Synthesis and Structural Characterization of a Pd^{2+} Complex with *p-tert*-Butylsulfinylcalix[4]arene

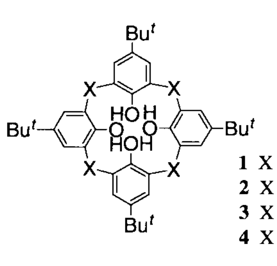
Naoya Morohashi,* Nobuhiko Iki, Sotaro Miyano,* Takashi Kajiwara,*† and Tasuku Ito†
Department of Biomolecular Engineering, Graduate School of Engineering, Tohoku University,
Aramaki-Aoba 07, Aoba-ku, Sendai 980-8579
†*Department of Chemistry, Graduate School of Science, Tohoku Universty, Sendai 980-8578*

(Received October 25, 2000; CL-000974)

Single-crystal X-ray analysis has shown that *p-tert*-butylsulfinylcalix[4]arene (H_4L) can bind Pd^{2+} ion by using either S or O atoms of bridging S=O groups in addition to phenolic oxygen atoms to form in $[Pd_2(H_2L)(H_3L)_2]$ complex.

Soon after the discovery of the practical method for the synthesis of *p-tert*-butylthiacalix[4]arene (**1**),[1] we have been engaged in the development of its novel functions and applications,[2] which are not attainable by the conventional methylene-bridged calix[4]arenes (e.g. **2**).[3] One of the most noteworthy features of **1** is the ability to bind various soft metal ions by virtue of the cooperative ligation of the epithio function and the phenoxide oxygens as revealed by solvent extraction studies and X-ray crystallography.[4,5]

The well-known ready oxidizability of an epithio function to the sulfinyl and/or sulfonyl group should be another attractive feature of **1**. Thus, we first showed that **1** can be oxidized to either *p-tert*-butylsulfinyl- (**3**) or *p-tert*-butylsulfonylcalix[4]arene (**4**) by controlling the amounts of $NaBO_3$ as the oxidizing agent.[6] Interestingly, conversion of S atoms to S=O groups allowed **3** to extract not only soft but also hard metal ions. Considering the fact that **1** can bind only soft metal ions as stated above, it seemed reasonable to presume that O atoms (hard donor) as well as S atoms (soft donor) of S=O groups of **3** should take part in the complexation with metal ions. For the first example to substantiate the hypothesis, herein we report the crystal structure of a **3**-Pd^{2+} complex to show the ligation by both S and O atoms.



1 X = S
2 X = CH_2
3 X = SO
4 X = SO_2

Treatment of **3** (H_4L) with a 4-fold excess of $Pd(OAc)_2$ in benzene afforded orange-colored complex. Vapor diffusion of MeOH into a solution of this complex in CH_2Cl_2 at room temperature gave a single crystal suitable for X-ray structural analysis.[7,8]

As shown in Figure 1, **3**-Pd^{2+} complex comprises one dianion (H_2L^{2-}) and two monoanion (H_3L^-) fused at the rims by two Pd^{2+} ions to have the composition of $[Pd_2(H_2L)(H_3L)_2]$ and C_2 symmetry with symmetry axis passing through the center of the cavity of H_2L^{2-}. As is well known in calix[4]arene chemistry, there are four conformational isomers according to the orientation of four phenyl rings, that is, cone, partial cone, 1,2-alternate, and 1,3-alternate isomers. In fact, H_2L^{2-} adopts 1,3-alternate conformation in the complex, whereas two H_3L^- do partial cone conformation (Figure 2). Distal aromatic rings are equivalent each other in H_2L^{2-}, whereas all of the four aromatic rings are not equivalent in H_3L^-. This indicates that there are six kinds of aromatic rings in $[Pd_2(H_2L)(H_3L)_2]$. Importantly, two coordination modes of the sulfinyl group are observed in the

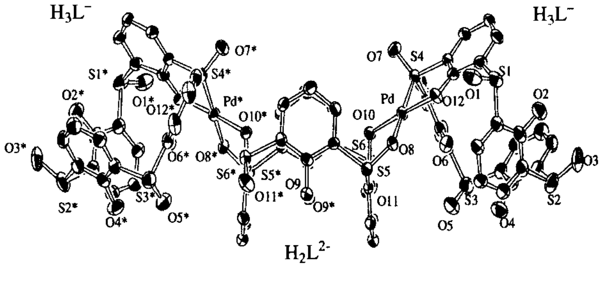
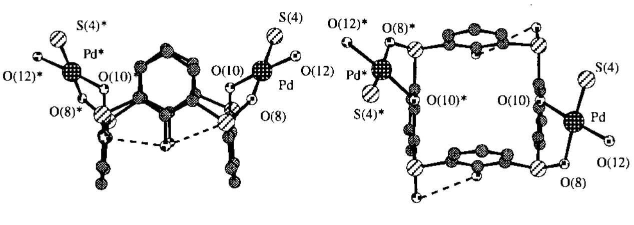
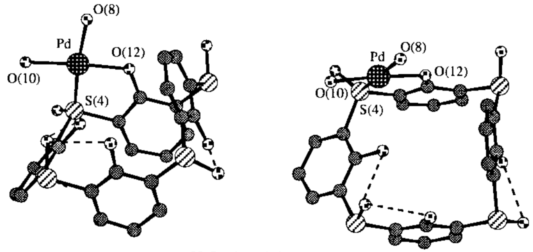


Figure 1. X-Ray structure of $[Pd_2(H_2L)(H_3L)_2]$. Bu*t* groups and H atoms are omitted for clarify.



H_2L^{2-} (1,3-alternate)



H_3L^- (partial cone)

Figure 2. Lateral (left) and top (right) views of the structures of H_2L^{2-} and H_3L^-. Bu*t* groups and H atoms are omitted for clarify.

complex. In H_2L^{2-}, sulfinyl and phenolate oxygen atoms coordinate to Pd^{2+} ion to form six-membered ring, whereas in H_3L^-, sulfinyl sulfur and phenolate oxygen coordinate to form five-membered ring.

In a square planer geometry, the bond length between Pd^{2+} and ligating atoms is 1.997(4) Å for Pd-O(12), 2.032(4) Å for Pd-O(10), 2.039(4) Å for Pd-O(8), and 2.1877(18) Å for Pd-S(4) (Table 1). The coordination of the S=O group affected the bond length: the S=O, in which O atom coordinates to Pd^{2+} ion, slightly elongates (1.529(4) Å) as compared to free S=O groups (av 1.503 Å). On the other hand, the S=O, in which S is doner to metal ion, shortens (1.457(4) Å).

Table 1. Selected bond distances (Å) and angles (deg) for $[Pd_2(H_2L)(H_3L)_2]$ complex

Pd-S(4)	2.1877(18)	O(8)-Pd-O(10)	94.80(15)
Pd-O(8)	2.039(4)	O(8)-Pd-O(12)	86.78(15)
Pd-O(10)	2.032(4)	O(12)-Pd-S(4)	87.01(12)
Pd-O(12)	1.997(4)	S(4)-Pd-O(10)	91.67(12)
S1-O(1)	1.492(5)		
S2-O(3)	1.509(6)		
S4-O(7)	1.457(4)		
S5-O(8)	1.529(4)		

Another noticeable structural feature of the complex is the intramolecular hydrogen bonding. It has been revealed that in the crystal state the free H_4L adopts 1,3-alternate conformation, which is stabilized by four pairs of OH···O=S hydrogen bondings between OH and the neighboring S=O.[9] The similar hydrogen bondings are observable in the complex between OH and S=O [O···O = av 2.732 Å] not participating in the coordination (Figure 2). It should be noted that the bifurcated one, OH···O(=S)···HO, exists in H_3L^-, which is caused by the *syn*-orientation of the two phenol rings.

The ^{1}H NMR of single crystal spesies $[Pd(H_2L)(H_3L)_2]$ dissolved in $CDCl_3$ exhibited six pairs of *meta* coupled doublets for aromatic protons and six singlet peaks of ^{t}Bu groups.[7] This suggests the existence of six kinds of aromatic rings and therefore C_2 symmetry of the complex is kept in solution. It should also be noted that four pair of intramolecular OH···O=S bonds are retained as judged by the δ_H values.

In conclusion, the X-ray structure analysis of $[Pd_2(H_2L)(H_3L)_2]$ complex has revealed that either S or O atoms of bridging S=O groups can bind cationic metal center. The crystallographic study of complexes of **3** with other metal ions (including hard Ti^{4+} ion) are now underway.

This work was supported by JSPS Research for the Future Program and by a Grant-in-Aid for Scientific Resarch on Priority Areas (No. 10208202) from the Ministry of Education, Science, Sports and Culture, Japan.

References and Notes

1 H. Kumagai, M. Hasegawa, S. Miyanari, Y. Sugawa, Y. Sato, T. Hori, S. Ueda, H. Kamiyama, and S. Miyano, *Tetrahedoron Lett.*, **38,** 3971 (1997).

2 N. Morohashi, N. Iki, T. Onodera, C. Kabuto, and S. Miyano, *Tetrahedron Lett.*, **41**, 5093, (2000), and references are cited therin.

3 C. D. Gutsche, "Calixarenes," in "Monographs in Supramolecular Chemistry," ed. by J. F. Stoddart, The Royal Society of Chemistry, Cambridge (1989); "Calixarenes - A Versatile Class of Macrocyclic Compounds," ed. by J. Vicens, V. Böhmer, Kluwer Academic, Dordrecht, (1991); C. D. Gutsche, "Calixarenes Revisited," in "Monographs in Supramolecular Chemistry," ed. by J. F. Stoddart, The Royal Society of Chemistry, Cambridge (1998).

4 N. Iki, N. Morohashi, F. Narumi, and S. Miyano, *Bull. Chem. Soc. Jpn.*, **71**, 1597, (1998).

5 N. Iki, N. Morohashi, C. Kabuto, and S. Miyano, *Chem. Lett.* **1999**, 219.

6 N. Iki, H. Kumagai, N. Morohashi, K. Ejima, M. Hasegawa, S. Miyanari, and S. Miyano, *Tetrahedron Lett.*, **39**, 7559, (1998); *cf.* G. Mislin, E. Graf, M. W. Hosseini, A. D. Cian, and J. Fischer, *Chem. Commun.*, **1998**, 1345.

7 To a solution of **3** (50.0 mg, 0.064 mmol) in benzene (5 mL) was added $Pd(OAc)_2$ (57.2 mg, 0.25 mmol). The reaction mixture was refluxed for 3 h. After cooling, the brown precipitate was collected by filtration, washed with hexane and dried in vacuo to give crude product. Orange single crystals were formed by recrystallization from CH_2Cl_2–MeOH solution. m.p. 318 °C (decomp.) IR (KBr) 3437(O–H), 2961(C–H),1001(S=O); ^{1}H NMR($CDCl_3$, 27 °C) δ 0.96 (s, 9H, CMe_3), 1.07 (s, 9H, CMe_3), 1.20 (s, 9H, CMe_3), 1.41 (s, 9H, CMe_3), 1.42 (s, 9H, CMe_3), 1.46 (s, 9H, CMe_3), 6.27 (d, 2H, J = 2.20 Hz, ArH), 6.83 (d, 2H, J = 2.31 Hz, ArH), 7.16 (d, 2H, J = 2.28 Hz, ArH), 7.35 (d, 2H, J = 2.47 Hz, ArH), 7.41 (d, 2H, J = 2.47 Hz, ArH), 7.58 (d, 2H, J = 2.31 Hz, ArH), 7.62 (d, 2H, J = 2.31 Hz, ArH), 7.64 (d, 2H, J = 2.20 Hz, ArH), 7.70 (d, 2H, J = 2.28 Hz, ArH), 8.16 (d, 2H, J = 2.31 Hz, ArH), 8.34 (d, 2H, J = 2.28 Hz, ArH), 8.38 (d, 2H, J = 2.28 Hz, ArH), 8.39 (s, 2H, OH), 8.64 (s, 2H, OH), 9.05 (s, 2H, OH), 9.93 (s, 2H, OH).

8 Single-crystal X-ray analysis on $[Pd_2(H_2L)(H_3L)_2]\cdot 12H_2O$ was performed on a Bruker Smart1000 system. A hemisphere of data was collected using a combination of ϕ and ω scans, with 0.3° frame widths. The data were corrected for absorption using an analytical technique. Crystal data: monoclinic, space group $C2/c$, a = 44.127(15) Å, b = 13.172(5) Å, c = 27.081(9) Å, β = 92.040(6)°, Z = 4, V = 15731(9) Å^3 T = 293 K, ρ(calc) = 1.174 g/cm^3, μ = 0.452 mm^{-1}, λ = 0.71073 Å, $2\theta_{max}$ = 45.2°, total data 30314, unique data 10262 (R_{int} = 0.0856), R/R_w [$I > 2\sigma(I)$] = 0.0698/0.1777. All non-hydrogen atoms refined anisotropically. Hydrogen atom positions were idealized and refined using a riding model. SHELXTL version 5.1 was used for structure solution, refinement based on F^2, and publication materials. Four t-butyl groups on the H_2L were disordered and were refined in two positions with equal occupancies.

9 G. Mislin, E. Graf, M. W. Hosseini, A. D. Cian, and J. Fisher, *Tetraedron Lett.*, **40**, 1129, (1999).