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AZAMACROCYCLIC Cr(III) COMPLEXES: SYNTHESIS AND SPECTROSCOPIC STUDIES

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ABSTRACT

The new tetra dentate aza-macrocyclic ligands LA prepared by 2,6 –diamino pyridine and 3-methyl-2,4-pentadione, Ligand LB prepared by 2,6-diamino-pyridine and 3-ethyl-2,4-pentadione, Ligand LC was prepared with the reaction of 5-bromo-2,3-diamino-pyridine with. 3-methyl-2,4-pentadione and Ligand LD were prepared with the reaction of 5-bromo-2,3-diamino-pyridine with 3-ethyl-2,4-pentadione. Ethyl Alcohol was used in the preparation of ligands as a solvent. All the Ligands were characterized with the help of elemental and spectral studies. Cr(III) complexes were prepared with these newly synthesized ligands. All the newly synthesized Chromium complexes are known to bind with overall composition $M(L)X_3$ [where {M Cr(III), X = Cl^-, & NO^-_3,}]. Cr(III) complexes are categorized by electronic spectral studies, Electron paramagnetic resonance spectroscopy, Infrared spectroscopy, mass spectroscopy, magnetic susceptibility measurements, and conductivity bridge measurements, and with the help of these studies Cr(III) complexes were allocated with octahedral geometry.

Keywords: Spectroscopic**,** Cr(III) Macrocyclic Complexes, 5-bromo-2,3-diaminopyridine, Tetradentate azamacrocyclic, 2,6- diamino-pyridine.

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INTRODUCTION

Inorganic, Bioinorganic, and Organic chemists have been greatly interested in the Macrocyclic world of Chemistry because of its great utility and exceptional potential.[1-3] The synthesis of macrocyclic complexes has medical, industrial, and analytical applications.[4] Complexation with Transition metal enhances the thermodynamic and kinetic stability of their complexes. Cr(III) Macrocyclic complexes synthesized with new aza macrocyclic tetra dentate ligands have been described with synthesis and spectral studies in this paper. These Cr(III) Macrocyclic complex's spectral studies can be used to further antifungal and antibacterial studies.

EXPERIMENTAL

Material

All AR-grade Chemicals are utilized and obtained from Sigma Aldrich. Salts of Cr(III) were acquired from Merck.

Synthesis of Ligands

Synthesis Elemental composition and chemistry of ligands are explained in prior papers.[5-8]

Preparation of Cr(III) Macrocyclic Complexes

Chromium(III) salt {(0.001) mole solution in hot ethanol} and correlated (LA, LB, LC LD) ligand respectively {(0.002) mole solution in hot ethanol} were mixed together with constant whipping. At 75-80^{0}C for 6 to 8 h, the mixture was refluxed and the colored complex precipitated on cooling. The colored complex was filtered and washed with ethanol. Cr(III) Complexes were dried with a vacuum over P_4O_{10}.

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Detection Methods

Physical Measurements

Carlo-Erba 1106 elemental analyzer is used to analyze C, H, and N (Table-1). ELICO (CM82T) conductivity bridge is used to measure Molar conductance. Gouy balance is used to measure Magnetic susceptibility with $CuSO_4.5H_2O$ at room temperature. JEOL-MS Route mass spectrometer was used to determine Electron impact mass spectrum. Perkin Elmer FTIR spectrum BX-II spectrophotometer is used to record Infrared spectral studies. Electronic spectral studies are done with the help of the Shimadzu UV Spectrophotometer. The EPR spectrum study was done at room temperature with an E_4-EPR spectrometer.

RESULTS AND DISCUSSION

The general composition of Cr(III) complexes was found {$[Cr(L)X_3]$ } {where (L = LA, LB, LC, LD) and (X = Cl^-, NO_3^-)} with the help of molar conductance measurements and C, H, and N elemental analysis of the Cr(III) complexes correlate to 1:1 electrolytes. As a consequence, $\{Cr(L)X_2\}X$ may be formulated for Cr(III) macrocyclic complexes.[9] Cr(III) nitrate complexes in the IR spectra show medium intense bands in the region at 1428-1430, 1260-1280, and 980-989 cm^{-1}, which are assigned to ν_3, ν_2, and ν_1 respectively. The nitrate groups proposed coordinated behavior with the Cr(III) metal ion which is located in the center in a unidentate fashion.[10-12] The band present at 1376-1390 cm^{-1} proposes an uncoordinated nitrate group in Cr(III) nitrate macrocyclic complex.[13-18]

Table-1: Element Composition of Macrocyclic Complexes of Cr(III)

Macrocyclic complexes of Cr(III)	Color	[Molar conductance] $\Omega^{-1}cm^2mol^{-1}$	Yield [%]	M.P. [^{0}C]	C, H, N [% found/calculated]			
					Cr	C	H	N
$[Cr(LA)Cl_2]Cl$ $CrC_{22}H_{26}N_6Cl_3$	Green	97	62	278	9.78 (9.77)	49.60 (49.62)	4.87 (4.88)	15.77 (15.78)
$[Cr(LA)(NO_3)_2]NO_3$ $CrC_{22}H_{26}N_9O_9$	Mehandi green	112	58	272	8.50 (8.49)	43.12 (43.13)	4.25 (4.24)	13.74 (13.72)
$[Cr(LB)Cl_2]Cl$ $CrC_{24}H_{30}N_6Cl_3$	Light green	102	60	280	9.30 (9.28)	51.40 (51.42)	5.34 (5.35)	14.98 (15.00)
$[Cr(LB)(NO_3)_2]NO_3$ $CrC_{24}H_{30}N_9O_9Br_2$	Light green	99	55	282	8.14 (8.12)	45.01 (45.00)	4.69 (4.68)	13.14 (13.12)
$[Cr(LC)Cl_2]Cl$ $CrC_{22}H_{24}N_6Br_2Cl_3$	Mehandi green	102	60	288	7.51 (7.53)	38.27 (38.26)	3.48 (3.47)	12.18 (12.17)
$[Cr(LC)(NO_3)_2]NO_3$ $CrC_{22}H_{24}N_9O_9Br_2$	Mehandi green	107	58	285	6.76 (6.75)	34.29 (34.28)	3.12 (3.11)	10.97 (10.90)
$[Cr(LD)Cl_2]Cl$ $CrC_{24}H_{28}N_6Br_2Cl_3$	Algae green	101	60	275	7.25 (7.24)	40.12 (40.11)	3.88 (3.89)	11.68 (11.69)
$[Cr(LD)(NO_3)_2]NO_3$ $CrC_{24}H_{28}N_9O_9Br_2$	Shiny green	98	56	272	6.52 (6.51)	36.10 (36.09)	3.51 (3.50)	10.51 (10.52)

The value of Magnetic moments for the Cr(III) macrocyclic complexes under study is near the spin. Around the Cr(III) ion, octahedral geometry is proposed by only value. Cr(III) {d^3, (S = $^3/_2$ the spin quantum number)}, $t_{2g}^3e_g^0$ is the strong ground configuration. $t_{2g}^2e_g^1$ is the excited configuration (six-fold orbital degeneracy) with $t_{2g}^1e_g^2$ being the other excited configuration (three-fold orbital degeneracy). ^4F and ^4P (the free ion split quartet term) in an octahedral field splits into $^4A_{2g}$, $^4T_{1g}$, $^4T_{2g}$, and $^4T_{1g}(P)$, respectively. Macrocyclic Cr(III) complexes in the electronic spectra show three bands in the range (Table-2) and DMF/DMSO was used as a solvent.

Table-2: Electronic Spectra with Magnetic Moment Values of the Macrocyclic Complexes of Chromium

Macrocyclic complexes of Cr(III)	μ_{eff} [BM]	Max. λ cm^{-1}]
$[Cr(LA)Cl_2]Cl$	3.88	15176, 18622, 22523
$[Cr(LA)(NO_3)_2]NO_3$	3.83	16556, 19120, 23809
$[Cr(LB)Cl_2]Cl$	3.80	15974, 19230, 24038
$[Cr(LB)(NO_3)_2]NO_3$	3.78	16835, 19193, 24096

[Cr(LC)Cl_2]Cl	3.85	16920, 19230, 23256
[Cr(LC)(NO_3)$_2$]NO_3	3.80	16722, 19230, 24038
[Cr(LD)Cl_2]Cl	3.81	15504, 19078, 21322

Transitions Allowed spin bands:

(ν_1) $^4A_{2g}$ [F] → $^4T_{2g}$ [F] (E = 10Dq)
(ν_2) $^4A_{2g}$ [F] → $^4T_{1g}$ [F] (E = 18Dq)
(ν_3) $^4A_{2g}$ [F] → $^4T_{1g}$ [P] (E= 12Dq + 15B), respectively.

The effective symmetry near the metal ion is D_{4h} is suggested as a transition displaying from the upgrading the triplet orbital degeneracy (symmetry is octahedral) with the expanded energy, and due to this reason the high split of first band C_{4v} symmetry has been ruled out. EPR spectrum is having an isotropic single broad line spectrum.[19-23] The expression used to calculate values is

$$g = 2.0023 [(1 - 4\lambda 0 / 10Dq]$$

(λ is considered as the metal ion complex spin-orbit coupling constant) (Table-3)

Table-3: EPR Spectra with Ligand Field Parameter

Macrocyclic complexes of Cr(III)	Dq [cm^{-1}]	B [cm^{-1}]	β	LFSE [$kJmol^{-1}$]	g_{iso}
[Cr(LA)Cl_2]Cl	1517	309.93	0.3376	217.49	1.9548
[Cr(LA)(NO_3)$_2$]NO_3	1655	223.92	0.2439	237.28	1.9587
[Cr(LB)Cl_2]Cl	1597	289.89	0.3158	228.96	1.9572
[Cr(LB)(NO_3)$_2$]NO_3	1683	204.84	0.2231	241.29	1.9595
[Cr(LC)Cl_2]Cl	1692	200.42	0.2183	242.58	1.9597
[Cr(LC)(NO_3)$_2$]NO_3	1672	218.64	0.2382	239.71	1.9592
[Cr(LD)Cl_2]Cl	1550	321.95	0.3507	222.22	1.9558
[Cr(LD)(NO_3)$_2$]NO_3	1689	199.71	0.2176	242.15	1.9596

With the help of Results and discussion suggested structure of Chromium Macrocyclic complexes

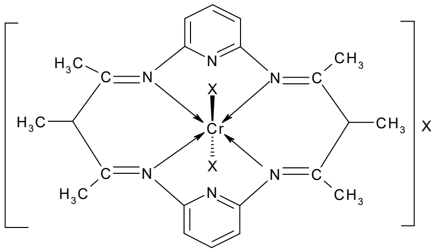

Fig.-1: Suggested Structure of the Chromium Macrocyclic Complexes with Ligand LA

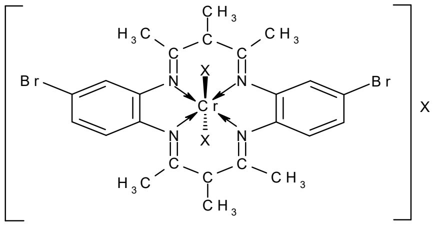

Fig.-2: Suggested Structure of the Chromium Macrocyclic Complexes with Ligand LB

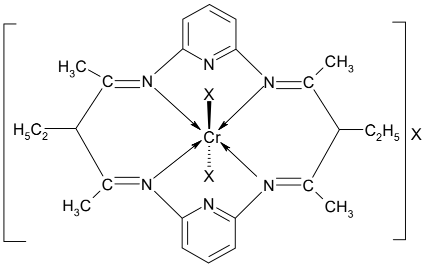

Fig-3: Suggested Structure of the Chromium Macrocyclic Complexes with Ligand LC

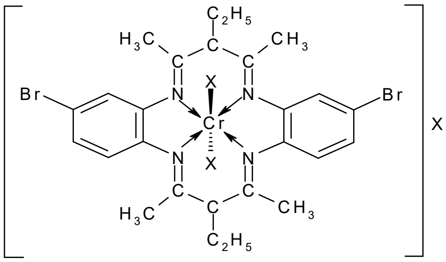

Fig-4: Suggested Structure of the Chromium Macrocyclic Complexes with Ligand LD

CONCLUSION

An octahedral geometry (Fig.-1 to 4) was found for Cr(III) macrocyclic complexes with tetra dentate ligands, with the support of electronic spectral studies, EPR, I.R, mass, magnetic susceptibility measurements, conductivity bridge measurements, and elemental analysis. These macrocyclic complexes of Cr(III) can be used for further studies of antimicrobial activities

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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