

Characterizations and X-ray Crystal Structure of Asymmetrical 2,4,9,11-Tetramethyl-1,5,8,12-monobenzotetraazacyclo[14]annulene Palladium(II) Complex

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It is reported that symmetrical dibenzotetraazacyclo[14]annulene are generally complexed with a variety of metals such as nickel, copper and cobalt.¹⁻⁷ The studies of the metal complexes of tetraazaannulene, which have been well known to possess chemical and thermal stability, have been of considerable attention because of their utilities as electrocatalysts or model compounds in biological system.⁸⁻¹⁴ Tetraazaannulenes as ligands prefer to coordinate with a metal ion in a square-planar fashion like porphyrines or phthalocyanines. Especially, palladium coordination complexes with macrocycle ligands such as tetraazaannulene or porphyrin typically prefer a square-planar arrangement as the most stable structure and are very resistive to chemical demetallation due to the stability of its square-planarity.¹⁵⁻¹⁷ The first X-ray structure of symmetrical tetraaza[14]annulene palladium(II) complex is reported by Tsutsui, M. *et al.* in 1979.¹⁸ The complexes reported in asymmetrical monobenzotetraaza[14]annulene are mostly to include nickel(II) ion.^{19,20} On the other hand, the palladium complex has scarcely been reported because it is not easy to prepare an asymmetrical free-based ligand in comparison to symmetrical free-based ligand. Herein, we synthesized and characterized a free-based asymmetrical 2,4,9,11-tetramethyl-1,5,8,12-monobenzotetraazacyclo[14]annulene (**L**) and its palladium complex (**[PdL]**) and determined the structure of the **[PdL]** by X-ray diffraction study.

Experimental Section

Materials. Ni(OAc)₂·4H₂O, 1,2-phenylenediamine, 1,2-diaminoethane, Pd(OAc)₂, NaCN and 2,4-pentandione were purchased from Aldrich and Fluka. The solvents such as CH₃CN, CH₃OH, CH₃CH₂OH, CH₂Cl₂ were refluxed over calcium hydride under nitrogen, and checked for purities by GC just before use. Dimethylsulfoxide (DMSO) was purchased from Merck and used without further more purification. Tetraethylammonium perchlorate (TEAP) used as supporting electrolyte was prepared and purified by the method described by Kolthoff and Coetzee.²¹

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Measurements. Elemental analyses (C, H, N) of the compounds prepared were carried out on a Carlo-Ebra, EA 1108 instrument. Infrared spectra were recorded on a Matteson Instruments, Inc. Galaxy 7020 A using KBr Pellets. ¹H-NMR (300 MHz) spectra were recorded on a Bruker instrument at room temperature and chemical shifts in CDCl₃ were given in ppm relative to tetramethylsilane as internal reference. Electronic absorption spectra were obtained on a Shimadzu UV-265 spectrophotometer.

Cyclic voltammetry was performed using a Bioanalytical System (BAS) CV-50W electrochemical analyzer and C2 cell stand at room temperature. The three electrodes system for the electrochemical measurements composed of the glassy carbon electrode as a working electrode, and Ag/Ag⁺ (0.01 M AgNO₃ in 0.1 M TEAP DMSO solution) as a reference electrode, and a platinum wire as an auxiliary electrode was used.

Synthesis: 2,4,9,11-Tetramethyl-1,5,8,12-monobenzotetraazacyclo[14]annulene (**L**). This ligand was prepared by modifying L'Eplattenier and Pugin's method.²² At first the asymmetrical 2,4,9,11-tetramethyl-1,5,8,12-monobenzotetraaza-cyclo[14]annulene nickel(II) as starting compound was prepared by the method reported in the literature.^{23,24} The complex (5.28 g, 0.015 mol) was dissolved in absolute ethanol (50 mL) and was treated excess anhydrous hydrochloric acid until the blue colored ligand salt precipitate. The reaction mixture was further stirred at room temperature for 18 h. The solid was filtered, dissolved in water (300 mL) and neutralized by addition of solid sodium cyanide. The yellow precipitate was recovered, washed with water, dried in *vacuo*. The red single crystal could be obtained by recrystallizing from a mixture (1 : 1) of dichloromethane and methyl alcohol. Yield 1.11 g (25%). Anal. Calcd. for C₁₈H₂₄N₄: C, 72.94; H, 8.16; N, 18.90%; Found: C, 72.78; H, 8.22; N, 18.93%. IR (KBr disc, cm⁻¹): ν(C=C), 1502; ν(C=N), 1562; ν(C₆H₆), 746. UV-vis: λ_{max} (nm) and ε_{max} (M⁻¹cm⁻¹) in CHCl₃ 322 and 36000. ¹H NMR (CDCl₃): 1.972, 2.101 (s) (methyl); 4.757(s) (methine); 3.443(s) (ethylene); 6.945 (m) (aromatic); 11.873 (br) (N-H).

2,4,9,11-Tetramethyl-1,5,8,12-monobenzotetraazacyclo[14]annulene palladium(II) (**[PdL]**). Pd(OAc)₂ (0.224 g, 0.001 mol) and free based ligand (**L**: 0.296 g, 0.001 mol) was

dissolved in acetonitrile (80 mL). The mixture was heated under reflux for 2 h with stirring and bubbled nitrogen gas for protecting from moisture. The reaction mixture was left to stand in refrigerator for 12 h. The solid was filtered and washed with acetonitrile. The product was chromatographed on aluminum oxide and eluted with chloroform. The yellow effluent was collected, evaporated to dryness in *vacuo* and dried. The dark brown crystal was obtained by recrystallizing from a mixture of dichloromethane and methyl alcohol (1 : 1). When the powder was yellow color but the crystal was dark brown. Yield 0.159 g (40%). Anal. Calcd. for $C_{18}H_{20}PdN_4$: C, 54.17; H, 5.02; N, 14.11%; Found: C, 53.79; H, 5.64; N, 14.11%. IR (KBr disc, cm^{-1}): ν (C=C), 1514; ν (C=N), 1569; ν (C_6H_6), 744. UV-vis: λ_{max} (nm) and ϵ_{max} ($M^{-1}cm^{-1}$) in $CHCl_3$, 374 and 19000, 432 and 11000. 1H NMR ($CDCl_3$): 2.187, 2.569 (s) (methyl); 4.998 (s) (methine); 3.773 (s) (ethylene); 6.820-7.514 (m) (aromatic).

X-ray crystallographic analysis: Preliminary examination and data collection for crystal of palladium(II) complex were performed with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) on an Enraf-Nonius CAD4 computer controlled *k*-axis diffracto-

Table 1. Crystal data and structure refinement for palladium(II) complex ([PdL])

Empirical formula	C ₁₈ H ₂₀ N ₄ Pd
Formula weight	398.78
Temperature	173(2) K
Wavelength	0.71073 \AA
Crystal system	Orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
Unit cell dimensions	a = 8.1003(12) \AA $\alpha = 90^\circ$ b = 8.2553(13) \AA $\beta = 90^\circ$ c = 24.416(4) \AA $\gamma = 90^\circ$
Volume	1632.7(4) \AA^3
Z	4
Density (calculated)	1.622 Mg/m ³
Absorption coefficient	1.141 mm ⁻¹
F(000)	808
Crystal size	0.38 × 0.28 × 0.25 mm ³
Theta range for data collection	1.67 to 28.32°
Index ranges	-10 ≤ h ≤ 10 -10 ≤ k ≤ 10 -32 ≤ l ≤ 23
Reflections collected	9553
Independent reflections	3837 [R(int) = 0.0283]
Completeness to theta = 28.32°	96.3%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7635 and 0.6710
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3837 / 0 / 212
Goodness-of-fit on F ²	1.096
Final R indices [I > 2σ(I)]	R1 = 0.0218, wR2 = 0.0571
R indices (all data)	R1 = 0.0228, wR2 = 0.0576
Absolute structure parameter	0.03(3)
Largest diff. peak and hole	0.583 and -0.755 e. \AA^{-3}

Table 2. Selected bond distances [\AA] and angles [$^\circ$] for palladium(II) complex ([PdL])

Pd-N(1)	1.977(2)	Pd-N(2)	1.978(2)
Pd-N(3)	1.966(2)	Pd-N(4)	1.957(2)
N(1)-C(1)	1.409(3)	N(1)-C(16)	1.343(3)
N(2)-C(2)	1.410(3)	N(2)-C(7)	1.341(3)
N(3)-C(9)	1.307(3)	N(3)-C(12)	1.461(4)
N(4)-C(13)	1.452(4)	N(4)-C(14)	1.391(4)
C(1)-C(2)	1.441(3)	C(1)-C(6)	1.393(3)
C(7)-C(8)	1.393(4)	C(7)-C(10)	1.517(3)
C(8)-C(9)	1.419(4)	C(9)-C(11)	1.508(4)
C(12)-C(13)	1.446(5)		
N(1)-Pd(1)-N(2)	83.75(8)	N(4)-Pd(1)-N(1)	96.21(9)
N(4)-Pd(1)-N(3)	83.78(9)	N(4)-Pd(1)-N(2)	177.61(9)
N(3)-Pd(1)-N(1)	178.11(9)	N(3)-Pd(1)-N(2)	96.19(9)
C(9)-N(3)-C(12)	122.5(2)	C(7)-N(2)-C(2)	127.3(2)
C(9)-N(3)-Pd(1)	123.43(18)	C(7)-N(2)-Pd(1)	120.62(17)
C(12)-N(3)-Pd(1)	113.56(19)	C(2)-N(2)-Pd(1)	111.49(15)
N(2)-C(2)-C(1)	115.3(2)	N(2)-C(7)-C(8)	123.3(2)
N(2)-C(7)-C(10)	121.9(2)	N(3)-C(9)-C(8)	122.4(2)
C(8)-C(7)-C(10)	114.8(2)	N(3)-C(9)-C(11)	120.8(2)
C(7)-C(8)-C(9)	130.4(2)	C(12)-C(13)-N(4)	113.7(2)
C(8)-C(9)-C(11)	116.7(2)		

meter equipped with a graphite crystal, incident-beam monochromator. Cell constants and orientation matrices for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections. The data were collected for Lorentz-polarization and absorption corrections were applied to the data. The structure was solved by direct methods using SHELXS-86 and refined by full-matrix least-squares calculations with SHELXL-97.^{25,26} The final cycle of the refinement converged with R = 0.0218 and wR = 0.0571. Crystal data, details of the data collection, and refinement parameters were listed in Table 1. The selected bond distances and angles were presented in Table 2.

Results and Discussion

The UV-visible spectra of the free ligand **L** and the complex [PdL] newly prepared were illustrated in Figure 1. The spectrum of the **L** showed only one peak at 322 nm ($\epsilon_{max} = 36000 M^{-1}cm^{-1}$) attributed to $\pi \rightarrow \pi^*$ transitions, while that of the [PdL] exhibited a band of ligand based at 374 ($\epsilon_{max} = 19000 M^{-1}cm^{-1}$) and a band at 432 nm ($\epsilon_{max} = 11000 M^{-1}cm^{-1}$) in $CHCl_3$. The latter band may be attributed to ligand to metal charge transfer (LMCT) from the highest occupied ligand molecular orbital to the lowest empty *d*-orbital of palladium. The LMCT band of the asymmetrical complex [PdL] shifted to higher energy than asymmetrical monobenzotetraazacyclo[14]annulene nickel(II) complex ($\lambda_{max} = 547 \text{ nm}$ and $\epsilon_{max} = 3000 M^{-1}cm^{-1}$) owing to the extended interaction by the larger *d*-orbital of palladium.¹³ In the 1H -NMR data, the characteristic peak (*N-H*) of free-based ligand appeared at 11.873 (s) ppm, while disappearing in the palladium(II) complex.

The cyclic voltammograms of the ligand **L** and the

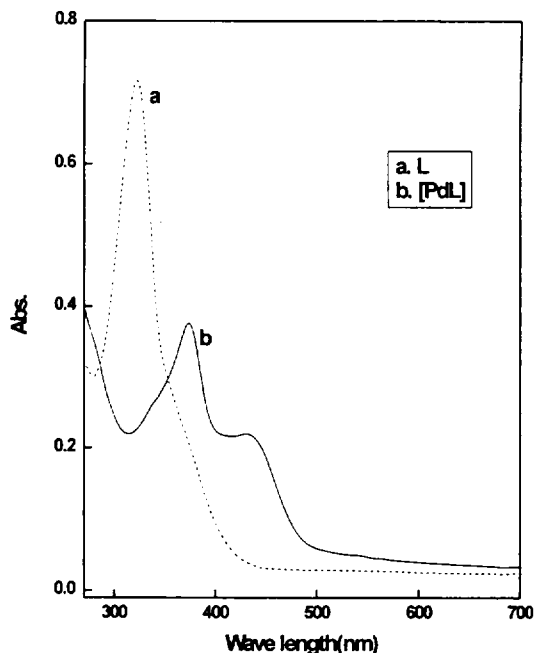


Figure 1. Electronic absorption spectra of free ligand and palladium(II) complex in chloroform solution at room temperature.

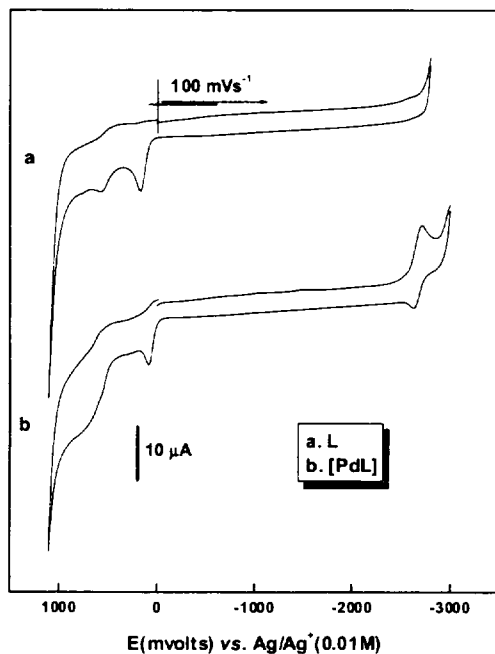


Figure 2. Cyclic voltammograms of free ligand and palladium(II) complex in a 0.1 M TEAP-DMSO solution at room temperature.

complex [PdL] measured in 0.1 M TEAP-DMSO solutions vs Ag/Ag^+ (0.01 M) at 25 °C and scan rates of 100 mVs^{-1} were shown in Figure 2. The L has only two irreversible

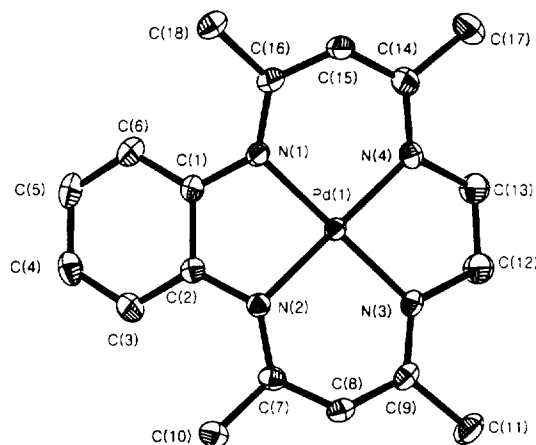


Figure 3. The molecular structure of palladium(II) complex.

oxidation peaks at +0.170 and +0.580 V. The [PdL] has two irreversible oxidation peaks by one electron at +0.090 and +0.700 V, respectively, and one quasi-reversible reduction peak by one electron of palladium-based ($\text{Pd}^{2+} \rightarrow \text{Pd}^+$) at -2.710 V. Such assignments of redox waves are supported by similar observation with asymmetrical monobenzotetraaza-cyclo[14]annulene nickel(II) complex.²⁷

The molecular structure of the complex [PdL] was drawn in Figure 3. Crystal data and refinement parameters and the selected bond distances and angles were presented in Tables 1 and 2, respectively. The average of four Pd-N bond distances was 1.970 Å that is longer than the corresponding Ni-N distances (1.870 Å) for symmetrical nickel(II) complex²⁸ but shorter than Pd-N distances (1.996 Å) for symmetrical palladium complex¹⁸ owing to different basicity for phenylenediamine and ethylenediamine. Such difference of bond distances might be attributed to the larger ionic radius of palladium. Also, the distances of N-C on the side of six-membered rings were 1.343 Å for N(1)-C(16), 1.341 Å for N(2)-C(7), 1.307 Å for N(3)-C(9) and 1.391 Å for N(4)-C(14), while for five-membered rings they were totally longer (1.409 Å for N(1)-C(1), 1.410 Å for N(2)-C(2), 1.461 Å for N(3)-C(12) and 1.452 Å for N(4)-C(13)). The average C-C distances in the six-membered chelate rings were 1.408 Å close to those of benzene (1.40 Å), reflecting some aromaticity that all π -electrons are somehow delocalized in the macrocycle ring. The average angles of N-Pd-N of five and six member rings were 83.76 and 96.20 Å, and N(3)-Pd-N(1) and N(4)-Pd-N(2) were 178.11 and 177.61°, respectively, indicating the geometry close to a square planar a little bit distorted. The coordination environment around the central palladium(II) atom showed a square planar geometry with four Pd-N bonds, which is very similar to that of symmetrical dibenzotetraazacyclo[14]annulene palladium(II) complex.

Supplementary material. Crystallographic data for the structural analysis have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number CCDC 222447. Copies of this

information can be obtained free of charge via E-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>; Tel: +44-1223-336031; Fax: +44-1223-336033.

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Cr(III)-Tetraaza Macrocylic Complexes Containing Auxiliary Ligands (Part I); Synthesis and Characterization of Cr(III)-Benzoato and Chlorobenzoato Macrocylic Complexes

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The reaction of *cis*-[Cr([14]-decane)(OH)₂]³⁺ ([14]-decane = *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) with auxiliary ligands {L_a = benzoate(bz) or chlorobenzoate(cbz)} leads to a new compound [Cr([14]-decane)(bz)₂]ClO₄ or [Cr([14]-decane)(cbz)₂]ClO₄. These complexes have been characterized by a combination of elemental analysis, conductivity, IR and Vis spectroscopy, mass spectrometry, and X-ray crystallography. The crystal structure of [Cr([14]-decane)(cbz)₂]⁺ was determined. The complex shows a distorted octahedral coordination environment with the macrocycle adopting a folded *cis*-V conformation. The angle N_{axial}-Cr-N_{axial} deviates by 14.5° from the ideal value of 180° for a perfect octahedron. The bond angle *cis*-O-Cr-O between the Cr(III) ion and the two carboxylate oxygen atoms of the monodentate *p*-chlorobenzoate ligands is close to 90°. The FAB mass spectra of the *cis*-[Cr([14]-decane)(L_a)₂]ClO₄ display peaks due to the molecular ions [Cr([14]-decane)(bz)₂-H]⁺, [Cr([14]-decane)(cbz)₂-2H]⁺ at *m/z* 578, 646, respectively.

Key Words : Macrocycle, Cr(III) complexes, Chlorobenzoate ligand, Crystal structure

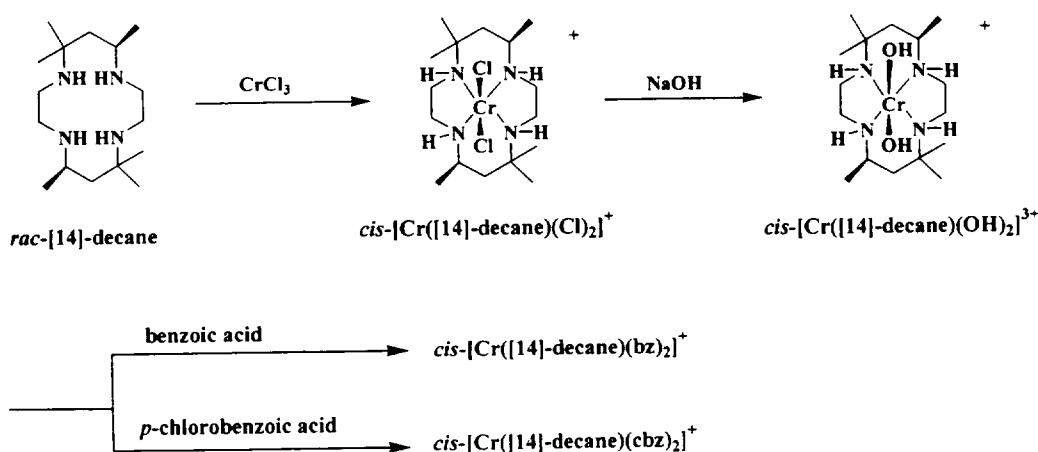
Introduction

Considerable interest exists in the successful application of the modified 1,4,8,11-tetraazacyclotetradecane cyclam, which can be used as models for a protein-metal binding site in biological systems¹⁻³ and as selective reagents of metallic ions.⁴⁻⁶ The DNA binding of Cr-macrocylic complexes is an area of great interest and activity, since these cleavage reagents potentially can be used for cancer therapy or as restriction nucleases.⁷⁻⁹

In recent years there have been many investigations of the synthesis, structures, and properties of various types of N-functionalized tetraaza macrocylic ligands and their

transition metal complexes.¹⁰⁻¹² In particular, the reactivity of nickel- or cobalt-macrocylic complexes toward Lewis bases like oxalate has been explored in detail.¹³⁻¹⁷ Eriksen and coworkers recently attempted to characterize the complex formation between carboxylic acids/carboxylates in particular acetic acid/acetate and macrocylic chromium complexes exemplified by *cis* complexes of *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (L_m = [14]-decane) and cyclam.¹⁸ However, much less attention has been given to the synthesis of the corresponding Cr-macrocylic complexes containing auxiliary ligands.¹⁹

In the present study, we describe the preparation and isolation of *cis*-[Cr([14]-decane)(L_a)₂]ClO₄ {L_a = benzoato



Scheme 1. Synthetic route of the *cis*-[Cr([14]-decane)(L_a)₂]⁺.

(bz⁻), chlorobenzoato (cbz⁻) (Scheme 1) and present the X-ray structure of the chlorobenzoato complex as well as the elemental and spectra analysis of benzoato and chlorobenzoato complexes. We have taken considerable interest in investigating the crystal structure of the complexes formed by Cr(III) and *rac*-form, [14]-decane with auxiliary ligands in *cis* position. These compounds are considered as quite attractive transition metal-macrocyclic complexes containing *cis* ligands, such as cisplatin, with antitumor activity.

Experimental Section

Measurements. Elemental microanalyses were performed using a LECO CHN-900 analyzer. The electronic absorption spectra of the complexes were acquired in DMF at 25 °C, using a HP model 8453 UV-VIS spectrophotometer. Conductivity measurements were carried out in DMF at 25 ± 1 °C, using an ORION 162 conductivity temperature meter. IR spectra were recorded using KBr pellets on a Bruker FSS66 FT-IR spectrometer. FAB-mass spectra were obtained on a JEOL JMS-700 Mass Spectrometer, using argon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV, and glycerol was used as the matrix. The mass spectrometer was operated in positive ion mode and mass spectra were calibrated by Alkali-CsI positive.

Preparation of starting materials. The *rac*-[14]-decane,^{20,21} *cis*-[Cr([14]-decane)(Cl)₂]Cl, and *cis*-[Cr([14]-decane)(OH)₂]⁺ solutions^{18,22} were prepared according to the literature procedure.

Preparation of *cis*-[Cr([14]-decane)(bz)₂]ClO₄·0.5H₂O. *cis*-[Cr([14]-decane)(OH)₂]⁺ solution (50 mL) was acidified with benzoic acid (9 g) in methanol (20 mL). To this was added a saturated aqueous NaClO₄ solution (20 mL) with stirring for 2 h under reflux, and the solution was allowed to stand at room temperature until a pink precipitate formed. The precipitate was filtered, washed twice with methanol and ether and dried *in vacuo*. Yield: 34%. Anal. Calcd (Found) % for C₃₀H₄₄N₄O₈Cl₃Cr·0.5H₂O: C, 52.44 (52.65); H, 6.89 (6.96); N, 8.15 (8.22). Λ_M (in DMF): 67.0 ohm⁻¹cm²mol⁻¹.

Preparation of *cis*-[Cr([14]-decane)(cbz)₂]ClO₄. *cis*-[Cr([14]-decane)(OH)₂]⁺ solution (10 mL) was acidified with a *p*-chlorobenzoic acid (1.6 g) dissolved in methanol (40 mL). The mixture was refluxed for 1 h. A saturated aqueous NaClO₄ solution (4 mL) was added to the above hot solution. The resulting mixture was stirred for 2 h under reflux and then cooled to room temperature. The pink precipitate was filtered, washed twice with methanol and ether and dried *in vacuo*. Yield: 50%. Anal. Calcd (Found) % for C₃₀H₄₄N₄O₈Cl₃Cr: C, 48.23 (48.29); H, 5.94 (6.06); N, 7.50 (7.57). Λ_M (in DMF): 67.1 ohm⁻¹cm²mol⁻¹.

Crystal Structure Determination. Crystals of *cis*-[Cr([14]-decane)(cbz)₂]ClO₄ suitable for X-ray diffraction study were grown from an acetonitrile : H₂O (1 : 1) solution of the complex. A pink crystal of complex was mounted on a glass fiber and coated with epoxy resin. The single crystal data for the complex were collected on a Kappa CCD

diffractometer equipped with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The crystallographic data, conditions for the collection of intensity data, and some features of the structure refinements are listed in Table 1. The intensity data were corrected for Lorentz and polarization effects. Absorption correction was not made during processing. Of the 7999 unique reflections measured, 7913 were considered to be observed ($F > 4\sigma(F)$) and were used in subsequent structure analysis. The structure was solved by the direct method²³ and refined by full-matrix least-squares refinement with use of the SHELXL-97 package program.²⁴ All non-hydrogen atoms were refined anisotropically. All hydrogen atoms except for the water hydrogen atoms were placed in the calculated positions with isotropic displacement parameters.

Crystallographic data for the structure reported here have been deposited with Cambridge Crystallographic Data Center (Deposition No. CCDC-236172). The data can be

Table 1. Crystallographic Data for *cis*-[Cr([14]-decane)(cbz)₂]ClO₄

Formula	C ₃₀ H ₄₄ N ₄ O ₈ Cl ₃ Cr
Formula weight	747.04
Radiation (Å)	Mo K(0.71073)
Crystal system	orthorhombic
Space group	<i>Pbca</i>
<i>a</i> (Å)	12.0930(10)
<i>b</i> (Å)	20.3580(10)
<i>c</i> (Å)	28.852
α (°)	90
β (°)	90
γ (°)	90
<i>V</i> (Å ³)	7103.1(7)
<i>Z</i>	8
<i>T</i> (K)	293(2)
<i>D</i> _{calc} (g cm ⁻³)	1.397
μ (mm ⁻¹)	0.600
no. unique data	7999
no. of obsd data ($F_0 > 4\sigma(F_0)$)	7913
no. variable	422
Goodness of fit	1.127
<i>R</i> (abs, all)	0.0977, 0.2172
<i>R</i> _w (obs, all)	0.1620, 0.3278

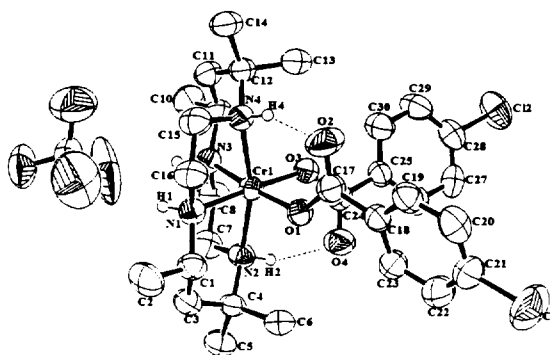


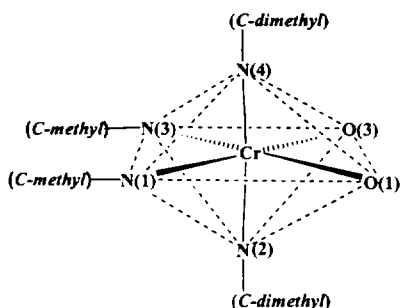
Figure 1. ORTEP plot of the *cis*-[Cr([14]-decane)(cbz)₂]ClO₄.

obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

Crystal Structure. An ORTEP drawing of the *cis*-[Cr([14]-decane)(cbz)₂]ClO₄ with the atomic labeling scheme is depicted in Figure 1. The selected bond distances and angles are listed in Table 2 and 3. The crystal structure of the present complex consists of monomeric cation of the indicated formula and noninteracting perchlorate anion. The monomeric cation, [Cr([14]-decane)(cbz)₂]⁺ shows a distorted octahedral environment, where the chromium(III) ion is coordinated by secondary amines of the macrocycle and by the two carboxylate oxygen atoms of the monodentate *p*-chlorobenzoate ligands in *cis* positions. The *rac*-form, [14]-decane readily folds to give *cis*-chromium(III) complexes with the (*RRRR*, *SSSS*) *sec*-NH configuration and two equatorial and one axial methyl substituents on each six-membered chelate ring. Therefore, two chlorobenzoates are bonded to the chromium(III) by monodentate ligand rather than single chlorobenzoate bonding by bidentate, forming a sterically stable six-coordinate complex. Here, the chlorobenzoate acted as bidentate ligand, forming a four-membered ring, over straining the structure, whereas the two chlorobenzoates function as a monodentate ligand, resulting in a more preferable structure.

The oxygen atoms from the chlorobenzoate ligands and two nitrogen donors (positions of *C*-methyl group) of the [14]-decane define the equatorial coordination plane (CrN₂O₂ *xy*-plane). Hexa-coordination is accomplished *via* the remaining two nitrogens of macrocyclic ligand (positions of *C*-dimethyl group) 1. The tetra-aza ligand is folded along the N(2)-Cr-N(4) axis (axial position). This configuration is often referred to as the Bosnich type-V stereochemistry.²⁵ A similar type of configuration was reported for *cis*-[Cr(cyclam)Cl(dmsO)]²⁺.²⁶ The Cr-N (secondary amines) bond distances are in the range of 2.115(5)-2.140(5) Å, and Cr-O (*p*-chlorobenzoate) distances are 1.964(4) Å and 1.973(4) Å²⁷⁻²⁹ (Table 2). The bond angles are N(1)-Cr-N(3),



1

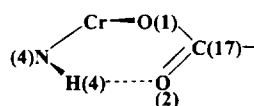
Table 2. Selected bond lengths (Å) for *cis*-[Cr([14]-decane)(cbz)₂]ClO₄

Cr(1)-O(1)	1.964(4)	Cr(1)-O(3)	1.973(4)
Cr(1)-N(1)	2.115(5)	Cr(1)-N(2)	2.140(5)
Cr(1)-N(3)	2.118(5)	Cr(1)-N(4)	2.131(5)
C(17)-O(2)	1.232(7)	C(24)-O(4)	1.238(7)
C(17)-O(1)	1.297(7)	C(24)-O(3)	1.288(7)
O(2)⋯N(4)	2.721(7)	O(4)⋯N(2)	2.791(7)

Table 3. Selected bond angles (°) for *cis*-[Cr([14]-decane)(cbz)₂]ClO₄

O(1)-Cr(1)-O(3)	89.2(2)	N(1)-Cr(1)-N(4)	82.8(2)
O(1)-Cr(1)-N(1)	87.7(2)	N(3)-Cr(1)-N(4)	87.7(2)
O(3)-Cr(1)-N(1)	176.5(2)	O(1)-Cr(1)-N(2)	97.9(2)
O(1)-Cr(1)-N(3)	173.9(2)	O(3)-Cr(1)-N(2)	91.7(2)
O(3)-Cr(1)-N(3)	84.8(2)	N(1)-Cr(1)-N(2)	87.3(2)
N(1)-Cr(1)-N(3)	98.4(2)	N(3)-Cr(1)-N(2)	83.3(2)
O(1)-Cr(1)-N(4)	92.3(2)	N(4)-Cr(1)-N(2)	165.5(2)
O(3)-Cr(1)-N(4)	98.8(2)		
O(2)-H(4)-N(4)	153.5(2)	O(4)-H(2)-N(2)	145.6(2)

N(2)-Cr-N(4) and O(1)-Cr-O(3) 98.4(2)°, 165.5(2)° and 89.2(2)°, respectively (Table 3). These values are well within the general trend with those found in the *cis*-forms of other tetraaza macrocyclic complexes of Cr(III).²⁶ An accepted fact is that in *cis* octahedral complexes of macrocycles of medium size (12-14 membered rings) the pattern of metal-ligand distance and the angle between the axial donors and the metal center are particularly affected by the cavity size.³⁰ In this complex, Cr-N(1; 2.115(5) Å) and Cr-N(3; 2.118(5) Å) distances are shorter than Cr-N(2, axial; 2.140(5) Å) and Cr-N(4, axial; 2.131(5) Å) and the angle N(2)-Cr-N(4) (165.5(2)°) is smaller than the ideal value of 180°, indicating that the donor atoms cannot achieve the axial positions of a perfect octahedron. By contrast, in *cis*-[Cr(cyclam)X₂] octahedral complexes, the angle N_{axial}-Cr-N_{axial} is closer to 180° than that of the title complex and the axial and equatorial distances have similar values.²⁹ The distances and angles were found to be O(2)⋯N(4) 2.721(7) Å, O(2)-H(4)-N(4) 153.5(2)°, O(4)⋯N(2) 2.791(7) Å, and O(4)-H(2)-N(2) 145.6(2)°, which reflect a hydrogen bonding.^{2,31,32} Under this situation, the self-organization seems to make the structure 2 more stable by the hydrogen bonding interaction, in which the carboxylate oxygen O(1) of *p*-chlorobenzoate anion is coordinated to the central Cr(III) and O(2) is H-bonded with H(4) to form a six-membered ring.



2

Electronic Absorption Spectra. The absorption spectra of *cis*-[Cr([14]-decane)(bz)₂]⁺ complex ion in DMF solution at room temperature is represented in Figure 2. Table 4 summarizes the electronic spectral data of *cis*-[Cr([14]-decane)(bz)₂]⁺, *cis*-[Cr([14]-decane)(cbz)₂]⁺, and [CrN₄(L_a)₂]³⁺ chromophores. There are overlapping absorption parts in the spectrum of the title complexes, including the two distinct bands. In *O_h* symmetry, three ligand field bands are expected for a *d³* ion ${}^4A_{2g} \rightarrow {}^4T_{2g}$, ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$ and the two electron transition ${}^4A_{2g} \rightarrow {}^4T_{1g}(P)$.³³ The two *d-d* bands of title complexes observed at 18200, 25390 cm⁻¹ can be related to the spin-allowed transitions, ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}$, respectively. The assignment of geometric configuration is confirmed by the *d-d* absorption spectra. The less symmetrical *cis*-isomers have much higher extinction coefficients than those of more symmetrical *trans*-isomers.³⁴

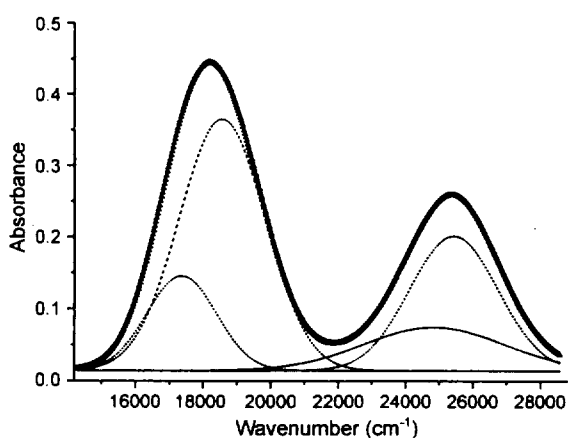


Figure 2. The electronic absorption spectrum of *cis*-[Cr([14]-decane)(bz)₂]⁺ClO₄·0.5H₂O in DMF solution at 298 K.

Table 4. Electronic transition spectral data of several Cr-macrocylic complexes

Complexes	ν , cm ⁻¹ (ϵ , M ⁻¹ cm ⁻¹)
<i>trans</i> -[Cr(cyclam)Cl ₂] ⁺ ^a	17483(19.9), 24570(35), 27397(41)
<i>trans</i> -[Cr(<i>meso</i> -[14]-decane)Cl ₂] ⁺ ^b	17422(25), 22727(27), 25840(47)
<i>trans</i> -[Cr(<i>meso</i> -[14]-decane)Br ₂] ⁺ ^b	16667(33), 24390(38), 26178(43)
<i>cis</i> -[Cr(cyclam)Cl ₂] ⁺ ^a	18904(111), 24752(106)
<i>cis</i> -[Cr([14]-decane)(NO ₂) ₂] ⁺ ^b	19084(202), 25641(116)
<i>cis</i> -[Cr([14]-decane)(bz) ₂] ⁺	18236(223), 25394(131)
<i>cis</i> -[Cr([14]-decane)(cbz) ₂] ⁺	18265(221), 25394(127)

^ataken from ref. 35. ^btaken from ref. 34.

Chromium complexes in tetragonal symmetry are expected to have four absorption bands in the *d-d* region, but each spectrum apparently has two major components. Thus, we

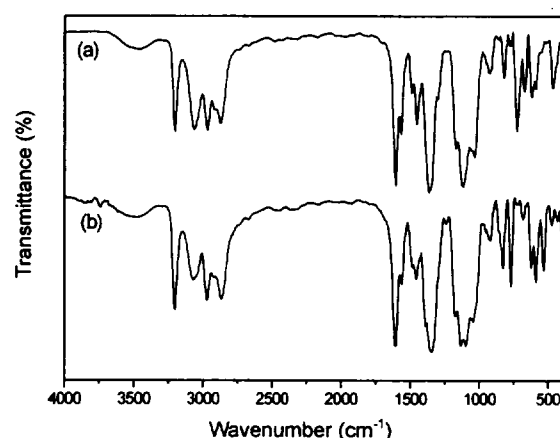


Figure 3. IR Spectra of (a) *cis*-[Cr([14]-decane)(bz)₂]⁺ClO₄·0.5H₂O and (b) *cis*-[Cr([14]-decane)(cbz)₂]⁺ClO₄.

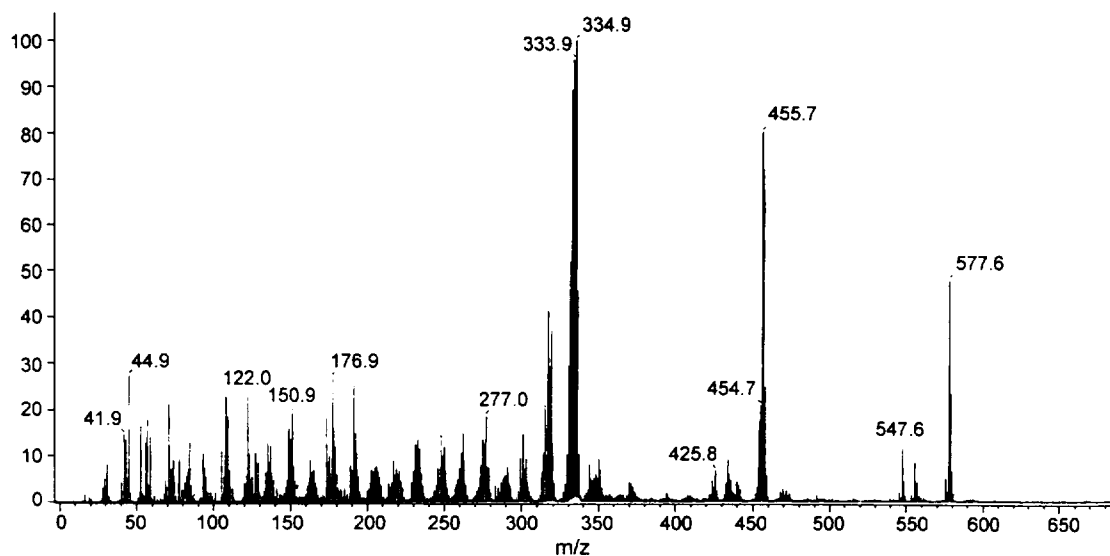


Figure 4. The FAB mass spectrum of the *cis*-[Cr([14]-decane)(bz)₂]⁺ClO₄·0.5H₂O.

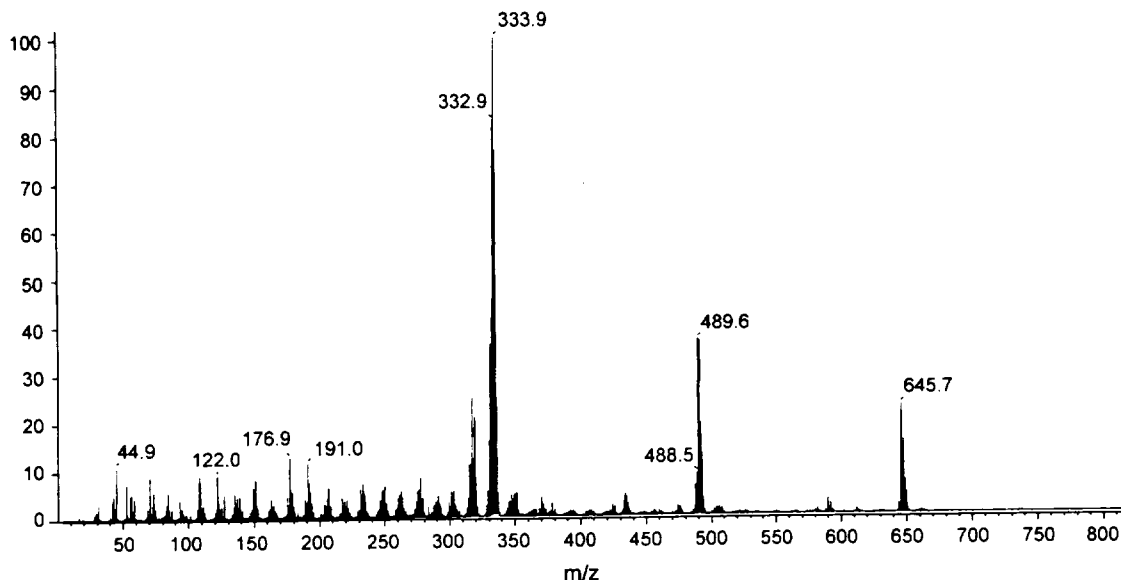


Figure 5. The FAB mass spectrum of the *cis*-[Cr([14]-decane)(cbz)₂]ClO₄.

and then added a minor component to reproduce the more suitable shape of the spectra in the region of interest. Finally, we performed least-squares fitting procedures, and the dotted lines in Figure 2 are Gaussian bands representing the approximate deconvolution of the spectra yielded by the calculations. The four peak positions calculated at 17364, 18562, 24848 and 25438 cm⁻¹ can be assigned to the ⁴E (⁴T_{2g} in O_h symmetry), ⁴B₂(⁴T_{2g}), ⁴E(⁴T_{1g}) and ⁴A₂(⁴T_{1g}), respectively.^{36,37} Similar procedures are also applied to *cis*-[Cr([14]-decane)(cbz)₂]⁺, taken 17644, 18853, 25052 and 25524 cm⁻¹.

Infrared and mass spectra. Three main features are observed in the IR spectra of the new two Cr(III) complexes: (1) The vibrations due to antisymmetric -NH-, -CH-, and Cr-N stretching mode in the macrocycle appear at *ca.* 3205, 2973, 474 cm⁻¹, respectively, and are common to two complexes.^{38,39} (2) In the title complexes, bands due to ν_{as}(COO⁻; antisymmetric mode) and ν_s(COO⁻; symmetric mode) of coordinated carboxylate (donor atom: O) occur at 1609 cm⁻¹ and -1367 cm⁻¹. Unidentate carboxylate complexes have much greater values, Δν (=ν_{as}(COO⁻) - ν_s(COO⁻); benzoate: 242 cm⁻¹, *p*-chlorobenzoate: 257 cm⁻¹) than the ionic carboxylate.⁴⁰ (3) The very strong absorption at near -1120 cm⁻¹ and -624 cm⁻¹ are assigned to ionic perchlorate (Figure 3).^{40,41} The values of molar conductance for *cis*-[Cr([14]-decane)(L_a)₂]ClO₄ measured in DMF or DMSO correspond to a 1 : 1 electrolyte (Λ_M = 67.0 ohm⁻¹cm²mol⁻¹), indicating that the auxiliary ligands in the Cr(III) complexes are not dissociated from the complex in these polar solvents.⁴²

In the FAB mass spectra of [Cr([14]-decane)(bz)₂]ClO₄ and [Cr([14]-decane)(cbz)₂]ClO₄ there is a peak at *m/z* 578, 646 corresponding to the molecular ions [Cr([14]-decane)(bz)₂-H]⁺, [Cr([14]-decane)(cbz)₂-2H]⁺, respectively (Figure

4 and 5). The molecular ion of the *cis*-[Cr([14]-decane)(bz)₂]ClO₄ and *cis*-[Cr([14]-decane)(cbz)₂]ClO₄ undergoes fragmentation to give species such as [Cr([14]-decane)(bz)-2H]⁺, [Cr([14]-decane)-H]⁺ and [Cr([14]-decane)(cbz)-2H]⁺, [Cr([14]-decane)-2H]⁺ at *m/z* 456, 335 and *m/z* 490, 334, respectively.

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