Vanadium(V) Complexes of 1,5,10-Tris(2,3-dihydroxybenzoyl)-1,5,10-triazadecane and Its Analogs

Alison Butler and Roger de la Rosa

Department of Chemistry, University of California, Santa Barbara, Santa Barbara, California 93106

Qizhi Zhou, Amrit Jhanji, and Carl J. Carrano*

Department of Chemistry, Southwest Texas State University, San Marcos, Texas 78666

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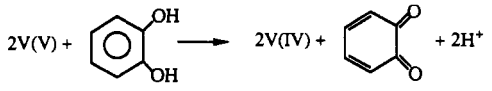
Vanadium(V) complexes of catechol and several polydentate analogs have been prepared and characterized in solution by optical and ^{51}V NMR spectroscopies as well by solution thermodynamic measurements. The vanadium(V) catecholate species displayed relatively sharp ^{51}V NMR signals in the range −164 to −268 ppm but in general were susceptible to decomposition by internal redox reactions yielding V(IV) and quinone, particularly in aqueous solution. The complexes of 1,5,10-tris(2,3-dihydroxybenzoyl)-1,5,10-triazadecane, and its sulfonated analog (3,4-LICAM and LICAMS) are an exception to this generalization and were quite stable. The sulfonated V(V)–LICAMS complex undergoes reversible protonations in aqueous solutions similar to those seen in the analogous Fe^{3+} complexes. The proton dependent formation constant for the reaction, $K^* = [V^{V}LICAMS]/[VO_2^+][LICAMS][H^+]$ has been measured, yielding a log K_{ML} of 24.2 (1) at 0.5 M in KNO_3 at 25 °C and pH 5.50.

Introduction

Interest in the interaction of vanadium with phenolates and catecholates stems in part from their widespread involvement in the bioinorganic chemistry of this element.[1] For example: (1) vanadium(III), -(IV), and -(V) are all thought to be bound to the serum protein, transferrin, via tyrosine ligands,[2-4] (2) the tunichromes are catechol derivatives thought to play an important role in the accumulation and storage of vanadium by marine organisms known as tunicates,[5] (3) the interaction of vanadium with tyrosine is thought to be responsible for the insulin mimetic effects of vanadate,[6] and (4) the reversal of vanadate inhibition of the Na,K ATPase by catecholamines is due to the binding of vanadium to the diol portion of the catecholamine.[7] Despite this interest, it is only recently that the coordination chemistry of V(III) and V(IV) with catechols has been properly elucidated.[8,9] The coordination chemistry of V(V) with these ligands remains somewhat more problematic. Early literature suggested that V(V) catecholates were incapable of existence, except as fleeting intermediates, due to a facile internal redox reaction.[10,11] This reaction, between a good oxidizing agent, V(V), and a modest reductant (the catechol), yields V(IV) and the corresponding quinone.



However in 1982 Cooper, Koh, and Raymond were able, in nonaqueous solvents, to isolate and unequivocally characterize octahedral V(V) "tris" complexes of catechol and some of its derivatives.[8] To our knowledge this still represents the only isolation and characterization of a V(V) tris(catechol) complex, although a number of V(V) mono- and bis(catecholates) are known.[12,13] In this report we extend the characterization of the simple V(V) catecholates to include ^{51}V NMR and solution thermodynamic measurements as well as expanding the number of such species by using hexadentate tricatecholate chelating agents, such as 1,5,10-tris(2,3-dihydroxybenzoyl)-1,5,10-triazadecane and the corresponding 1,4,7-triazaheptane, and 1,5,9-triazanonane derivatives (Chart I).[14]

Experimental Section

Synthesis. The ligand 1,5,10-tris(2,3-dihydroxybenzoyl)-1,5,10-triazadecane and its analogs were all prepared by a slight modification of the method of Fish et al.[15] Only the 3,4-LICAM(S) have been previously reported.[16] The materials were characterized by elemental analysis and infrared and proton NMR spectroscopies. Other polydentate catecholates were prepared as described by Raymond et al.[16,17] Sulfonation of ligands proceeded as previously reported.[16] Both the vanadium(IV) and -(V) tris(catecholates) or the *tert*-butyl-substituted analogs were prepared by the literature procedure.[8]

^{51}V NMR. The NMR experiments were done at room temperature using a General Electric GN 300 (frequency for V, 79.0 MHz) spectrometer equipped with a multinuclear broadband probe. Spectra were acquired unlocked, on nonspinning samples, under the following conditions: 90° pulse length; 10–20 μs for aqueous or methanolic vanadium(V)-containing solutions; pulse repetition rate 100 μs; spectral width 100 000 Hz. Typically about 5000 scans were necessary to obtain an acceptable signal to noise ratio on ca. 10^{-3} M vanadium(V) complex

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(14) Abbreviations used in this study: CAT = catechol; DTBC = di-*tert*-butylcatechol; PHEN = phenantholine; BPY = bipyridine; 3,4-LICAM = 1,5,10-tris(2,3-dihydroxybenzoyl)-1,5,10-triazadecane; 2,2-LICAM = 1,5,9-tris(2,3-dihydroxybenzoyl)-1,5,9-triazaheptane; 3,3-LICAM = 1,4,7-tris(2,3-dihydroxybenzoyl)-1,4,7-triazanonane; TRENCAM = *N,N',N''*-tris(2,3-dihydroxybenzoyl)tris(aminoethyl)amine; TIRON = 4,5-dihydroxy-*m*-benzenedisulfonate.
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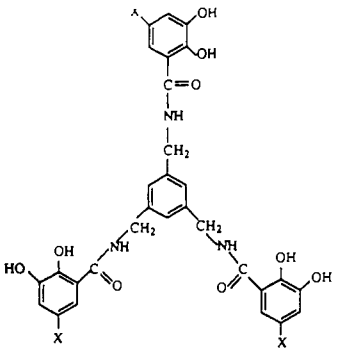
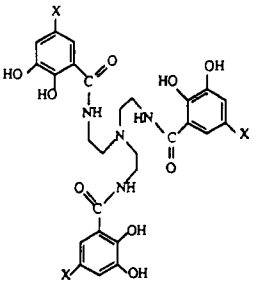
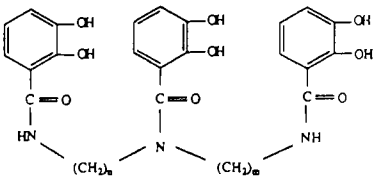
Chart I. Structures of Some of the Ligands Used in This Study



1,3,5 - N, N', N" - Tris(2,3-dihydroxylbenzoyl)triaminomethylbenzene



N ,N', N" - Tris(2,3-dihydroxylbenzoyl) triaminotriethylamine



N, N', N"- Tris (2,3-dihydroxylbenzoyl)
1,5,10-triazadecane (3,4-LiCAM)
and its analogs (2,2-LICAM and 3,3-LICAM)

n=m=2, 2,2-LICAM;

n=m=3, 3,3-LICAM;

n=3, m=4, 3,4-LICAM.

solutions. The free induction decays were obtained with 8K data points and were multiplied by an exponential filter function equivalent to a line broadening of 15–30 Hz prior to Fourier transformation. Chemical shifts are reported relative to neat $VOCl_3$ as an external reference.

Titrations. Potentiometric titrations at 25 °C and 1 M ionic strength (KNO_3) of both the free ligands and the vanadium complexes were conducted under a blanket of water-saturated nitrogen gas using a Corning Model 120 pH meter and a Cole-Palmer combination electrode. The electrode was standardized before each use with Fisher pH 4.00 and 7.00 buffers leading to estimated errors in pH readings of ±0.01 pH units. Formation constants were measured using solutions containing 2.5×10^{-4} M each of 3,4-LICAMS and sodium vanadate and varying concentrations of EDTA at μ = 0.5 M (KNO_3) and pH 5.50. The concentration of V(LICAMS) was determined from the absorption at 436 nm. The solutions were allowed to equilibrate for 3 days (the order of mixing of the components had no appreciable effect on the equilibrium values). The quoted constant is the average of six independent determinations at three different concentrations of EDTA.

Physical Methods. Proton NMR spectra were run in either $CDCl_3$ or D_2O on a Bruker 80 MHz FT NMR. Infrared spectra were recorded as KBr pellets on a PE 1600 FT-IR, while routine optical spectra utilized either an HP 8520 diode array or PE 553 rapid scan spectrophotometer. Near-IR data were obtained on a Perkin-Elmer NIR 330 spectrophotometer. Resonance Raman spectra of $[Et_3NH]_2[V(cat)_3]\cdot MeCN$ and $[Et_3NH][V(DTBC)_3]\cdot 1.5\,MeHO$ were obtained by Prof. Joann Sanders-Loehr, Oregon Graduate Institute of Science and Technology.

Table I. Optical and ^{51}V NMR Data for Spectra V(IV) and V(V) Catecholates

^{51}V NMR (δ)	solvent	ligand	λ_{max} (nm)		ϵ (M^{-1} cm^{-1})[a]
		V(V) Catecholates			
−235	CH_2Cl_2	$(dtbcat)_2bipy$	510	676	(22 400)
−202	CH_2Cl_2	$(dtbcat)_2phen$	516	675	(22 600)
−214	ACN/MEOH	dtbc	625	900	(17 000)
−245	$MEOH/H_2O$	3,4-LICAM	525	>825	(3150)
−268	ACN/MEOH	TRENCAM	630	815	(9875)
−476	H_2O, pH 4.0	TIRON	525	>825	(1300)
−164	H_2O, pH 5.0	3,4-LICAMS	448	812	(3830)
no[b]	H_2O, pH 2.0	3,4-LICAMS	510	890	(3920)
no[b]	H_2O, pH 5.0	3,3-LICAMS	436	800	nd[c]
no[b]	H_2O, pH 3.0	3,3-LICAMS	500	>825	nd
no[b]	H_2O, pH 2.0	TRENCAMS	540	>825	nd
		V(IV) Catecholates			
		Cat	552	650_{sh}	(9300)
		LICAM	572	675_{sh}	(2500)
		TRENCAM	580	640_{sh}	(7287)
		TIRON	580	675_{sh}	(nd)
		3,4-LICAMS	575	680_{sh}	(4275)
		TRENCAMS	570	640_{sh}	(nd)

[a] High-energy maxima. [b] no = not observed. [c] nd = not determined.

Results

Spectroscopy. Previous literature had suggested that authentic V(V) tris(catecholates) differ substantially in their optical spectra from the corresponding V(IV) complexes.[8] The V(V) complex was reportedly characterized by two widely separated and intense optical bands at ~625 and ~900 nm while the V(IV) species displayed two overlapping peaks of somewhat lower intensity centered at ~550 nm with a shoulder at 650 nm. After a larger series of multidentate vanadium catecholate complexes was examined (Table I) it appears that the aforementioned spectral differences are indeed quite characteristic of each oxidation state and thus optical spectroscopy provides an easy means to distinguish between them.

Although it appeared that V(V) complexes could be prepared for all the ligands studied, there were marked differences in their stabilities. In nonaqueous solvents the V(V) complexes were in general only stable for extended periods of time at nearly "neutral" pH. Addition of a base such as triethylamine to an acetonitrile or methanol solution of V(V) complex caused immediate reduction to the corresponding V(IV) tris(catecholate) as evidenced by the optical spectra. Acidification resulted in an initial color change from blue to a more violet tint, but this color rapidly faded, again yielding a V(IV) species. In aqueous solutions, the ligands TRENCAMS and MECAMS initially gave spectra indicative of V(V) tris(catecholates); however, these rapidly reverted to the features characteristic of V(IV) complexes. Different behavior was observed for the linear polycatecholates such as 3,4-LICAM and LICAMS, which gave blue to violet solutions with spectral features indicative of simple V(V) tris(catechols) only under acidic conditions. Raising the pH caused a shift to shorter wavelengths and a color change from violet to green. Since ^{51}V NMR indicates that the green complex still contains V(V), we believe it represents a hydrolyzed tris(catecholate) complex (vide infra).

Vanadium(V) catecholates are also amenable to investigation by ^{51}V NMR which should be sensitive to the coordination environment around the V(V). The well-characterized V(V) tris-(di-*tert*-butylcatecholate) shows a relatively sharp peak at −214 ppm in acetonitrile or methanol solution. This peak comes some 300 ppm below that of vanadate and other simple mono- and dioxovanadium(V) chelate complexes. The sharpness of the peak is consistent with the high symmetry of the tris(catecholate).

We examined several other complexes of V(V) with catechols and polycatecholates in nonaqueous solvents, all of which also displayed peaks in the −220 ± (40) ppm range (Table I). However, when we examined an analogous series of sulfonated, water-

Table II. Free Ligand Protonation Constants[a]

ligand	log K_1	log K_2	log K_3
3,4-LICAMS	8.59	7.03	6.21
3,3-LICAMS	8.36	7.42	6.42
2,2-LICAMS	7.08	6.66	5.22

[a] 25 °C, 1.0 M KNO_3, estimated error ≃ 0.02.

soluble, polycatecholates, at nearly neutral to slightly acidic pH, by ^{51}V NMR, only 3,4-LICAMS gave an NMR signal, which appeared at −164 ppm. As indicated by optical spectroscopy, both MECAMS and TRENCAMS were relatively unstable toward internal redox reactions, which results in reduction of the diamagnetic V(V) to paramagnetic V(IV), and thus a ^{51}V signal could not be observed. The simple disulfonated catechol TIRON did give a signal, but at −476 ppm, and it required a 50-fold excess of TIRON to vanadium.

In an attempt to understand the unique behavior of 3,4-LICAMS vis a vis TRENCAMS and MECAMS, further work concentrated on the series of new linear polycatecholamide sequestering agents. These were structurally similar to 3,4-LICAMS differing only in the chain length between the nitrogens in the backbone. These complexes are designated 3,3- and 2,2-LICAMS in keeping with the trivial nomenclature of Raymond et al.[16] However, neither of these two ligands gave a ^{51}V signal in aqueous solution, although optical spectroscopy indicated that V(V) complexes were indeed formed (vide infra).

Solution Thermodynamics. The six expected protonation reactions of the polycatecholates are known to fall into two groups of three protons each.[17,18] The more basic protonations occur above pH 11 and are therefore inaccessible to potentiometric methods. The constants for the more acidic protons were measured and are summarized in Table II. There is reasonable agreement between the values obtained for 3,4-LICAMS in this study and those obtained by Raymond et al.[18] The Raymond constants should be considered the more accurate, since we did not attempt to acquire the constants with the same level of precision obtained by the latter authors.[19] Comparison of the constants between members of the series 2,2-, 3,3-, and 3,4-LICAMS reveals a consistent increase in the first pK_a across the series.

Titration of a 1:1, 10^{-4}M solution of V(V) and the fully protonated 3,4-LICAMS ligand with standard base reveals three successive one-proton buffer regions within the 3–10 pH range (Figure 1). If the ligand were to release all six protons upon reaction with VO_3^- to form a trischelated catecholate according to reaction 1, the initial pH of the solution should be nearly neutral.

$$H_6L + VO_3^- \rightleftharpoons [VL]^- + 3H_2O \quad (1)$$

Since the solution is in fact at an acidic pH upon mixing, we postulate the rapid and nearly complete hydrolysis of the VL complex (eq 2). As the pH is raised the complex, VOHL is

$$[VL]^- + H_2O \rightleftharpoons [VOHL]^{2-} + H^+ \quad (2)$$

deprotonated to yield VOL which in turn can then undergo hydrolysis (eqs 3 and 4). Least-squares refinement of the

$$[VOHL]^{2-} \rightleftharpoons [VOL]^{3-} + H^+ \quad (3)$$

$$[VOL]^{3-} + H_2O \rightleftharpoons [VO_2HL]^{4-} + H^+ \quad (4)$$

potentiometric data using this model gives the protonation

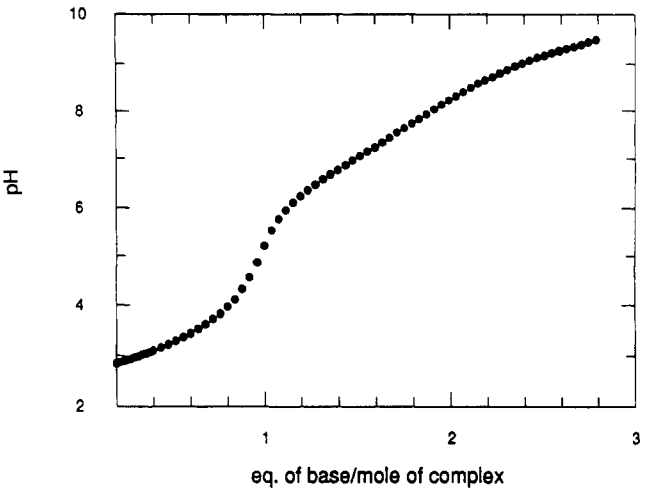


Figure 1. Titration of an approximately 10^{-4}M solution of V^V3,4-LICAMS with standard base, with other conditions as described in text.

Table III. V(V) Complex Protonation Constants (log K)

	log K		
ligand	spectrophotometric	potentiometric	^{51}V NMR
3,4-LICAMS	3.10 (2)[a]	3.16 (1)[b]	
		7.15 (3)	
		9.12 (4)	9.19 (2)
3,3-LICAMS	3.60 (5)	3.02 (2)[c]	
	7.95 (5)	7.31 (3)	
		9.17 (5)	
2,2-LICAMS	3.3 (2)	nd[d]	
	8.0 (2)	nd	
		nd	
3,4-LICAM	5.2 (1)		
3,3-LICAM	5.15 (5)		

[a] The numbers in parentheses represent estimated uncertainty in the last digit; conditions are as described in text. [b] The three protonation constants correspond to eqs 2–4, for the LICAMS series. Only reaction 2 is seen for the LICAM ligands. [c] Due to interference caused by ligand oxidation products formed upon reaction with the V(V), the protonation constants determined spectrophotometrically should be considered the more accurate. [d] nd = not determined.

constants listed in Table III. A distribution curve based on these constants is shown in Figure 2.

Potentiometric titrations on the vanadium(V) complexes of 3,3- and 2,2-LICAMS gave more ill-defined break points than 3,4-LICAMS. We attribute this to buffering by ligand oxdiation products. This hypothesis is supported by the fact that no ^{51}V NMR peaks are observed with these two ligand systems due to the presence of small amounts of V(IV) derived from the internal redox reaction. Nevertheless the amount of ligand oxidation appears to be relatively small as UV–vis spectra clearly indicating V(V) complexes are formed for all the systems and allowed accurate determination of some of the relevant protonation constants.

At pH values near 7 a stable, green solution was obtained from a mixture of 3,4-LICAMS and sodium vanadate. Above this pH the color of the solution faded to a pale yellow with ultimate re-formation of vanadate. Below pH 4 a reversible protonation occurred (Figure 3) yielding a violet species. Clear isosbestic points were evident at ~490 and ~800 nm. If the pH was lowered below 2 the violet color rapidly faded. From the change in the visible spectra as a function of pH, a Schwarzenbach analysis[20] indicated a single proton equilibrium with pK_a's of 3.10 (2) and 5.2 (1) for LICAMS and LICAM respectively. The increase in pK_a on going from the sulfonated to the unsulfonated analog is of a similar magnitude to that seen in the analogous iron

(18) Harris, W. R.; Raymond, K. N.; Weitl, F. L. *J. Am. Chem. Soc.* **1981**, *103*, 2667.

(19) In the present study pH was read to only two digit accuracy and the meter was calibrated by buffers rather than titration of standard acids, which allows direct pH meter readings of hydrogen ion *concentration*.

(20) Schwarzenbach, G.; Schwarzenbach, K. *Helv. Chim. Acta* **1963**, *46*, 1390.

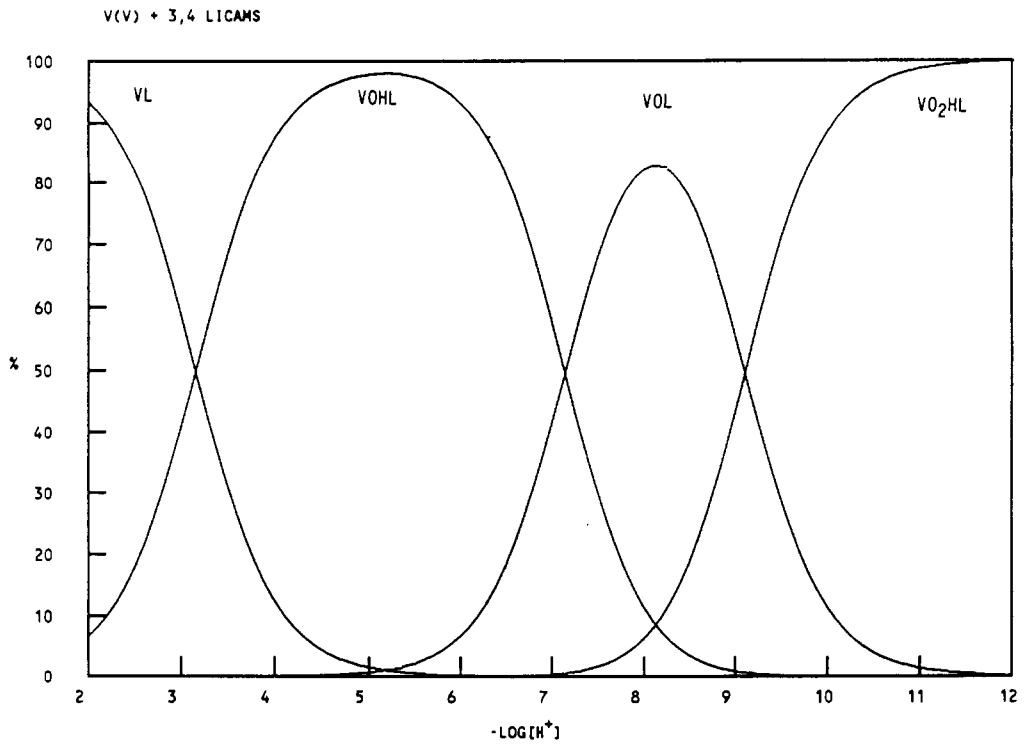


Figure 2. Distribution diagram for V^{V}LICAMS species as a function of pH. Conditions: [V] = [LICAMS] = 0.002 M; 25 °C; 1.0 M KNO_3. Data calculated using programs contained in: Martell, A. E.; Motekatis, R. J. *Determination and Use of Stability Constants*; VCH Publishers: Weinheim, Germany, 1992.

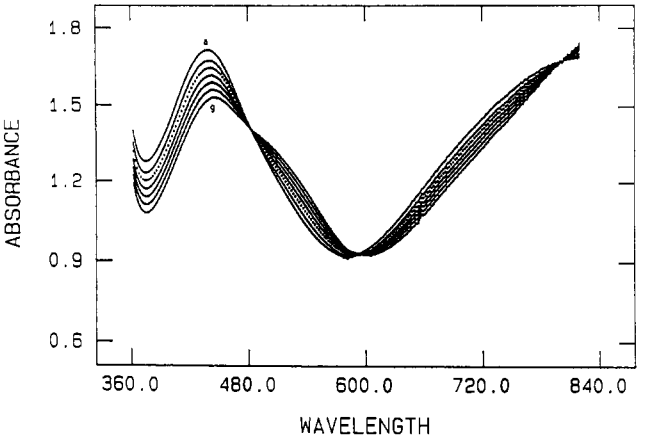


Figure 3. Optical spectra of V^{V}3,4-LICAMS as a function of pH over the range 4.27 (trace a) to 3.30 (trace g).

complexes.[18] Attempts at measuring the other protonations for 3,4-LICAMS via visible spectroscopy were thwarted by the overlapping of the constants and the small spectral changes that ensued. However in the case of the 3,3 and 2,2 derivatives we were able to measure a second protonation constant (Table III).

The ^{51}V NMR for V-3,4-LICAMS was also studied as a function of pH over the range from 4 to 10 (Figure 4). Between pH 4 and 8 no obvious NMR changes were observed, suggesting that the protonation equilibria identified by both spectrophotometric and potentiometric methods did not fundamentally change the coordination sphere of the V(V). However between pH 8 and 10 the primary peak at −164 ppm gradually diminished in intensity with concomitant growth of new peak near −320 ppm which shifted as a function of pH. At the highest measured pH (10.2) a small vanadate peak was also observable. Plotting the peak position as a function of pH leads to a pK_a of 9.19 (2) in good agreement with the final protonation constant evident from the potentiometric titration data.

Since to our knowledge there was no data available concerning the relative binding affinity of polycatecholates for V(V), we were prompted to determine the formation constant of V(V) 3,4-LICAMS in aqueous solution. As the complex is unstable at the low pH values needed to achieve a reasonable partition between the free metal ion and the ligand, direct potentiometric titration was deemed unsuitable. Instead the stability constant was estimated by competition with EDTA as described by eq 5. Thus

$$V^{V}\text{3,4-LICAMS} + EDTA^{4-} + 2H_2O \rightleftharpoons VO_2EDTA^{3-} + H_3LICAMS^{3-} + H^{+} \quad (5)$$

the partition equilibrium constant K_x is given by eq 6. Using the

$$K_x = \frac{[VO_2EDTA^{3-}][H_3LICAMS^{3-}][H^{+}]}{[V^{V}\text{3,4-LICAMS}][EDTA^{4-}]} \quad (6)$$

known equilibrium expression for VO_2EDTA^{3-}, eq 7, and

$$K_{ML}^{EDTA} = \frac{[VO_2EDTA^{3-}]}{[VO_2^{+}][EDTA^{4-}]} \quad (7)$$

combining with (6) give the pH-dependent conditional formation constant, K^* for V(V) LICAMS, eq 9.

$$K^* = \frac{K_{ML}^{EDTA}}{K_x} \quad (8)$$

$$K^* = \frac{[V^{V}LICAMS]}{[VO_2^{+}][H_3LICAMS^{3-}][H^{+}]} \quad (9)$$

Note the fact that we are expressing the deprotonated form of the free ligand as $3,4\text{-LICAMS}^{3-}$ even though LICAMS is actually a hexaprotic acid. This is necessary since we cannot directly measure the first three ligand protonations as they are so large. Essentially this means that the free ligand will not be more than triplely deprotonated under the experimental conditions. Using the appropriate mass balance equations and measuring the [V^{V}LICAMS] at 436 nm, we have evaluated K_x at pH 5.50.

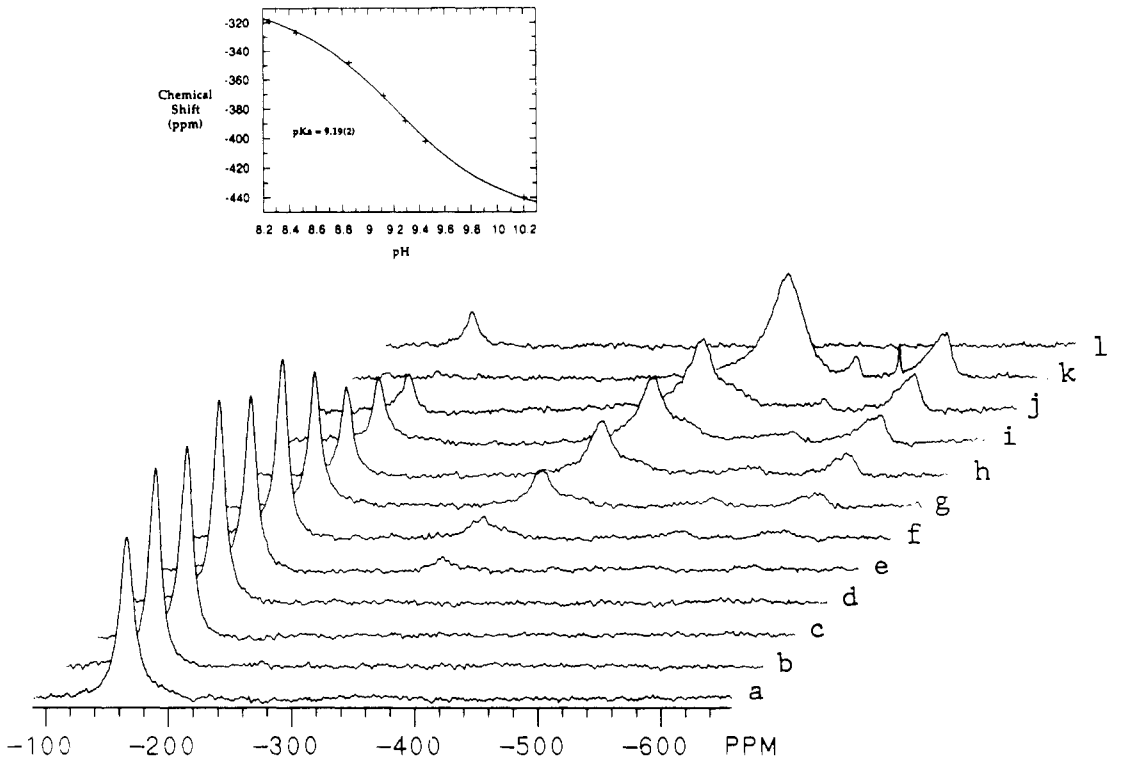


Figure 4. The pH dependence of the ^{51}V NMR spectrum of the vanadium(V) complex of 3,4-LICAMS. The complex was made in situ by the addition of 10.68 mM NH_4VO_3 and 17.72 mM 3,4-LICAMS in water; the initial pH was 4.49. The pH was raised by addition of NH_4OH and lowered with HCl. Conditions: (a) pH 4.49; (b) pH 5.04, after addition of NH_4OH; (c) pH 6.13; (d) pH 7.26; (e) pH 8.15; (f) pH 8.39; (g) pH 8.80; (h) pH 9.08; (i) pH 9.28; (j) pH 9.4; (k) pH 10.1; (l) pH 2.14, upon acidifying with HCl. The inset shows a fit of the data to a pK_a of 9.19.

Using log K_{ML} for VO_2EDTA^{3-} as 15.5,[21] we obtain a value for the conditional stability constant, K^*, for V^VLICAMS as log K_{ML} = 24.2 (1) at 25 °C, μ = 0.5 M, and pH = 5.50. It should be noted that while the proton-dependent formation constant measured here is a valid constant under the conditions, it is not directly comparable to standard formation constants which are written in terms of the completely deprotonated ligand, i.e. $LICAMS^{6-}$. Note also that the free metal ion is expressed as VO_2^+ since free V^{5+} is unknown at any pH.

Discussion

Spectroscopy. On the basis of both the intensity of the spectra ($\epsilon_m \approx 10^3$–10^4) and the fact that for V(V) at least, there are no d electrons, it has been suggested that the optical transitions observed for both oxidation states are LMCT in character. This assignment has now been confirmed by the presence of clear resonance-enhanced Raman peaks of the catecholate ligand upon 647-nm excitation into the respective optical bands. The resonance Raman spectra thus obtained were similar to those observed for Fe^{3+} catecholates and can be assigned in a similar way.[22]

It is tempting to speculate that the two peaks seen in the optical spectra of V(V) catecholates arise from transitions from the $p\pi$ orbitals of the ligand phenoxy oxygens into the empty t_{2g} and e_g orbitals on the metal. However this is unlikely to be the case for the same reasons previously outlined for the catechol complexes of high spin Fe^{3+}.[23] Exact assignment of these transitions will therefore require further work. As expected, sulfonation of the catechol rings pushes the LMCT transitions to higher energy due to the increasing negative charge on the complex, while protonation has the opposite effect. Comparison of the transition energies between the d^0 V(V) and the half-filled shell, high spin, d^5 Fe^{3+} analogs reveals that the former occur at lower energy due both to the increased positive charge on the central metal and the spin pairing required in the latter.[24]

Table I summarizes the ^{51}V NMR resonances for the known "tris" non-oxo vanadium catecholates along with those of the polydentate catechols from this study. Pecoraro and co-workers have already reported an extensive series of monocatecholato complexes of the general form LVO(cat).[25] It is apparent that all the non-oxo "tris-like" catechol complexes have ^{51}V NMR shifts that cluster at –230 ± 30 ppm. Beyond that it is difficult to discern any obvious trends vis a vis the influence of structural vs electronic effects on ^{51}V NMR shifts. The simple correlations between charge transfer transition energies and ^{51}V NMR shift reported by Pecoraro do not seem to apply, although we lack the necessary near-IR data on all but a few complexes.[25] Thus at this point in time it will be difficult to use ^{51}V NMR spectra of vanadium(V) catechols as a structural tool.

Solution Thermodynamics. Although it is of course impossible to directly derive any structural information from solution thermodynamic measurements, taken in concert with the NMR data we propose the following protonation scheme for V^V3,4-LICAMS:

$$[VL]^- \underset{-H_2O}{\overset{+H_2O}{\rightleftharpoons}} [VOHL]^{2-} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} [VOL]^{3-} \underset{-H_2O}{\overset{+H_2O}{\rightleftharpoons}} [VO_2HL]^{4-}$$

$$pK_a \qquad 3.16 \qquad 7.15 \qquad 9.12$$

This particular protonation scheme was chosen based on the observation that the ^{51}V NMR is largely unperturbed in the pH range 4–8, through which period other techniques indicate that protonation equilibria are established. This suggests that dramatic changes in the vanadium coordination sphere are unlikely. In

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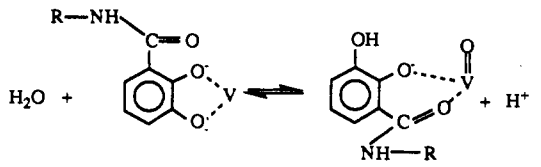
addition, the visible spectra of the violet species assigned as the tris(catecholate), VL is the most similar to that of the authentic tris(catecholates) which are all blue to violet in color (Table I). The exact nature of the hydrolyzed products are of course spectulative, but VOHL could be either a 7-coordinate vanadium hydroxo species or a vanadium oxo complex with a protonated catechol arm, perhaps similar to the salicylate mode of bonding proposed for protonated Fe^{3+}–LICAMS. It has been demonstrated conclusively by a variety of techniques that in the case of Fe^{3+} these protonations occur on the meta diol oxygen and cause a slippage from a catecholate to a salicylate mode of bonding.[26] Such a process could occur for V(V) as well, i.e.:



In the deprotonation of VOHL to VOL the proton ambiguity has been removed and an oxo–V(V) center seems reasonable. Above pH 9 hydrolysis to an oxo–hydroxo or dioxo V(V) center occurs which presumably results in concomitant loss of a ligand arm. The presence of this highly perturbed V(V) center results in the appearance of the new ^{51}V NMR features at ~−350 ppm and above. Finally, the magnitude of the measured formation constant indicates that while catechols are good ligands for vanadium, they are considerably poorer agents toward V(V) than Fe(III), i.e.:

$$\log K_{ML}^{Fe(LICAMS)} - \log K_{ML}^{FeEDTA} \approx 16$$

$$\log K_{ML}^{V(LICAMS)} - \log K_{ML}^{VO_2EDTA} \approx 9$$

Summary. Vanadium(V) complexes of a variety of polycatechol ligands have been prepared, and some are quite stable. For reasons perhaps related to their flexibility, the linear polycatecholates form more stable complexes than their cyclic analogs which tend to undergo internal redox reactions in aqueous solution. The V(V) catechol complexes of 3,4-LICAMS and its derivatives undergo protonation and hydrolysis reactions in solution which can be followed by ^{51}V NMR, UV–vis spectrophotometry and potentiometric titration. As expected polycatecholates are better ligands toward Fe^{3+} than V^{5+} as manifested by the formation constants and ease of hydrolysis of the latter.

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