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Linear Chain Formation by an Oxovanadium(V) Complex of *p*-Methylhexahomotrioxacalix[3]arene

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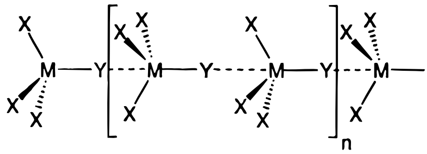
The oxovanadium(V) complex **4** can be readily synthesized by the reaction of the lithium salt of *p*-methylhexahomotrioxacalix[3]arene trianion **3** with $VOCl_3$. Infrared spectra indicate a terminal V═O for complex **4** in solution and V═O···V dative interactions in the solid state consistent with the formation of a μ-oxo-bridged linear chain polymer **1** (M = V, Y = O, X_3 = trianion of macrocycle **2a**). Vanadium-51 NMR spectra indicate increased shielding for the linear chain polymer in the solid state compared to complex **4** in solution. Complex **4** and its linear chain polymer are proposed to have the oxovanadium group contained within the cup of the macrocycle ligand as shown in structures **5** and **7**, respectively, where the cone represents macrocycle **2a**.

Introduction

Atom-bridged linear chain compounds[2−6] $[MX_n(\mu\text{-}Y)]_\infty$ (X_n = macrocycle or alkoxide ligands; Y = F, O, or N) have received much attention for their conductive,[2] liquid crystalline,[3] and nonlinear optical[4] properties. The μ-oxo- and μ-nitrido-bridged linear chain polymers $[MX_n(\mu\text{-}Y)]_\infty$ (Y = O, N) are particularly attractive as electro-optical materials, since linear chain formation results in one-dimensional alignment of the individual M−Y dipoles present in the asymmetrically μ-Y-bridged monomeric units (i.e. **1**). Tuning of the electronic properties of the X donors in such systems could potentially be used to modify the electro-optical properties of the linear chain polymers. In many of these systems, however, modification of the X ligand results in the formation of cyclic oligomers instead of linear chains.[7] For example, a number of $M(\equiv N)X_3$ complexes are known to form $[M(\mu\text{-}N)X_3]_\infty$ (M = Mo, W) linear chain polymers[4,6a,b] **1** (M = Mo, W; Y = N); however, modification of the X ligand results in μ-X-bridged dimers,[7a] as well as μ-nitrido bridged dimers,[7b] trimers,[7c] and tetramers.[7c−h] In contrast with simple X ligands (X = halide, alkoxide, aryloxides), macrocyclic systems (X = porphyrin, phthalocyanine, calix[4]arene) tend to favor linear chain formation over cyclooligomerization due to the coordination properties of the macrocycle ligands and their tendency to stack in the solid state.[2,3,5]



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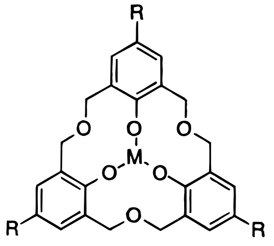
The reports of linear chain polymer formation by MYX_3 complexes[4,8] (X = halide or alkoxide; Y = O, N) has led us to consider the synthesis of the linear chain polymers **1**, where the X donors are the aryloxide oxygens in the hexahomotrioxacalix[3]arene macrocycles[9] **2**, abbreviated to oxacalix[3]arenes in this paper. The oxacalix[3]arenes are attractive X ligand candidates for the formation of the linear chains **1**, since they form complexes with a wide variety of metals[10−13] (i.e. $[M(L)(DMSO)]_2$, M = Sc, Y, Lu, La, and $[Ti(L)(O\textit{i}Pr)]_2$, where L = the trianion of macrocycle **2b**) and the shallow cupping[14] of the macrocycle ligand in these complexes is anticipated to favor stacking of the monomeric MYX_3 units in the solid state. In addition, the ease of variation of the macrocycle *para* substituents[9a,d] will allow a mechanism for fine tuning the properties of the linear chain polymers without loss of the linear chain structure.



2a: M= H_3, R= Me
2b: M= H_3, R=*t*Bu
3: M= Li_3, R= Me
4: M= VO, R= Me

In this paper, we describe the synthesis of the lithium salt of the *p*-methyloxacalix[3]arene trianion **3** and its use as a reagent in the synthesis of the oxovanadium(V) complex **4**. Complex **4** is observed to form *μ*-oxo-bridged linear chain polymers **1** (M = V, Y = O) in the solid state as evidenced by FTIR, NMR, and X-ray diffraction data.

Experimental Section

General Conditions. All solvents were dried using either calcium hydride or sodium−benzophenone ketyl and degassed. Methyllithium (1.4 M in hexanes) and $VOCl_3$ were purchased from Aldrich. *p*-Methyloxacalix[3]arene **2a** was prepared according to literature procedures.[9a] Complexes **3** and **4** were prepared and handled under inert atmosphere using either Schlenk or drybox techniques. Mass spectra (HR-FAB) were performed at the Midwest Center for Mass Spectrometry. Atomic absorption measurements were obtained on a Perkin−Elmer Model 303 spectrophotometer.

Solution NMR spectra were obtained on a Bruker AC-250 at 250.1 MHz for ^1H, 62.9 MHz for ^{13}C, and 65.8 MHz for ^{51}V, at 298 K using a 5 mm broadband probe. ^1H NMR spectra were referenced to TMS or protio solvent impurity, ^{13}C NMR spectra were referenced to the deuterated solvent, and ^{51}V NMR spectra were referenced to $VOCl_3$ in $CDCl_3$ ($\delta = 0.0$ ppm). Solid-state magic angle spinning (MAS) ^{51}V NMR spectra were recorded on a Bruker AMX400 and a ASX300 using 4 mm broadband MAS probes at resonant frequencies of 105.1 and 78.9 MHz, respectively. A standard Bloch decay using $\pi/6$ pulses, a 1 μs dwell, a 5 s decay and a spinning speed of 10 kHz was employed. An external $VOCl_3$ solution was used as reference ($\delta = 0.0$ ppm). Solid-state cross-polarized magic angle spinning (CPMAS) ^{13}C NMR spectra were obtained on a Bruker AMX400 at a resonant frequency of 100.6 MHz using a 2 ms contact time, 9 kHz spinning speed, and a 5 s recycle delay. The ^{13}C CPMAS-NMR spectra were referenced to the carbonyl ($\delta = 176.0$ ppm) in external crystalline glycine.

Synthesis of the Lithium Salt of *p*-Methyloxacalix[3]arene Trianion (3). In an inert atmosphere glovebox, 31.3 mg of CH_3Li (1.4 mmol) was added to a solution of 200 mg of *p*-methyloxacalix[3]arene **2a** (0.44 mmol) in 20 mL of diethyl ether. A white precipitate formed on stirring under inert atmosphere overnight. The solid was collected, washed with ether, and dried *in vacuo* for 24 h. Yield: 94%. ^1H NMR ($CDCl_3$): δ 7.03 (s, 6H, macrocycle 3,5-aryl protons), 4.62 (d, J = 10.0 Hz, 6H, macrocycle methylene protons), 4.24 (d, J = 10.0 Hz, 6H, macrocycle methylene protons), 2.10 (s, 9H, methyl protons). HRFAB (*o*-nitrophenyl octyl ether matrix): Calcd for $[C_{27}H_{27}Li_3O_6]_2$, m/z (M^+) 936.5; found, m/z (M^+) 936.6. Anal. Calcd for $C_{27}H_{27}Li_3O_6$: C, 69.25; H, 5.81; Li, 4.45. Found: C, 68.93; H, 5.82; Li, 4.40. Lithium analysis was performed by atomic absorption measurements of HNO_3 acidified solutions of **3**.

Synthesis of Oxovanadium(V)-*p*-Methyloxacalix[3]arene (4). In an inert-atmosphere glovebox, 32 mg of $VOCl_3$ (0.19 mmol) was added to a solution of 72 mg of trianion **3** (0.15 mmol) in 7 mL of $CHCl_3$. The solution immediately turned dark green and a white precipitate formed. The precipitate (LiCl) was removed by filtration, and 3 mL of THF was added to the filtrate. On sitting overnight, an orange solid formed which had a fibrous appearance. The solid was collected, washed with hexane, and dried *in vacuo* for 24 h. Yield: 81%. ^1H NMR ($CDCl_3$): δ 7.06 (s, 6H, macrocycle 3,5-aryl protons), 4.76 (d, J = 10.0 Hz, 6H, macrocycle methylene protons), 4.41 (d, J = 10.0 Hz, 6H, macrocycle methylene protons), 2.26 (s, 9H, methyl protons). ^{13}C NMR ($CDCl_3$): δ 169.9 (3C, 1-aryl), 132.4 (3C, 4-aryl), 130.5 (6C, 3,5-aryl), 124.1 (6C, 2,6-aryl), 71.9 (6C, CH_2), 20.5 (3C, methyl). ^{51}V NMR ($CDCl_3$): δ −320 ppm. ^{13}C NMR (solid, CPMAS, 100.6 MHz): δ 169.7 (3C, 1-aryl), 130.3 (3C, 4-aryl), 128.7 (6C, 3,5-aryl), 124.9 (6C, 2,6-aryl), 72.4 (6C, CH_2), 18.4 (3C, methyl). ^{51}V NMR (solid, MAS): δ −383 ppm (105.1 MHz), −385 ppm (78.9 MHz). FTIR ($CHCl_3$): $\nu_{V=O}$ 929 cm^{-1}. FTIR (KBr): $\nu_{V=O}$ 852 cm^{-1}. UV−visible (DMSO): λ (log ϵ) 383 nm (3.47). HRFAB (*o*-nitrophenyl octyl ether matrix): Calcd for $C_{27}H_{27}O_7V$, m/z (M^+) 514.12; found, m/z (M^+) 514.12.

X-ray powder diffraction data were collected for complex **4** on a Siemens D5000 X-ray powder diffractometer utilizing Cu Kα radiation ($\lambda_{av} = 1.5418$ Å) and equipped with a diffracted beam monochromator and a scintillation detector. Data were collected for a smear mount of the solid complex **4** over 10 h with a step size of 0.02 deg/step and a counting time of 10 s. A plot of relative intensity vs 2θ is shown in Figure 1, and a listing of the *d*-spacings of the observed peaks and their relative intensities are provided in Table 1.

Results and Discussion

The treatment of *p*-methyloxacalix[3]arene **2a** with 3 equiv of methyllithium in diethyl ether yields the lithium salt of the macrocycle trianion **3** in high yield. The room-temperature ^1H NMR spectrum of **3** displays a pair of doublets for the methylene protons (C_{3v} symmetry) which is consistent with a cupped[10−13] macrocycle ligand. There is no evidence for the equilibration of the macrocycle faces at high temperature (332 K). The mass spectral data are consistent with a dimeric complex. The lithium

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(14) The extent of cupping can be defined as the dihedral angle between the mean planes of the aryl rings with respect to the plane containing the aryloxide oxygens. The average dihedral angles for the $[M(L)(DMSO)]_2$ complexes are 45.2° (M = Sc), 52.2° (M = Lu), 52.6° (M = Y), and 54.9° (M = La)[10,11] and 40.3° for the $[Ti(L)(O\textit{i}Pr)]_2$ complex.[13]

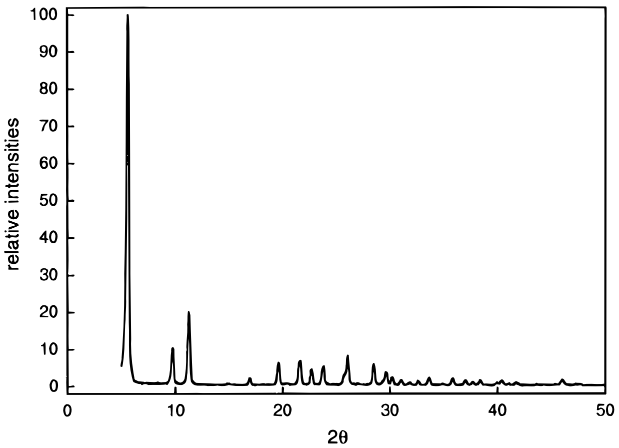


Figure 1. X-ray powder diffraction pattern for complex **4** in the solid state.

Table 1. X-ray Powder Diffraction Data (*d*-Spacing vs Relative Intensity) for Complex **4**

2θ	rel intensity	2θ	rel intensity
15.7354	100.00	2.3839	1.20
9.0711	10.34	2.3421	1.68
7.8505	20.03	2.2545	1.02
5.9102	0.73	2.2315	1.54
5.2261	2.08	2.194	0.77
4.5198	6.34	2.1602	1.01
4.3443	0.88	2.0709	0.48
4.1063	6.86	1.9981	0.64
3.9141	4.61	1.9707	1.81
3.7355	5.28	1.9226	0.69
3.4582	2.85	1.9078	0.67
3.4151	8.23	1.8056	0.67
3.302	0.65	1.754	0.54
3.1288	6.02	1.733	0.57
3.0105	3.85	1.7022	0.96
2.9565	2.43	1.6479	0.69
2.8765	1.62	1.6214	0.70
2.8106	1.06	1.5601	0.38
2.7409	1.46	1.5363	0.60
2.6605	2.37	1.5022	0.37
2.5664	0.71	1.4821	0.58
2.5026	2.15	1.4429	0.41
2.4248	1.60	1.2253	0.37

atoms in this complex are proposed to coordinate to the oxacalix[3]arene macrocycle via a pair of μ_2-aryloxo linkages and one ether linkage; dimer formation may occur by the formation of one or more μ_3-aryloxo linkages between the monomeric units.

The lithium salt of the macrocycle trianion **3** reacts readily with $VOCl_3$ in chloroform or THF to provide an orange/green solution of complex **4**. Only one oxovanadium(V) complex is formed in this reaction as evidenced by the presence of one set of macrocycle signals in ^{1}H NMR spectra of complex **1** and the single V=O stretch in IR spectra. The ^{1}H and ^{13}C NMR spectra indicate the macrocycle ligand in the complex possesses C_{3v} symmetry which is consistent with a cupped macrocycle ligand; no dynamic behavior was observed. Solution FTIR spectra of complex **4** exhibit an intense V=O stretch at 928 cm^{-1}; this $\nu_{V=O}$ is in the range (910−1010 cm^{-1}) typically observed for a terminal V=O.[3a−d,5a,c,15−17] Attempts to prepare complex **4** via the reaction of macrocycle **2a** with $VOCl_3$ in the presence of triethylamine resulted in decomposition of the macrocycle.

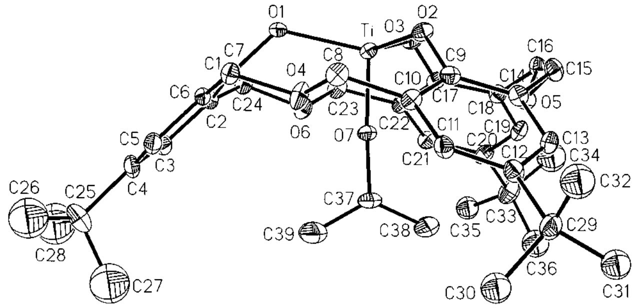
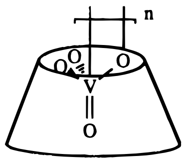
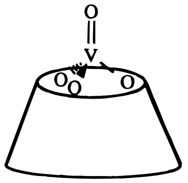


Figure 2. ORTEP diagram (20% probability) of the $[Ti(L)(O\textit{i}Pr)]_2$ monomer unit (L = trianion of macrocycle **2b**).

We propose that complex **4** has structure **5** where the cup represents the oxacalix[3]arene macrocycle ligand. Structure **5** has the oxo group within the cup of the macrocycle ligand and the metal is slightly displaced into the cup of the macrocycle. This structure has been proposed on the basis of the observation that metal ions coordinate to the oxacalix[3]arene macrocycles with the metal atom displaced into the cup of the macrocycle. An X-ray crystal structure of the monomer unit of the bis(μ-aryloxo)-bridged $[Ti(L)(O\textit{i}Pr)]_2$ complex (L = the trianion of macrocycle **2b**) is shown in Figure 2.[18] Since Ti(IV) and V(V) are similar in size, the $[Ti(L)(O\textit{i}Pr)]$ monomeric unit (Figure 2) is structurally analogous to the monomeric [V(=O)(L)] complex **4** (L = the trianion of macrocycle **2a**). The substitution of V(V) for Ti(IV) and an oxo group for the isopropoxide ligand in Figure 2 results in the "oxo-in" isomer (structure **5**) of complex **4**. The crystal structure for $V(=O)(OCH_2CH_2Cl)_3$ also provides support for the proposed structure **5**; the vanadium atom in the $V(=O)(OCH_2CH_2Cl)_3$ complex is displaced 0.3 Å out of the plane of the alkoxide oxygen atoms, and both the vanadium atom and oxo group are on the same side of this plane as the alkoxide ligands.[15] In contrast with the "oxo-in" isomer, the "oxo-out" isomer (structure **6**) has the oxo group and the aryloxide rings on opposite sides of the plane containing the phenolic oxygen atoms. The "oxo-out" structure **6** has precedence in the crystal structure of an oxotungsten(VI)−calix[4]arene complex ([W(=O)(L″)(DMF)]; L″ = the tetraanion of the calix[4]arene) which has its oxo group outside of the calix[4]arene macrocycle cup.[19] Although we believe complex **4** possesses the "oxo-in" structure **5**, we cannot exclude the possibility that this complex possesses the "oxo-out" structure **6**.



5 (n=1)
8 (n=2)



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A fibrous orange precipitate gradually forms from a THF or chloroform solution of complex **4** over several days. The filtrate

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(18) In a previous paper,[12] we proposed that the $[Ti(L)(O\textit{i}Pr)]_2$ complex was a mixture of a monomer and bis(μ-isopropoxo)-bridged dimer, with the isopropoxide ligand coordinated outside of the macrocycle cup. The crystal structure for this complex (Figure 2) clearly shows that the complex possesses bis(μ-aryloxo)-bridges involving O1 and that the isopropoxide ligand is contained within the macrocycle cup. This location of the isopropoxide ligand is consistent with the observed chemical shift (−0.16 ppm) for the *gem*-dimethyl groups, since the isopropoxide ligand would be in the shielding region of the macrocycle aryl rings.

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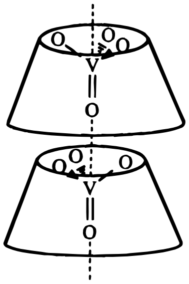
from the isolation of the orange solid frequently contained a green impurity which was presumed to be a V(IV) species on the basis its paramagnetically broadened ^{1}H NMR spectrum. The isolated orange solid is sparingly soluble in chloroform and THF but is soluble in DMSO or DMF; in all of these solvents, the complex dissolves to form a yellow/orange colored solution. The solid-state ^{13}C CPMAS spectrum of the orange solid is essentially identical (C_{3v} symmetry) to that of complex **4** in solution ($CDCl_3$) and exhibits narrow lines ($\Delta\nu = 100$ Hz) indicating high crystallinity. The HRFAB mass spectrum is consistent with the monomeric complex **4**. Attempts to obtain single crystals of complex **4** have been unsuccessful due to the tendency of the compound to form thin needles which are too small for a single-crystal X-ray analysis.

Several pieces of data indicate that the solid-state form of complex **4** is an asymmetric μ-oxo-bridged linear chain polymer **1** (M = V, Y = O, X_3 = trianion of macrocycle **2a**) which we propose to have structure **7**. The shift of the V=O stretch in FTIR spectra to lower energy ($\nu_{V=O}$ 852 cm^{-1}) in the solid state compared to solution ($\nu_{V=O}$ 928 cm^{-1}) is consistent with the formation of a μ-oxo-bridged structure in the solid state. A similar large shift is observed for other metal−oxo and −nitrido complexes on linear chain formation.[3−6] The low-energy $\nu_{V=O}$ observed for complex **4** in the solid state is in contrast with a related [V(=O)(O-4-tBuC$_6$H$_4$)$_3$] complex which exhibits a high-energy $\nu_{V=O}$ in the solid state (1020 cm^{-1}) and no evidence of linear chain formation.[17] The fiberlike morphology of the orange solid and the preferred orientation observed in the X-ray powder diffraction powder data (Table 1 and Figure 1) are consistent with the tendency for linear chains to favor crystallization in one dimension. In contrast, the dimeric metal complexes of the oxacalix[3]arenes ([M(L)(L′)]$_2$: L = trianion of macrocycle **2b**; M = Ti(IV), L′ = O*i*Pr; M = Sc(III), Lu(III), Y(III), and La(III), L′ = DMSO] tend to crystallize as plates.[10−13] Due to the severe preferred orientation and poor crystallinity of the linear chain polymer, indexing of the X-ray powder diffraction data was not possible. However, the strong reflection at a *d*-spacing of 15.7 Å ($2\theta = 5.62°$) resembles the anticipated diameter of the cupped macrocycle on the basis of the [Ti(L)(O*i*Pr)]$_2$ complex.[13] The low solubility of the solid state form of complex **4** is also consistent with a polymeric structure, since the [M(L)(L′)]$_2$ complexes[10−13] exhibit good solubility in organic solvents (i.e. $CHCl_3$, THF).



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The solid-state ^{51}V MAS spectrum for complex **4** is shown in Figure 3. A single sharp ($\Delta\nu = 500$ Hz), well-resolved isotropic chemical shift with the associated spinning sideband manifold is clearly evident in this spectrum. The ^{51}V nucleus has spin $^7/_2$ and may be influenced by second-order quadrupolar perturbations; the observed central isotropic chemical shift (denoted with Δ, Figure 3) is associated with the $+^1/_2$ to $-^1/_2$ transition. The measurement of the ^{51}V chemical shifts at both 105.1 MHz ($\delta_{obs} = -383$ ppm) and 78.9 MHz ($\delta_{obs} = -385$ ppm) allows the determination of the isotropic chemical shift ($\delta_{iso} = -380$ ppm) and the magnitude for the second order quadrupolar interaction, $(e^2qQ/h)(1 + \eta^2/3)^{1/2} = 3.4$ MHz.[20] The strength of the second order quadrupolar interactions is comparable to that observed in oxovanadium(V) alkoxide derivatives.[16] The isotropic ^{51}V chemical shift ($\delta_{iso} = -380$ ppm) for complex **4** in the solid state is upfield of the chemical shift observed for **4** in solution (−320 ppm).

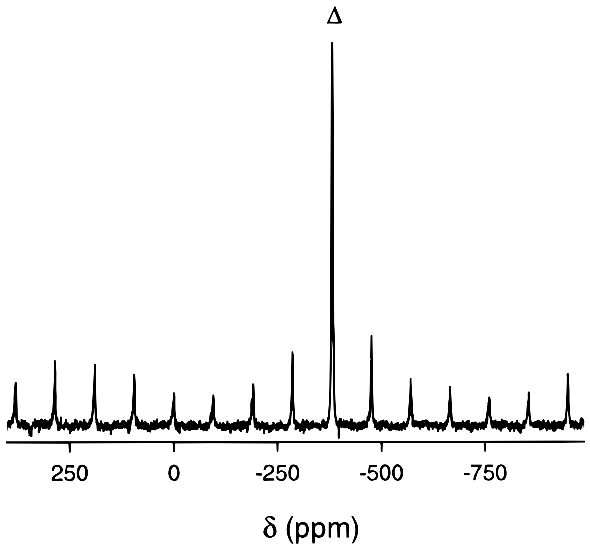

Figure 3. 105.1-MHz ^{51}V MAS-NMR spectrum for complex **4**. The symbol Δ denotes the isotropic chemical shift.

An increase in coordination number usually results in a deshielding of the vanadium center, whereas an increase in the electronegativity of the coordinating ligands increases the shielding.[15,16,21] In the case of the linear chain polymer **1**, the deshielding resulting from increased coordination number in the solid state (five-coordinate) vs solution (four-coordinate) may be compensated by the increased electronegativity of the ligands resulting from the V=O···V dative interaction and the lengthening[3a,5a] of the V=O bond on linear chain formation. To our knowledge, this is the first example of the use of ^{51}V NMR to probe linear chain formation by oxovanadium complexes.

The ease at which complex **4** forms μ-oxo-bridged linear chain polymers is in marked contrast with the tendency for oxovanadium(V) alkoxides to crystallize as bis(μ-alkoxo)-bridged dimers.[15,22] A similar tendency to form bis(μ-aryloxo)-bridged dimers is exhibited by metal complexes of the oxacalix[3]arenes (i.e. [M(L)(L′)]$_2$: L = trianion of macrocycle **2b**; M = Ti(IV), L′ = O*i*Pr; M = Sc(III), Lu(III), Y(III), and La(III), L′ = DMSO). The formation of the bis(μ-aryloxo)-

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(20) The observed ^{51}V chemical shifts may possess non-negligible contribution from second-order quadrupolar interactions such that the observed chemical shift is given by $\delta_{obs} = \delta_{iso} + \delta^{(2)}$. The second-order quadrupolar contribution ($\delta^{(2)}$) is given by eq 1, where e^2qQ/h and η are the principal component and asymmetry of the electrical field gradient tensor and ν_0 is the nuclear Larmor frequency. Field-dependent measurements of δ_{obs} allow the isotropic chemical shift and the magnitude of the second-order quadrupolar interaction to be evaluated. The central isotropic chemical shift was identified by obtaining spectra at different spinning speeds.

$$\delta^{(2)}\ (\mathrm{ppm}) = -2551\nu_0^{-2}(e^2qQ/h)^2(1 + \eta^2/3) \qquad (1)$$

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(22) Caughlan, C. N.; Smith, H. M.; Watenpaugh, K. *Inorg. Chem.* **1966**, *5*, 2131.

bridged dimer **8** by complex **4** can be excluded, since the solution and solid-state (CPMAS) ^{13}C NMR spectra of complex **4** indicate C_{3v} symmetry for the macrocycle. The solution C_{3v} symmetry is retained even at low temperatures (238 K) in contrast with the bis(μ-aryloxo)-bridged $[M(L)(DMSO)]_2$ dimers (M = Sc, Lu, Y, La) which exhibit C_s symmetry in this temperature region.[11,12]

Conclusion

The lithium salts of the oxacalix[3]arene macrocycle trianions **3** are useful reagents for the preparation of metal complexes of the macrocycles. In contrast with the decomposition of the oxacalix[3]arene macrocycles **2** in the presence of Lewis acidic metal halides, the macrocycle trianions **3** react to form metal complexes in high yield. Oxovanadium(V) complexes **4** of the oxacalix[3]arene macrocycles **2** can be readily synthesized by utilizing the macrocycle trianions **3**, and they exhibit the ability to form μ-oxo-bridged linear chain polymers **1** (M = V, Y = O) in the solid state. To our knowledge, this is the first report of linear chain formation by oxovanadium(V) complexes. Efforts are currently underway to synthesize oxovanadium(V) complexes **4** of other oxacalix[3]arene macrocycles **2** with the goal of obtaining X-ray-quality crystals of the complexes.

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