

Synthesis and Structural Characterization of a Dinuclear Palladium(II) Complex with *N,N',N'',N'''*-Tetrakis(2-*p*-toluenesulfonamidoethyl)cyclam

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Dinuclear palladium(II) complex with 1,4,8,11-tetrakis(2-*p*-toluenesulfonamidoethyl)-1,4,8,11-tetraazacyclotetradecane ($H_4tstaec$), $[Pd_2(tstaec)]$, was synthesized and characterized by elemental analysis and IR and UV–vis spectroscopies. The crystal structures of $H_4tstaec$ and $[Pd_2(tstaec)]$ were determined by single-crystal X-ray diffraction method. In the former ligand, the cyclam ring moiety takes a trans IV conformation with the tosyl arms pointing away from each other, whereas each palladium atom is bound by two nitrogen atoms of the cyclam moiety and two nitrogen atoms of the tosyl arms with Pd–Pd distance of 5.617(1) Å intervening the trans IV cyclam ring in the latter complex. DFT calculations were performed based on these crystal structures.

Macrocyclic polyamines with functional pendant arms and their metal complexes have attracted much attention over two decades, because they have been widely studied in various fields ranging from molecular recognition of anions or cations to potential applications in diagnostic and nuclear medicine.^{1,2} It is known that some additional donor groups of the pendant arms improve the thermodynamic and the kinetic stability of the metal complexes and this property is essential for in vivo applications.² Beside these, metal complexes of such macrocyclic ligands show interesting structural features depending on the functionalized side arms.¹ Previously, we and others reported on metal complexes with a fully N-substituted cyclam ligand by aminoethyl groups (cyclam = 1,4,8,11-tetraazacyclotetradecane), 1,4,8,11-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane (abbreviated as taec).³ Interestingly, this ligand does not form mononuclear metal species which are common in metal complexes of macrocyclic ligands, but invariably gives dinuclear metal complexes with coordination of the nitrogen atoms of the 2-aminoethyl groups and the cyclam ring. Two types of dinuclear structures, the chair form of the taec ligand in $[M_2(taec)]X_4$ ($M = Cr^{II}$, Ni^{II} , and Cu^{II} ; $X = ClO_4^-$, BF_4^- , and Br^-) and the boat form of the ligand in anion-bridged complexes of $[M_2X(taec)]Y_3$ ($M = Co^{II}$, Ni^{II} , Cu^{II} , Zn^{II} , and Cd^{II} ; $X = F^-$, Cl^- , Br^- , I^- , OH^- , and CO_3^{2-} ; $Y = ClO_4^-$, PF_6^- , $CF_3SO_3^-$, $B(C_6H_5)_4^-$, and Cl^-) have been found for metal complexes with taec. This can be ascribed to the high coordination ability of the primary amine nitrogen atoms of the pendant groups compared with those of the tertiary amine nitrogen atoms of the cyclam moiety. If all of the primary amines of the pendant arms are tosylated, the possibility of using the coordination of the macrocyclic ring to a metal ion arises as a way of forming a mononuclear species with the poor σ -donor ability of the secondary amine of the TsNH groups.⁴ In this study, we examined coordination properties of tetratosylated taec derivative, 1,4,8,11-tetrakis(2-

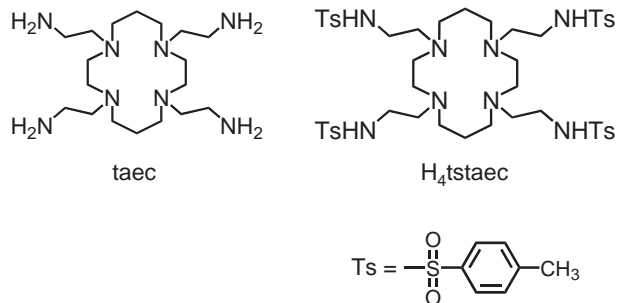


Chart 1.

p-toluenesulfonamidoethyl)-1,4,8,11-tetraazacyclotetradecane ($H_4tstaec$). Transition-metal complexes with N-tosylated ligands are scarce,⁴ although the tosylated amino groups are used as anion or cation recognition parts.^{5,6} The tetra-N-tosylation could hamper their coordinating ability; the characterization and properties of this ligand and its metal complexes have not been described, although tosylated taec is the precursor compound of taec. We report here, the synthesis and structural characterization of dinuclear palladium(II) complex with an N-tosylated macrocyclic ligand, $H_4tstaec$, together with the crystal structure of the free ligand, as well as a study of the electronic structures by density functional theory (DFT) calculations (Chart 1).

Experimental

Synthesis. Unless otherwise specified, all reagents were purchased commercially and used without further purification.

$H_4tstaec$. The macrocyclic ligand, $H_4tstaec$, was synthesized according to a method described in the literature^{3b} and obtained as white powder. The product was recrystallized from hot DMF to give colorless crystals. Anal. Found: C, 55.69; H, 7.05; N, 11.56%. Calcd for $C_{46}H_{68}N_8O_8S_4$ ($H_4tstaec$): C, 55.84; H, 6.93;

Table 1. Crystal Data and Data Collection Details

	H ₄ tstaec	[Pd ₂ (tstaec)]·2CH ₃ CN
Formula	C ₄₆ H ₆₈ N ₈ O ₈ S ₄	C ₅₀ H ₇₀ N ₁₀ O ₈ Pd ₂ S ₄
FW	989.32	1280.20
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	9.454(2)	14.484(2)
<i>b</i> /Å	13.546(2)	21.335(3)
<i>c</i> /Å	19.693(3)	8.947(1)
β /°	90.205(3)	92.861(3)
<i>V</i> /Å ³	2522.0(7)	2761.1(7)
<i>Z</i>	2	2
<i>D_c</i> /g cm ⁻³	1.30	1.54
<i>D_m</i> /g cm ⁻³	1.29	1.57
Crystal size/mm ³	0.25 × 0.20 × 0.10	0.35 × 0.30 × 0.15
μ (Mo K α)/mm ⁻¹	0.247	0.864
2 θ range/°	1.82–28.43	1.41–28.63
No. of reflections	15195	16980
No. of unique reflections		
with <i>I</i> > 2 σ (<i>I</i>)	5778	6425
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)] ^{a)}	0.0469, 0.1157	0.0419, 0.1069
Goodness-of-fit on <i>F</i> ²	0.903	0.953

a) $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

N, 11.33%. IR (KBr, cm⁻¹): ν (NH) 3259, ν_{as} (SO₂) 1328, ν_s (SO₂) 1164. ¹H NMR (DMSO-*d*₆, *T* = 298 K): δ 0.43 (4H, quintet, *J* = 6.1 Hz), 1.25 (8H, t, *J* = 4.5 Hz), 1.37 (8H, s), 1.51 (8H, t, *J* = 6.1 Hz), 1.53 (12H, s), 1.93 (8H, t, *J* = 4.5 Hz), 6.54 (8H, d, *J* = 8.1 Hz), 6.59 (4H, s), 6.82 (8H, d, *J* = 8.1 Hz).

[Pd₂(tstaec)]·CH₃CN. H₄tstaec (40 mg, 0.04 mmol) was dissolved in DMF (10 mL) at 60 °C. To this solution was added CH₃CN solution (2 mL) of palladium(II) acetate (18 mg, 0.08 mmol), and the mixture was heated at 60 °C for 10 min. On to the resulting yellow solution was layered acetonitrile (18 mL), and allowed to stand at room temperature to give orange crystals. Yield, 18.5 mg (38%). Anal. Found: C, 46.26; H, 5.60; N, 10.59%. Calcd for C₄₈H₆₇N₉O₈Pd₂S₄: C, 46.52; H, 5.45; N, 10.17%. IR (KBr, cm⁻¹): ν_{as} (SO₂) 1261, ν_s (SO₂) 1130. UV-vis: λ_{max} (ϵ /M⁻¹cm⁻¹, measured in DMF) 410 nm (858). ¹H NMR (DMSO-*d*₆, *T* = 353 K): δ 1.75 (12H, s), 1.86 (4H, m), 2.08 (8H, m), 2.42 (8H, m), 2.68 (8H, m), 2.98 (8H, m), 6.57 (8H, d, *J* = 7.9 Hz), 7.22 (8H, d, *J* = 7.9 Hz).

Measurements. Elemental analyses were conducted using a Thermo Finnigan FLASH EA 1112 series CHNS-O Analyzer. Infrared spectra were measured with a JASCO MFT-2000 FT-IR Spectrometer in the 4000–600 cm⁻¹ region. The electronic spectra were measured with a Shimadzu UV-vis-NIR Recording Spectrophotometer Model UV-3100. ¹H NMR spectra were recorded on a LA 400 spectrometer operating at 400.1 MHz for ¹H. Chemical shifts were referenced to the residual peaks of DMSO-*d*₆ (δ 2.49).

X-ray Crystallography. A preliminary examination was made and data were collected on a Bruker CCD X-ray diffractometer (SMART APEX) using graphite-monochromated Mo K α radiation at 20 °C. Crystal data and details concerning data collection are given in Table 1. The structure was solved by direct methods, and refined by full-matrix least-squares methods. The hydrogen atoms were inserted at their calculated positions and fixed there. All of the calculations were carried out on a Pentium IV Windows 2000 computer utilizing the SHELXTL software pack-

age.⁷ Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposit numbers CCDC-657151 and 657152. Copies of the data can be obtained free of charge via <http://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 336033; e-mail: deposit@ccdc.cam.ac.uk).

Computational Methods. Density functional theory (DFT) calculations were performed for H₄tstaec and [Pd₂(tstaec)]. The geometric parameters were given from X-ray diffraction analysis and the calculations were carried out by using Gaussian 03 (revision C.02) program.⁸ The geometries were optimized at the hybrid B3LYP level of DFT using the standard 3-21G* basis set for hydrogen, carbon, oxygen, nitrogen, and sulfur, and the LANL2DZ basis set for palladium. Excited-state energies and oscillator strengths were computed within the time-dependent density functional theory (TD-DFT) framework as implemented in the Gaussian 03 program.

Results and Discussion

Macrocyclic Ligand, H₄tstaec. The tosylated ligand, H₄tstaec, was prepared from a reaction of 1,4,8,11-tetraazacyclotetradecane with four equivalents of *N*-(*p*-toluenesulfonyl)aziridine in acetonitrile. The IR spectrum of H₄tstaec exhibits strong absorptions at 1328 and 1164 cm⁻¹ due to S–O stretching vibrations in addition to a ν (N–H) stretching band at 3259 cm⁻¹. Attempts to recrystallize from DMF gave colorless crystals suitable for single-crystal X-ray diffraction study. The crystal structure of H₄tstaec is shown in Figure 1. The asymmetric unit contains one-half of the H₄tstaec molecule, the macrocycle being centered on a crystallographic inversion center (Table 2). According to the stereochemical description of the cyclam ring introduced by Bosnich et al.,⁹ the relative orientation of the four nitrogen substituents can be ascribed to a trans IV configuration where two aminoethyl groups

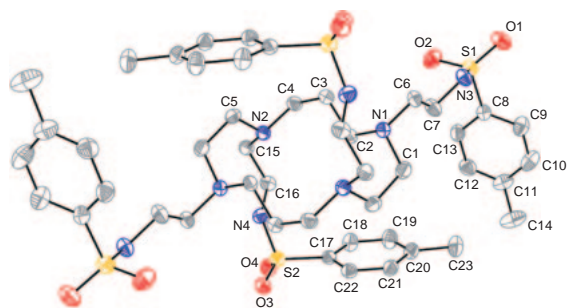


Figure 1. ORTEP drawing of the structure of $H_4tstaec$ showing the 25% probability thermal ellipsoids and atom labeling scheme. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (°) for $H_4tstaec^a$

N1–C2	1.463(3)	S1–O1	1.424(2)
N1–C1	1.469(3)	S1–O2	1.426(2)
N1–C6	1.472(2)	S1–N3	1.615(2)
N2–C4	1.463(2)	S1–C8	1.764(2)
N2–C5	1.452(3)	S2–O3	1.430(2)
N2–C15	1.460(3)	S2–O4	1.430(2)
N3–C7	1.463(2)	S2–N4	1.597(2)
N4–C16	1.461(3)	S2–C17	1.756(2)
O1–S1–O2	119.8(1)	C5–N2–C4	111.1(2)
O1–S1–N3	106.6(1)	C15–N2–C4	110.4(2)
O2–S1–N3	107.5(1)	C7–N3–S1	118.3(1)
O1–S1–C8	108.8(1)	C16–N4–S2	122.2(1)
O2–S1–C8	107.3(1)	N1–C1–C5'	114.4(2)
N3–S1–C8	106.1(1)	N1–C2–C3	112.4(2)
O3–S2–O4	119.4(1)	C2–C3–C4	112.8(2)
O3–S2–N4	107.1(1)	N2–C4–C3	115.0(2)
O4–S2–N4	106.8(1)	N2–C5–C1'	114.2(2)
O3–S2–C17	108.1(1)	N1–C6–C7	115.1(2)
O4–S2–C17	107.0(1)	N3–C7–C6	111.0(2)
N4–S2–C17	108.1(1)	C13–C8–S1	120.0(2)
C2–N1–C1	112.7(2)	C9–C8–S1	120.2(2)
C2–N1–C6	113.3(2)	N2–C15–C16	110.3(2)
C1–N1–C6	110.6(2)	N4–C16–C15	107.5(2)
C5–N2–C15	113.5(2)		

a) Prime refers to the equivalent position ($-x + 1$, $-y + 1$, $-z$).

separated by two methylene carbon atoms and the other two aminoethyl groups are oriented on opposite sides of the macrocyclic ring. Tosyl arms point away from each other in order to avoid their steric hindrance. As shown in Figure 2, this extended structure is hydrogen-bonded through the tosylated amino groups in the crystal, the closest contact being $N3 \cdots O4$ ($x - 1/2$, $-y + 1/2$, $z - 1/2$) of 3.030(2) Å.

Attempts were made to react the $H_4tstaec$ ligand with a variety of transition-metal salts including $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 4H_2O$, and $Cu(ClO_4)_2 \cdot 6H_2O$. Unfortunately no characterizable products could be isolated except for the starting materials in the case of simple 1:1 reaction, presumably due to the weak coordinating ability of the tosylated nitrogen atom with this sterically hindered system. However, we successfully isolated a metal complex when $H_4tstaec$ was treated with two

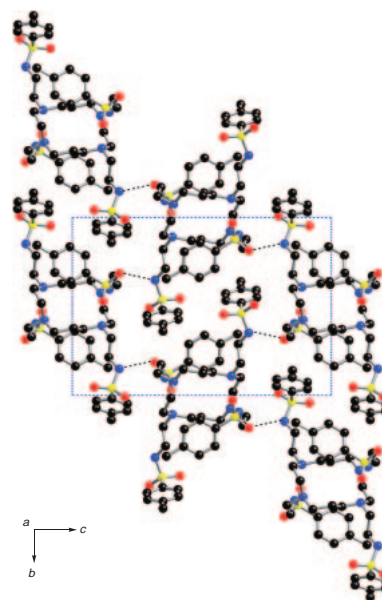


Figure 2. Crystal packing of $tstaec$.

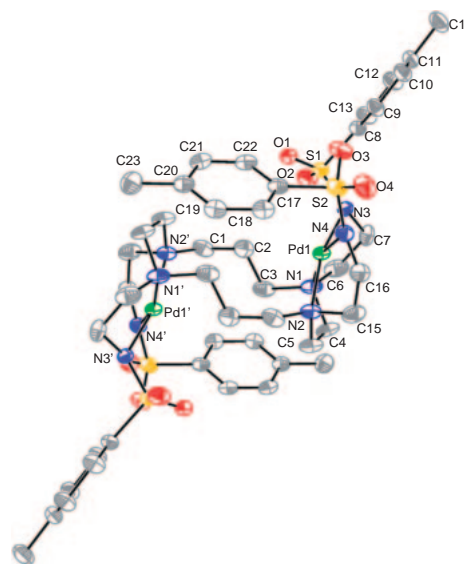


Figure 3. ORTEP drawing of the structure of $[Pd_2(tstaec)] \cdot 2CH_3CN$ showing the 25% probability thermal ellipsoids and atom labeling scheme. Hydrogen atoms are omitted for clarity.

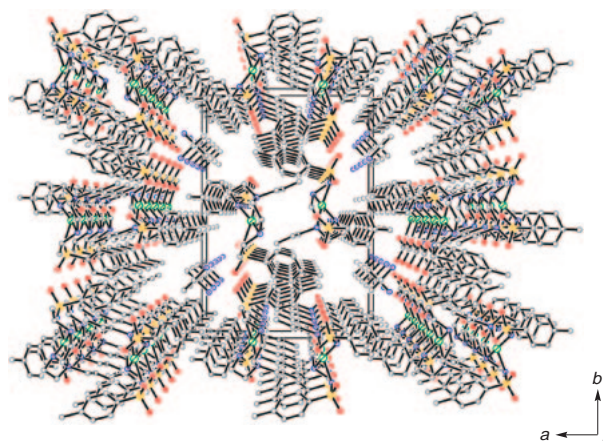
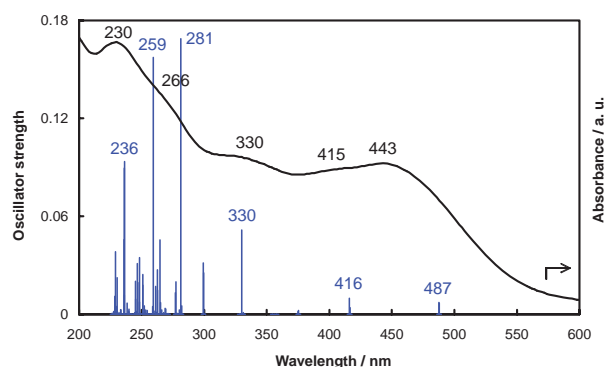
equivalent of palladium(II) acetate in DMF. Layering of acetonitrile to the DMF solution provided orange crystals of $[Pd_2(tstaec)] \cdot 2CH_3CN$. The 1H NMR spectra measured in DMSO for the $H_4tstaec$ ligand and the Pd^{II} complex confirms the ligand coordination in solution when we consider the difference between the spectral features in the range observed for the signals, in addition to the disappearance of the NH signal of the NHTs groups upon the complex formation. The crystal structure of $[Pd_2(tstaec)] \cdot 2CH_3CN$ was determined by X-ray structure analysis. A perspective view of $[Pd_2(tstaec)]$ is shown in Figure 3. Selected bond distances and angles are listed in Table 3. The dinuclear $[Pd_2(tstaec)]$ molecule possesses an inversion center. Each palladium atom

Table 3. Selected Bond Distances (Å) and Angles (°) for [Pd₂(tstaec)]·2CH₃CN^a

Pd1–N1	2.066(3)	S1–N3	1.580(3)
Pd1–N2	2.047(3)	N2–C1'	1.463(5)
Pd1–N3	2.042(3)	N2–C5	1.494(5)
Pd1–N4	2.034(3)	N2–C15	1.497(5)
C1–N2'	1.463(5)	N3–C7	1.486(5)
N1–C6	1.452(6)	S2–N4	1.589(3)
N1–C4	1.499(5)	N4–C16	1.465(5)
N1–C3	1.599(6)		
N1–Pd1–N2	86.0(1)	C1'–N2–Pd1	121.6(3)
N1–Pd1–N3	83.2(1)	C5–N2–Pd1	106.7(2)
N1–Pd1–N4	163.2(1)	C15–N2–Pd1	98.7(2)
N2–Pd1–N3	162.5(1)	C7–N3–S1	115.8(3)
N2–Pd1–N4	82.1(1)	C7–N3–Pd1	102.5(2)
N3–Pd1–N4	103.9(1)	S1–N3–Pd1	125.9(2)
C6–N1–C4	111.9(4)	O3–S2–O4	118.0(2)
C6–N1–C3	109.3(4)	O3–S2–N4	109.6(2)
C4–N1–C3	110.8(3)	O4–S2–N4	109.6(2)
C6–N1–Pd1	109.8(3)	N4–S2–C17	108.2(2)
C4–N1–Pd1	100.1(2)	C2–C3–N1	113.7(3)
C3–N1–Pd1	114.6(2)	C16–N4–S2	115.5(3)
C2–C1–N2'	118.9(4)	C16–N4–Pd1	110.5(2)
O1–S1–O2	116.9(2)	S2–N4–Pd1	131.2(2)
O1–S1–N3	108.8(2)	C5–C4–N1	113.3(3)
O2–S1–N3	112.3(2)	C4–C5–N2	113.3(3)
N3–S1–C8	106.6(2)	N1–C6–C7	111.2(4)
C1'–N2–C5	111.3(3)	N3–C7–C6	108.8(3)
C1'–N2–C15	107.5(3)	C16–C15–N2	111.2(4)
C5–N2–C15	110.1(3)	N4–C16–C15	109.0(3)

a) Prime refers to the equivalent position ($-x + 1$, $-y + 1$, $-z + 2$).

is coordinated to the two tertiary amino nitrogen atoms of the macrocycle and the two amido nitrogen atoms of the tosylaminoethyl arms. The Pd1...Pd1' distance is 5.617(1) Å. Although the coordination geometry around each palladium atom is square planar, the palladium atom deviates from the basal plane of N1, N2, N3, and N4 by 0.264 Å, presumably reflecting that the palladium(II) is too large to fit within the N₄-donor square plane. The Pd–N bond lengths range from 2.034(3) to 2.066(3) Å and are typical of such Pd–N bond lengths in other related complexes.¹⁰ The Pd1–N1 and Pd1–N2 bond lengths of 2.066(3) and 2.047(3) Å, respectively, are slightly longer than those of Pd1–N3 2.042(3) Å and Pd1–N4 2.034(3) Å, presumably as a consequence of different donor properties of the alkylated cyclam nitrogen and the deprotonated amido nitrogen atoms. It is known that the amido nitrogen atom binds to metal ion more strongly than the amino nitrogen atom.¹¹ It turns out that the cyclam skeleton keeps a trans IV configuration upon coordination of the tosylated amino groups to the two palladium atoms. This structure is comparable to the case of [M₂(taec)]X₄ complexes in chair form, in which the two metal atoms are bound by the nitrogen atoms of the cyclam ring and the pendant arms with a metal–metal separation of 5.267(2)–5.565(1) Å.^{3b,3e} However, the cyclam ring takes a trans III configuration in the taec complexes. A trans IV configuration can be found in related dinuclear metal complexes with the cyclam-based ligands, 1,4,8,11-tetrakis-

**Figure 4.** Crystal packing of [Pd₂(tstaec)]·2CH₃CN.**Figure 5.** Diffused reflectance spectra of [Pd₂(tstaec)]·CH₃CN with the TD-DFT calculated transition energies as absorption wavelengths in nm and oscillator strengths indicated by vertical lines for comparison.

[2-(salicylideneamino)ethyl]-1,4,8,11-tetraazacyclotetradecane and its substituted derivatives.¹² In these complexes, two metal atoms are well separated with a long Mn...Mn distance of 9.675(4)–10.097(3) Å because of the non-coordination of the cyclam-ring nitrogen atoms. Although the cyclam ring takes a similar trans IV configuration to H₄tstaec, the crystal structure of [Pd₂(tstaec)]·2CH₃CN is different from that of H₄tstaec. The coordination to the palladium atoms encountered in [Pd₂(tstaec)] also affects the spatial extension of the pendant arms, giving a cavity with 3.7 Å × 5.0 Å in the crystal, in which acetonitrile molecules are housed (Figure 4).

The diffuse reflectance spectrum of [Pd₂(tstaec)]·CH₃CN is shown in Figure 5. The spectrum is characterized by an intense band at 230 nm with some shoulders around 266 and 330 nm which may be charge-transfer transitions in origin, and broad absorptions around 415 and 443 nm, which can be associated with d–d transitions. This spectral feature is consistent with square-planar palladium(II) ion surrounded by N₄ donor atoms.¹³

The coordination of the tosyl groups could be caused by deprotonation of the tosylamide groups. We therefore decided to compare the electronic structure of H₄tstaec (as the protonated form) and [Pd₂(tstaec)] (as the deprotonated form) by DFT methods. DFT calculations were performed on optimized structures of the ligand and the palladium complex using

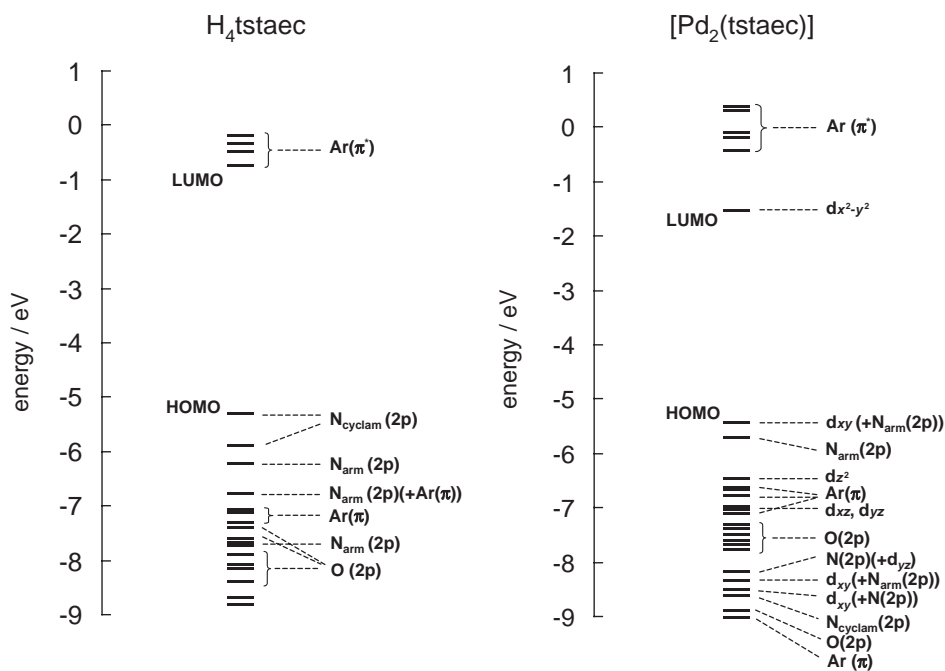


Figure 6. MO energy diagrams for $H_4tstaec$ (left) and $[Pd_2(tstaec)]$ (right).

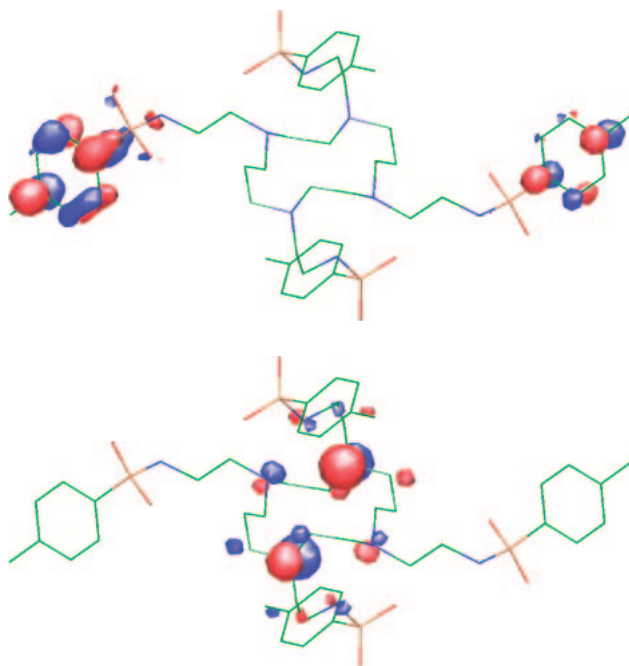


Figure 7. Calculated isosurface of HOMO (bottom) and LUMO (top) for $H_4tstaec$.

the coordinates obtained from the crystallographic data. The MO energy diagrams for $H_4tstaec$ and $[Pd_2(tstaec)]$ are shown in Figure 6. The molecular orbital surfaces generated by Gaussian 03 for $H_4tstaec$ show that the HOMO is indeed dominated by the 2p orbital of the nitrogen atoms of the cyclam ring. The LUMO is almost entirely made up of aromatic π^* orbitals of the tosyl pendant groups (The HOMO and LUMO diagrams for $H_4tstaec$ are shown in Figure 7.). Since each lobe of the 2p orbital of the four cyclam-ring-nitrogen

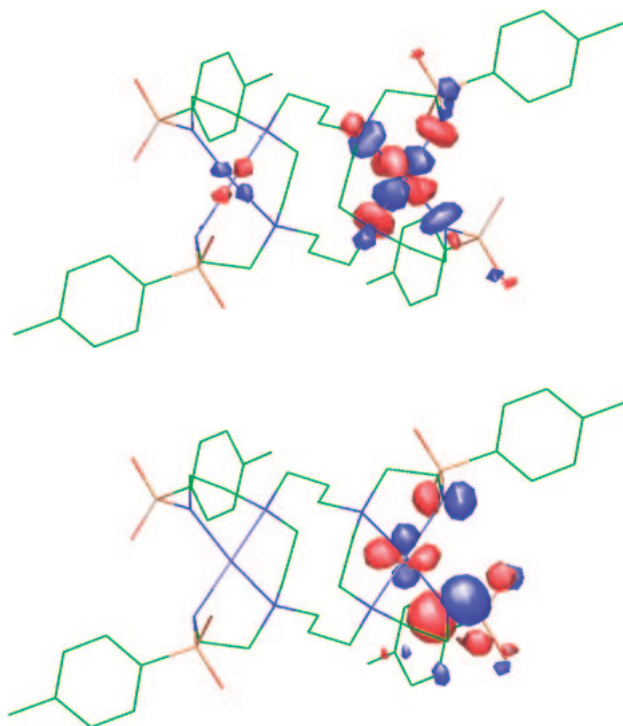


Figure 8. Calculated isosurface of HOMO (bottom) and LUMO (top) for $[Pd_2(tstaec)]$.

atoms directs in the alternating opposite direction, it is not hard to understand why the coordination of these cyclam-ring-nitrogen atoms is difficult to achieve in this ligand. The HOMO and LUMO diagrams for $[Pd_2(tstaec)]$ are shown in Figure 8. The HOMO is a metal d_{xy} orbital mixed with the nitrogen 2p orbitals of the deprotonated tosylamido groups. The LUMO is essentially metal-based empty $d_{x^2-y^2}$ orbital with some

contribution from the deprotonated tosylamido-nitrogen and cyclam-ring-nitrogen donors. As depicted in Figure 6, a relatively low lying cyclam-ring-nitrogen 2p orbital (HOMO-17, $N_{\text{cyclam}}(2p)$) compared with the HOMO of $H_4\text{tstaec}$ can be observed in $[\text{Pd}_2(\text{tstaec})]$. Presumably, the 2p orbital is stabilized by its coordination to the metal ion. To gain insight into the electronic transitions responsible for the observed UV-vis spectra of $[\text{Pd}_2(\text{tstaec})]$, TD-DFT calculations were performed using the Gaussian program suite. The transitions calculated at 487 and 416 nm may be compared to the experimental bands at about 443 and 415 nm (Figure 5). These bands are mainly d-d transitions composed of the HOMO ($\text{Pd}(d_{xy}) \rightarrow \text{LUMO}(\text{Pd}(d_{x^2-y^2}))$) and the HOMO-1 ($N(2p)$ with participation of the palladium d orbital) $\rightarrow \text{LUMO}$, respectively. The calculated transition at 330 nm can be ascribed to the experimental bands at 330 nm. This transition is mixed in character, with d-d (HOMO-5 ($\text{Pd}(d_{xz})$), HOMO-6 ($\text{Pd}(d_{yz})$) $\rightarrow \text{LUMO}$), and LMCT (HOMO-3 (aromatic π of the tosyl group) $\rightarrow \text{LUMO}$). The transitions with larger oscillator strengths at 281 and 259 nm may be assigned to the experimental shoulder bands at 266 nm. They can be described as charge-transfer transitions having the HOMO $\rightarrow \text{LUMO}+1$ (aromatic π^*) and the HOMO $\rightarrow \text{LUMO}+3$ (aromatic π^*). The calculated transition at 236 nm consists mainly of LMCT (the HOMO-10(O) $\rightarrow \text{LUMO}$). This may be responsible for the strong absorption at 230 nm in the experimental spectra. As a whole, the calculated values have a general resemblance to the experimental spectra.

In the present study we report the results of an investigation on an N-tosylated macrocyclic ligand with some metal ions. We could isolate only the palladium complex. The X-ray structure determination of the palladium complex shows that the tstaec ligand is octadentate and is coordinated to two palladium(II) ions similarly to the taec ligand, giving two planar N_4 donor atoms. It is to be noted that the deprotonated amido-nitrogen atoms bind more strongly to palladium(II) than do the tertiary amines, while alkylation of a secondary amine generally results in a reduction of its metal ion affinity due to steric factors. This fact suggests that the deprotonated form of the present ligand has a binding ability to metal ions. Among Pd^{2+} , Cu^{2+} , Ni^{2+} , and Co^{2+} ions, the highest tendency to promote amide deprotonation was observed for palladium(II) ion.¹⁴ This trend may be one of the reasons why only the palladium(II) species was isolated in the present system. We are now making an effort to synthesize metal complexes other than the palladium complex, although it seems to be difficult to isolate such species.

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