants for CT complexes of **S** with $\mathbf{V}^{4+}$, compared with the reference dicationic salts, i.e., derivatives of diethyl viologen, $\mathbf{EV}^{2+}$, and alkyldiammonium perchlorate salts, $\mathbf{P}_1{}^{2+}$−$\mathbf{P}_3{}^{2+}$ and $\mathbf{P}_5{}^{2+}$.

Results and Discussion

In dilute (∼10^{-5} mol dm^{-3}) acetonitrile solution, mixing **S** and $\mathbf{V}^{4+}$ produces solely a 1:1 complex.[7] At higher concentrations, the maximum of the CT absorption band is markedly red-shifted and its intensity increases as the excess of **S** over $\mathbf{V}^{4+}$ increases from ∼10^{-4} to ∼10^{-2} mol dm^{-3} (Figure 1). In contrast, the addition of $\mathbf{V}^{4+}$ to an equimolar solution of **S** and $\mathbf{V}^{4+}$ (∼10^{-3} mol dm^{-3}, which is the solubility limit for $\mathbf{V}^{4+}$) did not influence the position or intensity of the CT absorption band. This spectroscopic behavior enabled us to postulate the formation of a termolecular CT complex, $[\mathbf{S{\cdot}V{\cdot}S}]^{4+}$, between **S** and $\mathbf{V}^{4+}$ according to the following reaction scheme:

CHART 1



$$\mathbf{S} + \mathbf{V}^{4+} \xrightleftharpoons{K_{1V}} [\mathbf{S{\cdot}V}]^{4+} \tag{1}$$

$$[\mathbf{S{\cdot}V}]^{4+} + \mathbf{S} \xrightleftharpoons{K_{2V}} [\mathbf{S{\cdot}V{\cdot}S}]^{4+} \tag{2}$$

where K_{1V} and K_{2V} are the equilibrium constants.

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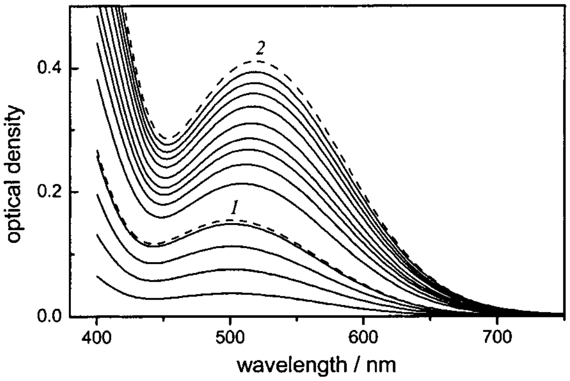


Figure 1. Absorption spectra in acetonitrile solution containing $\mathbf{V}^{4+}$ at a concentration of 4.0×10^{-4} mol dm^{-3} and **S** at concentrations ranging from 1×10^{-4} to 0.01 mol dm^{-3}. The dashed curves are the calculated spectra of complexes $[\mathbf{S{\cdot}V}]^{4+}$ (1) and $[\mathbf{S{\cdot}V{\cdot}S}]^{4+}$ (2) derived from the equilibration model discussed in the text.

The set of absorption curves shown in Figure 1 was constructed from these complexation equilibria using a matrix modeling method.[8] The model gave very small residual error for optical density, $\sigma_D < 0.001$, when $K_{1V} > 10^7$ mol^{-1} dm^3 and $K_{2V} = 1.6 \times 10^3$ mol^{-1} dm^3. Variation of K_{1V} in the stated range had virtually no effect on the value of K_{2V} or on the calculated spectra of the $[\mathbf{S{\cdot}V}]^{4+}$ or $[\mathbf{S{\cdot}V{\cdot}S}]^{4+}$ complexes, Figure 1. In addition, the calculated spectrum of $[\mathbf{S{\cdot}V}]^{4+}$ agreed exactly with the experimental spectrum measured when a large excess of $\mathbf{V}^{4+}$ over **S** was used. These facts, especially the small value of σ_D, support the assigned complexation stoichiometries.

Attempts to measure the equilibrium constant K_{1V} using direct spectrophotometric or fluorescence titration in dilute solution were unsuccessful because of the extremely high thermodynamic stability of the 1:1 $[\mathbf{S{\cdot}V}]^{4+}$ complex in acetonitrile. Therefore, a competing reaction methodology was employed to assess this constant. To find a suitable competing reactant, complexation of **S** with alkyldiammonium perchlorate salts $\mathbf{P}_1^{2+}$, $\mathbf{P}_2^{2+}$, $\mathbf{P}_3^{2+}$, and $\mathbf{P}_5^{2+}$ was studied. The absorption spectra obtained from solutions containing **S** at a constant total concentration and each of the alkyldiammonium perchlorate salts at various concentrations were analyzed using the same matrix modeling method. With $\mathbf{P}_2^{2+}$, $\mathbf{P}_3^{2+}$, and $\mathbf{P}_5^{2+}$, the spectroscopic data indicated a 1:1 complexation $[\mathbf{S{\cdot}P}_n]^{2+}$ between **S** and $\mathbf{P}_n^{2+}$ over the explored concentration range.[9] With $\mathbf{P}_1^{2+}$, a 1:2 complex involving one molecule of the biscrown stilbene with two $\mathbf{P}_1^{2+}$ salts $[\mathbf{P}_1{\cdot}\mathbf{S}{\cdot}\mathbf{P}_1]^{4+}$ was also formed when the salt concentration approached 10^{-3} mol dm^{-3}. The concentration-dependent spectra measured for **S** with $\mathbf{P}_1^{2+}$ were constructed from the following complexation model:

$$\mathbf{S} + \mathbf{P}_n^{2+} \xrightleftharpoons{K_{1P}} [\mathbf{S{\cdot}P}_n]^{2+} \tag{3}$$

$$[\mathbf{S{\cdot}P}_n]^{2+} + \mathbf{P}_n^{2+} \xrightleftharpoons{K_{2P}} [\mathbf{P}_n{\cdot}\mathbf{S}{\cdot}\mathbf{P}_n]^{4+} \tag{4}$$

where K_{1P} and K_{2P} are the equilibrium constants.

TABLE 1. Thermodynamic and Spectroscopic Parameters for the Complexes of S with $\mathbf{V}^{4+}$, $\mathbf{EV}^{2+}$, $\mathbf{P}_1^{2+}$, $\mathbf{P}_2^{2+}$, $\mathbf{P}_3^{2+}$, and $\mathbf{P}_5^{2+}$ [a]

	log K[b]	λ_{max}, nm	$\epsilon_{max} \times 10^{-3}$, mol^{-1} dm^3 cm^{-1}
S		336	37.5
$[\mathbf{S{\cdot}V}]^{4+}$	9.08	502	0.39
$[\mathbf{S{\cdot}V{\cdot}S}]^{4+}$	12.28	519	1.02
$[\mathbf{S{\cdot}EV}]^{2+}$	1.13	527	0.57
$[\mathbf{S{\cdot}P}_1]^{2+}$	5.83	336	34.9
$[\mathbf{P}_1{\cdot}\mathbf{S}{\cdot}\mathbf{P}_1]^{4+}$	8.48	332	38.8
$[\mathbf{S{\cdot}P}_2]^{2+}$	6.78	336	36.4
$[\mathbf{S{\cdot}P}_3]^{2+}$	7.58	334.5	37.0
$[\mathbf{S{\cdot}P}_5]^{2+}$	8.59	333.5	38.7

[a] In acetonitrile, 22 ± 2 °C. [b] For $[\mathbf{S{\cdot}V{\cdot}S}]^{4+}$, $K = K_{1V}K_{2V}$, and for $[\mathbf{P}_1{\cdot}\mathbf{S}{\cdot}\mathbf{P}_1]^{4+}$, $K = K_{1P}K_{2P}$. The stability constants are reproducible to within about ±20%.

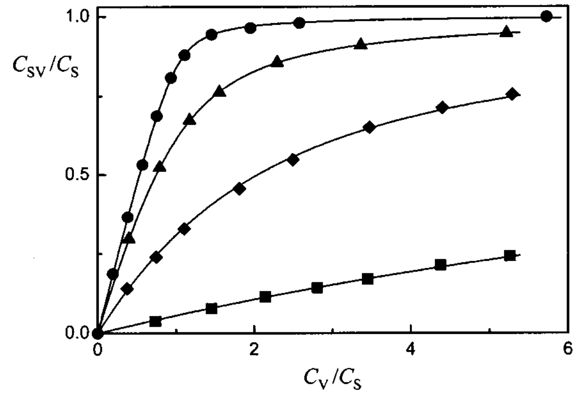


Figure 2. Relative concentration of the 1:1 charge-transfer complex $[\mathbf{S{\cdot}V}]^{4+}$ as a function of the relative concentration of acceptor salt $\mathbf{V}^{4+}$ in the presence of excess (1×10^{-3} mol dm^{-3}) $\mathbf{P}_1^{2+}$ (●), $\mathbf{P}_2^{2+}$ (▲), $\mathbf{P}_3^{2+}$ (◆) and $\mathbf{P}_5^{2+}$ (■) over **S** ($C_S = 2.0 \times 10^{-5}$ mol dm^{-3}). Solid curves are from the fits to eq 5.

The model gave a small residual error for optical density, $\sigma_D < 0.002$, when $K_{1P} = 10^5-10^6$ mol^{-1} dm^3 and $K_{2P} = 4.5 \times 10^2$ mol^{-1} dm^3. For the alkyldiammonium salts $\mathbf{P}_2^{2+}$, $\mathbf{P}_3^{2+}$, and $\mathbf{P}_5^{2+}$, estimates for K_{1P} were derived from the 1:1 complexation model (eq 3), yielding $K_{1P} = 10^6-10^7$ mol^{-1} dm^3 for $\mathbf{P}_2^{2+}$ and $K_{1P} > 10^7$ mol^{-1} dm^3 for $\mathbf{P}_3^{2+}$ and $\mathbf{P}_5^{2+}$. We failed to obtain more accurate estimations of the constants K_{1P} because of the very high stability of the 1:1 $[\mathbf{S{\cdot}P}_n]^{2+}$ complexes with $\mathbf{P}_3^{2+}$ and $\mathbf{P}_5^{2+}$ or because of the very small changes in the spectrum of **S** observed upon 1:1 complexation with $\mathbf{P}_1^{2+}$ (Supporting Information, Figure S2) and $\mathbf{P}_2^{2+}$. In fact, the magnitude of the observed spectral changes in the series decreased upon decreasing the length of the alkyl chain in the perchlorate salt $\mathbf{P}_n^{2+}$, probably because of an increase in the steric hindrance for effective two-center bonding in the corresponding 1:1 complexes. In $\mathbf{P}_1^{2+}$, the very large difference in the thermodynamic stability of the 1:1 ($[\mathbf{S{\cdot}P}_1]^{2+}$) and 1:2 ($[\mathbf{P}_1{\cdot}\mathbf{S}{\cdot}\mathbf{P}_1]^{4+}$) complexes of **S** with $\mathbf{P}_1^{2+}$ indicates that two-center bonding is still possible in the 1:1 complex, despite the relatively short length of the alkyl chain in $\mathbf{P}_1^{2+}$.

For $\mathbf{P}_2^{2+}$, a good estimation of K_{1P} (Table 1) was derived from fluorescence titration experiments. The fluorescence intensity from a solution of **S** was measured as a function of $\mathbf{P}_2^{2+}$ concentration.[10] On complete binding of the biscrown stilbene **S** with $\mathbf{P}_2^{2+}$ as a 1:1 complex, the emission intensity dropped by a factor of 2.6 (Supporting Information, Figure S1). The equilibrium constant was then obtained from nonlinear fitting of these data to a theoretical curve corresponding to a single equilibrium, as in eq 3.

To determine K_{1V} for complex $[\mathbf{S{\cdot}V}]^{4+}$ and K_{1P} for the complexes of **S** with $\mathbf{P}_1^{2+}$, $\mathbf{P}_3^{2+}$, and $\mathbf{P}_5^{2+}$, the concentration, C_{SV}, of the donor−acceptor 1:1 complex $[\mathbf{S{\cdot}V}]^{4+}$ was measured as a function of the concentration, C_V, of the acceptor $\mathbf{V}^{4+}$ in the presence of a large excess of the alkyldiammonium salt $\mathbf{P}_n^{2+}$ over **S**.[11] The resulting data (Figure 2) were fit to eq 5,

$$C_{SV} = \frac{1}{2}\left(x - \sqrt{x^2 - 4C_SC_V}\right), \quad x = C_S + C_V + C_PR \tag{5}$$

where C_S and C_P are total concentrations of **S** and $\mathbf{P}_n^{2+}$, respectively, and $R = K_{1V}^{-1}K_{1P}$ for the complexation model involving the equilibria of eqs 1 and 3 or $R = K_{1V}^{-1}K_{1P}(1 + K_{2P}C_P)$ for the model involving the equilibria of eqs 1, 3, and 4. Equation 5 is derived from the law of mass action and the material balance of the corresponding equations, provided that $C_S \ll C_P$ and $[\mathbf{S}] \ll C_{SV} + C_{SP} + C_{PSP}$, where C_{SP} and C_{PSP} are concentrations of $[\mathbf{S}\cdot\mathbf{P}_n]^{2+}$ and $[\mathbf{P}_n\cdot\mathbf{S}\cdot\mathbf{P}_n]^{4+}$, respectively. This condition is valid under the given experimental conditions.[11] The parameters R obtained from these fits were used, together with the known values of K_{1P} for $\mathbf{P}_2^{2+}$ and K_{2P} for $\mathbf{P}_1^{2+}$, to derive the equilibrium constants sought.

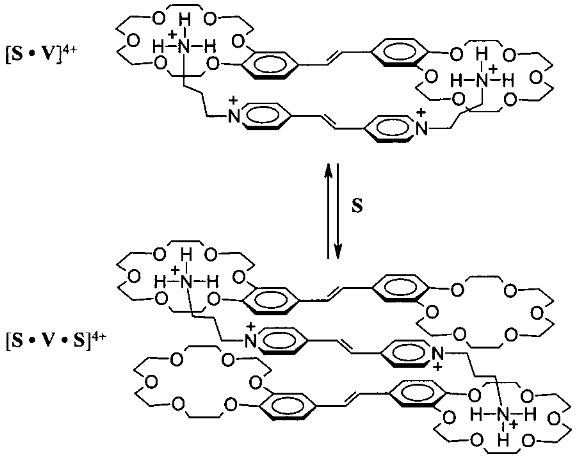
The equilibrium constant for complexation between **S** and $\mathbf{EV}^{2+}$ was also measured to evaluate the possible contribution of CT interactions on the thermodynamic stability of $[\mathbf{S}\cdot\mathbf{V}]^{4+}$. The addition of large amounts of **S** to a solution of $\mathbf{EV}^{2+}$ led to the appearance of an absorption band with the maximum at 527 nm (Supporting Information, Figure S3), indicating that **S** and $\mathbf{EV}^{2+}$ also produce a CT complex. The set of CT absorption spectra measured at various concentrations of the biscrown stilbene[12] was reconstructed well ($\sigma_D < 0.001$) from a 1:1 complexation model. These calculations gave the stability constant as well as the spectroscopic characteristics for complex $[\mathbf{S}\cdot\mathbf{EV}]^{2+}$.

The data derived from these spectroscopic studies are collected in Table 1. Among the compounds studied, bisammonium viologen $\mathbf{V}^{4+}$ gives the strongest 1:1 complex with the biscrown stilbene **S**, with a Gibbs free energy for complex formation of −12.2 kcal mol^{-1}. The relatively high thermodynamic stability of $[\mathbf{S}\cdot\mathbf{V}]^{4+}$ indicates that strong CT interactions between the complex components contribute significantly to ΔG. The entropy loss upon CT complexation in $[\mathbf{S}\cdot\mathbf{V}]^{4+}$ is lower than that in $[\mathbf{S}\cdot\mathbf{EV}]^{2+}$ because CT interactions are also encountered within the preorganized host−guest complex. Therefore, the contribution from CT interaction to ΔG for $[\mathbf{S}\cdot\mathbf{V}]^{4+}$ is likely to be larger than the ΔG value (−1.5 kcal mol^{-1}) found for $[\mathbf{S}\cdot\mathbf{EV}]^{2+}$.

It is more difficult to rationalize the unexpectedly high thermodynamic stability of the higher-order complex $[\mathbf{S}\cdot\mathbf{V}\cdot\mathbf{S}]^{4+}$, for which the Gibbs free energy is −16.5 kcal mol^{-1}. Some information on the structure of $[\mathbf{S}\cdot\mathbf{V}\cdot\mathbf{S}]^{4+}$ can be derived from a comparison of spectroscopic properties of $[\mathbf{S}\cdot\mathbf{V}]^{4+}$ and $[\mathbf{S}\cdot\mathbf{V}\cdot\mathbf{S}]^{4+}$. Generally, the expected spectroscopic shift of the CT complex absorption spectrum upon going from a bimolecular to a termolecular system is a red shift of the absorption maximum and an increase in intensity.[13] This behavior is typical of both symmetrical (D−A−D) and asymmetrical (D−D−A) donor D−acceptor A complexes.[14] These same shifts are observed, as expected, for the complexes of **S** with $\mathbf{V}^{4+}$. From theoretical estimations,[14] the increased absorptivity for D−D−A complexes should be less than 2. In the case of $[\mathbf{S}\cdot\mathbf{V}\cdot\mathbf{S}]^{4+}$, however, the absorptivity increased by a factor of 2.6, suggesting that this complex probably has a symmetrical structure.

The interaction of the crown units of **S** with the ammonium groups of $\mathbf{V}^{4+}$ plays a principal role in the formation of $[\mathbf{S}\cdot\mathbf{V}\cdot\mathbf{S}]^{4+}$, which is evidenced by the fact that no spectral changes indicative of higher-order CT complexes are observed when a large amount of 3,4,3′,4′-tetramethoxy stilbene[15] instead of **S** was added to a solution of the 1:1 $[\mathbf{S}\cdot\mathbf{V}]^{4+}$ CT complex. The possibility that each of the ammonium groups interacts simultaneously with two crown-ether units within $[\mathbf{S}\cdot\mathbf{V}\cdot\mathbf{S}]^{4+}$ seems to be unlikely because of steric reasons. Instead, it is most likely that the formation of $[\mathbf{S}\cdot\mathbf{V}\cdot\mathbf{S}]^{4+}$ occurs via the disruption of two-center host−guest bonding in the 1:1 $[\mathbf{S}\cdot\mathbf{V}]^{4+}$ complex, with one of the ammonium groups of $\mathbf{V}^{4+}$ being switched to a crown-ether unit of the second molecule of **S**, as shown in Scheme 1. The resulting significant gain in ΔG for 2:1 complexation can be explained only if one assumes that the geometry of $[\mathbf{S}\cdot\mathbf{V}]^{4+}$ is far from optimal for the two-center host−guest bonding required in the 1:1 complex and that shifting to the $[\mathbf{S}\cdot\mathbf{V}\cdot\mathbf{S}]^{4+}$ complex leads to a release of steric strain, thereby producing significant enthalpy gain.

SCHEME 1



Conclusions

Thus, bis(18-crown-6) stilbene **S** forms a strong 1:1 complex with the bisammonium viologen salt $\mathbf{V}^{4+}$ and with the bisalkylammonium perchlorate salts $\mathbf{P}_1^{2+}$, $\mathbf{P}_2^{2+}$, $\mathbf{P}_3^{2+}$, and $\mathbf{P}_5^{2+}$ in acetonitrile via two-center host−guest bonding. The 1:1 complex between **S** and $\mathbf{V}^{4+}$ has an increased thermodynamic stability because of strong charge transfer through a geometrically optimized interaction. Compounds **S** and $\mathbf{V}^{4+}$ are also able to form a termolecular CT complex $[\mathbf{S}\cdot\mathbf{V}\cdot\mathbf{S}]^{4+}$, which is likely to have a sandwich-type layered structure in which the acceptor salt is bound between two molecules of the biscrown stilbene.

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Supporting Information Available: Absorption spectra of complexes of **S** with $\mathbf{P}_1^{2+}$ and $\mathbf{P}_5^{2+}$, fluorescence titration curves, and data processing methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) The concentration of **S** was maintained at 4 × 10^{-6} mol dm^{-3} (5 cm quartz cell) or at 2 × 10^{-5} mol dm^{-3} (1 cm quartz cell); the concentration of the alkyldiammonium salt was varied from 0 to 1 × 10^{-3} mol dm^{-3} for $\mathbf{P}_2^{2+}$, $\mathbf{P}_3^{2+}$, and $\mathbf{P}_5^{2+}$ and to 0.02 mol dm^{-3} for $\mathbf{P}_1^{2+}$.

(10) The concentration of **S** was maintained at 1.0 × 10^{-6} mol dm^{-3} (1 cm quartz cell). The concentration of $\mathbf{P}_2^{2+}$ was varied from 0 to 2.0 × 10^{-5} mol dm^{-3}. Excitation and observation wavelengths were 343 and 393 nm, respectively. Optical densities at the excitation wavelength were ≤0.03.

(11) The concentrations of **S** and the perchlorate salts $\mathbf{P}_n^{2+}$ in a solution were maintained at 2.0 × 10^{-5} and 1.0 × 10^{-3} mol dm^{-3}, respectively. The concentration of $\mathbf{V}^{4+}$ was varied from 0 to 1 × 10^{-4} mol dm^{-3}. The concentration of $[\mathbf{S}\cdot\mathbf{V}]^{4+}$ was monitored by its optical density at 380–390 nm (5 cm quartz cell) in the region of the second absorption band of this complex. The contributions from all other species to the total optical density were negligible in comparison with that from the CT complex.

(12) The concentration of $\mathbf{EV}^{2+}$ was 4.8 × 10^{-3} mol dm^{-3}. The concentration of **S** was varied from 0 to 0.1 mol dm^{-3}. Measurements were conducted in a 0.1 cm quartz cell.

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