Cr(III)-Tetraaza Macrocyclic Complexes Containing Auxiliary Ligands (Part IV); Synthesis and Characterization of Cr(III)-Acetylacetonato, -Malonato and -Oxalato Macrocyclic Complexes

Jong Chul Byun[*] **and Chung Hun Han**

Department of Chemistry, Research Institute for Basic Sciences, Cheju National University, Jeju 690-756, Korea
[*]*E-mail: jchbyun@cheju.ac.kr*
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The reaction of *cis*-[Cr([14]-decane)(OH)$_2$]$^+$ ([14]-decane = *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-teraazacyclotetradecane) with auxiliary ligands {L$_a$ = acetylacetonate (acac), oxalate (ox) or malonate (mal)} leads to a new *cis*-[Cr([14]-decane)(acac)](ClO$_4$)$_2$·(1/2)H$_2$O (**1**), *cis*-[Cr([14]-decane)(ox)]ClO$_4$·(1/2)H$_2$O (**2**) or *cis*-[Cr([14]-decane)(mal)]ClO$_4$·(1/4)H$_2$O (**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)(acac)](ClO$_4$)$_2$·(1/2)H$_2$O reveals that central chromium(III) has a distorted octahedral coordination environment and two acetylacetonate-oxygen atoms are bonded to the chromium(III) ion in the *cis* positions. The angle N$_{axial}$-Cr-N$_{axial}$ deviates by 11° from the ideal value of 180° for a perfect octahedron. The bond angle O-Cr-O between the chromium(III) ion and the two acetylacetonate-oxygen atoms is close to 90°. The bond lengths of Cr-O between the chromium and the acetylacetonate-oxygen atoms are 1.950(3) and 1.954(2) 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 1560 {ν(C=O)}, 1710 {ν_{as}(OCO)} and 1660 cm^{-1} {ν_{as}(OCO)} attributed to the acac, ox and mal auxiliary ligands stretching vibrations, respectively.

Key Words : Macrocyclic Cr(III) complex, Acetylacetonato ligand, Crystal structure, Electronic absorption spectra

Introduction

The field of the macrocyclic chemistry of transition metals is developing very rapidly because of its applications[1] and importance in the area of coordination chemistry.[2] Macrocyclic ligand systems often exhibit unusual properties and sometimes mimic related natural macrocyclic compounds. There is currently considerable interest in complexes of polydentate macrocyclic ligands because of the variety of geometrical forms available and the possible encapsulation of the metal ion.[3]

Likewise, macrocyclic Schiff base ligands have received special attention because of their mixed hard-soft donor character and versatile coordination behavior,[4,5] and for their biological activities, *i.e.* toxicity against bacterial growth,[6] anticancerous[7] and other biochemical properties.[8,9]

The reduction of the carcinogen and mutagen chromate by cellular reductants results in the trapping of Cr(III) inside cells; a portion of this chromium is in the form of Cr(III)-DNA adducts.[10] The significance of these adducts in the carcinogenic and mutagenic potential of chromate is currently highly debated.[11] At low concentrations, Cr(III) binds preferentially to guanine-rich segments of DNA[12] and appears to bind primarily to guanine bases through N-7 and to PO2 groups of the backbone of DNA as shown by difference FT-IR spectra.[13] A more direct spectroscopic probe of Cr(III)-guanine complexes would be highly desirable.

β-Diketones and related derivatives are considered a class of very important ligands in the growth of coordination chemistry. Due to presence of two oxygen donor atoms and facile keto-enol tautomerism they easily coordinate with metal ions after deprotonating the enolic hydrogen atom and provide stable metal complexes with six-membered chelate rings.[14]

Due to the weak metal-oxygen bond usually found in metal acetylacetonates, a relatively stronger ligand can replace the acetylacetonato group to give a new type of complex. Replacement of one or both acetylacetonato groups depends upon the ligand to metal acetylacetonates {*e.g.* [MO$_2$(acac)$_2$], M = Mo, W, U} ratio taken, number of donating groups present in the ligand and electronic as well as steric properties of the ligand replacing acetylacetonato group. In this way metal acetylacetonates can act as starting materials to design various types of complexes with varying structural and chemical properties.[15]

The history of oxalates in coordination chemistry is long and a renewed interest can be noted in recent years.[16,17] The reason is the bis-chelating capability of the oxalates in combination with current efforts to prepare molecular based materials with higher dimensionality.[18,19]

And many recent reports have focused on the synthsis and structural characterization of polymeric transition metal compounds using malonate[20] or 2,2′-bipyrimidine[21] as

blocking and bridging ligands. The use of malonate as bridging ligand in copper(II) complexes has shown versatility of this dicarboxylate type ligand.[22] The variety of coordination modes of the malonate ligand accounts for the structural complexity of the malonate complexes. The ability of the carboxylato bridge to mediate significant ferro- or antiferromagnetic coupling between the paramagnetic centers enhances the interest in the malonate ligand, aiming at designing extended magnetic systems.[23]

The copper complexes of macrocyclic ligand (L_m = *trans*-5,7,12,14-tetramethyl-6,13-dinitro-1,4,8,11-tetraazacyclo-tetradecane) has recently been the subject of several chemical and structural studies.[24-27] 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.[24,25] It has been suggested that the axially oriented methyl groups prevent the coordination of solvent or counter ion ClO_4^- to the metal ion.[25] 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.

In addition the cobalt(III) complexes with tetraazamacro-cyclic ligands exist in the *cis* and *trans* configurations; only *cis* complexes have been observed in the presence of bidentate auxiliary ligands such as ethylenediamine or oxalate.[28] Very few crystal structures of cobalt-cyclam complexes have been reported.[29]

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.* 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-*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.[30,31] Eriksen *et al.* 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.[32] To our knowledge, few crystal structures of the Cr(III) complexes, *cis*-[Cr([14]-decane)(L_a)$_m$](ClO₄)$_n$ (L_a = auxiliary ligand) have been reported.[33] These patterns have led us to discuss physicochemical characterization and X-ray crystal structure of the type *cis*-[Cr([14]-decane) (L_a)$_m$](ClO₄)$_n$.

For some time we have been interested in the coordination chemistry of polydentate ligands. Recently we reported the preparation and characterization of several *cis*-[Cr([14]-decane)(L_a)$_m$](ClO₄)$_n$ complexes containing auxiliary ligands such as benzoate, chlorobenzoate and citrate anions.[33] In the light of above discussion, the present work concerns the synthesis and physicochemical characterization of a series of six-coordinate anion-bound Cr(III) complexes of the type *cis*-[Cr([14]-decane)L_a](ClO₄)$_n$ (L_a : n = 1; ox, mal, and n = 2; acac) (Scheme 1). And we also describe the crystal structure of *cis*-[Cr([14]-decane)(acac)](ClO₄)₂ complex.

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 the related compounds were prepared by literature methods.[33]

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
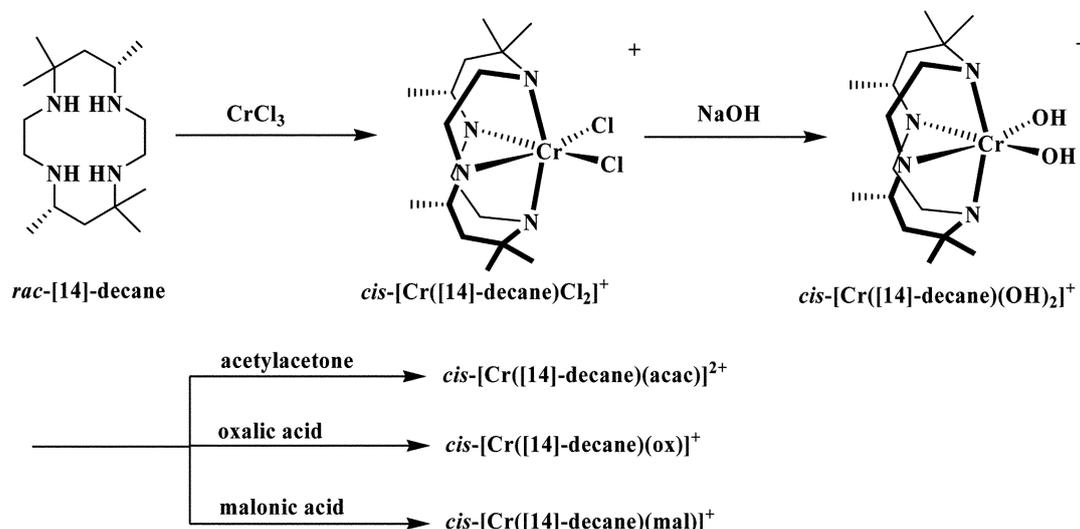
Scheme 1. Synthetic route of the *cis*-[Cr([14]-decane)(L_a)](ClO₄)$_n$ (L_a : n = 1; ox, mal, and n = 2; acac).

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)(acac)](ClO₄)₂·(1/2) H₂O (1). 4×10^{-3} M *cis*-[Cr([14]-decane)(OH)₂]⁺ solution (10 mL) and acetylacetone (2 mL) were mixed slowly with constant stirring overnight at room temperature. This solution was refluxed for 5 min in the presence of a saturated aqueous NaClO₄ solution (4 mL). On cooling a pink colored precipitate formed, which was filtered, washed twice with water and ether, and dried *in vacuo*. Yield: 68%. Anal. Calcd (Found) % for $C_{21}H_{42}N_4O_{10}Cl_2Cr\cdot(1/2)H_2O$: C, 39.20 (39.17); H, 6.89 (7.12); N, 8.71 (9.03). λ_M (DMF): 149 $ohm^{-1}cm^2mol^{-1}$.

Synthesis of *cis*-[Cr([14]-decane)(ox)]ClO₄·(1/2)H₂O (2). To a freshly prepared 4×10^{-3} M *cis*-[Cr([14]-decane)-(OH)₂]⁺ solution (10 mL), a solution of oxalic acid (2 g) in H₂O (20 mL) was slowly added in small portions, followed by dropwise addition of a saturated aqueous NaClO₄ solution (4 mL) with stirring, and solution was refluxed for 5 min. The resulting solution was allowed to stand in a refrigerator (~2 °C) until precipitates formed. The pink precipitates were filter, washed twice with ice-cold acetone, and dried in vacuo. Good quality crystals were obtained when the crude product was dissolved in the hot water (120 mL), followed by dropwise addition of a saturated aqueous NaClO₄ solution (12 mL) with constant stirring, and the resulting solution was allowed to stand in a refrigerator (~2 °C) until precipitates formed. Yield 84%. Anal. Calcd (Found) % for $C_{18}H_{36}N_4O_8ClCr\cdot(1/2)H_2O$: C, 40.57 (40.60); H, 7.00 (7.27); N, 10.51 (10.48). λ_M (DMF): 67.9 $ohm^{-1}cm^2mol^{-1}$.

Synthesis of *cis*-[Cr([14]-decane)(mal)]ClO₄·(1/4)H₂O (3). A similar procedure as that for **2** was followed with a 12 mL aqueous solution of malonic acid (2 g). Yield: 41%. Anal. Calcd (Found) % for $C_{19}H_{38}N_4O_8ClCr\cdot(1/4)H_2O$: C, 42.07 (42.09); H, 7.15 (6.97); N, 10.33 (10.32). λ_M (DMF): 70.3 $ohm^{-1}cm^2mol^{-1}$.

X-ray crystallography of complex. Crystals of *cis*-[Cr([14]-decane)(acac)](ClO₄)₂·(1/2)H₂O suitable for X-ray diffraction study were obtained by slow evaporation of acetonitrile : H₂O (1 : 1) solutions 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 6,975 unique reflections measured, 6,905 reflections in the range $1.35° \leq 2\theta \leq 27.48°$ were considered to be

Table 1. Crystallographic data for *cis*-[Cr([14]-decane)(acac)]-(ClO₄)₂·(1/2)H₂O

Formula	$C_{21}H_{43}Cl_2CrN_4O_{11}$
Formula weight	650.49
Temperature (K)	293(2)
Radiation (Å)	Mo Kα (0.71073)
Crystal system	monoclinic
Space group	C2/c
a (Å)	20.0210(10)
b (Å)	30.1120(10)
c (Å)	12.708
α (°)	90
β (°)	127.2170(10)
γ (°)	90
V (Å³)	6101.1(4)
Z	8
T (K)	293(2)
D_{calc} (gcm⁻³)	1.416
θ Range of data collected	1.35-27.48
F_{000}	2744
μ (mm⁻¹)	0.608
Independent reflections	6975 [R(int) = 0.0306]
no. of obsd data ($I > 2\sigma$(I))	6905
no. variable	362
Goodness of fit	1.105
R ($I > 2\sigma$(I))	$R = 0.0824$, $R_w = 0.2179$
R (all data)	$R = 0.1143$, $R_w = 0.22893$

$R = \Sigma \parallel F_0 \mid - \mid F_c \parallel / \Sigma \mid F_0 \mid$. $R_w = [\Sigma w(F_0^2 - F_c^2)^2 / \Sigma w(F_0^2)^2]^{1/2}$. $w = 1/[\sigma^2(F_0^2) + (0.2102P)^2 = 21.9446P]$, $P = (F_0^2 + 2F_c^2)/3$

observed ($I > 2\sigma(I)$) and were used in subsequent structure analysis. The structure was solved by the direct method,[34] and refined by full-matrix least-squares refinement with use of the SHELXL-97 package program.[35] 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 3, and the hydrogen bond lengths are given in Table 4.

Crystallographic data for the structure reported here have been deposited with Cambridge Crystallographic Data Center (Deposition No. CCDC 251035). 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)-tetraazacyclotetradecane complexes have been reported in the literature.[36] To our knowledge, this is the first reported crystal structure of a *cis*-[Cr([14]-decane)(acac)]-(ClO₄)₂·(1/2)H₂O complex containing auxiliary ligands, acac
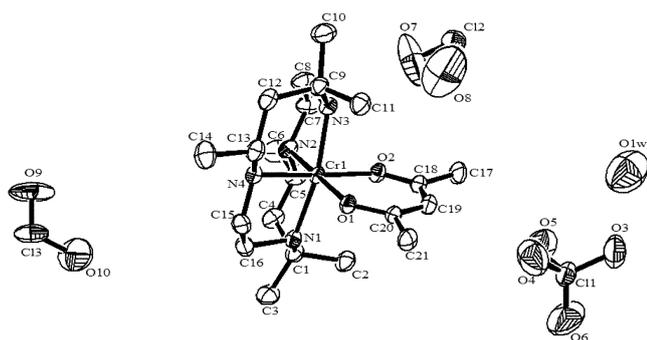
Figure 1. ORTEP plot of the *cis*-[Cr([14]-decane)(acac)]-(ClO₄)₂·(1/2)H₂O complex.

ion. The structure and labeling scheme for a bidentate acetylacetonato complex *cis*-[Cr([14]-decane)(acac)]-(ClO₄)₂·(1/2)H₂O is depicted in Figure 1. The crystal structure of this complex is made up of discrete *cis*-[Cr([14]-decane)(acac)]²⁺ cation, ClO₄⁻ anions and uncoordinated water molecule which are held together by electrostatic forces, hydrogen bonds and Van der Waals interactions. These results are backed up by the elemental analysis and molar conductivity ($\lambda_M = 149$ ohm⁻¹cm²mol⁻¹) which agreed with assignment of the structure as *cis*-[Cr([14]-decane)-(acac)](ClO₄)₂·(1/2)H₂O.

At monomeric cation *cis*-[Cr([14]-decane)(acac)]²⁺ chromium(III) ion is six-coordinated with the four secondary amines of the macrocycle and two acetylaceto-nate-oxygen atoms in *cis* position building a distorted octahedral environment. The oxygen atoms from the acac ligand 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) [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.[37] A similar type of configuration was reported for *cis*-[Cr(cyclam)Cl(dmso)]²⁺.[38]
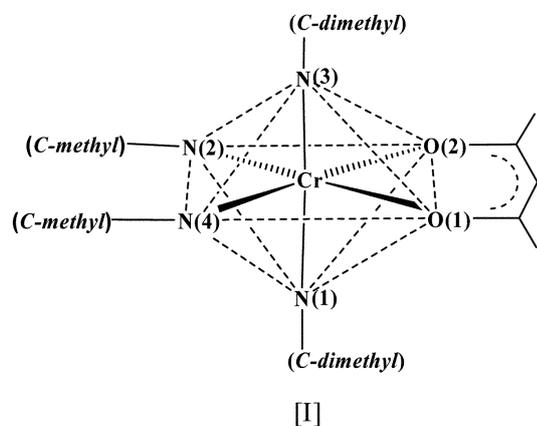
similar to that of [Cu(acac)(phen)(CH₃CN)]ClO₄ (phen = 1,10-phenanthroline)[41] and [Cu(acac)₂(quinoline)].[42] As observed in [Co(cyclam)(acac)](BF₄)₂,[43] the average bond angles {84.12(12)} of N-Cr-N of the five-membered chelate rings around the chromium(III) are smaller than those {89.04(13)°} of the six-membered ones (Table 3).

It is known that in *cis* octahedral complexes of macro-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.[44] In this complex Cr-N{2; 2.112(3) Å} and Cr-N{4; 2.107(3) Å} distances are shorter than Cr-N(1, axial; 2.130(3) Å) and Cr-N{3, axial; 2.133(3) Å} and the angle N(1)-Cr-N(3) {169.49(12)°} 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)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.[39]

In the coordinated environment of this complex, the longest Cr-N (secondary amines) and the shortest Cr-O bonds occupied *cis*-position. The O(1)-Cr-N(2) and O(2)-Cr-N(4) linkages are slightly bent {174.56(12) and 172.94(12)°}, whereas the bond angles of O(1)-Cr-O(2) and O(1)-Cr-N(3) are 89.85(11) and 99.95(12)°, respectively. The bidentate acetylacetonato ligand adopts the most stereochemically favorable orientation with respect to the macrocycle.

The delocalized C-C and C-O bond lengths for the acac chelate [II] in the title complex average 1.386(6) and 1.282(5) Å, respectively. The C-CH₃ bond lengths average 1.497(5) Å. The bond angles of Cr-O(1)-C(20), O(1)-Cr-O(2), C(18)-C(19)-C(20) and O(2)-C(18)-C(19) are 128.3 (2), 89.85(11), 124.2(3) and 124.9(3)°, respectively. These internal acac bond lengths and bond angles are in good agreement with those in related [Ru(acac)₂(*S*-BINAP)] {*S*-BINAP = *S*-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl} and [Ru(acac)₂ (diene)] complexes.[45]
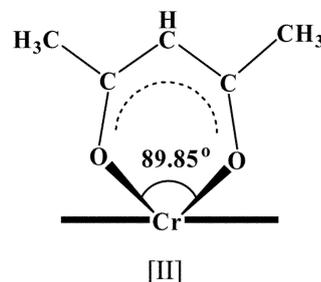

[I]

[II]

The Cr-N (secondary amines) bond distances are in the range of 2.107(3)-2.133(3) Å,[39,40] and Cr-O (acetylaceto-nate) distances are 1.950(3) and 1.954(2) (Table 2) which are

Analysis of the crystal packing of the title complex in the unit cell shows that there exist multiple hydrogen bonding interactions, resulting in a three-dimensional supramolecular network (Figure 2). The selected bond lengths are given in Table 4. The perchlorate anion is linked to the complex cation by the hydrogen bonds of the type N-H ···O with the secondary amine hydrogens of the macrocycle {N(2)···

Table 2. Selected bond lengths (Å) for *cis*-[Cr([14]-decane)(acac)]-(ClO$_4$)$_2$·(1/2)H$_2$O

Cr(1)-N(1)	2.130(3)	C(17)-C(18)	1.505(5)
Cr(1)-N(2)	2.112(3)	C(18)-C(19)	1.381(6)
Cr(1)-N(3)	2.133(3)	C(19)-C(20)	1.391(6)
Cr(1)-N(4)	2.107(3)	C(20)-C(21)	1.489(5)
Cr(1)-O(2)	1.950(3)	C(18)-O(2)	1.283(5)
Cr(1)-O(1)	1.954(2)	C(20)-O(1)	1.280(4)

Table 3. Selected bond angles (°) for *cis*-[Cr([14]-decane)(acac)]-(ClO$_4$)$_2$·(1/2)H$_2$O

|			
O(2)-Cr(1)-O(1)	89.85(11)	N(4)-Cr(1)-N(3)	88.76(12)
O(2)-Cr(1)-N(4)	172.94(12)	N(2)-Cr(1)-N(3)	83.86(13)
O(1)-Cr(1)-N(4)	85.34(11)	N(1)-Cr(1)-N(3)	169.49(12)
O(2)-Cr(1)-N(2)	86.46(12)		
O(1)-Cr(1)-N(2)	174.56(12)	C(20)-O(1)-Cr(1)	128.3(2)
O(2)-Cr(1)-N(1)	100.60(12)	C(18)-O(2)-Cr(1)	128.0(2)
O(1)-Cr(1)-N(1)	87.44(11)	O(1)-C(20)-C(19)	124.5(3)
O(2)-Cr(1)-N(3)	86.98(12)	O(1)-C(20)-C(21)	115.8(3)
O(1)-Cr(1)-N(3)	99.95(12)	O(2)-C(18)-C(19)	124.9(3)
		O(2)-C(18)-C(17)	115.3(4)
N(4)-Cr(1)-N(2)	98.69(12)	C(19)-C(18)-C(17)	119.8(4)
N(4)-Cr(1)-N(1)	84.37(12)	C(18)-C(19)-C(20)	124.2(3)
N(2)-Cr(1)-N(1)	89.31(13)	C(19)-C(20)-C(21)	119.7(3)

Table 4. Selected bond lengths (Å) for hydrogen bond of *cis*-[Cr([14]-decane)(acac)](ClO$_4$)$_2$·(1/2)H$_2$O

macrocycle-ClO$_4^-$ ion

N(2)···O(3) #1	3.001	N(4)···O(3) #1	3.057
N(3)···O(7)	3.042	N(1)···O(9) #2	3.009

water molecule – water molecule

Ow(1)···Ow(1) #3	2.643

Symmetry transformations used to generate equivalent atoms: #1; x, y, 1+z, #2; x, y, −1+z, #3; 1−x, y, −1/2−z

O(3); 3.001 Å, N(4)···O(3); 3.057 Å, N(3)···O(7); 3.042 Å, N(1) ···O(9); 3.009 Å}. These hydrogen bonds consolidate the structure of the present complex. Another interesting feature of the title complex resides in the formation of a three-dimensional layered structure in which lattice H$_2$O molecules present in the inter-layers. These uncoordinated waters form an intermolecular hydrogen bond {Ow(1)··· Ow(1); 2.643 Å}. In this lattice water connection it is interesting to compare the previous values reported for [Cu$_2$L$_c$(N$_3$)$_2$](ClO$_4$)·2H$_2$O (L$_c$ = hexaaza macrocycle) and [Co(piperazine)$_2$Cl$_3$]Cl·H$_2$O.[46,47]

Electronic absorption spectra. The reaction of anhydrous chromium(III) chloride with [14]-decane gives a good yield of a bluish-green complex *cis*-[Cr([14]-decane)-Cl$_2$]Cl.[48] Base hydrolysis of *cis*-[Cr([14]-decane)Cl$_2$]$^+$ has been studied.[30] The two moles of OH$^-$ ion are consumed per mole of *cis*-[Cr([14]-decane)Cl$_2$]$^+$ 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)$_2$]$^+$ solution. 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
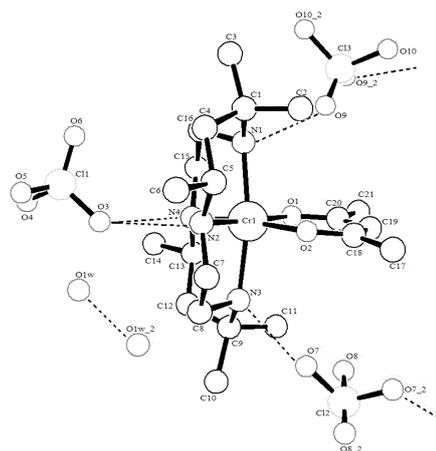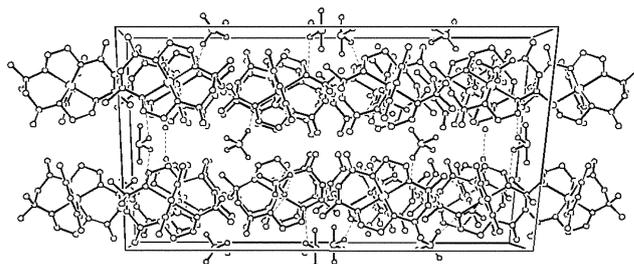
Figure 2. The molecular packing diagram of *cis*-[Cr([14]-decane)(acac)](ClO$_4$)$_2$·(1/2)H$_2$O along with the hydrogen bonds, indicated by broken lines that contribute to stabilize the lattice.

is in the range of 1 : 1 electrolyte. 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 HClO$_4$ solution to the aqueous *cis*-[Cr([14]-decane)(OH)$_2$]$^+$ complex solution. The absorption spectrum of this species is compared with several related compounds {*cis*-[{Cr([14]-decane)(μ-cit)}$_2$]$^{2+}$, *cis*-

Table 5. Electronic transition spectral data of *cis*-[Cr([14]-decane)-(acac)]$^{2+}$ and related Cr(III) complexes

Complexes	λ, nm (ε, M^{-1} cm^{-1})	ref.
cis-[Cr(cyclam)Cl$_2$]$^+$	529 (111), 404 (106)	a, b
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(cyclam)(NH$_3$)$_2$]$^{3+}$	468 (115), 355 (80)	a, b
cis-[Cr([14]-decane)(OH)$_2$]$^+$	609 (111), 380 (73)	b, c
cis-[Cr([14]-decane)(OH)(H$_2$O)]$^{2+}$	572 (130), 407 (53)	b, c
cis-[Cr([14]-decane)(H$_2$O)$_2$]$^{3+}$	529 (169), 388 (82)	b, c
cis-[Cr([14]-decane)(bz)$_2$]$^{+*}$	550 (223), 392 (131)	b
cis-[Cr([14]-decane)(cbz)$_2$]$^{+*}$	547 (221), 394 (127)	b
cis-[{Cr([14]-decane)(μ-cit)}$_2$]$^{2+*}$	532 (186), 385 (97)	d
cis-[Cr([14]-decane)(acac)]$^{2+}$	536 (190), 388 (269)	this work
cis-[Cr([14]-decane)(ox)]$^+$	533 (157), 386 (82)	this work
cis-[Cr([14]-decane)(mal)]$^+$	551 (164), 387 (71)	this work

a, b, c and d taken from ref. 30, 33, 48 and 61, respectively. *Abbreviations, bz, cbz and cit are benzoate, chlorobenzoate and citrate, respectively.

[Cr([14]-decane) (acac)]$^{2+}$, *cis*-[Cr([14]-decane)(ox)] $^+$, *cis*-[Cr([14]-decane)(mal)]$^+$} in Table 4. The first ligand field band ($^4A_{2g} \rightarrow {}^4T_{2g}$; O_h symmetry) of *cis*-[Cr([14]-decane)-(OH)$_2$]$^+$ complex solution is observed at 609 nm, while the second LF band ($^4A_{2g} \rightarrow {}^4T_{1g}$) is centered at 380 nm.[49,50] The molar absorptivities of the two *d-d* bands are substantially greater than those of the *trans* analogues, consistent with the given geometric assignment.

The absorption spectrum of the *cis*-[Cr([14]-decane)(ox)]$^+$ complex ion in DMF solution at room temperature is represented in Figure 3. Using octahedral notation for **1**, **2** and **3**, the two absorption bands are assigned as $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}(F)$.[50] 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 ~18750, ~25900 cm^{-1} can be related to the spin-allowed transitions, $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$, respectively.[51]

In order to obtain some points of reference for the splitting of the two bands, the band profiles were fitted by using four 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 18158, 19672, 24205 and 26481 cm^{-1} 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.[52,53] Similar procedures are also applied to *cis*-[Cr([14]-decane)-(acac)]$^{2+}$ and *cis*-[Cr([14]-decane)(mal)]$^+$, taken 18032, 19438, 25444, 26477 cm^{-1} and 17460, 18839, 25012, 26290 cm^{-1}, respectively.

Infrared spectra. The infrared spectra of *cis*-[Cr([14]-decane)(acac)](ClO$_4$)$_2$, *cis*-[Cr([14]-decane)(ox)]ClO$_4$ and *cis*-[Cr([14]-decane)(mal)]ClO$_4$ recorded at room temperature are presented in Figure 4. The infrared spectra of these

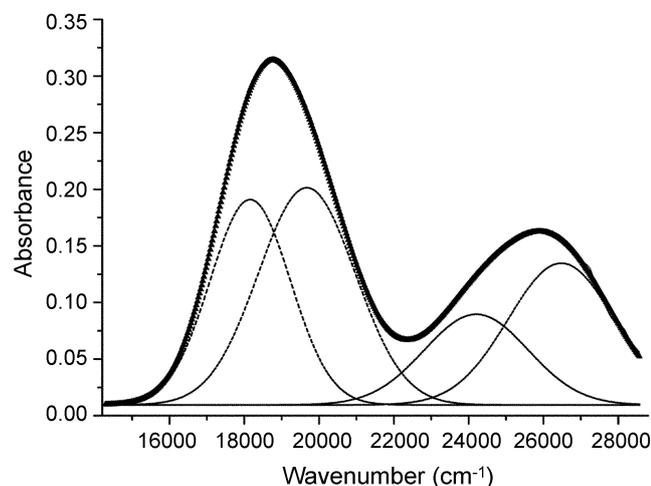**Figure 3**. The electronic absorption spectrum of 2.0 × 10^{-3} M *cis*-[Cr([14]-decane)(ox)]$^+$ in DMF solution at 298 K.

complexes, taken from KBr pellet, are in accord with the structure determined by X-ray diffraction. The IR spectra displayed N-H stretches from 3220 to 3080 cm^{-1}, C-H stretches from 2980 to 2890 cm^{-1}, and a strong ionic ClO$_4^-$ band at near 1100 cm^{-1} and 630 cm^{-1}.[51] The values of molar conductance for *cis*-[Cr([14]-decane)(acac)](ClO$_4$)$_2${λ_M (DMF) = 149 ohm^{-1}cm^{2}mol^{-1}}, *cis*-[Cr([14]-decane)(ox)]-ClO$_4$ {λ_M (DMF) = 67.9 ohm^{-1}cm^{2}mol^{-1}} and *cis*-[Cr([14]-decane)(mal)]ClO$_4$ {λ_M (DMF) = 70.3 ohm^{-1}cm^{2}mol^{-1}} measured in DMF correspond to a 1 : 2 (or 1 : 1) electrolyte, indicating that ClO$_4^-$ ions in the Cr(III) complexes are counter anions.[22,52]

As in [II], acetylacetone coordinate to a metal atom through the oxygen atoms. In this enol type of complex, the band due to the C-O stretching vibration occurs at lower frequencies, usually 1605-1560 cm^{-1}, than that due to the free acetylacetone C=O stretching vibration which occurs at 1640 cm^{-1}. A second strong band is observed near 1380 cm^{-1}. The band due to the C-H stretching vibration tends to higher frequencies than might be expected because of the new benzene-type environment in which it is found. The bands due to C-C stretching vibrations for complexes are found at about 1540 and 1290 cm^{-1}.[54]

The differences between the enol type acetylacetonate complexes (oxygen bound to metal) and the keto type (carbon bound) are as follow; (1) the γ-carbon hydrogen stretching frequency is lower by about 150-100 cm^{-1} in the keto form, (2) bands due to the asymmetric and symmetric C=O stretching vibrations appear at 1700-1650 cm^{-1} and 1650-1610 cm^{-1} respectively in the keto form, both bands being very strong, rather than the one at 1605-1560 cm^{-1} in the enol form.[54]

At the infrared spectrum for the title acac complex two peaks appearing in the 1560 and 1530 cm^{-1} assignable to the ν(C=O) and ν(C=C), respectively.[55] The corresponding peaks for [Cu(acac)$_2$] were observed at ~1578 and ~1528 cm^{-1}, indicating that the π-systems of the acac ligand are somewhat disturbed in the mixed ligand complex as compared with those in [Cu(acac)$_2$].[55,56,57]

For the oxalate ligand, various coordination modes via one, two, three or four oxygen atoms have been previously characterized.[58] The presence of oxalate at the *cis*-[Cr([14]-decane)(ox)] $^+$ accounts for the peaks at 1710 and 1680 cm^{-1} {antisymmetric ν_{as}(OCO) vibration} and bands at 1440 and 1380 cm^{-1} {symmetric ν_s(OCO) vibration}. The bending vibration corresponding to the δ(OCO) group is observed in the 1240 cm^{-1}. The number of ν_{as}(OCO) and ν_s(OCO) carboxylate stretchings and the wavenumber gap {$\Delta\nu = \nu_{as}$(OCO) $- \nu_s$(OCO) }between them suggest the presence of chelating coordination modes of the oxalato ligand.[33,59]

Dealing with the malonate absorptions, the patterns of the antisymmetric ν_{as}(OCO) (1660 cm^{-1}), symmetric ν_s(OCO) (1430, 1360 cm^{-1}) and bending δ(OCO) (1273 cm^{-1}) vibrations support the presence of chelating malonate in the title complex.[60,61]

FAB mass spectra. The FAB mass spectra of **1**, **2** and **3** consist of peaks due to the molecular ions *cis*-[Cr([14]-

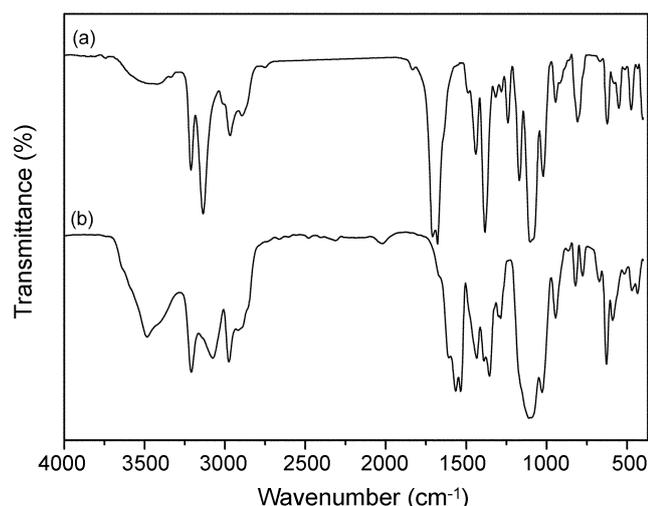**Figure 4**. IR spectra of (a) *cis*-[Cr([14]-decane)(ox)]ClO$_4$·(1/2)H$_2$O and (b) *cis*-[Cr([14]-decane) (acac)] (ClO$_4$)$_2$·(1/2)H$_2$O.

decane)(acac)]$^+$, *cis*-[Cr([14]-decane)(ox)]$^+$ and *cis*-[Cr([14]-decane)(mal)]$^+$, respectively. The molecular ions undergo fragmentation to give species such as *cis*-[Cr([14]-decane)]$^+$, *cis*-[Cr([14]-decane)]$^+$ and *cis*-[Cr([14]-decane)]$^+$. In the FAB mass spectra of **1**, **2** and **3** there is a peak at *m/z* 434, 424 and 438 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. This also accounts for the slight ambiguities in making assignments.[33,61,62] The molecular ion of **1**, **2** and **3** gives peak due to [Cr([14]-decane)]$^+$ at *m/z* 336.

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