

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

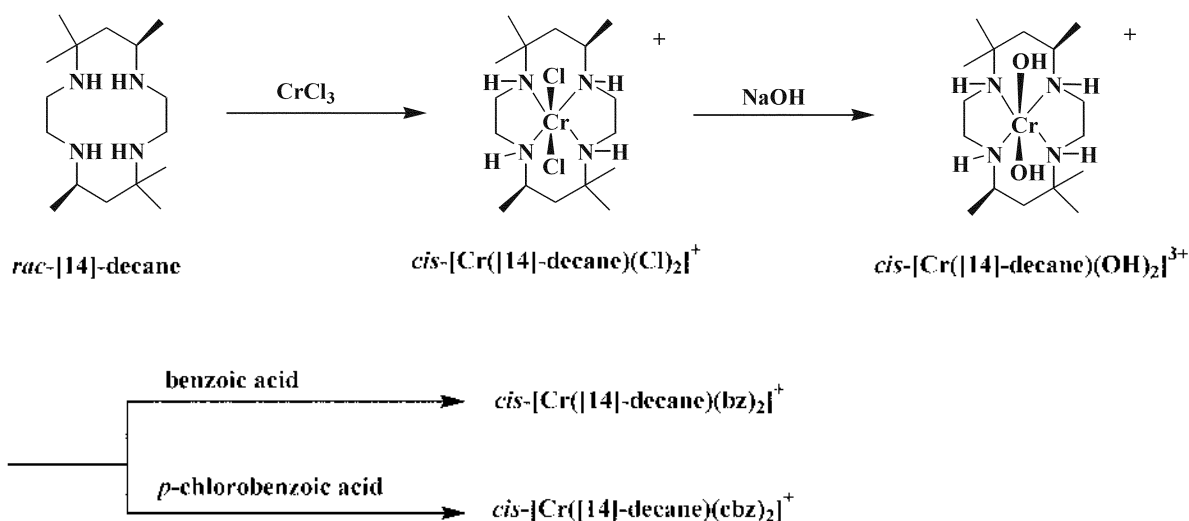
Introduction

Considerably 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-macrocyclic 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 macrocyclic ligands and their

transition metal complexes.¹⁰⁻¹² In particular, the reactivity of nickel- or cobalt-macrocyclic 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 macrocyclic 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-macrocyclic 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 J.FCO 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 C₃₀H₄₆N₄O₈ClCr·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 an 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

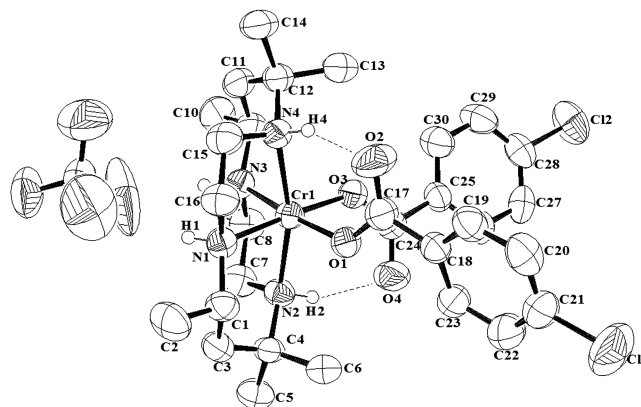


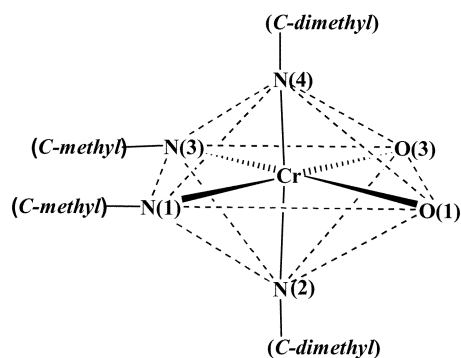
Figure 1. ORTEP plot of the *cis*-[Cr([14]-decane)(cbz)₂]ClO₄.

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 Boshich 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

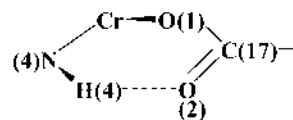
Table 2. Selected bond lengths (Å) for *cis*-[Cr([14]-decane)(cbz)₂]ClO₄

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]⁺ 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 ¹A_{2g} → ¹T_{2g}, ¹A_{2g} → ¹T_{1g}(F) and the two electron transition ¹A_{2g} → ¹T_{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, ¹A_{2g} → ¹T_{2g} and ¹A_{2g} → ¹T_{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.³¹

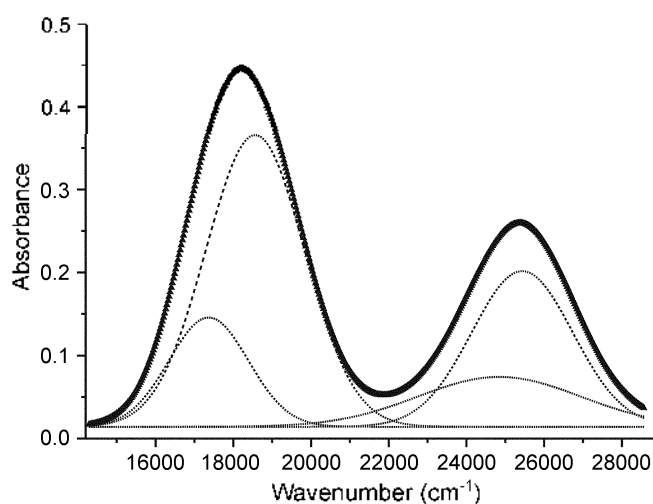


Figure 2. The electronic absorption spectrum of *cis*-[Cr([14]-decane)(bz)₂]⁺ClO₄·0.5H₂O in DMF solution at 298 K.

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

Complexes	ν, cm^{-1} ($\epsilon, \text{M}^{-1} \text{cm}^{-1}$)
<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] ^c	18236(223), 25394(131)
<i>cis</i> -[Cr([14]-decane)(cbz) ₂] ^c	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

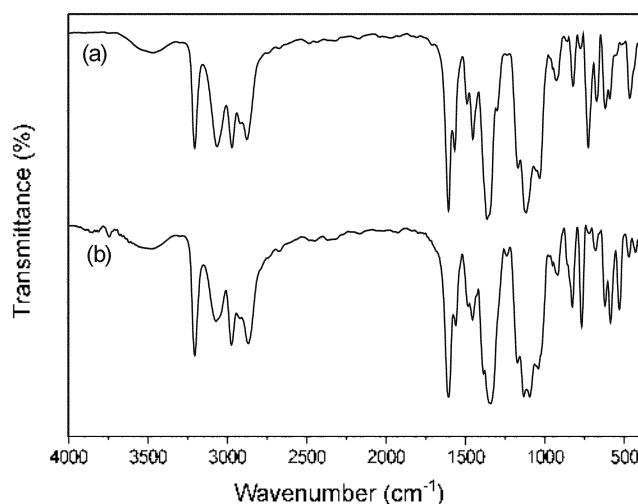


Figure 3. IR Spectra of (a) *cis*-[Cr([14]-decane)(bz)₂]⁺ClO₄·0.5H₂O and (b) *cis*-[Cr([14]-decane)(cbz)₂]⁺ClO₄.

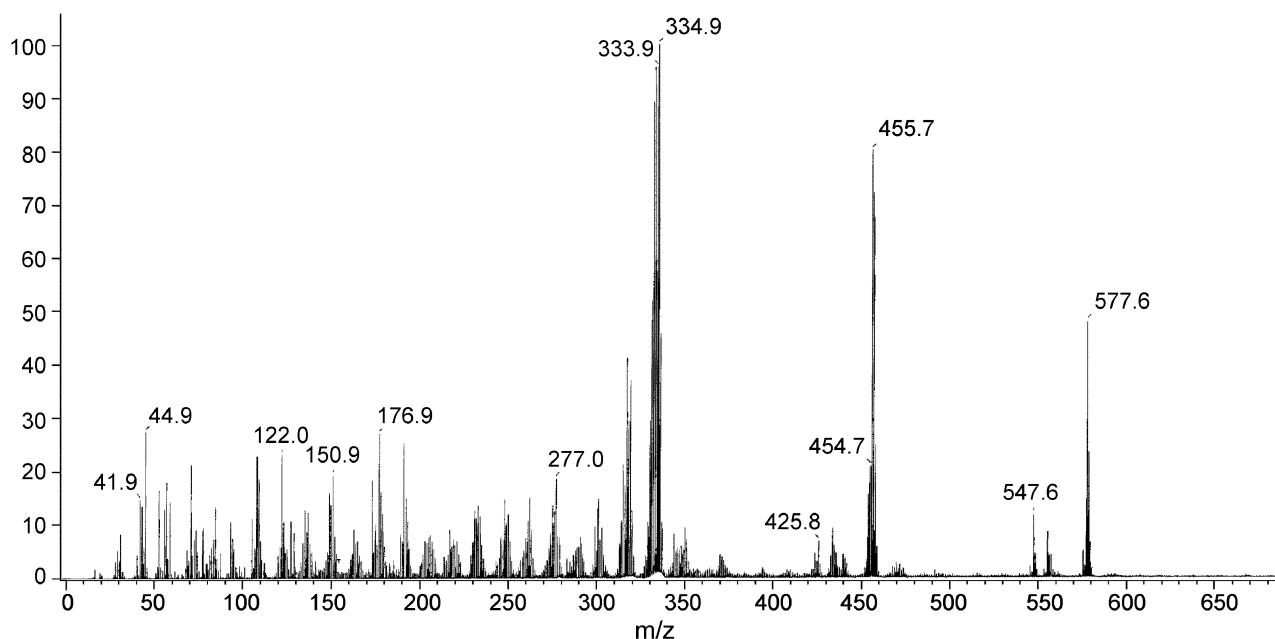


Figure 4. The FAB mass spectrum of the *cis*-[Cr([14]-decane)(bz)₂]⁺ClO₄·0.5H₂O.

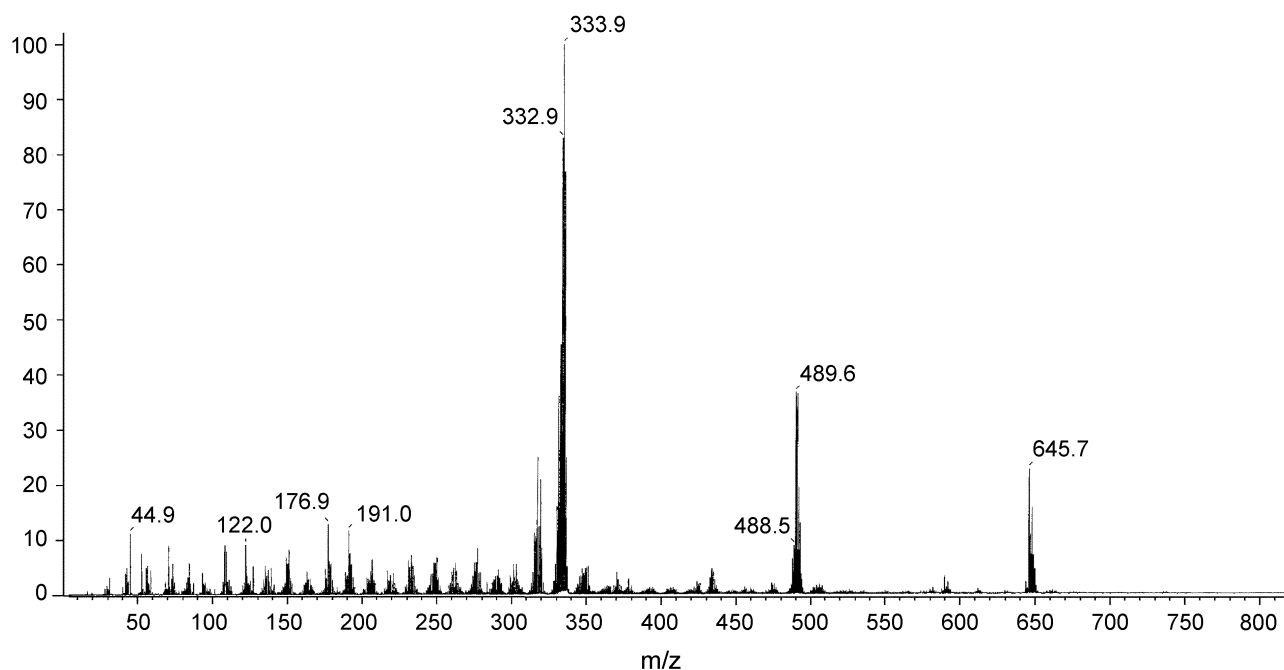


Figure 5. The FAB mass spectrum of the *cis*-[Cr([14]-decane)(cbz)₂]ClO₄.

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}), ⁴F(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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