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Intramolecular Electron Transfer in the N-Hydroxyethylethylenediaminetriacetatovanadium(II,IV) Binuclear Ion

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Abstract: The cross reaction of V(heedta)$^-$ (II) and VO(heedta)$^-$ (IV) forming a detectable (II,IV) precursor complex has been studied as a function of pH and temperature. At 298 K, $\mu = 0.20$, the following kinetic parameters have been measured: $k_1 =$ (II + IV outer-sphere electron transfer) = $(2.7 \pm 0.3) \times 10^4$ M^{-1} s^{-1}; k_2 ((II,IV) formation) = $(4.0 \pm 0.4) \times 10^4$ M^{-1} s^{-1}; k_{-2} ((II,IV) dissociation) = 2.0 ± 2.0 s^{-1}; k_3 ((II,IV) intramolecular electron transfer) = 25.5 ± 0.2 s^{-1}; $K_4 k_5$ ((II,IV) H$^+$ intramolecular electron transfer) = $(1.22 \pm 0.14) \times 10^7$ M^{-1} s^{-1}; k_6 (IV + (II,IV) outer-sphere electron transfer) = $(9.30 \pm 1.58) \times 10^3$ M^{-1} s^{-1}; k_7 (II + (II,IV) outer-sphere electron transfer) = $(4.61 \pm 0.79) \times 10^3$ M^{-1} s^{-1}; log K_2 (association constant for formation of (II,IV) from II + IV) = 4.30 ± 0.30. Temperature-dependent studies of the k_2, k_3, and $K_4 k_5$ paths reveal $\Delta H_2^\ddagger = 6.1 \pm 1.0$ kcal/mol, $\Delta S_2^\ddagger = -17 \pm 3$ eu; $\Delta H_3^\ddagger = 7.97 \pm 0.36$ kcal/mol, $\Delta S_3^\ddagger = -25.4 \pm 1.2$ eu; $\Delta H_{4,5}^\ddagger = -7.04 \pm 4.79$ kcal/mol, $\Delta S_{4,5}^\ddagger = -49.7 \pm 16.1$ eu. The V(heedta)$^-$/VO(Cydta)$^{2-}$ cross-reaction parameters comparable to $\Delta H_3^\ddagger$ and $\Delta S_3^\ddagger$ are 6.27 ± 0.44 kcal/mol and -30.4 ± 1.5 eu, respectively. The large negative $\Delta S_3^\ddagger$ value is discussed in terms of coordination rearrangements ($\Delta S_{CR}^\ddagger$) which limit intramolecular electron transfer. The reaction of Cr(heedta)$^-$/VO(heedta)$^-$ is found to be competitive with stopped-flow mixing and predominantly outer-sphere.

Introduction

Intramolecular electron transfer has been observed for the V(II,IV) binuclear complex formed from the inner-sphere component of the cross reaction of VO(heedta)$^-$ and V(heedta)$^-$ (heedta^{3-} = N-hydroxyethylethylenediaminetriacetate).[1] The V(III,III) binuclear ion, (heedta)-VOV(heedta)$^{2-}$, is the product of the electron transfer step. This species has been studied for its monomerization and formation reactions and its solution properties.[2] The V(III,III) complex is similar to the oxo-bridged (heedta)FeOFe(heedta)$^{2-}$ complex studied by Walling and Gray,[3,4] Wilkins[5] and Martell.[6]

The intramolecular electron transfer process within the V(II,IV)(heedta) binuclear complex is unusually slow by comparison with other inner-sphere systems.[1] A number of reports concerning intramolecular electron transfer within binuclear ions have appeared since the first report of Isied and Taube.[1,7-12] In general the reactant metal centers of the precursor complexes have been separated by means of bifunctional conjugated ligands. The only cases where electron transfer within a binuclear complex has been slow enough to allow detection of a precursor complex having the oxidant and reductant centers separated by a single atomic distance are the VO(heedta)$^-$/V(heedta)$^-$ cross reaction of our laboratory and Lane's report of the mercaptide bridged Cu(I)–Co(III) intermediate in the reduction of [Co(en)$_2$SCH$_2$CO$_2$]$^+$.[12] Electron transfer to Co(III) is often affected by the spin-state change in forming Co(II).[13a] The activation enthalpy in Lane's system is in agreement with a change in spin state as being rate determining.[14] Spin-state changes cannot affect the VO(heedta)$^-$/V(heedta)$^-$ system.[2] The explanation for the slow intramolecular electron transfer step must be found in a different phenomenon. Taube has inferred that entropy of activation which has been measured for many labile reactant pairs is dominated by the entropy costs to bring charged reactants together in solution in order to form the precursor complex.[15] His conclusion is based on the intramolecular electron transfer within (NH$_3$)$_5$CoLRu(NH$_3$)$_4$(H$_2$O)$^{5+}$ complexes (L = li-

gands related to 4,4'-bipyridine) where $\Delta S_{ET}{}^{\ddagger} = 0 \pm 2$ eu. The electron transfer is apparently adiabatic in the series of complexes which were studied since $\Delta H^{\ddagger}$ remains a constant 20.1 $\pm$ 0.2 kcal/mol with four different bridging ligands. We wish to report here the temperature dependence and competitive redox processes which are involved in the VO(heedta)$^-$/ V(heedta)$^-$ cross reaction. The bleaching of the V(II,IV) transient has a substantially more negative value for $\Delta S_{ET}{}^{\ddagger}$ than is observed by Taube or Lane for systems which do not require chelate structure rearrangements. The V(II,IV)-(heedta) intramolecular electron transfer appears to exhibit a ligand rearrangement controlled process. These observations are important in view of the coupling between structural factors and redox reactivities that are imposed on metalloprotein redox systems.

Experimental Section

Preparations. V(H$_2$O)$_6{}^{2+}$ and Cr(H$_2$O)$_6{}^{2+}$ were prepared by reduction of standardized solutions of VO(ClO$_4$)$_2$ and [Cr(H$_2$O)$_6$]-[(ClO$_4$)$_3$] over Zn/Hg. A slight excess of H$_3$heedta (enough to provide the total metal ion equivalents for 1 mol of Zn^{2+} per mol of V^{2+} or per 2 mol of Cr^{2+}) was added under N$_2$. The solutions were then adjusted to pH values near pH 5 by NaOH or HClO$_4$ or combined with pH-adjusted buffer solutions (phosphate, lutidine, Tris). All manipulations were carried out under N$_2$ by use of a gas manifold and syringe techniques. An Orion 601 digital pH meter was used to monitor the hydrogen ion concentration. A single probe, calibrated against commercial buffer standards, was mounted inside N$_2$-purged vessels for pH measurements. The ionic strength was maintained with NaClO$_4$ solutions standardized by the tetraphenylarsonium perchlorate gravimetric procedure. VO(heedta)$^-$ solutions were prepared by stoichiometric mixing of H$_3$heedta and VO(ClO$_4$)$_2$ followed by pH adjustment.

Catalysis Studies. Equivalent initial V(II) solutions were prepared by simultaneous reduction of VO(ClO$_4$)$_2$ solution over Zn/Hg and electrochemically by cathodic reduction at a Hg pool electrode. To effect a smooth electrochemical reduction of VO^{2+} to V^{2+} required the presence of 0.205 M NaCl in place of the usual NaClO$_4$ for ionic strength control. After complexation with the proper number of equivalents of H$_3$heedta for each of the reduced solutions of V^{2+}, the cross reaction was monitored using identical aliquots of a VO-(heedta)$^-$ solution. The course of the reaction exhibited identical total absorbances at all times throughout the runs. These systems were used as a test of potential catalytic impurities which might be present from contact with the Zn reduction source. No difference was obtained. The effect of stainless steel or platinum needles was also studied. Identical results were obtained from solutions exposed to stainless steel needles as for those exposed only to platinum. Catalysis of the (II,IV) bleaching was not induced by the presence of added V(heedta) or the (III,III) binuclear product.

Kinetic Studies. Solutions under N$_2$ were delivered to drive syringes of a Durrum D-110 stopped-flow spectrophotometer. The bleaching of the red V(II,IV) transient was monitored at 557 nm at various temperatures. The temperature was controlled by means of a Forma 2095 bath to ± 0.03 °C for the coolant liquid. The stopped-flow block was estimated at the extreme temperature limits of this study to be within ± 0.2 °C of the coolant temperature.

Data Analysis. Oscilloscopic photographs were obtained under conditions favorable to observation of the growth and decay of the V(II,IV) transient at 557 nm. The experimental value of A_∞ for the bleaching reaction was taken after 10 decay half-lives and prior to any discernible increase due to additional formation of the V(III,III) product via combination of V(III) monomers produced by the outer-sphere component. Plots of $-\ln (A_\infty - A_t)$ vs. time were linear in the decay portion of the absorbance-time curve. The slope was taken as the rate constant for the intramolecular electron transfer event. To estimate the rate constants applicable to the formation region required the use of the first-order rate constant for intramolecular electron transfer as an initial, but adjustable, parameter. When the best fit for several rate constants was sought by the computer procedure, described below, the value for the intramolecular electron transfer as the initial parameter remained within the computer-adjusted rate constants' error limits. However, the absorbance-time curve regenerated with the composite set of rate constants favored the formation
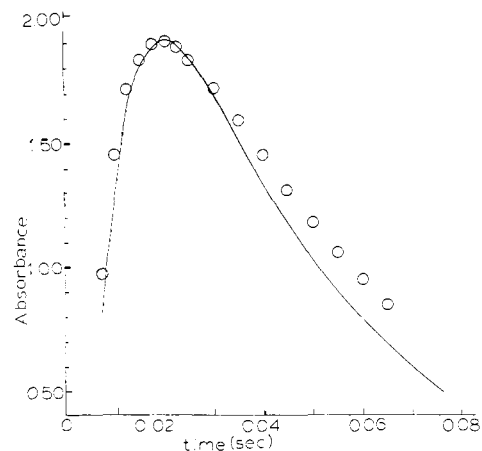

Figure 1. Formation and decay of V(II,IV)(heedta) binuclear ion: $\mu = 0.20$, $T = 25.0$ °C, pH 6.75. [V(heedta)$^-$] = [VO(heedta)$^-$] = 2.25 $\times$ 10^{-3} M; solid line = observed absorbance-time data; circles are computer-calculated absorbances using estimated rate constants as described in the text.

region in accuracy at the expense of the decay portion of the curve. See the circle points in Figure 1. Because the decay portion is of most interest in this work, the rate constants that are used to report intramolecular electron transfer activation parameters are those based on the experimental A_∞ and the first-order decay portion independent of the growth region or the approximations necessary to achieve the computer fitting.

Computer Data Analysis. The data obtained for the transient formation and bleaching were transferred to graph paper from oscilloscopic photographs. The absorbance-time data were manipulated by a first-order rate treatment in the bleaching portion of the curve and second-order reactions for the formation and outer-sphere components. Initial estimates for the rate of formation were made from the time to reach the peak in the absorbance-time curve ($\sim$22 ms). These data were fitted to the sum of differential equations by an iterative fourth-order Runge-Kutta algorithm program supplied by K. J. Johnson of the Department of Chemistry, University of Pittsburgh. Initialization of kinetic parameters for four competitive reactions were made based on the initial estimates for intramolecular electron transfer, growth of the intermediate, outer-sphere bleaching component, and product distribution between (III,III) binuclear ion and III monomer (see Results and Discussion). The kinetic constants were varied over a reasonable range of realistic and extreme values until a composite set of the best estimates to four rate constants and the extinction coefficient of the (II,IV) intermediate were obtained. These estimates included the best fit to the absorbance-time data and nearness to the peak-time maximum in absorbance. A tolerance in this parameter of 3 ms (10% of the rise time to maximum) was allowed. A ratio of the k's for outer-sphere redox path to substitution for inner-sphere reaction was set at 0.67 to agree with the product distribution of initial (III,III) ion and III monomer.

Results and Discussion

V(II,IV)(heedta) System. The bleaching reaction of the V(II,IV) binuclear ion was monitored at 557 nm by the stopped-flow method. Representative data at 25.0 °C, $\mu = 0.20$ (NaClO$_4$), is shown by the solid line in Figure 1. The inner-sphere component exhibits an acid-catalyzed and an uncatalyzed path.[1] The intramolecular electron transfer rate constant obeys the relationship of eq 1 as shown by the data at 25.4 °C (Figure 2) and data at 18.4, 22.0, and 30.8 °C (Table I). Values for a and b are compiled in Table II.

$$k_{obsd} = a + b[H_3O^+] \tag{1}$$

Application of the Eyring rate theory to the acid-independent (a) pathway and the [H$_3$O$^+$]-dependent (b) path are shown in Figures 3 and 4, respectively. The activation parameters are determined to be the following: (a) path $\Delta H^{\ddagger} = 7.97 \pm 0.36$ kcal/mol, $\Delta S^{\ddagger} = -25.4 \pm 1.2$ eu; (b) path $\Delta H^{\ddagger}$
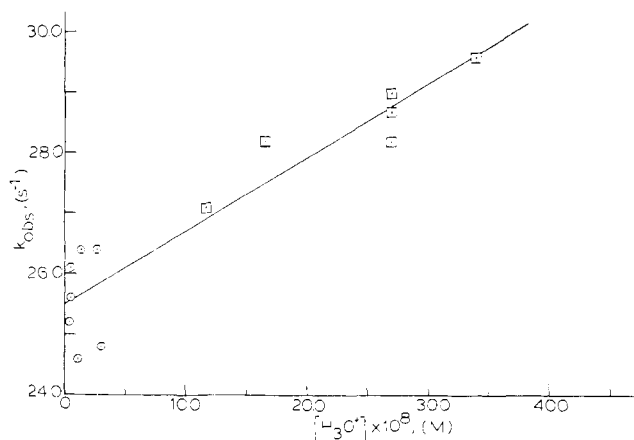
Figure 2. Bleaching rate of V(II,IV)(heedta) binuclear ion as enhanced by H_3O^+; $T = 25.4$ °C, $\odot$, [Tris buffer]$_{tot}$ = 0.126 M; $\square$, [phosphate buffer]$_{tot}$ = 0.050 M. $\mu = 0.20$ = (buffer + NaClO$_4$).

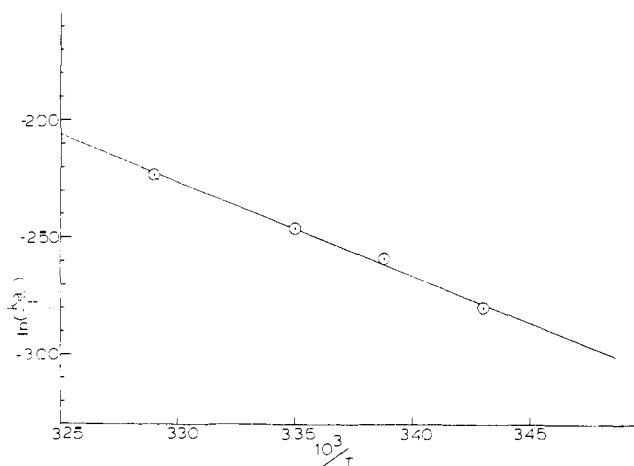**Figure 3.** Acid-independent bleaching reaction of V(Ii,IV)(heedta) binuclear ion; conditions given by Tables I and II.

Table I. Hydrogen Ion Dependence of the Intramolecular Electron Transfer of the V(II,IV)(heedta) Ion[a]

temp, °C	$[H_3O^+] \times 10^8$	k_{obsd}, s^{-1}	buffer
18.4	0.398	18.1	A
	0.436	17.6	A
	8.71	19.2	B
	14.1	18.5	B
	14.8	20.8	C
	15.9	19.8	C
	21.4	21.3	C
	36.3	22.5	B
22.0	0.316	22.2	A
	8.71	24.0	B
	15.5	23.9	C
	17.0	26.2	C
	21.4	26.2	C
25.4	33.9	29.6	C
	26.9	28.2	C
	26.9	28.7	C
	26.9	29.0	C
	16.6	28.2	C
	11.7	27.1	C
	3.09	24.8	A
	2.69	26.4	A
	1.38	26.4	A
	0.501	25.6	A
	0.457	26.1	A
	0.407	25.2	A
30.8	0.371	32.7	A
	2.88	36.7	A
	11.5	34.5	B
	19.5	34.1	C
	36.3	36.4	B

[a] $\mu = 0.20$ NaClO$_4$; buffers, A = Tris, B = lutidine, C = phosphate; [V(heedta)$^-$]$_i$ = [VO(heedta)$^-$]$_i$ = 2.25 × 10^{-3} M.

Table II. Acid-Independent and Dependent Kinetic Parameters at $\mu = 0.20$ (NaClO$_4$)

temp, °C	a, s^{-1}	$b \times 10^{-7}$, M^{-1} s^{-1}
18.4	17.8 ± 0.4	1.34 ± 0.23
22.0	22.1 ± 0.7	1.88 ± 0.51
25.4	25.5 ± 0.2	1.22 ± 0.14
30.8	32.8 ± 0.5	9.57 ± 2.28

= -7.04 ± 4.79 kcal/mol, $\Delta S^{\ddagger} = -49.7 \pm 16.1$ eu.

The decay of the (II,IV) binuclear species is dependent on the concentration of excess VO(heedta)$^-$ or V(heedta)$^-$ in the medium. The effect of excess monomer reagents on the intramolecular electron transfer rate constant is shown in Figure 5. The effect of excess monomer reagents on the decay of the V(II,IV) ion implies that the V(II,IV) ion has outer-sphere reactivities for the II and IV monomer components, separate from the outer-sphere reactivities of the monomers themselves, and the intramolecular decay component. The pseudo-first-order rate constant for intramolecular electron transfer in the presence of excess monomer reagents is given by the expression

$$k_{obsd} = d + e[\text{monomer}]_{excess} \qquad (2)$$

where $d = (a + b[H_3O^+])$ and [monomer]$_{excess}$ = [VO-(heedta)$^-$] or [V(heedta)$^-$] in excess of 1:1 stoichiometry at [monomer]$_{initial}$ > 2.25 × 10^{-3} M. The value of the coefficient (e) is found to be (9.30 ± 1.58) × 10^3 M^{-1} s^{-1} for the IV + (II,IV) reaction and (4.61 ± 0.79) × 10^3 M^{-1} s^{-1} for the II + (II,IV) reaction.

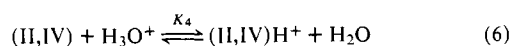The combined scheme for formation, decay, and outer-sphere reactivities is shown in Scheme I where II represents V(heedta)$^-$, IV represents VO(heedta)$^-$, III represents V(heedta)(H$_2$O), (II,IV) the (II,IV) binuclear ion, (III,III) the binuclear product, and (II,IV)H$^+$ the protonated intermediate associated with the acid-catalyzed path. Step 10 has been studied using authentic V(heedta)(H$_2$O).[2] It is slow

relative to all of the other steps and does not affect the observations and data analysis as described in the Experimental Section.

Scheme I

$$2H_3O^+ + II + IV \xrightarrow{k_1} 2III + 2H_2O \qquad (3)$$

$$II + IV \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (II,IV) \qquad (4)$$

$$(II,IV) \xrightarrow{k_3} (III,III) \qquad (5)$$

$$(II,IV) + H_3O^+ \overset{K_4}{\rightleftharpoons} (II,IV)H^+ + H_2O \qquad (6)$$

$$(II,IV)H^+ \xrightarrow{k_5} (III,III) + H_3O^+ \qquad (7)$$

$$IV + (II,IV) \xrightarrow{k_6} 2III + IV \qquad (8)$$

$$II + (II,IV) \xrightarrow{k_7} 2III + II \qquad (9)$$

$$2III \xrightarrow{slow} (III,III) \qquad (10)$$
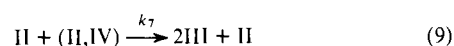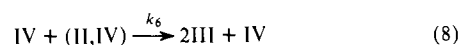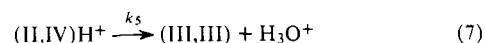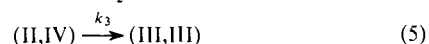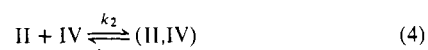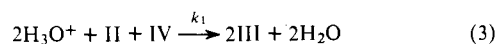
In order to obtain useful information concerning the formation of the (II,IV) binuclear complex it was necessary to use
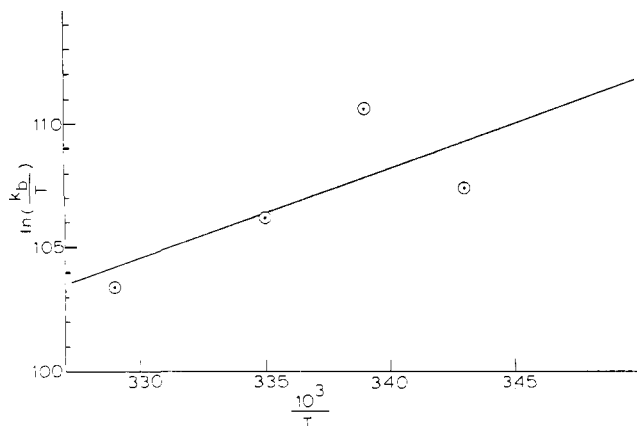
Figure 4. Acid-dependent bleaching reaction of V(II,IV)(heedta) binuclear ion; conditions given by Tables I and II.

Table III. Kinetic Rate Constants for Scheme I at 25.0 °C, μ = 0.20 (NaClO$_4$), pH 6.75

k_n	computer fit value of k
k_1	$(2.7 \pm 0.3) \times 10^4$ M^{-1} s^{-1}
k_2	$(4.0 \pm 0.4) \times 10^4$ M^{-1} s^{-1}
k_{-2}	2.0 ± 2.0 s^{-1}
k_3	28.0 ± 1.0 s^{-1} (computer fit)
k_3	27.5 ± 0.3 (data from Table II)
k_5K_4	$(1.22 \pm 0.14) \times 10^7$ M^{-1} s^{-1}
k_6	$(9.3 \pm 1.6) \times 10^3$ M^{-1} s^{-1}
k_7	$(4.6 \pm 0.8) \times 10^3$ M^{-1} s^{-1}

a computer fitting procedure as described in the Experimental Section. Under the conditions of an equal second-order reaction with [II]$_i$ = [IV]$_i$ = 2.25 × 10^{-3} M, pH $\simeq$ 7, the contribution from paths k_5, k_6, and k_7 are negligible. The system can be approximated by eq 3–5. Reiteration of the values for k_1, k_2, k_{-2}, and k_3 were made. The values obtained for the optimization of the various constants were relatively insensitive to k_{-2}. However, the best data were clearly those for k_{-2} in the range of 2.0 ± 2.0 s^{-1}. This value seems reasonable in that the (III,III) ion dissociates with an acid-independent rate term of 4.0 ± 1.0 s^{-1}. All of the Fe(III) dimer species of similar nature have dissociation parameters in the range of 5 ± 5 s^{-1}.[13] The value of k_3 was initially estimated as 26.0 ± 2.0 s^{-1} (cf. intercept in Figure 5). The best fit value of k_3 was found to be 28.0 ± 1.0 s^{-1} on a reiterative basis at pH 6.75. The agreement is excellent for the calculated value of 27.5 ± 0.3 s^{-1} at this pH from the data in Table II. The substitution rate for the formation of the (II,IV) ion was estimated from the growth portion of the absorbance–time curve; in this manner k_2 was estimated to be ~10^5 M^{-1} s^{-1}. The product distribution sets a value for the ratio of (k_1/k_2) = 0.67. An estimate can be made for k_1 on the basis of the independently studied magnitudes of k_6 and k_7. One would expect k_1 to be slightly larger than k_6 or k_7 based on electrostatic repulsion arguments. The k_1 path has $(-1)/(-1)$ partners while the k_6 or k_7 routes have $(-2)/(-1)$ pairs. The values of k_6 and k_7 were obtained from the slopes of Figure 5. Since $k_6 \sim 9.3 \times 10^3$ M^{-1} s^{-1} this was selected as an initial estimate of the lower limit of k_1. After a range of values were tested the best fit values were found to be k_1 = $(2.7 \pm 0.3) \times 10^4$ M^{-1} s^{-1} and k_2 = $(4.0 \pm 0.4) \times 10^4$ M^{-1} s^{-1}. The comparison to the experimental values of the absorbance to the (II,IV) intermediate using the rate constants of Table III are shown as circle points in Figure 1. From the concentration of the (II,IV) intermediate at the maximum as indicated by the computer data fit and the observed absorbance at the same time, an extinction coefficient for the (II,IV) transient was calculated to be 1360 ± 20 M^{-1} cm^{-1} at 557 nm.
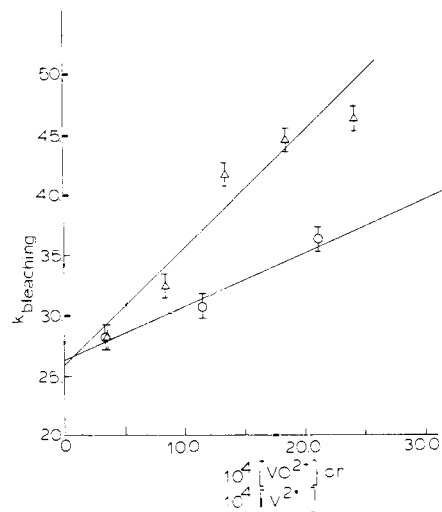

Figure 5. Bleaching rate of V(II,IV)(heedta) binuclear ion as enhanced by V(heedta)$^-$ and VO(heedta)$^-$ monomer complexes; μ = 0.20, T = 25.0 °C, pH 6.75; $\triangle$, [V(heedta)]$_i$ = 2.25 × 10^{-3} M; $\bigcirc$, [VO(heedta)$^-$]$_i$ = 2.25 × 10^{-3} M. Note: X axis represents the concentration of the V(II), $\bigcirc$, or V(IV), $\triangle$, heedta^{3-} complex.

Table IV. Variation of V(II,IV) Binuclear Reactions in Scheme I[a] as Determined by Computer Reiteration

temp, °C	$10^{-4} k_1$, M^{-1} s^{-1}	$10^{-4} k_2$, M^{-1} s^{-1}	k_{-2}, s^{-1}	k_3, s^{-1}
15.2	1.6	2.5	1.0	19.6
20.1	1.9	2.8	1.5	23.6
25.0	2.7	4.0	2.0	28.0
30.4	2.9	4.4	2.5	31.2

[a] μ = 0.20 NaClO$_4$; pH 6.75; [V(heedta)$^-$] = [VO(heedta)$^-$] = 2.25 × 10^{-3} M; kinetic constants ±10%.

The association constant for the (II,IV) ion from its II and IV monomers is found from the kinetic ratio of k_2/k_{-2} to be (2.0 ± 1.9) × 10^4 M^{-1}. The log K_2 is 4.30 ± 0.30 (μ = 0.20, t = 25.0 °C), which compares well with the association constant for the (III,III) dimer (3.74 ± 0.10) under equivalent conditions.[2] This would seem reasonable if the net electrostatic repulsions and solvation effects were similar for the (III,III) and (II,IV) ions.

The kinetic constants at other temperatures were estimated by a similar reiterative procedure. The results are summarized in Table IV. The activation parameters for the formation path (k_2) were determined by the Eyring treatment to be $\Delta H_2^\ddagger$ = 6.1 ± 1.0 kcal/mol, $\Delta S_2^\ddagger$ = −17 ± 3 eu. The value determined for $\Delta S_2^\ddagger$ is reasonable for the costs to aggregate two −1 ions.[15,13b] In this sense the assembly of the precursor complex in the VO(heedta)$^-$/V(heedta)$^-$ cross reaction is well behaved.[29]

The measured activation parameters for the (a) path correspond to the k_3 path of Scheme I. The value obtained for $\Delta S_3^\ddagger$ = −25.4 ± 1.2 eu is much more negative than the $\Delta S_{ET}^\ddagger$ = 0 ± 2 value found by Taube or Lane (see Table V). It would seem likely that the large negative $\Delta S^\ddagger$ term for the intramolecular electron transfer path is due to the coordination reorganization which is required to convert the precursor complex into a geometry more like that of the successor complex. It seems most likely that along the vanadium-vanadium axis the precursor differs from the successor, perhaps N-V-O-V-O for the precursor complex and N-V-O-V-N for the successor complex. The suggestion for the N-V-O-V-O orientation for the precursor complex is drawn from the solution structure of VO(heedta)$^-$ as supported by ESR data.[38] The product orientation may be achieved by ring opening at

Table V. Activation Parameters of Selected Electron Transfer Reactions

reaction pair	$\Delta H^{\ddagger}_{tot}$	$\Delta S^{\ddagger}_{tot}$	$\Delta H^{\ddagger}_{IET}{}^{a}$	$\Delta S^{\ddagger}_{IET}{}^{a}$	ref
$V(heedta)^-/VO(heedta)^-$	14.1 ± 1.4	-42 ± 4	8.0 ± 0.4	-25 ± 1	this work
$Cu^+/Co(en)_2(SCH_2CO_2)^+$			21.4 ± 0.4	1.0 ± 2.5	12
$(NH_3)_5CoLRu(NH_3)_4(H_2O)^{5+}$			20.2 ± 0.2	0 ± 2	15
$V(H_2O)_6{}^{2+}/VO(H_2O)_5{}^{2+}$	12.3	-16.5			20
$Cr(H_2O)_6{}^{2+}/VO(H_2O)_5{}^{2+}$	14.6 ± 0.8	17.6 ± 2.6			18
$Cr(H_2O)_6{}^{2+}/TiO^{2+}$	6.26 ± 1.5	-19.8 ± 0.5			21
$V(H_2O)_6{}^{2+}/TiO^{2+}$	12.7 ± 0.4	-14.6 ± 1.3			22
$Eu^{2+}/VO(H_2O)_5{}^{2+}$	2.83 ± 0.30	-33.4 ± 1.0			23
$Cu^+, H^+/VO(H_2O)_5{}^{2+}$	2.15 ± 0.08	-41.3 ± 0.5			24
$Mn(edta)(H_2O)^-/VO(H_2O)_3(OH)^+$	11.5 ± 1.0	-20 ± 3			15
$Mn(edta)(H_2O)^-/VO(heedta)^-$	11.8 ± 1.0	-7 ± 3			15
$Azurin(I)/Fe(CN)_6{}^{3-}$	-4.1	-52.0	3.6^b	-38.9^b	30
$Azurin(II)/Fe(CN)_6{}^{4-}$	5.9	-27.1	11.4^b	-16.6^b	30
$Azurin(II)/Fe(edta)^{2-}$	2.0	-37			31

^{a} IET = intramolecular electron transfer path as measured by the decay of an intermediate. ^{b} Calculated from $\Delta S^{\ddagger}_{tot}$, $\Delta H^{\ddagger}_{tot}$, and precursor association constants; ref 30.

the V(IV) end of the (II,IV) binuclear ion or by means of a concerted motion, without bond rupture, of one of the N donors into a position being vacated by H_2O. A carboxylate group could move into the initial N position. Support for the ring-opening sequence may be drawn from the presence of the acid-catalyzed pathway. A similar feature occurs in the $[H_3O^+]^2$-catalyzed pathway involving the proton-promoted intramolecular electron transfer within the Ru(II)-V(IV) binuclear ion, $(NH_3)_5RuOV(heedta)^+$.[37] In the $(NH_3)_5$-$RuOV(heedta)^+$ case rearrangements can occur only at the V(IV) site and the second-order H_3O^+ catalysis implicates at least one carboxylate as a site of proton attack. By analogy one would anticipate rearrangement requirements in the V(II,IV)(heedta) binuclear ion to be similar and localized at the V(IV) site. Since it is quite unlikely that both protons can occupy the oxo-bridging ligand in the activated complex for the $(NH_3)_5RuOV(heedta)^+$ intramolecular electron transfer, a structure with one proton on the bridging oxygen and one proton at one of the carboxylate groups is implicated.[37] For the acid-catalyzed pathway (b) $\Delta H^{\ddagger}$ is found to be -7.04 ± 4.79 kcal/mol and $\Delta S^{\ddagger} = -49.7 \pm 16.1$ eu. The parameter b equals K_4k_5. Under the assumption that the activation parameters for the k_5 step are similar to those of k_3, the contribution due to equilibrium (K_4) is found to be $\Delta H^° = -15.1 \pm 5.1$ kcal/mol, $\Delta S^° = -24.3 \pm 17.3$ eu. The large error bars and the assumption necessary to separate K_4 and k_5 obscure the meaning of these parameters. However, it may be concluded that protonation is reasonably exothermic with a negative entropy. These facts again suggest protonation at a basic carboxylate group for assisted ring opening. With labile reactant systems it is frequently impossible to separate the entropy costs for formation of the precursor complex, $\Delta S^{\ddagger}_{form}$, from that of the intramolecular electron transfer component, $\Delta S^{\ddagger}_{ET}$. In those systems where the precursor complex cannot be detected the total activation entropy for product formation, $\Delta S^{\ddagger}_{tot}$, is experimentally measured as the sum of $\Delta S^{\ddagger}_{form}$ and $\Delta S^{\ddagger}_{ET}$:

$$\Delta S^{\ddagger}_{tot} = \Delta S^{\ddagger}_{form} + \Delta S^{\ddagger}_{ET} \tag{11}$$

When structural rearrangements are minimal $\Delta S^{\ddagger}_{ET} \simeq 0$; the measured $\Delta S^{\ddagger}_{tot}$ then equals $\Delta S^{\ddagger}_{form}$ within experimental error.[15] In the case of intramolecular electron transfer between sites in binuclear ions or detectable precursor complexes $\Delta S^{\ddagger}_{ET}$ may be examined directly. The results of Taube's and Lane's experiments for complexes which require minimal bond rearrangements and coordination sphere changes imply that $\Delta S^{\ddagger}_{ET} \sim 0$ when a point charge or spherical model can describe the environments of the oxidant and reductant sites within the binuclear complex. The measurements for the

bleaching process of the V(II,IV)(heedta) ion as a function of temperature reveal a substantially more negative $\Delta S^{\ddagger}_{ET}$ $(-25.4 \pm 1.2$ eu). We propose to partition $\Delta S^{\ddagger}_{ET}$ into two terms: (1) a component related to the inner-sphere and solvation shell adjustment, $\Delta S^{\ddagger}_{reorg}$, which are normally considered with a point charge approximation, and (2) a term to account for structural rearrangement factors, $\Delta S^{\ddagger}_{CR}$, which are not accommodated by a point charge model for reactants proceeding to products:

$$\Delta S^{\ddagger}_{ET} = \Delta S^{\ddagger}_{reorg} + \Delta S^{\ddagger}_{CR} \tag{12}$$

Experimentally $\Delta S^{\ddagger}_{reorg} \sim 0$ for systems which closely follow the point charge approximation $(\Delta S^{\ddagger}_{CR} = 0)$ because $\Delta S^{\ddagger}_{ET} = \Delta S^{\ddagger}_{reorg} \simeq 0$. $\Delta S^{\ddagger}_{CR}$ is likely to be detectable only when its contribution is large because the uncertainty limits of activation entropy data are often large $(\pm 5-10$ eu). The effect produced by $\Delta S^{\ddagger}_{CR}$ would be more negative when the effective coordination number at one of the reactant metal sites changes. The effect would be particularly enhanced by the chelation of a metal center which introduces some differences in rigidity and preferred chelate geometries for the reactant and product oxidation states. The value for $\Delta S^{\ddagger}_{ET} = -25 \pm 1$ eu for the bleaching reaction of the V(II,IV) binuclear ion of this study may be attributed predominantly to the non-point charge component, $\Delta S^{\ddagger}_{CR}$. Redox events which involve V(IV) would be good candidates to reveal this effect because either oxidation or reduction changes the preferred coordination number. V(IV) in VO^{2+} is effectively five coordinate and V(III) complexes prefer six coordination. Nelson and Shepherd have observed a coordination rearrangement effect on $\Delta S^{\ddagger}_{tot}$ for the oxidation of VO^{2+} in aminocarboxylate environments by Mn(III) complexes.[16] In this case V(V) adopts six coordination with oxo ligands equatorial and trans to N donors compared to the axial VO^{2+} oxygen orientation.[17]

Cr(II)(heedta)$^-$/VO(heedta)$^-$ System. When Cr(heedta)$^-$ was used as the reductant for VO(heedta)$^-$ the electron transfer process was competitive with the mixing time of the stopped-flow device. Only a very small growth and decay curve could be detected on the 2 ms/div sweep of the oscilloscope. The products which were detected immediately after mixing and filling of a spectrophotometric cell were monomeric Cr(III)(heedta) and V(heedta) in phosphate buffer.[5,26] It would appear that with Cr^{II}(heedta)$^-$ the reduction of VO-(heedta)$^-$ is rapid and predominantly outer sphere. This result is similar to Espenson's observation that only about 10% of the redox events for the $Cr(H_2O)_6{}^{2+}/VO(H_2O)_5{}^{2+}$ reaction occurs with a Cr(III)-O-V(III) bridged intermediate.[18] The amplitude of the decay curve for the (heedta)CrOV(heedta)$^{2-}$ intermediate was too close to the noise level to allow a curve

fitting or any estimate of the extinction coefficient of the binuclear species. Subsequent to the net reduction of VO-(heedta)⁻, the system showed the slow increase expected for the formation of the V(III,III) ion.

V(heedta)⁻/VO(Cydta)²⁻ System. Ligand rearrangements about the metal center of M(Cydta)²⁻ complexes are generally slower than those about M(edta)²⁻ complexes.[19] An attempt to assess the effect of Cydta⁴⁻ on the intramolecular electron transfer path was made. Cydta⁴⁻ could not be used for the V(II) complex because addition of the Cydta⁴⁻ solution to complex V(H₂O)₆²⁺ resulted in a reduction of V(II) to the metallic state. This is in marked contrast to the stability of other V(II) aminocarboxylate complexes, e.g., heedta³⁻, edta⁴⁻, and nta³⁻. The cross reaction of V(heedta)⁻ and VO(Cydta)²⁻ was studied at pH 6.86. A larger component of the outer-sphere path was observed to be operative if the extinction coefficient of (heedta)VOV(Cydta)³⁻ is essentially the same as the V(II,IV)(heedta) binuclear ion. Only about one-fourth as much of the binuclear intermediate was detected (~14% inner sphere).

The temperature dependence of the bleaching process of the (heedta)VOV(Cydta)³⁻ species is shown in Figure 6 for the following measurements at $\mu = 0.20$ NaClO₄: (k, s⁻¹; T, °K) (50.9; 303.95), (40.2; 298.65), (31.7; 293.75), (26.5; 288.55), (23.3, 284.25). The activation parameters determined from this data are $\Delta H^{\ddagger} = 6.29 \pm 0.44$ kcal/mol, $\Delta S^{\ddagger} = -30.2 \pm 1.5$ eu. The values measured for this system are not substantially different from those of the acid-independent pathway of the V(II,IV)(heedta) ion. In this respect, it would suggest that rearrangements which would involve twisting or flexing of the ethylene bridge between N donors at the V(IV) site are not a large component of $\Delta S^{\ddagger}_{CR}$ for these systems. One would anticipate a much more negative value for $\Delta S^{\ddagger}_{ET}$ due to the rigidity of the cyclohexane component of Cydta⁴⁻ relative to heedta³⁻ with its less sterically hindered ethylene bridge.

Related Electron Transfer Systems. A comparison of the activation parameters which have been determined for a related series of electron transfer reactions is shown in Table V. The value measured for $\Delta S^{\ddagger}_{form} = -17 \pm 3$ eu for the VO-(heedta)⁻/V(heedta)⁻ reaction is close to the costs of assembly of the V²⁺/VO²⁺, Cr²⁺/VO²⁺, Cr²⁺/TiO²⁺, and V²⁺/TiO²⁺ transition states. The measured value for the activation enthalpy of formation of (II,IV) is 6.1 ± 1.0 kcal/mol. This is comparable to the activation enthalpy for diffusion of ions in water.[25,30] The total activation enthalpy for the V²⁺/VO²⁺ reaction as reported by Baker and Newton (12.3 kcal/mol) is quite similar to $\Delta H^{\ddagger}_{tot}$ for the VO(heedta)⁻/V(heedta)⁻ system. However, $\Delta S^{\ddagger}_{tot}$ is much more negative for the assembly and intramolecular electron transfer in the (II, IV(heedta) binuclear ion than for VOV⁴⁺, consistent with additional entropy factors associated with chelation. An inspection of Table V reveals that the Eu²⁺/VO²⁺ and Cu⁺, H⁺/VO²⁺ systems seem to have anomalously small values of $\Delta H^{\ddagger}_{tot}$ and negative values for $\Delta S^{\ddagger}_{tot}$. Espenson has shown that the $\Delta S^{\ddagger}_{tot}$ is consistent with the molar entropy of the transition for 4+ ions ($S^{\ddagger} \simeq -60$ to -80 eu).[23,24] The small values for $\Delta H^{\ddagger}_{tot}$ and $\Delta S^{\ddagger}_{tot}$ could also be reconciled if the products have energy surfaces which are more widely spaced than the corresponding surface for the reactants.[26] This would require a more highly solvated ion for Eu³⁺ or Cu²⁺ than for Eu²⁺. If the activated complex is more like the products, Eu³⁺ or Cu²⁺, solvation could also account for the $\Delta S^{\ddagger}_{tot}$ terms in the reduction of VO²⁺ by Eu²⁺ or Cu⁺. With Cu⁺ the possibility also exists for a negative component to $\Delta S^{\ddagger}_{tot}$ originating in the change of coordination number from 4 to 6. It is not possible to calculate $S^{\ddagger}$ for the V(heedta)⁻/VO(heedta)⁻ reaction by an accepted procedure because the molar entropies of the ions are not tabulated, nor are there reliable means to calculate S° for the complex ions.[27,28]
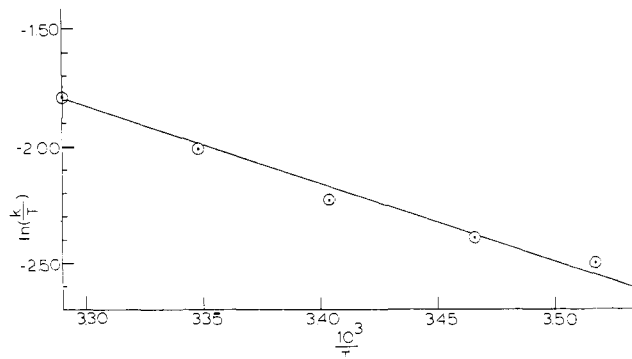

Figure 6. Total bleaching reaction for (heedta)VOV(Cydta)³⁻ ion; $\mu = 0.20$ (NaClO₄ + phosphate buffer), [V(heedta)⁻]ᵢ = 8.29 × 10⁻³ M; [VO(Cydta)²⁻]ᵢ = 8.29 × 10⁻³ M.

In spite of this acknowledged limitation we have utilized eq 13 and 14 with $r = 6.0$ Å for II and IV monomer complexes, $r = 12.0$ Å for (II,IV), to calculate a value of $S^{\ddagger}$ for (II, IV).[27,28]

$$S^{\circ} = \frac{3}{2} R \ln (\text{mol wt}) \frac{-270Z}{(r + 1.00)^2} + 37 \qquad (13)$$

$$S^{\ddagger} = \Delta S^{\ddagger}_{tot} + (\Sigma S^{\circ}_{react} - \Sigma S^{\circ}_{prod}) \qquad (14)$$

By this method we have found $S^{\ddagger} = -12$ eu for the (II,IV) complex. Although the reliability of the calculation may be questioned, a value of -12 eu to aggregate -1 reactant pairs falls into line with the series found for positive reactant pairs of charge product Q:[13c] ($\sim S^{\ddagger}$, Q) (-115, 6), (-90, 5), (-70, 4), (-35, 3), . . . , (-12, 1). Also the -17 ± 3 eu found for $\Delta S_2^{\ddagger}$ is close to the $-10Z_A Z_B$ value[13b] for the approach of monovalent anions[29] and the aggregation costs appear to be normal. The effect of rearrangement in metalloproteins on redox parameters is difficult to assess. Inevitably the measured values are composite effects of geometrical rearrangements and solvation effects which involve a variety of protein residues which extend beyond the immediate coordination spheres of the redox centers.[30,31,35,36] However, the reduction of the copper blue protein, azurin(II), by Fe(CN)₆⁴⁻ or Fe(edta)²⁻ as well as the oxidation of azurin(I) by Fe(CN)₆³⁻ appears to be entropy controlled for the electron transfer act within the outer-sphere precursor complexes of these systems.[30] The costs to achieve electron transfer from rearrangement factors are generally difficult to separate from solvation effects on the protein. For the azurin system the Cu(I) or Cu(II) center is protected from inner-sphere bridging by the protein; the copper center is separated from its redox partner by about 5 Å.[32-34] The small activation enthalpy implies that bonding rearrangement costs at the azurin site are relatively small. Structural factors can contribute a large negative activation entropy which controls the net redox reaction, e.g., -38.9 eu for the azurin(I)-Fe(CN)₆³⁻ electron transfer. Data concerning the effect of structural rearrangements and their effect on electron transfer intramolecular redox events for simple transition metal complexes have been absent prior to this report of the V(heedta)⁻/VO(heedta)⁻ reaction. Much further work is needed in this area to be of use in interpreting the magnitude of its contribution to the metalloprotein cases. These (II,IV) binuclear ion bleaching studies confirm that geometrical factors and coordination numbers preferred by given oxidation states of transition metal ions may be utilized to control rate processes such as electron transfer steps. It is possible to envision conformational equilibria which are adjusted by allosteric interactions with substrate or metabolites serving as a balance point for the redox reactivities of metalloproteins.

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Dynamics of Monocapped Octahedral [MoH(CO)$_2$(bidentate phosphine)$_2$]$^+$

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Abstract: The compounds [MoH(CO)$_2$(P–P)$_2$]$^+$ (P–P = R$_2$PC$_2$H$_4$ER$_2'$: R = R' = Me, E = P-dmpe; R = R' = Ph, E = P-diphos; R = Me, R' = Et, E = P-dmdepe; R = Me, R' = Ph, E = P-dmdPhpe, R = R' = Me, E = As-dmpdmae; R = R' = Ph, E = As-arphos; R = Ph, R' = Me, E = As-dPhpdmae) have a monocapped octahedral structure (*trans*-MoP$_4$(CO)$_2$ octahedron with hydride capping a PP(CO) face). Two NMR-differentiable exchange permutations exist for derivatives with symmetric phosphines, corresponding to pairwise and nonpairwise exchange of chelate ends. ^{1}H NMR line shapes for P–P = dmpe fit neither (similar to those for TaH(CO)$_2$(dmpe)$_2$), suggesting a mixed mechanism. Spectra for P–P = diphos agree well with those calculated for pairwise exchange, $\Delta H^{\ddagger} = 18.7 \pm 0.2$ kcal/mol, $\Delta S^{\ddagger} = 1.1 \pm 0.6$ eu. This corresponds to rotation of H about the CO–Mo–CO axis and constitutes detection of the monocapped octahedron $\rightleftharpoons$ pentagonal bipyramid interconversion. The related process in which H migrates between faces above and below the P$_4$ plane has been detected in [MoH(^{13}CO)$_2$(diphos)$_2$]$^+$. *cis*-Mo(CO)$_2$(P–P)$_2$ (P–P = dmdPhpe, dmpdmae, and dPhpdmae) is nearly isomerically pure, i.e., of the three possible isomers (C_2, C_2, and C_1), one C_2 isomer is predominant. Protonation at low temperature affords the hydride with "labels" mutually trans. Following first-order, reversible kinetics, this isomer converts to one with labels mutually cis; the activation parameters for this nonpairwise process are (P–P = dmdPhpe) $\Delta H^{\ddagger} = 18.0 \pm 0.4$ kcal/mol, $\Delta S^{\ddagger} = -4.2 \pm 1.5$ eu. The similarity of $\Delta H^{\ddagger}$ for the nonpairwise process to that for pairwise exchange suggests a nondissociative mechanism for the former. Moreover, similar stereochemical behavior was observed for all unsymmetric derivatives. Oxidation of C_2-*cis*-Mo(CO)$_2$-(dmdPhpe)$_2$ affords *trans*-[Mo^1(CO)$_2$(dmdPhpe)$_2$]$^+$. The Mo(I) cation is formed stereospecifically as the isomer with –PPh$_2$ groups mutually cis. This observation is consistent with the cis–trans isomerization which occurs on oxidation proceeding by a trigonal twist mechanism.

Seven-coordinate complexes generally exist as one of three commonly found geometries—the monocapped trigonal prism, the monocapped octahedron, and the pentagonal bipyramid.[1] The barriers to interconversion between idealized forms are thought to be small on both theoretical[1c,2] and empirical grounds. Intramolecular exchange in ML$_7$ complexes appears to be too rapid for measurement by NMR techniques; no report of quenched exchange has appeared.[3] However, limiting NMR spectra for systems having inequivalent or chelating ligands have been obtained for a number of compounds.[4] In general, the mechanisms for ligand exchange are poorly understood, with the exceptions of TaX(η^4-naphthalene)(dmpe)$_2$[41] and