



Research Article

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
## Synthesis and structural elucidation of alkylene dithiophosphate derivatives of macrocyclic complexes of Mn(II), Fe(III) and Co(III) having N<sub>2</sub>S<sub>2</sub> potential donors in 14 to 20- membered rings

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### ABSTRACT

Alkylene dithiophosphate derivatives of macrocyclic complexes of Mn(II) having

N<sub>2</sub>S<sub>2</sub> potential donors, of the general formula [M(L){S<sub>2</sub>P G}<sub>2</sub>] (where M= Mn(II),

Fe(III), & Co(III); L= Macrocyclic ligands, L<sup>1</sup>, L<sup>2</sup>, L<sup>3</sup>, L<sup>4</sup> and L<sup>5</sup> where G =

(CH<sub>3</sub>)<sub>2</sub> CCH<sub>2</sub>CH(CH<sub>3</sub>), CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>, CH<sub>2</sub>C(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>CH<sub>2</sub>, CH(CH<sub>3</sub>).(CH<sub>3</sub>)CH and C(CH<sub>3</sub>)<sub>2</sub>.(CH<sub>3</sub>)<sub>2</sub>C have been synthesized from the reaction of [M(L)Cl<sub>2</sub>/Cl<sub>3</sub>] with ammonium alkylene dithiophosphates in 1:2 molar ratios in THF. Fifteen new derivatives (1-15) have been synthesized by the combination of five macrocyclic complexes of 14-20 membered rings with different types of alkylene dithiophosphates. These complexes have been characterized by elemental analysis, molar conductance, molecular weight determinations & various spectroscopic techniques IR, <sup>31</sup>P NMR, electronic spectra, EPR, Mössbauer, mass spectra and X-ray powder diffraction. Molecular weight determination and magnetic measurements of these complexes indicate their monomeric nature. Octahedral structures have been proposed for these complexes, on the basis of <sup>31</sup>P NMR, electronic spectra and magnetic measurements in which two sulfur atoms and two nitrogen atoms of the macrocyclic ring coordinate to the central metal ion in square-planar geometry and each dithiophosphate moiety occupies the axial positions binding the central metal ion in unidentate manner.

**Key words:** Alkylene dithiophosphates, Macrocyclic complexes, mixed ligand complexes

### 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 other, these uses 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]. *In spite of vast innovations in macrocyclic chemistry and tremendous interest in mixed ligand complexes no macrocyclic complex having mixed ligand system was reported till our publications.* Alkylene dithiophosphates has been the area of our thrust since last many years [5-14]. Recently, we have reported mixed ligand macrocyclic complexes, having 14-20 and 22-28 membered rings, with dialkyl- & alkylene dithiophosphates and their biological and catalytic aspects [15-21]. In continuation to our above work we hereby report some novel macrocyclic complexes having mixed ligands: Synthesis and structural elucidation of alkylene dithiophosphate derivatives of macrocyclic complexes of Mn(II), Fe(III) and Co(III) having N<sub>2</sub>S<sub>2</sub> potential donors in 14 to 20- membered rings.

## EXPERIMENTAL SECTION

**Materials**

Metal salts and dicarboxylic acids of AR 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. Alkylene dithiophosphoric acids and their ammonium salts were prepared the methods reported earlier [5].

**Methods**

Microanalyses for carbon, hydrogen, nitrogen and sulphur were determined by SICART, Vallabh Vidyanagar. Mn(II), Fe(III), Co(III) and P were determined by standards methods [22]. The molecular weights were determined by the Rast camphor method. Infrared data were recorded on a Perkin-Elmer FT-IR spectrophotometer in KBr pellets. Magnetic data were recorded on Faraday balance. Electronic spectra were recorded on GBC 911 spectrophotometer in the 380-1000nm range using THF as a solvent. <sup>31</sup>P NMR spectra were recorded on 270 MHz spectrometer using CDCl<sub>3</sub> as a solvent and H<sub>3</sub>PO<sub>4</sub> as an external standard. FAB mass spectra were recorded on a JEOL SX 102/DA-6000 at 10 KV accelerating voltage spectrometer using nitro benzyl alcohol (NBA) matrix and Argon as the FAB gas. X-ray powder diffraction spectra of the compound was obtained on a Philips (Model P.W. 1840) diffractometer using Fe(K $\alpha$ ) target with Mg filter.

**Synthesis of Precursor Macrocyclic Complexes****Synthesis of Mn(II) complex of tetrabenzo[3,4,7,8,11, 12,15,16][6,14]diaz[1,9]dithiacyclohexadeca [2,5,10,13] tetraone**

A solution of manganese chloride (1.604g, 0.0081mol) in ~40ml methanol was reacted with *o*-aminothiophenol (2.028g, 0.0162mol) dissolved in 40ml methanol. This was followed by the addition of a methanolic solution (~40ml) of phthalic acid (2.70g, 0.0162mol). The reaction mixture was refluxed for 8-10 h. The off white precipitate obtained was filtered, washed with methanol and dried in vacuum. Yield: 4.24g, 82%; m.p.192°C, Anal. Calc. for C<sub>28</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>.MnCl<sub>2</sub>.(fw 635.9) : C, 52.83; H, 2.83; N, 4.40; S, 10.06; Mn, 8.48;. Found: C, 52.92; H, 2.81; N, 4.46; S, 10.18; Mn, 8.72.  $\lambda_{\text{max}}/\text{nm}(\text{edm}^3 \text{mol}^{-1} \text{cm}^{-1})$  542(34.0), 415(43.0), 345(50.4) , 310(61.6)  $\mu_{\text{eff}} = 5.94$ .B.M.

**Synthesis of Fe(III) complex of dibenzo[9,10,19,20] [8,18] diaza[1,11] dithiacycloicosa [2,17,12,17] tetraone**

A solution of ferric chloride (2.082g, 0.0077mol) in ~40ml methanol was reacted with *o*-aminothiophenol (1.934g, 0.0154mol) dissolved in 40ml methanol. This was followed by the addition of a methanolic solution (~40ml) of adipic acid (2.252g, 0.0154mol). The reaction mixture was refluxed for 8-10 h. The off white precipitate obtained was filtered, washed with methanol and dried in vacuum. Yield: 3.11g, 80%; m.p. 208°C , Anal. Calc. for C<sub>24</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>.FeCl<sub>3</sub>.(fw 632.3): C,45.54; H, 4.11; N, 4.42; S, 10.12; Fe, 8.82;. Found: C, 45.49; H, 4.07; N, 4.46; S, 10.06; Fe, 8.86.  $\lambda_{\text{max}}/\text{nm}(\text{edm}^3 \text{mol}^{-1} \text{cm}^{-1})$  782(33.4), 570(42.4), 458(44.2).  $\mu_{\text{eff}} = 5.96$  B.M.

**Synthesis of Co(III) complex of dibenzo[7,8,15,16] [6,14] diaza [1,9] dithiacyclohexadeca [2,5,10,13] tetraone**

A solution of cobalt chloride (1.186g, 0.0043mol) in ~40ml methanol was reacted with *o*-aminothiophenol (1.082g, 0.0086mol) dissolved in 40ml methanol. This was followed by the addition of a methanolic solution (~40ml) of succinic acid (1.028g, 0.0087mol). The reaction mixture was refluxed for 8-10 h. The off white precipitate obtained was filtered, washed with methanol and dried in vacuum. Yield: 2.24g, 78%; m.p. 205 °C, Anal. Calc. for C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>.CoCl<sub>3</sub>.(fw 551.4) : C, 41.42; H, 3.10; N, 4.83; S, 11.04; Co, 10.16;. Found: C, 41.46; H, 3.08; N, 4.80; S, 11.08; Co, 10.12.  $\lambda_{\text{max}}/\text{nm}(\text{edm}^3 \text{mol}^{-1} \text{cm}^{-1})$  515(58.2), 354(62.5).  $\mu_{\text{eff}} = 4.94$ .

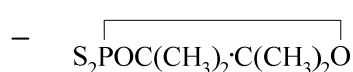
**Synthesis of Alkylene Dithiophosphate Derivatives of Macrocyclic Complexes**

Alkylene dithiophosphoric acids and their ammonium salts were prepared by the method as reported in our earlier communication [5].

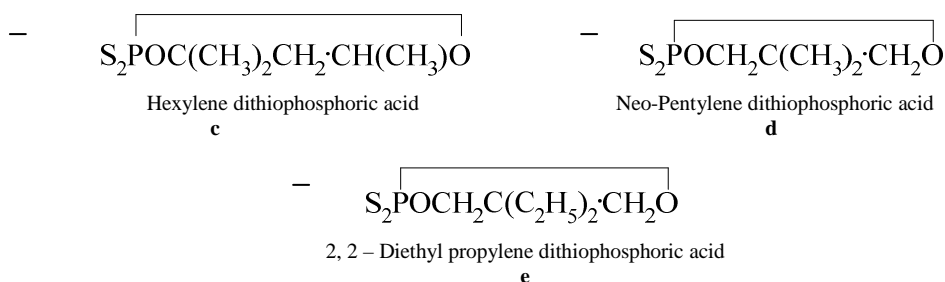
The symbols of the alkylene dithiophosphate anions, of their ammonium salts, used for the synthesis of mixed ligand macrocyclic complexes have been depicted by **a-e** through the script.



Butylene dithiophosphoric acid  
**a**



Teramethylethylene/Pinacolene dithiophosphoric acid  
**b**



### Synthesis of tetramethylethylene dithiophosphate derivative of Mn(II) macrocyclic complex of tetrabenzotetraaza[3,4,7,8,11,12,15,16][6,14] diaza[1,9]dithiacyclohexadeca [2,5,10,13]tetraone

Macrocyclic complex mentioned above (1.137g, 0.0017mol) was dissolved in THF & was reacted with methanolic solution of ammonium tetramethylethylene dithiophosphate (0.780g, 0.0034mol) in 1:2 molar ratios. Reaction mixture was refluxed for ~ 2h at 90 °C. On cooling the off white crystal of dithiophosphate derivative were separated out, which were filtered through G-3 filtering funnel. This crude product was washed several times with methanol by vigorous shaking in filtration funnel to remove the ammonium chloride formed during the reaction. Product was dried in vacuum and was crystallized by THF/C<sub>2</sub>H<sub>5</sub>OH mixture (1:1). Yield: 1.12g, 74%; m.p.196°C, Anal. Calc. for C<sub>30</sub>H<sub>38</sub>N<sub>2</sub>O<sub>8</sub>P<sub>2</sub>S<sub>6</sub>.MnCl<sub>2</sub>.(fw 862.9): C, 41.71; H, 4.40; N, 3.24; S, 22.14; Mn, 6.36;. Found: C, 41.68; H, 4.62; N, 3.28; S, 22.19; Mn, 6.39. Molar conductance  $\Lambda_M$  (DMSO, 25°C)10.0 ohm<sup>-1</sup>cm<sup>2</sup> mol<sup>-1</sup>. Selected IR data( KBr, cm<sup>-1</sup>)v1685m, 1552m, 1256m, 648w (amide I, II, III and IV respectively, v3145w(N-H), v1040m(P)-O-C , v890mP-O-(C), v950s ring vibrations, v710s(P=S), v560w(P-S), v420s (Mn-N) and v 326w(Mn-S).  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) 545(32.0), 415(42.6), 345(49.6), 315(62.0).  $\mu_{\text{eff}} = 5.96$  B.M.. Mass spectra(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH) m/z 863.9 [MnL<sup>1</sup> b<sub>2</sub>, 100%]<sup>+</sup>; m/z 652.9 [b<sub>2</sub>, 30%]<sup>+</sup>; m/z 441.9 [b<sub>2</sub>, 30%]<sup>+</sup>; m/z 360 [M-2C<sub>6</sub>H<sub>5</sub>-CO-NH- CO- S, 90%]<sup>+</sup> and m/z 152 [M-2C<sub>6</sub>H<sub>6</sub>, 40%]<sup>+</sup>.

### Synthesis of diethylpropylene dithiophosphate derivative of Fe(III) macrocyclic complex of dibenzotetraaza[9,10,19,20] [8,18]diaza[1,11]dithiacycloicosa [2,7,12,17]tetraone

The precursor macrocyclic complex mentioned above (1.22g, 0.0019mol) was dissolved in THF and was reacted with methanolic solution of ammonium diethylpropylene dithiophosphate (0.932g, 0.0038mol) in 1:2 molar ratios. The reaction mixture was refluxed for ~4h at 90 °C. On cooling derivative was separated out, which were filtered through G-3 filtered funnel. This crude product was washed several times with methanol by vigorous shaking in filtration funnel to remove the ammonium chloride formed during the reaction product was dried in vacuum and was crystallized with THF/C<sub>2</sub>H<sub>5</sub>OH mixture (1:1). Yield: 1.40g, 71%; m.p. 204°C, Anal. Calc. for (C<sub>38</sub>H<sub>54</sub>N<sub>2</sub>O<sub>8</sub>P<sub>2</sub>S<sub>6</sub>.Fe)Cl.(fw 1011.3): C, 45.09; H, 5.34; N, 2.76; P, 6.13; S, 18.98; Fe, 5.51; Cl, 3.51;. Found: C, 46.02; H, 5.30; N, 2.72; P, 6.17; S, 18.88; Fe, 5.48; Cl, 3.54; Molar conductance  $\Lambda_M$  (DMSO, 25°C) 42.0 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. Selected IR data (KBr, cm<sup>-1</sup>)v1690s, 1585s, 1270s, 695w, (amide I, II, III and IV respectively, v3167m(N-H), v1075m (P)-O-C, v890mP-O-(C), v985s ring vibrations, v670s(P=S), v580w(P-S), v460s (Fe-N) and v345w(Fe-S).  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) 778(32.8), 562(40.4), 462(45.2).  $\mu_{\text{eff}}=5.96$  B.M.. Mass spectra. (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH) m/z 1012.3[FeL<sup>4</sup>e<sub>2</sub>, 100%]<sup>+</sup>; m/z 787.3 [e<sub>2</sub>, 40%]<sup>+</sup>; m/z 562.3 [e<sub>2</sub>, 38 %]<sup>+</sup>; m/z 262[2NH-CO-CH<sub>2</sub>-CH<sub>2</sub>- CH<sub>2</sub>-CO-S, 90%]<sup>+</sup>; m/z 156[2C<sub>6</sub>H<sub>6</sub>, 40%]<sup>+</sup>; m/z 102[-CH<sub>2</sub>-CH<sub>2</sub>- CH<sub>2</sub>-CO-S, 47%]<sup>+</sup>; and m/z 57[-NH-CO-CH<sub>2</sub>, 45%]<sup>+</sup>.

### Synthesis of tetramethylethylene dithiophosphate derivative of Co(III) macrocyclic complex of dibenzotetraaza[7,8,15,16][6,14] diaza[1,9] dithiacyclohexadeca [2,5,10,13]tetraone

The precursor macrocyclic complex mentioned above (1.27g, 0.0020mol) was dissolved in THF and was reacted with methanolic solution of ammonium butylene dithiophosphate (0.9269g, 0.0040mol) in 1:2 molar ratios. The reaction mixture was refluxed for ~4h at 90 °C. On cooling derivative were separated out, which were filtered through G-3 filtered funnel. This crude product was washed several times with methanol by vigorous shaking in filtration funnel to remove the ammonium chloride formed during the reaction product was dried in vacuo and was crystallized with THF/C<sub>2</sub>H<sub>5</sub>OH mixture (1:1). Yield: 1.42g, 70%; m.p. 202°C, Anal. Calc. for (C<sub>32</sub>H<sub>42</sub>N<sub>2</sub>O<sub>8</sub>P<sub>2</sub>S<sub>6</sub>.Fe)Cl.(fw 930.4) : C, 41.27; H, 4.51; N, 3.01; P, 6.66; S, 20.63; Co, 6.33; Cl, 3.81;. Found: C, 41.18; H, 4.49; N, 3.04; P, 6.62; S, 20.67; Co, 6.30; Cl, 3.86; Molar conductance  $\Lambda_M$  (DMSO, 25°C) 43.0 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. Selected IR data (KBr, cm<sup>-1</sup>)v1690s, 1574m, 1275s, 680w, (amide I, II, III and IV respectively, v3215w(N-H), v1058m (P)-O-C , v880mP-O-(C), v1000s ring vibrations, v670s(P=S), v540w(P-S), v460s (Co-N) and v380w(Co-S).  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) 520(60.2), 350(63.2).  $\mu_{\text{eff}} = 5.02$  B.M.. <sup>31</sup>P, 98.28. Mass spectra. (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH) m/z 931.4 [CoL<sup>2</sup>b<sub>2</sub>, 100%]<sup>+</sup>; m/z 720.4 ; [b<sub>2</sub>, 39%]<sup>+</sup>; m/z 509.4 ; [b<sub>2</sub>, 37 %]<sup>+</sup>; m/z 262[2NH-CO-CH<sub>2</sub>-CH<sub>2</sub>-CO-S, 89%]<sup>+</sup>; m/z 156[2C<sub>6</sub>H<sub>6</sub>, 38%]<sup>+</sup>; m/z 74[-CH<sub>2</sub>-CO-S, 48%]<sup>+</sup>; and m/z 57[-NH-CO-CH<sub>2</sub>, 42%]<sup>+</sup>.

Other derivatives were also prepared by same method. Their analytical data and physical properties have been depicted in Table-1.

Table 1. Analytical data of alkylene dithiophosphate derivatives of macrocyclic complexes of Mn(II), Fe(III) and Co(III)

No.	Compound [Molecular formula] (Empirical Formula)	Found ( Calcd.)						M.p. °C	M.W.
		%C	%H	%N	%P	%S	%M		
1	[MnL <sup>1</sup> c <sub>2</sub> ] (C <sub>30</sub> H <sub>38</sub> N <sub>2</sub> O <sub>8</sub> P <sub>2</sub> S <sub>6</sub> .Mn)	41.64 (41.71)	4.42 (4.40)	3.21 (3.24)	7.23 (7.18)	22.27 (22.24)	6.31 (6.36)	202	874 (862.9)
	[MnL <sup>2</sup> b <sub>2</sub> ] (C <sub>32</sub> H <sub>42</sub> N <sub>2</sub> O <sub>8</sub> P <sub>2</sub> S <sub>6</sub> .Mn)	43.17 (43.09)	4.75 (4.71)	3.10 (3.14)	6.89 (6.95)	21.59 (21.54)	6.11 (6.16)		206 (890.9)
3	[MnL <sup>3</sup> d <sub>2</sub> ] (C <sub>32</sub> H <sub>42</sub> N <sub>2</sub> O <sub>8</sub> P <sub>2</sub> S <sub>6</sub> .Mn)	43.16 (43.09)	4.68 (4.71)	3.09 (3.14)	6.90 (6.95)	21.59 (21.54)	6.19 (6.16)	200	881.2 (890.9)
	[MnL <sup>4</sup> e <sub>2</sub> ] (C <sub>38</sub> H <sub>54</sub> N <sub>2</sub> O <sub>8</sub> P <sub>2</sub> S <sub>6</sub> .Mn)	46.69 (46.76)	5.58 (5.53)	2.97 (2.87)	6.39 (6.35)	19.63 (19.69)	5.68 (5.63)		204 (890.9)
5	[MnL <sup>5</sup> b <sub>2</sub> ] (C <sub>40</sub> H <sub>54</sub> N <sub>2</sub> O <sub>8</sub> P <sub>2</sub> S <sub>6</sub> .Mn)	48.70 (48.63)	4.21 (4.25)	2.86 (2.83)	6.30 (6.28)	19.51 (19.45)	5.61 (5.56)	202	910.4 (930.9)
	[FeL <sup>1</sup> c <sub>2</sub> ]Cl (C <sub>30</sub> H <sub>38</sub> N <sub>2</sub> O <sub>8</sub> P <sub>2</sub> S <sub>6</sub> .Fe)Cl	40.10 (40.03)	4.26 (4.22)	3.14 (3.11)	6.91 (6.89)	21.39 (21.34)	6.18 (6.20)		201 (899.3)
7	[FeL <sup>2</sup> b <sub>2</sub> ]Cl (C <sub>32</sub> H <sub>42</sub> N <sub>2</sub> O <sub>8</sub> P <sub>2</sub> S <sub>6</sub> .Fe)Cl	41.48 (41.41)	4.58 (4.53)	3.06 (3.02)	6.72 (6.68)	20.64 (20.70)	6.05 (6.01)	205	910.4 (927.3)
	[FeL <sup>3</sup> d <sub>2</sub> ]Cl (C <sub>32</sub> H <sub>42</sub> N <sub>2</sub> O <sub>8</sub> P <sub>2</sub> S <sub>6</sub> .Fe)Cl	41.47 (41.41)	4.50 (4.53)	3.07 (3.02)	6.62 (6.58)	20.78 (20.70)	6.03 (6.01)		211 (927.3)
9	[FeL <sup>4</sup> e <sub>2</sub> ]Cl (C <sub>38</sub> H <sub>54</sub> N <sub>2</sub> O <sub>8</sub> P <sub>2</sub> S <sub>6</sub> .Fe)Cl	46.02 (45.09)	5.30 (5.34)	2.72 (2.76)	6.70 (6.13)	18.88 (18.98)	5.48 (5.51)	209	1023.7 (1011.3)
	[FeL <sup>5</sup> a <sub>2</sub> ]Cl (C <sub>36</sub> H <sub>54</sub> N <sub>2</sub> O <sub>8</sub> P <sub>2</sub> S <sub>6</sub> .Fe)Cl	44.71 (44.66)	3.54 (3.51)	2.91 (2.89)	6.44 (6.40)	19.88 (19.85)	5.72 (5.76)		210 (967.3)
11	[CoL <sup>1</sup> c <sub>2</sub> ]Cl (C <sub>30</sub> H <sub>38</sub> N <sub>2</sub> O <sub>8</sub> P <sub>2</sub> S <sub>6</sub> .Co)Cl	39.92 (39.89)	4.19 (4.21)	3.14 (3.10)	6.90 (6.87)	21.23 (21.27)	6.56 (6.52)	203	916.8 (902.4)
	[CoL <sup>2</sup> b <sub>2</sub> ]Cl (C <sub>32</sub> H <sub>42</sub> N <sub>2</sub> O <sub>8</sub> P <sub>2</sub> S <sub>6</sub> .Co)Cl	41.18 (41.27)	4.49 (4.51)	3.04 (3.01)	6.62 (6.66)	20.67 (20.63)	6.30 (6.33)		206 (930.4)
13	[CoL <sup>3</sup> d <sub>2</sub> ]Cl (C <sub>32</sub> H <sub>42</sub> N <sub>2</sub> O <sub>8</sub> P <sub>2</sub> S <sub>6</sub> .Co)Cl	41.32 (41.27)	4.53 (4.51)	3.03 (3.01)	6.70 (6.66)	20.67 (20.63)	6.30 (6.33)	202	922.4 (930.4)
	[CoL <sup>4</sup> e <sub>2</sub> ]Cl (C <sub>38</sub> H <sub>54</sub> N <sub>2</sub> O <sub>8</sub> P <sub>2</sub> S <sub>6</sub> .Co)Cl	44.88 (44.95)	5.34 (5.32)	2.78 (2.76)	6.14 (6.11)	18.88 (18.92)	5.78 (5.80)		211 (1014.4)
15	[CoL <sup>5</sup> a <sub>2</sub> ]Cl (C <sub>36</sub> H <sub>54</sub> N <sub>2</sub> O <sub>8</sub> P <sub>2</sub> S <sub>6</sub> .Co)Cl	44.48 (44.51)	3.48 (3.50)	2.86 (2.88)	6.41 (6.39)	19.80 (19.78)	6.04 (6.07)	216 (970.4)	982.4 (970.4)

## RESULTS AND DISCUSSION

Manganese chloride reacts with *o*-aminothiophenol and dicarboxylic acids in 1:2:2 molar ratios in methanol to afford white or off-white complexes as shown below:

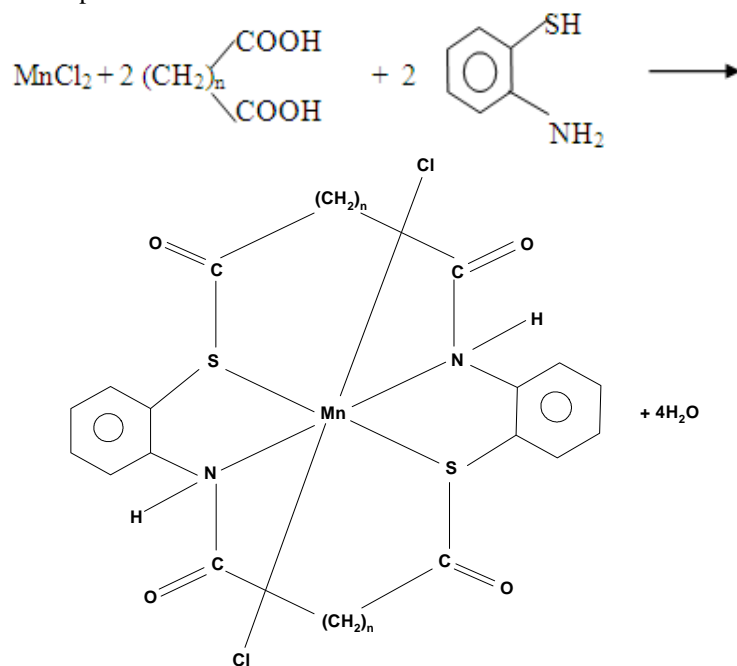


Fig. 1 Tentative Structure of Macrocyclic Complexes of Mn(II)

Similarly FeCl<sub>3</sub> and CoCl<sub>3</sub> reacts with *o*-aminothiophenol and dicarboxylic acids in 1:2:2 molar ratios in methanol to afford green and orange complexes as shown below:

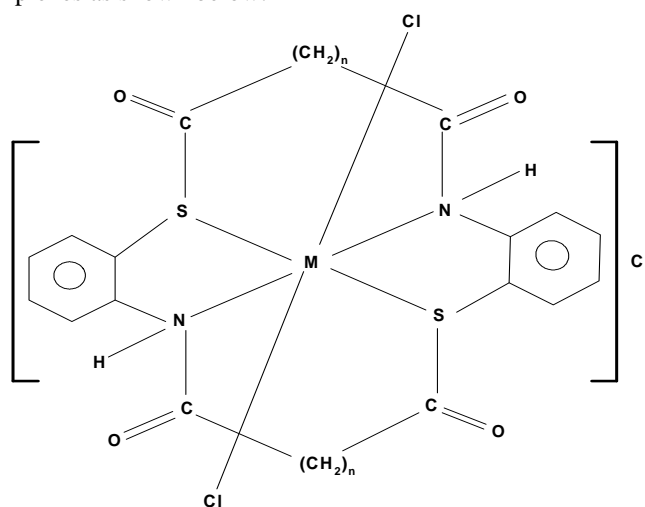


Fig. 2 Tentative Structure of Macrocyclic Complexes of Fe(III), Co(III).

$n = 1, 2, 3, 4$  or  $(\text{CH}_2)_n = o\text{-C}_6\text{H}_4$ ; L= macrocyclic ligands L<sup>1</sup>, L<sup>2</sup>, L<sup>3</sup>, L<sup>4</sup>, L<sup>5</sup>.

L<sup>1</sup>= macrocyclic ligand derived from *o*-aminothiophenol and malonic acid ( $n=1$ ); **{Dibenzo[ 6,7,13,14][5,12]diaza [1,8]dithiacyclotetradeca [2,4,9,11]tetraone}**.

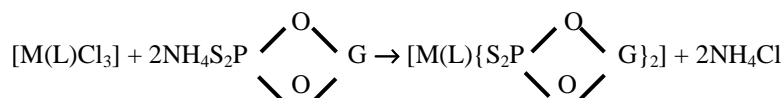
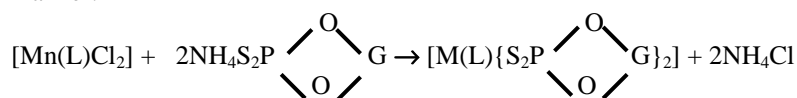
L<sup>2</sup>=macrocyclic ligand derived from *o*-aminothiophenol and succinic acid ( $n=2$ ); **{Dibenzo[ 7,8,15,16] [ 6,14] diaza [1,9] dithiacyclohexadeca [ 2,5,10,13]tetraone}**.

L<sup>3</sup>=macrocyclic ligand derived from *o*-aminothiophenol and glutaric acid ( $n=3$ ); **{Dibenzo[8,9,17,18] [7,16] diaza [1,10] dithiacyclooctadeca [ 2,6,11,15]tetraone}**.

L<sup>4</sup>=macrocyclic ligand derived from *o*-aminothiophenol and adipic acid ( $n=4$ ); **{Dibenzo[9,10,19,20] [8,18] diaza [1,11] dithiacycloicosa [ 2,7,12,17]tetraone}**.

L<sup>5</sup>=macrocyclic ligand derived from *o*-aminothiophenol and phthalic acid ( $(\text{CH}_2)_n = o\text{-C}_6\text{H}_4$ ); **{Tetrabenzo[3,4,7,8,11,12,15,16] [6,14] diaza [1,9]dithiacyclohexadeca [2,5,10,13] tetraone}**.

The above macrocyclic complexes were reacted with a methanolic solution of ammonium alkylene dithiophosphates in 1:2 molar ratios to afford the alkylene dithiophosphate derivatives of the macrocyclic complexes in the following manner:



The reaction mixture was refluxed for ~4 h. On cooling, the crystals of the dithiophosphate derivative were separated out.

Except for THF and DMSO, these derivatives are insoluble in common organic solvents. All derivatives are white or off-white of Mn(II), green of Fe(III) and Orange or brown of Co(III) solids and melt with at high temperatures (196-206). Molecular weight determinations indicate their monomeric nature. The molar conductance of 10<sup>-3</sup>M solutions in DMSO lies in the range (08-12) ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup> showing that these complexes are non-electrolyte.

The IR spectra of the macrocyclic complexes, the four bands in the region 1690-1650 (s), 1587-1530 (m), 1275-1250 (s) and 695-632 (w) cm<sup>-1</sup> have been ascribed to the amide I, amide II, amide III and amide IV in-plane deformation vibrations, respectively [23]. A broad band in the region 3278-3145 cm<sup>-1</sup> has been assigned to the ν(NH) 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 1075-1040 cm<sup>-1</sup> and 890-850 cm<sup>-1</sup> may be assigned to (P)-

O-C and P-O-(C) stretching vibrations, respectively [24]. The band present between 1000-945  $\text{cm}^{-1}$  may be attributed to the ring vibrations of dioxaphospholanes and dioxaphosphorinanes respectively, which are probably coupled with C-C stretching vibrations [25]. A weak band present in the region 580-540  $\text{cm}^{-1}$  has been attributed to P-S symmetric and asymmetric vibrations. A strong band observed in the region 710-650  $\text{cm}^{-1}$ , which also appears in ammonium alkylene dithiophosphates at around the same region, is attributed to the P=S moiety. This indicates the unidentate behavior of the dithiophosphate moieties [26]. The presence of sharp and weak bands in the region 480-420  $\text{cm}^{-1}$  and 377-318  $\text{cm}^{-1}$  have been assigned to  $\nu(\text{M-N})$  and  $\nu(\text{M-S})$  vibrations, respectively [8-27].

Due to the paramagnetic nature of Mn, Fe, and Co in an octahedral geometry,  $^1\text{H}$  NMR spectra of its complexes cannot be observed as easily as those of diamagnetic complexes. We have reported earlier the  $^1\text{H}$  NMR of some paramagnetic Ni(II) complexes [7,8]. During the present investigations, it was not possible to obtain the  $^1\text{H}$  NMR spectra for the present complexes.

$^{31}\text{P}$  NMR spectra of some compounds could be recorded, however. The spectra recorded on a 270MHz spectrometer using  $\text{CDCl}_3$  as a solvent and  $\text{H}_3\text{PO}_4$  as an external standard. As we reported earlier [7,8,15-17] the position of the  $^{31}\text{P}$  chemical shift is not influenced by the paramagnetic nature of the metal ion as influenced in the  $^{31}\text{P}$  NMR spectra. During the present investigations also the values of  $^{31}\text{P}$  chemical shift in these derivatives are not influenced by the presence of unpaired electrons. The values of chemical shift of the newly synthesized compounds are reported in the data after their synthesis. The chemical shift values of five membered dioxaphospholane derivatives lie between 78–80.28 and six membered dioxaphosphorinane derivatives lie in the range 84.24-98.28 which is expected for monodentate moieties. The chemical shift values do not show any significant change from their parent alkylene dithiophosphoric acids. This indicates again the monodentate nature of alkylene dithiophosphate moieties attached to the central metal ion [26]. The chemical shift does not depend on the nature of the metal ion.

Electronic spectra were recorded on a GBC 911 spectrophotometer in the range 380-1000 nm using THF as a solvent. In manganese four bands were observed at 543-555( $\nu_1$ ) ( $\epsilon$ : 32.0-33.2), 410-416( $\nu_2$ ) ( $\epsilon$ : 39.3-43.4), 344-350( $\nu_3$ ) ( $\epsilon$ : 48.0-51.2) and 308-315( $\nu_4$ ) ( $\epsilon$ : 60.6-63.2)nm, respectively. These bands may be assigned to the transitions  $^6\text{A}_{1g} \rightarrow ^4\text{T}_{1g} (^4\text{G})$ ,  $^6\text{A}_{1g} \rightarrow ^4\text{E}_g$ ,  $^4\text{A}_{1g} (^4\text{G})$ ,  $^6\text{A}_{1g} \rightarrow ^4\text{E}_g (^4\text{D})$  and  $^6\text{A}_{1g} \rightarrow ^4\text{T}_{1g} (^4\text{P})$ , respectively. These transitions indicate the six-coordination of the central manganese ion. Three bands were observed, for Fe(III) complexes, at 786-795( $\nu_1$ ) ( $\epsilon$ : 34.8-35.2), 570-580( $\nu_2$ ) ( $\epsilon$ : 40-43) and 450-459( $\nu_3$ ) ( $\epsilon$ : 46.0-48.1) nm, respectively. These bands may be assigned to the transitions  $^6\text{A}_{1g} \rightarrow ^4\text{T}_{1g} (\text{G})$ ,  $^6\text{A}_{1g} \rightarrow ^4\text{T}_{2g} (\text{G})$  and  $^6\text{A}_{1g} \rightarrow ^4\text{A}_{1g} (\text{G})$ , respectively. These transitions indicate the six-coordination of the central iron atom. For Co(III) complexes two bands were observed at 510-520( $\nu_1$ ) ( $\epsilon$ : 55-60) and 350-355( $\nu_2$ ) ( $\epsilon$ : 60-63.1),nm, respectively. These bands may be assigned to the transitions  $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$  and  $^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$ , respectively. These transitions indicate the six-coordination of the central cobalt atom [28].

Table 2. X-ray powder diffraction data of  $[\text{MnL}^1\text{b}_2]$

Peak No.	2 $\theta$ (deg.) obs.	d-spacing (obs.) ( $\text{\AA}$ )	h	K	l
1	21.4	3.5639	2	8	1
2	23.7	3.1452	2	1	4
3	25.2	3.1486	0	2	5
4	27.6	3.0461	5	3	0
5	28.9	2.6439	3	9	1
6	30.2	2.8667	0	2	5
7	31.6	2.5797	1	5	5
8	32.2	2.7107	2	7	6
9	32.8	2.4275	0	10	4
10	33.6	2.3138	5	11	4
11	35.1	2.16.1	4	4	1
12	37.4	2.1056	2	1	5
13	40.2	2.1360	0	2	5
14	41.8	2.1193	4	4	1
15	42.6	2.1107	3	10	2
16	42.9	1.9870	0	12	4
17	43.8	1.8764	4	4	1
18	46.2	1.8987	1	5	3
19	46.8	1.8390	3	10	2
20	47.8	1.7849	2	7	6
21	51.8	1.6721	4	11	4
22	80.2	1.6105	1	12	3
23	82.6	1.5496	6	4	1

$a=12.1422$ ,  $b=24.2075$ ,  $c=16.9065$  Orthorhombic system.

The magnetic susceptibility was measured by a VSM balance using Hg [Co(CNS)<sub>4</sub>] as calibrate. Pascal constants were used for diamagnetic corrections. The Mn(II) complexes show magnetic moment values of 5.92- 5.96 B.M. at room temperature, which correspond to five unpaired electrons, as expected for high spin Mn(II) complexes. The magnetic moment values of Fe(III) complexes lie between 5.89- 5.92 and of Co(III) complexes between 4.02- 5.02, respectively expected for octahedral Fe(III) and Co(III) complexes [29,30].

The lattice dynamics of the compound [MnL<sup>1</sup>b<sub>2</sub>] has been ascertained by recording the X-ray diffraction. The observed 2θ angles, "d" values and h, k, l values are recorded. The data suggest an orthorhombic lattice for the derivatives.

Refined values: a = 12.1422, b = 24.2075, c = 16.9065, α = β = γ = 90(Orthorhombic systems) max dev. 2θ = 0.2. Data have been presented in Table-2.

The FBA mass spectra of two representative compounds were recorded in nitrobenzyl alcohol (NBA) matrix.

[MnL<sup>4</sup>d<sub>2</sub>] shows the molecular ion peak at m/e = 979.7 (Calcd. mole. wt.918.9) with 100% relative abundance which confirm the formation of the neopentylene derivative of macrocyclic complex. The other important fragments are at m/e 720 and 520 due to the loss of two [d]<sup>+</sup> respectively. In addition, the spectrum contains a very strong (91% relative abundance) peak at m/e 290 for loss of two [NH-CO-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>- CO- S]<sup>+</sup> and a peak at m/e 156 for loss of two [C<sub>6</sub>H<sub>6</sub>]<sup>+</sup>. The peak at m/e 57 indicates loss of [NHCOCH<sub>2</sub>]<sup>+</sup> and the peak at m/e 88 indicates the loss of [CH<sub>2</sub>CH<sub>2</sub>COS]<sup>+</sup>

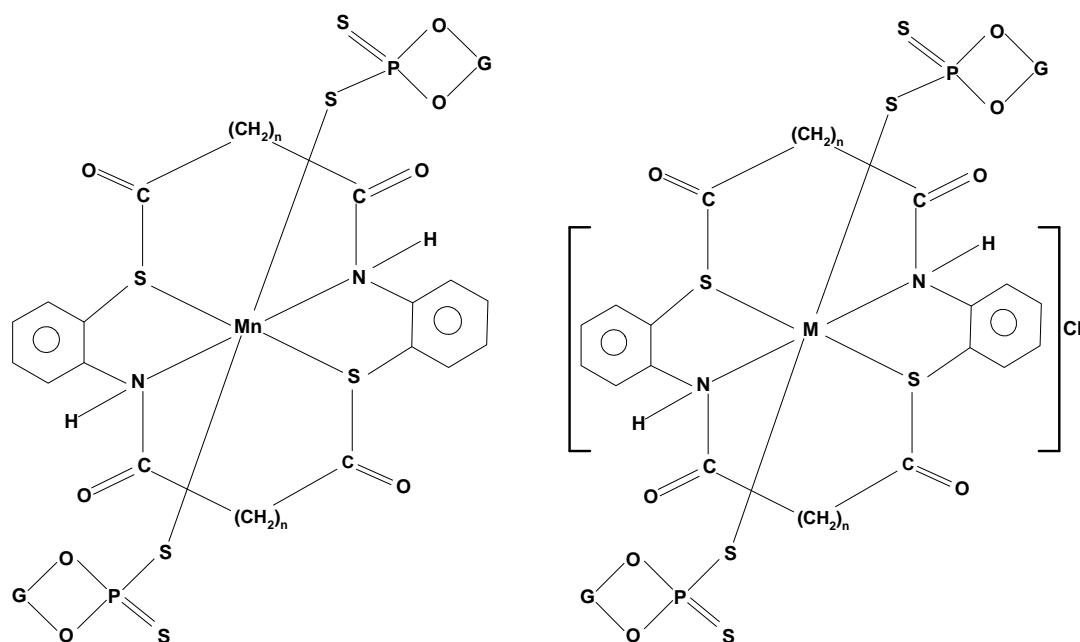
[MnL<sup>5</sup>c<sub>2</sub>] shows the molecular ion peak at m/e = 987.9(Calcd. mole. wt. 986.9) with 100% relative abundance which confirm formation of the hexylene derivative of macrocyclic complexes.. The other important fragments are at m/e 777 and 566 due to the loss of two [c]<sup>+</sup> respectively. In addition, the spectrum contains very strong (80% relative abundance) peak at m/e 234 for loss of two [NH-CO-CH<sub>2</sub>-CO-S]<sup>+</sup> and a peak at m/e 156 for loss of two [C<sub>6</sub>H<sub>6</sub>]<sup>+</sup>

EPR spectra of the powdered Mn(II) complexes at room temperature depict an isotropic signal consisting of a pattern of six doublets. The g<sub>eff</sub> values of the complexes are 2.0020 and 2.0011 respectively. This is in accordance with the other six coordinated Mn(II) complexes [31]. EPR spectra of two Fe(III) complexes [FeL<sup>3</sup>d<sub>2</sub>] and [FeL<sup>4</sup>e<sub>2</sub>] show a strong g ~ 2 signal with a weak signal g ~ 5.7 which could be interpreted in terms of six coordinated Fe(III) complexes undergoing departure from a purely axial symmetry and a low value of the Zero Field Splitting parameter D (0.1 to 0.2 cm<sup>-1</sup>) as suggested by the computer simulated EPR plots given by Collision and Powell for octahedral FeO<sub>6</sub> chelates [32].

Mössbauer spectra of two iron(III) [FeL<sup>3</sup>d<sub>2</sub>] (8) and [FeL<sup>4</sup>e<sub>2</sub>] (9) compounds were recorded ~at room temperature. The isomer shift values (δ) are 0.58 mms<sup>-1</sup> for (8) and 0.62 for (9) mms<sup>-1</sup>. The quadruple splitting lie between 0.52- 0.77 mm s<sup>-1</sup>. The range of line width varies from 0.30-0.33. The isomer shift values are typical as for other iron(III) complexes having substantial covalency in Fe(III) ligand bond [33,34].

## CONCLUSION

The above spectral and magnetic data indicate the octahedral geometry shown in Figure 4 for the above derivatives in which two sulphur atoms and two nitrogen atoms of the macrocyclic rings coordinate to the central manganese ion in square-planar geometry, and each dithiophosphate moiety occupies the axial positions binding to the central manganese ion in a unidentate manner through strong electrostatic attraction Figure 4. In the macrocyclic complexes of Fe(III) and Co(III) one chloride ion remains outside the coordination sphere.



M=Mn(II), Fe(III) and Co(III), n = 1, 2, 3, 4 or  $(\text{CH}_2)_n = o\text{-C}_6\text{H}_4\text{-}$

where G =  $(\text{CH}_3)_2\text{CCH}_2\text{CH}(\text{CH}_3)$ ,  $\text{CH}_2(\text{CH}_3)_2\text{CH}_2$ ,  $\text{CH}_2\text{C}(\text{C}_2\text{H}_5)_2\text{CH}_2$ ,

$\text{HC}(\text{CH}_3)(\text{CH}_3)\text{CH}$  and  $\text{C}(\text{CH}_3)_2(\text{CH}_3)_2\text{C}$

FIG. 4. Tentative structure of the alkylene dithiophosphate derivatives of macrocyclic complexes.

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