Zinc(II) Slides on a Ligand Surface: The X-Ray Crystal Structure and Dynamic Behavior in Solution of [Zn(H$_2$L)(tacn)]**

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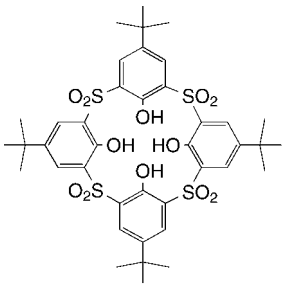
Calix[4]arenes have been extensively investigated in supramolecular and molecular-recognition chemistry.[1–3] Substituents on the body and/or on the rims give calixarenes remarkable abilities to coordinate to metal ions, which enables the synthesis of new organic–inorganic assemblies. We have reported dinuclear nickel(II) and cobalt(II) complexes containing a *p-tert*-butylsulfonylcalix[4]arene (H_4L); $[M_2(L)(H_2O)_2(dmf)_4]$ (M = Co (**1**), Ni (**2**); dmf = dimethylformamide).[4, 5]



In complexes **1** and **2**, L^{4-} adopts the 1,2-alternate conformation, and acts as a bis-tridentate chelating ligand in the solid state.[4] Free H_4L in solution has shown temperature-dependent conformational dynamics.[6] Herein, we found that in [Zn(H$_2$L)(tacn)] (**3**; tacn = 1,4,7-triazacyclononane), the zinc(II) cation forces H_2L^{2-} to adopt a cone conformation in solution and that the $\{Zn(tacn)\}^{2+}$ moiety moves smoothly on the approximate plane created by eight donor oxygen atoms, from two phenol groups, two phenoxy groups, and four sulfonyl groups. We report here the synthesis and the solution and solid state structure of **3**, together with its dynamic behavior in solution.

A stoichiometric reaction of zinc(II) acetate dihydrate and H_4L in $CHCl_3$ resulted in the formation of a white precipitate. The precipitate was treated with TACN in DMF, and colorless crystals of **3**·DMF were obtained from this solution.

The solid-state structure of **3** is shown in Figure 1. In **3**, the zinc(II) cation is in an octahedral environment and is coordinated by H_2L^{2-} and TACN, both in a tridentate *fac*-fashion. The former coordinates to the Zn center in a cone conformation, through two deprotonated phenoxy oxygen atoms (O1 and O4) and one sulfonyl oxygen atom (O2), with bond lengths of 2.1229(19), 2.0729(18), and 2.1572(17) Å, respectively. The length of $O_{sulfonyl}$–Zn is slightly longer than those of the $O_{phenoxy}$–Zn bonds. However, no other complexes with $O_{sulfonyl}$–Zn bonds have been reported.[7] The same coordination mode is found in complexes **1** and **2**, and $H_{4-n}L^{n-}$ commonly acts as a tridentate facial ligand through two phenoxy oxygen atoms and one sulfonyl oxygen atom. The other sites of the Zn center are occupied by the N_3 atom donor set from the TACN ligand, with interatomic distances of 2.152(2), 2.133(3), and 2.111(2) Å. The conformation of the calix[4]arene depends strongly on several factors, such as the number of metal ions (one in **3**, two in **1** and **2**), and the size of the supporting ligand(s) (bulky TACN in **3**, relatively small DMF and H_2O molecules in **1** and **2**). When $H_{4-n}L^{n-}$ adopts a tridentate *fac*-coordination mode, the 1,3-alternate conformation is not possible, but the other three conformations, cone, partial cone,[8] and 1,2-alternate,[4] are possible. In **3**, steric hindrance between the TACN and the noncoordinating phenol groups is avoided by adoption of the cone conformation (see Figure 1, bottom). As a result, the four $O_{phenoxy}$ atoms (O1, O4, O7, and O10) and the four axial $O_{sulfonyl}$ atoms (O2, O5, O8, and O11) are arranged in a coplanar manner, with maximum deviations from the mean plane of −0.40 Å for O7 and 0.52 Å for O8. As discussed below, the zinc(II) cation moves around on the O_8 plane in solution. One *t*Bu group from a neighboring complex is included in the cavity formed by four phenyl groups (self-clathration) and thus, in the solid state, **3** is a dimer. Compound **3** has a pseudo-mirror plane, including the Zn, N3, S1, and S3, which divides the complex into two quasi-equivalent parts.

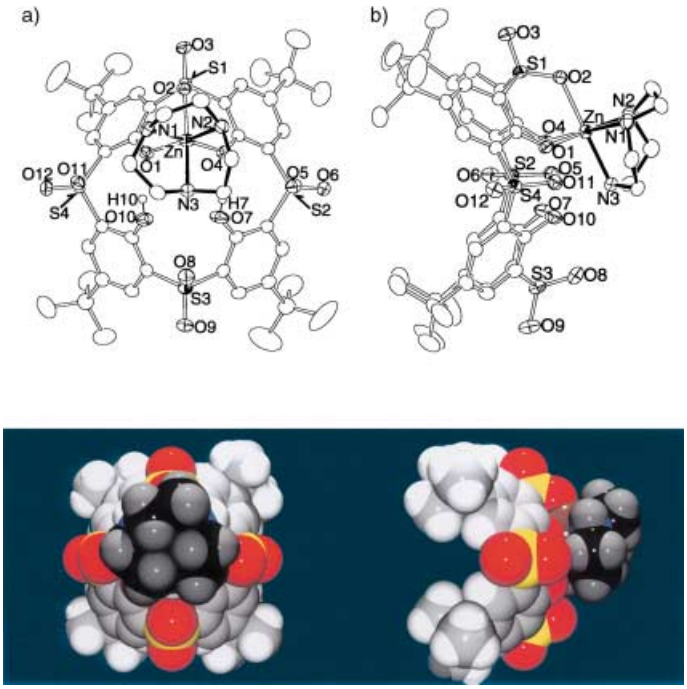


Figure 1. ORTEP drawing with thermal ellipsoids at 50% probability (top) and space-filling drawing (bottom) of the complex **3**. a) Top view and b) side view. Selected bond lengths [Å]: Zn–O1 2.1229(19), Zn–O4 2.0729(18), Zn–O2 2.1572(17), Zn–N1 2.152(2), Zn–N2 2.133(3), Zn–N3 2.111(2), S1–O2 1.4508(19). Average S–O (excluding O2) 1.437.

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[**] H_4L = *p-tert*-Butylsulfonylcalix[4]arene (an analogue of *p-tert*-butylcalix[4]arene in which the bridging methylene groups are replaced by sulfonyl moieties) and tacn = 1,4,7-triazacyclononane. This work was supported by a Grant-in Aid for Scientific Research (Nos. 10149102 and 11740366) from the Ministry of Education, Science, Sports and Culture, Japan, as well as by JSPS Research for the Future Program.

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Two protons of phenol groups were found near O7 and O10 by differential-Fourier search. The O–H bonds are directed toward the $O_{phenoxy}$ atoms, which forms hydrogen bonds between O4–O7 and O10–O1, respectively. These hydrogen bonds help to stabilize the cone conformation.

In CD_2Cl_2, a 1:1 mixture of **3** and free H_4L, or TACN, the two ^{1}H NMR spectra only show superposition of the signals arising from each component up to 40 °C, which implies that neither ligand exchange nor ligand dissociation occurs in solution below room temperature. Figure 2a shows the

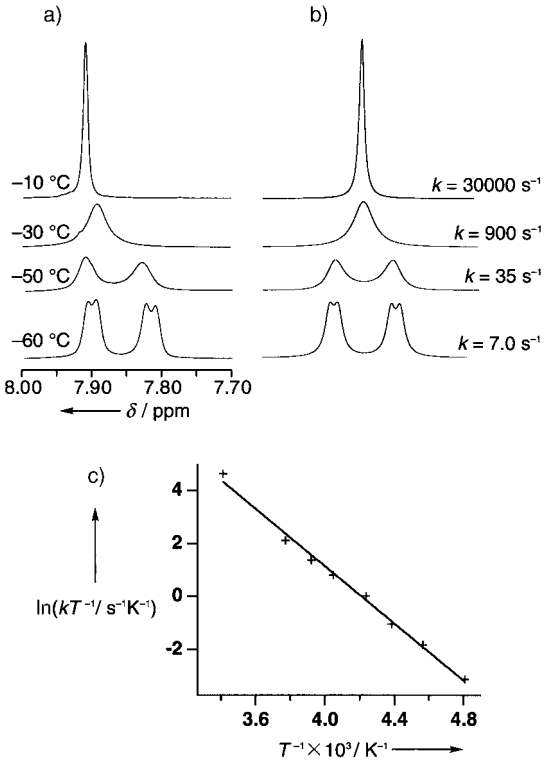

Figure 2. a) Temperature-dependent ^{1}H NMR spectra of the aromatic region of **3** in CD_2Cl_2, b) simulated spectra, and c) an Eyring plot.

temperature dependence of the ^{1}H NMR spectrum of **3** in the aromatic region. At −60 °C, the spectrum of **3** shows four singlet peaks with equal intensities at $\delta_H = 7.90$, 7.88, 7.81, and 7.80, which are assigned to the *meta* protons of the phenyl rings. This observation indicates the presence of two chemical environments for the phenyl rings, shown in Figure 3 as one ring with H_a and H_b and another ring with H_c and H_d, and also implies the presence of a mirror plane which divides the calix[4]arene into two equivalent parts. Hence, compound **3** in solution assumes a structure similar to that in the solid state. As the temperature is raised, the four peaks broaden gradually and coalesce, with a slight shift downfield. At room temperature the spectrum of **3** shows only one sharp peak, which indicates that all of the *m*-H atoms are chemically equivalent at this temperature.[9] Since ligand dissociation does not take place under these conditions, the temperature-dependent behavior is understandable only if the zinc(II) cation moves on the O_8 plane on the ^{1}H NMR spectroscopy timescale.[10] The spectra were analyzed by a conventional dynamic-NMR spectroscopic method[11], based on a model involving "the circular sliding of the zinc(II) ion over the O_8 surface" (Figure 3). The spectra simulated from this model are shown in Figure 2b, along with rate constants for the sliding process from one site to the adjoining site. Activation parameters are estimated from an Eyring plot (Figure 2c) to be $\Delta H^{\ddagger} = 45(1)$ kJ mol^{-1} and $\Delta S^{\ddagger} = -8(6)$ J mol^{-1} K^{-1}, respectively. The small negative entropy change may indicate that the sliding process occurs by an associative mechanism, which involves an additional Zn^{II}–O bond formation, or by a concerted mechanism, accompanied by fast phenol O–H bond rearrangements. In this temperature range, the methylene protons of the TACN give rise to only two quartet peaks in the ^{1}H NMR spectrum, which can be assigned to two kinds of protons, near to and far from the zinc(II) cation. This result indicates that the six methylene groups of the TACN are equivalent, even at low temperatures. Only a slight broadening of the peaks was observed at −60 °C.

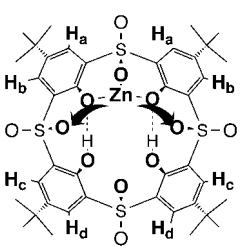

Figure 3. A schematic drawing of the Zn^{II} cation-sliding model used for the analyses. The TACN and protons (except for the *m*-H atoms of the phenyl groups, and two phenol moieties) are omitted.

Herein, we have synthesized a novel mononuclear complex of zinc(II) ion with a dianionic sulfonylcalix[4]arene, and have investigated its structure both in the solid state and in solution. In solution, **3** maintains the cone conformation and it was found that the zinc(II) ion smoothly slides on the ligand surface on the NMR spectroscopy timescale. Calixarene–metal complexes have been regarded as models for oxo-surfaces, on which chemical transformations are assisted or catalyzed.[12] Our results may provide useful information in understanding the bond-forming and bond-breaking steps in such models.

Experimental Section

3: To a chloroform solution (3 mL) of H_4L (8.49 mg, 0.01 mmol), zinc(II) acetate dihydrate (2.19 mg, 0.01 mmol) in chloroform (2 mL) was added. The colorless solution was heated under reflux for 1 h and was evaporated to dryness. The resulting white residue was then treated with TACN (0.01 mmol) in DMF (1 mL). Colorless blocks of **3**·DMF were obtained by slow evaporation at room temperature, in 54% yield.

Crystal-structure determination of [Zn(H_2L)(tacn)]·dmf (**3**·dmf): A colorless prism (ca. 0.45 × 0.18 × 0.08 mm) was analyzed with a Bruker SMART CCD-based diffractometer at 213 K with $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). Monoclinic, space group $P2_1/n$, $a = 20.0157(18)$, $b = 11.4413(10)$, $c = 23.233(2)$ Å, $\beta = 102.198(2)°$, $V = 5200.3(8)$ Å^3, $Z = 4$, $\rho_{calc} = 1.424$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.700$ mm^{-1}, $F(000) = 2352$. ω-scans, 30785 reflections measured ($2\theta_{max} = 50°$), of which 9203 were independent and 7205 were observed [$I > 2\sigma(I)$], 674 refined parameters, $R = 0.0401$, $wR2 = 0.1076$[$I > 2\sigma(I)$], residual electron density max./min. 0.703/−0.290 e Å^{-3}, max./min. transmission 0.910/0.766. Data reduction was performed with the SAINT software, which corrects for Lorentz and polarization factors. Absorption corrections were applied with SADABS, supplied by G. Sheldrick (Universität Göttingen). The structure was solved by direct methods with SHELXS-97[13] and refined by the least-squares method on F^2, SHELXL-97,[14] incorporated in SHELXTL-PC version 5.10. All non-hydrogen atoms were refined anisotropically. Hydrogens were calculated by geometrical methods and refined by using a riding model, except for the two phenol protons which were found by differential-Fourier analysis near O7 and O10, and refined isotropically. CCDC 176743 contains the

supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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