Inorg. Chem. **1995**, *34*, 5641−5645

Synthesis, X-ray Structure, and Dynamic Behavior of a Scandium−Oxacalix[3]arene Complex

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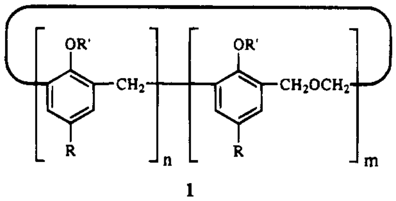
Received March 31, 1995⊗

The coordination of Sc(III) to the oxacalix[3]arene macrocycles has been investigated. Reaction of Sc(trifluoromethanesulfonate)$_3$ with *p-tert*-butyloxacalix[3]arene, **2**, in the presence of triethylamine results in the formation of the neutral complex $[Sc_2L_2(dmso)_2]\cdot 2dmso\cdot acetone$, **3**, where L is the trianion of *p-tert*-butyloxacalix[3]arene. The colorless crystals of **3**, chemical formula $C_{41.5}H_{60}O_{8.5}S_2Sc$, are monoclinic, space group $P2_1/n$, with $a = 15.938(6)$ Å, $b = 11.328(3)$ Å, $c = 25.075(7)$ Å, $\beta = 94.62(1)°$, and $Z = 4$; R refined to 0.112. The single-crystal X-ray structure of **3** indicates the complex is dimeric with two μ-aryloxo linkages. The macrocycle in **3** coordinates as a trianionic, eight electron donor to scandium through each of the aryloxide oxygens and one ether linkage. Variable temperature ^1H NMR studies provide evidence for a dynamic isomerization of **3** on the NMR time scale.

Introduction

Calixarenes have been extensively examined for their ability to form metal complexes and to extract metal ions from aqueous solutions.[1-4] Examples of Ti^{4+}, Fe^{3+}, Co^{2+}, WO^{4+}, and Eu^{3+} complexes of calix[*n*]arenes (**1a**: R = *t*-Bu, R′ = H, *n* = 4, 6, or 8, *m* = 0) have been reported.[1] The bishomooxacalix[4]arenes (**1b**: R = *t*-Bu, R′ = H, *n* = 3, *m* = 1) form complexes with UO_2^{2+}, Y^{3+}, and Eu^{3+}.[2] Calix[*n*]arenes (**1a**) and O-alkylated calix[*n*]arenes (**1**: R = *t*-Bu, R′ = alkyl, $CH_2CO_2CH_3$, *n* = 4, 6, and 8, *m* = 0) have been reported to extract metals from aqueous solutions and to transport metals across a liquid−liquid membrane.[3,4]



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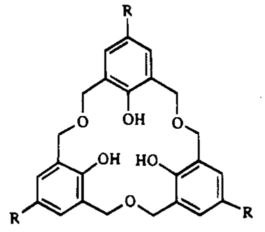
In contrast to the numerous studies of metal complexation by calix[*n*]arenes and bishomooxacalix[4]arenes, there have been only limited studies on the metal complexing ability of the hexahomotrioxacalix[3]arenes **2**, abbreviated "oxacalix[3]arenes" in this paper.[5,6] Recently, we reported a new synthesis of the *p*-R-oxacalix[3]arenes **2** (R = *t*-Bu, *i*-Pr, Et, Me, Cl) that provides the macrocycles in good yields and allows for a thorough study of their metal-complexing ability.[5] The *p*-chlorooxacalix[3]arene **2** (R = Cl) is observed to complex sodium ions in the absence of base and to complex sodium ions and potassium ions with greater affinity than lithium ions in the presence of triethylamine. The more electron-rich *p*-alkyloxacalix[3]arenes **2** (R = *t*-Bu, *i*-Pr, Et, CH_3) exhibit binding of alkali metals only in the presence of a strong base (OH^-).[5] We have also reported the isolation and characterization of a titanium complex of the *p-tert*-butyloxacalix[3]arene **2** (R = *t*-Bu) and a mechanistic study of its dynamic isomerization.[6]



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In this paper, we describe the synthesis, X-ray structure, and dynamic behavior of a scandium complex, **3**, of the *p-tert*-butyloxacalix[3]arene macrocycle. This is the first X-ray structure of a metal complex of an oxacalix[3]arene.

⊗ Abstract published in *Advance ACS Abstracts*, October 1, 1995.

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Experimental Section

General Procedures. All solvents were dried using either calcium hydride or sodium benzophenone ketyl and degassed. *p-tert*-Butyloxacalix[3]arene and scandium trifluoromethanesulfonate [Sc(OTf)$_3$] were prepared by literature procedures.[5,7] The scandium complex **3** was prepared and handled under inert atmosphere using either Schlenk or drybox techniques. NMR spectra were recorded on a Bruker AC-250 at resonant frequencies of 250 and 62.9 MHz for ^{1}H and ^{13}C, respectively. Chemical shifts were referenced to either tetramethylsilane or protio solvent impurity. Attached proton test experiments were carried out on ^{13}C NMR spectra so that negative peaks [APT(−)] and positive peaks [APT(+)] correspond to carbon atoms possessing an odd and even number of hydrogens, respectively. Elemental analyses were performed by Galbraith Laboratories.

Synthesis of [Sc$_2$L$_2$(dmso)$_2$]·2dmso·acetone (3). In an inert atmosphere glovebox a solution of 34 mg of Sc(OTf)$_3$ (0.071 mmol) in 50 μL of dmso was added to a solution of 34 mg of *p-tert*-butyloxacalix[3]arene (0.064 mmol) and 30 mg of triethylamine (0.29 mmol) in 4 mL of acetone. A white precipitate formed upon stirring under inert atmosphere for 3 h. The solid was collected, washed with acetone, and dried *in vacuo* for 24 h. Yield: 55%. A suitable crystal for single crystal X-ray analysis was obtained overnight by performing the same procedure except the dmso volume was increased to 1 mL and the stirring was eliminated after 5 min. The ^{1}H and ^{13}C NMR spectra for the precipitate and the crystals were identical. ^{1}H NMR (dmso-d_6, 298 K): δ 6.97 (s, 6H, 3,5-aryl protons), 4.80 (d, J = 8.7 Hz, 6H, methylene protons), 4.14 (d, J = 8.7 Hz, 6H, methylene protons), 1.16 (s, 27H, *tert*-butyl protons). ^{13}C NMR (dmso-d_6, 298 K): δ 161.5 (3C, 1-aryl), 138.9 (3C, 4-aryl), 126.3 (6C, 3,5-aryl), 125.8 (6C, 2,6-aryl), 72.1 (6C, CH$_2$), 33.3 (3C, C(CH$_3$)$_3$), 31.7 (9C, C(CH$_3$)$_3$). ^{1}H NMR (toluene-d_8, 298 K): δ 7.18 (s, 2H, 3,5-aryl protons), 7.16 (s, 2H, 3,5-aryl protons), 7.15 (s, 2H, 3,5-aryl protons), 6.51 (d, J = 8.3 Hz, 2H, methylene protons), 5.82 (d, J = 9.1 Hz, 2H, methylene protons), 4.84 (d, J = 8.3 Hz, 2H, methylene protons), 4.27 (d, J = 9.1 Hz, 2H, methylene protons), 4.21 (d, J = 8.7 Hz, 2H, methylene protons), 4.08 (d, J = 8.7 Hz, 2H, methylene protons), 1.30 (s, 18H, C(CH_3)$_3$), 1.21 (s, 9H, C(CH_3)$_3$), 0.42 (s, 6H, (CH_3)$_2$SO). ^{13}C NMR (toluene-d_8, 298 K): δ 163.0 (2C, APT(+), 1-aryl), 158.9 (1C, APT(+), 1-aryl), 141.6 (1C, APT(+), 4-aryl), 137.1 (2C, APT(+), 4-aryl), 130.1 (2C, APT(+), 2,6-aryl), 129.5 (2C, APT(−), 3,5-aryl), 128.6 (2C, APT(−), 3,5-aryl), 128.2 (2C, APT(+), 2,6-aryl), 127.8 (2C, APT(−), 3,5-aryl), 126.9 (2C, APT(+), 2,6-aryl), 75.6 (2C, APT(+), CH$_2$), 74.5 (2C, APT(+), CH$_2$), 72.9 (2C, APT(+), CH$_2$), 34.4 (2C, APT(−), (CH$_3$)$_2$SO), 34.3 (3C, APT(+), C(CH$_3$)$_3$), 32.5 (6C, APT(−), C(CH$_3$)$_3$), 32.2 (3C, APT(−), C(CH$_3$)$_3$). Anal. Calcd for $C_{41.5}H_{60}O_{8.5}S_2Sc$: C, 62.00; H, 7.52. Found: C, 62.28; H, 7.64.

X-ray Crystallographic Studies. A colorless, monoclinic needle used for X-ray study (0.23 × 0.23 × 0.81 mm) was sealed in a glass capillary under nitrogen. A total of 6639 independent reflections (R_{int} = 1.89%) were measured on a Siemens R3m/V diffractometer using graphite monochromated Mo Kα radiation, with ω scan mode, $2\theta_{\max}$ = 47°. After absorption correction (semiempirical), the structure was solved by direct methods using SHELXTL PC and refined by the full-matrix least-squares method[8] ; scattering factors were taken from ref 9. The octants of data collected were h, k, $\pm l$. Anisotropic thermal parameters were refined for all non-hydrogen atoms except those in which the final difference Fourier map displayed signs of disorder (*tert*-butyl group on phenyl ring **B**, sulfur and methyls of the coordinated dmso, Figure 1). The asymmetric unit has a stoichiometry of ScL(dmso)·dmso·0.5acetone. No corrections for extinction were made. Hydrogen atoms were calculated and allowed to ride on the carbon atom to which they were bonded with fixed U values. The final agreement factors were R = 0.113 and R_w = 0.112 for 3300 observed reflections having $F > 2.0\sigma(F)$, the function minimized being $\sum w(\Delta F^2)$ [statistical weights derived from $w^{-1} = \sigma(F) + 0.0030F^2$]. Crystallographic data and basic details of data collection for **3** are presented in Table 1.

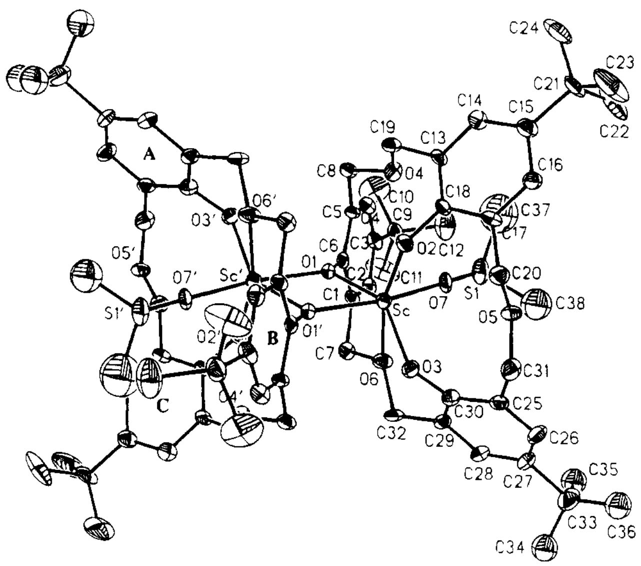

Figure 1. ORTEP drawing of [Sc$_2$L$_2$(dmso)$_2$]·2dmso·acetone (**3**). Ellipsoids are drawn at the 20% probability level. Primed and unprimed symbols denote atoms related by an inversion center.

Table 1. Crystallographic Data for [Sc$_2$L$_2$(dmso)$_2$]·2dmso·acetone (**3**)

chem formula: $C_{41.5}H_{60}O_{8.5}S_2Sc$	space group: $P2_1/n$
fw = 804.0	T = 20 °C
a = 15.938(5) Å	λ = 0.710 73 Å
b = 11.328(3) Å	ρ_{calcd} = 1.183 g cm^{-3}
c = 25.075(7) Å	μ = 30.3 cm^{-1}
β = 94.62(1)°	transm = 0.873−0.929
V = 4513(2) Å^3	$R(F_o)^a$ = 0.113
Z = 4	$R_w(F_o)^b$ = 0.112

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

Results and Discussion

Synthesis and Characterization of [Sc$_2$L$_2$(dmso)$_2$]·2dmso·acetone (3). The reaction of *p-tert*-butyloxacalixarene **2** (R = *t*-Bu) with Sc(OTf)$_3$ in a dmso/acetone mixture and an excess of triethylamine readily affords complex **3** as a colorless, amorphous powder. X-ray quality crystals could be prepared by increasing the dmso concentration. The powder and the crystals were the same compound based on ^{1}H NMR spectra.

The overall molecular configuration of **3** and the atom numbering system are given in Figure 1, and Tables 1−3 summarize the crystallographic results.

The structure determination of complex **3** was complicated by the high thermal motion and associated disorder of the *tert*-butyl group and the dmso molecules, however it was well defined in respect to the metal environment and core atoms of the ligand. The complex is a dimer with C_i symmetry that possesses a Sc$_2$(μ-O)$_2$ core where two aryloxide oxygens (O1 and O1′) are the bridging oxygens, Figure 1. The scandium centers are distorted octahedra with the aryloxide oxygens (O1, O2, O3 and O1′, O2′, O3′) occupying meridional coordination sites. The fifth and sixth coordination sites are occupied by one of the macrocycle ether oxygens (O6 and O6′) and unidentate dmso ligands (O7 and O7′), as indicated in Figure 1. Important bond distances and angles for **3** are given in Table 3. The Sc−O1 [2.101 Å] and Sc−O1′ [2.150 Å] bond distances are longer than the Sc−O2 and Sc−O3 bond distances (1.979 and 1.960 Å) as expected for μ-phenoxo linkages. The Sc−O2 and Sc−O3 bond distances are also longer than those (*ca.* 1.87 Å) observed for the related monomeric complex [Sc(2,6-di-*tert*-butyl-4-methylphenoxide)$_3$] that possesses bulky arylox-

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Table 2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^3) for [$Sc_2L_2(dmso)_2$]·2dmso·acetone (**3**)

atom	x	y	z	*U*(eq)[a]
Sc	746(6)	1090(2)	11(1)	39(1)
O1	545(5)	−717(6)	−137(3)	33(3)
O2	433(5)	1959(7)	−660(3)	52(3)
O3	839(5)	2235(7)	599(3)	50(3)
O4	1230(6)	−166(7)	−1253(3)	56(3)
O5	1581(5)	3995(8)	−129(3)	51(3)
O6	1585(6)	51(7)	774(3)	63(4)
C1	1744(8)	−1724(10)	256(4)	40(5)
C2	2487(8)	−2387(11)	202(5)	48(5)
C3	2680(8)	−2800(11)	−290(6)	48(5)
C4	2174(9)	−2483(11)	−722(5)	48(5)
C5	1467(8)	−1808(10)	−690(4)	39(5)
C6	1230(8)	−1430(10)	−189(4)	38(4)
C7	1555(8)	−1259(10)	802(5)	51(5)
C8	966(9)	−1358(10)	−1177(4)	51(5)
C9	3514(9)	−3455(13)	−346(6)	63(6)
C10	3394(12)	−4372(17)	−786(8)	141(11)
C11	3810(12)	−4155(19)	169(7)	143(11)
C12	4187(11)	−2625(17)	−496(8)	125(10)
C13	913(9)	1823(11)	−1521(5)	46(5)
C14	1277(8)	2314(11)	−1935(5)	55(5)
C15	1560(9)	3478(13)	−1928(5)	62(6)
C16	1432(8)	4101(11)	−1451(5)	55(5)
C17	1064(8)	3614(11)	−1040(4)	46(5)
C18	789(8)	2434(11)	−1061(5)	41(5)
C19	649(9)	574(11)	−1562(5)	51(5)
C20	952(9)	4317(12)	−542(5)	59(6)
C21	2007(12)	4033(14)	−2383(6)	78(7)
C22	2971(14)	3977(21)	−2252(8)	174(14)
C23	1815(17)	5335(17)	−2449(8)	172(14)
C24	1882(16)	3399(19)	−2892(7)	182(15)
C25	1860(9)	3720(12)	807(5)	51(5)
C26	2554(10)	4104(13)	1118(5)	66(6)
C27	2959(9)	3388(15)	1505(5)	69(6)
C28	2687(9)	2252(12)	1557(5)	54(5)
C29	1977(9)	1860(11)	1233(5)	47(5)
C30	1553(9)	2609(12)	873(5)	46(5)
C31	1445(10)	4475(12)	375(5)	68(6)
C32	1685(9)	626(11)	1298(4)	53(5)
C33	3733(11)	3889(15)	1887(6)	100(7)
C34[b]	3590	3629	2438	115(5)
C35[b]	4490	2979	1857	115(5)
C36[b]	3909	5165	1790	115(5)
O7	1979(5)	1137(8)	−174(3)	55(3)
S1	2866(5)	931(8)	−267(4)	81(3)
C37[b]	3070	889	−895	266(16)
C38[b]	3372	2235	−25	163(9)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] These atoms were of the disordered *tert*-butyl group and methyls of the dmso and were not refined; however, isotropic thermal parameters were refined.

ide ligands.[10] The Sc–OAr bond distances in the latter compound may be shorter as a result of greater π-donation in the apparent six electron complex than in the 12 electron complex **3**. The Sc–O2 and Sc–O3 bond lengths are consistent with values (*ca.* 2.02 Å) reported for the 12 electron complex, [$Sc(pic)_2(OH_2)_4$](pic)(Hpic)·8.2H_2O.[11]

The macrocycle ligand in **3** adopts a "cup" conformation similar to the metal complexes of calix[4]arenes and homooxacalix[4]arenes where the metal is the base of the cup.[1,2] In addition to the coordinating dmso, there is a dmso molecule included in each of the dimer's macrocyclic "cups". Dihedral angles (Table 3) can be used to define the pitch of the cup where a greater dihedral angle indicates a steeper cup. The dihedral angles for **3** indicate that the aryl rings (Figure 1: rings **A** and **B**) adjacent to the coordinated ether linkage (O6) are steeper than the aryl ring (Figure 1: ring **C**) adjacent to the noncoordinating ethers (O4 and O5). The binuclear species **3** is remarkably similar in structure to the dimeric europium complex of the bishomooxacalix[4]arene macrocycle (**1b**), [$Eu_2(HL)_2(dmso)_2$]·2acetone, reported by Harrowfield and co-workers where HL is the trianion of macrocycle **1b**.[2a] Both ligands adopt a cup conformation about the metal. The bishomooxacalix[4]arene macrocycle utilizes all of its five donor atoms, whereas the oxacalix[3]arene macrocycle in **3** utilizes only four of its six donor atoms. Molecular modeling studies indicate that the coordination of all six atoms of the oxacalix[3]arene macrocycle is possible only with larger metals.[12] The dihedral angles for the europium dimer (60.3, 49.7, 54.9, and 62.8°) indicate an

Table 3. Selected Bond Lengths (Å), Angles (deg), and Dihedral Angles[a] (deg) for [$Sc_2L_2(dmso)_2$]·2dmso·acetone (**3**)

Sc–O1	2.101(8)	Sc–O7	2.055(8)
Sc–O2	1.979(8)	Sc–O1′	2.150(8)
Sc–O3	1.960(8)	Sc–Sc′	3.427(5)
Sc–O6	2.535(8)		
O1–Sc–O2	108.0(3)	O3–Sc–O6	74.7(3)
O1–Sc–O3	141.1(3)	O3–Sc–O7	97.9(3)
O1–Sc–O6	75.2(3)	O3–Sc–O1′	92.0(3)
O1–Sc–O7	96.9(3)	O6–Sc–O7	74.1(3)
O2–Sc–O3	108.0(3)	O6–Sc–O1′	104.5(3)
O2–Sc–O6	162.7(3)	O7–Sc–O1′	169.2(3)
O2–Sc–O7	88.6(3)	O1–Sc–O1′	72.6(3)
O2–Sc–O1′	92.5(3)	Sc–O1–Sc′	107.4(3)
ΦA	58.3(3)	ΦC	34.9(3)
ΦB	42.5(3)		

[a] Angle between the mean planes of the aryl rings and the plane defined by O1, O2, and O3.

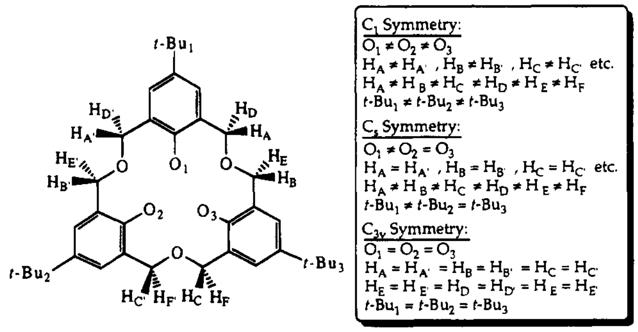

Figure 2. Effect of macrocycle symmetry on atom equivalencies.

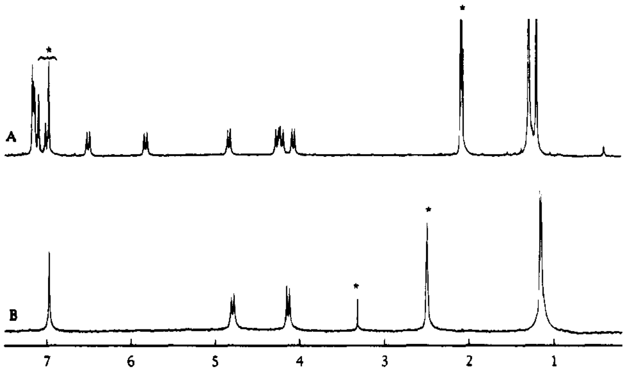

Figure 3. ^1H NMR spectra of [$Sc_2L_2(dmso)_2$]·2dmso·acetone (**3**) at 298 K: (A) spectrum in toluene-d_8, (B) spectrum in dmso-d_6. Asterisks indicate protio solvent impurity and water.

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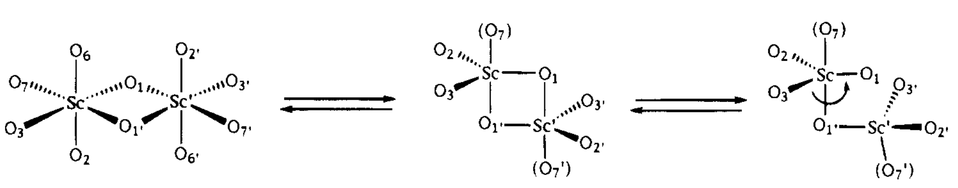
[12] Molecular modeling performed on PCMODEL, Serena Software, Bloomington, IN.



A
Low temperature
C_1 symmetry
$O_1 \neq O_2 \neq O_3$

B
Room temperature
C_s symmetry
$O_2 = O_3$

C
High temperature
C_{3v} symmetry
$O_1 = O_2 = O_3$

Figure 4. Proposed mechanisms for the dynamic behavior of complex **3**. Macrocycle labeling is the same as in Figures 1 and 2. The symmetry groups describe the macrocycle symmetry.

overall steeper cup than in **3**. Both complexes are triple inclusion complexes, with one metal atom, one O-coordinated dmso, and one solvent molecule included in the cup of the macrocycle. The included dmso molecules were omitted from Figure 1 for clarity. In contrast with **3**, the europium dimer included acetone instead of dmso. The overall shallower cup in **3** apparently allows for the inclusion of the larger dmso molecule.

^{1}H NMR Studies. As we have previously reported, ^{1}H and ^{13}C NMR spectra of oxacalix[3]arene metal complexes can serve as sensitive indicators of the metal's coordination environment.[6] In the following discussion, the "local" symmetry of the oxacalix[3]arene ligand will be discussed as opposed to the overall symmetry of the dimeric complex. Although the X-ray structure of complex **3** indicates local C_1 symmetry for the macrocycle ligand, this symmetry is inconsistent with the solution ^{1}H and ^{13}C NMR spectra of complex **3** in a noncoordinating solvent (toluene-d_8) at 298 K (Figure 3A). As shown in Figure 2, C_1 symmetry would result in complete asymmetry of the macrocycle ligand, thus each of the macrocycle methylene protons would be inequivalent and a total of twelve doublets would be observed in the ^{1}H NMR spectrum. The presence of six doublets for the methylene protons as observed in the ^{1}H NMR spectrum for **3**, Figure 3A, indicates the macrocycle possesses a mirror plane (C_s symmetry) on the NMR time scale. The aromatic and *tert*-butyl ^{1}H NMR signals and the ^{13}C NMR spectrum are also consistent with the presence of a mirror plane through the macrocycle ligand. The presence of only one signal at 0.42 ppm for the coordinated and included dmso molecules indicates that dmso decoordination and exchange is rapid on the NMR time scale.

As the temperature is lowered to 180 K, the macrocycle methylene, *tert*-butyl, and aromatic signals broaden and begin to separate. When the temperature is raised to 373 K, the macrocycle methylene doublets broaden and coalesce. At the highest temperature, the macrocycle methylene region simplified to a sharp doublet at 4.18 ppm and a broad signal at 5.72 ppm. In addition to these changes in the macrocycle methylene region, the pair of *tert*-butyl signals and the three 3,5-aryl signals collapse to singlets. This spectrum for the macrocycle methylene region is consistent with a higher coalescence temperature for the downfield macrocycle methylene signal, possibly resulting from a larger chemical shift range for the exchanging protons responsible for the broadened signal. A similar dynamic behavior and different coalescence temperatures for the macrocycle methylene protons was observed for a titanium complex of macrocycle **2** (R = *t*-Bu).[6] The high temperature spectrum for complex **3** is consistent with the macrocycle possessing C_{3v} symmetry on the NMR time scale (Figure 2, O1 = O2 = O3).

The ^{1}H NMR spectrum of **3** in the coordinating solvent dmso-d_6 consists of singlets for the 3,5-aryl and *tert*-butyl protons, and the macrocycle methylene protons appear as a pair of doublets (Figure 3B). This spectrum is consistent with the macrocycle possessing C_{3v} symmetry. No dynamic behavior was observed in the temperature range 290 to 360 K.

Solution Structure and Dynamic Behavior of Complex 3. We propose that complex **3** is dimeric in toluene existing as either structure **A** or **B** (Figure 4), and it dissociates in dmso to the six-coordinate monomeric complex **4** or **5** (L = dmso).[13,14] Structure **A** is identical to the solid state structure of complex **3** with octahedral scandium centers. The alternative structure **B** has trigonal or tetrahedral scandium centers and is consistent with the room temperature ^{1}H NMR spectrum in toluene-d_8. Structure **A** is also consistent with the ^{1}H NMR spectrum provided that dynamic isomerization results in rapid exchange of O2 and O3, and O4 and O6 on the NMR time scale. Such a dynamic process could occur through dissociation of O6 and formation of **B** as an intermediate (Figure 4). The broadened peaks in the low temperature (180 K) spectrum of **3** suggests that such a dynamic process may be occurring in solution.

The high temperature ^{1}H NMR spectrum of **3** in toluene-d_8 is consistent with **A** or **B** provided that the aryloxide oxygens (O1, O2, and O3) and the ether oxygens (O4, O5, and O6) are exchanging on the NMR time scale. This dynamic behavior could occur through cleavage of a μ-aryloxide linkage to form a ring-opened intermediate **C** (Figure 4). The intermediate **C** could then undergo rotation about the remaining μ-aryloxide linkage (Sc$-$O1′) which would result in exchange of the aryloxide and ether oxygens.

When a sample of **3** in toluene-d_8 is titrated with dmso-d_6, the six methylene doublets gradually decrease in intensity and a new pair of doublets at 4.80 ppm and 4.14 ppm appear and increase in intensity until they are the only species present at high dmso concentrations. The chemical shifts of the new doublets are different than the signals (4.18 and 5.72 ppm) in the high temperature spectrum in toluene-d_8. This result indicates that the solution species in toluene and dmso are different, since they are both present throughout the titration. The final spectrum in the titration resembles the spectrum of **3** in dmso-d_6 (Figure 3B). The monomeric complexes **4** and **5** are consistent with the dmso-d_6 spectrum provided that the ether linkages and dmso ligands in **5** are undergoing rapid exchange on the NMR time scale.

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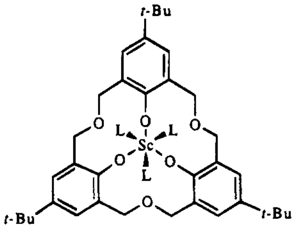
(13) Solution molecular weight measurements were not conducted on complex **3** since the acetone and included dmso molecules would contribute to the colligative properties of a solution of **3**. The calculated molecular weight for a solution of the dimeric complex **3** and 2 equiv of dmso molecules is identical to a monomeric complex with two coordinated dmso ligands, for example **5**. Removal of the dmso from complex **3** would require heating at high temperatures *in vacuo*. This was not attempted since the macrocycle **2** (R = *t*-Bu) decomposes at elevated temperatures.

(14) Most scandium complexes are six coordinate. Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1980; p 996.



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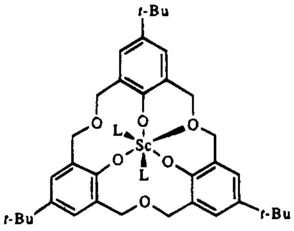

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Conclusions

Complex **3** is the first structurally characterized metal complex of an oxacalix[3]arene. The macrocycle ligand in complex **3** serves as a trianionic, eight electron donor to the scandium center through the coordination of the aryloxide oxygen atoms and one ether linkage. Variable temperature ^{1}H NMR experiments indicate dynamic behavior for complex **3** which is consistent with rapid decoordination of the ether linkage at room temperature and cleavage of a μ-aryloxide linkage at high temperature.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Sandia National Laboratories are also acknowledged for financial support of this research through the Sandia-University Research Program. The NSF Chemical Instrumentation Program is acknowledged for providing a low field NMR spectrometer. We would like to thank Dr. Zsolt Bencze for providing samples of macrocycle **2** (R = *t*-Bu) and to acknowledge Dr. Todd Alam for many helpful discussions.

Supporting Information Available: Tables of atom coordinates, bond lengths and angles, thermal parameters, hydrogen coordinates, and least squares planes and a stereoview of complex **3** (14 pages). Ordering information is given on any current masthead page.

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