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Shaping the Cavity of the Macrocyclic Ligand in Metallocalix[4]arenes: The Role of the Ligand Sphere

Udo Radius[†]

Institut für Anorganische Chemie, Engesserstrasse, Geb. 30.45, D-76128 Karlsruhe, Germany

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The coordination form of calix[4]arene ligands and therefore the cavity of the macrocyclic ligand can be controlled by other ligands in transition metal calix[4]arene complexes, if strong directing coligands such as oxo groups are used. This paper describes the synthesis and characterization of the d^0 transition metal complexes [Cax(OMe)$_2$O$_2$-TiCl$_2$] **1** (monoclinic, space group $P2_1/c$, lattice constants $a = 21.639(4)$, $b = 20.152(3)$, $c = 12.750(3)$ Å, $\beta = 95.68(3)$, $V = 5532.6(19)$ Å^3) and [Cax(OMe)$_2$O$_2$MoO$_2$] **2** (monoclinic, space group $P2/c$, lattice constants $a = 12.433(3)$, $b = 16.348(3)$, $c = 24.774(5)$ Å, $\beta = 99.15(3)$, $V = 4971.6(17)$ Å^3). Whereas in **1** the calix[4]arene ligand adopts an *elliptically distorted cone* conformation, the macrocyclic ligand binds in a paco-like conformation to the metal center of **2**, in the solid state and in solution. This was predicted by density functional theory calculations on models of different isomers of **1** and **2**: *cis,cone*-**1′**,**2′**, *trans,cone*-**1′**,**2′**, and *cis,paco*-**1′**,**2′**. According to these calculations, the energetic difference of 72.9 kJ/mol between both *cis*-dioxomolybdenum compounds is quite pronounced in favor of the cis,paco isomer, and 28.0 kJ/mol for the titanium compounds in favor of the cis,cone isomer.

Introduction

Calixarenes and related macrocycles[1] have received considerable attention for their host−guest chemistry and their ability to bind metals, so there is currently much interest in the synthesis and structural characterization of new metallocalixarenes.[2] The simplest of the calixarenes, the calix[4]arene system, usually binds in an tetradentate fashion, and retains its cone-like appearance in square pyramidal complexes of the type [CaxO$_4$-ML] (Cax = carbonhydride backbone of the *p*-*t*-Bu-calix[4]-arene, $C_{44}H_{52}$; L = monodendate ligand) or in octahedral complexes [CaxO$_4$ML$_2$], if both ligands L are oriented trans to each other. In this configuration, one of the ligands coordinates *endohedrally* to the metal atom and is located in the cage of the calix[4]arene ligand. For group 6 chemistry, imido compounds [CaxO$_4$M(NR)L′] (R = *t*-Bu, Mes; L′ = NCMe, CN-*t*-Bu, etc.) are good examples for such a coordination of the calix[4]arene ligand.[3] Furthermore, it has been found in mononuclear complexes that the calix[4]arene is capable of adopting alternative conformations in binding to metal centers, usually in an *elliptical cone* conformation, in which the calix[4]arene oxygen atoms adopt cis and trans sites in octahedral [CaxO$_4$-ML$_2$] complexes. In these compounds, the ligands L are mutually cis oriented, as has been found, for example, in the structurally characterized molybdenum[4] or tungsten[5] dichlorides [CaxO$_4$MCl$_2$]. According to density functional theory (DFT) calculations, the cis isomer of [CaxO$_4$MoCl$_2$] is approximately 18.1 kJ/mol higher in energy as compared to the trans compound, and a detailed analysis has shown that this difference in energy is almost exclusively due to the deformation energy needed to distort the calix[4]arene ligand.[6] Floriani and coworkers have shown that the conversion of *cis*-[CaxO$_4$WCl$_2$] into the thermodynamically more favorable trans isomer is facilitated by reactions with Lewis acids such as AlCl$_3$ or WCl$_6$.[5b] However, at this point we were inspired from our calculations to further investigate the possibilities coordination chemistry provides to direct the coordination behavior of calix-[4]arene ligands and to shape the cavity of the calix[4]arene ligands in transition metal complexes. To differentiate coordination sites in the macrocyclic ligand, we were planning to use the anions of calix[4]arene ethers [Cax(OMe)$_2$(OH)$_2$] or [Cax-(OMe)(OH)$_3$] as ligands in octahedral d^0 transition metal complexes of the type [Cax(OMe)$_2$O$_2$ML$_2$], [Cax(OMe)$_2$O$_2$-MLL′], or [Cax(OMe)O$_3$MLL′]. To avoid any influence of occupied transition metal d orbitals for our investigation of the role of the ligands L and L′, we decided to use metals M in their highest oxidation state. First results of our studies are presented in this publication.

Experimental Section

General. All reactions and subsequent manipulations involving organometallic reagents were performed under argon or nitrogen atmosphere using standard Schlenk techniques. The preparation of

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[†] E-mail: uradius@achibm6.chemie.uni-karlsruhe.de.

(1) (a) Gutsche, C. D. *Calixarenes*; Royal Society of Chemistry: Cambridge, 1989. (b) *Calixarenes*: *A Versatile Class of Macrocyclic Compounds*; Vincens, J., Böhmer, V., Eds.; Kluwer Academic Publ.: Dordrecht, 1991. (c) *Calixarenes 50th Anniversary: Commemorative Issue*; Vincens, J., Asfari, Z., Horrowfield, J. M., Eds.; Kluwer Academic Publ.: Dordrecht, 1994. (d) Gutsche, C. D. *Calixarenes Revisited*; Royal Society of Chemistry: Cambridge, 1998. (e) *Calixarenes in Action*; Lucinat, M., Ungaro, R., Eds.; Imperial College: London, 2000. (f) Lumetta, G. J.; Rogers, R. D.; Gopalan, A. S. *Calixarenes for Separations*; American Chemical Society: Washington, DC, 2000.

(2) (a) Floriani, C. *Chem. Eur. J.* **1999**, *5*, 19. (b) Wieser, C.; Dieleman, C. B.; Matt, D. *Coord. Chem. Rev.* **1997**, *165*, 93. (c) Roundhill, D. M. *Prog. Inorg. Chem.* **1995**, *43*, 533.

(3) (a) Radius, U.; Attner, J. *Eur. J. Inorg. Chem.* **1999**, 2221. (b) Gibson, V. C.; Redshaw, C.; Clegg, W.; Elsegood, M. R. J. *J. Chem. Soc., Chem. Commun.* **1995**, 2371. (c) Gibson, V. C.; Redshaw, C.; Clegg, W.; Elsegood, M. R. J. *J. Chem. Soc., Chem. Commun.* **1998**, 1969.

(4) Radius, U.; Attner, J. *Chem. Eur. J.* **2001**, *7*, 783.

(5) (a) Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1991**, *30*, 4465. (b) Giannini, L.; Solari, E.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1999**, *38*, 1438.

(6) Radius, U. Unpublished results.

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samples for spectroscopy was accomplished by using a Braun MB 150 BG-I glovebox. Solvents were dried according to standard procedures, stored over activated 4 Å molecular sieves and degassed prior to use. Deuterated solvents were obtained from Aldrich Inc. (all 99 at. % D), dried according to standard procedures, and stored over activated 4 Å molecular sieves. NMR spectra were recorded on a Bruker AC 250 at 298 K. ^{13}C NMR spectra were broad-band proton decoupled (^{13}C{^{1}H}). Standard DEPT-135 experiments were recorded to distinguish $-CH_3$ and $-CH$ type carbons from $-C$ or $-CH_2$ type carbons in the ^{13}C NMR spectrum. Residual solvent peaks used as internal standards were as follows: $CDCl_3$, 7.24 ppm; C_6D_6, 7.16 ppm (^{1}H); or natural-abundance carbon signal at 77.0 ppm for $CDCl_3$ and 128.0 ppm for C_6D_6 (^{13}C). EI/MS spectra were recorded on a Varian MAT 3830 (70 eV). Elemental analyses were performed by the microanalytical laboratory of the author's department. *p*-*t*-Bu-calix[4]arene, *p*-*t*-Bu-calix[4]arene dimethyl ether,[7] $[MoO_2Cl_2]$,[8] and $[TiCl_4(thf)_2]$[9] were prepared as described in the literature.

Computational Details. All density functional calculations reported in this article were carried out by using the TURBOMOLE set of programs, developed by Ahlrichs and co-workers, within the RI-J approximation.[10,11] Standard SV(P) basis sets and auxiliary basis sets as implemented in the TURBOMOLE package were used for all atoms.[11,12] The acronym SV(P) (split valence plus polarization) refers to TURBOMOLE split valence basis sets, augmented by a shell of polarization functions. Quasi-relativistic pseudopotentials were used for Mo.[13] All calculations were performed including gradient corrections, Becke's nonlocal correction for exchange, and Perdew's nonlocal correction for correlation to the local density approximation part of the density functional.[14]

Experimental Details. Synthesis of $[Cax(OMe)_2O_2TiCl_2]$ 1.[15] A slurry of 7.08 g (10.5 mmol) of $Cax(OMe)_2(OH)_2$ and 3.49 g (10.5 mmol) of $[TiCl_4(thf)_2]$ in 100 mL of toluene was stirred for 24 h at 60 °C. After cooling to room temperature, all volatiles were removed in vacuo and the residue was suspended in 40 mL of hexane. The product was filtered off, washed with small amounts of hexane, and dried in vacuo. $[Cax(OMe)_2O_2TiCl_2]\cdot C_7H_8$: dark red solid, yield 8.10 g (87%). Crystals suitable for X-ray analysis were grown by the slow diffusion of hexane into saturated toluene solutions of **1**.

Anal. Calcd. for $C_{46}H_{58}Cl_2O_4Ti\cdot C_7H_8$: C, 71.86; H, 7.51. Found: C, 71.18; H, 7.17. ^{1}H NMR (C_6D_6): $\delta = 0.68$ (s, 18 H, C(CH_3)$_3$), 1.39 (s, 18 H, C(CH_3)$_3$), 3.19 (d, 4 H, $^2J_{HH} = 13.4$ Hz, CH_2), 4.19 (s, 6 H, OCH_3), 4.60 (d, 4 H, $^2J_{HH} = 13.4$ Hz, CH_2), 6.82 (s, 4 H, Ar-H_m), 7.17 (s, 4 H, aryl-H_m). ^{13}C NMR (C_6D_6): $\delta = 30.59$, 31.87 (C(CH$_3$)$_3$), 33.81, 34.54 (C(CH$_3$)$_3$), 34.64 (CH$_2$), 71.23 (OCH$_3$), 124.85, 127.31 (Ar-C_m), 130.26, 131.64 (Ar-C_o), 144.44, 154.96 (Ar-C_p), 158.06, 165.53 (Ar-C_i). EI/MS *m/z* (%): 792 (1) $[M]^+$, 757 (5) $[M - CH_3]^+$, 742 (100) $[M - CH_3 - Cl]^+$.

Synthesis of $[Cax(OMe)_2O_2MoO_2]$ 2. In 20 mL of toluene 1.44 g (2.13 mmol) of $Cax(OMe)_2(OH)_2$ was dissolved and deprotonated with 2.7 mL of an 1.6 M solution of BuLi in hexane. The resulting solution was added to a solution of 423 mg (2.13 mmol) of $[MoO_2Cl_2]$, dissolved in a mixture of 20 mL of toluene and 2 mL of dimethoxyethane. The reaction mixture turned immediately red. It was stirred for 30 min at room temperature and for another 12 h at 100 °C. After filtration, all volatile components were removed under reduced pressure to give a red, oily solid. Addition of 15 mL of acetonitrile under gentle warming afforded a yellow, insoluble material, which was filtered off and dissolved in 10 mL of Et_2O. After 2 days at −40 °C 1.28 g (1.60 mmol, 75%) of **2** was obtained in the form of yellow crystals. Crystals suitable for X-ray analysis were grown from from either diethyl ether or acetonitrile solutions of **2**.

Anal. Calcd. for $C_{46}H_{58}O_6Mo$: C, 68.81; H, 7.28. Found: C, 68.76; H, 7.33. ^{1}H NMR (C_6D_6) $\delta = 0.79$ (s, 3 H, OCH_3), 1.06 (s, 9 H, C(CH_3)$_3$), 1.19 (s, 9 H, C(CH_3)$_3$), 1.20 (s, 18 H, C(CH_3)$_3$), 3.31 (d, 2 H, CH_2, $^2J_{HH} = 12.2$ Hz), 3.45 (d, 2 H, CH_2, $^2J_{HH} = 12.2$ Hz), 4.18 (s, 3 H, OCH_3), 4.76 (d, 4 H, CH_2, $^2J_{HH} = 12.2$ Hz), 7.09, 7.11, 7.22, 7.23 (s, 8 H, Ar−H). ^{1}H NMR ($CDCl_3$) $\delta = 0.78$ (s, 3 H, OCH_3), 1.18 (s, 9 H, C(CH_3)$_3$), 1.34 (s, 18 H, C(CH_3)$_3$), 1.42 (s, 9 H, C(CH_3)$_3$), 3.56 (d, 2 H, CH_2, $^2J_{HH} = 14.8$ Hz), 3.59 (d, 2 H, CH_2, $^2J_{HH} = 12.0$ Hz), 4.48 (d, 2 H, CH_2, $^2J_{HH} = 14.8$ Hz), 4.55 (s, 3 H, OCH_3), 4.77 (d, 2 H, CH_2, $^2J_{HH} = 12.0$ Hz), 7.16, 7.18, 7.34, 7.36 (s, 8 H, Ar−H). ^{13}C NMR ($CDCl_3$) $\delta = 31.3$, 31.7, 31.8 (C(CH$_3$)), 32.1 (CH$_2$), 34.2, 34.5, 34.5 (C(CH$_3$)), 35.9 (CH$_2$), 63.7, 66.3 (OCH$_3$), 125.1, 125.6, 125.7, 127.3 129.9, 131.8, 132.9, 134.2 (Ar-C_o and Ar-C_m), 146.0 (Ar-C_i), 148.5, 149.6, 150.0 (Ar-C_p), 158.0, 160.3 (Ar-C_i). EI/MS *m/z* (%): 804.3 (100) $[M^+]$, 789.3 (59) $[M^+ - CH_3]$, 773.3 (59) $[M^+ - OCH_3]$.

X-ray Crystallography. $[Cax(OMe)_2O_2TiCl_2]\cdot 2C_7H_8$ $1\cdot 2C_7H_8$. Stoe-IPDS diffractometer (Mo Kα radiation); $T = 203(2)$ K; data collection and refinement, SHELXS-97[16] and SHELXL-97;[17] monoclinic, space group $P2_1/c$, lattice constants $a = 21.639(4)$, $b = 20.152(3)$, $c = 12.750(3)$ Å, $\beta = 95.68(3)$, $V = 5532.6(19)$ Å^3, $Z = 4$, μ(Mo Kα) = 0.295 mm^{-1}, $2\Theta_{max} = 49.8$; 9554 independent reflections measured ($R_{ind} = 0.042$), of which 7655 were considered observed with $I > 2\sigma(I)$; maximum/minimum residual electronic density 0.959 and −0.661 e/Å^3; 577 parameters (Ti, O, anisotropic, C anisotropic except for disordered *t*-Bu groups, the positions of the H atoms were calculated for idealized positions); $R_1 = 0.054$; $wR_2 = 0.160$.

$[Cax(OMe)_2O_2MoO_2]\cdot 1.5Et_2O$ $2\cdot 1.5Et_2O$. Stoe-STADI IV diffractometer (Mo Kα radiation), $T = 203(2)$ K; data collection and refinement, SHELXS-97[16] and SHELXL-97;[17] monoclinic, space group $P2/c$, lattice constants $a = 12.433(3)$, $b = 16.348(3)$, $c = 24.774(5)$ Å, $\beta = 99.15(3)$, $V = 4971.6(17)$ Å^3, $Z = 4$, μ(Mo Kα) = 0.313 mm^{-1}, $2\Theta_{max} = 52.1$°; 9859 independent reflections measured, of which 8078 were considered observed with $I > 2\sigma(I)$; maximum/minimum residual electronic density 0.893 and −0.830 e/Å^3; 510 parameters (Mo, O, N, anisotropic, C anisotropic except disordered *t*-Bu groups, the positions of the H atoms were calculated for idealized positions); $R_1 = 0.062$; $wR_2 = 0.168$.

Results

It has long been recognized that coordinated ligands may have significant influence upon metal−ligand bonding within a complex, particularly for those ligands in trans positions.[18] The term "trans influence" was originally used to describe this ground-state phenomenon of the tendency of a ligand to selectively weaken (and in most cases to elongate) the bond

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(7) Arduini, A.; Casnati, A. *Macrocycle Synthesis, A Practical Approach*; Oxford University Press: New York, 1996.

(8) (a) Colton, R.; Tomkins, I. B. *Aust. J. Chem.* **1965**, *18*, 447. (b) Colton, R.; Tomkins, I. B.; Wilson, P. W. *Aust. J. Chem.* **1964**, *17*, 496. (c) Gibson, V. C.; Kee, T. P.; Shaw, A. *Polyhedron* **1990**, *9*, 2293.

(9) Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135.

(10) (a) Ahlrichs, R. TURBOMOLE. In *Enzyclopedia of Computational Chemistry*; v. R. Schleyer, P., Ed.; Wiley: Chichester, 1998; Vol. 5, p 3123. (b) Ahlrichs, R.; v. Arnim, M. TURBOMOLE, parallel implementation of SCF, density functional, and chemical shift modules. In *Methods and Techniques in Computational Chemistry*; Clementi, E., Corongiu, G., Eds.; STEF; Cagliary, 1995.

(11) (a) Treutler, O.; Ahlrichs, R. *J. Chem. Phys.* **1995**, *102*, 346. (b) Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, *242*, 652. (c) Eichkorn, K.; Weigand, F.; Treutler, O.; Ahlrichs, R. *Theor. Chim. Acta* **1997**, *97*, 119.

(12) (a) Haase, F.; Ahlrichs, R. *J. Comput. Chem.* **1993**, *14*, 907. (b) Weigand, F.; Häser, M. *Theor. Chem. Acc.* **1997**, *97*, 331. (c) Weigand, F.; Häser, M.; Patzelt, H.; Ahlrichs, R. *Chem. Phys. Lett.* **1998**, *294*, 143. (d) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.

(13) Andrae, D.; Häussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123.

(14) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200. (c) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822. Erratum: Perdew, J. P. *Phys. Rev. B* **1986**, *34*, 7406.

(15) The synthesis of $[Cax(OMe)_2O_2TiCl_2]$ **1** by a different procedure was published before: Zanotti-Gerosa, A.; Solari, E.; Giannini, L.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chim. Acta* **1998**, *270*, 298.

(16) Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Solution*; Universität Göttingen, 1997.

(17) Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; Universität Göttingen, 1997.

(18) Coe, B. J.; Glenwright, S. J. *Coord. Chem. Rev.* **2000**, *203*, 5.

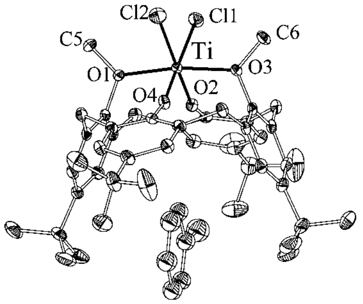

Figure 1. ORTEP plot of the molecular structure of $[Cax(OMe)_2O_2TiCl_2]$ **1**. Anisotropic thermal ellipsoids are shown at the 40% probability level. Disorders of *t*-Bu groups are not resolved in the drawing. Hydrogen atoms are omitted for clarity.

trans to itself.[19] Thus, several rules are known to govern the geometry and the ligand site occupation in six-coordinate d^0 complexes of the type $[ME_2L_2X_2]$, where L is a neutral donor ligand, in this case the ether groups of the calix[4]arene ligand, and X is a monoanionic ligand, i.e., the alkoxide groups of the calix[4]arene. The ligand E varies depending on the metal atom one uses across the transition series. For group 4 metals, E is a monoanionic ligand, e.g., halogens, whereas for group 6 metals, E has to be a dianionic ligand, e.g., oxo, imido, or sulfido. In the following we want to restrict our discussion to two simple groups of octahedral d^0 complexes, compounds of the type $[Cax(OMe)_2O_2MCl_2]$ (M = group 4 metal) and $[Cax(OMe)_2O_2M'O_2]$ (M′ = group 6 metal).

The calix[4]arene ligand in complexes $[Cax(OMe)_2O_2MCl_2]$ usually adopts an *elliptical distorted cone* conformation in the solid state and in solution, in which both chlorine ligands are mutually in cis position. This was shown by Floriani and coworkers for $[Cax(OMe)_2O_2ZrCl_2]$[20] and can be confirmed for the analogous titanium compound $[Cax(OMe)_2O_2TiCl_2]$ **1**. The most powerful tool to investigate this behavior in solution is ^1H NMR spectroscopy, where a signal pattern for the calixarene ligand is found, which is typical for the macrocyclic ligand in a local C_{2v} symmetry: two signals for the protons of the *tert*-butyl groups at 0.68 and 1.39 ppm in an integration ratio of 1:1, two doublets for the diastereotopic protons of the methylene bridges at 3.19 and 4.60 ppm with coupling constants of 13.4 Hz, and resonances of the aryl protons at 6.82 and 7.17 ppm. In addition, there is one signal for the protons of the methoxy groups at 4.19 ppm, shifted significantly to lower field as compared to the signals of the calix[4]arene ether at 3.46 ppm.

The result of the crystal structure determination of **1** is shown in Figure 1. Selected bond lengths and bond angles are given in Table 2. Complex **1** crystallizes in the space group $P2_1/c$ with two molecules of toluene per formular unit. One of these solvent molecules is *endohedrally* located in the calix[4]arene pocket.

Table 1. Crystallographic Data[a]

	$1\cdot 2C_7H_8$	$2\cdot 1.5Et_2O$
formula	$C_{60}H_{74}Cl_2O_4Ti$	$C_{52}H_{73}MoO_{7.5}$
weight, g·mol^{-1}	978.0	914.0
temp, K	190(2)	203(2)
wavelength, Å	0.71073	0.71073
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2/c$
a, Å	21.639(4)	12.433(3)
b, Å	20.152(4)	16.348(3)
c, Å	12.750(3)	24.774(5)
β, deg	95.68(3)	99.15(3)
V, Å^3	5532.6(19)	4971.6(17)
Z	4	4
density, g·cm^{-3}	1.170	1.221
μ(Mo Kα), mm^{-1}	0.295	0.313
F(000)	2076	1948
GOF	1.092	1.063
R_{ind} [$I > 2\sigma(I)$]	$R_1 = 0.0540$ $wR_2 = 0.1604$	$R_1 = 0.0622$ $wR_2 = 0.1681$
R_{ind} (all data)	$R_1 = 0.0653$ $wR_2 = 0.1675$	$R_1 = 0.0773$ $wR_2 = 0.1855$

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 2. Selected Bond Lengths (pm) and Angles (deg) in $[Cax(OMe)_2O_2TiCl_2]$ **1**

Ti−Cl(1)	234.4(1)	Ti−Cl(2)	236.1(1)
Ti−O(1)	210.1(2)	Ti−O(2)	180.6(2)
Ti−O(3)	213.3(2)	Ti−O(4)	178.3(2)
Cl(1)−Ti−Cl(2)	88.2(1)	O(1)−Ti−O(3)	170.8(1)
O(2)−Ti−Cl(2)	176.2(1)	O(4)−Ti−Cl(1)	175.9(1)
Ti−O(1)−C(10)	116.6(1)	Ti−O(2)−C(20)	153.5(2)
Ti−O(3)−C(30)	115.6(1)	Ti−O(4)−C(40)	163.8(2)
Ti−O(1)−C(5)	128.6(2)	Ti−O(3)−C(6)	128.9(2)

The metal atom in **1** is octahedrally coordinated with two ether and alkoxo oxygen atoms of the calix[4]arene ligand and two chlorine atoms, which are mutually in cis positions. The angles of the groups trans to each other are close to 180° (O(1)−Ti−O(3), 170.8(1)°; O(2)−Ti−Cl(2), 176.2(1)°; O(4)−Ti−Cl(1), 175.9(1)°); the angle Cl(1)−Ti−Cl(2) is 88.2(1)°. The Ti−O distances of 178.3(2) and 180.6(2) pm to the oxygen atoms of the phenolate and 210.1(2) and 213.3(2) pm, respectively, to the oxygen atoms of the ether groups as well as the Ti−Cl bond lengths are unexceptional.[21−23] A similar ligand sphere was found in $[TiCl_2(O\text{-}2,6\text{-}Me_2C_6H_3)_2(thf)_2]$ **A**,[22] but due to the constraints of the calix[4]arene ligand, **1** cannot adopt the favorable arrangement realized in this compound. The oxygen atoms of the alkoxo and the ether ligands are in **A** almost ideally arranged in a plane, in such a way that the neutral ligands are trans to the better donor groups $[RO]^-$. The alkoxide ligands are mutually in cis, and the chlorine atoms in trans position, with an angle Cl−Ti−Cl of 165.0(3)°.

The calix[4]arene ether ligand cannot adopt an ideal cone conformation in the complex because of the different functionalities, ether and alkoxy groups, in the molecule. This is demonstrated, for example, by different Ti−O−C angles of 116.6(1)° and 115.6(1)° in the ether unit and 153.5(2)° and 163.8(2)° in the phenolate. The different Ti−O bond lengths and Ti−O−C bond angles lead automatically to an *elliptical* deformation of the ligand, which is now ideally formed to host the toluene molecule.

Computational quantum chemistry is now an established chemist's tool and may be used as an analytical instrument in a similar sense that an NMR spectrometer or X-ray diffractometer can be used to resolve structures. However, it is also useful before experiments are performed, and one of the most appealing

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(19) Pidcock, A.; Richards, R. E.; Venanzi, L. M. *J. Chem. Soc. A* **1966**, 1707.

(20) (a) Giannini, L.; Solari, E.; Zanotti-Gerosa, A.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Angew. Chem.* **1996**, *108*, 79; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 85. (b) Giannini, L.; Caselli, L.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C.; Re, N.; Sgammellotti, A. *J. Am. Chem. Soc.* **1997**, *119*, 9198.

(21) Kanehisa, N.; Kai, Y.; Yasuda, H.; Nakayama, Y.; Takei, K.; Nakamura, A. *Chem. Lett.* **1990**, 2167.

(22) Okuda, J.; Fokken, S.; Kang, H.-C.; Massa, W. *Chem. Ber.* **1995**, *128*, 221.

(23) (a) Tararov, V. I.; Hibbs, D. E.; Hursthouse, M. B.; Ikonnikov, N. S.; Abdul Malik, K. M.; North, M.; Orizu, C.; Belekon, Y. N. *J. Chem. Soc., Chem. Commun.* **1998**, 387. (b) Corden, J. P.; Errington, W.; Moore, P.; Wallbridge, M. G. H. *J. Chem. Soc., Chem. Commun.* **1999**, 323.

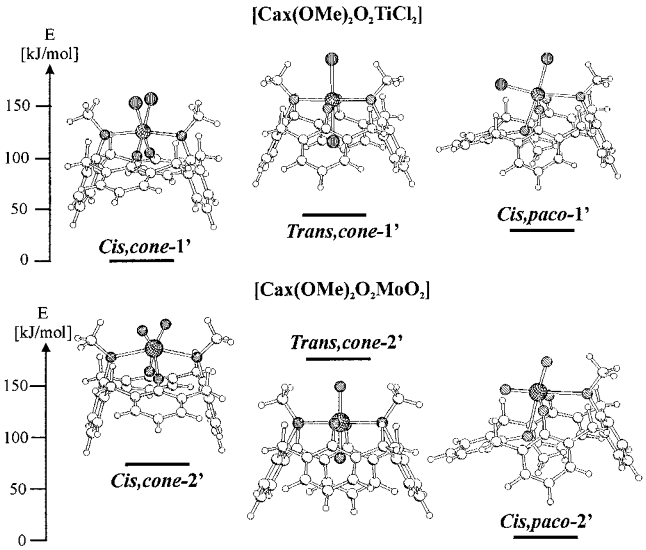

Figure 2. Relative energies of the cis,cone isomer (left), trans,cone isomer (middle), and cis,paco isomer (right) of [Cax′(OMe)$_2$O$_2$TiCl$_2$] **1′** (top) and [Cax′(OMe)$_2$O$_2$MoO$_2$] **2′** (Cax′ = CH backbone of *p-H*-calix[4]arene, C$_{28}$H$_{20}$) according to DF calculations (RIDFT/SVP/BP86).

benefits of computational quantum chemistry is its predictive power to assist synthesis and characterization of new compounds. To estimate the energetic differences of possible isomers of [Cax(OMe)$_2$O$_2$TiCl$_2$] **1**, DF calculations were performed on models of these compounds. To save computer time, the *tert*-butyl groups of the calix[4]arene ligand were replaced by hydrogen atoms. The results of our computations on the models [Cax′(OMe)$_2$O$_2$TiCl$_2$] **1′** (Cax′ = CH backbone of *p-H*-calix[4]arene, C$_{28}$H$_{20}$) are summarized in the upper part of Figure 2.

We took three different isomers into consideration for the computations: The first one is *cis,cone*-**1′**, a model of the experimentally verified complex, in which the calix[4]arene ligand coordinates in an *elliptically distorted cone* conformation and the two chlorine atoms arrange mutually in cis positions. In *trans,cone*-**1′**, the calix[4]arene ligand also coordinates in an *elliptically distorted cone* conformation, but both chlorine ligands are trans to each other. Furthermore, we have found another interesting isomer from the isomers possible within the geometrical restrictions given by the calix[4]arene ligand, *cis,paco*-**1′**. In this isomer the chlorine atoms are mutually in the cis position, but the calix[4]arene ligand is coordinated in a form which reminds one of a *partial cone* (paco) conformation of the calix[4]arene. The ether groups of the calix[4]arene ligand are trans with respect to the chlorine atoms. As a consequence, one of the methoxy groups is located *inside* the cavity of the calix[4]arene ligand leading to an “up, up, up, down” arrangement of the aryloxy units of the macrocycle.

The geometry optimization of *cis,cone*-**1′** converges to almost within a C_{2v} symmetrical energy minimum structure, which is in good agreement with the result of the X-ray analysis of **1**. The Ti−O distances of 184.22 and 216.32 pm are slightly overestimated as compared to 180.6(2), 178.3(2) pm and 213.3(2), 210.1(2) pm in **1**, but within the error margins of the method employed here. *Trans,cone*-**1′** is 45.5 kJ/mol higher in energy as compared to *cis,cone*-**1′**, and *cis,paco*-**1′** is energetically situated between these isomers, 28.0 kJ/mol higher in energy than *cis,cone*-**1′**.

Compounds of the general type [MO$_2$X$_2$L$_2$] (M = Mo, W) are known to adopt a distorted octahedral environment with both oxo ligands cis to each other in order to maximize the back-donation into the unoccupied t$_{2g}$ set of orbitals. In most cases, the arrangement of the anionic ligands X and the neutral ligands L is very strictly driven by the *trans influence* of the oxide ligands in a way, that the weakest π-bonding donor atom coordinates trans to the oxo group.[24] Thus, the ligands L are usually bonded cis to each other and trans to the oxygen atom; the monoanionic X ligands are trans to each other and cis with respect to the oxygen atoms.[25] However, there are exceptions known for this [M(*cis*-O$_2$)(*trans*-X$_2$)(*cis*-L$_2$)] arrangement.[26] In the case of group 6 calix[4]arene ether complexes [Cax(OMe)$_2$O$_2$MO$_2$], a *trans*-oxo compound complex seems to be very unfavorable compared to the *cis*-oxo compounds and a stable (*trans*-X$_2$)(*cis*-L$_2$) configuration seems to be possible only for an cis,paco-like conformation of the calix[4]arene ligand. To put the qualitative considerations in a more precise framework, we performed DF calculations on model compounds [Cax′(OMe)$_2$O$_2$MoO$_2$] of dioxo calix[4]arene molybdenum(VI) complexes, on *cis,cone*-**2′**, *trans,cone*-**2′**, and *cis,paco*-**2′** as shown in the lower part of Figure 2. These computations confirm the general picture given above. The lowest energy isomer is *cis,paco*-**2′**, 72.9 kJ/mol higher in energy lies *cis,cone*-**2′**, and *trans,cone*-**2′** is 172.9 kJ/mol above *cis,paco*-**2′**. In contrast to the titanium complexes, the energetic differences between these isomers are very pronounced, which demonstrates impressively the strong directing effects of the oxo ligand O^{2-} in transition metal complexes in their highest oxidation state. Furthermore, the cis,paco isomer seems to be strongly favorable with respect to a possible cis,cone or trans,cone isomer.

To confirm our computations experimentally, we have reacted molybdenum dioxo dichlorides with calix[4]arene dimethyl ether under different sets of conditions. The reaction of the dilithiated calixarene ether with the dimethoxyethane adduct of [MoO$_2$Cl$_2$], prepared in situ, affords after workup a yellow powder of composition C$_{46}$H$_{58}$O$_6$Mo in 75% yield, as confirmed by elemental analysis and mass spectroscopy. The proton NMR spectrum of this compound shows a signal pattern typical for a local C_s symmetry of the calix[4]arene ligand, and this was a

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[24] Nugent, W. A.; Mayer, J. M. *Metal−Ligand Multiple Bonds*; Wiley: New York, 1988.

[25] See, for example: X = halogen: (a) Florian, L. R.; Corey, E. R. *Inorg. Chem.* **1968**, *7*, 722. (b) Fenn, R. H. *J. Chem. Soc. A* **1969**, 1764. (c) Pierpont, C. G.; Downs, H. H. *Inorg. Chem.* **1977**, *16*, 2970. (d) Kamenar, B.; Penavic, M.; Korpar-Colig, B.; Markovic, B. *Inorg. Chim. Acta* **1982**, *65*, L245. (e) Bowen, S. M.; Duesler, E. N.; McCabe, D. J.; Paine, R. T. *Inorg. Chem.* **1985**, *24*, 1191. (f) Coddington, J. M.; Taylor, M. J. *J. Chem. Soc., Dalton Trans.* **1990**, 41. (g) Gahagan, M.; Mackie, R. K.; Cole-Hamilton, D. J.; Cupertino, D. C.; Harman, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1990**, 2195. (h) Dreisch, K.; Adersson, C.; Ståhlhandske, C. *Polyhedron* **1991**, *10*, 2417. (i) Dreisch, K.; Adersson, C.; Håkansson, M.; Jagner, S. *J. Chem. Soc., Dalton Trans.* **1993**, 1045. (j) Sens, I.; Stenger, H.; Müller, U.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1992**, *610*, 117. (k) Taylor, M. J.; Jirong, W.; Rickard, C. E. F. *Polyhedron* **1993**, *12*, 1433. (l) Arnaiz, F. J.; Aguado, R.; Sanz-Aparicio, J.; Martinez-Ripoll, M. *Polyhedron* **1994**, *13*, 2745. (m) Baird, D. M.; Yang, F. L.; Kavanaugh, D. J.; Finness, G.; Dunbar, K. R. *Polyhedron* **1996**, *15*, 2597. X = alkyl: (n) Schrauzer, G. N.; Hughes, L. A.; Strampach, N.; Robinson, P. R.; Schlemper, E. O. *Organometallics* **1982**, *1*, 44. (o) Schrauzer, G. N.; Hughes, L. A.; Schlemper, E. O.; Ross, F.; Ross, D. *Organometallics* **1983**, *2*, 1163. (p) Schrauzer, G. N.; Schlemper, E. O.; Liu, N. H.; Wang, Q.; Rubin, K.; Zhang, X.; Long, X.; Chin, C. S.; *Organometallics* **1986**, *5*, 2452. (q) Zhang, C.; Schlemper, E. O.; Schrauzer, G. N. *Organometallics* **1990**, *9*, 1016. X = OR, SR: (r) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021. (s) Piarulli, U.; Williams, D. N.; Floriani, C.; Gervasio, G.; Viterbo, D. *J. Chem. Soc., Dalton Trans.* **1995**, 3329. (t) Lang, R. F.; Ju, T. D.; Hoff, C. D.; Bryan, J. C.; Kubas, G. J. *J. Am. Chem. Soc.* **1994**, *116*, 9747.

[26] See, for example: (a) Dreisch, K.; Adersson, C.; Ståhlhandske, C. *Polyhedron* **1992**, *11*, 2143. (b) Dreisch, K.; Adersson, C.; Ståhlhandske, C. *Polyhedron* **1993**, *12*, 303.

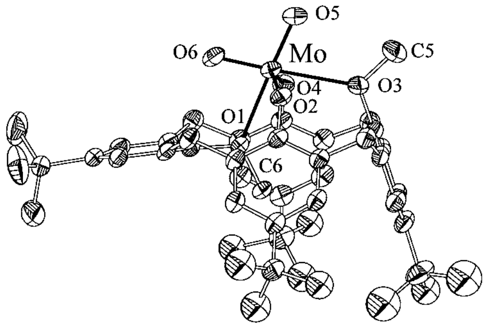

Figure 3. ORTEP plot of the molecular structure of $[Cax(OMe)_2O_2MoO_2]$ **2**. Anisotropic thermal ellipsoids are shown at the 40% probability level. Disorders of *t*-Bu groups are not resolved in the drawing. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Lengths (pm) and Angles (deg) in $[Cax(OMe)_2O_2MoO_2]$ **2**

Mo−O(1)	239.4(3)	Mo−O(2)	191.6(3)
Mo−O(3)	255.9(3)	Mo−O(4)	192.0(3)
Mo−O(5)	169.4(3)	Mo−O(6)	169.0(3)
O(1)−Mo−O(2)	76.50(10)	O(1)−Mo−O(3)	101.55(10)
O(1)−Mo−O(4)	76.46(10)	O(1)−Mo−O(5)	177.72(12)
O(1)−Mo−O(6)	80.66(12)	O(2)−Mo−O(3)	76.52(10)
O(2)−Mo−O(4)	137.16(12)	O(2)−Mo−O(5)	103.66(15)
O(2)−Mo−O(6)	103.49(14)	O(3)−Mo−O(4)	77.17(10)
O(3)−Mo−O(5)	76.32(10)	O(3)−Mo−O(6)	177.68(10)
O(4)−Mo−O(5)	102.14(14)	O(4)−Mo−O(6)	104.16(14)
O(5)−Mo−O(6)	101.47(15)		

first indication that the calix[4]arene ligand in $[Cax(OMe)_2O_2MoO_2]$ **2** coordinates in a paco-like mode to the metal atom. The different protons of the *tert*-butyl groups split to signals at 1.18, 1.34, and 1.42 ppm in an integration ratio of 1:2:1. Four doublets can be found for the diastereotopic protons of the methylene bridges at 3.56 and 4.48 ppm as well as 3.59 and 4.77 ppm with coupling constants of 14.8 and 12.0 Hz, respectively. For the aryl protons, four signals are detectable. Most significantly, we observe two signals for the methoxide groups of the calix[4]arene ether: One is at 4.18 ppm and therefore comparable to the chemical shift of 4.19 ppm found in **1**, whereas the other resonance is significantly shifted at 0.79 ppm. This value does not change much in different solvents; for example, this signal is detectable in $CDCl_3$ at 0.79 ppm and in C_6D_6 at 0.78 ppm. We attribute it to the methyl group of the *endohedrally* coordinated ether unit of the calix[4]arene ligand. Similar shifts to higher fields of *endohedrally* coordinated groups due to ring current effects of the calix[4]arene phenyl rings have been recognized earlier by ourselves and others.[3,27]

Crystals suitable for X-ray crystal structure analysis of **2** have been prepared from diethyl ether and acetonitrile solutions. The molecular structure is in both cases almost identical and is shown in Figure 3 for **2** in $\mathbf{2}\cdot 1.5Et_2O$. Selected bond distances and angles are given in Table 3. In the solid state, the calix[4]arene dimethyl ether ligand in **2** also does not bind in an *elliptically distorted cone* conformation, but in a paco-like form as predicted by theory and suggested for solutions of **2** by NMR spectroscopy. Six oxygen atoms of two alkoxide ligands RO^- and two ether ligands R_2O of the calix[4]arene ligand, and two oxo ligands O^{2-}, coordinate to the molybdenum atom to give a significantly distorted octahedral coordination geometry. The molybdenum−oxygen bond lengths of Mo−O(2) 191.6(3) pm, Mo−O(4) 192.0(3) pm to the alkoxide groups and Mo−O(5) 169.4(3) pm, Mo−O(6) 169.0(3) pm to the oxo ligands are unexceptional. The molybdenum oxygen distances to the ether groups of Mo−O(1) 239.4(3) pm and of Mo−O(3) 255.9(3) pm are considerably longer, especially Mo−O(3). $Mo-O_{ether}$ bond lengths of 235.8−242.6 pm have been observed for related compounds $[MoO_2(met)_2]$ (metH = 2-methoxyethanol) or $[MoO_2(pyr)_2]$ (Hpyr = tetrahydropyran-2-methanol).[28] However, the Mo−O(5) distance is very large, probably due to geometrical constraints of the calix[4]arene ligand, and suggests only weak interaction of O(3) with the metal atom.

The strong trans influencing ability of the multiply bonded oxo ligand explains the disposition of the ligands. The oxo ligands are coordinated cis to each other with an angle O(5)−Mo−O(6) of 101.47(15)°, increased from an idealized value of 90° to maximize π overlap to the high-valent molybdenum atom. The phenoxide units of the calix[4]arene ligand are in cis position to the oxides and trans to each other. Interestingly, the angle O(2)−Mo−O(4) of 137.16(12)° is significantly smaller than 180°, and is much closer to a tetrahedral angle. The ether groups are aligned in trans position to the oxo ligands, the angles $O_{oxo}-Mo-O_{ether}$ being 177.72(12)° and 177.68(10)°.

Discussion

The coordination form of calix[4]arene ligands and therefore the cavity of the macrocyclic ligand can be controlled by other ligands in transition metal calix[4]arene complexes, if strong directing coligands such as oxo groups are used. In this paper, we have focused from a theoretical and an experimental point of view on d^0 transition metal complexes $[Cax(OMe)_2O_2TiCl_2]$ **1** and $[Cax(OMe)_2O_2MoO_2]$ **2**. In these compounds, the chloride and oxide coligands are oriented cis to each other, but they have clearly distinct features in calix[4]arene binding. Whereas in **1** the calix[4]arene ligand adopts an *elliptically distorted cone* conformation, the macrocyclic ligand binds in a paco-like conformation to the metal center of **2**. DF calculations on models of different isomers of **1** and **2** clearly show that this phenomenon is mainly driven by the coligands employed in the complexes and exists in the solid state and in solution, as confirmed by X-ray crystallography and NMR spectroscopy. We expect this effect to be quite general. During our work there was a report by Young and co-workers on complexes $[Cax(OR)_2O_2MOCl_2]$ (M = Mo, W; R = Me, Et), in which the oxo ligand directs the ether group of the calix[4]arene ligand into the trans postion, and we observed similar behavior in monomethyl ether complexes of the type $[Cax(OMe)O_3MOCl]$ (M = Mo, W).[6] According to our DF calculations the energetic difference of 72.9 kJ/mol between both *cis*-dioxomolybdenum compounds is quite pronounced in favor of the cis,paco isomer. For the titanium compounds, on the other side, the energetic difference is much smaller, 28.0 kJ/mol, in favor of the cis,-cone isomer, and therefore one can anticipate *paco*-calix[4]arene ligands also in titanium complexes if directing ligands stronger than chloride are used.

Macrocyclic complexes are used as templates in multicomponent assembly processes and as synthetic molecular receptors for guest molecules, and calixarenes as well as metallocalixarenes have been used extensively for this type of chemistry. As our results show, the choice of the coligands in metallocalixarene ethers might be of crucial importance here. In compound **1** the calix[4]arene is able to host, for example, a solvent molecule in the hydrophobic pocket (as shown in Figure 2). This pocket is occupied in complex **2** by the methyl group of one of the ether units of the calix[4]arene ligand. For this

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(27) Acho, J. A.; Doerrer, L. H.; Lippard, S. J. *Inorg. Chem.* **1995**, *34*, 2542.

(28) Lehtonen, A.; Sillanpää, R. *Acta Chem. Scand.* **1999**, *53*, 1078.

compound the directing coligands totally change the character and the host properties of the calix[4]arene.

Molybdenum complexes containing the *cis*-dioxomolybdenum(VI) unit coordinated to ligands having nitrogen, oxygen, or sulfur donors are extensively investigated because such complexes are proposed as model compounds for the active sites in a number of oxo transfer molybdoenzymes.[29] Currently, we are investigating the potential of **2** to facilitate oxo transfer processes as well as the influence of the ether ligand size on the conformation of the calix[4]arene ligand bound on the *cis*-[MoO_2] unit.

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Supporting Information Available: Crystallographic data (final atomic coordinates with esd's for non-hydrogen atoms, complete table of bond distances and angles, anisotropical thermal parameters) for complexes **1** and **2**, details of the calculations of **1′** and **2′**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-163111 and CCDC-163112. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: 44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[29] Collison, D.; Garner, C. D.; Joule, J. A. *Chem. Soc. Rev.* **1996**, 25.