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Template Synthesis, Structural Elucidation and Biological Activities of Mixed Ligand Macrocyclic Complexes of Cr (III)

C. P. Bhasin* and B. N. Thakkar

*Department of Chemistry, Hemchandracharya North Gujarat University, Patan-384265, (Gujarat) **INDIA**

Email: cpbhasin@yahoo.com

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ABSTRACT

Alkylene dithiophosphate derivatives of macrocyclic complexes of Cr(III) having N_4S_4 potential donors, of the general formula, $[Cr(L)\{S_2P(O)(O)G\}_2]Cl$ where L=macrocyclic ligands L^1, L^2, L^3, L^4, L^5 and G=$CH_3–CH–CH–CH_3$, $(CH_3)_2–C–C–(CH_3)_2$, $(CH_3)_2C–CH_2–CH(CH_3)$, CH_2-C $(CH_3)_2$-CH_2 and CH_2-$C(C_2H_5)_2$-CH_2 *have been synthesized from the reaction of* $[Cr(L)X_2]_X$ *where X = Cl^-, NO_3^- or CH_3CHOO^-, with ammonium alkylene dithiophosphates in 1:2 molar ratios in THF. These complexes have been characterized by elemental analysis, molar conductance, molecular weight determinations, IR,* ^{31}P *NMR, electronics spectra and magnetic measurements. The anti-microbial of these derivatives have been studied by screening them Aspergillus flavus, fusarium oxysporum, Trichoderma harzianum and bacteria like Salmonella typhi and Bacillus subtili. Alkylene dithiophosphate derivatives were found to be more fungitoxic and antibacterial than their corresponding macrocylic complexes.*

Keywords: Macrocyclic complexes, *bis*-(2-aminophenyl) disulphide, Cr(III).

INTRODUCTION

The chemistry of macrocyclic ligands is a fascinating area of intense study for inorganic chemists. The possibility to tailor –make different types of macrocycles for specific use has promoted much of this interest. Among others, these include for biological systems, therapeutic reagents for the treatment of metal intoxication, synthetic ionophores and the selective extraction of heavy and precious metals[1-4]. Inspite of vast innovation in macrocyclic chemistry and tremendous interest in mixed ligand complexes, no mixed ligand macrocyclic complex was reported till our publications. Alkylene dithiophosphates has been the area of our thrust since last three decades [5-14]. Considering the importance of mixed ligand macrocyclic complexes, we reported synthesis, characterization, antimicrobial and catalytic aspects of mixed ligand macrocyclic complexes of Cr(III), Mn(II), Fe(III), Co(III), Ni(II), Cu(II), Cd(II), Sn(II) and Pb(II) with dialkyl- and alkylene dithiophosphates having N_2S_2 potential donors in 22 to 28 membered

rings[15-31]. We have also reported the macrocyclic complexes of Ni(II) and Sn(II) with dialkyl- and alkylene dithophosphate having N_4S_4 potential donors in 22-28 membered rings[17,24,28-30]. In continuation to the above work we hereby report the synthesis, characterization and antimicrobial aspects of alkylene dithiophosphate derivatives of macrocyclic complexes of Cr(III) having N_4S_4 potential donors in 22 to 28 membered rings.

MATERIALS AND METHODS

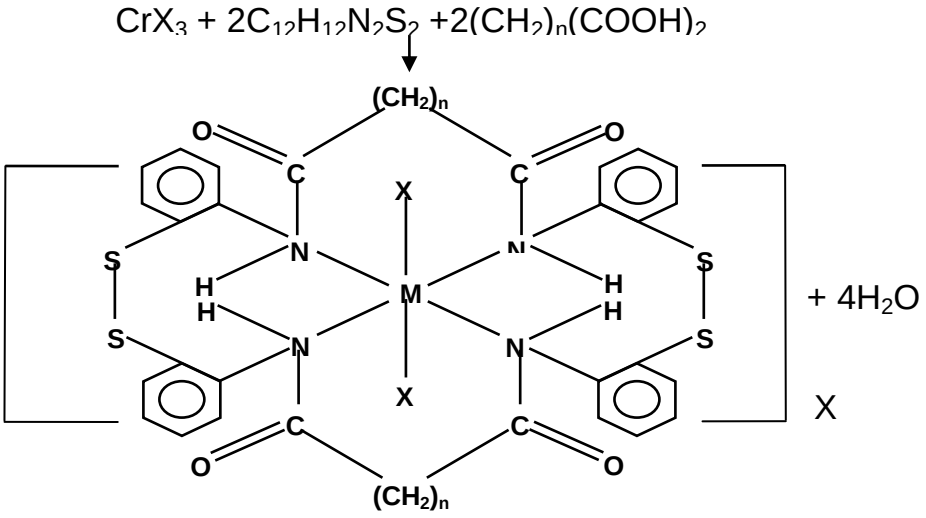
All the Chromium salt and dicarboxilic acids of A.R. grade were obtained from S,D. fine chemicals and were used without further purification. *o*-Aminothiophenol was used as obtained from Merck. Solvents were purified and dried by standard methods. The chelating ligand *bis*-(2-aminophenyl) disulphide was synthesized by the dimerization of the o-aminothiophenol by H_2O_2 as reported in the literature [32]. Ammonium alkylene dithiophosphates were prepared by the method as we reported in our earlier communication [6].

Microanalyses for carbon, hydrogen, nitrogen and sulphur were determined from SICART, Vallabh Vidyanagar. Chromium and phosphorus were estimated by standard method [33]. The molecular weights were determined by Rast Camphor method. Infrared data were recorded on a Perkin-Elmer FT-IR spectrophotometer as KBr pellets. ^{31}P NMR spectra were recorded on a Jeol 300 MHz spectrometer using DMSO-d_6 as a solvent and TMS as an internal standard. ^{31}P NMR spectra were recorded on the same instrument using DMSO-d_6 as a solvent and H_3PO_4 as an external standard.

Synthesis of butylene dithiophosphate derivative of {Tetrabenzo[2,3,11,12,15,16,24,25][4,10,17,23] tetra aza [1,13,14,26] tetrathaicyclohexai-cosane[5,9,18,22]tetraone}: Precursor macrocyclic complex mentioned above in parenthesis (3.04 g, 0.0038 mol) was dissolved in THF and was reacted with methanolic solution of ammonium butylene dithiophosphate (1.57 g, 0.0078 mol) in 1:2 molar ratio. Reaction mixture was refluxed for ~5 h on oil bath on cooling the green crystals of dithiophosphate derivatives were separated out, which were filtered through G-3 filtering funnel. This crude product was washed several times with methanol, by vigrous shaking in filtration funnel, to remove the ammonium nitrate formed during the reaction. Product was dried under vacuum and was crystallized with THF / C_2H_5OH mixture.

RESULTS AND DISCUSSION

Reaction of Chromium (M = Cr(III)) salts with *bis*-(2-aminophenyl) disulphide and various dicarboxylic acids in 1:2:2 molar ratio in methanol to afford off white or light yellow complexes as shown below :



X=Cl^-,NO_3^- or CH_3CHOO^- and L = L^1, L^2, L^3, L^4, L^5. n = 1, 2, 3, 4 or $(CH_2)_n$ = *o*-$C6H_4$-

Figure 1. Tentative Structure of Macrocyclic Complexes of Cr(III)

L = Macrocyclic ligands L^1,L^2,L^3,L^4 and L^5

L^1= Macrocyclic ligand derived from *bis*-(2-aminophenyl)disulphide and malonic acid (n=1), **22- membered ring; {Tetrabenzo[2,3,9,10,13,14,20,21][4,8,15,19]tetraaza [1,11,12,22]tetrathiacyclodiicosane[5,7,16,18] tetraone}.**

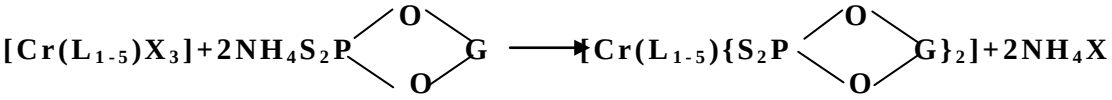
L^2= Macrocyclic ligand derived from *bis*-(2-aminophenyl)disulphide and succinic acid (n=2), **24- membered ring; {Tetrabenzo[2,3,10,11,14,15,22,23][4,9,16,21]tetraaza [1,12,13,24]tetrathiacyclotetraicosane[5,7,17,20]tetraon}.**

L^3= Macrocyclic ligand derived from *bis*-(2-aminophenyl) disulphide and glutaric acid (n=3), **26- membered ring; {Tetrabenzo[2,3,11,12,15,16,24,25][4,10,17,23]tetraaza [1,13,14,26]tetrathiacyclohexaicosane[5,9,18,22]tetraone}.**

L^4 = Macrocyclic ligand derived from *bis*-(2-aminophenyl) disulphide and adipic acid(n=4), **28- membered ring. {Tetrabenzo[2,3,12,13,16,17,26,27][4,11,18,25]tetraaza [1,14,15,28]tetrathiacyclooctaicosane[5,10,19,24]tetraone}.**

L^5 = Macrocyclic ligand derived from *bis*-(2-aminophenyl) disulphide and phthalic acid ($(CH_2)_n$ = *o*-C_6H_4-), **24- membered ring; {Hexabenzo[2,3,6,7,10,11,14,15,18,19,22,23][4,9,16,21]tetraaza [1,12,13,24]tetrathiacyclotetraicosane[5,8,17,20]tetraone}.**

The above macrocyclic complexes of Cr(III) in the THF were reacted with a methanolic solution of ammonium alkylene dithiophosphates in 1 : 2 molar rations to afford the alkylene dithiophosphate derivatives of the macrocyclic Cr(III) complexes in the following manner :



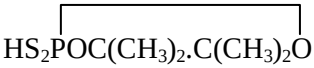
G = CH_3–CH–CH-CH_3, $(CH_3)_2C$ - C$(CH_3)_2$, $(CH_3)_2C$-CH_2-CH(CH_3), CH_2-$C(CH_3)_2$-CH_2 **and** CH_2-$C(C_2H_5)_2$-CH_2.

IUPAC names have been mentioned in parenthesis in hold letters. The formula of the alkylene dithiophosphoric acid used for the synthesis of mixed ligand macrocyclic complexes have been depicted below.

$HS_2POCH(CH_3).CH(CH_3)O$

Butylene dithiophosphoric acid

(2-Mercapto-2-thiono-4,5 dimethyl 1,2,3-dioxaphospholane)



$HS_2POC(CH_3)_2.C(CH_3)_2O$

Tetramethylethylene dithiophosphoric acid

(2-Mercapto-2-thiono-4,4,5,5-tetremethyl-1,3,2-dioxaphospholane)

$HS_2POC(CH_3)_2CH_2.CH(CH_3)O$
Hexylene dithiophosphoric acid
(2-Mercapto-2-thiono-4,4,6-trimethyl-1,3,2-dioxaphosphorinane)

$HS_2POCH_2C(CH_3)_2.CH_2O$
Neo-pentylene (2,2-dimethlpropylene) dithiophosphoric acid
(2-Mercapto-2-thiono-5,5 dimethyl 1,3,2-dioxaphosphorinane)

$HS_2POCH_2C(C_2H_5)_2.CH_2O$
2,2-Diethylpropylene dithiophosphoric acid
(2 Mercapto-2-thiono-5,5 diethyl 1,3,2-dioxaphosphorinane)

Except THF and DMSO, these derivatives are insoluble in almost all organic solvents. All derivatives are yellow or light yellow in color. The molar conductance of 10^{-3} M solution in DMSO lie in the range 36-44 $ohm^{-1}cm^2mol^{-1}$, showing that these complexes are 1:1 electrolyte The molecular weight determinations indicate their monomeric nature. The Analytical Data of Alkylene Dithiophosphate Derivatives of Macrocyclic Complexes of Cr(III) ar presented in table 1.

Infrared Spectra: In the macrocyclic complexes, the four bands in the region 1638-1680 (s), 1516-1582(m), 1240-1272(s) and 648-690 (w) cm^{-1} have been ascribed to the amide I, amide II, amide III and amide IV in-plane deformation vibrations, respectively [34]. A broad band in the region 3104-3189(m) cm^{-1} has been assigned to the ν(N-H) vibration of the secondary amino group. These bands do not show any significant change from their parent macrocyclic complexes. Two bands present in the region 1040-1072 cm^{-1} and 888-840 cm^{-1} may be assigned to (P)-O-C and P-O-(C) stretching vibrations, respectively [35]. The band present between 999-954 cm^{-1} may be attributed to the ring vibrations of dioxaphospholanes and dioxaphosphorinanes respectively, which are probably coupled with C-C stretching vibrations [36,37]. A weak band present in the region 570-538 cm^{-1} has been attributed to P-S symmetric and asymmetric vibrations. A strong band observed in the region 728-680 cm^{-1}, which also appears in ammonium alkylene dithiophosphates at 128 around the same region, is attributed to the P=S moiety. This indicates the unidentate behavior of the dithiophosphate moieties The presence of sharp and weak bands in the region 483-418 cm^{-1} and 364-320 cm^{-1} have been assigned to ν(Cr-N) and ν(Cr-S) vibrations, respectively [7,8,38].

Table-1- Analytical Data of Alkylene Dithiophosphate Derivatives of Macrocyclic Complexes of Cr(III)

Sr. No.	Compound	Analysis % Found (Calcd.)									
		C	H	N	P	S	Cr	Cl	Molecular Wight Found (Calcd.)	Conductivity ^M $Ohm^{-1}Cm^2Mol^{-1}$	M.P. (decomp.) ^0C
1	$[Cr(L_1)\ S_2POC(CH_3)_2CH_2.CH(CH_3)O\}_2]$ $(C_{42}H_{48}N_4P_2S_8O_8Cr)Cl$	44.54 (44.15)	4.29 (4.20)	5.11 (4.90)	5.57 (5.43)	22.15 (22.42)	4.66 (4.55)	3.25 (3.10)	1136 (1141.5)	38	203
2	$[Cr(L^1)\{S_2POCH(CH_3).CH(CH_3)O\}_2]$ $(C_{38}H_{40}N_4O_8P_2S_8Cr)NO_3$	41.05 (41.00)	3.66 (3.59)	6.26 (6.29)	5.59 (5.57)	23.06 (23.02)	4.69 (4.67)	-	1105 (1112)	44	204
3	$[Cr(L^1)\{S_2POC(CH_3)_2.C(CH_3)_2O\}_2]$ $(C_{42}H_{48}N_4O_8P_2S_8Cr)(CH_3COO)$	50.44 (50.47)	4.08 (4.12)	4.75 (4.80)	5.28 (5.32)	21.88 (21.97)	4.48 (4.46)	-	1149 (1165)	36	199

4	$[Cr(L^2)\{S_2POCH_2C(C_2H_5)_2.CH_2O\}_2]$ $(C_{46}H_{56}N_4O_8P_2S_8Cr)Cl$	46.04 (46.09)	4.58 (4.67)	4.72 (4.67)	5.15 (5.17)	21.30 (21.37)	4.42 (4.34)	2.88 (2.96)	1186 (1197.5)	37	211
5	$[Cr(L^2)\{S_2POC(CH_3)_2.C(CH_3)_2O\}_2]$ $(C_{44}H_{52}N_4O_8P_2S_8Cr)NO_3$	44.16 (44.14)	4.48 (4.34)	5.79 (5.85)	5.22 (5.18)	21.37 (21.40)	4.39 (4.34)	-	1191 (1196)	42	205
6	$[Cr(L^2)\{S_2POCH_2C(CH_3)_2.CH_2O\}_2]$ $(C_{42}H_{48}N_4O_8P_2S_8Cr)(CH_3COO)$	50.45 (50.47)	4.36 (4.37)	4.77 (4.80)	5.29 (5.32)	21.89 (21.97)	4.41 (4.46)	-	1175 (1165)	41	208
7	$[Cr(L^3)\{S_2POC(CH_3)_2CH_2CH(CH_3)O\}_2]$ $(C_{46}H_{56}N_4O_8P_2S_8Cr)Cl$	46.02 (46.09)	4.59 (4.67)	4.62 (4.67)	5.13 (5.17)	21.31 (21.37)	4.41 (4.34)	2.94 (2.96)	1182 (1197.5)	39	211
8	$[Cr(L^3)\{S_2POCH_2C(C_2H_5)_2.CH_2O\}_2]$ $(C_{48}H_{60}N_4O_8P_2S_8Cr)NO_3$	46.05 (46.00)	4.72 (4.79)	5.55 (5.59)	5.89 (4.95)	20.39 (20.44)	4.08 (4.15)	-	1274 (1252)	40	202
9	$[Cr(L_3)\{S_2POC(CH_3)_2.C(CH_3)_2O\}_2]$ $(C_{46}H_{56}N_4P_2S_8O_8Cr)(CH_3COO)$	52.74 (52.79)	4.80 (4.83)	4.51 (4.58)	5.03 (5.07)	20.94 (20.96)	4.29 (4.25)	-	1232 (1221)	43	208
10	$[Cr(L^4)\{S_2POCH(CH_3).CH(CH_3)O\}_2]$ $(C_{44}H_{52}N_4O_8P_2S_8Cr)Cl$	45.16 (45.14)	4.46 (4.44)	4.75 (4.78)	5.33 (5.30)	21.78 (21.88)	4.41 (4.44)	2.96 (2.99)	1177 (1169.5)	41	201
11	$[Cr(L^4)\{S_2POC(CH_3)_2.C(CH_3)_2O\}_2]$ $(C_{48}H_{60}N_4O_8P_2S_8Cr)NO_3$	45.12 (45.09)	4.54 (4.57)	5.69 (5.71)	5.10 (5.06)	20.89 (20.91)	4.26 (4.24)	-	1211 (1224)	38	204
12	$[Cr(L^4)\{S_2POCH_2C.(CH_3)_2.CH_2O\}_2]$ $(C_{46}H_{56}N_4O_8P_2S_8Cr)(CH_3COO)$	53.78 (53.80)	4.01 (4.04)	4.50 (4.48)	4.93 (4.96)	20.46 (20.49)	4.13 (4.16)	-	1234 (1249)	40	206
13	$[Cr(L^5)\{S_2POC(CH_3)_2.C(CH_3)_2O\}_2]$ $(C_{52}H_{52}N_4O_8P_2S_8Cr)Cl$	49.26 (49.30)	4.14 (4.10)	4.39 (4.42)	4.79 (4.89)	20.28 (20.22)	4.07 (4.10)	2.80 (2.76)	1242 (1265.5)	44	209
14	$[Cr(L^5)\{S_2POC(CH_3)_2CH_2.CH(CH_3)O\}_2]$ $(C_{52}H_{52}N_4O_8P_2S_8Cr)NO_3$	48.32 (48.29)	4.10 (4.02)	5.38 (5.41)	4.83 (4.79)	19.76 (19.81)	4.07 (4.02)	-	1288 (1292)	38	204
15	$[Cr(L^5)\{S_2POCH(CH_3).CH(CH_3)O\}_2]$ $(C_{48}H_{44}N_4O_8P_2S_8Cr)(CH_3COO)$	54.46 (54.50)	3.85 (3.81)	4.61 (4.54)	5.16 (5.02)	20.79 (20.76)	4.23 (4.11)	-	1210 (1233)	40	207

[a]Analytical and physico-chemical data of precursor macrocyclic com plexes.

^{31}P NMR: ^{31}P NMR spectra of a few compounds were recorded on 300 MHz spectrometer using DMSO-d_6 as a solvent and H_3PO_4 as an external standard. ^{31}P NMR spectra of few representative compounds could be recorded. The chemical shift values do not show any significant change from their respective ammonium Alkylene dithiophospate moieties attached to the central chromium ion [39,40]. The values of chemical shift of the newly synthesized compounds are depicted in table 2.

Magnetic Susceptibility: The magnetic moment of the complexes is given in table 2. The Magnetic susceptibility was measured by VSM balance using $Hg[Co(CNS)_4]$ as a calibrant. Pascal constants where used for diamagnetic corrections. The Cr(III) complexes show magnetic movement values of 3.90-4.04 B.M. at room temperature, which correspond to three unpaired electron expected for high spin Cr(III) complexes [41,42].

Table 2- Physico-Chemical Data of Alkylene Dithiophosphate Derivatives of Macrocyclic Complexes of Cr(III)

^{31} P NMR Chemical shift (δ)	Magnetic Moments μ_{eff} (B. M.)	Electronic Spectra λ_{max} (nm) ($\varepsilon dm^3 mol^{-1} cm^{-1}$)	
		ν_1	ν_2
94.72	3.92	580 (32.88)	414 (44.19)
91.00	4.02	578 (31.11)	414 (44.82)
91.14	3.98	586 (29.58)	414 (40.18)
94.09	3.96	579 (32.39)	415 (40.59)
90.22	4.01	584 (32.18)	422 (42.95)
73.89	3.98	578 (31.84)	419 (43.06)
75.12	3.94	585 (31.96)	415 (41.25)
96.66	4.02	583 (32.78)	422 (42.52)
94.02	4.00	578 (30.69)	420 (42.37)
90.88	3.96	580 (29.70)	408 (41.75)
91.28	3.98	586 (32.62)	412 (42.69)
77.19	3.94	580 (29.37)	430 (42.84)
73.81	4.02	585 (31.04)	428 (44.89)
92.69	4.00	590 (33.60)	418 (41.69)
93.11	3.99	588 (32.84)	414 (41.55)

Electronic Spectra: The electronic spectra were recorded on a GBC 911 spectrophotometer in the range 380-1000 nm using THF as a solvent. In Chromium two bands were observed at 578- 590 (ν1) (ε : 31.11 - 33.60) and 408 - 430, (ν2) (ε : 41.75 - 42.84) nm, respectively. These bands may be assigned to the transitions $^4T_{2g}(F) \leftarrow {}^4A_{2g}$ and $^4T_{1g}(P) \leftarrow {}^4A_{2g}$ respectively. These transitions indicate the six-coordination of the central chromium ion [43]. Data have been presented in table 2.

APPLICATIONS

Antimicrobial Activity: The antimicrobial activity of *bis*-(2-aminopheny) disulfide, dicarboxylic acids, Chromium salts and the precursor macrocyclic complexes (L^1 to L^5) has been reported in our earlier communication[15]. Like their precursor macrocyclic complexes, the antifungal activity of dialkyldithiophosphate derivatives has been tested against three fungi, *Aspergillus flavus, Fusarium oxysporum* and *Trichoderma harzianum.* The screening data for the average percentage inhibition of the fungi at 100, 125 and 200 ppm concentration. The values obtained suggest that the alkylene dithiophosphate derivatives of macrocyclic complexes are more fungitoxic than their precursor macrocyclic complexes as well as the alkylene dithiophospharic acids. Further, the data also indicate that with the increase in the concentration, the fungitoxicity also increases. The antibacterial activity against two bacteria, namely *Salmonella* typhi and *Bacillus* subtili, were tested by the inhibition zone technique[15,16]. The values suggest that the alkylene dithiophosphate derivatives of macrocyclic

complexes are more antibacterial than their precursor macrocyclic complexes (CrL^1-CrL^5). The Antifungal Activity and Antibacterial Activity of Alkylene Dithiophosphate Derivatives of Macrocyclic Complexes of Cr(III) is given in table 3.

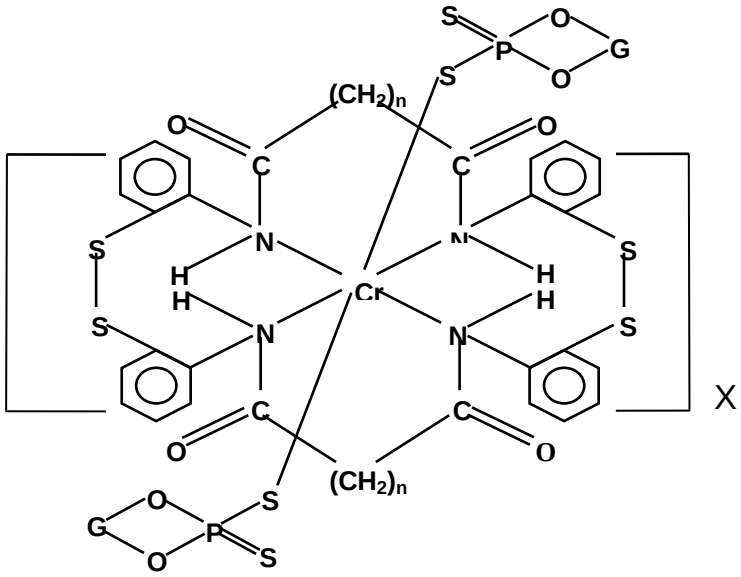
Table 3- Antifungal Activity And Antibacterial Activity of Alkylene Dithiophosphate Derivatives of Macrocyclic Complexes of Cr(III)

Sr. No.	Compound	Average % of Inhibition after 72 h at 30± 2°C									percentage growth inhibition after 24 hours at 30 ± 2°C (conc. in ppm)			
		Aspergillus flavus			*Fusarium oxysporum*			*Alternaria alternata*			*Bacillus Subtili*		*Salmonella typhi*	
		100	125	200	100	125	200	100	125	200	500	1000	500	1000
A	Bavistin (Standard)	91	95	99	90	94	99	91	95	99	-	-	-	-
B	Streptomycin	-	-	-	-	-	-	-	-	-	98	99	98	99
C	*bis*-(2-aminopheny) disulfide	30	34	40	31	35	39	32	37	41	11	13	10	12
D	$CrCl_3.6H_2O$	31	35	41	30	37	42	30	36	40	10	14	12	14
E	$Cr(NO_3)_3.9H_2O$	32	37	42	30	35	42	31	36	41	11	15	12	17
F	$Cr(CH_3COO)_3H_2O$	36	42	30	34	40	30	35	41	43	10	15	13	19
G	HOOC-CH_2-COOH	18	20	21	21	24	27	22	25	29	6	8	6	9
H	HOOC-$(CH_2)_2$-COOH	21	24	28	22	26	29	21	24	27	8	10	8	12
I	HOOC-$(CH_2)_3$-COOH	21	25	29	22	26	29	22	25	29	9	11	8	13
J	HOOC-$(CH_2)_3$-COOH	20	23	26	21	24	27	22	26	29	8	11	7	12
K	HOOC-C_6H_4-COOH	22	24	27	23	26	29	21	24	28	10	13	11	14
L	$HS_2POC(CH_3)_2CH_2CH(CH_3)O$	61	65	66	70	72	74	75	68	70	17	22	20	24
M	$HS_2POC(CH_3)_2C(CH_3)_2O$	62	64	65	66	72	73	75	66	72	17	21	20	24
N	$HS_2POCH_2C(CH_3)_2CH_2O$	72	74	68	65	70	72	74	71	73	22	24	24	27
	Complex													
1	$[Cr(L_1)\ S_2POC(CH_3)_2CH_2.CH(CH_3)O\}_2]$ $(C_{42}H_{48}N_4P_2S_8O_8Cr)Cl$	51	56	61	50	55	60	52	56	61	38	40	40	42
2	$[Cr(L^1)\{S_2POCH(CH_3).CH(CH_3)O\}_2]$ $(C_{38}H_{40}N_4O_8P_2S_8Cr)NO_3$	53	59	64	52	56	61	52	57	61	40	44	41	46
3	$[Cr(L^1)\{S_2POC(CH_3)_2.C(CH_3)_2O\}_2]$ $(C_{42}H_{48}N_4O_8P_2S_8Cr)(CH_3COO)$	50	54	62	51	56	63	51	54	60	39	42	40	44
4	$[Cr(L^2)\{S_2POCH_2C(C_2H_5)_2.CH_2O\}_2]$ $(C_{46}H_{56}N_4O_8P_2S_8Cr)Cl$	53	57	61	55	59	63	52	56	60	35	39	36	42
5	$[Cr(L^2)\{S_2POC(CH_3)_2.C(CH_3)_2O\}_2]$ $(C_{44}H_{52}N_4O_8P_2S_8Cr)NO_3$	52	55	60	51	56	61	50	56	62	38	44	40	46
6	$[Cr(L^2)\{S_2POCH_2C(CH_3)_2.CH_2O\}_2]$ $(C_{42}H_{48}N_4O_8P_2S_8Cr)(CH_3COO)$	52	58	61	53	59	63	50	54	61	42	46	40	44
7	$[Cr(L^3)\{S_2POC(CH_3)_2CH_2CH(CH_3)O\}_2]$ $(C_{46}H_{56}N_4O_8P_2S_8Cr)Cl$	52	56	60	52	57	63	51	56	62	41	45	42	46

8	$[Cr(L^3)\{S_2POCH_2C(C_2H_5)_2.CH_2O\}_2]$ $(C_{48}H_{60}N_4O_8P_2S_8Cr)NO_3$	51	55	62	50	55	61	51	57	62	42	46	38	42
9	$[Cr(L_3)\{S_2POC(CH_3)_2.C(CH_3)_2O\}_2]$ $(C_{46}H_{56}N_4P_2S_8O_8Cr)(CH_3COO)$	55	57	63	52	57	63	51	56	61	40	43	38	42
10	$[Cr(L^4)\{S_2POCH(CH_3).CH(CH_3)O\}_2]$ $(C_{44}H_{52}N_4O_8P_2S_8Cr)Cl$	54	59	63	56	61	65	55	59	63	41	45	40	46
11	$[Cr(L^4)\{S_2POC(CH_3)_2.C(CH_3)_2O\}_2]$ $(C_{48}H_{60}N_4O_8P_2S_8Cr)NO_3$	53	59	62	51	56	62	52	57	62	38	43	40	46
12	$[Cr(L^4)\{S_2POCH_2C.(CH_3)_2.CH_2O\}_2]$ $(C_{46}H_{56}N_4O_8P_2S_8Cr)(CH_3COO)$	51	56	62	50	55	60	51	56	62	40	45	41	46
13	$[Cr(L^5)\{S_2POC(CH_3)_2.C(CH_3)_2O\}_2]$ $(C_{52}H_{52}N_4O_8P_2S_8Cr)Cl$	51	55	64	52	58	61	53	58	64	39	44	40	45
14	$[Cr(L^5)\{S_2POC(CH_3)_2CH_2.CH(CH_3)O\}_2]$ $(C_{52}H_{52}N_4O_8P_2S_8Cr)NO_3$	52	57	62	53	58	63	51	55	61	42	47	41	47
15	$[Cr(L^5)\{S_2POCH(CH_3).CH(CH_3)O\}_2]$ $(C_{48}H_{44}N_4O_8P_2S_8Cr)(CH_3COO)$	52	57	60	51	55	60	53	57	64	40	45	41	46

CONCLUSIONS

The above spectral data indicate the octahedral geometry (Fig. 2) for the above derivatives in which four nitrogen atoms of the macrocyclic ring coordinate to the central (M = Cr(III)) ion in the square planar form and each dithiophosphate moiety occupies the axial position binding the central metal (M = Cr(III)) ion in unidentate manner through strong electrostatic attraction.



n = 1, 2, 3, 4 or $(CH_2)_n$= *o*-C_6H_4-

where G = $(CH_3)_2CCH_2CH(CH_3)$, $CH_2(CH_3)_2CH_2$, $CH_2C(C_2H_5)_2CH_2$, $HC(CH_3)$ $(CH_3)CH$ and $C(CH_3)_2(CH_3)_2C$

Fig.2. Tentative Structure of the Alkylene DithiophosphateDerivatives of Macrocyclic Complexes of Cr(III)

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