

Synthetic and Structural Studies of Some Polynuclearchelate of [Zn(II)-MADTCB]₂ 4H₂O

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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 Zn(II) hydrazinium dithiocarbamate hydrazinium dithiocarbamate and mercapto acetic acid. They have been characterized on the basis of elemental, thermal, magnetic, spectral and Mössbauer studies.

Keywords : hydrazinium, dithiocarbamate, hydrazinium, dithiocarbamate

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 Polychelate derived from Zn(II) hydrazinium dithiocarbamate used as ligand 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. Zinc complex [Zn(II)-MADTCB]₂ .xH₂O derived from hydrazinium dithiocarbamate and used as ligand were prepared in three steps.

Preparation of hydrazinium dithiocarbamate: ⁽²⁾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 Zn(II): ⁽¹⁾ A solution of hydraziniumdithiocarbamate (0.56gm, 0.004 mole) in water (15ml) was added dropwise with stirring to a solution of zincacetate (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 Zn(II) complex: A mixture of, solution of dithiocarbamate

Zn(II) complex (10gm, 0.035 mole) [Zn(II)- MADTCB]₂ 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 [Zn(II)- MADTCB]₂ obtained was found to be insoluble in almost all organic solvent.

Preparation of Polynuclear chelates of VO(IV), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II): Suspension of [Zn(II)- MADTCB]₂ 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 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.

Table 1 Analytical Data of ligand [Zn(II)- MADTCB]₂ 4H₂O and its Polynuclear Chelate in % found (calcd.)

Compound	M	Zn	C	H	N	S
[Zn(II)-MADTCB] ₂ .4H ₂ O	26.53(27.80)	14.69(13.89)	1.63(1.56)	11.42(10.49)	39.18(38.68)
[VO(IV)-(Zn(II)-MADTCB) ₂] _n .5H ₂ O	8.10(8.78)	20.66(21.05)	11.44(11.68)	2.54(2.65)	8.90(7.85)	30.32(31.65)
[Mn(II)-(Zn(II)-MADTCB) ₂] _n .4H ₂ O	8.9(9.03)	21.06(22.05)	11.66(10.68)	2.59(2.38)	9.07(8.78)	31.11(32.05)
[Fe(III)-(OH)(Zn(II)-MADTCB) ₂] _n .4H ₂ O	9.06(10.15)	21.03(22.25)	11.65(11.25)	2.58(2.68)	9.06(8.76)	31.06(31.68)
[Co(II)-Zn(II)-MADTCB) ₂] _n .4H ₂ O	9.50(10.65)	20.98(21.48)	11.59(10.68)	2.57(2.78)	9.01(8.65)	31.91(31.65)
[Ni(II)-(Zn(II)-	9.50	20.98(11.59(2.57(2	9.01(8	31.91(

MADTCB) ₂] _n .H ₂ O	(10.65)	21.48)	10.68)	.78)	.65)	31.65)
[Cu(II)-(Zn(II)-MADTCB) ₂] _n .5H ₂ O	10.08(11.05)	20.80(21.63)	11.52(10.60)	2.56(2.96)	8.96(8.65)	30.72(31.66)
[Zn(II)-(Zn(II)-MADTCB) ₂] _n .4H ₂ O	31.10(32.15)	11.48(11.98)	2.55(2.02)	8.93(8.26)	30.62(31.29)

N-H vibration generally occurs at 3000-3100 cm⁻¹. 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 NH₂ group vibration in the ligand spectrum suggests that mercaptoacetic acid substituted at NH₂ position by replacing the hydrogen of NH₂ group. Also -NH₂ 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 cm⁻¹(3,4,5)

-CSS-M In dithiocarbamate the asymmetric CS₂ stretching frequency occur at 1000 cm⁻¹, with disulphur chelation a single ν(C=S) is usually found, whereas when unidentate sulphur coordination occurs this band is splitted (3,6). [Ni(II)-MADTCB)₂]_n.4H₂O ligand and its polynuclear chelates exhibit intense and sharp bands with well defined shoulders at 990-995 cm⁻¹ which indicates unidentate coordination of sulphur to metal. -N-N stretching vibration has been sensitive in the region 900- 1100 cm⁻¹(7). -C-S stretching vibration in the range 600- 700 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 (8). All polynuclear chelates and ligand display very broad band in the range 3600-3200 cm⁻¹. All polynuclear chelate exhibits vibration frequency in the range 355- 460 cm⁻¹, 470-560 cm⁻¹ and 200-335 cm⁻¹ which may be assigned to M-N, M-O and M-S frequency respectively. In VO(IV) chelate frequency observed at 980 cm⁻¹ is due to asymmetric stretching vibration(9)

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

Table 2 Magnetic and Spectral Data of [M²⁺-(Zn(II)-MADTCB)₂]_n.xH₂O

Sr No	Coordination Polymers	μ _{eff} . B.M.	Absorption nm	Bands kK	Assignment	References
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1	[Zn(II)-MADTCB) ₂] _n .4H ₂ O	Diamagnetic	860 475	11.627(s) 21.05(sh)	C.T. C.T.	
2	[VO(IV)-(Zn(II)-MADTCB) ₂] _n .4H ₂ O	0.75	850 820-705 585 510 400	11.76(s) 12.20-14.20(b) 17.00(a) 19.60(sh) 25(sh)	² B ₂ - ² E C.T. ² B ₂ - ² B ₁ C.T. ² B ₂ - ² A ₁	10, 11, 12, 13
3	[Mn(II)-(Zn(II)-MADTCB) ₂] _n .4H ₂ O	5.10	450 875 510 400	22.22(sh) 11.42(s) 19.60(sh) 25.00(b)	C.T. C.T. ⁶ A _{1g} - ⁴ T _{2g} (4G) ⁶ A _{1g} - ⁴ A ₁ ⁴ E _g (G)	14, 10
4	[Fe(III)-(OH)(Zn(II)-MADTCB) ₂] _n .5H ₂ O	3.1	860 500 430	11.62 20.00 23.25	⁶ A _{1g} - ⁴ T _{1g} ⁶ A _{1g} - ⁴ T _{2g} ⁶ A _{1g} - ⁴ E _g ⁶ A _{1g} - ⁴ T _{1g}	15, 16, 17, 18,
5	[Co(II)-(Zn(II)-MADTCB) ₂] _n .4H ₂ O	4.60	800 500 585	12.50 20.00 17.70	⁴ T _{1g} (F)- ⁴ T _{1g} (P) ⁴ T _{1g} (F)- ⁴ A _{2g} (F) ⁴ T _{1g} (F)- ² A _{2g}	16, 19, 20
6	[Ni(II)-(Zn(II)-MADTCB) ₂] _n .5H ₂ O Square planar Ni(II) metal	3.4	875 560	11.42 17.85	³ A _{2g} (F)- ³ T _{2g} (F) ³ A _{2g} (F)- ³ T _{1g} (F)	21, 22 19
7	[Cu(II)-(Zn(II)-MADTCB) ₂] _n .4H ₂ O	0.9	750 700-600 450	13.30 14.28-16.66(b) 22.22(sh)	C.T. ² B _{1g} - ² A _{1g} - ² B _{2g} - ² E _g	
8	[Zn(II)-(Zn(II)-MADTCB) ₂] _n .4H ₂ O	Diamagnetic	480 875	20.83 11.42	C.T. C.T.	

In Mössbauer study of [Fe(III)-(OH)(Zn(II)-MADTCB)₂]_n.5H₂O coordination polymer δ value (0.62) mms⁻¹ lies within the range expected for typical Fe(III) high spin state complexes. However, it exhibits comparatively large ΔEQ (0.997mms⁻¹) suggesting large distortion presumably due to axial octahedral distortion.

X-ray diffraction pattern of [Ni(II)-(Zn(II)-MADTCB)₂]_n.5H₂O

has been studied. Diffractogram of coordination polymers are given in Table3. 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 3 complex may have orthorhombic unit cell. The cell parameters have been calculated using equation.

$$\sin^2\theta_{hkl} = Ah^2 + Bk^2 + Cl^2.$$

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

Table 3 X- ray Diffraction Data of [Ni(II)-(Zn(II)-MADTCB)₂]_n5H₂O

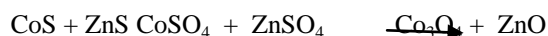
a= 9.958 b= 5.340 c= 7.352

n	2θ Obs.	2θ Cal.	H	K	L	d Obs.
1	29.50	29.53	3	0	1	3.028
2	29.50	29.50	0	1	2	3.028
3	38.25	38.25	2	2	0	2.353
4	40.50	40.50	0	1	3	2.227
5	55.25	55.20	5	1	2	1.663
6	63.50	63.54	5	2	2	1.465
7	65.50	65.49	1	3	3	1.425
8	65.50	65.50	4	1	4	1.425
9	76.50	76.54	8	0	0	1.245
10	76.50	76.52	1	4	2	1.245

Thermogravimetric study of [Zn(II)- MADTCB]₂ 4H₂O complex shown in **Fig-3**. as curve A. Mass loss upto 100⁰ C corresponds to loss of four molecules of water of hydration. Beyond this temperature gradual mass loss occur around 410⁰ C indicate decomposition of the free part of the ligand. Residue formed at 410⁰C may corresponds to formation of ZnS. Residue formed at 575⁰C may be of ZnO. [VO(IV)-(Zn(II)- MADTCB)₂]_n 5H₂O undergoes continuous weight loss upto 125⁰C indicates evolution of five hydrated water molecule. Then there is gradual mass loss upto 450⁰C. Mass left at this temperature corresponds to the formation of metal sulphide. Beyond 450⁰C small rise in weight is observed which may be due to the formation of metal sulphate from sulphide.

[Mn(II)-(Zn(II)- MADTCB)₂]_n 4H₂O polynuclear chelate loss 12% mass below 100⁰C corresponds to four hydrated water molecule. After this polynuclear chelate undergoes decomposition slowly and contiously. Residue formed near 440⁰C corresponds to sulphide of manganese and zinc. Steady curve is observed in the range 440⁰C to 575⁰C. TG curve of [Fe(III)-(OH)(Zn(II)- MADTCB)₂]_n 5H₂O polynuclear chelate undergoes three step degradation process. First step below 130⁰C corresponds to five hydrated water molecules. Gradual mass loss is observed upto 300⁰C. From 300⁰C- 440⁰C mass increase and at around 440⁰C again mass loss is observed. Beyond 440⁰C thermogram attains constant level. Residue obtained at the end may corresponds to the formation of FeS and ZnS. [Co(II)-(Zn(II)- MADTCB)₂]_n 4H₂O polynuclear chelate loss four hydrated water molecules near 130⁰C. After this polynuclear chelate undergoes continuous degradation upto 450⁰C to 610⁰C. Thermogram attains costant level. Beyond 610⁰C thermogram shows rise in weight upto 690⁰C,

followed by continuous weight loss upto 850⁰C and attains constant level. This changes may indicate the formation of



[Ni(II)-(Zn(II)- MADTCB)₂]_n 5H₂O polynuclear chelate loss five hydrated water molecules below 100⁰C. After this dehydration polynuclear chelate is stable upto 300⁰C and then it undergoes continuous mass loss upto 525⁰C. Residue formed corresponds to NiS and ZnS. Beyond 600⁰C rapid gain in weight is observed and maintained constant level upto 625⁰C. Rise in weight is may be due to formation of ZnSO₄ and NiSO₄. [Cu(II)-(Zn(II)-MADTCB)₂]_n 5H₂O polynuclear chelate degrade in two steps. In first step five hydrated molecules loss below 100⁰C. After 150⁰C this dehydrated polynuclear chelate undergoes gradual mass loss. Residue formed at 525⁰C may corresponds to ZnS and CuS. Beyond this increase in weight is observed which may be due to the formation of ZnSO₄ + CuSO₄. [Zn(II)-(Zn(II)- MADTCB)₂]_n 4H₂O poly nuclear chelate loss four hydrated water molecule around 100⁰C. After this chelate is stable upto 325⁰C and then it undergoes continuous mass loss and finally the residue formed near 700⁰C corresponds to ZnS.

From the TG data activation energy values of coordination polymers by using Sharp-Wentwoth method are given in Table 4

Table 4 Activation Energy of [M' -(Zn(II)- MADTCB)₂]_n xH₂O Polynuclear Chelates.

Sr No	Coordination Polymers	Activation Energy (KCal/mole)	
		Temperature range	Room Temp. – 150 ⁰ C
1	[Zn(II)- MADTCB] ₂ 4H ₂ O	9.212	2.303
2	[VO(IV)-(Zn(II)- MADTCB) ₂] _n 5H ₂ O	6.580	2.150
3	[Mn(II)-(Zn (II)- MADTCB) ₂] _n 4H ₂ O	6.909	4.187
4	[Fe(III)-(OH)(Zn(II)- MADTCB) ₂] _n 5H ₂ O	9.212	5.257
5	[Co(II)-(Zn (II)- MADTCB) ₂] _n 4H ₂ O	--	--
6	[Ni(II)-(Zn (II)- MADTCB) ₂] _n 5H ₂ O	8.3757	6.579
7	[Cu(II)-(Zn (II)- MADTCB) ₂] _n 5H ₂ O	11.844	2.4031
8	[Zn(II)-(Zn (II)- MADTCB) ₂] _n 4H ₂ O	--	--

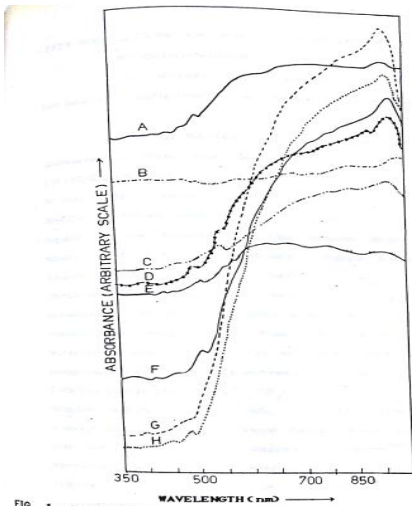


FIG. 1 - DIFFUSE REFLECTANCE SPECTRA OF
A = $(VOCl_4) \cdot (ZnCl_2) \cdot (MADTCB)_2 \cdot n \cdot 4H_2O$, B = $(CoCl_2) \cdot (ZnCl_2) \cdot (MADTCB)_2 \cdot n \cdot 4H_2O$,
C = $(NiCl_2) \cdot (ZnCl_2) \cdot (MADTCB)_2 \cdot n \cdot 4H_2O$, D = $(FeCl_3) \cdot (OH) \cdot (ZnCl_2) \cdot (MADTCB)_2 \cdot n \cdot 5H_2O$,
E = $(CoCl_2) \cdot (ZnCl_2) \cdot (MADTCB)_2 \cdot n \cdot 4H_2O$, F = $(MnCl_2) \cdot (ZnCl_2) \cdot (MADTCB)_2 \cdot n \cdot 4H_2O$,
G = $(ZnCl_2) \cdot (MADTCB)_2 \cdot 4H_2O$, H = $(ZnCl_2) \cdot (ZnCl_2) \cdot (MADTCB)_2 \cdot n \cdot 4H_2O$.

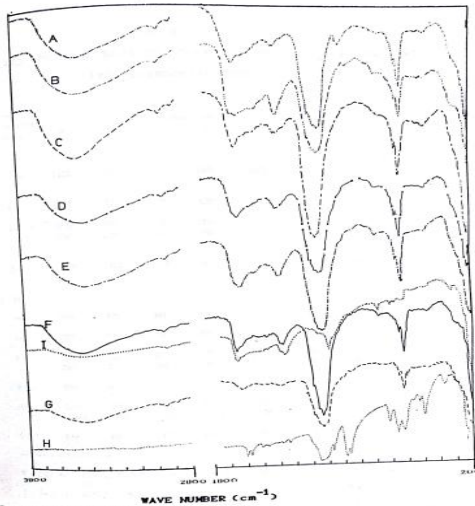


FIG. 2 - INFRARED SPECTRA OF
A = $(VOCl_4) \cdot (ZnCl_2) \cdot (MADTCB)_2 \cdot n \cdot 5H_2O$, B = $(MnCl_2) \cdot (ZnCl_2) \cdot (MADTCB)_2 \cdot n \cdot 4H_2O$,
C = $(FeCl_3) \cdot (OH) \cdot (ZnCl_2) \cdot (MADTCB)_2 \cdot n \cdot 4H_2O$,
D = $(CoCl_2) \cdot (ZnCl_2) \cdot (MADTCB)_2 \cdot n \cdot 4H_2O$,
E = $(NiCl_2) \cdot (ZnCl_2) \cdot (MADTCB)_2 \cdot n \cdot 4H_2O$, F = $(CoCl_2) \cdot (ZnCl_2) \cdot (MADTCB)_2 \cdot n \cdot 5H_2O$,
G = $(ZnCl_2) \cdot (ZnCl_2) \cdot (MADTCB)_2 \cdot n \cdot 4H_2O$, H = $(ZnCl_2) \cdot (MADTCB)_2 \cdot 4H_2O$,
I = $(ZnCl_2) \cdot (Dteb)_2$.

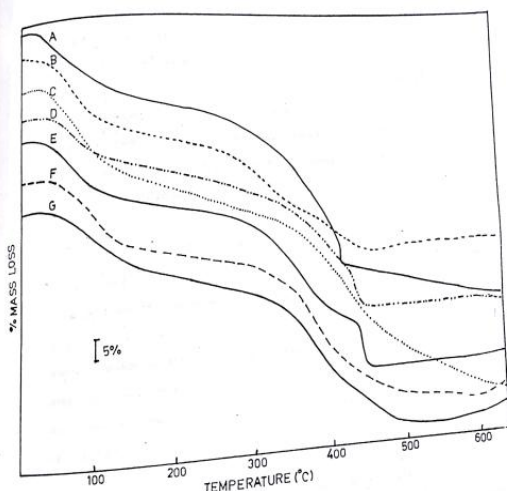


FIG. 3 - THERMOGRAVIMETRIC ANALYSIS OF
A = $(ZnCl_2) \cdot (MADTCB)_2 \cdot 4H_2O$, B = $(VOCl_4) \cdot (ZnCl_2) \cdot (MADTCB)_2 \cdot n \cdot 5H_2O$,
C = $(ZnCl_2) \cdot (ZnCl_2) \cdot (MADTCB)_2 \cdot n \cdot 4H_2O$, D = $(MnCl_2) \cdot (ZnCl_2) \cdot (MADTCB)_2 \cdot n \cdot 4H_2O$,
E = $(ZnCl_2) \cdot (ZnCl_2) \cdot (MADTCB)_2 \cdot n \cdot 4H_2O$, F = $(NiCl_2) \cdot (ZnCl_2) \cdot (MADTCB)_2 \cdot n \cdot 4H_2O$,
G = $(FeCl_3) \cdot (OH) \cdot (ZnCl_2) \cdot (MADTCB)_2 \cdot n \cdot 5H_2O$,
H = $(CoCl_2) \cdot (ZnCl_2) \cdot (MADTCB)_2 \cdot n \cdot 5H_2O$.

The tentative structure for polymers is as follows.

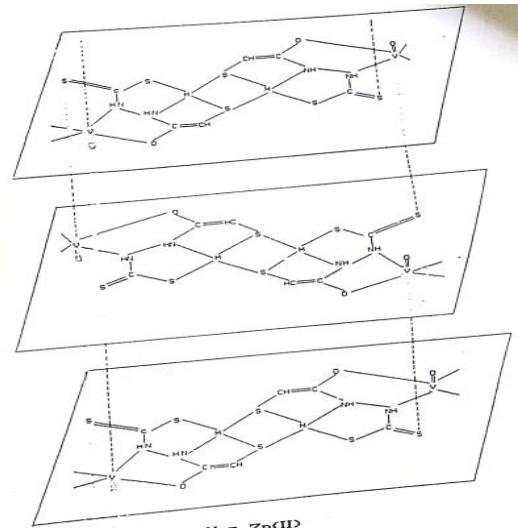


Fig.4 M = Zn(II)

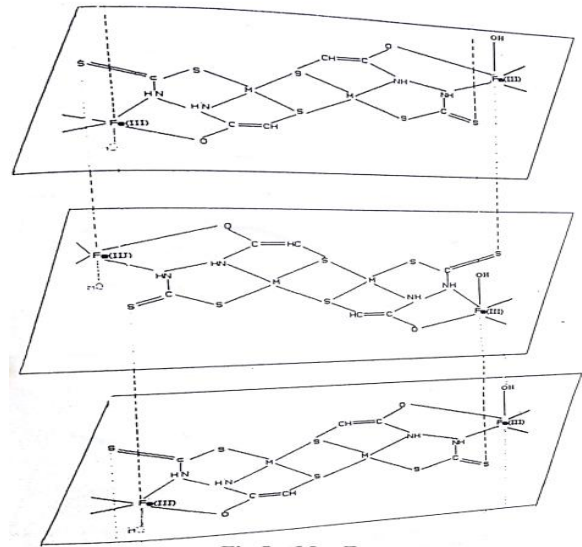


Fig.5 M = Zn

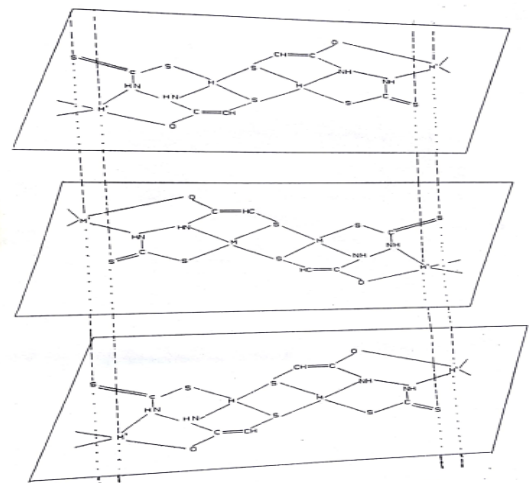


Fig.6 M = Zn(II)
M' = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)

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