a fundamental point of interest in this study is the identification of the origin of the oxo ligand in the Cr(VI) oxo diperoxo products. Direct experimental evidence for a possible oxygen atom transfer from H_2O_2 could have been obtained by reacting Cr(IV) with labeled H_2O_2. Experimental difficulties arising from the secondary reaction of $OCr(O_2)_2L$ type complexes precluded such labeling studies.

The decomposition of oxodiperoxochromium(VI) generated by the reaction of H_2CrO_4 and H_2O_2 has already been investigated.[3] The decomposition of $OCr(O_2)_2(en)$ has been studied, and the kinetic data are presented in Supplementary Table II, which in turn shows that whereas the pseudo-first-order rate constants, k_s, are independent of $[H_2O_2]$, they exhibit a zero- as well as a first-order dependence on $[H^+]$ as seen in Figure 4. These data are consistent with the second stage in the Cr(IV)–H_2O_2 reaction corresponding to an acid-assisted self-decomposition of the blue oxodiperoxochromium(VI) complexes rather than any bimolecular process involving H_2O_2. A wide variety of mechanistic pathways involving the formation of $OCr^V(O_2)_2L^+$, $OCr^{IV}(O_2)L$, $OCr^{III}L^+$, O_2^-, and O_2H intermediates can be visualized. Due to the complicated nature of the system, unambiguous identification of the nature of intermediates formed, if any, during the decomposition of $OCr^{VI}(O_2)L$ type complexes to Cr(III) products appears difficult. Previous studies on analogous Cr(VI) diperoxo systems seem to suggest that Cr(V) intermediates with sufficient lifetime for detection of ESR may not be formed.[3] Our data on the second-stage kinetics are not inconsistent with the either of the two mechanistic pathways discussed by earlier workers in cases of related complexes.[3]

In summary, the results of this study show that the H_2O_2 reaction with $Cr^{IV}(O_2)_2L$ affords blue $Cr(O)(O_2)_2L$ intermediates through possibly an inner-sphere pathway involving $Cr^{IV}(O_2)_2$-$L{\cdot}H_2O_2$ type adducts, which later decompose to Cr(III) products.

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Supplementary Material Available: Listings of kinetic data (4 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Stanford University, Stanford, California 94305

Coordination Chemistry and Redox Properties of Polypyridyl Complexes of Vanadium(II)

John C. Dobson and Henry Taube*

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Polypyridyl vanadium(II) complexes of the type $[V^{II}(trpy)(bpy)(L)]^{n+}$ (trpy = 2,2′:6′,2″-terpyridine; bpy = 2,2′-bipyridine; L = Cl, H_2O, CH_3CN) have been synthesized and characterized by a combination of elemental analyses, FAB mass spectroscopy, cyclic voltammetry, and UV-vis spectroscopy. The substitution chemistry and redox properties of the ions were investigated by cyclic voltammetry. The $E_{1/2}$ values of the V(III/II) couples have been compared to those of the structurally equivalent ions of Ru(II) and Os(II) to assess the extent of π-back-bonding in d^3 V(II) systems. The reactivity of the V(II) ions toward dioxygen and CO_2 is discussed in terms of the development of redox catalysts for the activation of small molecules.

Introduction

The development of the coordination chemistry of vanadium(II) has been hindered by the susceptibility of the V(II) species to oxidation. As the techniques for manipulating air-sensitive complexes have become more commonplace, the number of synthetic routes to complexes other than the aqua ions and tris chelate complexes of vanadium(II) has gradually increased.[1] Di- and trivalent complexes of vanadium are of increasing interest because of their potential applications in the reversible binding of dioxygen,[2] multielectron redox catalysis,[3] and modeling of intermediates formed in the hydrodesulfurization of crude oils.[4]

Our interest in low-valent vanadium chemistry dates back two decades when it was discovered in our laboratories[5] that V(II) complexes, when acting as 1e reductants, differ from other structurally analogous first-row M(II) polypyridyl complexes. For $[V^{II}(bpy)_3]^{2+}$ and $[V^{II}(trpy)_2]^{2+}$ (bpy = 2,2′-bipyridine; trpy = 2,2′:6′,2″-terpyridine) it was shown that upon oxidation to V(III) in aqueous solution the coordination sphere is in every instance disrupted and that the V(III) species formed is unstable with respect to oxidation to V(IV). An estimate of $E°$ for the $[V(bpy)_3]^{3+/2+}$ couple was made on the basis of the Marcus cross-relation theory. Since that time, Saji and Aoyagui have reported[6] polarographic data for $[V^{II}(bpy)_3]^{2+}$ and, more recently, Shah and Maverick have reported the results of cyclic voltammetric studies.[3a,c] However, redox potential data for complexes of V(II) remain extremely limited.[7] Herein we report the results we have obtained in a study of coordination and redox chemistry of polypyridyl complexes of V(II) containing a single labile coordination site, i.e. $[V^{II}(trpy)(bpy)(L)]^{n+}$. Of special interest to us are substitution processes that leave much of the coordination sphere intact and any evidence to be obtained on the extent of π-back-bonding in d^3 V(II) systems. We hope to compare the results with the wealth of information known for d^6 systems. In addition, it was hoped that the reactivity of the complexes with dioxygen would be amenable to detailed kinetic and mechanistic investigation. The reactivity to dioxygen of divalent complexes of the first-row metals (Cr^{II}, Fe^{II}, Co^{II}) has been studied extensively,[8] but considerably less is known about kinetics and mechanism of dioxygen reactivity with V(II).[2d] In an equally important but opposite sense is the potential reactivity of the low-valent V(I) and V(0) species, which, in principle, can be generated by chemical or electrochemical

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reduction of V(II). Of particular interest in this regard is the recent surge in the study of systems capable of the electrocatalytic reduction of small molecules such as CO_2.[9]

Experimental Section

Materials. Vanadium(III) chloride, 2,2′-bipyridine (bpy), and bis(triphenylphosphoranylidene)ammonium chloride (PPN^+Cl^-) were purchased from Aldrich Chemical Co. Ammonium hexafluorophosphate and 2,2′:6′,2″-terpyridine (trpy) were purchased from Sigma Chemical Co. Electrochemical grade tetra-*n*-butylammonium hexafluorophosphate (TBAH) was purchased from Fluka Chemical Co. Acetone was dried over B_2O_3 and purified by vacuum distillation.[10] Diethyl ether was distilled under argon over NaK alloy. Dichloromethane (anhydrous, Aldrich Chemical Co.) was distilled under argon over P_2O_5. Acetonitrile (Burdick and Jackson spectrograde, 0.001% H_2O) was used as supplied. HPLC grade water was purchased from J. T. Baker Chemical Co. All solvents were deoxygenated by purging with argon, and reactions were carried out under argon atmosphere in a Vacuum Atmospheres Corp. glovebox or by using standard Schlenk techniques.

Preparations. **V^{III}(trpy)Cl_3.** The procedure described here is a modification of one that has been reported.[11] To 1.00 g (6.36 mmol) of VCl_3 dissolved in 50 mL of CH_3CN was added 1.78 g (7.62 mmol) of 2,2′:6′,2″-terpyridine. The solution was stirred for 4 h, after which time the color of the suspension/solution had changed from purple to brown. The brown solid was collected by filtration, washed with 3 × 5 mL of anhydrous diethyl ether, and dried in vacuo. [In the presence of a large excess of trpy, over extended reaction times a green filtrate was observed that gave λ_{max} = 674 nm, consistent with formation of $V(trpy)_2^{2+}$.[5]] Yield: 2.21 g, 91%. Anal. Calcd for $VC_{15}N_3H_{11}Cl_3$: C, 46.13; H, 2.84; N, 10.76; Cl, 27.23. Found: C, 46.33; H, 3.00; N, 10.79; Cl, 26.98.

$V^{III}(O_3SCF_3)_3$. This complex was prepared as mentioned by Verma et al.[12] To 100 mg (0.636 mmol) of VCl_3 under argon in a Schlenk tube was added 3 mL of CF_3SO_3H. The solution was heated to reflux for 3 h, after which time the pale green solid that had formed was isolated by filtration and dried in vacuo. Yield: 300 mg, 95%. Anal. Calcd for $VC_3F_9O_9S_3$: C, 7.23; S, 19.31; V, 10.23. Found: C, 7.38; S, 19.13; V, 10.00.

$[V^{II}(trpy)_2](O_3SCF_3)_2$. To a stirred suspension of 50 mg (0.13 mmol) of V(trpy)Cl_3 and 45 mg (0.19 mmol) of 2,2′:6′,2″-terpyridine in 12 mL of acetone was added 99 mg (0.38 mmol) of $Ag(O_3SCF_3)$. The initial brown suspension had turned purple after 10 min. With time the solution color changed to green. After 2 h the reaction mixture was filtered through a fine glass frit to remove the AgCl precipitate. The green filtrate was pipetted into 150 mL of stirred diethyl ether to precipitate a green solid, which was collected by filtration. The crude product was recrystallized by vapor diffusion of diethyl ether into acetone or CH_2Cl_2. Disproportionation was evident as the green crystals of the desired complex were accompanied by a small amount of a colorless coprecipitate attributable to the corresponding V(IV) disproportionation product. The complex could also be prepared by the addition of excess, 2,2′:6′,2″-terpyridine to $V^{III}(O_3SCF_3)_3$ in CH_2Cl_2.

$[V^{II}(trpy)(bpy)(Cl)](ZnCl_4)_{0.5}$. To 100 mg (0.26 mmol) of V(trpy)Cl_3 in 25 mL of acetone over zinc amalgam was added 40 mg (0.26 mmol) of 2,2′-bipyridine. The suspension was stirred for 15 h. After this time the dark green solid that had formed was collected by filtration, washed with 3 × 3 mL of diethyl ether and dried in vacuo. Yield: 116 mg. Anal. Calcd for $VC_{25}H_{19}N_5Cl_3Zn_{0.5}$: C, 51.82; H, 3.31; N, 12.09; Cl 18.36; Zn, 5.64. Found: C 50.22; H, 3.43; N, 11.24; Cl, 17.97; Zn, 5.48.

$[V^{II}(trpy)(bpy)(OH_2)](O_3SCF_3)_2\cdot H_2O$. To 10 mL of 0.1 M CF_3SO_3H(aq) was added 100 mg of $[V^{II}(trpy)(bpy)(Cl)](ZnCl_4)_{0.5}$. The solution was allowed to stand for 1 h, after which time the precipitate that formed was isolated by filtration and dried in vacuo. The PF_6^- salt of the same complex can be obtained by the addition of a saturated solution of NH_4PF_6(aq) after only 15 min. Anal. Calcd for $VC_{27}H_{23}N_5S_2F_6O_8$: C, 41.87; H, 2.99; N, 9.04; S, 8.28. Found: C, 41.69; H, 2.72; N, 8.85; S, 7.88; Cl, 0.09.

$[V^{II}(trpy)(bpy)(CH_3CN)](PF_6)_2$. To 5 mL of CH_3CN was added 50 mg (0.067 mmol) of $[V^{II}(trpy)(bpy)(OH_2)](PF_6)_2$. The solution was allowed to stir for 10 min, after which time the solution was pipetted into 125 mL of stirred diethyl ether to precipitate the complex. The blue solid was collected by filtration and dried in vacuo.

$[V^{III}(bpy)_2Cl_2][V^{III}(bpy)Cl_4]$. The previously described preparation of this complex[11,13] was modified as follows: To 158 mg (1.00 mmol) of VCl_3 and 317 mg (2.03 mmol) of 2,2′-bipyridine was added 10 mL of acetone. The reaction mixture was allowed to stir for 4 h, after which time a light brown solid was collected by filtration, washed with 3 × 1 mL of acetone and dried in vacuo. Yield: 345 mg, 88%. Anal. Calcd for $V_2C_{30}H_{24}N_6Cl_6$: C, 46.01; H, 3.09; N, 10.73; Cl, 27.1; V, 13.01. Found: C, 46.05; H, 3.05; N, 10.66; Cl, 26.83; V, 12.72.

$[V^{IV}(trpy)(bpy)(O)](PF_6)_2$. To 12 mL of H_2O in a Schlenk tube was added 50 mg (0.067 mmol) of $[V^{II}(trpy)(bpy)(OH_2)](PF_6)_2$. O_2 was bubbled over the stirred solution. After 30 min the solution color had changed from deep green to violet. After 6 h the solution color had turned to light green with formation of a small amount of a light green precipitate. Saturated NH_4PF_6(aq) was added dropwise to complete precipitation, and the solid was isolated by filtration, washed with 3 × 1 mL of diethyl ether, and dried in vacuo. Yield: 47 mg. Anal. Calcd for $VC_{25}H_{19}F_{12}N_5OP_2$: C, 40.23; H, 2.57; N, 9.38; P, 8.3. Found: C, 39.67; H, 2.65; N, 9.15; P, 8.01.

Measurements. UV–vis spectra were recorded in quartz cells at room temperature on either a Beckman Model 5270 spectrophotometer or a Hewlett-Packard Model 8452A diode array spectrophotometer. Infrared spectra were recorded on an IBM 98 FTIR spectrometer. X-band EPR spectra were recorded at room temperature in quartz capillary tubes on a Bruker Model ER 220D-SRC spectrometer. Cyclic voltammetric experiments were performed under argon by using a PAR Model 173 potentiostat with a PAR Model 175 universal programmer as a sweep generator. Measurements were made in a cell outfitted with a Pt^0 working electrode (~0.07 cm^2), a Pt^0 auxiliary electrode, and a reference electrode consisting of a Au^0 button electrode immersed in a 1,2-dimethoxyethane (DME) solution containing 0.5 M NaO_3SCF_3 separated from the main cell by a Vycor frit. No correction was made for junction potential effects. The reference was calibrated with the ferrocene/ferrocenium couple ($E°$ = 0.55 V vs NHE) kept in situ. Microanalyses were performed by Chemical Analytical Services, Berkeley, CA. Fast atom bombardment (FAB) mass spectrometry of air-sensitive samples was performed by the University of California Mass Spectrometry Laboratory, CA, under the direction of Dr. Julie Leary. The details of the instrumentation can be found elsewhere.[14]

Results and Discussion

Syntheses. Two preparative routes to polypyridyl complexes of vanadium(II) were uncovered with VCl_3 serving as the starting material in each case. The first route centered on the instability of V(III) with respect to disproportionation. In CH_2Cl_2 suspensions containing V^{III}(trpy)Cl_3,[15] 2,2′:6′,2″-terpyridine (trpy), and 3 equiv of $Ag(O_3SCF_3)$, V(III) is unstable with respect to disproportionation and formation of $[V^{II}(trpy)_2]^{2+}$ and a V^{IV}(O) species. The source of oxygen in the V(IV) disproportionation product is unknown but is presumed to be trace H_2O. The former product was characterized by fast atom bombardment (FAB) mass spectrometry, UV–vis spectroscopy,[5] and cyclic voltammetry, while the latter species was identified as V(IV) by its characteristic eight-line EPR spectrum with $\langle g \rangle$ = 1.97 and its characteristic IR band ν(V=O) at 957 cm^{-1}. Solutions of $V^{III}(O_3SCF_3)_3$ and excess trpy in CH_2Cl_2 also undergo a disproportionation reaction to give identical products, despite measures to keep water content to a minimum (see Experimental Section).

The second route involves the chemical reduction (Zn/Hg) of acetone suspensions containing V^{III}(trpy)Cl_3 and 1 equiv of 2,2′-bipyridine (bpy) to give $[V^{II}(trpy)(bpy)(Cl)]^+$. Substitution of Cl^- leads to cations of the type $[V(trpy)(bpy)(L)]^{n+}$ (e.g., L = H_2O, CH_3CN). Salts of this type were characterized by a combination of elemental analyses, FAB mass spectra, UV–vis

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(9) See, for instance: *Catalytic Activation of Carbon Dioxide*; Ayers, W. M., Ed.; ACS Symposium Series 363; American Chemical Society: Washington, DC, 1988; and references therein.

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(15) V(trpy)Cl_3 is sparingly soluble in both polar and nonpolar organic solvents. It does, however, readily dissolve in neat CF_3SO_3H with the evolution of HCl(g). A green solid can be isolated from solution by filtration following the addition of diethyl ether. Elemental analyses (Found: C, 31.26; H, 1.81; N, 6.06; S, 13.46; Cl, 0.14; V, 6.10) are consistent with the retention of the terpyridyl ligand and show that essentially no chloride remains. Given the affinity of Cl^- for V(III), it is a noteworthy observation that the terpyridyl ligand is preferentially retained. Refluxing this solid in CF_3SO_3H leads to formation of V$(O_3SCF_3)_3$ with loss of the terpyridyl ligand.

Table I. Major Ions Observed in the FAB Spectra of Polypyridyl V(II) Complexes

complex	ion, *m/z* (rel intens)
$[V^{II}(trpy)(bpy)(Cl)]^+(ZnCl_4)_{0.5}^-$	$[V^{II}(trpy)(bpy)(Cl)]^+$, 475 (50); $[V^{II}(trpy)(Cl)]^+$, 319 (100); $[V^{II}(bpy)(Cl)]^+$, 242;[a] $[V^{II}(trpy)(bpy)]^+$, 440 (9)
$[V^{II}(trpy)(bpy)(OH_2)]^{2+}(PF_6)_2^{2-}$	$[V^{II}(trpy)(bpy)(PF_6)]^+$, 585 (100); $[V^{I}(trpy)(bpy)(OH_2)(S)]^+$, 578 (30);[b] $[V^{I}(trpy)(bpy)(S)]^+$, 560 (42);[b] $[V^{I}(trpy)(bpy)(PF_6)(S)]^+$, 705 (9);[b] $[V^{II}(trpy)(bpy)]^+$, 440
$[V^{II}(trpy)_2]^{2+}(O_3SCF_3)_2^{2-}$	$[V^{II}(trpy)_2(O_3SCF_3)]^+$, 666 (30); $[V^{I}(trpy)_2]^+$, 517 (100); $[V^{II}(trpy)(O_3SCF_3)]^+$, 433 (27)

[a] The relative intensity is obscured by the sulfolane matrix, which has peaks at *m/z* 241, 361, 481, and 601. [b] S is the solvent sulfolane (MW = 120).

spectra, and cyclic voltammetry.

FAB Spectra. Table I summarizes the results obtained for the FAB positive ion analyses on three air-sensitive polypyridyl vanadium(II) complexes. The *m/z* values given correspond to the species containing the principal isotope ^{51}V. The FAB positive ion spectrum of $[V^{II}(trpy)(bpy)(Cl)]^+$ features a molecular cation peak at *m/z* 475 and fragmentation peaks at *m/z* 319 and 242 corresponding to the $(M - bpy)^+$ and $(M - trpy)^+$ cations, respectively. A much less intense peak appears for the $(M - Cl)^+$ cation at *m/z* 440. The FAB spectra of the dications $[V^{II}(trpy)(bpy)(OH_2)](PF_6)_2$ and $[V^{II}(trpy)(bpy)(CH_3CN)](PF_6)_2$ do not contain a molecular ion peak. Instead, both complexes show peaks at *m/z* 585 corresponding to the $[V^{II}(trpy)(bpy)(PF_6)]^+$ monocation fragment. Both complexes yield reduced vanadium(I) fragments containing the solvent. For the aqua complex these peaks appear at *m/z* 705, 578, and 560. The mechanism of the reduction process in the FAB experiment is unknown. However, reduction of 2+ ions to 1+ ions in both field desorption and FAB spectra of metal complexes has precedent.[16,17] In particular, the major peak in the positive ion FAB spectrum of $[Os^{II}(trpy)_2](PF_6)_2$ is $[Os(trpy)_2]^+$ at *m/z* 658.[17] Consistent with this result is the observed reduction of vanadium(II) to vanadium(I) in the FAB spectrum of $[V^{II}(trpy)_2](O_3SCF_3)_2$. For this complex, the most intense ion, $[V^{I}(trpy)_2]^+$, is observed at *m/z* 517. Less intense peaks are also observed at *m/z* 666 and 433 for $[V^{II}(trpy)_2(O_3SCF_3)]^+$ and $[V^{II}(trpy)(O_3SCF_3)]^+$, respectively.

Electrochemistry. The redox properties of the vanadium(II) complexes were investigated by cyclic voltammetry (CV), and the results are summarized in Table II. The results of the electrochemical studies and FAB spectra are consistent with six-coordinate pseudooctahedral geometry about the V(II) center. The cyclic voltammogram of $[V^{II}(trpy)(bpy)(Cl)]^+$ in CH_3CN/0.1 M TBAH (Figure 1a) shows reversible waves at $E_{1/2} = -0.97$ and -1.20 V vs NHE attributable to the $[V(trpy)(bpy)(Cl)]^{+/0}$ and $[V(trpy)(bpy)(Cl)]^{0/-1}$ couples. A third quasi-reversible wave at $E_{1/2} = 0.17$ V is assigned to the $[V(trpy)(bpy)(Cl)]^{2+/+}$ couple. The oxidation to $[V^{III}(trpy)(bpy)(Cl)]^{2+}$ is not chemically reversible; a small cathodic wave at $E_{p,a} = -0.47$ V appears at the expense of the cathodic wave of the $[V(trpy)(bpy)(Cl)]^{2+/+}$ couple. The pattern of redox changes observed is consistent with previous observations on $[V(bpy)_3]^{2+}$ by Saji and Aoyagui[6] and by Shah and Maverick.[3a,c] The lowering of the potential of the V(III/II) couple for $[V(trpy)(bpy)(Cl)]^{2+/+}$ (0.17 V) relative to that for $[V(trpy)_3]^{3+/2+}$ (0.50 V) is consistent with replacement of a pyridyl ligand by an anionic Cl^- ligand in the inner coordination sphere. The replacement of a second pyridyl ligand by Cl^- further decreases the potential, the V(III/II) couple for $[V(bpy)_2(Cl)_2]^{+/0}$ appearing at $E_{1/2} = -0.28$ V.

The nature of the irreversibility of the $[V(trpy)(bpy)(Cl)]^{2+/+}$ couple was investitaged in further detail. The magnitude of the irreversible wave at $E_{p,c} = -0.47$ V relative to the V(III/II) couple

Table II. Redox Potential Data for Polypyridyl Complexes of Ru, Os, and V

	redox couple, V vs NHE[a]				
	$E°_{ox}$	$E°_{red}$			
species	M(III/II)	2+/+	+/0	0/−1	ref
$Ru(trpy)_2^{2+}$	1.51	−1.03	−1.27	−1.71	18
$Os(trpy)_2^{2+}$	1.21	−1.01			19
$V(trpy)_2^{2+}$	0.46	−0.70	−0.85	−1.38	this work
$V(trpy)(bpy)(CH_3CN)^{2+}$	0.52	−0.85	−1.09		this work
$Ru(trpy)(bpy)(Cl)^+$	1.05		−1.11		20
$Os(trpy)(bpy)(Cl)^+$	0.68				21
$V(trpy)(bpy)(Cl)^+$	0.17		−0.97	−1.20	this work
$Ru(bpy)_2Cl_2$	0.54				22
$Os(bpy)_2Cl_2$	0.20				23
$V(bpy)_2Cl_2$[b]	−0.28				this work
trpy				−1.92	18
bpy				−1.88	24

[a] All values reported in CH_3CN solution with either 0.1 M tetra-*n*-butylammonium hexafluorophosphate or tetraethylammonium perchlorate as electrolyte unless otherwise noted. [b] The V(III/II) couple for the cation of $[V(bpy)_2Cl_2][V(bpy)(Cl)_4]$ was measured in CH_2Cl_2/TBAH. Assignment of the V(II/I) and V(I/0) redox couples is precluded by the irreversible redox chemistry associated with the V-containing counterion.

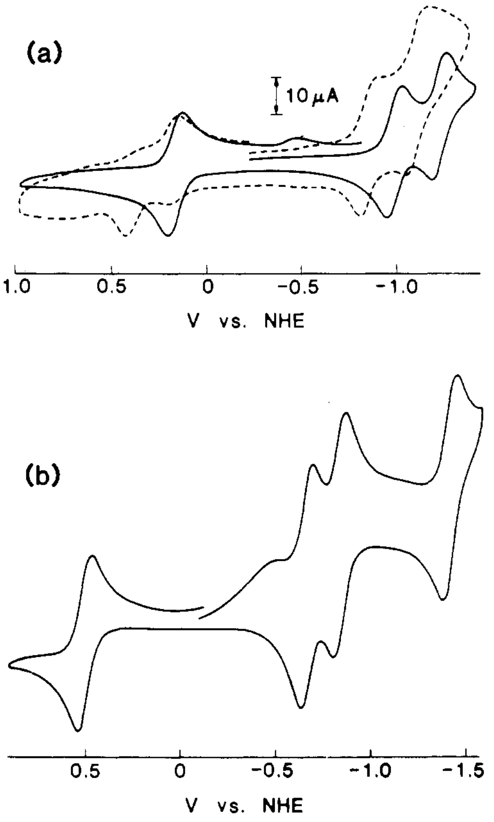

Figure 1. Cyclic voltammograms: (a) $[V^{II}(trpy)(bpy)(Cl)]^+$ in CH_3CN/0.1 M TBAH (scan rate 200 mV/s) (—) and the same solution 30 min after the addition of NaO_3SCF_3 (---); (b) $[V^{II}(trpy)_2]^{2+}$ in acetone/0.1 M TBAH (scan rate 200 mV/s).

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Table III. UV-Vis Spectral Data for Complexes of the Type $[V^{II}(trpy)(bpy)L]^{n+}$

complex	λ_{max}, nm (ϵ, $M^{-1}\ cm^{-1}$)	solvent
$[V^{II}(trpy)(bpy)(Cl)]^+(ZnCl_4)_{0.5}{}^-$	808 (4000), 425 (2600), 400 (2725), 376 (2650)	CH_3CN
$[V^{II}(trpy)(bpy)(CH_3CN)]^{2+}(PF_6)_2{}^{2-}$	678 (3800), 420 s (2350), 400 s (3150), 380 (3250)	CH_3CN
$[V^{II}(trpy)(bpy)(OH_2)]^{2+}(PF_6)_2{}^{2-}$	750 (4000), 425 (3400), 400 (3400), 378 (3750)	H_2O

is independent of scan rate and is also independent of concentration over the range 5×10^{-3} to 1×10^{-4} M. The ratio of peak currents $i_{p,a}/i_{p,c}$ for the V(III/II) couple is enhanced in the presence of added bases such as pyridine. This is accompanied by an increased amplitude in the irreversible wave at −0.47 V. These observations are consistent with those previously described by Shah and Maverick, who concluded that for $[V(phen)_3]^{2+}$ the formation of an oxo-bridged binuclear species is promoted in the presence of base.[3a] By analogy, for the $[V(trpy)(bpy)(Cl)]^+$ system in the presence of base, this process likely involves initial aquation (from trace H_2O in CH_3CN) of V(III)

$$[V^{II}(trpy)(bpy)(Cl)]^+ \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [V^{III}(trpy)(bpy)(Cl)]^{2+} \xrightarrow[+H_2O]{-Cl} [V^{III}(trpy)(bpy)(OH_2)]^{3+}$$

followed by base-assisted binuclear formation

$$2[V^{III}(trpy)(bpy)(OH_2)]^{3+} + 2B \rightarrow [(trpy)(bpy)V^{III}(O)V^{III}(bpy)(trpy)]^{4+} + 2BH^+$$

The amplitude of the reduction wave at −0.47 V was found to be enhanced by the addition of PPN^+Cl alone; it is postulated that, upon oxidation to V(III), Cl^- displaces one pyridyl ring of the terpyridyl ligand and that this pyridyl ring can act as a base to assist binuclear formation.

In Figure 1b is shown the cyclic voltammogram of $[V^{II}(trpy)_2](O_3SCF_3)_2$. Reversible waves are observed for the $[V(trpy)_2]^{3+/2+}$, $[V(trpy)_2]^{2+/+}$, and $[V(trpy)_2]^{+/0}$ couples. An additional reversible couple can be observed at $E_{1/2} = -1.42$ V and is assigned to the $[V(trpy)_2]^{0/-1}$ couple. The appearance of four 1e redox couples for the $[V(trpy)_2]^{2+}$ complex is expected on the basis of the results of previous electrochemical studies on $[Fe(trpy)_2]^{2+}$, $[Ru(trpy)_2]^{2+}$, and $[Co(trpy)_2]^{2+}$.[18,25]

A question arises whether the excess electrons of the reduced species occupy a metal dπ orbital or a ligand π^* orbital. Extensive work by Saji and Aoyagui[6b] has shown that the standard heterogeneous rate constant for a redox system of $M(bpy)_3$, where the excess electron occupies the ligand π^* orbital, falls within 0.1–0.3 cm s^{-1}, while when the excess electron occupies a metal dπ orbital, it falls within 0.8–1.3 cm s^{-1}. This classification holds irrespective of $E_{1/2}$ potentials, oxidation states, ionic charges, and electrode type. The difference in rate constants for the two groups is believed to be related to the differences in the inner-sphere reorganization energy. On the basis of the published data for $[V(bpy)_3]^{2+}$, the excess electrons of the polypyridyl complexes of vanadium(II) reported here are taken to occupy metal dπ orbitals, a conclusion that is supported by comparisons still to be made.

Electronic Spectra. In the energy range covered in our studies, two charge-transfer transitions have been identified[20] for $[V^{II}(bpy)_3]^{2+}$, one in the region of 650 nm, the other at a shorter wavelength and to a different π^* level, each showing vibrational fine structure. The same general features are observed in the spectrum of $[V^{II}(trpy)(bpy)(Cl)]^+$ shown in Figure 2. The intervals, 1.6×10^3 cm^{-1}, corresponding to the fine structure shown by the envelope at higher energy can easily be read and are close to the stretching vibrations ν(C=C) and ν(C=N) within the 2,2′-bipyridyl and 2,2′:6′,2″-terpyridyl ring systems.[21] The (0,0) transition in the lower energy band for $[V^{II}(bpy)_3]^{2+}$ is reported at 651 nm.[20a] There is apparently a large shift in the energy of this transition in replacing one pyridyl ligand by a chloride ion. In Table III the band maxima that we have observed in our spectrophotometric studies are summarized. Of the three species we have characterized, the large shift to lower energies is observed only for the chloro complex.

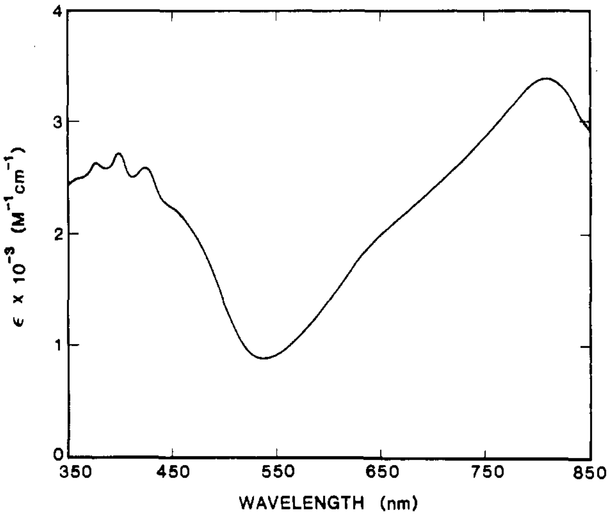

Figure 2. Visible spectrum of a solution containing 1.1×10^{-4} M $[V^{II}(trpy)(bpy)(Cl)]^+$ in CH_3CN.

Substitution. Cyclic voltammetric monitoring of an acetonitrile solution containing 10^{-3} M $[V^{II}(trpy)(bpy)(Cl)]^+$ gave no evidence for ligand loss over a period of 1 h. However, an aqueous solution of the same complex is rapidly ($t_{1/2} < 5$ min) converted to $[V^{II}(trpy)(bpy)(OH_2)]^{2+}$. The aqua complex in water is easily precipitated by the addition of saturated NH_4PF_6(aq). The aqua ligand, in turn, is readily ($t_{1/2} < 2$ min) replaced in acetonitrile to yield $[V^{II}(trpy)(bpy)(CH_3CN)]^{2+}$. All three complexes are stable in traditionally noncoordinating solvents such as CH_2Cl_2. Several substitution processes were monitored by cyclic voltammetry: (1) The addition of 1 equiv of PPN^+Cl^- to a solution containing 10^{-3} M$[V^{II}(trpy)(bpy)(CH_3CN)]^{2+}$ in CH_3CN leads to quantitative formation of $[V^{II}(trpy)(bpy)(Cl)]^+$. The affinity of Cl^- over the π-acceptor ligand CH_3CN for V(II) suggests that π-back-bonding interactions with the d^3 metal center for the sixth ligand L in the $[V^{II}(trpy)(bpy)(L)]^{n+}$ systems are minimal. This is expected given the greater π-accepting ability of the trpy and bpy ligands, which occupy the remaining five coordination sites. (2) The $[V(trpy)(bpy)(CH_3CN)]^{3+/2+}$ couple is irreversible in acetone, the reduction wave being absent. This suggests that acetone is better able to stabilize V(III) and thus replaces CH_3CN. (3) Although $[V^{II}(trpy)(bpy)(Cl)]^+$ is substitutionally inert for extended periods in CH_3CN/TBAH, NaO_3SCF_3 causes NaCl to precipitate with concomitant formation of $[V^{II}(trpy)(bpy)(CH_3CN)]^{2+}$. The resultant V(III/II) couple under these conditions is irreversible as seen in the dashed-line cyclic voltammogram in Figure 1a. Upon oxidation to V(III), the CH_3CN ligand is replaced by $CF_3SO_3{}^-$ to form $[V^{III}(trpy)(bpy)(O_3SCF_3)]^{2+}$. When the metal is rereduced to V(II), the $CF_3SO_3{}^-$ ligand is replaced by CH_3CN to give $[V^{II}(trpy)(bpy)(CH_3CN)]^{2+}$. (4) The cyclic voltammogram of $[V^{II}(trpy)(bpy)(OH_2)]^{2+}$ in CH_2Cl_2/0.1 M TBAH shows an irreversible oxidation wave at $E_{p,a} = 0.48$ V vs NHE. The electrochemical reduction of $[V^{II}(trpy)(bpy)(OH_2)]^{2+}$ reveals broad, quasi-reversible waves at −1.05 and −1.38 V and leads to the formation of a reversible couple at $E_{1/2} = 0.17$ V. The redox potential of the newly observed couple is identical with that of the $[V^{II}(trpy)(bpy)(Cl)]^{2+/+}$ redox couple and suggests that the

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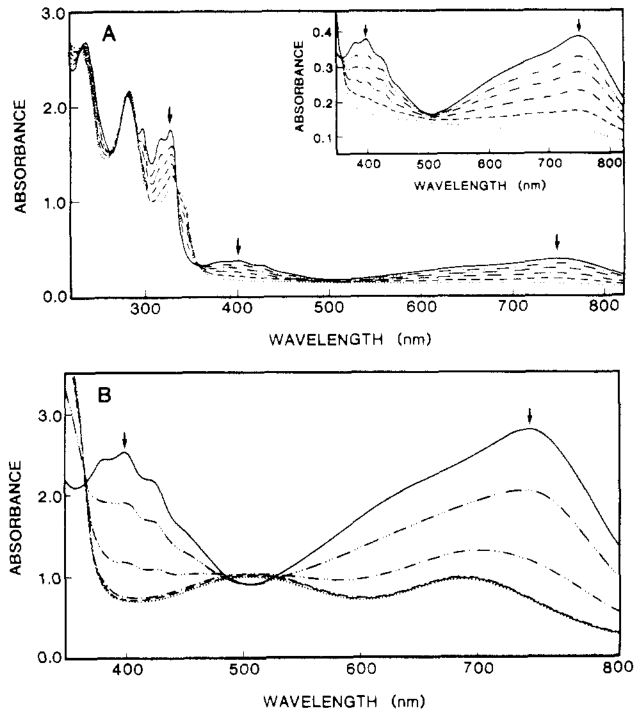

Figure 3. UV-vis spectra recorded during the air oxidation of $[V^{II}(trpy)(bpy)(OH_2)]^{2+}$ in H_2O: (A) solution containing 9.6×10^{-5} M $[V^{II}(trpy)(bpy)(OH_2)]^{2+}$ (spectra recorded every 2 min from $t = 0$ to $t = 10$ min); (B) solution containing 1.6×10^{-3} M $[V^{II}(trpy)(bpy)(OH_2)]^{2+}$ (spectra recorded every 3 min from $t = 0$ to $t = 15$ min).

reduction processs leads to a net abstraction of Cl from the solvent.

Reactivity with O_2. All the (polypyridyl)vanadium(II) complexes are easily oxidized in the presence of O_2. With $[V(trpy)(bpy)(OH_2)^{2+}$ as reductant, the reaction was monitored spectrophotometrically. In dilute solutions ($<10^{-4}$ M) of $[V^{II}(trpy)(bpy)(OH_2)]^{2+}$ the oxidation proceeds with no sign of an intermediate (Figure 3A). In more concentrated solutions ($>10^{-3}$ M) the reaction proceeds through a purple intermediate (Figure 3B). The two broad absorption bands centered at 505 and 685 nm in the spectrum of the intermediate suggest binuclear formation of the μ-oxo ion $[(trpy)(bpy)V^{III}(O)V^{III}(bpy)(trpy)]^{4+}$. This assignment is made by comparison of the electronic spectrum of the μ-oxo ion $[\{V^{III}(bpy)_2Cl\}_2O]^{2+}$, which has two broad absorption bands centered at 525 and 625 nm.[28,29] The disappearance of the purple intermediate in Figure 3b is relatively slow, and the intermediate can still be detected after 1 h. We conclude that the final product is the oxo complex $[V^{IV}(trpy)(bpy)(O)]^{2+}$ on the basis of elemental analyses, infrared spectroscopy ($\nu(V^{IV}{=}O)$ observed at 980 cm^{-1}), and the characteristic eight-line pattern in the EPR spectrum (Figure 4) with $\langle g \rangle = 1.97$. The data show that at high concentrations the oxidation of $[V^{II}(trpy)(bpy)(OH_2)]^{2+}$ to $[V^{IV}(trpy)(bpy)(O)]^{2+}$ is inhibited by the formation of the μ-oxo ion $[(trpy)(bpy)V^{III}(O)V^{III}(trpy)(bpy)]^{4+}$. We have found that the reaction of $[V^{IV}(trpy)(bpy)(O)]^{2+}$ with $[V^{II}(trpy)(bpy)(OH_2)]^{2+}$ is rapid under our conditions, yielding a species whose visible spectrum is indistinguishable from that of the purported μ-oxo ion. The chemistry we have observed is not out of line with the conclusions reached by Bielski et al.[2d] on the mechanism of the reaction of $V^{2+}(aq)$ with O_2, in which it is suggested that $VO^{2+}(aq)$ is the initial product of oxidation, the μ-oxo V(III) species being formed in the subsequent reaction of $VO^{2+}(aq)$ with $V^{2+}(aq)$.[30]

The $[V^{IV}(trpy)(bpy)(O)]^{2+}$ ion in CH_3CN showed no oxidative reactivity with organic substrates such as 2-propanol and styrene and no apparent reactivity with PPh_3 even after the reaction mixture was heated to 40 °C for several hours. Acetonitrile solutions containing the V(IV) species are air stable for days. Solutions saturated with O_2 showed a color change from light green to dark yellow over a period of 4 days. A ^1H NMR spectrum in CD_3CN of the evaporated residue showed resonances between 7 and 10 ppm, consistent with the formation of a diamagnetic V(V) species with a coordinated (trpy)(bpy) environment.

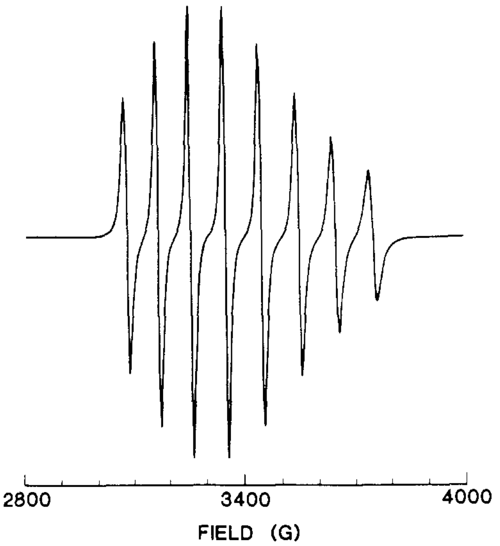

Figure 4. EPR spectrum (in CH_3CN, room temperature) of $[V^{IV}(trpy)(bpy)(O)](PF_6)_2$.

Attempted Reaction with CO_2. The reduced V(I) and V(0) species of the type $[V(trpy)(bpy)(L)]^{n+}$ were investigated for possible reactivity with CO_2. Polypyridyl complexes of Re, Ru, Os, Ir, and Co exhibit electrocatalytic behavior toward the reduction of CO_2 as a result of cycling through the polypryidyl ligand-based reductions.[9] Abruna and co-workers[25] have shown that thin films of electropolymerized $Co(v\text{-}trpy)_2{}^{2+}$ (v-trpy = 4'-vinyl-2,2':6',2''-terpyridine) are active in the electrocatalytic reduction of CO_2 and conclude that an available coordination site is necessary for catalytic activity. For the $Co(v\text{-}trpy)_2{}^{n+}$ system it is postulated that one pyridyl ring of the tridentate terpyridyl ligand is displaced upon reduction, thereby providing this coordination site. For complexes of the type $[V(trpy)(bpy)(L)]^{n+}$ it was hoped that the ligand L would be sufficiently labile to provide a necessary coordination site for CO_2 reduction to occur. In CH_3CN, CH_2Cl_2, or acetone solutions saturated with $CO_2(g)$, the reduced forms of the ions $[V(trpy)_2]^{2+}$, $[V(trpy)(bpy)(Cl)]^+$, $[V(trpy)(bpy)(OH_2)]^{2+}$, and $[V(trpy)(bpy)(CH_3CN)]^{2+}$ were all inactive toward the electrocatalytic reduction of CO_2 on the cyclic voltammetric time scale (scan rate 20 mV/s). The lack of reactivity toward CO_2 may be due, in part, to the nature of the MO occupied upon reduction. For the vanadium complexes reported here it was shown that this MO is largely $d\pi$(metal) in character. For the reported Co, Ru, Os, and Ir complexes the reductions occur in an MO that is largely antibonding π^*(ligand) in character.

General Discussion. As suggested also by other work, the unit [V(trpy)(bpy)] with vanadium in both the 2+ and 3+ oxidation states retains its integrity in a wide range of solvents, thus enabling the study of relative affinities of various ligands for the metal center. The most striking result of the limited work we have done along these lines bears on the affinity of the metal centers for CH_3CN. We have observed that Cl^-, even at 10^{-3} M, essentially completely replaces the CH_3CN solvate of the V(II) complex with CH_3CN as solvent, while $CF_3SO_3^-$ does not. When V is in the oxidation state 3+, even the latter nucleophile, though at low concentration, also replaces CH_3CN in neat CH_3CN. Acetone replaces CH_3CN on V(III) in neat acetone as solvent, but there is also partial replacement in CH_3CN as solvent with acetone at about the 2 M level. Because of the electron-withdrawing effects of the N-heterocycle ligands, a decrease in lability of the sixth ligand is expected. The substitution rates nonetheless are quite rapid so that if the rates are to be measured spectrophotomet-

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rically, rapid mixing procedures would be needed.

The result quoted above that $[V^{II}(trpy)(bpy)]^{2+}$ has a low affinity for CH_3CN, which is expected to be a better π acid than Cl^-, suggests that back-bonding does not play an important role in its binding to a sixth ligand. This does not mean, however, that back-bonding is unimportant in the chemistry of V(II), but must only mean that the back-bonding capacity of $[V^{II}(trpy)(bpy)]^{2+}$ is depleted by the π-acid polypyridyl groups already attached. The degree to which V(II)(πd^3) participates in back-bonding compared to that for the much more completely studied πd^6 cases is a point of some interest. The potentials of the V(III/II) couples for the different cases have a bearing on this, but because the potentials also involve the V(III) state, it is not as direct a measure as would be desirable. Nevertheless, it is of interest to compare the changes in the potentials for corresponding Ru, Os, and V couples (Table II). For the change from $M(trpy)_2^{2+}$ to $M(trpy)(bpy)Cl^+$, $-\Delta E_{1/2}$ values for the three systems are 0.46, 0.53, and 0.29 V, respectively; for the change from $M(trpy)(bpy)Cl^+$ to $M(bpy)_2Cl_2$, $-\Delta E_{1/2}$ values are 0.51, 0.48, and 0.45 V. If the change in potential absent back-bonding is much the same for the three cases, as seems likely because the same oxidation states are involved, the results can be taken to show that the stabilization of V(II) by back-bonding is substantial even though only three πd electrons are involved in this case.

The data for the continued reduction of the $M(trpy)_2$ moiety support the conclusion reached earlier, on other grounds, that the reduced states in the case of vanadium are more strongly metal based than in the case for either Ru or Os.

Taguchi et al. have shown that O_2 oxidizes species such as $[V^{IV}(\beta\text{-dik})(bpy)(O)]^+$ to V(V) on the time scale of hours.[31] Because of the stabilization of the V(V) product by the negative charge of the coordinated diketonate ion, the resulting V(V) species is expected to be less reactive as an oxidizing agent than the products resulting from the oxidation of $[V^{IV}(trpy)(bpy)(O)]^{2+}$. Cationic V(V) is a quite potent oxidant. In acidic aqueous solution, 1 M H^+ and above, the dominant form of V(V) is VO_2^+. For the reaction of VO_2^+ with cyclobutanol (aldehyde as product) in 1 M $HClO_4$ at 25 °C, the specific rate is measured as 2.1×10^{-3} $M^{-1}\ s^{-1}$.[32] Although aqueous V(V) does not oxidize benzene, it oxidizes aromatic compounds such as naphthalene[33] and toluene.[34] For the oxidation of toluene in 2 M H_2SO_4 at 30 °C, (product unspecified) k is reported as 5×10^{-4} $M^{-1}\ s^{-1}$.

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Contribution from the Department of Chemistry,
Grinnell College, Grinnell, Iowa 50112

Equilibrium and Kinetic Studies of Monoaqua Complexes of Platinum(II). 3. Acid–Base Properties and Dimerization of $[Pt(amino\ acid)(Me_2SO)(OH_2)]^+$ Species

Luther E. Erickson,* Ingrid E. Burgeson, Eric Eidsmoe, and Russell G. Larsen

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The acid dissociation and dimerization reactions of platinum(II) complexes of general formula $[Pt(amino\ acid)(Me_2SO)(H_2O)]^+$, for the amino acids glycine, sarcosine, and *N,N*-dimethylglycine (dmg), were investigated by potentiometric and NMR methods. Data are reported for the pK_a at 35 °C and for the equilibrium (K_d) and rate constants (k_d and k_{-d}) for the dimerization reaction over a range of temperatures. Approximate values for these quantities at 35 °C are $pK_a = 4$, $K_d = 100$ M, $k_d = 10^{-2}$ $M^{-1}\ s^{-1}$, and $k_{-d} = 10^{-4}\ s^{-1}$, with the dmg complex having the smallest pK_a and K_d and the largest k_{-d}. The significance of these data for species distribution as a function of pH, total platinum concentration, and pCl, for dimerization and trimerization of aqua species derived from cisplatin, and for potential reactions with other ligands is examined.

Introduction

Previous papers in this series have reported results of our study of the formation, by hydrolysis, of the monoaqua species formed from the monochloro species of general formula *cis*(*N*,*S*)-[Pt(amino acid)$(Me_2SO)Cl]$[1] and of the dimerization of the monoaqua species $[Pt(dien)(H_2O)]^{2+}$.[2] This paper describes our subsequent determination of the pK_a values and the rate and equilibrium constants for the dimerization of *cis*(*N*,*S*)-[Pt(amino acid)$(Me_2SO)(H_2O)]^+$, where amino acid = glycine (gly), sarcosine (sar), or *N*,*N*-dimethylglycine (dmg). The acid–base properties of the aqua species are intimately connected with the dimerization reaction, since the dimerization is most favored at pH = pK_a. In light of that observation, the dimerization reaction is most appropriately written

$$Pt\text{–}OH + Pt\text{–}OH_2^+ \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} Pt\text{–}OH\text{–}Pt^+ + H_2O \qquad (1)$$

where $Pt\text{–}OH_2^+$ and Pt–OH denote the aqua species and its deprotonated conjugate base, while $Pt\text{–}OH\text{–}Pt^+$ denotes the μ-OH-bridged dimer. The equilibrium constant for this reaction, K_d, is given by $K_d = [Pt\text{–}OH\text{–}Pt^+]/[Pt\text{–}OH_2^+][Pt\text{–}OH] = k_d/k_{-d}$.

The pK_as of aqua species were determined by potentiometric pH titrations. Since the dimerization reactions are relatively fast under typical titration conditions, both K_d and K_a could be estimated from the titration curves by allowing pH equilibration after each addition of base.[2] Although rate data for the dimerization reaction could also be obtained from the rate of equilibration of the pH after each addition of NaOH, a more direct NMR method was ultimately employed as the preferred method to determine rate and equilibrium constants for the dimerization reaction. Both equilibrium and rate data for dimerization were also obtained as a function of temperature to permit calculation of thermodynamic data and activation parameters for the dimerization reactions.

Experimental Section

Starting Materials. The *cis*(*N*,*S*)-[Pt(amino acid)$(Me_2SO)Cl]$ compounds were obtained as the thermodynamically favored and/or less soluble isomers in the reaction of $K[Pt(Me_2SO)Cl_3]$ with the amino acid anions in a 1:1 ratio.[3] The neutral compounds were isolated from the

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