Coordination of Epithio Groups of *p-tert*-Butylthiacalix[4]arene in a Zn^{2+} Complex Studied by X-Ray Crystallography

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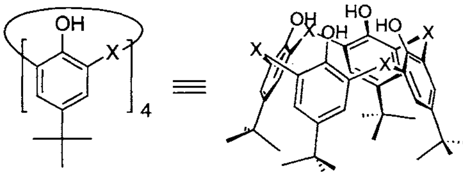
(Received November 12, 1998; CL-980862)

Single-crystal X-ray analysis has shown that *p-tert*-butylthiacalix[4]arene (H_4L) binds to Zn^{2+} ion by bridging sulfur atoms in addition to phenolic oxygen atoms to form $[Zn_4L(H_2L)_2]$.

A wide variety of metal complexes of *p-tert*-butylcalix[4]arene (CA) have been synthesized and studied by X-ray crystallography, which has revealed the coordination of phenolic oxygen atoms.[1] To the best of our knowledge, however, CA itself has not been reported to be able to bind metal ions in solvent extraction. In a previous paper, we first reported a convenient, one-step synthesis of *p-tert*-butylthiacalix[4]arene (TCA, H_4L) in a satisfactory yield, in which *o,o'* positions of four *p-tert*-butylphenol units are bridged by epithio groups instead of methylene groups.[2] Since then, we have been engaged in a project to develop novel functions of TCA such as complexation property with metal ions[3–5] and organic compounds[6] and chiral differentiation ability.[7]



CA : X = CH_2 ; **TCA** (H_4L) : X = S

As one of the remarkable results of the replacement of CH_2 by S, we demonstrated that TCA can quantitatively extract transition metal ions such as Co^{2+}, Cu^{2+} and Zn^{2+} from an aqueous phase into chloroform.[3] We confirmed that CA shows little extraction ability under the comparable reaction conditions as has been reported in the literature.[3] Therefore, a question arises how TCA binds metal ions without the aid of the supplementary ligating groups such as ester, amide or carboxy as required in case of CA.[8] Herein we studied the structure of a TCA-Zn^{2+} complex by X-ray crystallography to answer this question.

We synthesized the TCA-Zn^{2+} complex *via* solvent extraction protocol.[3] Briefly, aqueous solution (10 cm^3) containing 7.5×10^{-2} M Zn^{2+} and 0.5 M Tris-HCl buffer (pH = 8.0) and chloroform solution (10 cm^3) of 5.0×10^{-2} M TCA are shaken together for 24 h to form TCA-zinc(II) complex quantitatively. The aliquot of the organic phase was filtered through Omnipore JH Filter (0.5 µm, Millipore), evaporated to dryness and dissolved into 20 cm^3 of dry benzene under nitrogen. Half of the solvent was evaporated by heating on an oil bath, which was followed by addition of 10 cm^3 of anhydrous methanol. The solution was allowed to cool and stand at room temperature to obtain colorless crystals of TCA-Zn^{2+} in 48 h.[9] The crystal was air sensitive so that intensity data were measured in a capillary filled with the mother liquor.[10]

As shown in Figure 1, TCA-Zn^{2+} complex comprises one L^{4-} and two H_2L^{2-} in cone conformation fused at the lower rim by four Zn^{2+} ions to have the composition of $[Zn_4L(H_2L)_2]$[11] and C_2 symmetry with the symmetry axis passing through the

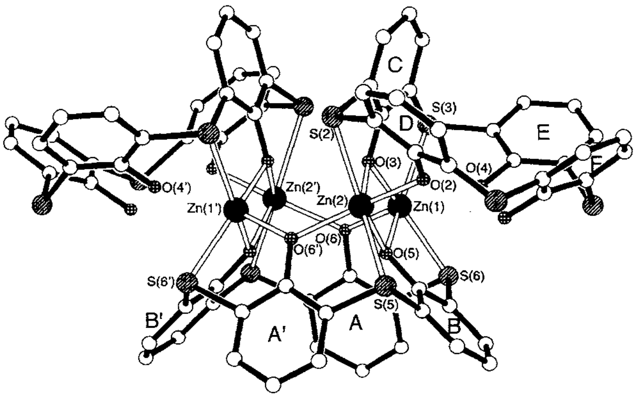


Figure 1. Molecular structure of $[Zn_4L(H_2L)_2]$. Hydrogen atoms, Bu^t groups, and included benzenes are omitted. Selected bond length (Å) and angles (°): Zn(1)–S(3) 2.527(4), Zn(1)–O(3) 1.969(8), Zn(1)–O(6) 2.028(7), Zn(1)–S(6) 2.436(4), Zn(1)–O(5) 2.041(8), Zn(2)–S(5) 2.651(4), Zn(2)–O(3) 2.058(8), Zn(2)–O(6') 2.051(7), Zn(2)–S(2) 2.675(4), Zn(2)–O(2) 2.056(8), Zn(2)–O(5) 2.035(8), S(3)–Zn(1)–S(6) 112.9(1), S(3)–Zn(1)–O(3) 82.6(3), S(3)–Zn(1)–O(5) 153.9(2), S(3)–Zn(1)–O(6) 104.5(2), S(6)–Zn(1)–O(3) 156.4(2), S(6)–Zn(1)–O(5) 82.1(2), S(6)–Zn(1)–O(6) 86.7(2), O(3)–Zn(1)–O(5) 77.4(3), O(3)–Zn(1)–O(6) 107.3(3), O(5)–Zn(1)–O(6) 97.3(3), S(2)–Zn(2)–S(5) 130.1(1), S(2)–Zn(2)–O(2) 76.9(3), S(2)–Zn(2)–O(3) 76.0(2), S(2)–Zn(2)–O(5) 151.5(2), S(2)–Zn(2)–O(6') 95.7(2), S(5)–Zn(2)–O(2) 80.2(3), S(5)–Zn(2)–O(3) 150.7(3), S(5)–Zn(2)–O(5) 77.7(2), S(5)–Zn(2)–O(6') 80.0(2), O(2)–Zn(2)–O(3) 96.3(3), O(2)–Zn(2)–O(5) 107.0(3), O(2)–Zn(2)–O(6') 146.3(3), O(3)–Zn(2)–O(5) 75.5(3), O(3)–Zn(2)–O(6') 114.0(3), O(5)–Zn(2)–O(6') 95.1(3). Atoms denoted ' are related to their counterparts by the symmetry operator: $1-x$, y, $1/2-z$.

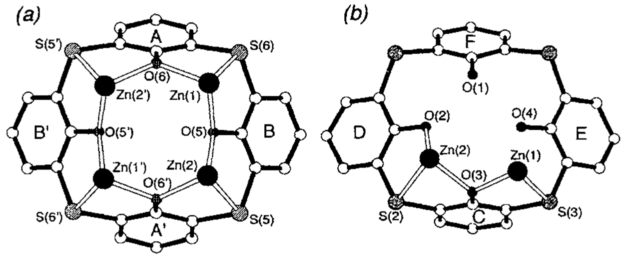


Figure 2. Top view of the TCA moieties of the $[Zn_4L(H_2L)_2]$ complex. (*a*) L^{4-}, (*b*) H_2L^{2-}. For clarity, all hydrogen atoms and Bu^t groups are omitted.

center of the cavity of L^{4-}. The inclusion of benzene molecules in the crystal lattice was observed (not drawn in Figure 1). There are two kinds of coordination environment of five and six coordination. In a distorted square pyramidal coordination geometry, Zn(1) and Zn(1') are coordinated to one epithio S-donor and two phenolate O-donors belonging to L^{4-} and one epithio S-donor and one phenolate S-donor belonging to H_2L^{2-}. The bond length between Zn^{2+} and ligating atoms is in the range of 1.97 ~ 2.04 Å for Zn-O and 2.44 ~ 2.53 Å for Zn-S. Hence the distance between Zn(1 or 1') and O(4 or 4'), which is located below the bottom of the square pyramid, was too large (2.43 Å) for Zn-O bond, there seems no coordination bond between them. On the other hand, Zn(2) and Zn(2') are coordinated to one epithio S-donor and two phenolate O-donors of both L^{4-} and H_2L^{2-} in a distorted octahedral coordination geometry, where the bond length between Zn^{2+} and ligating atoms is larger in the range of 2.04 ~ 2.06 Å for Zn-O and 2.65 ~ 2.68 Å for Zn-S.

Both L^{4-} and H_2L^{2-} form five membered chelated rings with Zn^{2+} (Figure 2). The L^{4-} coordinating to four Zn^{2+} is slightly flattened and has C_2 symmetry, in which the interplanar angles for two sets of facing aromatic rings are 47.20° (rings A versus A') and 89.86° (rings B versus B') (Figure 2a). The H_2L^{2-} is somewhat more distorted having no symmetry with interplanar angles of 111.25° (rings D versus E) and 43.38° (rings C versus F) (Figure 2b). The two residual phenolic protons in H_2L^{2-} are seemingly hydrogen bonded to each other [O(1)...O(4) 2.56 Å] and with a phenolate oxygen [O(1)...O(2) 2.49 Å] which is coordinated to Zn^{2+} ion.

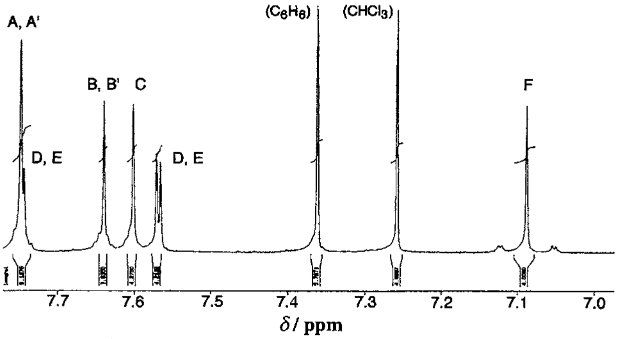


Figure 3. ^1H NMR spectrum of the crystal species, $[Zn_4L(H_2L)_2]$, dissolved in $CDCl_3$ (27 °C). The $CHCl_3$ peak was from the impurity in $CDCl_3$, while the C_6H_6 was from the included benzene molelules in the crystal lattice.

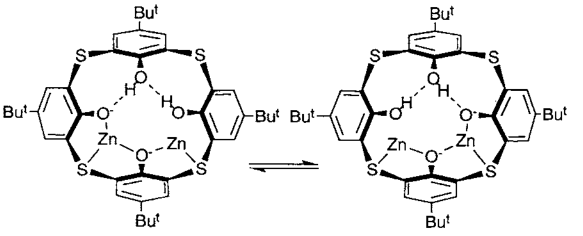


Figure 4. Tautomerism in H_2L^{2-} moiety of the $[Zn_4L(H_2L)_2]$ complex.

The ^1H NMR of the single crystal species $[Zn_4L(H_2L)_2]$ measured as a solution dissolved in $CDCl_3$ exhibited four singlets and one pair of *meta* coupled doublets for the aromatic protons (Figure 3).[9] This suggests the existence of five kinds of aromatic rings as assigned in Figure 3 and therefore the higher symmetry than the one in the crystal structure. This is best understood by assuming the tautomerism between five and six coordinated Zn^{2+} ions in H_2L^{2-} moiety as shown in Figure 4. Namely, formation and breaking of two hydrogen bonds and one O-Zn^{2+} coordination bond occur simultaneously. As a result, $[Zn_4L(H_2L)_2]$ has C_{2v} symmetry in solution state.

The X-ray structure analysis of $[Zn_4L(H_2L)_2]$ complex has proven the contribution of epithio S to bind Zn^{2+} ion, as has been suggested previously by solvent extraction and NMR study.[3] Among calixarenes and the analogues, the characteristic of TCA to coordinate to metal ions by bridging X group is unique, which must be impossible in case of X = CH_2.

The authors wish to thank Dr. H. Takizawa and Dr. K. Ueda, Tohoku University, for their kind assistance to measure X-ray reflection intensity. This work was supported by Grant-in-Aid for Scientific Research (No. 09750940) from the Ministry of Education, Science, Sports and Culture, Japan.

References and Notes

1 See *e.g.*; S. R. Dubberley, A. J. Blake, and P. Mountford, *J. Chem. Soc., Chem. Commun.*, **1997**, 1603; and literatures cited therein.
2 H. Kumagai, M. Hasegawa, S. Miyanari, Y. Sugawa, Y. Sato, T. Hori, S. Ueda, H. Kamiyama, and S. Miyano, *Tetrahedron Lett.*, **38**, 3971(1997).
3 N. Iki, N. Morohashi, F. Narumi, and S. Miyano, *Bull. Chem. Soc. Jpn.*, **71**, 1597(1998).
4 N. Iki, H. Kumagai, N. Morohashi, K. Ejima, M. Hasegawa, S. Miyanari, and S. Miyano, *Tetrahedoron Lett.*, **39**, 7559 (1998).
5 N. Iki, F. Narumi, T. Fujimoto, N. Morohashi, and S. Miyano, *J. Chem. Soc., Perkin Trans. 2*, **1998**, 2745.
6 N. Iki, T. Fujimoto, and S. Miyano, *Chem. Lett.*, **1998**, 625.
7 N. Iki, F. Narumi, T. Suzuki, A. Sugawara, and S. Miyano, *Chem. Lett.*, **1998**, 1065.
8 See literatures cited in reference 3.
9 Elemental analysis and selected spectroscopic data. Mp >360°C. Found: C, 59.32; H, 5.54; S, 15.59%. Anal. Calcd for $C_{120}H_{136}O_{12}S_{12}Zn_4$: C, 59.64; H, 5.67; S, 15.92%. ^1H NMR ($CDCl_3$): δ 1.05 (s, 18H, Bu^t), 1.18 (s, 18H, Bu^t), 1.22 (s, 18H, Bu^t), 1.22 (s, 18H, Bu^t), 1.23 (s, 36H, Bu^t), 7.09 (s, 4H, Ar-H), 7.57 (d, 4H, Ar-H, J_{meta} 2.5 Hz), 7.60 (s, 4H, Ar-H), 7.64 (s, 4H, Ar-H), 7.74 (d, 4H, Ar-H, J_{meta} 2.5 Hz), 7.75 (s, 4H, Ar-H), 13.8 (s, 4H, OH). ^{13}C NMR ($CDCl_3$): δ 31.08, 31.31, 31.35, 31.49, 31.57 [$C(CH_3)_3$], 33.83, 34.09, 34.13, 34.17 [$C(CH_3)_3$], 118.60, 120.04, 120.79, 121.30, 121.92 (*ipso* C_{Ar} with respect to S), 133.10, 133.63, 134.29, 135.97, 136.49, 136.72 (*ipso* C_{Ar} with respect to H), 140.05, 140.11, 141.11, 141.33, 142.37 (*ipso* C_{Ar} with respect to Bu^t), 157.42, 158.12, 158.48, 159.54, 160.36 (*ipso* C_{Ar} with respect to OH).
10 Crystallographic Data: $C_{120}H_{136}O_{12}Zn_4S_{12} \cdot 7(C_6H_6)$, *FW* = 2963.42, Monoclinic, a = 33.59(1) Å, b = 23.19(1) Å, c = 26.50(1) Å, β= 126.89(2)°, V = 16512(11) Å^3, Mo–*Kα* radiation (λ = 0.71069 Å), space group *C2/c* (No. 15), Z = 4, D_{calc} = 1.192 g/cm^3, T = 296 K, μ (Mo–Kα) = 7.80 cm^{-1}, No. of measured reflection = 5692 (2θ < 55°), final R = 0.066, R_w = 0.078 for 5212 observed reflections ($I_o > 3\sigma (I_o)$), GOF = 1.83. The molecule has a crystallographic two-fold axis symmetry. Out of five independent *tert*-butyl groups, two groups were found as disorder, which were refined isotropically. Finally, a total of seven benzene, which are included in the crystal lattice molecules, were found for one $[Zn_4L(H_2L)_2]$ molecule.
11 It should be noted that the composition of the TCA-Zn^{2+} complex was changed to $[Zn_4L(H_2L)_2]$ upon crystallization of $[Zn(H_2L)]$ which had been obtained by solvent extraction.[3]