

## Synthetic and Structural Studies of Some Coordination Polymers by Using DBMAB Ligand

**Chandrashekhar P Kalambe** 

\*Department of Chemistry, Government College of Engineering, Chandrapur cpkalambe@rediffmail.com

Abstract : Coordination Polymers of VO(IV), Mn(II), Fe(III), Co(II), Ni(II), and Zn(II) were prepared by using Ligand DBMAB derived from O - Dianisidine and mercapto acetic acid. They have been characterized on the basis of elemental, magnetic, thermal, spectral and Mossabuer studies.

Keywords : VO(IV), Mn(II), Fe(III), Co(II), Ni(II), and Zn(II)

Coordination polymers have very interesting properties, which make them useful for various applications in science and technology. Coordination polymers have good thermal stability and catalytic activity, which enhance the development of polymeric materials either from polymeric or monomeric ligand. This communication describes the preparation and characterization of chelate prepared from [DBMAB] 3,3Dimethoxy,1,1 Bis- (mercaptoacetamido) benzidine, derived from and o-dianisidene mercaptoacetic acid with Metal VO(IV),Mn(II),Fe(III),Co(II),Ni(II), and Zn(II).

## Experimental

All metal acetate and chemicals used were of A. R. grade. All solvents were purified by distillation.

Solution of o-dianisidene (25 g, 0.1 mole) was dissolved in benzene (400 ml) and mercaptoacetic acid (20.00 ml, 0.3 mole) was added to it. The mixture was refluxed for three hours.The reaction mixture was cooled to room temperature and product was filtered and dried. Product was crystallized from benzene. m.p. 80° C. Coordination polymers were prepared by dissolving equimolar mixture of metal acetate (in case of iron and vanadium ferric chloride and vanadyl sulphate respectively) and ligand in dimethyl formamide separately. The reaction mixture was refluxed for about 2 hours.the product obtained was filtered and washed with number of times with hot dimethylformamide (DMF) and then with hot absolute alcohol to remove unreacted ligand and metal salt.

Elemental analysis, magnetic susceptibility measurement at room temperature, diffuse reflectance spectra,

thermogravimetric analysis and Mössbauer study and XRD carried out for characterization of chelate.

## **Result and Discussion**

Elemental analysis data (Table 1) are of the polychelates correspond to general formula ML or [ML]n.

			r		
Compound	М	С	Н	N	S
MAAN		54.78(55.	4.92(5.1	7.05(7.1	15.85(16.
		10)	0)	4)	33)
[VO(IV)-	11.77(12.	44.34(43.	4.15(4.1	6.46(5.8	14.78(14.
DBMAB] <sub>n</sub> 5	78)	26)	3)	9)	05)
$H_2O$					
[Mn(II)-	13.06(13.	45.60(43.	4.27(3.9	6.65(5.8	15.20(15.
DBMAB]	36)	26)	7)	9)	33)
<sub>n</sub> 3H <sub>2</sub> O					
[Fe(III)-	13.05(13.	45.25(44.	4.26(4.0	6.60(6.5	15.21(15.
DBMAB]	89)	66)	5)	8)	05)
<sub>n</sub> H <sub>2</sub> O					
[Co(II)-	13.88(14.	45.17(44.	4.23(4.0	6.58(6.0	15.05(14.
DBMAB] <sub>n</sub>	25)	75)	3)	5)	89)
[Ni(II)-	13.87(14.	45.12(44.	4.22(3.8	6.53(6.2	15.00(14.
DBMAB] <sub>n</sub>	40)	13)	9)	5)	80)
[Zn(II)-	14.68(15.	44.75(42.	4.19(3.8	6.52(6.2	14.90(14.
DBMAB]	26)	78)	5)	3)	06)
<sub>n</sub> H <sub>2</sub> O					

Table 1 Analytical Data of ligand and chelate in % found(calcd.)

-C-O-H vibration frequency of DBMAB exhibits a broad band around 3230 cm<sup>-1</sup> which is known to be lowered due to intra and inter molecular hydrogen bonding <sup>[1,2]</sup>. –N-H shows band at 2920 cm<sup>-1</sup> which may assign to stretching frequency. This frequency also appeared in coordination polymer which indicates non participation of NH group in the coordination. Broad and weak band around 2600 cm<sup>-1</sup> suggest -S-H stretching vibration <sup>[3]</sup>. This band disappears after formation of coordination polymers. Band observed at 680 cm<sup>-1</sup> attributed to the C-S vibration. On coordination with metal this band shift to higher frequency region and appears in the range 680-800 cm<sup>-1</sup>. C=O band with well defined shoulder 1620 cm<sup>-1</sup> in the ligands. In the chelate shoulder disappear and frequency of the band shifted to lower region indicates wide delocalization of electronic charge.<sup>[4,5]</sup> All



coordination polymers display a very broad bands in the range 3100-3600 cm<sup>-1</sup> which may be due to stretching vibration of hydroxyl bridge or due to overlapping of stretching vibration of hydrated water molecules. M=O frequency appears in the range 472-620 cm<sup>-1[6,7]</sup> and M-S in 310-350 cm<sup>-</sup>. In VO(IV) chelate frequency observed at 1030 cm<sup>-1</sup> is due to asymmetric stretching vibration<sup>[8]</sup>

Magnetic moment and Electronic Spectral data and its interpretation discuss in Table 2

Sr	Coordina	μef	Absor	Bands	Assign	Sugge	Ref
No	tion	fe.	р	kK	ment	sted	ere
	Polymers	В.	tion			Geom	nce
		М.	nm			etry	s
1	[	1.8	855	11.07	${}^{2}B_{2}-{}^{2}E$	Octah	8
	VO(IV)-	5	770	13.0		edral	
	DBMAB		550	18.88	${}^{2}B_{2}-{}^{2}B_{1}$	geom	
	$]_n 5H_2O$		400	25.00	${}^{2}B_{2}-{}^{2}A_{1}$	etry	
2	[ Mn(II)-	6.1	820	12.20	${}^{6}A_{1g} - {}^{4}T_{1g}$	Octah	9
	DBMAB	0	550	18.18	(G)	edral	15
	] <sub>n</sub> H <sub>2</sub> O				<sup>6</sup> A <sub>1g</sub> -	geom	10
					<sup>6</sup> A <sub>1g',</sub> <sup>4</sup> E <sub>g</sub>	etry	
					(4D)		
3	[ Fe(III)-	6.1	860	11.62	${}^{6}A_{1g} - {}^{4}T_{1g}$	Octah	11
	DBMAB	0	500	20.00	${}^{6}A_{1g} - {}^{4}T_{2g}$	edral	12
	$]_n 2H_2O$		435	23.00	${}^{6}A_{1g} - {}^{4}T_{2g}$	geom	
						etry	
4	[Co(II)-	5.4	625-	16.00-	${}^{4}T_{1g}$ (F) –	Octah	
	DBMAB	8	555	18.00	${}^{4}A_{2g}$	edral	12,
	$]_n H_2O$		833	12.00	${}^{4}T_{1g}$ (F) –	geom	13
			440	22.72	${}^{4}T_{1g}(P)$	etry	14
					${}^{4}T_{1g}$ (F) –		
					${}^{4}T_{2g}(F)$		
5	[Ni(II)-	2.6	870	11.50	${}^{3}A_{2g}$ –	Octah	15
	DBMAB	8	600	16.66	${}^{3}T_{2g}(F)$	edral	
	]n H2O		400	25.00	${}^{3}A_{2g}$ –	geom	
					${}^{3}T_{1g}(F)$	etry	

Table 2 Magnetic and Spectral Data of [M (II)-MAAN]<sub>n</sub>

Mössbauer study of [Fe(III)-DBMAB]<sub>n</sub> 2H<sub>2</sub>O polymer shows well resolved doublet. Isomer shift ( $\partial$ ) value found to be 6.02mms<sup>-1</sup>. Five 3 d electron are equally populated. Therefore, no valancy contribution should be expected for qudrupole splitting. In case of perfect cubic symmetry no qudrupole splitting should be observed. However, polymeric structure ligand is enough to cause the distortion and hence net electric field gradient (EFG) is generated due to ligand contribution giving rise to  $\Delta$ EQ 0.96.

 ${}^{3}A_{2g}$  ${}^{3}T_{1g}(P)$ 

Thermogravimetric study of  $[M-(II)-DBMAB]_n$  polymers shown in Fig-3. In  $[VO (IV)-DBMAB]_n.4H_2O$  polymer undergoes degradation around 100  $^{0}C$  to 150  $^{0}C$ . This loss may be due to hydrated water and free part of organic ligand. After this gradual mass losses is observed upto  $410^{0}$  C followed by rapid decrease in weight. Residue formed at  $425^{\circ}$ Cthis stage corresponds to vanadyl sulphide which further undergoes oxidation. During the oxidation of sulphide to vanadyl sulphate increase in weight is observed beyond  $625^{\circ}$ C.

[Mn(II)- DBMAB]<sub>n</sub>.4H<sub>2</sub>O from the curve polymer undergoes decomposition in four steps. The first step may corresponds to loss of four hydrated water molecules. After this dehydrated polymer again loss its weight suddenly at 200  $^{\circ}$ C. This may be due to free part of organic ligand. From 250  $^{\circ}$ C to 325  $^{\circ}$ C stable species is formed which looses it's mass rapidly and the residue may be of MnS + MnSO<sub>4</sub> at about 380  $^{\circ}$ C. This may be due to oxidation of metal sulphide to metal sulphate. [Fe(III)-DBMAB]<sub>n</sub>.H<sub>2</sub>O decompose in two steps in first steps gradual mass loss at around 100  $^{\circ}$ C may be due to free part of organic ligand and hydrated water molecules. Rapid mass loss observed from 175  $^{\circ}$ C to 250  $^{\circ}$ C and thermogram attains constant level upto 700  $^{\circ}$ C. Residue formed at 250  $^{\circ}$ C may be of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.

**[Co(III)- DBMAB]**<sub>n</sub>**.H**<sub>2</sub>**O** polymer shows loss of one molecule of water of hydration below 100  $^{\circ}$ C. Beyond 175 $^{\circ}$ C to 350  $^{\circ}$ C thermogram attain constant level. Residue obtained in the range 350 $^{\circ}$ C to 600 $^{\circ}$ C may be the mixture of Co(SCN)<sub>2</sub> + CoS.

[Ni(II)- DBMAB]<sub>n</sub>. Polymer undergo degradation in one step and attains constant level beyond 375 <sup>o</sup>C to 600 <sup>o</sup>C. After this 600 <sup>o</sup>C increase in weight is observed which may be due to oxidation of metal sulphide to metal sulphate. [Zn(II)-DBMAB]<sub>n</sub>.2H<sub>2</sub>O Polychelate degrade in one step and lossess hydrated water molecule around 100<sup>o</sup>C and then form dehydrated species upto 325 <sup>o</sup>C . After this sudden loss in weight is observed and beyond 400 <sup>o</sup>C constant levels attains by the thermogram. The residue formed at 400 <sup>o</sup>C is may be of ZnS and ZnSO<sub>4</sub>.

From the TG data activation energy values of coordination polymers by using Sharp-Wentwoth method are given in Table 3

Table 3 Activation Energy of [M-(II)- DBMAB]\_nxH2OCoordination Polymers

Sr No	Coordination Polymore	Activation Energy ( KCal/mole) Temprature range			
	Coordination Polymers	$150^{\circ} \mathrm{C} - 450^{\circ} \mathrm{C}$	Room Temp. – 150 <sup>0</sup> C		
1	[VO(IV)- DBMAB] <sub>n</sub> .5H <sub>2</sub> O	1.910	7.360		
	[Mn(II)- DBMAB] <sub>n</sub> .H <sub>2</sub> O	5.117	2.510		
	[Fe(III)- DBMAB] <sub>n</sub> .H <sub>2</sub> O	3.176	2.763		
	[Co(III)- DBMAB] <sub>n</sub>	11.050	12.660		
	[Ni(II)- DBMAB] <sub>n</sub>	2.760	2.228		
	[Zn(II)- DBMAB] <sub>n</sub> .H <sub>2</sub> O	13.160			



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F = (Fe(III) -(OHD DBMAB) H20, G = [VOCIVD -DBMAB] "5HSO, H = [MCCIID -DBMAB] H\_0, I = [Co(II) -DBMAB], J = [NI(II) -DBMAB],



WAVE NUMBER (cm

TAVE NUMBER (CH ) FIG. 2 - INFRARED SPECTRA OF A = [VOCIVO-DBHAB]\_BH\_20, B = [NnCIID-DBHAB]\_BH\_20, C = [FeCIID-COHD DBHAB]\_H\_20, D = [CoCIID-DBHAB]\_N, E = [NLCIID-DBHAB]\_N, F = [ZnCIID-DBHAB]\_H\_20, - DBHAB. G = DBMAB.



FIG. 3 - THERMOGRAVIMETRIC ANALYSIS OF A = [Vo(IV) -DBMAB]\_SH\_O, B = [Mn(II) -DBMAB]\_SH\_O, C = [Fe(III) - (OHDDBMAB]\_H\_O, D = [Co(II) -DBMAB E = [NL(II) -DBMAB]\_N, F = [Zn(II) -DBMAB]\_H\_O. H20, The tentative structure for polymers is as follows.









Fig 5



Where R = Mn(II), Co(II), Ni(II) and Zn(II)





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