Syntheses and Characterization of Cr(III)-Hydrogensalicylato and -Hydroxonitrophenolato Tetraaza Macrocyclic Complexes

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Chromium(III) complexes, *cis*-[Cr([14]-decane)(HOC$_6$H$_4$COO)$_2$]ClO$_4$ **I** and *cis*-[Cr([14]-decane)(OH) (OC$_6$H$_4$NO$_2$)]ClO$_4$·H$_2$O **II** ([14]-decane = *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-teraazacyclotetradecane) are synthesized and structurally characterized by a combination of elemental analysis, conductivity, IR and VIS spectroscopy, and X-ray crystallography. The complexes crystallizes in the monoclinic space groups, *C*2$_1$/*a* in **I** and *P*2$_1$/*n* in **II**. Analysis of the crystal structure of complex **I** reveals that central chromium(III) ion has a distorted octahedral coordination environment and two hydrogensalicylato ligands are unidentate to the chromium(III) ion *via* the carboxyl groups in the *cis*-position. For monomeric complex **I** the hydrogensalicylato coordination geometry is as follows: Cr-O(average) = 1.984(3) Å; Cr-N range = 2.105(3)-2.141(4) Å; C(24)-O(4) = 1.286(5) Å; N(2)-Cr-N(4) (equatorial position) = 96.97(15)°; N(1)-Cr-N(3) (axial position) = 168.27(15)°; O(1)-Cr-O(4) = 85.70(13)°. The crystal structure of **II** has indicated that chromium(III) ion is six-coordinated by four secondary amines of the macrocycle, hydroxide anion and nitrophenolate anion.

Key Words : Macrocyclic Cr(III) complex, Crystal structure, Salicylate, Nitrophenolate

Introduction

The complexes of transition metal ions with macrocyclic ligands are significant because of their resemblance with many natural systems, such as porphyrins and cobalamines.[1] The main interest in the macrocycles arise due to their use in labeling monoclonal antibodies with radioactive metals[2,3] and for cancer diagnoses[4,5] as well as with paramagnetic ions for magnetic resonance imaging.[6]

Among the large group of macrocyclic complexes used for the synthesis of porphyrin systems, there are planar tetraaza complexes of copper(II), nickel(II) and chromium(III). This is helped above all by the square symmetry of the metal ion, owing to which there are another two free coordinating sites at the axial positions. Access to the metal ion is very easy when there are no substituents at the macrocyclic ring. This situation changes with the growth and character of substituents, which may present steric hindrance, preventing any coordination to the metal ion. Cyclam, [14]-decane {*meso*- and *rac*-(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane)} and their substituted derivatives are the widespread tetraaza macrocyclic ligands.[7-9]

Salicylic acid, its derivatives and metal salicylates have been used for many years as anti-inflammatory, antipyretic and analgesic drugs in medicine.[10-13] Salicylate is the active component of aspirin and has been found to induce phenotypic multiple antibiotic resistance in various bacteria.[14] Nitrophenols, a compound that is of intense theoretical interest,[15,16] are used to manufacture drugs (*e.g.* acetaminophen), fungicides, insecticides, and dyes and to darken

leather. Contact with eyes causes irritation in humans.[17]

In aqueous solutions, the salicylic acid affords hydrogensalicylate (Hsal = 2-HOC$_6$H$_4$CO$_2^-$; pK$_{a1}$ = 2.97) and salicylate (sal = $^-$OC$_6$H$_4$CO$_2^-$; pK$_{a2}$ = 13.7) ions. From a coordination standpoint, salicylate is a versatile ligand, displaying a variety of bonding modes. The hydrogensalicylate anion can bind to metals as unidentate carboxylate, bidentate chelating by employing one carboxylate oxygen and hydroxyl oxygen atoms or bidentate bridging carboxylate ligand.[18-20] The bisdeprotonated anion $^-$OC$_6$H$_4$CO$_2^-$ regularly chelates through the hydroxyl and one of the carboxylate oxygen atoms.[21,22] The X-ray structures of several mononuclear metal(II) complexes of salicylate derivatives with *N*-donor ligands have been reported.[10,11,23] It has been found that the increase of acidity of the alkylcarboxylate ligands or of the basicity of the basic ligands promotes formation of monomeric complexes.[10]

Pyridine carboxylic acids and their derivatives possess very interesting pharmaceutical properties and constitute an important group of anthelmintics and vitamins.[24] Chromium 3-pyridine carboxylate and 2-pyridine carboxylate are currently used as food supplements.[25] The nutritional role of chromium(III) has been established of mammals for the maintenance of normal glucose, lipid and protein metabolism.[26,27] The naturally occurring ligands and their coordination compounds seem to be implied in the therapeutic activity displayed by drugs containing transition metal ions or the ligand itself.[28] Cr(III) or Cr(VI) reacts with many naturally occurring ligands forming several isomeric complexes due to the high affinity of Cr(III) for N, O and/or S donor atoms.[29,30] Therefore, the chemistry of chromium with

such ligands is obviously of great importance.[31,32] Despite these results very little is known about the composition and structure of the biologically active forms of chromium.

In the light of above discussion, we describe herein the preparation, spectroscopic characteriztion and crystal structure of the first chromium(III) macrocyclic complex, *cis*-[Cr ([14]-decane) $(HOC_6H_4COO)_2$]ClO_4 **I** and *cis*-[Cr([14]-decane)(OH)$(OC_6H_4NO_2)$]$ClO_4\cdot H_2O$ **II** containing auxiliary ligands (L_a = $HOC_6H_4CO_2^-$ or $^-OC_6H_4NO_2$) in its coordination sphere (Schemes 1 and 2). The interactions between Cr(III) and these ligands are of great importance in view of the presumed role of the Cr-N, O bond in the biochemical processes. These compounds are also interesting for their role as unique models in studying complex formation with various substrates.

Experimental Section

General methods. All chemicals were commercial analytical reagents and were used without further purification. For the spectroscopic and physical measurements, organic solvents were dried and purified according to the literature methods.[33] Macrocyclic *rac*-[14]-decane ligand,[34] *cis*-[Cr ([14]-decane)Cl_2]Cl and *cis*-[Cr([14]-decane)(OH)$_2$]$^+$ solution [35,36] were prepared according to the literature methods previously reported. Microanalyses of C, H, and N was carried out using LECO CHN-900 analyzer. Conductance measurement of the complex was performed in DMF at 25 ± 1 °C using an ORION 162 conductivity temperature meter. IR spectrum was recorded with a Bruker FSS66 FT-IR spectrometer. Electronic absorption spectrum was measured at 25 °C on a HP model 8453 UV-VIS Spectrophotometer.

Synthesis of *cis*-[Cr([14]-decane)$(HOC_6H_4COO)_2$]ClO_4 (I). An aqueous solution of $HClO_4$ (70%, *ca*. 1 mL) was mixed with a freshly prepared 4×10^{-3} M *cis*-[Cr([14]-decane)(OH)$_2$]$^+$ solution (10 mL). To this solution was slowly added a salicylic acid (1.38 g) with stirring at room temperature and the resulting mixture was refluxed for 2 h. The pink solution was left undisturbed at room temperature for 10 h. Pink product was obtained which was then washed
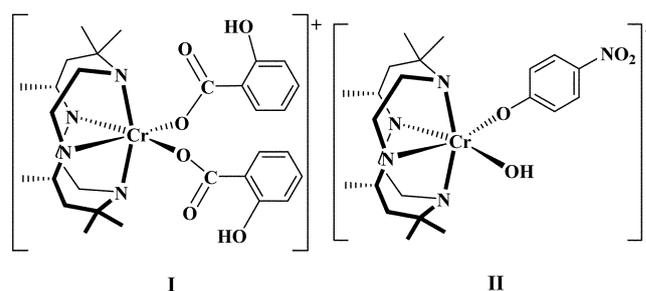

Scheme 2. Structures of the prepared *cis*-[Cr([14]-decane)(HOC$_6$H$_4$COO)$_2$]ClO$_4$ (**I**) and *cis*-[Cr([14]-decane)(OH)(OC$_6$H$_4$NO$_2$)]ClO$_4$·H$_2$O (**II**)

thoroughly with ethanol and finally dried *in vacuo*. Yield: 35%. Anal. Calcd (Found) % for $C_{30}H_{46}N_4O_{10}ClCr$: C, 50.74 (49.89); H, 6.53 (6.22); N, 7.89 (7.94). λ_M(DMF): 69.2 ohm^{-1}cm^{2}mol^{-1}.

Synthesis of *cis*-[Cr([14]-decane)(OH)(OC$_6$H$_4$NO$_2$)]-ClO$_4$·H$_2$O (II). To a freshly prepared *cis*-[Cr([14]-decane)(OH)$_2$]$^+$ solution, a solution of 4-nitrophenol (1.46 g) in methanol (30 mL) was slowly added in small portions, followed by dropwise addition of a saturated aqueous NaClO$_4$ solution (2 mL) with stirring, and refluxed for 2 h. The resulting solution was allowed to stand in a room temperature until dark green precipitates formed. The precipitates were filter, washed twice with methanol, and dried *in vacuo*. Yield 77%. Anal. Calcd (Found, %) for $C_{22}H_{41}N_5O_8ClCr\cdot H_2O$: C, 43.39 (43.20); H, 7.12 (7.38); N, 11.50 (11.55). λ_M (DMF): 66.9 ohm^{-1}cm^{2}mol^{-1}.

X-ray crystallography of complex. Crystals of **I** and **II** suitable for X-ray diffraction study were obtained by slow evaporation of acetonitrile : H$_2$O (1 : 1) solutions of each complex. A pink crystal of complexes 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 Kα radiation (λ = 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 polari-
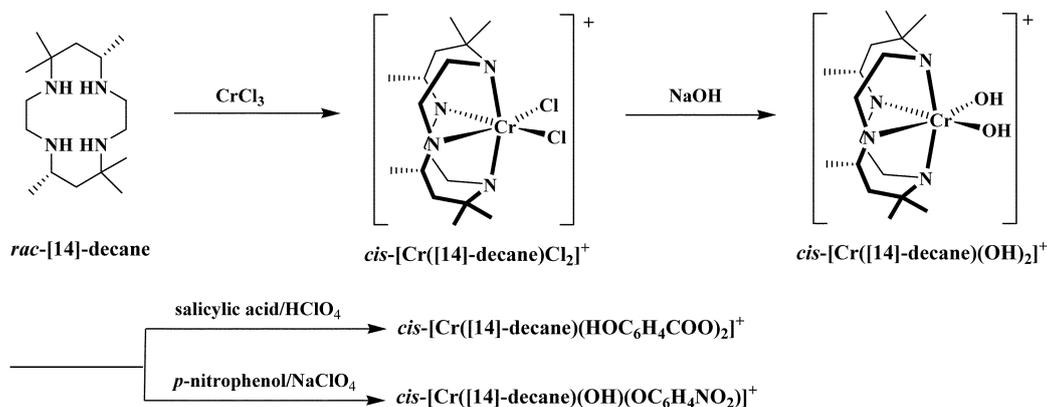
Scheme 1. Synthetic route of the *cis*-[Cr([14]-decane)(HOC$_6$H$_4$COO)$_2$]$^+$ and *cis*-[Cr([14]-decane)(OH) (OC$_6$H$_4$NO$_2$)]$^+$ complexes.

Characterization of Cr(III)-Macrocyclic Complexes

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Table 1. Crystallographic data and structure refinement for *cis*-[Cr([14]-decane)(HOC$_6$H$_4$COO)$_2$]ClO$_4$ (**I**) and *cis*-[Cr([14]-decane)(OH)(OC$_6$H$_4$NO$_2$)]ClO$_4$·H$_2$O (**II**)

	I	II
Empirical formula	C$_{30}$H$_{46}$ClCrN$_4$O$_{10}$	C$_{22}$H$_{43}$ClCrN$_5$O$_9$
Formula weight	710.16	609.06
T / K	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$C2_1/a$	$P2_1/n$
a / Å	15.9787(5)	10.735(5)
b / Å	11.2818(4)	13.832(5)
c / Å	19.9362(8)	19.382(5)
α / °	90	90
β / °	110.806(2)	81.979(5)
γ / °	90	90
V / Å^3	3359.5(2)	2849.8(18)
Z	4	4
Reflections collected	13835	8333
Independent reflections	7718	5380
Goodness-of-fit on F^2	1.032	1.03
Final R_1, wR_2 [I >2$\sigma(I)$]	0.0655, 0.1633	0.0823, 0.2286
R indices (all data)	0.1667, 0.2419	0.1717, 0.3046

$R = \Sigma||F_0|-|F_c||/\Sigma|F_0|$, $R_w = [\Sigma w(F_0{}^2-F_c{}^2)^2/\Sigma w(F_0{}^2)^2]^{1/2}$

Table 2. Selected bond lengths (Å) and angles (°) for *cis*-[Cr([14]-decane)(HOC$_6$H$_4$COO)$_2$]ClO$_4$ (**I**) and *cis*-[Cr([14]-decane)(OH)-(OC$_6$H$_4$NO$_2$)]ClO$_4$·H$_2$O (**II**)

I		II	
Cr-N(2)	2.105(3)	Cr-N(2)	2.119(4)
Cr-N(4)	2.111(4)	Cr-N(1)	2.145(5)
Cr-N(1)	2.128(4)	Cr-N(4)	2.146(6)
Cr-N(3)	2.141(4)	Cr-N(3)	2.153(5)
Cr-O(4)	1.974(3)	Cr-O(1)	1.912(5)
Cr-O(1)	1.993(3)	Cr-O(2)	1.931(4)
O(4)-Cr-O(1)	85.70(13)	O(1)-Cr-O(2)	92.89(19)
O(4)-Cr-N(1)	95.43(13)	O(9)-Cr-N(2)	86.8(2)
O(1)-Cr-N(1)	92.64(14)	O(2)-Cr-N(2)	174.47(18)
O(4)-Cr-N(2)	174.08(14)	O(1)-Cr-N(1)	89.7(2)
O(1)-Cr-N(2)	88.41(14)	O(2)-Cr-N(1)	101.93(18)
O(4)-Cr-N(3)	92.92(13)	O(1)-Cr-N(4)	176.87(17)
O(1)-Cr-N(3)	96.19(13)	O(2)-Cr-N(4)	85.4(2)
O(4)-Cr-N(4)	88.92(14)	O(1)-Cr-N(3)	99.3(2)
O(1)-Cr-N(4)	174.58(14)	O(2)-Cr-N(3)	86.18(19)
N(2)-Cr-N(4)	96.97(15)	N(2)-Cr-N(1)	83.59(18)
N(2)-Cr-N(1)	84.26(14)	N(2)-Cr-N(4)	95.2(2)
N(4)-Cr-N(1)	88.55(15)	N(1)-Cr-N(4)	88.1(2)
N(2)-Cr-N(3)	88.28(14)	N(2)-Cr-N(3)	88.44(19)
N(4)-Cr-N(3)	83.37(14)	N(1)-Cr-N(3)	167.6(2)
N(1)-Cr-N(3)	168.27(15)	N(4)-Cr-N(3)	83.2(2)
C(4)-N(1)-Cr	106.9(3)	C(4)-N(1)-Cr	106.4(4)
C(2)-N(1)-Cr	123.8(3)	C(2)-N(1)-Cr	123.3(4)
C(5)-N(2)-Cr	103.9(3)	C(5)-N(2)-Cr	103.4(3)
C(6)-N(2)-Cr	120.3(3)	C(6)-N(2)-Cr	116.0(4)
C(12)-N(3)-Cr	107.5(3)	C(9)-N(3)-Cr	123.7(4)
C(10)-N(3)-Cr	123.1(3)	C(12)-N(3)-Cr	106.2(4)
C(13)-N(4)-Cr	104.8(3)	C(13)-N(4)-Cr	105.0(4)
C(15)-N(4)-Cr	119.3(3)	C(14)-N(4)-Cr	118.6(4)
C(17)-O(1)-Cr	128.6(3)	C(17)-O(2)-Cr	140.8(4)
C(24)-O(4)-Cr	131.5(3)	O(4)-N(5)-O(3)	123.8(6)

zation effects. Absorption correction was not made during processing. Of the 13,835 and 8,333 unique reflections measured of complexes **I** and **II**, 7,718 and 5,380 reflections in the range 1.09° ≤ 2θ ≤ 27.53° and 1.81° ≤ 2θ ≤ 27.28° were considered to be observed ($I > 2\sigma(I)$), respectively and were used in subsequent structure analysis. The structure was solved by the direct method, [37] and refined by full-matrix least-squares refinement with use of the SHELXL-97 package program.[38] All atoms of the monomeric chromium (III) complex were refined anisotropically. All the hydrogen atoms were first found in difference electron density maps, and then placed in the calculated sites and included in the final refinement in the riding model approximation with displacement parameters derived from the parent atoms to which they were bonded. Selected bond lengths and bond angles are presented in Table 2, and the hydrogen bond lengths and angles are given in Table 3.

Crystallographic data for the structure reported here have been deposited with Cambridge Crystallographic Data Centre {Deposition Nos. CCDC-277016 (**I**) and 277015 (**II**)}. The data can be 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

Description of crystal structure. Only a few chromium (III)-hexamethyl tetraazacyclotetradecane complexes have been reported in the literature.[39] To the best of our knowledge, these are the first reported crystal structures of complexes **I** and **II**. The structures and labeling schemes for

a unidentate hydrogensalicylato complex **I** and nitrophenolato complex **II** are depicted in Figures 1 and 2, respectively. The crystal structure of complex **I** is made up of discrete *cis*-[Cr([14]-decane)(HOC$_6$H$_4$COO)$_2$]$^+$ cation and ClO$_4{}^-$ anion. The structure **II** consists of [Cr([14]-decane)(OH)-(OC$_6$H$_4$NO$_2$)]$^+$, ClO$_4{}^-$ and H$_2$O which are held together by electrostatic forces and hydrogen bonding interactions.

At monomeric cation of **I** chromium(III) ion is six-coordinated with the four secondary amines of the macrocycle and two unidentate hydrogensalicylate-oxygen atoms in *cis* position building a distorted octahedral environment. The complex **II** is similar to that observed in **I**, while the chromium(III) ion is coordinated with a hydroxide ion and a nitrophenolate ion in *cis* fashion. The oxygen atoms from the hydrogensalicylato ligands and two nitrogen donors (positions of *C-methyl* group) of the [14]-decane define the equatorial coordination plane (CrN$_2$O$_2$ *xy*-plane) (Scheme 3). Hexa-coordination is accomplished *via* the remaining two nitrogens (positions of *C-dimethyl* group) of macro-

Table 3. Selected bond lengths (Å) and bond angles (°) for hydrogen bonds of *cis*-[Cr([14]-decane) (HOC$_6$H$_4$COO)$_2$]ClO$_4$ (**I**) and *cis*-[Cr([14]-decane)(OH)(OC$_6$H$_4$NO$_2$)]ClO$_4$·H$_2$O (**II**)

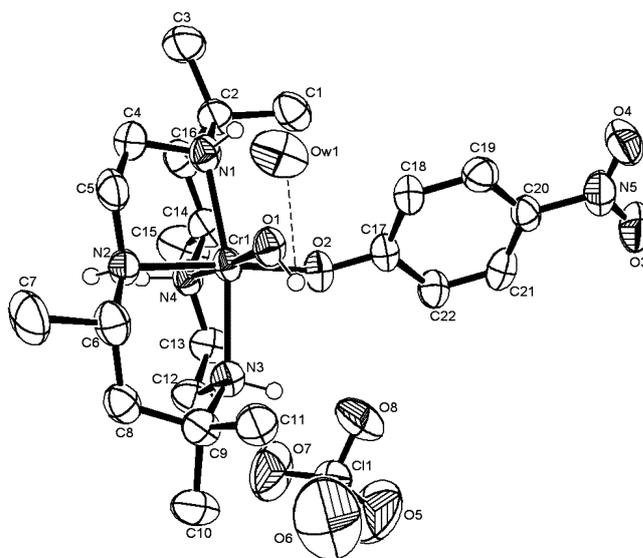| *cis*-[Cr([14]-decane) (HOC$_6$H$_4$COO)$_2$]ClO$_4$ (**I**)		
macrocycle-auxiliary ligand (Hsal)		
N(1)-O(2)	2.783	N(1)-H(1)-O(2)	150.09
N(3)-O(5)	2.816	N(3)-H(3)-O(5)	151.03
intramolecular interaction (auxiliary ligand)		
O(2)-O(3)	2.568	O(2)-H(3d)-O(3)	144.98
O(5)-O(6)	2.561	O(5)-H(6d)-O(6)	144.95
macrocycle-ClO$_4^-$ ion		
N(2)-O(8)	3.069	N(2)-H(2)-O(8)	168.13
cis-[Cr([14]-decane)(OH)(OC$_6$H$_4$NO$_2$)]ClO$_4$·H$_2$O (**II**)		
macrocycle-water		
N(2)-Ow(1) [#]	3.010	N(2)-H(2)-Ow(1)	162.00
N(4)-Ow(1) [#]	2.974	N(4)-H(4)-Ow(1)	169.79
auxiliary ligand-water		
O(1)-Ow(1)	2.652	O(1)-H(1d)-Ow(1)	61.73

Symmetry transformations used to generate equivalent atoms: [#]; 1.5–x, –1/2+y, 1.5–z
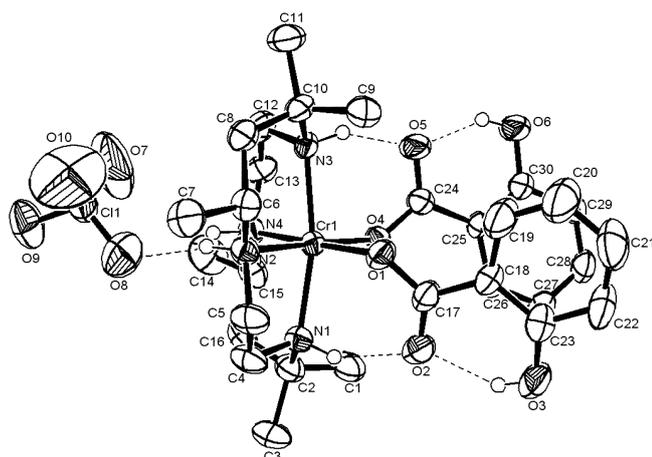
Figure 1. ORTEP drawing with atom-labelling scheme for *cis*-[Cr([14]-decane)(HOC$_6$H$_4$COO)$_2$]ClO$_4$ (**I**).

cyclic ligand. The tetraaza ligand is folded along the N(1)-Cr-N(3) axis (axial position). This configuration is often referred to as the Bosnich type-V stereochemistry.[40] A similar type of configuration was reported for *cis*-[Cr-(cyclam)Cl(dmso)]$^{2+}$.[41]

In both investigated crystal structures, the average Cr-N (secondary amines) bond lengths are 2.131(4) Å,[42] and Cr-O bond lengths are in the range of 1.912(5)-1.993(3) Å (Table 2) which are similar to that of [Zn(Hsal)$_2$(bipy)(CH$_3$OH)] (bipy = 2,2'-bipyridyl)[43] and {*trans*-[Cu(Hsal)$_2$(4,4'-bipy)]-(DMF)}$_n$.[44] As observed in [Co(cyclam)(acac)](BF$_4$)$_2$,[45] the average bond angles {83.82(14)° in **I** and 83.40(10)° in **II**} of N-Cr-N of the five-membered chelate rings around the chromium(III) are smaller than those {88.42(15)° in **I** and 88.27(11)° in **II**} of the six-membered ones (Table 2).

It is known that in *cis* octahedral complexes of macro-

Figure 2. ORTEP drawing with atom-labelling scheme for *cis*-[Cr([14]-decane)(OH)(OC$_6$H$_4$NO$_2$)] ClO$_4$·H$_2$O (**II**).

cycles 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.[46] In complex **I** Cr-N{2; 2.105(3) Å} and Cr-N{4; 2.111(4) Å} bond lengths are shorter than Cr-N{1, axial; 2.128(4) Å} and Cr-N{3, axial; 2.141(4) Å}. However, in complex **II** Cr-N(1) and Cr-N(4) bond lengths have the same magnitude due to the shortening of the Cr-O(1) {1.912(5) Å}. The angles N(1)-Cr-N(3) {168.27(15)° in complex **I** and 167.6(2) ° in complex **II**} are smaller than the ideal value of 180°, indicating that the donor atoms are not able to achieve the axial positions of a perfect octahedron. By contrast, in *cis*-[Cr(cyclam)X$_2$] octahedral complexes, the angle N$_{axial}$-Cr-N$_{axial}$ is closer to 180° than that of the title complexes and the axial and equatorial distances have similar values.[42]

In the coordinated environment of these complexes, the longest Cr-N (secondary amines) and the shortest Cr-O bonds occupied *cis*-position. In complex **I** the O(1)-Cr-N(4) and O(4)-Cr-N(2) linkages are slightly bent {174.58(14) and 174.08(14)°}, whereas the bond angles of O(1)-Cr-O(4), O(1)-Cr-N(3) and O(4)-Cr-N(1) are 85.70(13), 96.19(13) and 95.43(13)°, respectively. The bond angles in complex **II** are comparable with those in complex **I**, but in complex **II** the O(1)-Cr-O(2), O(2)-Cr-N(1) and O(1)-Cr-N(3) angles of 92.89(19), 101.93(18) and 99.3(2)°, respectively, are larger than the corresponding values found in complex **I**. The C(17)-O(1), C(17)-O(2) and C(23)-O(3) bond lengths in complex **I** are 1.293(6), 1.251(6) and 1.336(6) Å, respectively. The bond angles of Cr-O(1)-C(17), Cr-O(4)-C(24), O(1)-C(17)-O(2) and O(4)-C(24)-O(5) are 128.1(3), 131.5(3), 122.5(5) and 123.1(5)° respectively. These bond lengths and bond angles are similar to those in related [Zn(Hsal)$_2$-(bipy)(CH$_3$OH)],[43] {*trans*-[Cu(Hsal)$_2$(4,4'-bipy)](DMF)}$_n$[44] and [Cu(Im)$_2$(sal)$_2$] (Im = imidazole).[47]

Analysis of the crystal packing of complex **I** in the unit cell shows that there exist multiple hydrogen bonding

(*C-dimethyl*)
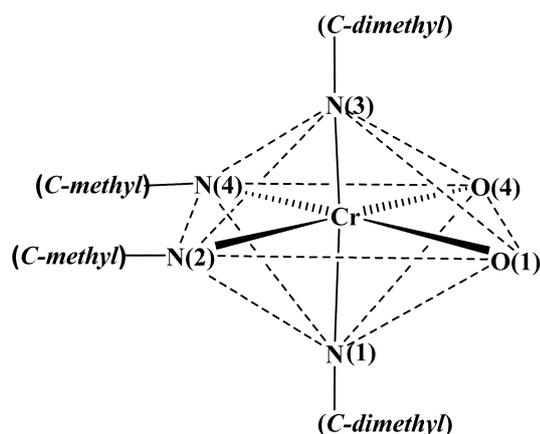
Scheme 3. Optimized structure of Cr(III) macrocyclic complex *cis*-[Cr([14]-decane)(HOC$_6$H$_4$COO)$_2$] ClO$_4$ (**I**).

interactions (Table 3). The overall crystal packing and the conformation of the compounds are stabilized by the inter- and /or intramolecular hydrogen bonding. In complex **I** the uncoordinated carboxyl oxygen O(2) of the unidentate hydrogensalicylates is not only involved in a quasi-aromatic hydrogen bonded rings within salicylate group utilizing C(17), C(18), C(23), O(3) and *ortho*-hydroxyl proton {O(3)-H} attached to O(3), but also assists in the generation of a second rings involving N(1), Cr, O(1), C(17) and secondary amine hydrogen {N(1)-H} of the macrocycle. Also, a very similar structural configuration prevails for the uncoordinated carboxyl oxygen O(5). Traditional hydrogen bonding interaction also exist between the secondary amine hydrogen of the macrocycle and one oxygen atom of a perchlorate anion.

The selected bond lengths and bond angles for hydrogen bonds in complex **I** are given in Table 3. We are able to observe hydrogen bonding of the secondary amine hydrogens of the macrocycle with both the uncoordinated carboxylate oxygens {N(1)-O(2); 2.783 Å, N(3)-O(5); 2.816 Å, N(1)-H(1)-O(2); 150.09°, N(3)-H(3)-O(5); 151.03°} and the ClO$_4^-$ ion {O(2)-O(3); 2.568 Å, O(5)-O(6); 2.561 Å, O(2)-H(3d)-O(3); 144.98°, O(5)-H(6d)-O(6); 144.95°}, in addition of the intramolecular hydrogen bonding between the *ortho*-hydroxyl group in the salicylate anions and the uncoordinated carboxylate oxygens {N(2)-O(8); 3.069 Å, N(2)-H(2)-O(8); 168.13 °}. These results compare favorably with analogous distances and angles in others [Zn(Hsal)$_2$-(bipy)(CH$_3$OH)][43] and {[Cu(phen)$_2$(Hsal)]Hsal·H$_2$O}.[48]

In the crystal lattice of **II** there is one water molecule as solvent of crystallization, which is clustered together with *cis*-[Cr([14]-decane)(OH)(OC$_6$H$_4$NO$_2$)]$^+$ cation (Table 3). It is noteworthy that the hydrophilic parts, nitrophenolato ligands of the structure are placed in the close proximity. It is clearly seen that coordination to metals of nitrophenolato ligand has significant influence on C(17)-O(2) bond length {1.323(7) Å in **II**}. The average C-O bond lengths are 1.311 (2) Å, 1.305(3) Å and 1.293 in Mg(OC$_6$H$_4$NO$_2$)·8H$_2$O,[49] [Co(NH$_3$)$_6$] (OC$_6$H$_4$NO$_2$)$_3$·4H$_2$O[50] and [Cu(dipyam)-(OC$_6$H$_4$NO$_2$)(μ-OCH$_3$)]$_2$ (dipyam = 2,2'-dipyridylamine),[51] respectively.

In complex **II** the lattice water is bonded to the proton of the secondary amine of the macrocycle, N(2)-Ow(1) = 3.010 Å and N(4)-Ow(1) = 2.974 Å, in addition of the hydrogen bond between lattice water and hydrogen of hydroxo ligand, O(1)-Ow(1) = 2.652 Å.

Spectroscopic properties. A DMF solution of *cis*-[Cr([14]-decane)(OH)$_2$]ClO$_4$ displayed a molar conductance of 71.4 ohm^{-1}cm^{2}mol^{-1}, which is in the range of 1 : 1 electrolyte.[52] Undoutedly, the conductivity measurements of complexes **I** (λ_M = 69.2 ohm^{-1}cm^{2}mol^{-1}) and **II** (λ_M = 66.9 ohm^{-1}cm^{2}mol^{-1}) in DMF solution are also consistent with 1 : 1 electrolyte behavior. The first ligand field band ($^4A_{2g} \rightarrow$ $^4T_{2g}$; O_h symmetry) of *cis*-[Cr([14]-decane)(OH)$_2$]$^+$ solution is observed at 612 nm, while the second ligand field band ($^4A_{2g} \rightarrow$ $^4T_{1g}$) is centered at 379 nm.[53,54] The electronic spectra of DMF solution of complexes show two spin-allowed *d-d* transition peaks 541 and 391 nm in **I** (578 and 473 nm in **II**), indicative of a distorted octahedral stereochemistry around the chromium(III) ion.[55] Table 4 summarizes the electronic spectral data of *cis*-[Cr([14]-decane)(HOC$_6$H$_4$COO)$_2$]$^+$ *cis*-[Cr([14]-decane)(bz)$_2$]$^+$, *cis*-[Cr([14]-decane)(cbz)$_2$]$^+$, *cis*-[{Cr([14]-decane)(μ-cit)}$_2$]$^{2+}$, *cis*-[Cr([14]-decane)(NCS)$_2$]$^+$, *cis*-[Cr([14]-decane)(N$_3$)$_2$]$^+$, *cis*-[Cr([14]-decane)(caa)$_2$]$^+$, *cis*-[Cr([14]-decane)(acac)]$^{2+}$ and related octahedral Cr(III) complexes.[56] Such bands are resolved by Gaussian Analysis and the four peak positions calculated at 18030, 18553, 24195, and 25726 cm^{-1} in **I** (16578, 18368, 20741 and 21793 cm^{-1} in **II**) can be assigned to the $^4E(^4T_{2g}$ in O_h symmetry), $^4B_2(^4T_{2g})$, $^4E(^4T_{1g})$ and $^4A_2(^4T_{1g})$, respectively.[57,58(b)]

The infrared spectra of complexes **I** and **II**, taken from KBr pellet, show common absorption bands characteristic of the tetraaza macrocyclic ligand (Figure 3). The IR data of complexes **I** and **II** are in accord with the structure determined by X-ray diffraction. In complex **I** the IR spectra displayed N-H stretches {ν(N-H)} at 3194 and 3084 cm^{-1}, C-H stretches {ν(C-H)} of macrocyclic ligand at 2,976 and 2887 cm^{-1}, and a strong ionic ClO$_4^-$ band at near 1120 cm^{-1} and 623 cm^{-1}.[55] On complexation the position of n(N-H) bands shifted to lower frequency compared to the macrocyclic ligand and a new bands appear at near 461 and 444 cm^{-1} attribute to ν(Cr-N), it provides, strong evidence for the involvement of nitrogen in coordination.[58]

OH stretching vibration bands corresponding to coordinated OH$^-$ ligand and OH of uncoordinated water molecule are present at 3560 and 3512 cm^{-1}, respectively, for complex **II**.[59] The strong bands at 1494 and 1302 cm^{-1} in the spectrum of **II** are associated with the -NO$_2$ asymmetric and symmetric stretching vibration bands in nitrophenolate group.[59] In addition, complex **II** has been characterized by a perchlorate absorption at 1111 and 625 cm^{-1} as well as Cr-N bands at 488 and 419 cm^{-1}.

The typical peak of salicylic acid appearing in the region of 1700-1650 cm^{-1} is absent, which shows a complete deprotonation of the carboxyl groups. The asymmetric and symmetric stretching vibration bands of hydrogensalicylate group appear at 1628, 1387 cm^{-1}, respectively.[60] The splitt-

Table 4. Electronic transition spectral data of **I**, **II**, and related octahedral Cr(III) complexes

Complexes	λ, nm (ε, M^{-1} cm^{-1})	refs.
cis-[Cr(cyclam)(H$_2$O)$_2$]$^{3+}$	483 (126), 370 (38)	a, b
cis-[Cr(cyclam)(H$_2$O)(NH$_3$)]$^{3+}$	476 (110), 362 (87)	a, b
cis-[Cr([14]-decane)(OH)$_2$]$^+$	612 (123), 379 (85)	b
cis-[Cr([14]-decane)(OH)(H$_2$O)]$^{2+}$	575 (138), 393 (62)	b
cis-[Cr([14]-decane)(H$_2$O)$_2$]$^{3+}$	540 (160), 388 (79)	b
cis-[Cr([14]-decane)(cbz)$_2$]$^{+\ *}$	547 (221), 394 (127)	b
cis-[{Cr([14]-decane)(μ-cit)}$_2$]$^{2+*}$	532 (186), 385 (97)	b
cis-[Cr([14]-decane)(NCS)$_2$]$^+$	541 (135), 406 (78)	b
cis-[Cr([14]-decane)(caa)$_2$]$^{+\ *}$	537 (201), 390 (108)	b
cis-[Cr([14]-decane)(acac)]$^{2+\ *}$	536 (190), 388 (269)	b
cis-[Cr([14]-decane)(ox)]$^{+\ *}$	533 (157), 386 (82)	b
cis-[Cr([14]-decane)(mal)]$^{+\ *}$	551 (164), 387 (71)	b
cis-[Cr([14]-decane)(HOC$_6$H$_4$COO)$_2$]$^+$	541 (223), 391 (134)	this work
cis-[Cr([14]-decane)(OH)(OC$_6$H$_4$NO$_2$)]$^+$	578 (172), 473sh (326)	this work

a, b and c taken from refs. 55 (a, c) and 55 (d), respectively. *Abbreviations, cbz, cit, caa, acac, ox, and mal are chlorobenzoate, citrate, chloroacetate, acetylacetonate, oxalate and malonate, respectively.
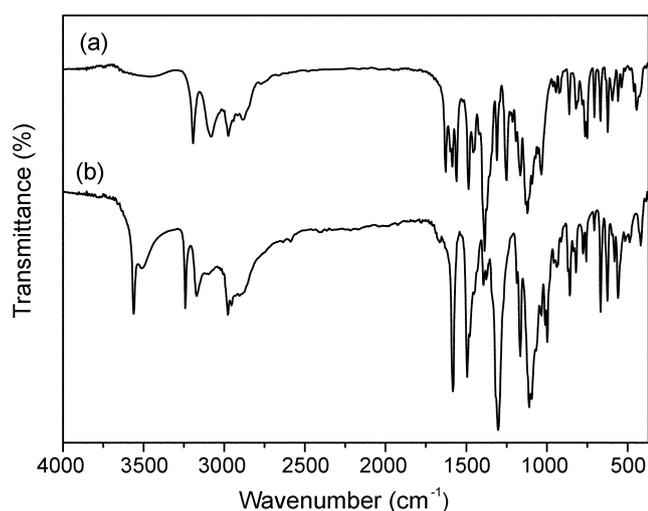

Figure 3. IR spectrum of the (a) *cis*-[Cr([14]-decane)(HOC$_6$H$_4$COO)$_2$]ClO$_4$ (**I**) and (b) *cis*-[Cr([14]-decane)(OH)(OC$_6$H$_4$NO$_2$)]-ClO$_4$·H$_2$O (**II**).

ing of the vibration bands of salicylate group indicates that the COO$^-$ groups function in different coordination fashions. The asymmetric ν_{as}(COO$^-$) vibration band is observed in the high frequency, which is probably due to the polarization of the carboxyl groups and the inequivalence of two Cr(III)-O bonds.[61] The difference between the symmetric and asymmetric stretches, $\Delta\nu$ {= ν_{as}(COO$^-$)- ν_s(COO$^-$)} are on the order of 213 cm^{-1}, indicating that carboxylate groups are either free or coordinated to the metal ion in a monodentate fashion.[62] The aforementioned assignments are in agreement with previous results for citrate complexes of various metals.[63]

However, the above carboxylate bands undergo different shifts depending on the interacting metal. The strongest changes are observed for the ν_{as}(COO$^-$), which is one of the most intense in the IR spectra. In the case of sodium salicylate, this band is split in two components appearing at

1597 and 1583 cm^{-1}. But in the case of Fe^{3+} and Cu^{2+} complexes the ν_{as}(COO$^-$) mode is markedly weakened. This variation may indicate a significant change in the symmetry of these modes induced by the intraction with the metal.[60]

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