Cr(III)-Tetraaza Macrocyclic Complexes Containing Auxiliary Ligands (Part III); Synthesis and Characterization of Cr(III)-Isothiocyanato, -Azido and -Chloroacetato Macrocyclic Complexes

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The reaction of *cis*-[Cr([14]-decane)(OH$_2$)$_2$]$^+$ ([14]-decane = *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-teraazacyclotetradecane) with auxiliary ligands {L$_a$= isothiocyanate (NCS$^-$), azide (N$_3$$^-$) or chloroacetate(caa)} leads to a new *cis*-[Cr([14]-decane)(NCS)$_2$]ClO$_4$·H$_2$O (**1**), *cis*-[Cr([14]-decane)(N$_3$)$_2$]ClO$_4$ (**2**) or *cis*-[Cr([14]-decane)(caa)$_2$]ClO$_4$ (**3**). These complexes have been characterized by a combination of elemental analysis, conductivity, IR and Vis spectroscopy, mass spectrometry, and X-ray crystallography. Analysis of the crystal structure of *cis*-[Cr([14]-decane)(NCS)$_2$]ClO$_4$·H$_2$O reveals that central chromium(III) has a distorted octahedral coordination environment and two NCS$^-$ anions are bonded to the chromium(III) ion *via* the N-donor atom in the *cis* positions. The angle N$_{axial}$-Cr-N$_{axial}$ deviates by 13° from the ideal value of 180° for a perfect octahedron. The bond angle N-Cr-N between the Cr(III) ion and the two nitrogen atoms of the isothiocyanate ligands is close to 90°. The bond lengths of Cr-N between the chromium and NCS$^-$ groups are 1.964(5) and 2.000(5) Å. They are shorter than those between chromium and nitrogen atoms of the macrocycle. The IR spectra of **1**, **2** and **3** display bands at 2073, 1344 and 1684 cm^{-1} attributed to the NCS$^-$, N$_3$$^-$ and caa groups stretching vibrations, respectively.

Key Words : Cr(III) macrocyclic complex, Cr(III) isothiocyanato complex, Crystal structure, Absorption spectra

Introduction

Binding of auxiliary ligand (chlorobenzoate, citrate, chloroacetate, NO, CO, imidazole, SCN$^-$, and N$_3$$^-$) to transition metal proteins has been widely employed as a method to obtain structural or mechanistic information on the metal sites.[1] For instance, the azide ion has been used in binding studies on amine oxidases,[2] superoxide dismutase,[3] galactose oxidase,[4] laccase,[5] and ascorbate oxidase.[6] In such cases binding of anions such as azide, thiocyanate and bromide to copper(II) is generally accompanied by the appearance of LMCT transitions in the visible or near-UV region and produce changes in the EPR spectra that may potentially very useful for empirical correlations between spectra and structure.[7-9]

The geometry and coordination mode of NCS$^-$ and N$_3$$^-$ in copper complexes is strongly influenced by the electronic and steric effects around Cu atom.[10] It has been shown that octahedral copper complexes with two NCS$^-$ or N$_3$$^-$ ions in the axial positions can be prepared only when the four equatorial positions are occupied by sterically hindered nitrogen donor ligands.[11] The copper complexes of macrocyclic ligand (L$_m$ = *trans*-5,7,12,14-tetramethyl-6,13-dinitro-1,4,8,11-tetraazacyclotetradecane) has recently been the subject of several chemical and structural studies.[12-15] This ligand forms square planar complex with the copper(II) ion, [Cu(L$_m$)](ClO$_4$)$_2$, which provides a rare example of square

planar coordination of tetraazamacrocyclic copper(II) complexes.[12,13] It has been suggested that the axially oriented methyl groups prevent the coordination of solvent or counter ion ClO$_4$$^-$ to the metal ion.[13] However, there is plenty of space for coordination of small auxiliary ligands such as NCS$^-$, N$_3$$^-$ or NO to the axial positions resulting in the formation of five- or six-coordinate copper complexes.

Recent field monitoring studies indicate that haloacetic acids are widespread in the environment and have generated interest in investigating their sources, environmental fate, persistence, and disposition.[16] In this context Grodzicki *et al.*[17] have reported synthesis, molecular structure, spectroscopic and magnetic properties of the copper(II) chloroacetate complexes with 5,7-dimethyl-1,2,4-triazolo-[1,5-α]-pyrimidine (dmtp) and 5,7-diphenyl-1,2,4-triazolo-[1,5-α]-pyrimidine (dptp), Cu$_2$(CH$_2$ClCOO)$_4$(dmtp)$_2$ and Cu$_2$-(CH$_2$ClCOO)$_4$(dptp)$_2$. Huskens *et al.*[18] have described a study of the coordination of Ln(III) with the three chloroacetate, acrylate and propiolate with the use of potentiometry, calorimetry and multinuclear NMR spectroscopy.

Currently only limited synthetic work has been carried out on chromium(III) complexes of macrocyclic ligand, *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (= [14]-decane) and 1,4,8,11-tetraazacyclotetradecane (cyclam) containing auxiliary ligands. House *et al.*[19,20] have described the preparation of a variety of Cr(III) complexes, *cis*-[Cr([14]-decane)(L$_a$)$_2$]L$_a$ (L$_a$ = NCS$^-$, Br$^-$ and N$_3$$^-$) of C-
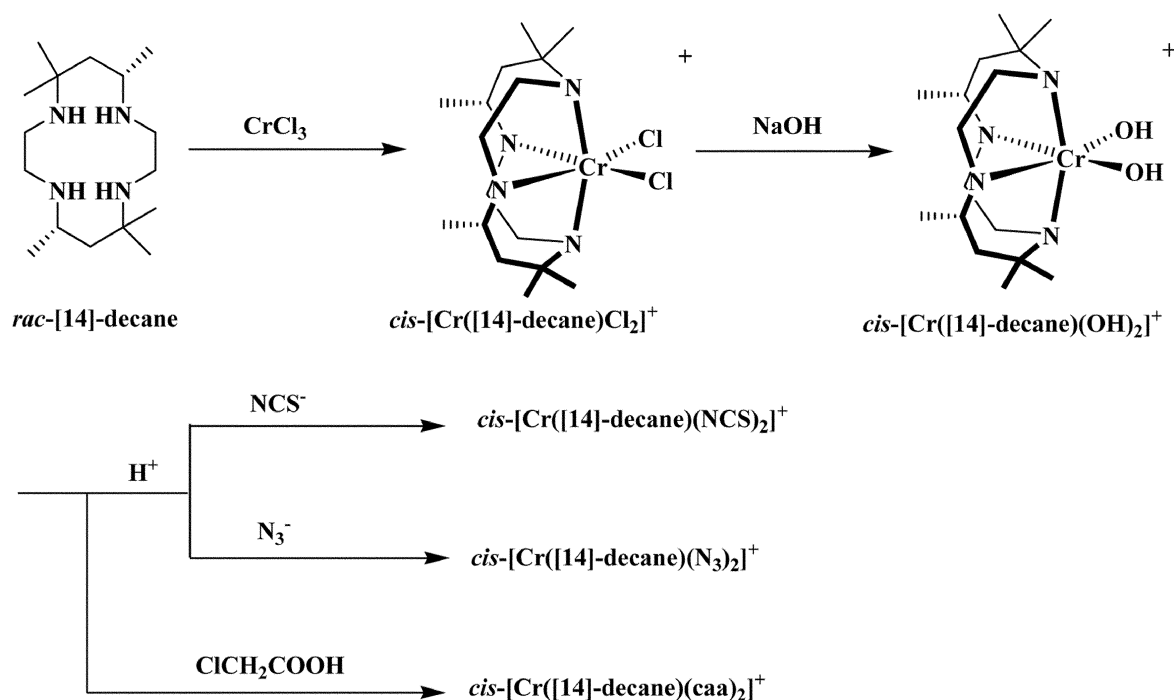
Scheme 1. Synthetic route of the *cis*-[Cr([14]-decane)(L_a)$_2$]ClO$_4$ (L_a = NCS$^-$, N$_3^-$ and caa).

meso and C-*racemic* diastereoisomers. C-*racemic* type readily folds to give *cis*-complexes with the (*RRRR, SSSS*) *sec*-NH configuration and two equatorial and one axial methyl substituent on each six-membered chelate ring. Eriksen *et al.*[21] have recently attempted to characterize the complex formation between carboxylic acids/carboxylates, in particular acetic acid/acetate and *cis*-[Cr([14]-decane)-(Cl)$_2$]Cl. To our knowledge, few crystal structures of the Cr(III) complexes, *cis*-[Cr([14]-decane)(L_a)$_2$]Y (L_a = NCS$^-$, N$_3^-$ ClCH$_2$COO$^-$ and Y = ClO$_4^-$) have been reported. These patterns have led us to discuss X-ray crystal structure of the type *cis*-[Cr([14]-decane)(L_a)$_2$]Y.

In the light of above discussion, this work performs synthesis and physicochemical characterization of a series of six-coordinate anion-bound Cr(III) complexes of the type *cis*-[Cr([14]-decane)(L_a)$_2$]ClO$_4$ (L_a = NCS$^-$, N$_3^-$ ClCH$_2$-COO$^-$) (Scheme 1). And we also describe the crystal structure of Cr(III) macrocyclic complex containing SCN$^-$ ions.

Experimental Section

General methods. All reagents and chemicals were purchased from commercial sources. Solvents used for electrochemical and spectroscopic studies were purified by standard procedures. Nanopure quality water was used throughout this work. *cis*-[Cr([14]-decane)(OH)$_2$]$^+$ solution and related compounds were prepared by literature methods.[22]

Microanalyses of C, H, and N were carried out using LECO CHN-900 analyzer. Conductance measurements of the complexes were performed in DMF at 25 ± 1 °C using an ORION 162 conductivity temperature meter. IR spectra

were recorded with a Bruker FSS66 FT-IR spectrometer as KBr pellets. Electronic absorption spectra were measured at 25 °C on a HP model 8453 UV-VIS Spectrophotometer. 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.

Synthesis of *cis*-[Cr([14]-decane)(NCS)$_2$]ClO$_4$·H$_2$O (1). 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 a 50 mL aqueous solution of NaSCN (0.83 g) and a saturated aqueous NaClO$_4$ solution (4 mL) were added dropwise with constant stirring. After the addition the resulting mixture was stirred thoroughly for 4 h. The pink solution was left undisturbed at room temperature for 1 h to give pink product, and then the product was washed with ice-cold acetone and finally dried *in vacuo*. Yield: 58%. Anal. Calcd (Found) % for C$_{18}$H$_{36}$N$_6$O$_4$ClS$_2$Cr·H$_2$O: C, 37.92 (37.98); H, 6.72 (7.03); N, 14.74 (14.44). λ_M (DMF): 91.9 ohm^{-1}cm^{2}mol^{-1}.

Synthesis of *cis*-[Cr([14]-decane)(N$_3$)$_2$]ClO$_4$ (2). A similar procedure as that for **1** was followed with a 50 mL aqueous solution of NaN$_3$ (0.65 g). Yield: 75%. Anal. Calcd (Found) % for C$_{16}$H$_{36}$N$_{10}$O$_4$ClCr: C, 36.96 (36.98); H, 6.98 (6.94); N, 26.94 (26.48). λ_M (DMF): 73.6 ohm^{-1}cm^{2}mol^{-1}.

Synthesis of *cis*-[Cr([14]-decane)(caa)$_2$]ClO$_4$ (3). To a 10 mL solution containing 4×10^{-3} M *cis*-[Cr([14]-decane)(OH)$_2$]$^+$, a 20 mL aqueous solution of chloroacetic acid (1 g) was added slowly with stirring at room temperature, after being stirred for 1h, a saturated aqueous NaClO$_4$ solution (4 mL) was added dropwise with constant

stirring. The resulting mixture was stirred thoroughly for 2 h under reflux and then cooled to room temperature. The pink precipitate was washed with ice-cold water and dried *in vacuo*. Yield: 90%. Anal. Calcd (Found) % for $C_{20}H_{40}N_6O_8Cl_3Cr \cdot H_2O$: C, 38.56 (38.51); H, 6.47 (6.70); N, 8.99 (9.09). λ_M (DMF): 66.2 ohm^{-1}cm^{2}mol^{-1}.

Caution: Metal azide complexes are potential explosives. Only a small amount of material should be prepared and handled with caution.

X-ray crystallography of complex. Crystals of *cis*-[Cr([14]-decane)(NCS)₂](ClO₄)₂·H₂O suitable for X-ray diffraction study were obtained by slow evaporation of 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 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 polarization effects. Absorption correction was not made during processing. Of the 6,039 unique reflections measured, 6,030 reflections in the range $1.93° \le 2 \le 27.48°$ were considered to be observed ($I > 2\sigma(I)$) and were used in subsequent structure analysis. The structure was solved by the direct method,[23] and refined by full-matrix least-squares refinement with use of the SHELXL-97 package program.[24] All atoms of the monomeric chromium(III) complex were refined anisotropically, but the water hydrogens were refined isotropically. The

water hydrogens were difficult to find in the difference maps, but surprisingly easy to refine to very reasonable positions. Selected bond lengths and bond angles are presented in Table 2 and 3, and the hydrogen-bond lengths and angles are given in Table 4.

Crystallographic data for the structure reported here have been deposited with Cambridge Crystallographic Data Center (Deposition No. CCDC-249656). 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

Preparation of *cis*-[Cr([14]-decane)(OH)₂]⁺ solution. The reaction of anhydrous chromium(III) chloride with [14]-decane gives a good yield of a bluish-green complex *cis*-[Cr([14]-decane)Cl₂]Cl.[25] Base hydrolysis of *cis*-[Cr([14]-decane)Cl₂]⁺ has been studied.[19] The two moles of OH⁻ ion are consumed per mole of *cis*-[Cr([14]-decane)Cl₂]⁺ complex in the pH range 7.8-9.4, and the final visible absorption spectrum is identical to that obtained from *cis*-[Cr([14]-decane)(OH)]⁺ solution. A DMF solution of *cis*-[Cr([14]-decane)(OH)₂]ClO₄ displayed a molar conductance of 71.4 ohm^{-1}cm^{2}mol^{-1}, which is in the range of 1 : 1 electrolyte.[19] This complex ion can be used to prepare a large variety of other complexes containing auxiliary ligands.

It shows that the absorption bands shift to shorter wavelength on addition of HClO₄ solution to the aqueous *cis*-[Cr([14]-decane)(OH)₂]⁺ complex solution. The absorption spectrum of this species is compared with several related compounds in Table 5. The first LF band ($^4A_{2g} \rightarrow {}^4T_{2g}$; O_h symmetry) of *cis*-[Cr([14]-decane)(OH₂)₂]³⁺ solution is observed at 529 nm, while the second LF band ($^4A_{2g} \rightarrow {}^4T_{1g}$) is centered at 388 nm.[26] The molar absorptivities of the two *d-d* bands are substantially greater than those of the *trans* analogues, consistent with the given geometric assignment.[19]

Description of crystal structure. Only a few chromium (III)-tetraazacyclotetradecane complexes have been reported in the literature.[27,28] To our knowledge, this is the first reported crystal structure of a *cis*-[Cr([14]-decane)(NCS)₂]-ClO₄·H₂O complex containing auxiliary ligands, NCS⁻ ions. Like the azide ligand, the pseudohalide NCS⁻ ion has been known to coordinate to metals in both terminal and bridging modes. The thiocyanato group has received most of the major attention due to its versatility as a ligand and to the wide variety of magnetic properties of its compounds.[29] The structure and labeling scheme for isothiocyanato (N-donor) complex *cis*-[Cr([14]-decane)(NCS)₂]²⁺ is depicted in Figure 1. The crystal structure of this complex is composed of monomeric cation of the indicated formula and noninteracting perchlorate anions. These results are backed up by the elemental analysis and molar conductivity (λ_M = 91.9 ohm^{-1}cm^{2}mol^{-1}) which agreed with assignment of the structure as *cis*-[Cr([14]-decane)(NCS)₂](ClO₄)·H₂O.

Table 1. Crystallographic Data for *cis*-[Cr([14]-decane)(NCS)₂]-ClO₄·H₂O

Formula	$C_{18}H_{38}N_6O_5S_2ClCr$
Formula weight	570.11
Radiation (Å)	Mo Kα (0.71073)
Crystal system	orthorhombic
Space group	*Cbca*
a (Å)	15.295
b (Å)	16.4850(10)
c (Å)	21.0490(10)
α (°)	90
β (°)	90
γ (°)	90
V (Å³)	5307.3(4)
Z	8
T (K)	293(2)
D_{calc} (gcm^{-3})	1.427
θ Range of data collected	1.93-27.48
F_{000}	6039
μ (mm^{-1})	0.728
no. of obsd data (I > 2σ(I))	6030
no. variable	304
Goodness of fit	1.008
R	0.0762
R_w	0.2196

$R = \Sigma \parallel F_0| - |F_c\parallel/\Sigma|F_0|$. $R_w = [\Sigma w(F_0{}^2 - F_c{}^2)^2/\Sigma w(F_0{}^2)^2]^{1/2}$. $w = 1/[\sigma^2(F_0{}^2) + (0.1485P)^2 + 0.0000P]$, $P = (F_0{}^2 + 2F_c{}^2)/3$
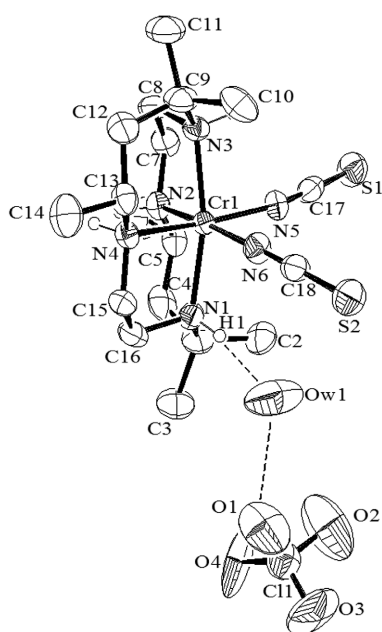
Figure 1. ORTEP plot of the *cis*-[Cr([14]-decane)(NCS)$_2$]ClO$_4$·H$_2$O complex.

The monomeric cation, [Cr([14]-decane)(NCS)$_2$]$^+$ shows a distorted octahedral environment, where the chromium(III) ion is coordinated by secondary amines of the macrocycle and by the two nitrogen atoms of the auxiliary ligand NCS$^-$ ions in *cis* positions. The nitrogen atoms from the NCS$^-$ 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). Hexa-coordination is accomplished *via* the remaining two nitrogens of macrocyclic ligand (positions of *C-dimethyl* group) I. The tetra-aza 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.[30] A similar type of configuration was reported for *cis*-[Cr(cyclam)Cl(dmso)]$^{2+}$.[31]

I
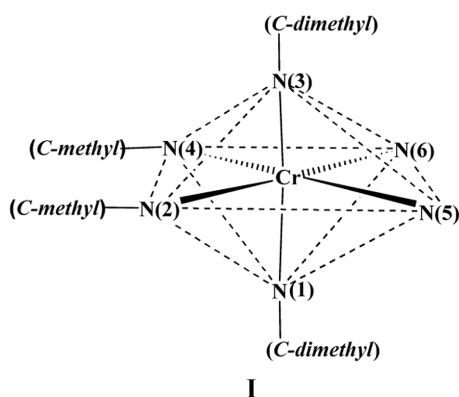
The Cr-N (secondary amines) bond distances are in the range of 2.103(4)-2.147(4) Å, and Cr-N (isothiocyanate) distances are 1.964(5) and 2.000(5) (Table 2).[32-34] The bond angles N(1)-Cr-N(3), N(2)-Cr-N(4) and N(5)-Cr-N(6) are 167.5(2)°, 97.1(2)° and 88.0(2)°, respectively (Table 3).

These values are well within the general trend with those found in the *cis*-forms of other tetraaza macrocyclic complexes of Cr(III).[31] It is known 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.[35] In this complex Cr-N {2; 2.103(4) Å} and Cr-N {4; 2.104(4) Å} distances are shorter than Cr-N {1, axial; 2.147(4) Å} and Cr-N {3, axial; 2.132(4) Å} and the angle N(1)-Cr-N(3) {167.5(2)°} is 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 complex and the axial and equatorial distances have similar values.[34]

In the coordinated environment of this complex, the longest Cr-N (secondary amines) and the shortest Cr-N (isothiocyanate) bonds occupied *cis*-position. The two NCS ligands keep their linearity, N-C-S bond angles are 177.3(6)° and 178.1(5)°, whereas the Cr-N(5)-C(17) and Cr-N(6)-C(18) linkages are slightly bent {165.0(4)° and 167.3(5)°}. Each NCS ligand adopts the most stereochemically favorable orientation with respect to the macrocycle. These data are similar to that reported for other complexes, (NiL-1)$_3$-[Fe(NCS)$_6$]$_2$ (L-1 = 5,6,12,13,-Me$_4$-[14]-4,11-dieneN$_4$)[36] and [Ge(tmtaa)(NCS)$_2$] (tmtaa = 5,14-dihydro-6,8,15,17-tetramethyldibenzo[*b, i*] [1,4,8,11]tetraazacyclotetradecine).[37] The bond length of N(6)-C(18) {1.139(7) Å} is about 0.077 Å shorter than that of N(5)-C(17) {1.216(7) Å}.

The non-coordinated thiocyanate group is well-ordered with C-N and C-S distances of 1.168(9) and 1.620(7) Å, compared with the coordinated isothiocyanato moiety C-N and C-S distances of 1.216(7), 1.139(7) Å and 1.589(7), 1.632(7) Å in the title complex, respectively. Those of the isothiocyanato group are comparable to those reported for [Ge(tmtaa)(NCS)$_2$] having distances 1.176(9), 1.164(8) Å and 1.597(8), 1.592(8) Å, respectively.[37] The presence of terminal isothiocyanato ligands in the title complex is in accordance with the concept of hard-soft acids and bases of Pearson.

There have been reports that the hydrogen bond systems in the related tetraaza metallo-macrocycles play an important role in reinforcing the coordination of the axial ligands as well as in determining the whole structures of the molecules and the coordination geometries about the central metals.[38-40] As shown in Figure 2 and Table 4, there are three types of intermolecular hydrogen bonds. The counter ion ClO$_4^-$ and

Table 2. Selected bond lengths (Å) for *cis*-[Cr([14]-decane)-(NCS)$_2$]ClO$_4$·H$_2$O

Cr(1)-N(1)	2.147(4)	Cr(1)-N(6)	2.000(5)
Cr(1)-N(2)	2.103(4)	N(5)-C(17)	1.216(7)
Cr(1)-N(3)	2.132(4)	N(6)-C(18)	1.139(7)
Cr(1)-N(4)	2.104(4)	C(17)-S(1)	1.589(7)
Cr(1)-N(5)	1.964(5)	C(18)-S(2)	1.632(7)

Table 3. Selected bond angles (°) for *cis*-[Cr([14]-decane)-(NCS)$_2$]ClO$_4$·H$_2$O

N(5)-Cr(1)-N(6)	88.0(2)	N(5)-Cr(1)-N(1)	102.5(2)
N(5)-Cr(1)-N(2)	87.3(2)	N(6)-Cr(1)-N(1)	87.3(2)
N(6)-Cr(1)-N(2)	172.4(2)	N(2)-Cr(1)-N(1)	87.9(2)
N(5)-Cr(1)-N(4)	172.8(2)	N(4)-Cr(1)-N(1)	83.4(2)
N(6)-Cr(1)-N(4)	88.2(2)	N(3)-Cr(1)-N(1)	167.5(2)
N(2)-Cr(1)-N(4)	97.1(2)	C(17)-N(5)-Cr(1)	165.0(4)
N(5)-Cr(1)-N(3)	87.3(2)	C(18)-N(6)-Cr(1)	167.3(5)
N(6)-Cr(1)-N(3)	100.9(2)	N(5)-C(17)-S(1)	178.1(5)
N(2)-Cr(1)-N(3)	84.8(2)	N(6)-C(18)-S(2)	177.3(6)
N(4)-Cr(1)-N(3)	87.4(2)		

Table 4. Selected bond lengths (Å) and bond angles (°) for hydrogen bond of *cis*-[Cr([14]-decane)(NCS)$_2$] ClO$_4$·H$_2$O

macrocycle-ClO$_4^-$ ion			
N(4)-O(3)(1/2-x, y, 1/2+z)	2.989	N(4)-H(4)-O(3)	160.59
macrocycle-water molecule			
N(1)-Ow(1)	2.879	N(1)-H(1)-Ow(1)	167.48
Water molecule-ClO$_4^-$ ion			
Ow(1)-O(1)	2.879		

aquo molecule form hydrogen bonds of the type N-H···O with the secondary amine hydrogens of the macrocycle {N(4)-O(3) (1/2 − x, y, 1/2 + z); 2.989 Å, N(1)-Ow(1); 2.879 Å}. The structure of the compound is further consolidated by another hydrogen bond of the type O-H···O between the aquo molecule and oxygen atom of the ClO$_4^-$ ion {O$_w$(1)-O(1); 2.879 Å}. These interactions result in a formation of polymeric chains in the packing of the title compound (Figure 2). Namely, the ordered perchlorate anion and aquo molecule participate in mediating between the *cis*-[Cr([14]-decane)(NCS)$_2$]$^{2+}$ units to form the polymeric chains through hydrogen bonds. Hydrogen bonding interactions through macrocyclic N-H groups, anions and aquo molecules are crucial for the formation of supramolecular polymers. It is generally understood that the directionality and strength of interactions are essential to assemble building blocks in polymeric chemistry, and usually a hydrogen bond is the interaction of choice.[41-43]

Electronic absorption spectra. The absorption spectrum of the *cis*-[Cr([14]-decane)(NCS)$_2$]$^+$ complex ion in DMF solution at room temperature is represented in Figure 3. Table 5 summarizes the electronic spectral data of *cis*-[Cr([14]-decane)(NCS)$_2$]$^+$, *cis*-[Cr([14]-decane)(N$_3$)$_2$]$^+$, *cis*-[Cr([14]-decane)(caa)$_2$]$^+$ and related Cr(III) complexes. The values of molar conductance for *cis*-[Cr([14]-decane)-(NCS)$_2$]ClO$_4$ {λ_M (DMF) = 91.9 ohm^{-1}cm^{2}mol^{-1}}, *cis*-[Cr([14]-decane)(N$_3$)$_2$]ClO$_4$ {λ_M (DMF) = 73.6 ohm^{-1}cm^2 mol^{-1}} and *cis*-[Cr([14]-decane)(caa)$_2$]ClO$_4$ {λ_M (DMF) = 66.2 ohm^{-1}cm^{2}mol^{-1}} measured in DMF or DMSO correspond to a 1 : 1 electrolyte, indicating that the auxiliary ligands in the Cr(III) complexes are not dissociated from the complex in these polar solvents.[22,44]

Using octahedral notation for **1**, **2** and **3**, the two absorption bands are assigned as $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow$
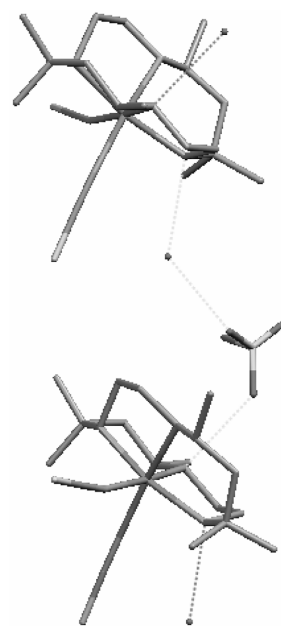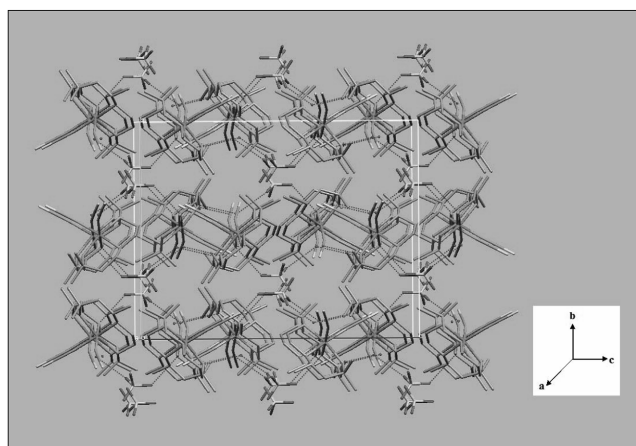
Figure 2. The molecular packing diagram of *cis*-[Cr([14]-decane)-(NCS)$_2$]ClO$_4$·H$_2$O along with the hydrogen bonds, indicated by broken lines that contribute to stabilize the lattice.

$^4T_{1g}$(F).[27] There are overlapping absorption parts in the spectra of the title complexes including the two distinct bands. Three ligand field bands are expected for a d^3 ion, $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$(F) and the two electron transition $^4A_{2g} \rightarrow {}^4T_{1g}$(P) in octahedral and pseudo octahedral symmetry.[26] The two *d-d* bands of title complexes observed at ~18620, ~25640 cm^{-1} can be related to the spin-allowed transitions, $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$, respectively.[45]

It is noteworthy that the *d-d* band for *cis*-[Cr([14]-decane)(caa)$_2$]$^+$ is at a higher energy than that for the *cis*-[Cr([14]-decane)(NCS)$_2$]$^+$ and *cis*-[Cr([14]-decane)(N$_3$)$_2$]$^+$ (Table 5). The caa therefore lies higher in the spectrochemical series than NCS$^-$ and N$_3^-$ ions, consistent with a higher s-donor strength for caa. This LF strength is in accord with that previously found in the corresponding complexes.[19]

In order to obtain some points of reference for the splitting of the two bands, the band profiles were fitted by using four

Table 5. Electronic transition spectral data of *cis*-[Cr([14]-decane)-$(L_a)_2$]ClO$_4$ (L_a = NCS$^-$, N$_3^-$ and caa) and related Cr(III) complexes

| Complexes	λ, nm (ε, M^{-1} cm^{-1})	refs.
cis-[Cr(cyclam)Cl$_2$]$^+$	529 (111), 404 (106)	a
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)	b
cis-[Cr(cyclam)(NH$_3$)$_2$]$^{3+}$	468 (115), 355 (80)	b
cis-[Cr([14]-decane)(OH)$_2$]$^+$	609 (111), 380 (73)	c
cis-[Cr([14]-decane)(OH)(H$_2$O)]$^{2+}$	572 (130), 407 (53)	c
cis-[Cr([14]-decane)(H$_2$O)$_2$]$^{3+}$	529 (169), 388 (82)	c
cis-[Cr([14]-decane)(bz)$_2$]$^+$**	548 (223), 394 (131)	d
cis-[Cr([14]-decane)(cbz)$_2$]$^+$**	547 (221), 394 (127)	d
cis-[Cr([14]-decane)(NCS)$_2$]$^+$	541 (135), 406 (78)	this work
cis-[Cr([14]-decane)(N$_3$)$_2$]$^+$	572 (213), 426 (127)	this work
cis-[Cr([14]-decane)(caa)$_2$]$^+$	537 (201), 390 (108)	this work

a, b, c, d taken from ref. 26(a), 26(b), 25, and 22, respectively. **Abbreviations, bz and cbz are benzoate and chlorobenzoate ions, respectively
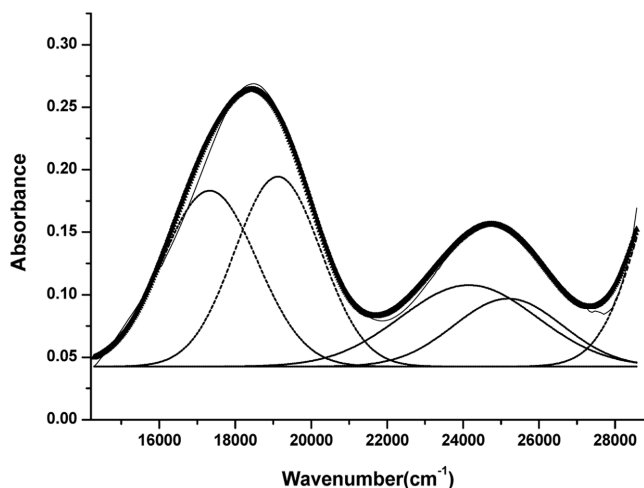
Figure 3. The electronic absorption spectrum of 2.0 × 10^{-3} M *cis*-[Cr([14]-decane)(NCS)$_2$]$^+$ in DMF solution at 298 K.

Gaussian curves, as seen in Figure 3. Finally, we performed least-squares fitting procedures, and the dotted lines in Figure 3 are Gaussian bands representing the approximate deconvolution of the spectrum yielded by the calculations. The four peak positions calculated at 17990, 18690, 25140 and 25970 cm^{-1} can be assigned to the ^{4}E(^{4}T$_{2g}$ in O_h symmetry), ^{4}B$_2$(^{4}T$_{2g}$), ^{4}E(^{4}T$_{1g}$) and ^{4}A$_2$(^{4}T$_{1g}$), respectively.[46,47] Similar procedures are also applied to *cis*-[Cr([14]-decane)-(N$_3$)$_2$]$^+$ and *cis*-[Cr([14]-decane)(caa)$_2$]$^+$, taken 16862, 18241, 23432, 24428 cm^{-1} and 17967, 19058, 24724, 25814 cm^{-1}, respectively.

Infrared spectra. The infrared spectra of *cis*-[Cr([14]-decane)(NCS)$_2$]ClO$_4$, *cis*-[Cr([14]-decane)(N$_3$)$_2$]ClO$_4$ and *cis*-[Cr([14]-decane)(caa)$_2$]ClO$_4$ recorded at room temperature are presented in Figure 4. The IR spectra displayed N-H stretches from 3200 to 3000 cm^{-1}, C-H stretches from 3000 to 2900 cm^{-1}, and a strong ionic ClO$_4^-$ band at near 1100 cm^{-1} and 630 cm^{-1}.[48]

Thiocyanate is an ambidentate ligand and has a schizo-
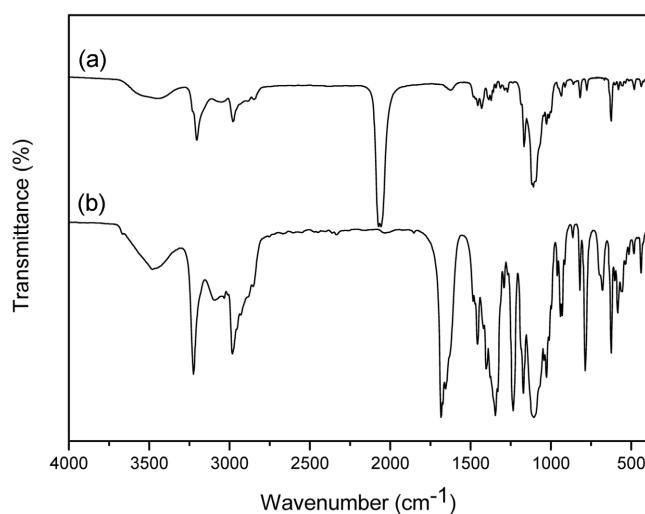
Figure 4. IR spectra of (a) *cis*-[Cr([14]-decane)(NCS)$_2$]ClO$_4$·H$_2$O and (b) *cis*-[Cr([14]-decane)(caa)$_2$]ClO$_4$.

phrenic preference to Cd(II) exhibiting both N and S bonding modes. Out of four SCN$^-$ ions around the Cd centre in the [Cd(eti)(SCN)$_2$]$_n$ {eti = 1-ethyl-2-(p-tolylazo)imidazole} two are S-bonded and two are N-bonded.[49] The IR spectrum of [Cu(glycinato)(NCS)(H$_2$O)]$_n$ complex shows a very strong band at 2100 cm^{-1} due to the ν(C-N) mode, in addition to two medium bands at 809 and 770 cm^{-1} related to ν(C-S). Bridging *N,S*-thiocyanato groups exhibit two ν(C-N) bands above and below 2100 cm^{-1} as well as two ν(C-S) bands.[50,51] The absorption vibrations due to the N-coordinated NCS$^-$ group in *cis*-[Cr([14]-decane)(NCS)$_2$]ClO$_4$ appear at 2073 and 818 cm^{-1}, which is consistent with the X-ray structural results of the complex.

In general, the transition metal complexes containing a terminal azide ligand exhibit an intense antisymmetric stretching frequency, ν_{as}(N$_3^-$) at ~2090 cm^{-1} and a symmetric mode, ν_s(N$_3^-$) at ~1350 cm^{-1} and defomation band at ~620 cm^{-1}.[52] Metal-ligand stretching bands occur in the far infrared range. The peaks in the range 481-410 cm^{-1} can be assigned to the Cr-N(cyclam) stretching mode.[48] The absorption peak at 2081 cm^{-1} in the *cis*-[Cr([14]-decane)-(N$_3$)$_2$]ClO$_4$ is assigned to the antisymmetric stretching mode of azide. The symmetric stretching frequency, ν_s(N$_3^-$) and deformation band, δ(N$_3^-$) are observed at 1344 and 636 cm^{-1}, respectively. The Cr-N ([14]-decane) stretching mode is also appeared 482 and 435 cm^{-1}.

The IR spectrum of the *cis*-[Cr([14]-decane)(caa)$_2$]ClO$_4$ II contains an absoption at 1684 and 1346 cm^{-1} due to antisymmetric and symmetric stretching vibration band of the carboxylic groups with stretching bands of the Cr-N at 484 and 439 cm^{-1}.[53,54] In addition, the bands at 1107 and 625 cm^{-1} are originated from the uncoordinated ClO$_4^-$ ion. The differences between the symmetric and antisymmetric stretches, $\Delta\nu$ {= ν_{as}(COO$^-$) − ν_s(COO$^-$)} are on the order of 200 cm^{-1}, indicating that carboxylate groups are either free or coordinated to the metal ion in a monodentate fashion.[48] The aforementioned assignments are in agreement with

previous results for citrate complexes of various metals.[51,55]

cis-[Cr([14]-decane)(caa)₂]⁺
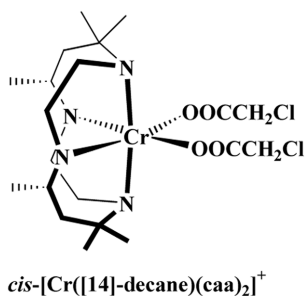
II

FAB mass spectra. The FAB mass spectra **1**, **2** and **3** show peaks due to the molecular ions *cis*-[Cr([14]-decane)-(NCS)₂]⁺, *cis*-[Cr([14]-decane)(N₃)₂]⁺ and *cis*-[Cr([14]-decane)-(caa)₂]⁺, repectively. The molecular ions undergo fragment-ation to give species such as *cis*-[Cr([14]-decane)(NCS)]⁺, *cis*-[Cr([14]-decane)(N₃)]⁺ and *cis*-[Cr([14]-decane)(caa)]⁺. In the FAB mass spectra of 1, 2 and 3 there is a peak at *m/z* 452, 420 and 522 corresponding to the molecular ions, respectively. These major peaks are associated with peaks of mass one or two greater or less, which are attributed to protonated/deprotonated forms.[56-58] This also accounts for the slight ambiguities in making assignments. The molecular ion of the *cis*-[Cr([14]-decane)(NCS)₂]ClO₄ give peaks due to [Cr([14]-decane)(NCS)]⁺ and [Cr([14]-decane)]⁺ at *m/z* 393 and 334, respectively. In the mass spectrum of *cis*-[Cr([14]-decane)(N₃)₂]ClO₄ the peaks observed at *m/z* 377 and 334 are due to fragments [Cr([14]-decane)(N₃)]⁺ and [Cr([14]-decane)]⁺, respectively. In the *cis*-[Cr([14]-decane)(caa)₂]ClO₄ there are two fairly strong peaks at *m/z* 428 and 335, which may be assigned to [Cr([14]-decane)(caa)]⁺ and [Cr([14]-decane)]⁺, respectively.

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