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Pd(II) Complexes with thiacalix[4]-arene and -aniline; subtle, but distinct influences of phenol and aniline units on the 3-D structure †

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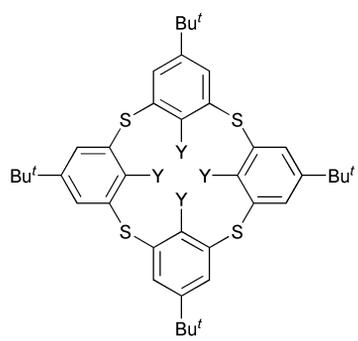
The Pd(II) complexes of thiacalix[4]aniline (TCAn) and thiacalix[4]arene (TCAr), in which four aniline and phenol units are linked by four sulfides at the *o*,*o*′-positions, respectively, were prepared by simply heating the ligands with $Pd(II)(OAc)_2$ in $CHCl_3$ or benzene at reflux and structurally characterized by X-ray diffraction methods. In TCAn, two thiacalix ligands adopting a pinched-cone conformation are fused at the narrower rims to coordinate to two Pd(II) ions by amide NH^- and the adjacent S atoms. In contrast for TCAr, two ligands coordinate to two Pd(II) ions with phenolate O^- and thioether S atoms at the narrower rims. Four sets of hydrogen bonding between the O^- and free OH cause a deviation of the Pd(II) centers from the square coordination plane and also lead the conformation of the calix to be more cone-like to provide enough space to accommodate guest CH_3CN molecules.

Introduction

Control of the three-dimensional structure of molecules by non-covalent interactions such as coordination and hydrogen bonding is a major topic in supramolecular chemistry mimicking the function of biomolecules.[1] Owing to the macrocyclic structure and ease of modification of the phenol unit, calixarenes have been utilized as a scaffold to construct artificial enzymes *via* introduction of functional groups responsible for molecular recognition and chemical transformation.[2] Recently, we have reported a facile one-step synthesis of *p-tert*-butylthiacalix[4]arene (TCAr)[3] endowed with four bridging-sulfurs in place of the methylene bridges of "classical" calixarenes, providing additional binding sites for metal ions.[4] Thus, the coordination chemistry of TCAr has been studied by solvent extraction[5] and crystallography[6] with a wide variety of metal ions. Very recently, we synthesized another member of the calix family, *p-tert*-butylthiacalix[4]aniline (TCAn), by replacing the phenolic OH of TCAr with NH_2,[7] which should open a new host–guest chemistry based on aniline rather than the conventional calixarene chemistry based on phenol. Consequently, TCAn has been revealed to have a specific binding ability to Pd(II) and Au(III) ions among 41 kinds of metal ions examined,[8] making a sharp contrast to TCAr which binds to a wide variety of soft metal ions.[5] The clear difference in the selectivity prompted us to isolate and characterize the structure of the 2 : 2 TCAn-Pd(II) complex, revealing the coordination of the amide N as well as the thioether S. Herein we report the details of the structural features of the complex, comparing with a similar 2 : 2 complex of TCAr-Pd(II) obtained recently, which contrasts the difference between the characteristics of phenol and aniline functions to bring about differences in the three-dimensional structure and inclusion ability of the thiacalix scaffolds.



TCAr, H_4tcar; Y = OH
TCAn, H_4tcan; Y = NH_2

Results and discussion

The Pd(II) complex of TCAn (H_4tcan) was readily synthesized by heating a mixture of $Pd(OAc)_2$ and TCAn in chloroform at reflux. A single crystal of the complex was revealed to be $[Pd_2(H_2tcan)_2]$ with two TCAn ligands being fused at the narrower rim by coordination to two Pd(II) ions (Fig. 1a). The structural features are summarized in Table 1. The complex has approximate C_{2h} symmetry with an axis through two Pd(II) ions, showing that the two TCAn ligands are almost structurally identical. Interestingly, the TCAn ligand in the complex adopts a typical pinched-cone conformation, in which the torsion angles between two distal benzene rings are 122.6 and 4.3°. This contrasts sharply with the 1,3-alternate conformation of free TCAn in the solid state.[7] Thus, it can be said that the binding of the two Pd(II) ions forces all four amino groups to come onto the same side of the plane containing the four S atoms. From the viewpoint of coordination, two TCAn ligands provide Pd(II) ions with a *trans*-square planar coordination geometry *via* two sets of N,S atoms (see Table 1). Strikingly, each TCAn ligand is dianionic H_2tcan^{2-}, in which a pair of amino groups release each proton to make an amide $-HN^-$ to coordinate to the Pd(II) center with one of the adjacent bridging sulfurs (Fig. 1b). In general, the formation of a Pd(II)-amide complex is not so common, because Pd(II) with a filled d_{z^2} orbital is not

† The X-ray structure for thiacalix[4]aniline-Pd(II) was first reported in a communication.[8]

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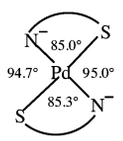
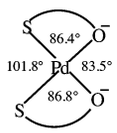
Table 1 Comparison of structural parameters of Pd(II) complexes of TCAn and TCAr

Properties	TCAn (H_4tcan)[a]	TCAr (H_4tcar)
Complex formula	$[Pd_2(H_2tcan)_2]\cdot 3.5CHCl_3$	$[Pd_2(H_2tcar)_2\cdot 2CH_3CN]\cdot 2CH_3CN\cdot 2CH_2ClCH_2Cl\cdot 6H_2O$
Molecular symmetry	Approx. C_{2h} symmetry (the axis through Pd–Pd)	Exact C_i symmetry (the center at the midpoint between two Pd atoms) and approx. C_{2h} symmetry (the axis through the center of the cone)
Conformation of calix ligands	Pinched cone	Intermediate between cone and pinched cone
torsion angles between distal phenyl groups/°	122.6, 4.3	145.4, 75.0
deviation of sulfur atoms from planarity/Å	0.043	0.605
Coordination geometry (with bond angles)		
	trans-square planar	*cis*-square planar
coordination bond lengths/Å	Pd–S 2.29, Pd–N 2.00	Pd–S 2.29, Pd–O 2.00
deviation of the Pd atom from the coordination plane/Å	0.02	0.17

[a] Values are averaged between two H_2tcan^{2-} units or two Pd(II) centers.

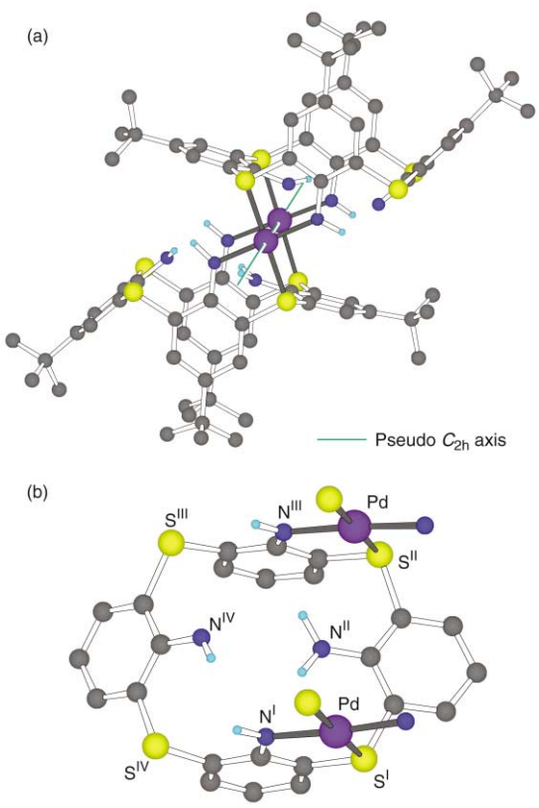


Fig. 1 X-Ray structure of $[Pd_2(H_2tcan)_2]$ (a) and top view of a thiacalix framework with two Pd(II) centers (b). Protons on carbon atoms are not shown for clarity. Protons of the free NH_2 groups were not fully found due to somewhat diffused peaks.

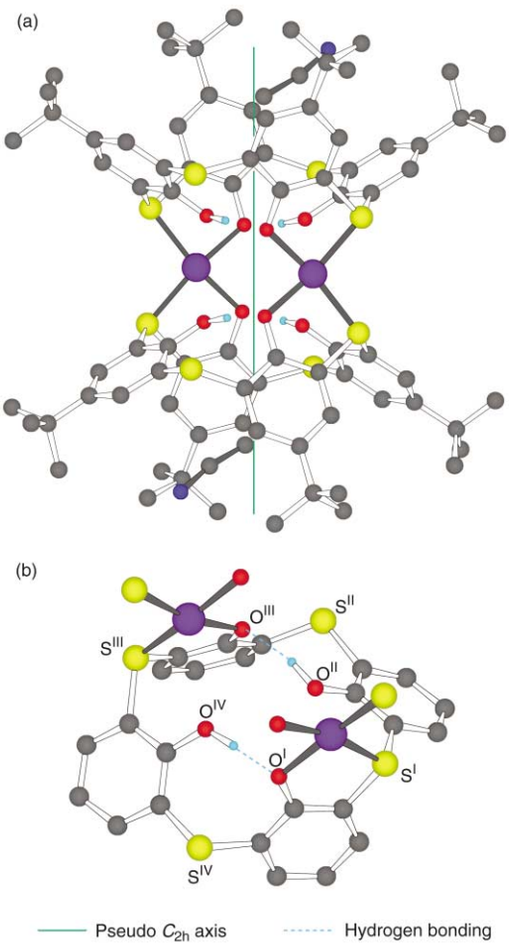


Fig. 2 X-Ray structure of $[Pd_2(H_2tcar)_2]$ (a) and top view of a thiacalix framework with two Pd(II) centers (b). Protons on carbon atoms are not shown for clarity.

able to accept π-donation from the lone-pair electrons of the hard amide moiety.[9] Therefore, Pd(II)-amide complexes have conventionally been prepared with the aid of a base to promote deprotonation of the amine followed by the introduction into a palladium complex to displace a leaving ligand.[10] In this context, $[Pd_2(H_2tcan)_2]$ is one of the quite rare examples of Pd(II)-amide complexes to be assembled spontaneously by only heating a mixture of the components in chloroform. Also noted is the regioselectivity of the binding sites of Pd(II) to the TCAn ligand. Among eight possible neighboring N,S-donor sets, two sets consisting of two proximal S (S^I,S^{II}) and the distal two N atoms (N^I,N^{III}), which are linked to S^I and S^{II}, respectively, bind to the Pd(II) ions (Fig. 1b). This in turn brings H_2tcan^{2-} an approximate σ-plane of the pseudo C_{2h} symmetry.

A Pd(II) complex of TCAr (H_4tcar) was also synthesized from a mixture of $Pd(OAc)_2$ and TCAr in benzene by the same method to form $[Pd_2(H_2tcan)_2]$. The solid-state structure of a single crystal of the complex shows a double cone structure fused at the narrower rim of the calix similar to $[Pd_2(H_2tcan)_2]$ (Fig. 2). In addition, the composition of the complex was

revealed to be $[Pd_2(H_2tcar)_2]$, implying that each TCAr ligand also releases two protons, to become the dianion H_2tcar^{2-}, to bind to two Pd(II) ions. Besides these similarities, however, a scrutiny of the structures revealed some differences of $[Pd_2(H_2tcar)_2]$ from $[Pd_2(H_2tcan)_2]$:

(1) The molecular symmetry: although $[Pd_2(H_2tcar)_2]$ has an approximate C_{2h} symmetry, the pseudo symmetry axis passes through the center of the cone, not through the pair of Pd(II) ions. Also, the complex has an exact C_i symmetry with a center of inversion at the midpoint of two Pd ions, meaning that the two TCAr ligands are identical.

(2) The three-dimensional structure of the calix ligand: H_2tcar^{2-} adopts a conformation intermediate between cone and pinched-cone (see Table 1 for the torsion angles), thus having enough space to accommodate a guest molecule, CH_3CN, in each cavity. This contrasts well with the rectangular cavity of $[Pd_2(H_2tcan)_2]$ with no guest molecules inside. Another noticeable feature concerning the molecular conformation is that the four bridging sulfur atoms of $[Pd_2(H_2tcar)_2]$ deviate significantly from the mean plane in an up-down-up-down manner (Table 1). This is hardly observed in the $[Pd_2(H_2tcan)_2]$, suggesting that little strain should arise in the TCAn framework due to complexation.

(3) Coordination geometry: each Pd(II) center of $[Pd_2(H_2tcar)_2]$ adopts an approximate square planar coordination geometry in a *cis*- rather than *trans*-fashion, with a pair of O^-,S-donor sets provided by two H_2tcar^{2-}. In addition, the Pd(II) ion floats *ca.* 0.17 Å from the average plane of the four donor atoms.

(4) The regioselectivity of the Pd(II)-binding sites in the TCAr ligand: among eight possible O^-,S-donor sets, two sets (O^I,S^I and O^{III},S^{III}) located distally to one another bind to the Pd(II) ions (Fig. 2b), which brings a pseudo C_{2h} axis as well as the above-mentioned "twist" of the S_4 plane to H_2tcar^{2-}.

(5) Hydrogen bonding: intramolecular hydrogen bonding was found between free phenolic OH and coordinating phenolate O^- ($O^{IV} \cdots O^I$ and $O^{II} \cdots O^{III}$): O ··· O = av. 2.58, O–H = av. 0.99, O ··· H = av. 1.61 Å, O–H ··· O = av. 169°. In contrast, no such interaction was found between free NH_2 and coordinating NH^- in $[Pd_2(H_2tcan)_2]$. Considering the higher basicity of NH^- than that of O^-, the higher ability of H-donation of OH than NH_2 may be the main contributor to hydrogen bonding.

Taking these facts into account, it is concluded that the difference in the three-dimensional structure of the complexes results from the regioselectivity of the metal-binding sites in the thiacalix ligands. What then determines the regioselectivity? In the $[Pd_2(H_2tcan)_2]$ complex, the two Pd(II) centers tend to adopt planar-square coordination geometry by requiring the H_2tcan^{2-} to provide the same coordination environment on both sides of the pseudo σ-plane (Fig. 1b). On the other hand, the dianion H_2tcar^{2-} is stabilized by two O–H ··· O hydrogen bondings (Fig. 2b). Therefore, Pd(II) prefers the binding sites to form pseudo C_2 symmetry in order not to disturb the existing hydrogen bonding. In other words, coordination to the Pd(II) ions and intramolecular hydrogen bonding play a "tug-of-war" to distort both the ligand moiety and the coordination geometry in the $[Pd_2(H_2tcar)_2]$ complex. On the whole, the phenol and aniline units in the thiacalix scaffold show good contrast in their differing roles to control the three-dimensional structure of the complexes *via* coordination and/or hydrogen bonding, which leads to the difference in the inclusion ability of the resulting complexes.

Experimental

Synthesis

TCAn-Pd(II) complex. To a solution of *p-tert*-butylthiacalix[4]aniline (H_4tcan, 0.12 g, 0.17 mmol) in $CHCl_3$ (15 ml) was added $Pd(OAc)_2$ (45 mg, 0.20 mmol) and the mixture was then refluxed for 72 h. The dark-red reaction mixture was evaporated to dryness and washed with benzene (20 ml) to give a crude product. Recrystallization from $CHCl_3$–MeOH solution afforded dark-green needles (31.0 mg, 23%). Single crystals for X-ray analysis were obtained by slow liquid diffusion of $CHCl_3$–MeOH. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 0.89 (s, 18H, ^{t}Bu), 1.29 (s, 9H, ^{t}Bu), 1.37 (s, 9H, ^{t}Bu), 4.16 (s, 2H, NH), 4.54 (s, 2H, NH), 5.42 (s, 2H, NH), 6.71 (d, 2H, J = 2.1 Hz, ArH), 6.99 (d, 2H, J = 2.1 Hz, ArH), 7.55 (s, 2H, ArH), 7.86 (s, 2H, ArH); FTIR (KBr, cm^{-1}): 3441 (NH), 3341 (NH), 2961 (CH).

TCAr-Pd(II) complex. A mixture of *p-tert*-butylthiacalix[4]arene (H_4tcar, 0.10 g, 0.14 mmol), PhH (10 ml) and $Pd(OAc)_2$ (125 mg, 0.55 mmol) was heated at reflux for 6 h. After filtration, the residue was washed with hexane, then dried *in vacuo* to give a brown powder (30.2 mg, 27%). Single crystals for X-ray analysis were obtained by slow vapor diffusion of CH_3CN into a 1,2-dichloroethane solution of the powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.00 (s, 36H, ^{t}Bu), 1.29 (s, 36H, ^{t}Bu), 6.81 (d, 4H, J = 2.1 Hz, ArH), 7.24 (d, 4H, J = 2.1 Hz, ArH), 7.52 (d, 4H, J = 2.5 Hz, ArH), 7.59 (d, 4H, J = 2.5 Hz, ArH), 12.07 (s, 4H, OH); FTIR (KBr, cm^{-1}): 3431 (OH), 2963 (CH).

X-Ray structral analyses

Crystallographic structure determinations were performed on a Rigaku/MSC Mercury CCD diffractometer using Mo-Kα radiation (λ = 0.71069 Å). All calculations were performed using the software package TeXsan (v. 1.11).[11] The structure was solved by direct methods with SIR92 [12] and refined by full-matrix least-squares methods with SHELXL-97.[13] All non-hydrogen atoms were refined anisotropically.

Crystal data for TCAn-Pd(II). $C_{83.5}H_{103.5}S_8N_8Pd_2Cl_{10.5}$, M = 2060.83, monoclinic, a = 16.0963(4), b = 35.1851(4), c = 17.7567(9) Å, β = 104.0085(4)°, U = 9757.4(6) Å^3, T = 230 K, space group $P2_1/c$, Z = 4, μ(Mo-Kα) = 8.72 cm^{-1}, 64044 reflections measured, 17047 unique (R_{int} = 0.030). Final R_1 = 0.052 for 11045 data [$I > 2\sigma(I)$] and wR_2 = 0.150 for all data.

Crystal data for TCAr-Pd(II). $C_{92}H_{124}O_{14}S_8N_4Pd_2Cl_4$, M = 2121.10, monoclinic, a = 13.0224(7), b = 31.4980(2), c = 13.5987(7) Å, β = 107.0044(4)°, U = 5334.1(4) Å^3, T = 223 K, space group $P2_1/c$, Z = 2, μ(Mo-Kα) = 6.51 cm^{-1}, 65670 reflections measured, 10836 unique (R_{int} = 0.032). Final R_1 = 0.041 for 7592 data [$I > 2\sigma(I)$], wR_2 = 0.119 for all data.

CCDC reference numbers 192371 for TCAr-Pd(II) and 192372 for TCAn-Pd(II).

See http://www.rsc.org/suppdata/dt/b2/b208317e/ for crystallographic data in CIF or other electronic format.

Acknowledgements

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