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Spectral studies with coordination behaviour of (NO₃) and (NCS) anions and EPR parameters of chromium(III) complexes which have different chromospheres macrocyclic ligands: Synthesis and electronic spectroscopy

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Abstract

New macrocyclic ligands were prepared and chromium(III) stability in the macrocyclic cavities are reported. Two of them have four-coordinate $[N_2O_2]:[N_4]$, third one has five-coordinate $[N_2O_2S]$ and the last one has six-coordinate $[N_4O_2]$ donor macrocyclic cavities. These macrocyclic ligands have been synthesized with their chromium(III) complexes which have mononuclear nature and their structural features have been discussed on the basis of: elemental analysis, magnetic moment, electronic, IR, ¹H NMR, and EPR spectral studies. All the chromium(III) complexes show magnetic moments in the range of 3.74–3.80 B.M. corresponding to high-spin configuration. However, the interaction of oxygen to the chromium ion in complexes is much weaker than that of other donor atoms. The spin–orbit coupling parameter, *z*, gives no significance because the splitting of doublet transition lines are too large to be explained by spin–orbit coupling. The β values (0.75–0.79) indicate the covalent character, which is due to the presence of σ bond between the metal/ligand. λ values indicate that the complexes under study have substantial covalent character and their *g*-values have also been calculated by using spin–orbital coupling constant (λ). (0) 2006 Elsevier B.V. All rights reserved.

Keywords: Macrocyclic ligands; ¹H NMR; IR; EPR; Chromium(III) complexes

1. Introduction

The synthesis of macrocyclic ligands and their transition metal complexes is a growing area of research in inorganic and bioinorganic chemistry in view of their presence in many biologically significant systems [1–3]. Macrocyclic metal complexes are considered to be the model of metalloporphyrins and metallocorrins due to their intrinsic structural properties. The synthesis and study of macrocycles have undergone tremendous growth and their complexation chemistry with a wide variety of metal ions has been extensively studied [4,5]. In particular, chromium(III) complexes are quite useful for this purpose since they are so kinetically inert that various complexes could be isolated and show three spin allowed transition bands and a number

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of clearly defined spin forbidden transitions specially based on UV-vis absorption [6,7].

The biological significance of chromium is still a matter of considerable discussion [8–10]. The glucose tolerance factor (GTF) [11], an active chromium(III) substance, has never been isolated in pure form, and the other biological product containing chromium, called low molecular weight chromium (LMWCr) [12,13], which was obtained in milligram amounts. Its structure has not as yet been determined and here is still some skepticisms in the literature regarding any positive role for chromium(III) in biological systems [14].

As the ternary complexes seem to be better models for the chromium(III) active substances than the binary ones, in this paper we report the isolation of the chromium(III) complexes with the mixture of organic skeleton containing macrocyclic ligands.

Macrocycles find wide applications in medicine, cancer diagnosis and in treatment of tumors, in metal ion techniques

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Fig. 1. Structures of macrocyclic ligands.

and treatment of kidney stone. Macrocyclic ligands have been used successfully for diverse processes such as separation of ions by transport through artificial and natural membrane, liquid–liquid or solid–solid phase transfer reaction, preparation of ion-selective electrodes, isotope separation and in the understanding of some natural processes through mimicry of metalloenzymes [15,16].

In this article we have developed some new chromium(III) complexes with the mixture of organic skeleton containing macrocyclic ligands (Fig. 1). Namely Ligand L^1 : 2,4-diphenyl-1,5-diaza-8,12-dioxo-6,7:13,14-dibenzocyclotetradeca-1,4-di-

ene $[N_2O_2]$ ane; ligand L^2 : 2,4,9,11-tetraphenyl-6,13-dimethyl-1,5,8,12-traazacyclotertr-adeca-1,4,8,11-tetraene $[N_4]$ ane; ligand L^3 : 1,7-diaza-4-monothia-10,14-dioxo-8,9:15,16-cyclohexadecane $[N_2O_2S]$ ane and ligand L^4 : 4,13-diaoxo-1,7,10,16terazacyclooctadecane $[N_4O_2]$ ane.

2. Experimental

2.1. 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 were carried out on a Carlo-Erba 1106 Elemental Analyzer. Molar conductance was measured on an ELICO conductivity bridge (Type CM82T). Magnetic susceptibility measurements were made on Gouy Balance at room temperature using $CuSO_4.5H_2O$ 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 chromium(III) complexes were recorded as powder samples at room temperature on an E-4 EPR spectrometer using DPPH as the g-marker.

2.2. Preparation and characterization of macrocyclic ligands

The proposed chemical structures of the prepared macrocyclic ligands were in good agreement with the stoichiometries concluded from their analytical, ¹H NMR, and IR spectral data and related structures are given in Fig. 1.

2.2.1. Ligand L^1 : 2,4-diphenyl-1,5-diaza-8,12-dioxo-6,7:13,14-dibenzocyclotetradeca-1,4-diene[N_2O_2]ane

To an EtOH solution of (25 ml) dibenzoylmethane (0.05 mol), an EtOH solution (25 ml) of 1,2-di(*o*-aminophenoxy)propane (0.05 mol) was added in the presence of a few drops (~1 ml) of conc. HCl. The solution was refluxed on a water bath at ~82 °C for 3–4 h. The solution was then concentrated to half of it's volume under reduced pressure and kept over night at ~5 °C. The off-white crystals formed were filtered, washed with EtOH, and dried under a vacuum over P_4O_{10} .

For L^1 Formula: $C_{30}H_{26}N_2O_2$. C 80.69 (80.10); H 5.87 (5.12): N: 6.27 (6.10).

Table 1 H NMR spectral data of the macrocyclic ligands $L^1,\,L^2,\,L^3$ and L^4

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Ligand	Phenyl	Benzene (subst.)	—NH	Ph-CH2-Ph	—O—CH ₂	-S-CH ₂	-NH-CH ₂
$L^1 C_{30} H_{26} N_2 O_2$	7.1–7.25 (10H, m)	7.1–6.9 (2H, m) (2H, d, <i>J</i> =7.2) (2H, d, <i>J</i> =7.1) (2H, m)	_	4.1 (2H, s)	3.4 (4H, m)	-	-
$\begin{array}{c} L^2 C_{36} H_{36} N_4 \\ L^3 C_{19} H_{24} N_2 O_2 S \end{array}$	7.20–7.30 (20H, m) –	- 7.2-6.5 (4H, m) (2H, d, J =7.2) (2H, d, J =7.0)	– 5.2 (2H, s)	4.4 (4H, m) -	– 3.2 (4H, m)	– 2.8 (4H, s)	– 3.2 (4H, m)
$L^4 C_{12} H_{28} N_4 O_2$	_	-	9.2 (4H, s)	-	3.25 (8H, m)	-	3.2 (16H, m)

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Table 2
Important I.R. absorption bands (cm ^{-1}) of nitrato and thiocyanato chromium(III) complexes of L ¹ , L ² , L ³ , and L ⁴

Compound	$\upsilon_{C=N}$	$v_{ m Ni-N}$	$v_{ m Ni-O}$	$v_{\rm Ni-S}$	v_{NO_3}	$v_{ m NCS}$
$[Cr(L^1)(NO_3)_2](NO_3)$	1610	624	510	_	1421, 1309 and 1385	_
$[Cr(L^2)(NO_3)_2](NO_3)$	1601	615	-	-	1420, 1301 and 1384	-
$[Cr(L^3)(NO_3)](NO_3)_2$	-	611	520	310	1420, 1308 and 1382	_
$[Cr(L^4)](NO_3)_3$	-	625	-	-	1385	_
$[Cr(L^1)(NCS)_2](NCS)$	1607	618	511	-		2084, 2050
$[Cr(L^2)(NCS)_2](NCS)$	1602	620	-	-		2081,2051
$[Cr(L^3)(NCS)](NCS)_2$	-	622	514	315		2089, 2049
$[Cr(L^4)](NCS)_3$	-	620	-	-		2052

Table 3 Analytical data of chromium(III) complexes

Complexes/empirical formula	Yield (%)	Molar conductance $\Omega cm^2 mol^{-1})$	Color	Elemental analysis calcd. (found%)			
				Cr	С	Н	N
$\overline{[Cr(L^1)(NO_3)_2](NO_3) CrC_{30}H_{26}N_5O_{11}}$	40	86.0	Green	7.60 (7.50)	52.64 (52.32)	3.83 (3.56)	10.23 (10.11)
[Cr(L ²)(NO ₃) ₂](NO ₃) CrC ₃₆ H ₃₆ N ₇ O ₉	45	94.0	Dark green	6.82 (6.74)	56.69 (56.12)	4.76 (4.41)	12.86 (12.45)
[Cr(L ³)(NO ₃)](NO ₃) ₂ CrC ₁₉ H ₂₄ N ₅ O ₁₁ S	56	165	Dark green	8.93 (8.63)	39.18 (39.01)	4.15 (4.12)	12.02 (11.99)
[Cr(L ⁴)](NO ₃) ₃ CrC ₁₂ H ₂₈ N ₇ O ₁₁	50	245	Green	10.43 (10.12)	28.92 (28.56)	5.66 (5.23)	19.67 (19.32)
[Cr(L ¹)(NCS) ₂](NCS) CrC ₃₃ H ₂₆ N ₅ O ₂ S ₃	58	90.0	Reddish-brown	7.73 (7.45)	58.91 (58.65)	3.90 (3.65)	10.41 (10.26)
[Cr(L ²)(NCS) ₂](NCS) CrC ₃₉ H ₃₆ N ₇ S ₃	54	93.0	Green	6.92 (6.68)	62.38 (62.11)	4.83 (4.74)	13.06 (12.99)
$[Cr(L^3)(NCS)](NCS)_2 CrC_{21}H_{24}N_7O_2S_4$	61	189	Dark green	10.02 (9.98)	34.73 (34.65)	5.44 (5.33)	18.90 (18.48)
$[Cr(L^4)](NCS)_3 CrC_{15}H_{28}N_7O_2S_3$	65	250	Dark green	10.69 (10.22)	37.02 (36.85)	5.80 (5.45)	20.15 (20.01)

2.2.2. Ligand L²: 2,4,9,11-tetraphenyl-6,13-dimethyl-1,5,8,12-traazacyclotertr-adeca-1,4,8,11-tetraene [N₄]ane

This ligand prepared as reported earlier [5].

2.2.3. Ligand L^3 : 1,7-diaza-4-monothia-10,14-dioxo-8,9:15,16-cyclohexadecane[N_2O_2S]ane

To an EtOH solution (25 ml) of bis(2-chloroethayl)ether (0.05 mol), an EtOH solution (25 ml) of 1,2-di(o-aminophenoxy)propane (0.05 mol) was added. The resulting solution was refluxed on a water bath at \sim 72 °C for 5–6 h. The solution was then concentrated to half of it's volume under reduced pressure and kept overnight at \sim 5 °C. The off-white crystals formed were filtered, washed with EtOH, and dried

under a vacuum over P_4O_{10} . L³ Formula: $C_{19}H_{24}N_2O_2S_1$ C: 66.25 (66.12); H: 7.02 (6.95), N: 8.13 (8.11).

2.2.4. Ligand L^4 :

4,13-dioxo-1,7,10,16-teraazacyclooctadecane[N₄O₂]ane

To an EtOH solution (20 ml) of bis(2-chloroethayl)thiol (0.05 mol), an EtOH solution (20 ml) of diaminoethane (0.05 mol) was added. The resulting solution was refluxed on a water bath at \sim 72 °C for 3–4 h. The solution was then concentrated to half of it's volume under reduced pressure and kept overnight at \sim 5 °C. The white crystals formed were filtered, washed with EtOH, and dried under a vacuum over P₄O₁₀. L⁴ Formula: C₁₂H₂₈N₄O₂ C: 55.35, (55.23); H: 10.84, (10.47); N: 21.52 (21.0).

Table 4

Magnetic moment, electronic spectral data of the chromium(III) complexes with all ligands in DMSO

Complexes	Magnetic moments (B.M.)	υ_2	v_1	Transitions	
$\begin{tabular}{ cr(L^1)(NO_3)_2](NO_3) \\ [Cr(L^1)(NCS)_2](NCS) \\ [Cr(L^2)(NO_3)_2](NO_3) \\ [Cr(L^2)(NCS)_2](NCS) \\ [Cr(L^3)(NO_3)](NO_3)_2 \\ [Cr(L^3)(NCS)](NCS)_2 \end{tabular}$	3.80	17241	11235		
	3.74	17543	11235		
	3.79	16393	11098	${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{2g}(F)$	
	3.75	16949	11764		
	3.80	18181	17494	and $4 \wedge (\mathbf{E}) 4\mathbf{T} (\mathbf{E})$	
	3.74	16806	11764	$A_{2g}(F) \rightarrow T_{1g}(F)$	
$[Cr(L^4)](NO_3)_3$	3.79	17857	12048		
$[Cr(L^4)](NCS)_3$	3.75	16499	11627		



Fig. 2. UV spectra of the complexes $[Cr(L^3)(NO_3)](NO_3)_2$ for A and $[Cr(L^3)(NCS)](NCS)_2$ for B.



Fig. 3. UV spectra of the complexes $[Cr(L^4)](NO_3)_3$ for A and $[Cr(L^4)](NCS)_3$ for B.

All the ligands were also characterized by ¹H NMR and the ¹H NMR spectral data are giving in Table 1.

2.3. Preparation of chromium(III) complexes

EtOH solution of (25 ml) corresponding macrocylic ligands L^1 , L^2 , L^3 or L^4 was added to an EtOH solution of the (20 ml)



Fig. 4. EPR spectra of the complex $[Cr(L^1)(NO_3)_2](NO_3)$.



Fig. 5. E.P.R. spectrum of the complex [Cr(L³)(NCS)](NCS)₂.



Fig. 6. EPR spectrum of the complexes $[Cr(L^4)](NCS)_3$ for A and $[Cr(L^4)](NO_3)_3$ for B.



Fig. 7. Structure of the complex $[Cr(L^1)(NCS)_2](NCS)$.

hydrated chromium(III) salts (1m mol). 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 over night at \sim 5 °C. The colored crystals formed were filtered off, washed with EtOH and finally dried in a vacuum desiccator over P₄O₁₀.

3. Results and discussion

3.1. IR spectra of the chromium(III) complexes

The infrared spectrum of these ligands L^1 and L^2 show bands at 1610–1601 cm⁻¹ which may be assigned to C=N respectively [1]. The IR spectra of both L^3 and L^4 ligands show characteristic bands at 3280–3310 cm⁻¹ corresponding to v (NH). On complexation these bands shift to the lower frequency ~10 cm⁻¹. It proved diversion of electron clouds from the nitrogen donor of C=N and NH groups, thereby resulting in the formation of the metal nitrogen bond and related data are given in Table 2.

In the IR spectrum of L^3 , bands due to Ph–O–CH₂– at 520–510 cm⁻¹ are also shift to lower side on complexation and it also indicates the formation of metal–oxygen/sulphur bond. Due to the formation of new bonds, another new bands appeared in



Fig. 8. Structure of the complex $[Cr(L^1)(NO_3)_2](NO_3)$.



Fig. 9. Structure of the complex $[Cr(L^2)(NCS)_2](NCS)$.

the low frequency region for (Ni–O) at $520-510 \text{ cm}^{-1}$, (Ni–S) at $315-310 \text{ cm}^{-1}$ and (Ni–N) at $624-611 \text{ cm}^{-1}$ [1].

3.1.1. Bands due to thiocyanate anions

In the IR spectra of thiocyanato complexes of L^1 , L^2 and L^3 ligands show N-bonded coordination and shows band shows at 2089–2081 cm⁻¹ and second type coordination corresponds to uncoordinated behaviour of this group and shows band at 2051–2049 cm⁻¹. Thus, these result proved two types of coordination behaviour of this group in these complexes.

 L^4 complex shows band at 2052 cm⁻¹ which is corresponding to uncoordinated nature of this ion [3].

3.1.2. Bands due to nitrate anions

In the IR spectra nitrato complexes of ligand L^1 and L^2 show bands at 1421–1420 and 1301–1309 cm⁻¹ corresponding to monodentate nature of this group and also show a sharp band at 1385–1384 cm⁻¹ which is corresponding to uncoordi-



Fig. 10. Structure of the complex $[Cr(L^2)(NO_3)_2](NO_3)$.



Fig. 11. Structure of the complex $[Cr(L^3)(NCS)_2](NCS)$.

nated nature of this group. Thus, these result proved two types of coordination behaviour of this group in these complexes.

 L^4 complex shows band at 1385 cm⁻¹ which is corresponding to uncoordinated nature of this ion.

4. Results and discussion

4.1. Chromium(III) complexes

The isolated complexes are stable in air, completely soluble in DMSO. All of the complexes are found to have the composition $Cr(L)(X)_3$ (where L = Ligands L¹, L², L³, and L⁴X = SCN and NO₃). The elemental analysis data obtained for the complexes are listed in Table 3.

All the complexes show magnetic moment corresponding to three unpaired electrons (i.e. 3.74–3.80 BM), which is approximately equal to spin only value [1].

All the complexes show molar conductances in the range of 86–94, 165–189 and 245–250 Ω^{-1} cm² mol⁻¹ as 1:1, 1:2 and 1:3 electrolytes. Therefore, these complexes may be formulated as [Cr(L¹ or L²)(X₂)]X, [Cr(L³)X]X₂ and [Cr(L⁴)]X₃, respectively. H¹ NMR spectra of the complexes are also studied and compared with the H¹ NMR spectra of their macrocyclic ligands, which proved metal to ligand complexation.



Fig. 12. Structure of the complex $[Cr(L^3)(NO_3)](NO_3)_2$.



Fig. 13. Structures of $[Cr(L^4)](NO_3)_3$.

4.2. Electronic spectroscopy

The electronic spectra of the complexes recorded in DMSO and the observed values are reported with their possible transitions [17,18]. Table 4 and Figs. 2 and 3.

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

4.3. Ligand field parameters

Various ligand field parameters Dt, Ds, Dq, B, C, λ and β have been calculated and their values have a good agreement with data earlier reported [1]. The values of the ligand field parameters are consistent with octahedral geometry for the complexes. However, the interaction of oxygen to the chromium in complexes are 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 spin-orbit coupling parameter, *z*, gives no significance because the splitting of doublet transition lines are too large to be explained by spin-orbit coupling [19,20].

The β values (0.75–0.79) indicate the covalent character, which is due to the presence of σ bond between the metal/ligand. Δ values indicate the energy difference between the principle bands, which are formed due to ligand field absorption. This



Fig. 14. Structures of [Cr(L⁴)](NCS)₃.

type of complexes may have either C_{4v} or D_{4h} symmetry which is arising from the lifting of the degeneracy of the orbital triplet (in octahedral symmetry) in the order of increasing energy or assuming D_{4h} symmetry. The C_{4v} symmetry has been ruled out because of higher splitting of the first band. This suggests that it possess distorted octahedral geometry around the metal ion.

4.4. EPR spectra of chromium(III)

The EPR spectra of the complexes were recorded (Figs. 4–6) as polycrystalline sample as well as solution at room temperature at different frequency. The *g*-values are calculated by using the expression, $g = 2.0023(1 - 4\lambda/10 \text{ Dq})$ where λ is the spin–orbit coupling constant for the metal ion [21,22]. Owen [23] gives the reduction of the spin–orbit coupling constant from the free ion value, 90 cm⁻¹ for chromium(III) can be employed as a measure of metal–ligand covalency. The values of λ indicate that the complexes under study have substantial covalent character. *g*-values have been calculated and found in the range of 1.95–1.99 which correspond to six 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 chromium(III) ions.

5. Conclusion

A series of chromium(III) complexes with macrocyclic ligands have been prepared and fully characterized. The coordinating behavior in the complexes of chromium(III) effected by the coordination stereochemistry of the macrocyclic ligands NCS and NO₃. Due to these coordinating sites of the ligands are affecting coordination behaviors of the NO₃ and NCS ions. On the basis of above studies suggested structures of the complexes are given in Figs. 7–14.

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