

Chromium(III) Complexes with Different Chromospheres Macrocyclic Ligands: Synthesis and Spectroscopic Studies

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Symmetric tetradentate (L^1) and asymmetric pentadentate (L^2) macrocyclic ligands that possess 2 dissimilar coordination sites were prepared. One has a 4-coordinate (N_4) and the other has a 5-coordinate (N_2O_3S) donor set. Trivalent Cr(III) complexes were synthesized with L^1 and L^2 and their structures were investigated using elemental analyses and magnetic moment, electronic, IR, 1H NMR, ^{13}C NMR and EPR spectra. All the Cr(III) complexes show magnetic moments corresponding to a high-spin configuration. Δ values indicate the energy difference between the principle bands, which are formed due to ligand field absorption. The spin-orbit coupling parameter, z , gives no significance because the splitting of doublet transition lines is too large to be explained by spin-orbit coupling. λ values indicate that the complexes under study have a substantial covalent character. g -values were also calculated using the spin-orbital coupling constant, λ .

Key Words: Macrocyclic ligands, 1H NMR, ^{13}C NMR, IR, EPR, Cr(III) complexes.

Introduction

Transition metals play a central role in the construction of molecular materials, which display magnetic properties and find applications in material and supramolecular chemistry and biochemistry¹⁻⁴. Cr(III) complexes of macrocyclic ligands are well known for their biological importance as well as their anticarcinogenic, antibacterial, and antifungal properties⁵. There are numerous Cr(III) complexes, which have been well characterized, providing a fertile set of model small molecule oxidants for inquiry. Cr(III) complexes with O, N and S donor macrocyclic ligands can increase the activity of insulin by binding to a small chromium binding protein⁹. There is some controversy surrounding the exact biochemical forms and the action of Cr(III) in biological systems; the topic has been the subject of many experimental reports and continues to be investigated. Cr(III) biochemistry provide a basis for novel therapies based on metal complexes. One unknown fact in this complex problem is the role that chromium may play in the regulation of glucose metabolism; the molecular

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basis of chromium action in biological systems has not been explained, while the toxicology of Cr(VI) has been well characterized. An understanding of the biochemistry and action of Cr(III) continue to elude researchers within this field⁷⁻¹⁵. In this study we have developed some new Cr(III) complexes with macrocyclic ligands containing different donor atoms, namely- L¹: 1,5-diaza-8,12-dioxa-6,7:13,14-dibenzocyclotetradecane and L²: 1,7-diaza-10,14-dioxa-4-thia-8,9:15,16-dibenzocyclohexadeca-2,6-dione.

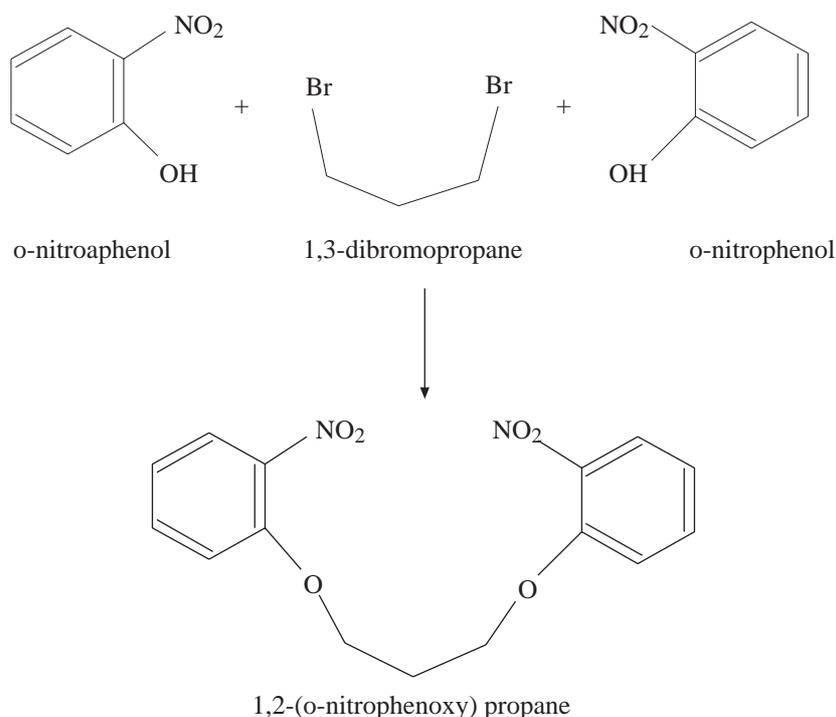
Experimental

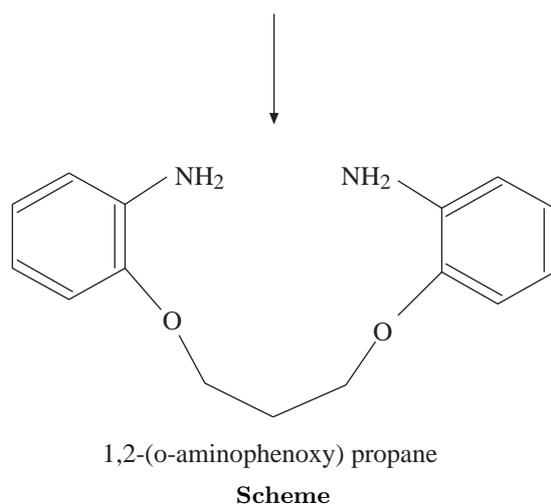
Materials and instrumentation

All the chemicals used in the present investigation were of AR grade, purchased from Sigma Chemical Co, USA. Elemental analysis (CHN) of these complexes was carried out on a Carlo-Erba 1106 Elemental Analyzer. Molar conductance was measured on an ELICO conductivity bridge (Type CM82T). Magnetic susceptibility measurements were performed on a Gouy Balance at room temperature using CuSO₄.5H₂O as calibrant. Infrared spectra were recorded on a Perkin Elmer 137 instrument as KBr pellets. Electronic spectra were recorded in DMSO solution on a Shimadzu UV mini-1240 spectrophotometer. EPR spectra of the Cr(III) complexes were recorded as powder samples at room temperature on an E-4 EPR spectrometer using DPPH as the g-marker.

Preparation of macrocyclic ligands

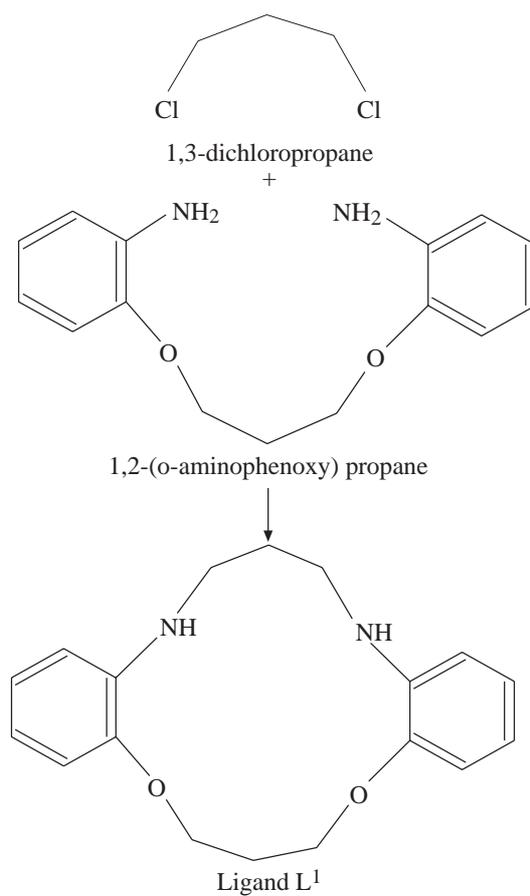
Preparation of diamines: This diamine is prepared by the method reported earlier¹.





(ii) Preparation of macrocyclic ligands:

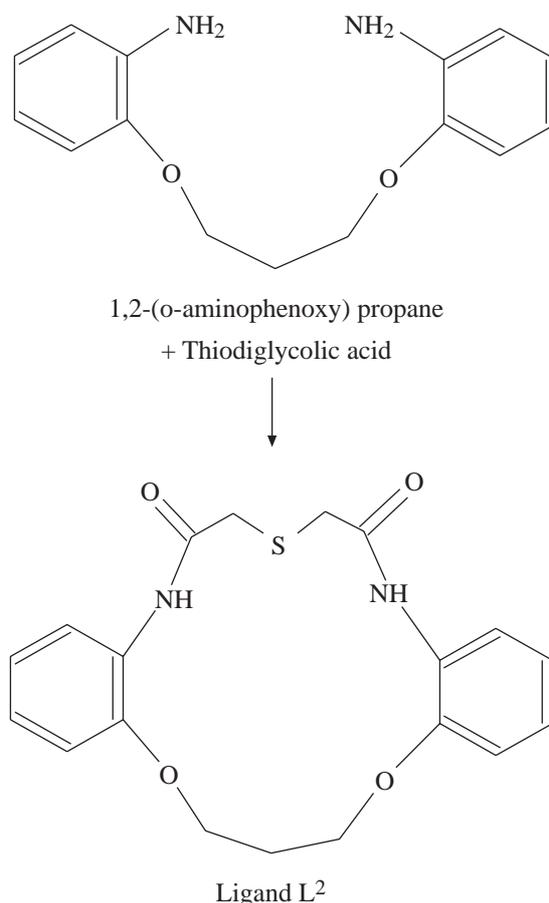
A hot (~50 °C) EtOH solution (20 mL) of 1,2-di(*o*-aminophenoxy) propane (0.1 mmol) and a hot EtOH solution (20 mL) of an equimolar amount of corresponding dichloropropane or thiodiglycolic acid (0.1 mmol) were mixed in a 100 mL round bottom flask.



Preparation of 1,5-diaza-8,12-dioxa-6,7:13,14-dibenzocyclo tetradecane (L¹)

Scheme

The resulting solution was refluxed on a water bath at $\sim 80^\circ\text{C}$ for several hours and the progress of the reaction was ascertained by noting the liberated water azeotropically. The solution was then concentrated to half of its volume under reduced pressure and kept overnight at $\sim 5^\circ\text{C}$. The crystals formed were filtered, washed with EtOH solution and dried in a vacuum desiccator over P_4O_{10} .



Preparation of 1,7-diaza-10,14-dioxa-4-thia-8,9:15,16-dibenzocyclohexadeca-2,6-dione (L^2)

Scheme

The proposed chemical structures of the prepared macrocyclic ligands were in good agreement with the stoichiometries concluded from their analytical data, ^1H NMR, ^{13}C NMR and IR spectral data. L^1 is white and L^2 is pale yellow.

Ligand L^1 m.p. 182°C . ^1H NMR: (CDCl_3) δ : 7.0 (2H, d), 7.1 (2H, m), 6.5 (4H, m), 6.80 (2H, d, $J = 7.6$), 3.7 (4H, m, NH- CH_2), 3.6 (4H, m, O- CH_2), 3.4 (2H, m), 3.2 (2H, m, - CH_2) and ^{13}C NMR (CDCl_3): 121.01-122.04, 122.10-124.50 (C_6H_4); 144.50-146.0 to 148.0-150.5 (C_6H_4); 150-152 (NH- C_6H_4); 61.2 (- CH_2 -); 62.5-66.20 (- CH_2 - CH_2 - CH_2 -).

Ligand L^2 m.p. 165°C . ^1H NMR: (CDCl_3) δ : 7.2 (4H, m), 6.8 (2H, d, $J = 7.1$), 6.5 (2H, d, $J = 6.7$), 3.8 (2H, s, NH); 3.1 (2H, m, - CH_2 -), 3.0 (4H, s, - CH_2 -), 2.8 (6H, m, - CH_2 -) and ^{13}C NMR (CDCl_3): 122.5-125.5 (C_6H_4); 136.5-137.0 (C_6H_4); 152.0-152.5 (NH- C_6H_4); 122.0-124.5 (C_6H_4); 170.5-172.1 (C=O); 66.50-65.10 (-O- CH_2 - CH_2 - CH_2 -), 30.5 (-S- CH_2 -).

Preparation of Cr(III) complexes

EtOH solution of (25 mL) corresponding macrocyclic ligands was added to an EtOH solution of the (20 mL) hydrated Cr(III) salts (1 mmol). The resulting solution was refluxed on a water bath at 75-85 °C for several hours. The solution was then concentrated to half of its volume under reduced pressure and kept overnight at ~5 °C. The colored crystals formed were filtered off, washed with EtOH and finally dried in a vacuum desiccator over P₄O₁₀.

Results and Discussion

IR spectra

The IR spectra of both ligands show characteristic bands at 3306-3285 cm⁻¹ corresponding to ν (NH). On complexation these bands shift to the lower frequency 3300-3269 cm⁻¹. This indicates diversion of electron clouds from the nitrogen of NH group, thereby resulting in the lowering of the NH stretching frequency. The Ph-O-CH₂-group shows bands in the IR spectra at 301-490 cm⁻¹ in both ligands, which also shift to the lower side on complexation. This shifting of impotent bands confirms the mode of chelation through the C-O-C, C-S-C and -C-NH-C- groups, which are acting as coordinating sites. New bands appeared in the low frequency region for (Ni-O) at 521-535 cm⁻¹, (Ni-S) at 639-662 cm⁻¹ and (Ni-NH) at 510-515 cm⁻¹, which give good evidence of metal/donor bonds in the studied complexes¹⁷ (Table 1).

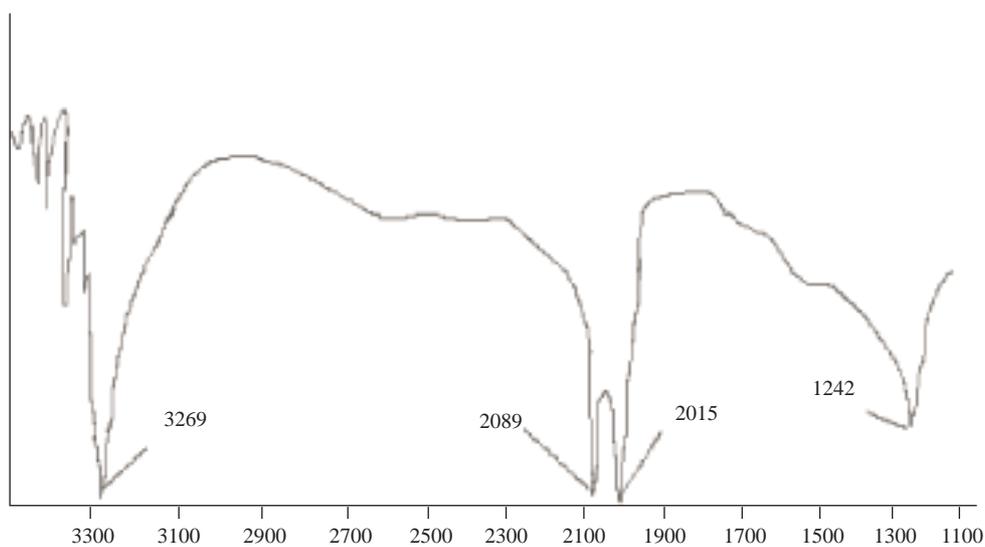


Figure 1. IR spectrum of [Cr(L²)](NCS)(NCS)₂.

Bands due to anions

The IR spectra of the thiocyanato complexes of both ligands show different types of coordination mode due to this group. The complex of ligand L¹ shows bands at 2090 cm⁻¹ corresponding to the N-bonded thiocyanato group, but the complex of L² shows 2 strong absorption bands, one at 2015 cm⁻¹ corresponding to uncoordinated behavior and the other at 2089 cm⁻¹ for corresponding N bonded thiocyanate¹⁸ (Figure 1).

The nitrate complex of ligand L^1 shows bands at 1420 and 1308 cm^{-1} corresponding to the monodentate nature of this group, but the complex of L^2 shows bands at 1420, 1382 and 1308 cm^{-1} corresponding to the monodentate and uncoordinated nature of this ion¹⁹.

Table 1. Important IR absorption bands (cm^{-1}) of L^1 and L^2 with their Cr(III) complexes.

Compound	ν_{NH}	ν_{C-S-C}	ν_{Ni-O}	ν_{Ni-S}	ν_{NO_3}	ν_{NCS}
$C_{29}H_{26}N_4(L^1)$	3285	-	-	-	-	-
$C_{29}H_{26}N_4Cr(NO_3)_3$	3267	-	-	-	1420, 1308	-
$C_{29}H_{26}N_4Cr(NCS)_3$	3200	-	-	-	-	2090
$C_{18}H_{18}N_2O_4S(L^2)$	3306	662	535	370	-	-
$C_{18}H_{18}N_2O_4SCr(NO_3)_3$	3258	658	521	365	1420, 1382 and 1308	-
$C_{18}H_{18}N_2O_4SCr(NCS)_3$	3269	639	1242	361	-	2089, 2015

Cr(III) complexes

The isolated complexes are stable in air, completely insoluble in water and common organic solvents, but completely soluble in DMSO. All of the complexes are found to have the composition $Cr(L)(X)_3$ (where L = Ligands L^1 and L^2 , X = SCN and NO_3). The elemental analyses data obtained for the complexes are listed in Table 3. The complexes show a magnetic moment corresponding to 3 unpaired electrons (i.e. 3.74-3.80 BM), which is approximately equal to a spin-only value²⁰.

All the complexes show molar conductances in the range 86-94 and 165-189 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ as 1:1 and 1:2 electrolytes. Therefore, these complexes may be formulated as $[Cr(L^1)(X_2)]X$ and $[Cr(L^2)X]X_2$ respectively. 1H NMR spectra of the complexes are also studied and compared with the 1H NMR spectra of their macrocyclic ligands, which proved metal to ligand complexation.

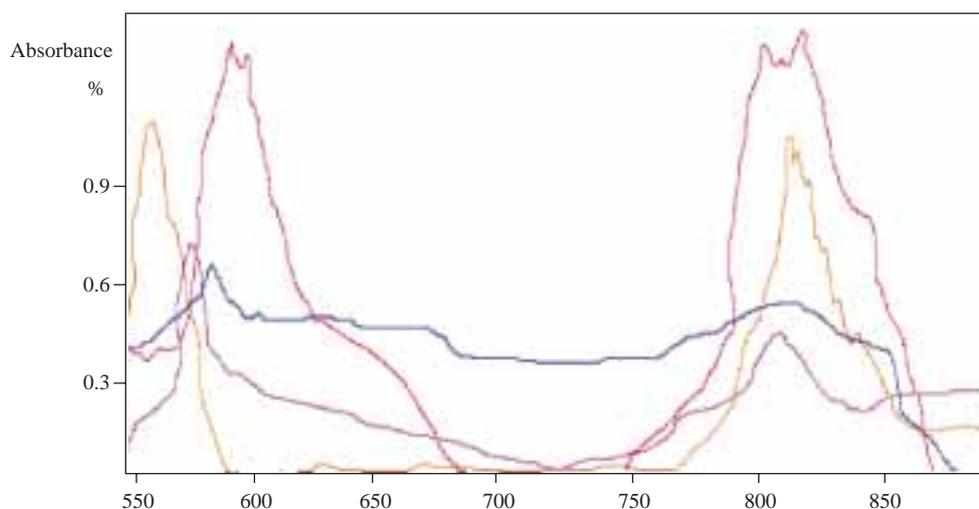


Figure 2. Electronic spectra of all the Cr(III) complexes.

The electronic spectra of the complexes recorded in DMSO (HPLC grade) and the observed values are reported with their possible transitions²¹ (Table 2 and Figure 2).

The positions of the important bands indicate that these complexes exhibit 6-coordinate octahedral geometry, consistent with D_{4h} symmetry around the metal ion.

Table 2. Magnetic moment and electronic spectral data of the Cr(III) complexes in DMSO.

Complexes	Magnetic moments (B.M.)	ν_1	ν_2	Transitions
CrL ¹ (NO ₃) ₃	3.80	17857	12422	${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$
CrL ¹ (NCS) ₃	3.74	17543	12269	and
CrL ² (NO ₃) ₃	3.79	17241	12315	${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$
CrL ² (NCS) ₃	3.75	16949	12195	

Ligand field parameters

Various ligand field parameters Dt (701-743), Ds (5800-6544), Dq (1686-1682), B (605-740), C (2400-2941), λ (44–53) and β (0.80-0.84) were calculated and their values are listed in brackets with the parameters. The values of the ligand field parameters are consistent with octahedral geometry for the complexes¹. However, the interaction between oxygen and the chromium in complexes is much weaker than that of other donor atoms. The ligand field strength, $10 Dq$, can be estimated roughly for each ligand by the relationship of nonlinear, anisotropic ligands. The ligand field parameters from the best-fit parameter set yield the Δ values. Large variance of the spin-orbit coupling parameter, z , gives no significance because the splitting of doublet transition lines is too large to be explained by spin-orbit coupling²².

The β values indicate the covalent character, which is due to the presence of a σ bond between the metal and ligand. Δ values indicate the energy difference between the principle bands, which are formed due to ligand field absorption. This type of complex may have either C_{4v} or D_{4h} symmetry, which arises from the lifting of the degeneracy of the orbital triplet (in octahedral symmetry) in the order of increasing energy and assuming D_{4h} symmetry¹³. C_{4v} symmetry was ruled out because of the higher splitting of the first band. This suggests that it possesses distorted octahedral geometry around the metal ion.

EPR spectra

The EPR spectra of the complexes were recorded (Figures 3-5) as a polycrystalline sample as well as solution at room temperature at different frequencies. The g -values are calculated by using the expression, $g = 2.0023(1 - 4\lambda / 10 Dq)$, where λ is the spin-orbit coupling constant for the metal ion²³. Owen²⁴ states that the reduction of the spin-orbit coupling constant from the free ion value 90 cm^{-1} for Cr(III) can be employed as a measure of metal-ligand covalency. The values of λ indicate that the complexes under study have a substantial covalent character. g -values were calculated and found in the range of 1.97-1.99, corresponding to 6-coordinated geometry. It is possible to define a covalency parameter analogous to the nephelauxetic parameter, which is the ratio of the spin-orbit coupling constant for the complex and the free Cr(III) ions.

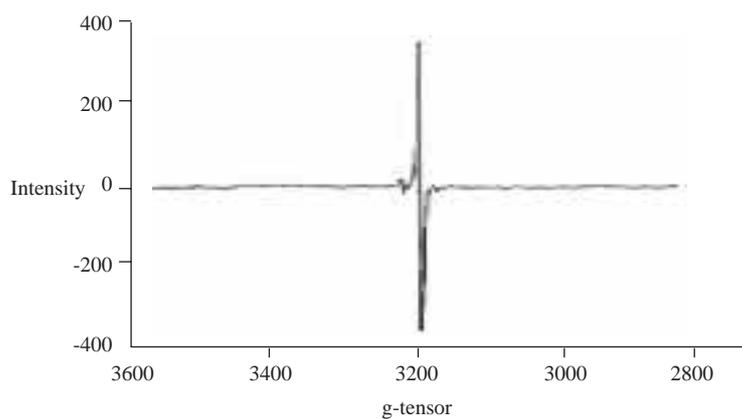


Figure 3. EPR spectrum of $[\text{Cr}(\text{L}^1)(\text{NCS})_2](\text{NCS})$.

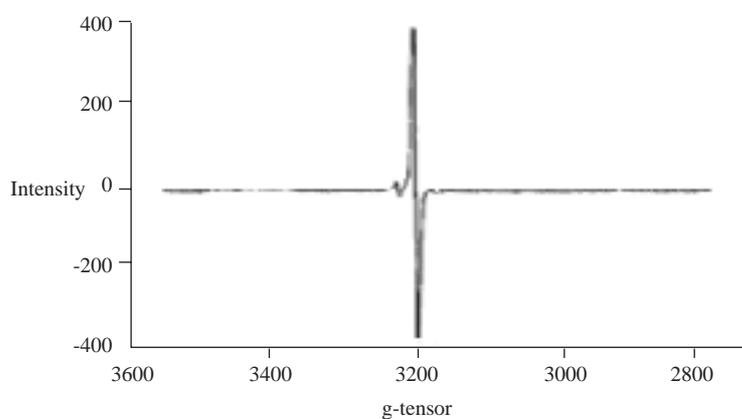


Figure 4. EPR spectrum of $[\text{Cr}(\text{L}^2)(\text{NCS})](\text{NCS})_2$.

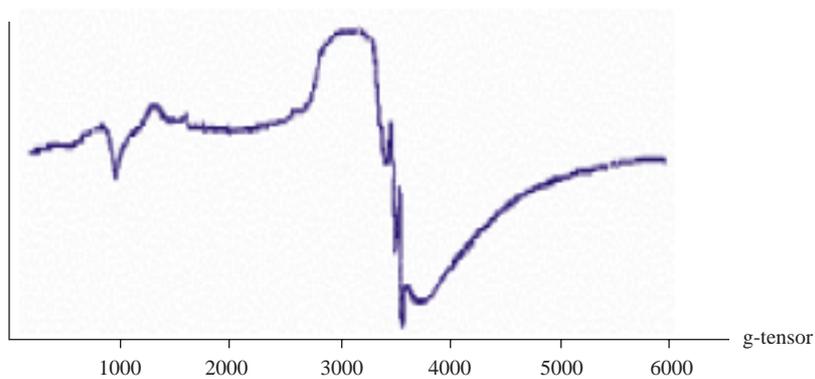
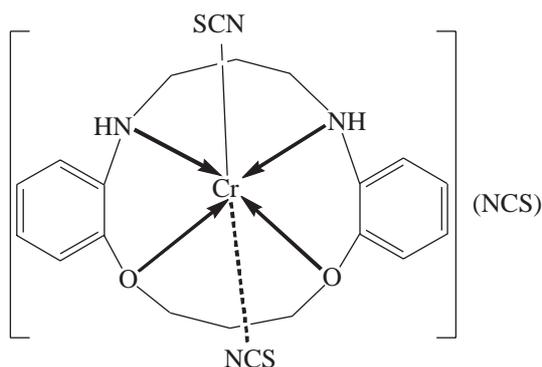
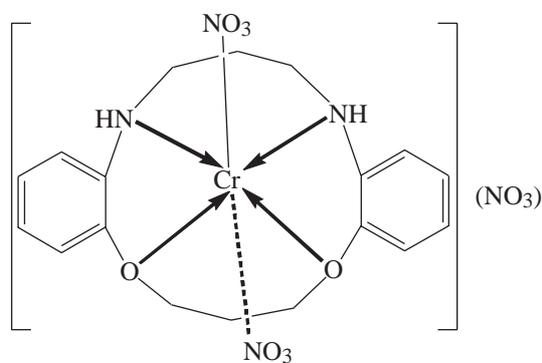


Figure 5. EPR spectrum of $[\text{Cr}(\text{L}^1)(\text{NO}_3)](\text{NO}_3)_2$ in solution.

Table 3. Elemental analysis data calculated (found).

Compound	% C	% H	% N	% Cr
$C_{29}H_{26}N_4(L^1)$	80.90 (80.65)	6.09 (6.04)	13.01 (12.85)	-
$C_{29}H_{26}N_7CrO_9$	52.10 (52.00)	3.92 (3.55)	14.67 (14.50)	7.78 (7.61)
$C_{32}H_{26}N_7CrS_3$	58.52 (58.40)	3.99 (3.50)	14.93 (14.71)	7.92 (7.65)
$C_{18}H_{18}N_2O_4S(L^2)$	60.32 (60.20)	5.06 (4.90)	7.82 (7.73)	-
$C_{18}H_{18}N_5O_{13}S$	36.25 (36.00)	3.04 (2.80)	11.74 (11.55)	8.27 (8.01)
$C_{21}H_{18}N_5O_4S_4$	45.64 (45.50)	3.28 (3.10)	12.67 (12.55)	9.41 (9.25)

**Figure 6.** Suggested structure of the complex $[Cr(L^1)(NCS)_2](NCS)$.**Figure 7.** Suggested structure of the complex $[Cr(L^1)(NO_3)_2](NO_3)$.

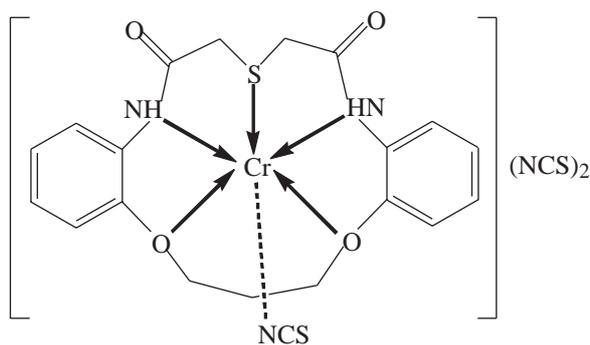


Figure 8. Suggested structure of the complex $[\text{Cr}(\text{L}^2)(\text{NCS})](\text{NCS})_2$.

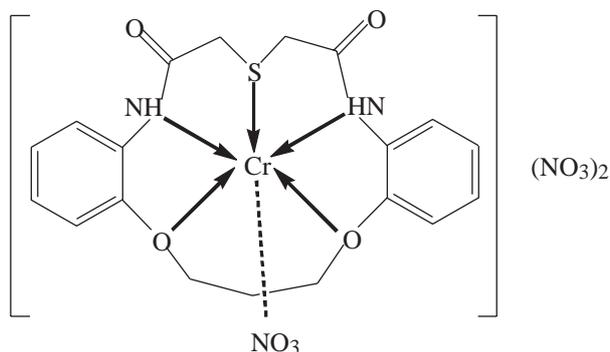


Figure 9. Suggested structure of the complex $[\text{Cr}(\text{L}^2)(\text{NO}_3)](\text{NO}_3)_2$.

Conclusion

A series of Cr(III) complexes with macrocyclic ligands were prepared and fully characterized. The coordinating behavior of both ligands does not affect the coordinating nature of Cr(III) ion with different metal salts. However the numbers of coordinating sites of the ligands do affect the coordination behavior of the NO_3 and NCS ions. On the basis of the above studies, suggested structures of the complexes are given in Figures 6-9.

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