Generalizing the Metallacrown Analogy: Ligand Variation and Solution Stability of the V^VO 9-Metallacrown-3 Structure Type

Brian R. Gibney, Ann J. Stemmler, Steffen Pilotek, Jeff W. Kampf, and Vincent L. Pecoraro*

Willard H. Dow Laboratories, Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109-1055

In previous reports, salicylhydroxamic acid (H_3shi) was used as a stabilizing ligand for metallacrowns, metal complexes with a structural analogy to crown ethers. An important goal for generalizing the metallacrown analogy was to prepare organic ligands with a wide variety of functional groups that retain a high-yield synthesis for a predicted metallacrown structural motif. The organic ligands used in this study ((4-hydroxysalicyl)hydroxamic acid, (5-deuterio- and (3,5-dideuteriosalicyl)hydroxamic acid, and 3-hydroxynaphthohydroxamic acid) demonstrate in principle this objective. Each of these ligands will form the generalized $9\text{-}MC_{(VO^{3+})N}\text{-}3$ structure previously reported with $9\text{-}MC_{(VO^{3+})N(shi)}\text{-}3$ in high-yield syntheses. The deuterio analogs are used to assign the ^1H NMR spectrum of $9\text{-}MC_{(VO^{3+})N(shi)}\text{-}3$, **1**, the 3-hydroxynaphthohydroxamic acid (H_3nha) dramatically increases the metallacrown bulk, and (4-hydroxysalicyl)hydroxamic acid adds an additional chelating atom that may allow further modification of the metallacrown to append functional groups capable of binding to clean metal surfaces or forming metallomesogens. The X-ray structure of $9\text{-}MC_{(VO^{3+})N(nha)}\text{-}3$, **4**, shows that the fundamental structural parameters of **1** are maintained. A variety of analytical methods including molecular weight determinations using mass spectroscopy and vapor pressure osmometry and solution probes such as ^1H and ^{51}V NMR and UV–vis spectroscopy allow us to conclude that the generalized $9\text{-}MC_{(VO^{3+})N}\text{-}3$ structure is retained in solution for the entire series of compounds. The concentration dependence of the visible spectra of the complexes changes linearly over a wide range of concentrations and in a variety of solvents demonstrating that the complexes do not dissociate even at relatively low concentrations (≥ 200 μM). Ligand-exchange studies between metallacrowns show that the metallacrowns are dynamic in methanol (exchange is complete after 10 h with $k = 0.31 \pm 0.02$ h^{-1}) but relatively inert in acetonitrile (no exchange after 48 h). Complex **1** has been used to prove the solution stability of the metallacryptate **7** in methanol. The observations that significant modifications to the organic portion of the metallacrown can have minor effects on metallacrown stoichiometry and ring geometry, that the molecules retain their structure in solution, and that ligand exchange is slow or nonexistent in organic solvents suggest that the preparation of organic ligands with new functional groups that can append nanosized metallacrowns to metal surfaces or organic polymers is a reasonable goal. X-ray parameters for $9\text{-}MC_{(VO^{3+})N(nha)}\text{-}3$, **4**, $C_{48}H_{53}N_8O_{17}V_3$, 1166 g/mol: crystal system monoclinic, $P2_1/n$ (No. 14), $a = 15.539(3)$ Å, $b = 20.512(5)$ Å, $c = 16.576(5)$ Å, $\beta = 106.77(2)°$, $V = 5059(2)$ Å^3, $Z = 4$, 11421 data collected with 5° < 2θ < 55°, 8693 data with $F_o \pm 4\sigma(F)$, $R = 0.0524$, $R_w = 0.0792$.

Introduction

The "metallacrown analogy"[1] is a useful synthetic rationale for the design and preparation of multinuclear complexes with moderate valent metals. Figure 1 illustrates conceptually the "analogy" that one may substitute heteroatoms such as transition metals and nitrogen atoms at positions occupied by methylene groups in the parent crown ether[2–5] complexes. This leads to a new class of molecules with features distinct from simple organic crowns[6] such as strong visible absorption spectra, magnetism, and redox activity. Furthermore, the hydroximate oxime oxygen atoms are far more basic than aliphatic ether oxygen atoms, which leads to complexation of moderate valent transition metals in the metallacrown cavity. Complexes with Mn(III), Fe(III), V(V), Cu(II), and Ga(III) in the ring positions have been prepared using the ligand salicylhydroxamic acid, a tetradentate chelating agent that confers stability to the metal ensemble.[7–12] A wide

variety of metals including Na(I), Mn(II), Mg(II), Fe(III), and Cu(II) have been sequestered into the metallacrown cavity. Added complex stability is obtained by bridging anions such as acetate, sulfate, or chloride between the encapsulated and ring metals. In fact one can consider metallacrowns as binding not just a metal but rather metal salts such as $Fe^{III}(OAc)_3$, $Fe^{III}(SO_4)_2^-$, or Mn^{II}-$(OAc)_2$.[1,7,9] In addition to the wide range of metals that may be incorporated into either ring or encapsulated positions, a variety of structural motifs including 9-MC-3,[10] 12-MC-4,[7] 15-MC-5,[13] and metallacryptates[12] have been prepared. It is clear that the metallacrown analogy can lead to extremely rich coordination chemistry when one considers the controlled variability of composition, structure, and physical properties possible in this system.

Even considering the virtually endless combinations of ring metal, encapsulated metal, ring size, and bridging anion types that can be prepared using the salicylhydroxamic acid ligand, the metallacrown analogy cannot fulfill a wide variety of applications until the stabilizing organic ligand can be modified significantly to allow, for example, attachment to electrode surfaces or formation of mesogenic phases. Recognizing the limitations of

● Abstract published in *Advance ACS Abstracts,* November 15, 1993.

(1) Lah, M. S.; Pecoraro, V. L. *Comments Inorg. Chem.* **1990,** *11,* 59.

(2) Pedersen, C. J. *J. Am. Chem. Soc.* **1967,** *89,* 2495.

(3) Pederson, C. J. *J. Am. Chem. Soc.* **1967,** *89,* 7017.

(4) Pedersen, C. J. *Angew. Chem., Int. Ed. Engl.* **1988,** *27,* 1021.

(5) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1988,** *27,* 89.

(6) Hiraoka, M. *Crown Compounds: Their Characteristics and Applications;* Elsevier Scientific: New York, 1982.

(7) Lah, M. S.; Pecoraro, V. L. *J. Am. Chem. Soc.* **1989,** *111,* 7258.

(8) Lah, M. S.; Pecoraro, V. L. *Inorg. Chem.* **1991,** *30,* 878.

(9) Lah, M. S.; Kirk, M. L.; Hatfield, W.; Pecoraro, V. L. *J. Chem. Soc., Chem. Commun.* **1989,** 1606.

(10) Pecoraro, V. L. *Inorg. Chim. Acta* **1989,** *155,* 171.

(11) Gibney, B. R.; Kampf, J. W.; Kessissiglou, D. P.; Pecoraro, V. L. To be submitted for publication in *Inorg. Chem.*

(12) Lah, M. S.; Gibney, B. R.; Tierney, D. L.; Penner-Hahn, J. E.; Pecoraro, V. L. *J. Am. Chem. Soc.* **1993,** *115,* 5857.

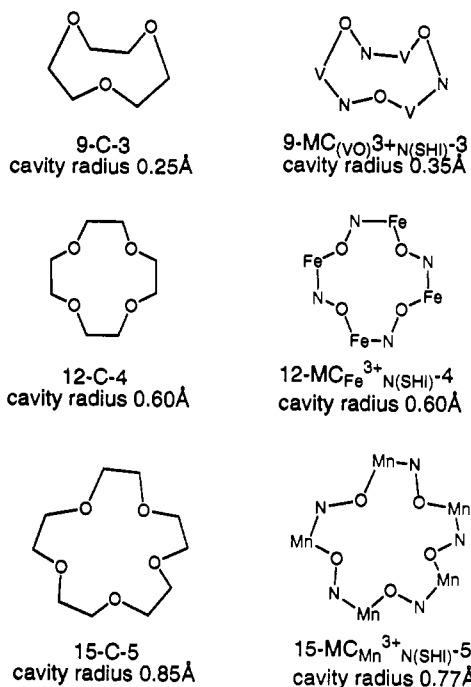(13) Kessissiglou, D. P.; Kampf, J. W.; Pecoraro, V. L. *Polyhedron,* in press.

Figure 1. Metallacrown analogy used as a design concept for the preparation of moderate valent transition metal complexes.
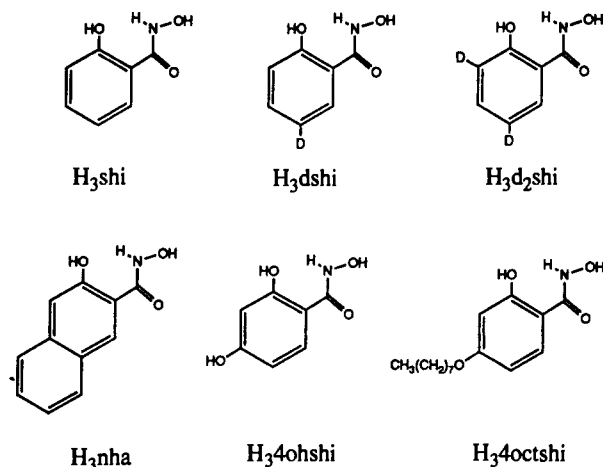

Figure 2. Ligands used in this study. Abbreviations key is given in the text.

metallacrowns built solely on salicylhydroxamic acid, we have begun preparing ligands that will retain the essential features necessary for metallacrown ring formation while allowing for enlargement of the molecule and/or addition of useful functional groups to the cluster. Inherent in these studies is establishing whether one can synthesize in high yield a metallacrown of desired structure from a new organic precursor.

Another important aspect of metallacrown chemistry is the solution integrity of the materials. X-ray structures of the metallacrowns demonstrate definitively the structural analogy in the solid state; however, this technique does not speak to the stability of the materials in various solvents. For example, metallacrowns could dissociate when dissolved and then reassemble on crystallization or precipitation. Furthermore, even if the molecules are stable, one would like to know whether the metal and ligand components of the complexes are in fast ligand exchange since this should impact the mechanism of metal complexation into the encapsulated position and the ability to prepare and isolate mixed ligand metallacrowns.

In this contribution we address a series of these points including the following: (a) Can the 9-MC-3 structure type be obtained from structurally related hydroxamic acid ligands? (b) Do the

vanadium 9-MC-3 complexes retain the nuclearity that is seen in the solid state in a variety of solvents? (c) What is the rate of ligand exchange between metallacrowns in a variety of solvents? (d) Are vanadium metallacrowns stable in the presence of excess ligand? (e) Can vanadium metallacrowns be used as a probe of solution integrity and exchange rate for other more complex metallacrowns.

Experimental Section

Materials. Salicylhydroxamic acid (H$_3$shi), vanadyl sulfate, sodium acetate, 3-hydroxynaphthoic acid, 3,5-diiodosalicylic acid, 5-iodosalicylic acid, 2,4-dihydroxybenzoic acid, and hydroxylamine hydrochloride were obtained from Aldrich Chemical Co. All other chemicals and solvents were reagent grade.

Abbreviations Used: H$_3$shi = salicylhydroxamic acid; H$_3$dshi = (5-deuteriosalicyl)hydroxamic acid; H$_3$d$_2$shi = (3,5-dideuteriosalicyl)-hydroxamic acid; H$_3$nha = 3-hydroxy-2-naphthohydroxamic acid; H$_3$4-ohshi = 2,4-dihydroxybenzohydroxamic acid.

The nomenclature for metallacrowns is as follows: M′$_{m′}$A$_a$[X-MC$_{M^{n+}H(Z)}$-Y], where X and Y indicate ring size and number of oxygen donor atoms, MC specifies a metallacrown, M and n+ are the ring metal and its oxidation state, H is the identity of the remaining heteroatom bridge, and (Z) is an abbreviation for the organic ligand containing the hydroximate functionality. There are m′ captured metals (M′) and a bridging anions (A) bound to the ring oxygens and metals, respectively. A vacant metallacrown is described by the VO^{3+} analogue 9-MC$_{(VO^{3+})N(nha)}$-3. The core structure is a nine-membered ring with VO^{3+} and N replacing methylene carbons. The organic ligand used is the triply deprotonated form of naphthohydroxamic acid (nha). A metal-encapsulated metallacrown is represented by Mn^{II}(OAc)$_2$[12-MC$_{Mn^{3+}N(shi)}$-4]. This molecule has the core structure of 12-crown-4 with the carbon atoms replaced by Mn(III) and N atoms throughout the ring. Salicyl-hydroxamic acid (shi) confers stability to the ring. An Mn(II) is captured by the hydroximate oxygen, and there are two bridging acetates linking two ring metals to the captured metal. Additional descriptors of chirality for the ring and captured metal ions will not be discussed here. The nomenclature for metallacryptates is as follows: M″$_{m″}$[M′$_{m′}${(X-MC$_{M^{n+}H(X)}$-Y)$_2$(Z)$_z$}]}, where there are m′ atoms of M′ in the metallacryptand cavity, m″ atoms of M″ capping the metallacryptate, and z atoms of Z forming the bridge between fused metallacrown ring metals. All other symbols are defined as for metallacrowns.

The supporting organic ligand has three protonation states and several ligation modes. The hydroxamic acid is the fully protonated uncoordinated ligand.[14] A single deprotonation of the ligand leads to the hydrox*a*mate that can ligate to a metal via the hydrox*a*mate carbonyl oxygen and oxime oxygen in a five-membered chelate. Double deprotonation of hydroxamic acid moiety yields the hydrox*i*mate which can also form a five-membered chelate. Fully deprotonated, shi^{3-} has several distinct modes of metal coordination, two of which are observed in metallacrown structures. First, a hydrox*i*mate chelate can be formed by the hydrox*i*mate oxygens. Second, the six-membered imino–phenolate chelate can be formed from the phenolate oxygen and hydrox*i*mate nitrogen. In cases where the metallacrown encapsulates a metal, the oxime oxygen of the hydrox*i*mate bridges from the ring metal to the core metal.

Preparation of Ligands and Complexes. 3-Hydroxy-2-naphthohy-droxamic acid. 3-Hydroxy-2-naphthoic acid (18.8 g, 100 mmol) was refluxed in 300 mL of absolute ethanol with 5 mL of concentrated sulfuric acid for 18 h. Periodic water removal was achieved via a Dean–Stark trap (5 × 15 mL). The resulting solution was cooled to room temperature, and solvent was removed by flash evaporation. Ethyl-3-hydroxy-2-naphthoate[15] crystallized during this process. Recrystallization from methanol gave 54.0 g (62.5% yield) of ethyl 3-hydroxy-2-naphthoate. Condensation of 3-hydroxy-2-naphthoate (24.5 g, 115 mmol) with hydroxylamine hydrochloride (15.98 g, 230 mmol) and KOH (19.3 g, 345 mmol) in 300 mL of methanol yielded the potassium salt of 3-hydroxy-2-naphthohydroxamic acid (H$_3$nha). This salt was dissolved in 1.25 M CH$_3$COOH in MeOH and crystallized to yield 18.7 g of 3-OH-2-nha (46% yield based on ester). ^{1}H-NMR (CD$_3$OD, 300 MHz): δ 7.12 (s, 1H), 7.21 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 7.4 Hz, 1H), 7.58 (d, J = 8.3 Hz, 1H), 7.75 (d, J = 8.3 Hz, 1H), 8.29 (s, 1H). ^{13}C-NMR (CD$_3$-

(14) Ventura, O. N.; Rama, J. B., Turi, L.; Dannenberg, J. J. *J. Am. Chem. Soc.* **1993**, *113*, 5754.

(15) Franczyk, T. S.; Czerwinski, K. R.; Raymond, K. N. *J. Am. Chem. Soc.* **1992**, *114*, 8138–8146.

OD): δ 111.8, 121.0, 123.8, 126.5, 128.2, 128.4, 129.5, 129.7, 137.6, 157.4, 167.5. Mass spectroscopic molecular weight: calcd for $C_{11}H_9N_1O_3$, m/e 203.0582; obsd, m/e 203.0580.

(5-Deuteriosalicyl)hydroxamic acid and (3,5-Dideuteriosalicyl)hydroxamic Acid. (5-deuteriosalicyl)hydroxamic acid and (3,5-dideuteriosalicyl)hydroxamic acid were prepared by the same method. The synthesis is described for (3,5-dideuteriosalicyl)hydroxamic acid. Selective ring deuteration of 3,5-diiodosalicylic acid was accomplished by modified literature procedure.[16] The 3,5-dideuteriosalicylic acid was converted to the methyl ester in 86% yield from 3,5-dideuteriosalicylic acid. GC-MS and ¹H-NMR confirmed the purity of the ester as >98%. The ester was condensed with hydroxylamine in methanolic KOH analogous to the H_3nha synthesis. The reaction mixture was flash evaporated to an oil after 24 h and triturated with ether. The powder was dissolved in 1.25 M acetic acid in methanol. The (3,5-dideuteriosalicyl)hydroxamic acid began to precipitate upon cooling and was washed with water and ether. Purity (>95%) was evaluated by ¹H and ¹³C NMR. Yield from starting iodosalicylic acid was 49.1%. Mass spectroscopic molecular weight: calcd for $C_7H_5D_2N_1O_3$, m/e 153.0426; obsd, m/e 153.0423.

For (5-deuteriosalicyl)hydroxamic acid the yield was 62.3% overall. Purity (>95%) was evaluated by ¹H and ¹³C NMR. Mass spectroscopic molecular weight: calcd for $C_7H_6D_1N_1O_3$, m/e 154.0489; obsd, m/e 154.0483.

2,4-Dihydroxybenzohydroxamic Acid. Methyl 2,4-dihydroxybenzoate was prepared by a literature procedure.[17] Purity (>95%) was evaluated by ¹H and ¹³C NMR and GC-MS. 2,4-Dihydroxybenzohydroxamic acid was prepared by literature method.[17] Purity (>95%) was evaluated by ¹H NMR. ¹³C-NMR (CD₃OD): δ 103.8, 106.8, 108.6, 129.8, 162.3, 163.4, 169.2. Mass spectroscopic molecular weight: calcd for $C_7H_7N_1O_4$, m/e 169.0375; obsd, m/e 169.0383.

9-MC$_{(VO^{3+})N(shi)}$-3, 1, 9-MC$_{(VO^{3+})N(shi)}$-3, 2, and 9-MC$_{(VO^{3+})N(d2shi)}$-3, 3. The metallacrowns 1–3 were synthesized as described previously for 1.[10]

9-MC$_{(VO^{3+})N(nha)}$-3, 4. To a solution of 20 mg (0.1 mmol) of H_3nha in DMF was added a solution of 15 mg (0.09 mmol) of vanadyl sulfate in DMF. The reaction was allowed to stir for 1 h before being filtered. Vapor diffusion of ether in the DMF solution resulted in 20 mg of X-ray-quality crystals (60% yield). Scale up of this reaction leads to gram quantities of microcrystalline 4. Anal. Calcd for 4: V, 13.1; C, 49.4; H, 4.5; N, 9.6. Found: V, 13.1; C, 49.6; H, 4.6; N, 9.6.

9-MC$_{(VO^{3+})N(4-obshi)}$-3, 5. Vanadyl sulfate (0.81 g, 5 mmol) was added to a solution of 2,4-dihydroxybenzohydroxamic acid (0.84 g, 5 mmol) in 200 mL of MeOH. The solution was stirred 3 h and then filtered. Slow evaporation gave 982 mg (72% yield) of dark purple crystaline prisms. Anal. Calcd for 5: C, 35.9 H, 3.7; N, 5.2. Found: C, 35.9; H, 3.7; N, 5.3.

Na{Na₂[Na{(12-MC$_{Ga^{3+})N(shi)}$-4)₂(OH)₄}]}, 6, and Na{Na₂[Na{(12-MC$_{Ga^{3+})N(d2shi)}$-4)₂(OH)₄}]}, 7. The metallacryptates were prepared as previously described for 6.[12]

Methods. ¹H NMR spectra of the model complexes were obtained on a Bruker 360 MHz FT-NMR spectrometer operating in the quadrature detection mode (¹H frequency, 360.1 MHz). ⁵¹V NMR spectra were collected by using a one-pulse sequence with a 90° pulse of 9.9 ms. Between 3000 and 10 000 transients were accumulated over a 50-kHz bandwidth for each sample. The spectra contained 8K data points, and the signal to noise ratio was improved by apodization of the free induction decay, which introduced a negligible 10–20-Hz line broadening. Chemical shifts were referenced to TMS or resonances due to residual protons present in the deuterated solvents.

UV–visible spectra were recorded on a Perkin-Elmer Lambda 9 UV/vis/near-IR spectrophotometer equipped with a Perkin-Elmer 3600 data station. Infrared spectra were obtained on a Nicolet 60-SX FT-IR as KBr pellets. Positive and negative FAB mass spectra were acquired by the University of Michigan Mass Spectroscopy Facility. Elemental analyses were performed by the Microanalysis Laboratory in the Department of Chemistry at the University of Michigan. Vapor pressure osmometry was performed by Galbraith Laboratories using CH₃CN maintained at 45 °C. Vapor pressure readings for three solution concentrations were plotted to obtain a zero concentration vapor pressure from which a molecular weight was calculated.

(16) McCubbin, J. A.; Moir, R. Y.; Neville, G. A. *Can. J. Chem.* **1970**, *48*, 942–947.
(17) Scott, A. W.; Kearse, W. O. *J. Org. Chem.* **1940**, *5*, 598.
(18) Siemens Analytical Services, Madison, WI, 1988.

Table I. Summary of Crystallographic Data for 9-MC$_{(VO^{3+})N(nha)}$-3, 4

formula	$C_{48}H_{53}N_8O_{17}V_3$	V, Å³	5059(2)
mol wt	1166.8	cryst sys	monoclinic
a, Å	15.539(3)	space group	$P2_1/n$ (No. 14)
b, Å	20.512(5)	Z	4
c, Å	16.576(5)	radiation (λ, Å)	Mo Kα (0.7107)
α, deg	90.0	temp, K	176
β, deg	106.77(2)	Rᵃ	0.0524
γ, deg	90.0	R_wᵇ	0.0792

ᵃ $R = \sum \|F_o - F_c\|/|F_c|$. ᵇ $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Collection and Reduction of X-ray Data. Suitable crystals of 4 were obtained as described above. These crystals were mounted in glass capillaries. Intensity data were obtained at 176 K on a Siemens R3 diffractometer using Mo Kα radiation (0.7107 Å) monochromatized from a graphite crystal whose diffraction vector was parallel to the diffraction vector of the sample. Three standard reflections were measured every 97 reflections. Modified crystal and data parameters are given in Table I. Intensity data were collected using θ/2θ scans. The data were reduced, the structure solved, and the model refined using the SHELXTL PLUS[18] program package. Computations were carried out on a VAX Station 3500. In the subsequent refinement, the function $\sum w(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The agreement indices $R_1 = \sum \|F_o| - |F_c\|/|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|]^{1/2}$ were used to evaluate the results. Atomic scattering factors are from The International Tables for X-Ray Crystallography. Hydrogen atoms were placed using a riding model at 0.96 Å from bonded carbon atoms and allowed to refine to a common U(H) of 0.104(3) Å². Unique data and final R indices are reported in Table I. Fractional atomic coordinates for 4 are given in Table II. Selected bond distances and angles for this compound are provided in Table III.

Results

Description of Structure of 9-MC$_{(VO^{3+})N(nha)}$-3, 4. The vanadium metallacrown formed with the naphthohydroximato ligand, illustrated in Figure 3, is remarkably similar to the previously described 9-MC$_{(VO^{3+})N(shi)}$-3, 1.[10] The complex is of the 9-metallacrown-3 type with all of the vanadium ions, as the VO³⁺ unit, in the metallacrown ring having the +5 oxidation state. The metallacrown core is constructed with three naphthohydroximato (nha³⁻) ligands linked through the three vanadium ions. The nha³⁻ acts as a binucleating tetradentate ligand with carbonyl and hydroximate oxygen atoms (O2 and O3, respectively) bound to one vanadium and phenolate oxygen (O1) and hydroximate nitrogen (N1) atoms bound to an adjacent vanadium. This organization results in a [V–N–O–]₃ ring system that is analogous to a 9-crown-3 with the carbon atoms replaced by V(V) and N. The vanadium ions are six coordinate with the remaining coordination site being filled by DMF. The ring vanadium atoms are separated by 4.67 Å. Other important distances and angles are provided in Table III.

The structure of the nine-membered ring core of 4 is similar to that described for 1 and the iron metallacrown Fe(OAc)₃[9-MC$_{(Fe^{3+})N(shi)}$-3].[9] The vanadium separation is identical to that seen in the previous vanadium and iron structures; however, the cavity radius of 4 (0.42 Å) is slightly greater than that of 9-MC$_{(VO^{3+})N(shi)}$-3 (0.35 Å) and Fe(OAc)₃[9-MC$_{(Fe^{3+})N(shi)}$-3] (0.35 Å). Furthermore, the metallacrown ring oxygens are further separated in 4 (5.70 Å) vs 1 (5.43 Å). Despite these changes, the vanadium complex 4 still does not efficiently bind a transition ion in the capping position. This probably reflects the low affinity of the metallacrown ring oxygens for transition metal ions in the absence of the acetate groups that provide additional stabilization of the capping iron in the tetramer. The vanadium cluster cannot form the bridging acetate mode since the terminal oxo group blocks this metal coordination site.

The formation of 9-MC$_{M^{3+}N}$-3 structures is dependent on the stereochemistry of the ring metal ions. The nha ligands adopt a cis propeller configuration in the 9-MC$_{M^{3+}N}$-3 compounds. This

Table II. Fractional Atomic Coordinates and U(eq) Values (Å^2) for 9-MC$_{(VO^{3+})N(nha)}$-3, **4**

atom	x	y	z	U(eq)^a	atom	x	y	z	U(eq)^a
V1	0.23264(4)	0.11361(3)	0.14126(3)	0.0159(2)	C11	0.1328(2)	0.1911(2)	−0.0036(2)	0.016(1)
V2	0.08715(4)	0.30707(3)	0.07013(4)	0.0162(2)	C12	0.1113(2)	0.3673(2)	−0.0769(2)	0.017(1)
V3	0.40108(4)	0.31705(3)	0.18058(3)	0.0154(2)	C13	0.0655(2)	0.3742(2)	−0.1614(2)	0.019(1)
O1	0.1942(2)	0.0604(1)	0.0484(1)	0.0190(7)	C14	0.1101(3)	0.3674(2)	−0.2239(2)	0.020(1)
O2	0.0910(2)	0.2434(1)	−0.0311(1)	0.0173(7)	C15	0.0632(3)	0.3719(2)	−0.3113(2)	0.026(1)
O3	0.1302(2)	0.2284(1)	0.1232(1)	0.0175(7)	C16	0.1075(3)	0.3614(2)	−0.3712(2)	0.030(1)
O4	0.0683(2)	0.3700(1)	−0.0169(2)	0.0186(7)	C17	0.2004(3)	0.3462(2)	−0.3479(2)	0.028(1)
O5	0.3452(2)	0.3542(1)	0.0564(1)	0.0176(7)	C18	0.2476(3)	0.3425(2)	−0.2640(2)	0.023(1)
O6	0.2792(2)	0.3294(1)	0.1714(1)	0.0169(7)	C19	0.2040(2)	0.3539(2)	−0.2007(2)	0.018(1)
O7	0.4955(2)	0.2966(1)	0.1338(1)	0.0186(7)	C20	0.2508(2)	0.3501(2)	−0.1146(2)	0.017(1)
O8	0.3347(2)	0.1360(1)	0.0598(1)	0.0180(7)	C21	0.2067(2)	0.3566(2)	−0.0537(2)	0.015(1)
O9	0.3211(2)	0.1853(1)	0.1914(1)	0.0180(7)	C22	0.2603(2)	0.3490(2)	0.0347(2)	0.015(1)
O10	0.2104(2)	0.0975(1)	0.2163(2)	0.0225(8)	C23	0.4801(2)	0.2752(2)	0.0542(2)	0.016(1)
O11	0.0745(2)	0.3422(1)	0.1518(2)	0.0230(8)	C24	0.5252(2)	0.3020(2)	0.0012(2)	0.018(1)
O12	0.4329(2)	0.3027(1)	0.2796(1)	0.0220(8)	C25	0.5056(2)	0.2825(2)	−0.0840(2)	0.018(1)
O13	0.3495(2)	0.0424(1)	0.1813(2)	0.0218(8)	C26	0.5474(2)	0.3112(2)	−0.1412(2)	0.023(1)
O14	−0.0479(2)	0.2853(1)	0.0307(2)	0.0212(8)	C27	0.5251(3)	0.2913(2)	−0.2239(2)	0.026(1)
O15	0.4502(2)	0.4105(1)	0.2015(1)	0.0205(8)	C28	0.4609(3)	0.2419(2)	−0.2543(2)	0.025(1)
O16	0.1787(2)	0.0524(2)	0.4721(2)	0.047(1)	C29	0.4195(3)	0.2129(2)	−0.2012(2)	0.022(1)
O17	0.7319(2)	0.1162(2)	0.9637(2)	0.048(1)	C30	0.4407(2)	0.2322(2)	−0.1154(2)	0.018(1)
N1	0.1587(2)	0.1798(1)	0.0795(2)	0.0170(9)	C31	0.3986(2)	0.2030(2)	−0.0591(2)	0.019(1)
N2	0.2190(2)	0.3342(1)	0.0926(2)	0.0170(9)	C32	0.4173(2)	0.2241(2)	0.0231(2)	0.0153(9)
N3	0.3641(2)	0.2226(1)	0.1464(2)	0.0163(8)	C33	0.3704(2)	0.1921(2)	0.0775(2)	0.016(1)
N4	0.4489(2)	−0.0287(2)	0.1530(2)	0.025(1)	C34	0.3798(3)	0.0112(2)	0.1297(2)	0.023(1)
N5	0.5189(2)	0.4993(2)	0.1695(2)	0.022(1)	C35	0.4951(3)	−0.0410(2)	0.2410(2)	0.031(1)
N6	−0.1828(2)	0.2700(2)	−0.0643(2)	0.0209(9)	C36	0.4805(4)	−0.0640(2)	0.0908(3)	0.045(2)
N7	0.3092(2)	0.0266(2)	0.4426(2)	0.032(1)	C37	0.4864(2)	0.4400(2)	0.1534(2)	0.020(1)
N8	0.8698(3)	0.0948(2)	0.9450(3)	0.049(2)	C38	0.5135(3)	0.5331(2)	0.2456(2)	0.030(1)
C1	0.1871(2)	0.0792(2)	−0.0315(2)	0.016(1)	C39	0.5543(3)	0.5346(2)	0.1085(2)	0.028(1)
C2	0.2129(2)	0.0372(2)	−0.0853(2)	0.021(1)	C40	−0.0951(2)	0.2743(2)	−0.0436(2)	0.021(1)
C3	0.2139(2)	0.0581(2)	−0.1669(2)	0.019(1)	C41	−0.2317(3)	0.2795(2)	−0.0016(2)	0.029(1)
C4	0.2475(3)	0.0175(2)	−0.2208(2)	0.025(1)	C42	−0.2371(3)	0.2595(2)	−0.1519(2)	0.031(1)
C5	0.2484(3)	0.0390(2)	−0.2986(2)	0.025(1)	C43	0.2203(3)	0.0308(2)	0.4248(3)	0.041(2)
C6	0.2163(2)	0.1019(2)	−0.3273(2)	0.024(1)	C44	0.3692(3)	0.0455(2)	0.5239(3)	0.037(2)
C7	0.1845(2)	0.1428(2)	−0.2767(2)	0.020(1)	C45	0.3506(4)	0.0032(3)	0.3795(3)	0.050(2)
C8	0.1821(2)	0.1219(2)	−0.1957(2)	0.018(1)	C46	0.7818(4)	0.0996(3)	0.9209(4)	0.059(2)
C9	0.1529(2)	0.1629(2)	−0.1408(2)	0.018(1)	C47	0.9184(5)	0.1088(3)	1.0348(4)	0.069(3)
C10	0.1568(2)	0.1434(2)	−0.0601(2)	0.016(1)	C48	0.9210(5)	0.0674(3)	0.8959(5)	0.088(4)

^{a} $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

Table III. Selected Bond Distances (Å) and Angles (deg) for 9-MC$_{(VO^{3+})N(nha)}$-3, **4**

Distances				
V=O			**V–O(oxime)**	
V1–O10	1.599(2)		V1–O9	1.863(2)
V2–O11	1.595(2)		V2–O3	1.866(2)
V3–O12	1.600(2)		V3–O6	1.873(2)
V–N			**V–O(phenolate)**	
V1–N1	2.039(3)		V1–O1	1.892(2)
V2–N2	2.050(3)		V2–O4	1.895(2)
V3–N3	2.053(3)		V3–O7	1.894(2)
V–O(carbonyl)			**V–O(DMF)**	
V1–O8	2.158(2)		V1–O13	2.065(3)
V2–O2	2.141(2)		V2–O14	2.059(2)
V3–O5	2.130(2)		V3–O15	2.056(3)

Angles^a			
O1–V1–N1	82.3–82.1 (82.6)	O1–V1–O9	151.8–154.6 (153.4)
O1–V1–O8	80.3–81.5 (81.0)	O1–V1–O10	107.7–109.4 (108.3)
O1–V1–O13	88.9–89.3 (89.1)	O9–V1–N1	84.8–86.9 (86.0)
O9–V1–O8	75.3–75.8 (75.6)	O9–V1–O10	96.1–97.2 (96.6)
O9–V1–O13	98.4–101.8 (99.7)	O8–V1–ON1	90.7–93.8 (92.6)
O8–V1–O10	167.6–168.5 (168.1)	O8–V1–O13	81.1–82.9 (81.9)
O10–V1–N1	94.9–97.6 (95.9)	O10–V1–O13	90.2–91.6 (90.8)
O13–V1–N1	169.2–171.8 (170.6)	V1–N1–O3	120.7–121.6 (121.2)
N1–O3–V2	118.8–120.3 (119.8)		

^{a} The range of chemically equivalent angles is provided. The average is given in parentheses. The angles are referenced to the V1 coordination sphere (e.g., (O1–V1–N1) = (O4–V2–N2) = (O7–V3–N3)).

is in contrast to 12-MC$_{M^{3+}N}$-4 complexes previously described that have hydroximate ligands in a planar geometry. The 9-MC$_{M^{3+}N}$-3 motif is chiral since absolute stereochemical isomerism can be described for the vanadium coordination sphere. Both Λ and Δ isomers are possible at each of the ring positions

of the 9-MC$_{M^{3+}N}$-3. The five-membered ring is formed by the hydroximate group, while a six-membered ring is formed through the substituted iminophenolate. This leads to an asymmetric propeller configuration for the V(V). The possible isomers are Λ or Δ using the skew line convention for compounds with C_2 or pseudo-C_2 axes. Only the ΛΛΛ or ΔΔΔ isomers will complete the nine-membered ring system. Therefore, the chirality at one metal center imposes the identical chirality on the remaining two ring metal ions. The ΔΔΔ isomer is shown in Figure 3.

One final structural comment on **4** is warranted. As depicted in Figure 4 for 9-MC$_{(VO^{3+})N(shi)}$-3 and 9-MC$_{(VO^{3+})N(nha)}$-3, the aromatic rings of the shi and nha ligands are directed away from the cavity of the metallacrown. In the case of **1**, a hydrophobic cavity reminiscent of calixarenes is developed on the opposite side of the molecule. The arrows on **1** show how one might expect the cylinder to lengthen and broaden on going to the longer naphthoic ring system. Thus, extension of the aromatic ring system should lead to a larger hydrophobic cavity that might confer recognition of hydrophobic molecules. Surprisingly, this is not the case in the solid state since **4** sustains a significant twisting of the naphthyl ring with respect to the metallacrown core. While the cylinder of 9-MC$_{(VO^{3+})N(nha)}$-3 elongates with respect to **1** due to the naphthoic ring, it does not cause a broadening of the hydrophobic cavity. Instead, the naphthoic rings collapse to fill the space of the cylinder. The T-shaped interaction has been described previously for aromatic systems. The origins of this effect have been discussed both experimentally and theoretically for benzene, anthracene, and naphthalene in crystals and in solution.[19] While steric factors (repulsive interactions) appear to play a part in this alignment in the crystal
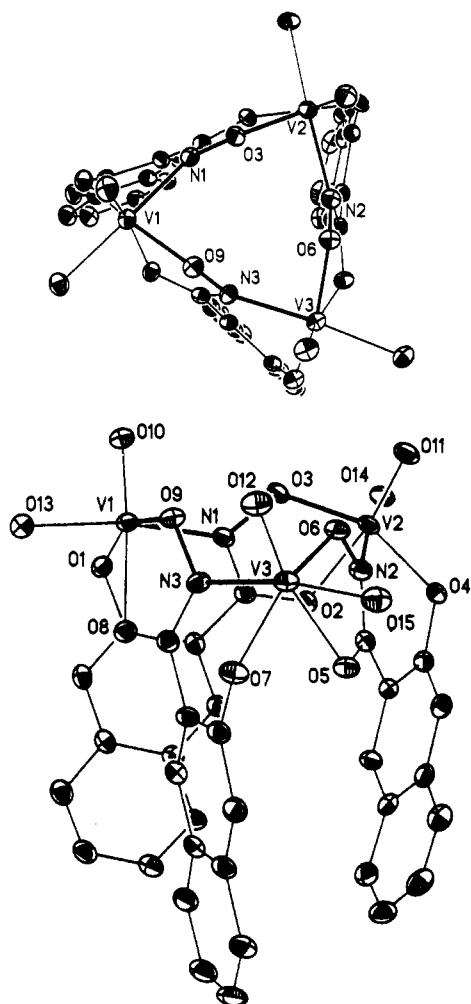
(19) Williams, D. E. *Acta Crystallogr.* **1980**, *A36*, 715.

Figure 3. ORTEP diagrams of 9-MC$_{(VO^{3+})N(nha)}$-3, **4**, with thermal ellipsoids at 50% probability: Top, top view of **4** emphasizing the metallacrown ring and orientation of naphthoic rings; bottom, side view of metallacrown illustrating the cylinder formed by the naphthyl rings. Only the oxygen atoms of the DMF molecules are shown.

structure of benzene, the deviation from flatness in the stacking of large aromatic units, expected to optimize van der Waal forces, are mitigated by small, but significant, partial charges that are manifested by the molecular quadrupole moment.[20] Bartell has calculated that carbon has a 0.14 electron surplus while hydrogen has a 0.14 electron deficit in benzene.[21] These charges dominate short-range interactions between aromatic rings. In the case of **4**, significant twisting of the planes of the naphthyl groups result. While the electric quadrupole effect adequately explains the observed distortion in the solid state, it is difficult to assess whether a hydrophobic cavity more similar to that originally predicted (calixarene-like) would develop when **4** is dissolved in solvents such as methanol, DMF, or acetonitrile where other competing factors become available.

Titration of H₃shi with VOSO₄ in DMF or Acetonitrile. Addition of H₃shi to a VOSO₄ solution in DMF leads to air oxidation of the metal to V⁵⁺ and an increased absorbance in the visible spectrum. The titration curve for the addition of 1–5 equiv of H₃shi is shown as Figure 5. Initial additions of ligand lead to minor absorption changes; however, once 1 equiv of ligand has been added the solution turned indigo blue (λ_{max} = 522 and 600 nm). Subsequent ligand addition leads to a new complex as the spectrum red shifts (λ_{max} = 525 nm) until 3 equiv of ligand
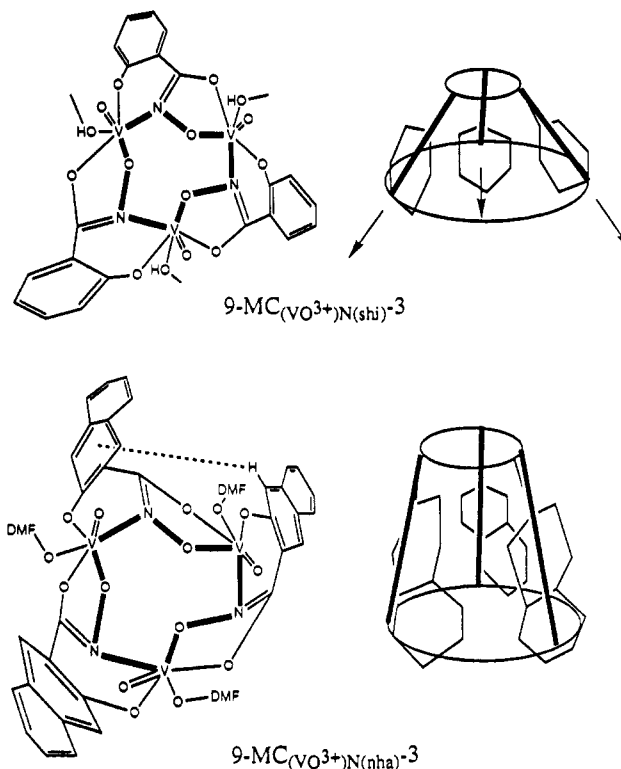
(20) Battaglia, M. R.; Buckingham, A. D.; Williams, J. H. *Chem. Phys. Lett.* **1981**, *78*, 421.
(21) Bartell, L. S.; Sharkey, L. R.; Shi, X. *J. Am. Chem. Soc.* **1988**, *110*, 7006.

9-MC$_{(VO^{3+})N(shi)}$-3

9-MC$_{(VO^{3+})N(nha)}$-3

Figure 4. Diagrams of 9-MC$_{(VO^{3+})N(shi)}$-3, **1** (top left), and 9-MC$_{(VO^{3+})N(nha)}$-3, **4** (bottom left). The phenolate rings of **1** are splayed out generating a cylinder that is reminiscent of calixerenes (top right). Hypothetically, elongation of this cylinder (along the direction of the arrows) with naphthohydroxamic acid should lead to a lengthening of the cylinder and a significant broadening of the base. In contrast, the naphthyl rings of **4** are pulled into the cavity (bottom right) leading to an elongated cylinder that has a compressed base. The quadrupolar interaction between the ring hydrogens and the aromatic ring current, shown for only one interaction on the bottom left, leads to this highly compacted structure.
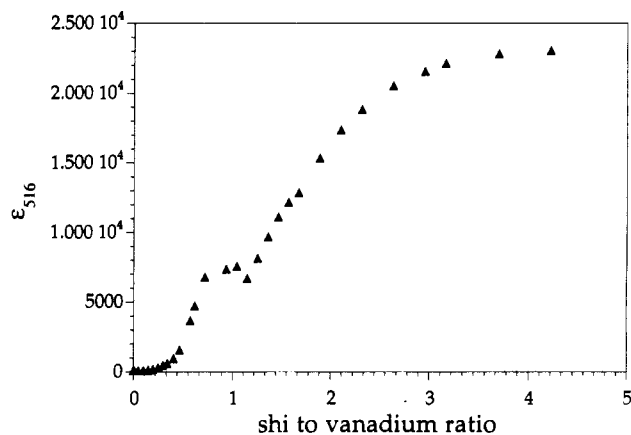

Figure 5. Plot of ϵ_{516} vs concentration of H₃shi for a 0.5 mM VOSO₄ solution in DMF.

are added at which time the final spectrum with λ_{max} = 520 nm results. Similar results are observed in acetonitrile.

The titration curve is consistent with the formation of tris-(hydroximate) complexes of the type V(Hshi)₃⁻ or related protonated species.[22,23] The plateau region is most simply explained as a region of stability for the 9-MC$_{(VO^{3+})N(shi)}$-3 structure where there is a ligand to metal ratio equal to one. The 1:1 ligand to metal species can be assigned to 9-MC$_{(VO^{3+})N(shi)}$-3 by UV–vis and ¹H and ⁵¹V NMR. It is unlikely that the only

(22) Pande, K. N.; Tandon, S. G. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1509.
(23) Fisher, D. C.; Barclay-Peet, S. J.; Balfe, C. A.; Raymond, K. N. *Inorg. Chem.* **1989**, *28*, 4399–4406.
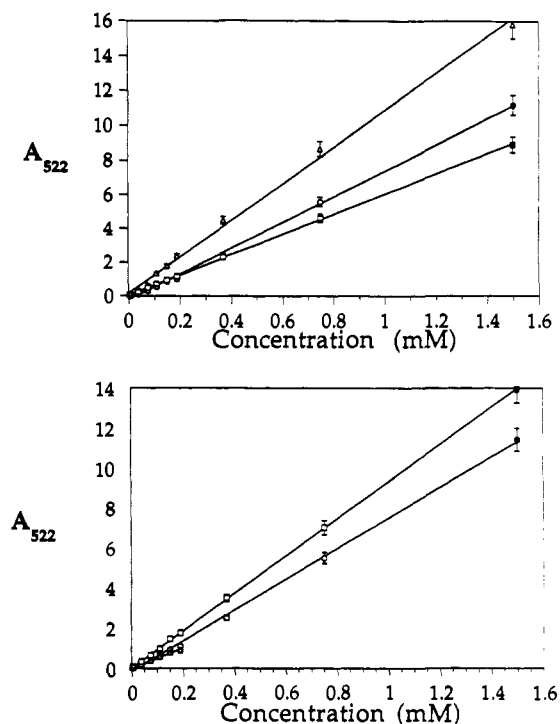
Figure 6. Plots of A_{522} vs concentration in methanol (O), acetonitrile (□) and DMF (△) for **1** (top) and **4** (bottom).

equilibrium in this system is between the 9-MC$_{(VO^{3+})N(shi)}$-3 and tris complexes. This is substantiated by the complex ^{1}H and ^{51}V NMR observed upon addition of ligand to 9-MC$_{(VO^{3+})N(shi)}$-3. Both bis and tris complexes can also be observed; however, these spectra are not as clean (new resonances at –349, –363, –377 and –410 ppm develop) as those of the pure 9-MC$_{(VO^{3+})N(shi)}$-3 (single resonance at –228 ppm) since a variety of ligand protonation states and metal complex isomers are possible. These resonances are in the range previously reported for the oxochlorobis(*N*-phenylbenzohydroximate)vanadium(V) complex (–283 ppm[24]). Therefore, we cannot address at this point whether the ligand is bound in these cases as the hydroximate or iminophenolate of shi^{3-}, as the hydroximate of Hshi^{2-}, or as the hydroxamate of H$_2$shi$^-$. On the bases of the downfield shift of the ^{51}V NMR signals, it is likely, however, that the hydroximate or hydroxamate complexes are the dominant species.

Structural Integrity Dependence on Concentration. Serial dilutions of standard 1.5 mM solutions of **1** and **4** in methanol, acetonitrile, and DMF confirm that both metallacrowns retain their integrity in these solution at ≥ 0.1 mM concentrations. Plots of absorbance at 522 nm versus [**1**] in acetonitrile, methanol, and DMF are shown as Figure 6. Nearly identical results are obtained for **4** in any of the three solvents (the solubility of **4** in DMF is 0.27 mM so that the dilution curve in Figure 6 is limited to concentrations equal to or below this value). The concentration variation leads to a linear change in absorbance across this range of concentrations. Only in methanol at the lowest 9-MC$_{(VO^{3+})N(shi)}$-3 concentrations does one see any deviation from linearity. This may be due to the higher water content in methanol, which is known to cause decomposition of the metallacrowns. The extinction coefficients that are determined from the slopes of these lines for each metallacrown in the three solvents are provided in Table IV.

Molecular Weight Determination. Vapor pressure osmometry was used to evaluate the solution integrity of the complexes **1** and **4**. In CH$_3$CN, **1** gave 652, (VO(shi))$_3$ = 651, and **4** gave 817, (VO(nha))$_3$ = 801. These values demonstrate conclusively that the metallacrowns are intact in CH$_3$CN. The similarity in optical

(24) Weidemann, C.; Priebsch, W.; Rehder, D. *Chem. Ber.* **1989**, *122*, 235.

absorption spectra and ^{1}H and ^{51}V NMR spectra for these and related compounds speaks to the integrity of all materials in this range of solvents.

Ligand Exchange between Vanadium Metallacrowns. The ligand exchange between **1** and **4** in methanol and acetonitrile and **1** and **5** in DMF was monitored by ^{1}H NMR using the chemical shift values for H$_3$shi, H$_3$nha, H$_3$4-ohshi, **1**, **4**, and **5** that are provided in Table V. There is no evidence for ligand exchange between **1** and **4** in acetonitrile since, after 42 h, all the proton peaks may be assigned either to 9-MC$_{(VO^{3+})N(shi)}$-3 or 9-MC$_{(VO^{3+})N(nha)}$-3. An identical result is observed in the ligand-exchange experiment between **1** and **5** in DMF as no exchange can be detected within 48 h. Thus, not only is metallacrown structure retained by **1** and **4** in acetonitrile and **1** and **5** in DMF but it also appears that rapid dissociation equilibria that would scramble the ligands is not operative. Quite different results are obtained in methanol, where the ^{1}H NMR shows relatively rapid exchange that is complete in ≈6 h. In addition, the spectra point toward the formation of 9-MC$_{(VO^{3+})N(shi)(nha)2}$-3 and 9-MC$_{(VO^{3+})N(shi)2(nha)}$-3 since there are new resonances that are not present for **1** or **4** or for the ligands in protonated or deprotonated forms. The assignment of these resonances to mixed-ligand vanadium metallacrowns is confirmed by FAB-MS, which has mass peaks for **1**, **4**, and both mixed-ligand metallacrowns. The ^{1}H NMR spectra of the reactions in acetonitrile and methanol are provided in the supplementary material.

Kinetic information for the vanadium metallacrowns in methanol was obtained by following the loss in signal intensity over time either for the doublet at 7.77 ppm for **4** or the singlet at 6.56 ppm for **4**. These resonances were chosen since there was no overlap with any of the new peaks that grew in over the course of the experiment. The integration of the area under the peak, A, was calibrated against an internal standard (a DMF resonance at 7.97 ppm). The results of these experiments are shown in Figure 7 where log $[(A - A_\infty)/(A_0 - A_\infty)]$ vs time (in hours) is plotted for both of the resonances that were monitored. The slopes for the best fit lines are 0.31 ± 0.02 h^{-1}. This treatment indicates that the approach to the equilibrium mixture is first order with an overall rate constant that is equal to the sum of the individual first-order rate constants from each participating species.

Ligand Exchange between Metallacrowns. The observation that **1** is kinetically labile in methanol allows it to be used as a probe of the integrity of other metallacrowns in solutions containing methanol. The ligand exchange between **1** and **7** in acetonitrile was monitored by ^{1}H NMR. Ligand exchange between **1** and **7** was not observed in acetonitrile even after several days, which is expected since **1** and **4** did not exchange under these conditions. Due to the poor solubility of **7** in methanol, a 1:1 mixture of acetonitrile:methanol was used for exchange reactions. Whereas the two vanadium metallacrowns, **1** and **4**, undergo ligand exchange with a $t_{1/2}$ ≈ 5 h, **1** and **7** show no evidence of ligand exchange after 10 h. Since there is no thermodynamic penalty for this reaction, and since **1** is labile, the lack of ligand exchange between **1** and **7** must be due to the kinetic inertness of **7**. The solution integrity of **7** has already been proven[12] under noncompetitive conditions, but these experiments provide additional evidence for the stability of **7** in solution. Experiments are underway to ascertain the ligand exchange rates of other metallacrowns in various solvent systems containing methanol.

Discussion

An important goal for generalizing the metallacrown analogy is that new organic ligands can be synthesized that may confer interesting or useful properties onto a metallacrown of desired structure. To satisfy this desire one must be able both to prepare organic ligands with a wide variety of functional groups and to

Table IV. UV–Vis and ^{51}V NMR Parameters for 9-MC$_{(VO^{3+})N}$-3 Derivatives

| complex	UV–vis: λ_{max} (ϵ^a)			^{51}V NMR: δ^b (ν^c)
	methanol	acetonitrile	DMF	
1	522 (7560), 614 (6690)	522 (5960), 614 (6660)	522 (10 700), 600 (12 100)	−233 (1200)
4	522 (7670), 583 (7960)	522 (9330), 620 (10400)	522 (5330), 614 (5830)	−228 (2200)
5	515 (6540), 600 (6600)	531 (8848), 615 (10162)	547 (6587), 600 (6827)	−235 (1100)

^{a} Extinction coefficient in M^{-1} cm^{-1} per cluster. ^{b} In ppm vs an external VOCl$_3$ standard. Collected in acetonitrile. ^{c} Line widths in hertz.

Table V. ^{1}H NMR Parameters in Acetonitrile for H$_3$shi, H$_3$nha, 9-MC$_{(VO^{3+})N}$-3, and Na{Na$_2$[Na{(12-MC$_{Ga^{3+}N(d_2shi)}$-4)$_2$(OH)$_4$}]} Complexes

compd	3H	4H	5H	6H
		shi		
H$_3$shi	6.92	7.41	6.87	7.47
H$_3$dshi	6.92	7.41		7.47(s)
H$_3$d$_2$shi		7.41(s)		7.47(s)
1	6.75	7.41	6.68	6.78
2	6.75	7.41		6.78(s)
3		7.41(s)		6.78(s)
6	6.79	7.19	6.65	7.65
7		7.19(s)		7.65(s)
		4-ohshi		
4-ohshi	6.38(s)		6.39(d)	7.56(d)
5	6.79(s)		7.46(d)	6.78(d)
		nha		
H$_3$nha	7.05 (s), 7.20 (t), 7.34 (t), 7.61 (d), 7.76 (d), 8.25 (s)			
4	6.70 (s), 6.83 (d), 7.13 (s), 7.18 (t), 7.47 (t), 7.77 (d)			

Figure 7. Plot of log $[(A - A_\infty)/(A_0 - A_\infty)]$ vs time (in hours) for a mixture of **1** and **4** in methanol. The peak areas (A) of the ^{1}H NMR resonances were monitored at 6.56 ($\triangle$) and 7.77 ($\blacksquare$) ppm.

be certain that a high-yield synthesis for a desired metallacrown structural motif exists with these ligands. The metallacrowns reported in this contribution demonstrate in principle both of these objectives. The organic ligands used in this study and shown in Figure 2 include (5-deuterio- and (3,5 dideuteriosalicyl)-hydroxamic acid, (4-hydroxysalicyl)hydroxamic acid, and 3-hydroxynaphthohydroxamic acid. Each of these ligands will form the generalized 9-MC$_{(VO^{3+})N}$-3 structure in high-yield syntheses. While the deuterio derivatives provide little steric or electronic modification (however, they are extremely useful for probing solution integrity and dynamics), the 3-hydroxynaphthohydroxamic acid and (4-hydroxysalicyl)hydroxamic acid complexes establish that significant ring alterations either to increase size, change the electronic nature, or add additional functional groups that are potential ligands and/or sites of further modification are amenable to this approach. Preparation of a metallacrown with H$_3$nha was of particular importance since a previous report demonstrated the existence of a V^{V}O$_2$(H$_2$nha)$_2$ complex.[25] However, the X-ray structure of **4** shown in Figure 3 convincingly shows that not only stoichiometry but also fundamental structural parameters of the 9-metallacrown-3 ring are maintained. The recognition that severe changes in the organic scaffolding can have minor effects on metallacrown stoichiometry and ring geometry suggests that the synthesis of new functional groups that can append metallacrowns to metal surfaces,[26] or organic polymers or form metallomesogens[27] is a reasonable goal. For example, studies are underway to characterize the liquid crystallinity of metallacrowns formed with (4-(octyloxy)salicyl)-hydroxamic acid (prepared by a modification of the synthesis of H$_3$4-ohshi) and to attach pyridyl groups (e.g., (4-((3′-pyridylmethyl)amino)salicyl)hydroxamic acid) so that metallacrowns may be appended to clean metal surfaces.

Before one can use metallacrowns as precursors for inorganic mesogens or to modify surfaces, one must ascertain whether the structure of the complex determined in the solid state is maintained when the metallacrown has been dissolved. Often, this can be
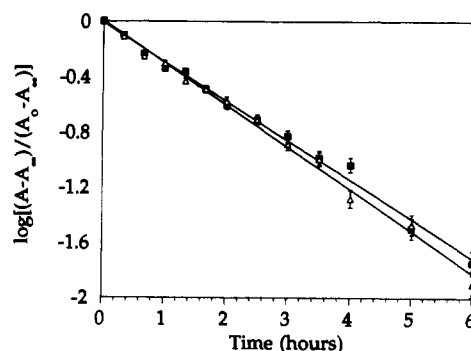
a difficult task; however, in this case data from a variety of analytical methods allow us to conclude that the generalized 9-MC$_{(VO^{3+})N}$-3 structure is retained. Molecular weight determinations using mass spectroscopy and vapor pressure osmometry are consistent with the crystallographically determined 9-MC$_{(VO^{3+})N(shi)}$-3 and 9-MC$_{(VO^{3+})N(nha)}$-3 stoichiometries. The clean proton and vanadium NMR signals demonstrate that there is only one species in solution that must have the molecular weight determined above. The concentration dependence of the visible spectra of the complexes changes linearly over a wide range of concentrations and in a variety of solvents demonstrating that the complexes do not dissociate at lower concentrations ($\geq$200 mM). Furthermore, addition of excess ligand decomposes the metallacrown in favor of the vanadium tris(hydroximate) complex in a stoichiometric reaction (i.e., 6 equiv of ligand/1 equiv of 9-MC$_{(VO^{3+})N(shi)}$-3 are required to form the tris complex). On bases of these results, we are confident that the class of 9-MC$_{(VO^{3+})N}$-3 structures are stable in acetonitrile and dry DMF and to some extent in methanol.

In the future we hope to isolate mixed-ligand metallacrowns whereby a single functionality would be incorporated into the metal complex. In order to isolate this target, ligand exchange between metallacrowns must be slow or nonexistent. We have examined the rate of ligand exchange between **1** and **4** in acetonitrile to evaluate the lability of the hydroximate ligands. Mixing equimolar solutions of **1** and **4** in acetonitrile results in no detectable ligand exchange after 48 h. However, ligand exchange in **1** and **4** can be observed in methanol and monitored conveniently by ^{1}H NMR. Significant scrambling of shi and nha is observed after only 30 min and is essentially complete after 48 h. The apparent first-order rate constant is 0.31 h^{-1}. These data demonstrate that the metallacrown ligands are dynamic in a good donor solvent such as methanol but appear to be locked into the metallacrown complex in poorer donors such as acetonitrile. Future work in the latter solvent may lead to isolation of the desired mixed-ligand metallacrowns.

Inherent to the future application of all metallacrowns is the question of solution integrity and dynamics. While molecular weight measurements and NMR spectroscopy can assess the structural question, the question of dynamics is not as easily addressed. Fortunately, the 9-metallacrown-3 motif provides a useful probe for metallacrown dynamics in solvents containing methanol. Ligand-exchange experiments using **1** with metallacrowns based on dshi or d$_2$shi circumvents thermodynamic

(25) Ostrobrod, B. G.; Markman, A. L. *Tr. Tashkent. Politekh. Inst.* **1971**, *74*, 13.

(26) Bard, A. J.; Abruña, H. D.; Chidsey, C. E.; Faulkner, L. R.; Feldberg, S. W.; Itaya, K.; Majda, M.; Melroy, O.; Murray, R.; Porter, M.; Soriaga, M. P.; White, H. S. *J. Phys. Chem.* **1993**, *97*, 7147.

(27) Maitlis, P. W.; Hudson, S. A. *Chem. Rev.* **1993**, *93*, 861.

barriers and allows for convenient study of ligand exchange by NMR. The 1:1 ligand to metal stoichiometry of **1** obviates the problem during ligand-exchange studies of metallacrowns reacting with excess ligand to form mononuclear species. In addition, the low affinity of **1** for captured metals and bridging anions allows ligand-exchange kinetics to be determined directly without complications from encapsulated metal/bridging anion-exchange processes. Using this approach we have shown that the metallacryptate **7**, which has previously been shown to retain its solution structure, is also kinetically inert in acetonitrile/methanol mixtures. The combination of the known exchange rates and the diamagnetism of **1** makes it a powerful probe of metallacrown solution dynamics.

Conclusions

An important goal for generalizing the metallacrown analogy was to prepare organic ligands with a wide variety of functional groups that retain a high-yield synthesis for the parent metallacrown structural motif. The organic ligands used in this study ((4-hydroxysalicyl)hydroxamic acid, (5-deuterio- and (3,5-dideuteriosalicyl)hydroxamic acid, and 3-hydroxynaphthohydroxamic acid) demonstrate in principle this objective. Each of these ligands will form the generalized 9-MC$_{(VO^{3+})N}$-3 structure previously reported with 9-MC$_{(VO^{3+})N(shi)}$-3 in high-yield syntheses. The X-ray structure of 9-MC$_{(VO^{3+})N(nha)}$-3, **4**, shows that the fundamental structural parameters of **1** are maintained. A variety of analytical methods including molecular weight determinations using mass spectroscopy and vapor pressure osmometry and solution probes such as ^{1}H and ^{51}V NMR and UV–vis spectroscopy

allow us to conclude that the generalized 9-MC$_{(VO^{3+})N}$-3 structure is retained in solution for the entire series of compounds. The concentration dependence of the visible spectra of the complexes changes linearly over a wide range of concentrations and in a variety of solvents demonstrating that the complexes do not dissociate even at relatively low concentrations ($\geq$200 mM), while ligand-exchange studies show that the metallacrowns are dynamic in methanol but relatively inert in acetonitrile. These two features, thermodynamic stability and relative kinetic inertness, are critical to the further exploitation of the metallacrown analogy for the purposes of preparing metallomesogens or metallopolymers. The observations that significant modifications to the organic portion of the metallacrown can have minor effects on metallacrown stoichiometry and ring geometry, that the molecules retain their structure in solution, and that ligand exchange is slow or nonexistent in organic solvents suggests that the preparation of organic ligands with new functional groups that can append nanosized metallacrowns to metal surfaces or in liquid crystals is a reasonable goal.

Supplementary Material Available: Tables 6–10, providing a complete crystallographic summary, anisotropic thermal parameters of all non-hydrogen atoms, fractional atomic positions and thermal parameters for hydrogen atoms, a complete set of bond distances, and a complete set of bond angles for **4**, Figure S1, providing a complete numbering scheme for all atoms, and Figure S2, showing the ^{1}H NMR for the mixing experiments between **1** and **4** in acetonitrile and methanol (13 pages). Ordering information is given on any current masthead page.