

# Synthetic and Structural Studies of Some Polynuclearchelate of [Cd(II)-MADTCB]<sub>2</sub> H<sub>2</sub>O

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**Abstract :** Coordination Polymers of VO(IV), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) were prepared by using Ligand Cd(II) hydrazinium dithiocarbamate hydrazinium dithiocarbamate and mercapto acetic acid. They have been characterized on the basis of elemental, thermal, magnetic, spectral and Mössbauer studies. Polynuclear chelate have very interesting properties, which make them useful for various applications in science and technology. These polymeric chelate 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 Polychelate derived from Cd(II) hydrazinium dithiocarbamate used as ligand with Metal VO(IV), Co(II), Ni(II), Cu(II) and Zn(II).

Keywords : . Polynuclear chelate, alcohol, water, VO(IV), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II)

## Experimental

All metal acetate and chemicals used were of A. R. grade. All solvents were purified by distillation. Cadmium complex [Cd(II)-MADTCB]<sub>2</sub> .xH<sub>2</sub>O derived from hydrazinium dithiocarbamate and used as ligand were prepared in three steps.

**Preparation of hydrazinium dithiocarbamate:** <sup>(2)</sup> To the solution of (32 ml, 1mole) hydrazine hydrate in ice cold ethanol (50 ml), carbondisulphide (30ml, 0.5 mole) was added dropwise. The alcohol mixture was stirred constantly at 0°C for about 30 minutes. The product was washed with alcohol and crystallized from water.

**Preparation of Bis-(dithio carbazato) complex of Cd(II):** <sup>(1)</sup> A solution of hydraziniumdithiocarbamate (0.56gm, 0.004 mole) in water (15ml) was added dropwise with stirring to a solution of cadmiumacetate (0.002 mole) in water (25ml) containing 5 M acetic acid (1ml). The stirring was continued for further 10 minutes. The precipitated metal complex was filtered, washed first with water, then with alcohol and dried in vacuum over potassiumhydroxide

**Preparation of Di-(μ-mercaptoacetodithiocarbazato N,S) di Cd(II) complex:** A mixture of, solution of dithiocarbazato Cd(II) complex (10gm, 0.035 mole) [Cd(II)- MADTCB]<sub>2</sub> in hot dimethyl sulphoxide (50 ml) and mercaptoacetic acid (5.1 ml, 0.1 mole) was digested on water bath for about an hour. The product obtained was washed several times with hot water followed by alcohol and dried in air. The ligand [ Cd(II)-

MADTCB]<sub>2</sub> obtained was found to be insoluble in almost all organic solvent.

**Preparation of Polynuclear chelates of VO(IV), Co(II), Ni(II), Cu(II) and Zn(II):** Suspension of [Zn(II)- MADTCB]<sub>2</sub> ligand in dimethylformamide and metal acetate (in DMF), in equimolar proportion, was refluxed for about 10 hours. The products thus obtained were filtered and washed several times with hot water followed by dimethylformamide.

Elemental analysis, magnetic susceptibility measurement at room temperature, diffuse reflectance spectra, thermogravimetric analysis 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]<sub>n</sub>.

**Table 1 Analytical Data of ligand [ Cd(II)- MADTCB]<sub>2</sub> H<sub>2</sub>O and its Polynuclear Chelate in % found (calcd.)**

Compound	M	Cd	C	N	S
[ Cd(II)-MADTCB] <sub>2</sub> .H <sub>2</sub> O	....	38.35(39.65)	11.96(12.16)	9.58(8.65)	32.82(33.08)
[VO(IV)-( Cd(II)-MADTCB) <sub>2</sub> ] <sub>n</sub> .5H <sub>2</sub> O	7.05(8.12)	30.98(31.65)	8.86(9.61)	7.74(8.05)	26.55(27.00)
[Co(II)-(Cd(II)-MADTCB) <sub>2</sub> ] <sub>n</sub> .4H <sub>2</sub> O	8.25(8.90)	31.32(31.90)	8.69(9.99)	7.83(8.16)	26.85(27.05)
[Ni(II)-( Cd(II)-MADTCB) <sub>2</sub> ] <sub>n</sub> .4H <sub>2</sub> O	8.25(9.15)	31.32(32.23)	8.79(9.95)	7.83(8.15)	26.8(27.03)
[Cu(II)-( Cd(II)-MADTCB) <sub>2</sub> ] <sub>n</sub> .H <sub>2</sub> O	8.30(7.86)	32.00(33.31)	9.86(10.73)	7.98(8.20)	26.96(26.00)
[Zn(II)-( Cd(II)-MADTCB) <sub>2</sub> ] <sub>n</sub> .H <sub>2</sub> O	9.01(10.18)	31.06(32.25)	9.35(10.75)	7.76(7.15)	26.62(25.86)

N-H vibration generally occurs at 3000-3100 cm<sup>-1</sup>. In ligand these are absent whereas in the metal hydrazinium dithiocarbamate, which are used to derived the ligand, these bands (intense and sharp) are observed. Disappearance of NH<sub>2</sub> group vibration in the ligand spectrum suggests that mercaptoacetic acid substituted at NH<sub>2</sub> position by replacing the hydrogen of NH<sub>2</sub> group. Also - NH<sub>2</sub> vibration is not reappeared in the polychelate.

-C-N- vibration with the unidentate sulphur coordination, the frequency of C-N stretching vibration has been observed in the range 1440-1500  $\text{cm}^{-1}$ <sup>(3,4,5)</sup>

-CSS-M In dithiocarbamate the asymmetric  $\text{CS}_2$  stretching frequency occur at 1000  $\text{cm}^{-1}$ , with disulphur chelation a single  $\nu(\text{C}=\text{S})$  is usually found, whereas when unidentate sulphur coordination occurs this band is splitted<sup>(3,6)</sup>. [Ni(II)-MADTCB]<sub>2</sub>.4H<sub>2</sub>O ligand and its polynuclear chelates exhibit intense and sharp bands with well defined shoulders at 990- 995  $\text{cm}^{-1}$  which indicates unidentate coordination of sulphur to metal. -N-N stretching vibration has been sensitive in the region 900-1100  $\text{cm}^{-1}$ <sup>(7)</sup>. -C-S stretching vibration in the range 600- 700  $\text{cm}^{-1}$  has been observed in ligand and their polynuclear chelate. This band has well defined shoulder and shifted to higher frequency region, which may be probably because of drainage of the electrons from the sulphur to metal ion on coordination. -C=O bands appear in the region 1645-1610. The shift of bands toward the low frequency region indicates wide delocalization of electronic charge in newly formed chelate ring<sup>(8)</sup>. All polynuclear chelates and ligand display very broad band in the range 3600-3200  $\text{cm}^{-1}$ . All polynuclear chelate exhibits vibration frequency in the range 355- 460  $\text{cm}^{-1}$ , 470-560  $\text{cm}^{-1}$  and 200-335  $\text{cm}^{-1}$  which may be assigned to M-N, M-O and M-S frequency respectively. In VO(IV) chelate frequency observed at 980  $\text{cm}^{-1}$  is due to asymmetric stretching vibration<sup>[9]</sup>

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

**Table 2 Magnetic and Spectral Data of [M'-( Zn(II)-MADTCB)<sub>2</sub>]<sub>n</sub>.xH<sub>2</sub>O**

Sr No	Coordination Polymers	$\mu_{\text{eff}}$ . B.M.	Absorption nm	Bands kK	Assignment	References
1	[Cd(II)-MADTCB] <sub>2</sub> .4H <sub>2</sub> O	Diamagnetic	550 875	18.18 11.42	C.T. C.T.	
2	[VO(IV)-(Cd(II)-MADTCB) <sub>2</sub> ] <sub>n</sub> 5H <sub>2</sub> O	1.63	865 740 550 400	11.60 13.50 18.18 25.00	<sup>2</sup> B <sub>2</sub> - <sup>2</sup> E -- <sup>2</sup> B <sub>2</sub> - <sup>2</sup> B <sub>1</sub> <sup>2</sup> B <sub>2</sub> - <sup>2</sup> A <sub>1</sub>	11, 12,13 14, 15
3	[Co(II)-(Cd(II)-MADTCB) <sub>2</sub> ] <sub>n</sub> 4H <sub>2</sub> O	3.82	840 475 550	11.90 21.05 18.18	<sup>4</sup> T <sub>1g</sub> (F)- <sup>4</sup> T <sub>1g</sub> (P) <sup>4</sup> T <sub>1g</sub> (F)- <sup>4</sup> A <sub>2g</sub> (F) <sup>4</sup> T <sub>1g</sub> (F)- <sup>4</sup> A <sub>2g</sub>	16,17 18,19 20
4	[Ni(II)-(Cd(II)-MADTCB) <sub>2</sub> ] <sub>n</sub> 5H <sub>2</sub> O	3.80	850 540	11.76 18.50	<sup>3</sup> A <sub>2g</sub> (F)- <sup>3</sup> T <sub>2g</sub> (P)  <sup>3</sup> A <sub>2g</sub> (F)- <sup>3</sup> T <sub>1g</sub> (F)	18, 20, 19
5	[Cu(II)-(Cd(II)-MADTCB) <sub>2</sub> ] <sub>n</sub>	1.61	800 714- 620 550	12.50 14.00- 16.66 18.18	<sup>2</sup> B <sub>1g</sub> - <sup>2</sup> A <sub>1g</sub> <sup>2</sup> B <sub>1g</sub> <sup>2</sup> B <sub>2g</sub> <sup>2</sup> B <sub>1g</sub> - <sup>2</sup> E <sub>g</sub>	10

X-ray diffraction pattern of [Cu(II)-(Cd(II)-MADTCB)<sub>2</sub>]<sub>n</sub>H<sub>2</sub>O and [Zn(II)-(Cd(II)-MADTCB)<sub>2</sub>]<sub>n</sub>2H<sub>2</sub>O

have been studied. Diffractogram of coordination polymers are given in Table3and Table4. From the diffractogram it has been

observed that complexes are poorly crystalline and hence it is very difficult to assign their crystal structure. However on the basis of analysis of experimental data as give in Table 3and Table 4 complex may have orthorhombic unit cell. The cell parameters have been calculated using equation.

$$\text{Sin}^2\Theta \text{ hkl} = \text{Ah}^2 + \text{Bk}^2 + \text{Cl}^2.$$

$$\text{Where } A = \frac{\lambda^2}{4a^2}, \quad B = \frac{\lambda^2}{4b^2}, \quad C = \frac{\lambda^2}{4c^2}$$

**Table 3 X- ray Diffraction Data of [Cu(II)-(Cd(II)-MADTCB)<sub>2</sub>]<sub>n</sub>H<sub>2</sub>O**

a= 7.554                      b= 11.837                      c= 5.594

n	2 $\Theta$ Obs.	2 $\Theta$ Cal.	H	K	L	d Obs.
1	32.00	32.00	0	0	2	2.797
2	35.50	35.50	0	2	2	2.529
3	40.00	40.00	3	1	1	2.254
4	57.25	57.26	2	2	3	1.609
5	72.00	72.01	2	0	4	1.312
6	74.50	74.50	5	5	0	1.274

**Table 4 X- ray Diffraction Data of [Zn(II)-(Cd(II)-MADTCB)<sub>2</sub>]<sub>n</sub>2H<sub>2</sub>O**

a= 5.963                      b= 4.898                      c= 5.274

n	2 $\Theta$ Obs.	2 $\Theta$ Cal.	H	K	L	d Obs.
1	34.00	34.00	0	0	2	2.637
2	41.75	41.75	1	1	2	2.163
3	59.25	59.25	0	3	1	1.560
4	74.50	74.52	4	2	0	1.274
5	76.50	76.51	1	1	4	1.245

Thermogravimetric study of [Cd(II)-MADTCB]<sub>2</sub>H<sub>2</sub>O complex shown in **Fig-3**. as curve A shows that there is negligible mass loss upto 220<sup>o</sup>C. Beyond this temperature is rapid weight loss ,due to simultaneous destruction of organic matter and oxidation of sulphide and metal to sulphate and metal oxide respectively. Residue at 560<sup>o</sup>C may corresponds for mixture of CdSO<sub>4</sub> , CdS and CdO. A slight increase in weight indicates the oxidation of sulphide to sulphate. Thermogram of [VO(IV)-(Cd(II)-MADTCB)<sub>2</sub>]<sub>n</sub>5H<sub>2</sub>O polynuclear chelate shows rapid weight loss upto 125<sup>o</sup>C which may be corresponds to five molecules of water of hydration. After this mass loss simultaneous destruction of organic matter and oxidation of sulphide and metal, to sulphate and oxide respectively is attained around 700<sup>o</sup>C. A residue can be considered as mixture of sulphate, sulphide and oxide of vanadium and cadmium. Decomposition of [Co(II)-(Cd(II)-MADTCB)<sub>2</sub>]<sub>n</sub>4H<sub>2</sub>O polynuclear chelate occur in three stages. Initial weight loss in first stage may be due to loss of four hydrated water molecules below 100<sup>o</sup>C, followed by gradual mass loss of dehydrated polymer. In the temperature range 475-525<sup>o</sup>C residue obtained, may be due to mixture of CoS and CdS.

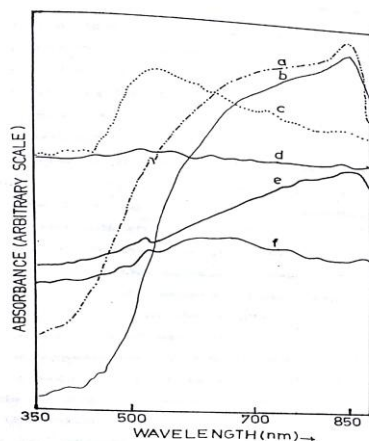
Beyond 525<sup>o</sup>C rapid increase in mass is observed. This increase in mass may indicate the oxidation of metal sulphide to sulphate.

[Ni(II)-(Cd(II)- MADTCB)<sub>2</sub>]<sub>n</sub> 5H<sub>2</sub>O Polychelate loss five hydrated water molecules below 125<sup>o</sup>C. After this dehydrated polychelate undergoes gradual mass loss upto 440<sup>o</sup>C and then rapid fall in weight at 490<sup>o</sup>C. Residue at around temperature 490<sup>o</sup>C corresponds to the formation of NiS + CdS. Increase in weight observed beyond 490<sup>o</sup>C which followed by decrease in weight. This increase in weight may be due to oxidation of metal sulphide to metal sulphate while decrease in weight may be due to decomposition of sulphate to oxide. [Cu(II)-(Cd(II)-MADTCB)<sub>2</sub>]<sub>n</sub> polychelate shows mass loss from 300<sup>o</sup>C. After this gradual mass loss upto 425<sup>o</sup>C observed. Beyond 440<sup>o</sup>C thermogram attains constant level. Residue may be mixture of sulphate, sulphide and oxide of Cu(II) and Cd(II). [Zn(II)-(Cd(II)- MADTCB)<sub>2</sub>]<sub>n</sub> 2H<sub>2</sub>O polynuclear chelate undergoes degradation gradually upto 300<sup>o</sup>C. After this, rapid fall in weight is observed followed by decrease in weight. Residue in the temperature range 540-860<sup>o</sup>C may be taken as mixture of sulphate, sulphide and oxide of Zn(II) and Cd(II).

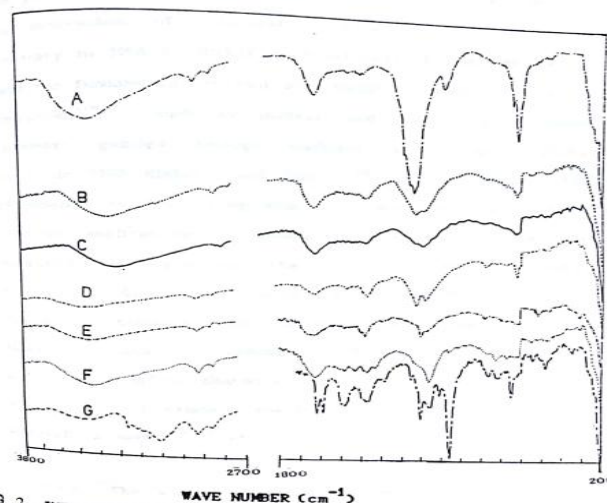
From the TG data activation energy values of coordination polymers by using Sharp-Wentworth method are given in Table 5

**Table 5 Activation Energy of [M' -(Cd(II)- MADTCB)<sub>2</sub>]<sub>n</sub> xH<sub>2</sub>O Polynuclear Chelates.**

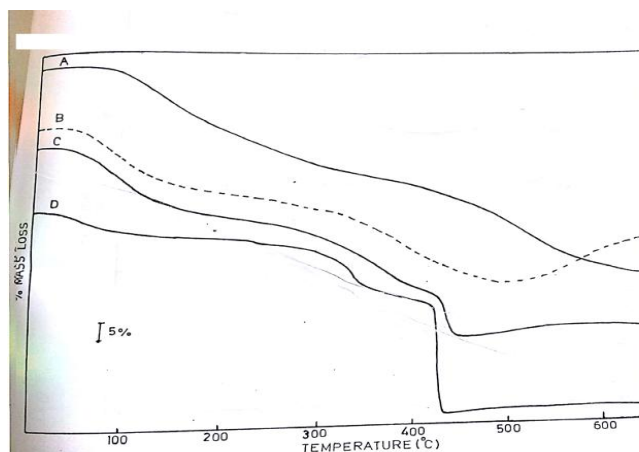
Sr No	Coordination Polymers	Activation Energy ( KCal/mole)	
		Temperature range	Room Temp. - 150 <sup>o</sup> C
1	[Cd(II)- MADTCB) <sub>2</sub> ] <sub>n</sub> H <sub>2</sub> O	--	--
2	[VO(IV)-(Cd(II)-MADTCB) <sub>2</sub> ] <sub>n</sub> 5H <sub>2</sub> O	5.527	3.543
3	[Co(II)-( Cd (II)-MADTCB) <sub>2</sub> ] <sub>n</sub> 4H <sub>2</sub> O	6.511	4.863
4	[Ni(II)-( Cd (II)-MADTCB) <sub>2</sub> ] <sub>n</sub> 5H <sub>2</sub> O	7.409	6.023
5	[Cu(II)-( Cd (II)-MADTCB) <sub>2</sub> ] <sub>n</sub> H <sub>2</sub> O	15.353	6.448
6	[Zn(II)-( Cd (II)-MADTCB) <sub>2</sub> ] <sub>n</sub> 2H <sub>2</sub> O	--	--



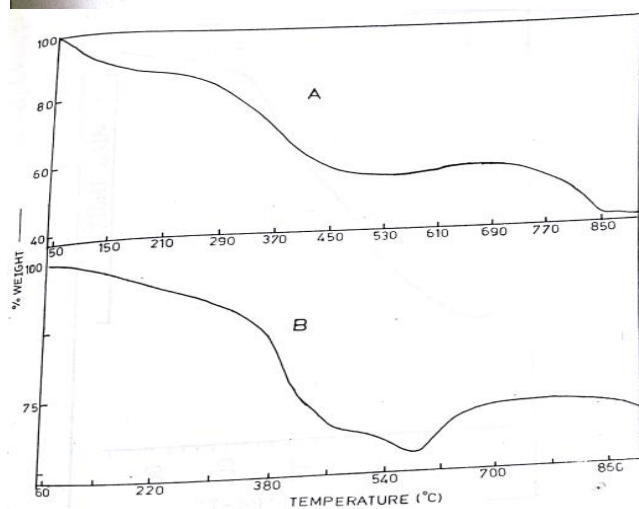
**FIG. 1 - DIFFUSE REFLECTANCE SPECTRA OF**  
a = [Zn(II)-(Cd(II)-MADTCB)<sub>2</sub>]<sub>n</sub> H<sub>2</sub>O, b = [Cd(II)-MADTCB)<sub>2</sub>]<sub>n</sub> H<sub>2</sub>O,  
c = [VO(IV)-(Cd(II)-MADTCB)<sub>2</sub>]<sub>n</sub> 5H<sub>2</sub>O, d = [Co(II)-(Cd(II)-MADTCB)<sub>2</sub>]<sub>n</sub> 4H<sub>2</sub>O,  
e = [Ni(II)-(Cd(II)-MADTCB)<sub>2</sub>]<sub>n</sub> 5H<sub>2</sub>O, f = [Cu(II)-(Cd(II)-MADTCB)<sub>2</sub>]<sub>n</sub> H<sub>2</sub>O.



**FIG. 2 - INFRARED SPECTRA OF**  
A = [VO(IV)-(Cd(II)-MADTCB)<sub>2</sub>]<sub>n</sub> 5H<sub>2</sub>O, B = [Co(II)-(Cd(II)-MADTCB)<sub>2</sub>]<sub>n</sub> 4H<sub>2</sub>O,  
C = [Ni(II)-(Cd(II)-MADTCB)<sub>2</sub>]<sub>n</sub> 5H<sub>2</sub>O, D = [Cu(II)-(Cd(II)-MADTCB)<sub>2</sub>]<sub>n</sub> H<sub>2</sub>O,  
E = [Zn(II)-(Cd(II)-MADTCB)<sub>2</sub>]<sub>n</sub> 2H<sub>2</sub>O, F = [Cd(II)-MADTCB)<sub>2</sub>]<sub>n</sub> H<sub>2</sub>O,  
G = [Cd(II)-(Cd(II)-MADTCB)<sub>2</sub>]<sub>n</sub>.



**FIG. 3 - THERMOGRAVIMETRIC ANALYSIS OF**  
A = [Co(II)-(Cd(II)-MADTCB)<sub>2</sub>]<sub>n</sub> 4H<sub>2</sub>O,  
B = [VO(IV)-(Cd(II)-MADTCB)<sub>2</sub>]<sub>n</sub> 5H<sub>2</sub>O, C = [Ni(II)-(Cd(II)-MADTCB)<sub>2</sub>]<sub>n</sub> 5H<sub>2</sub>O,  
D = [Cu(II)-(Cd(II)-MADTCB)<sub>2</sub>]<sub>n</sub> H<sub>2</sub>O.



**FIG. 4 - THERMOGRAVIMETRIC ANALYSIS OF**  
A = [Co(II)-(Zn(II)-MADTCB)<sub>2</sub>]<sub>n</sub> 4H<sub>2</sub>O,  
B = [Zn(II)-(Cd(II)-MADTCB)<sub>2</sub>]<sub>n</sub> 2H<sub>2</sub>O.

The tentative structure for polymers is as follows.

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