

Synthetic and Structural Studies of Some Polynuclearchelate

Chandrashekhar P Kalambe

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

Coordination Polymers of VO(IV), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) were prepared by using Ligand Ni(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. Present communication describes the preparation and characterization of Polychelate derived from Ni(II) hydrazinium dithiocarbamate used as ligand with Metal 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. Nickel complex [Ni(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 drop wise. 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 Ni(II): ⁽¹⁾ A solution of hydraziniumdithiocarbamate (0.56gm, 0.004 mole) in water (15ml) was added dropwise with stirring to a solution of nickelacetate (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 Ni(II) complex: A mixture of, solution of dithiocarbazato Ni(II) complex (10gm, 0.035 mole) [Ni(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 [

Ni(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 [Ni(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 [Ni(II)- MADTCB]₂ and its chelate in % found (calcd.)

Compound	M	Ni	C	H	N	S
[Ni(II)-MADTCB] ₂ .4H ₂ O	24.68(25.90)	15.06(14.64)	1.67(1.20)	11.71(10.18)	40.16(41.26)
[VO(IV)-(Ni(II)-MADTCB) ₂] _n .3H ₂ O	8.26(8.32)	20.12(20.85)	11.66(11.15)	2.60(2.30)	9.07(8.87)	31.77(32.03)
[Mn(II)-(Ni(II)-MADTCB) ₂] _n .4H ₂ O	9.25(9.32)	19.50(20.15)	11.90(11.13)	2.64(2.34)	9.25(9.32)	31.73(32.68)
[Fe(III)-(Ni(II)-MADTCB) ₂] _n .4H ₂ O	9.25(9.32)	19.50(20.15)	11.90(11.13)	2.64(2.34)	9.25(9.32)	31.73(32.68)
[Co(II)-(Ni(II)-MADTCB) ₂] _n .H ₂ O	9.68(10.05)	19.37(19.80)	11.82(12.05)	2.95(3.05)	9.19(8.85)	31.52(30.52)
[Ni(II)-(Ni(II)-MADTCB) ₂] _n .4H ₂ O	29.05(30.15)	11.82(10.89)	2.95(2.06)	9.25(8.87)	31.73(32.73)
[Cu(II)-(Ni(II)-MADTCB) ₂] _n .H ₂ O	10.56(11.78)	19.18(18.56)	9.70(10.78)	2.60(2.36)	9.10(9.15)	31.21(32.22)
[Zn(II)-(Ni(II)-MADTCB) ₂] _n .3H ₂ O	10.60(11.98)	19.25(18.76)	9.72(9.89)	2.65(2.38)	9.75(9.27)	31.25(33.25)

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]₂.4H₂O 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 [(M'-Ni(II)-MADTCB)₂]_n.xH₂O

Sr No	Coordination Polymers	μ _{eff} · B.M.	Absorption nm	Bands kK	Assignment	References
1	[Ni(II)-MADTCB] ₂ .4H ₂ O	2.65	875 725 500 400	11.42(sh) 13.79(sh) 20.00(w) 25.00	³ A _{2g} (F)- ³ T _{2g} (F) ³ A _{2g} (F)- ³ T _{1g} (F) ³ A _{2g} -E _g ³ A _{2g} (F)- ³ T _{1g} (P)	10 11
2	[VO(IV)-(Ni(II)-MADTCB) ₂] _n .3H ₂ O	1.80	900 675 600	11.00(m) 14.87(w) 16.66(w)	² B ₂ - ² e _g ² B ₂ - ² B ₁ ² B ₂ - ² A ₁	12, 13, 14, 15
3	[Mn(II)-(Ni(II)-MADTCB) ₂] _n .4H ₂ O	5.08	900 825 450 410 615	11.12 12.12 22.22(w) 24.40(w) 16.25(w)	c.t. ⁶ A _{1g} - ⁴ T _{1g} (4G) ⁶ A _{1g} - ⁴ E _g ⁶ A _{1g} - ⁴ E _g (4D) ¹ A _{1g} - ¹ B _{1g}	16, 17, 18

	Inside Ni(II)					
4	[Fe(III)-(OH)(Ni(II)-MADTCB) ₂] _n .4H ₂ O	4.30	825 650 550	12.12(w) 15.38(w) 18.18(w)	⁶ A _{1g} - ⁴ T _{1g} ⁶ A _{1g} - ⁴ T _{2g}	19, 20
5	[Co(II)-(Ni(II)-MADTCB) ₂] _n .H ₂ O	5.10	835 550- 660 500	12.00(b) 15.00- 18.00(w) 18.18(w)	⁴ T _{1g} (F)- ⁴ T _{1g} (P) ⁴ T _{1g} (F)- ⁴ A _{2g} ⁴ T _{1g} (F)- ⁴ T _{2g}	21
6	[Ni(II)-(Ni(II)-MADTCB) ₂] _n .4H ₂ O Square planar Ni(II) metal	3.32	875 800 700 590	12.40(w) 12.50 14.30(w) 17.00(b)	³ A _{2g} (F)- ³ T _{2g} (F) ³ A _{2g} (F)- ³ T _{1g} (F) ¹ A _{1g} - ¹ B _{1g}	16, 18, 22
7	[Cu(II)-(Ni(II)-MADTCB) ₂] _n .4H ₂ O Inside Ni(II)	1.65	550- 455	18.00- 22.00 13.00	² B _{1g} - ² A _{1g} ² B _{1g} - ² B _{2g} ² B _{1g} - ¹ B _{1g}	14, 21

In Mössbauer study of [Fe(III)-(OH)(Ni(II)-MADTCB)₂]_n.4H₂O

polymer three line spectrum has been observed. It can be resolved into doublets arising due to Fe(II) and Fe(III) states. It seems that besides Fe(III) complex a Fe(II) complex is also formed. Because of reducing properties of sulphur Fe(III) --- Fe(II) reduction may occur. ΔEQ 2.95mms⁻¹ may be due to Fe(II) state and observed smaller ΔEQ 1.023mms⁻¹ may be due to Fe(III) state. Such ΔEQ in Fe(III) complex indicates large distortion. The distortion may be due to axial elongation. The observed δ values of 0.54 and 1.505 mms⁻¹ also corresponds to Fe(III) and Fe(II) in high spin state respectively.

X-ray diffraction pattern of [VO(IV)-(Ni(II)-MADTCB)₂]_n.3H₂O and [Mn(II)-(Ni(II)-MADTCB)₂]_n.4H₂O

have been studied. Diffractogram of coordination polymers are given in Table 3 and Table 4 respectively. 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 and Table 4 complexes may have orthorhombic unit cell. The cell parameters have been calculated using equation.

$$\sin^2\Theta hkl = Ah^2 + Bk^2 + Cl^2.$$

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

Table 3 X- ray Diffraction Data of [VO(IV)-(Ni(II)-MADTCB)₂]_n3H₂O

a= 2.388		b= 7.006		c= 36.797		
n	2θ Obs.	2θ Cal.	H	K	L	d Obs.
1	40.20	40.20	1	1	2	2.243
2	46.00	46.00	1	2	0	1.973
3	46.00	46.03	0	3	10	1.973
4	55.00	55.00	1	3	0	1.670
5	66.88	88.88	1	4	3	1.403
6	65.50	85.48	0	4	15	1.425
7	68.50	88.49	1	0	22	1.370
8	74.00	73.95	0	3	24	1.281
9	76.25	76.26	0	1	29	1.249

Table 4 X- ray Diffraction Data of [Mn(II)-(Ni(II)-MADTCB)₂]_n4H₂O

a= 17.328		b= 5.183		c= 3.271		
n	2θ Obs.	2θ Cal.	H	K	L	d Obs.
1	59.25	58.25	0	1	2	1.580
2	80.30	60.30	2	1	2	1.535
3	68.00	68.00	1	2	2	1.379
4	73.25	73.34	13	1	0	1.292
5	73.25	73.26	1	4	0	1.292
6	76.50	76.53	11	2	1	1.245
7	76.50	76.41	9	0	2	1.245

Thermogravimetric study of [Ni(II)- MADTCB)₂ 4H₂O complex shown in **Fig-3**. as curve A. mass loss upto

120⁰ C corresponds to loss of four molecules of water of hydration. Beyond this temperature gradual mass loss occur around 350⁰ C indicate decomposition of the free part of the ligand .There is inflexion at 425⁰ C.

[VO(IV)-(Ni(II)- MADTCB)₂]_n 3H₂O undergoes continuous weight loss. Near 475-550⁰ C TG curve shows little arrest. Percentage weight loss in this temperature range indicates the formation of metasulphides. Beyond this temperature 550⁰C the TG curve again shows continuous mass loss and finally residue at 725⁰C corresponds to mix oxide i.e. NiO and V₂O₅. [Mn(II)-(Ni(II)- MADTCB)₂]_n 4H₂O polynuclear chelate shows decomposition in three steps. First step polymer losses 12.00% mass loss below 100⁰C. This mass loss may be due to four hydrated water molecules. After this gradual mass loss is observed upto 475⁰C which is indicative of decomposition of free part of ligand. Beyond 475⁰C, the TG curve attains a constant level followed by gradual mass loss. Finally 45% residue left at 725⁰C may be of Mn(SCN)₂ and Ni(SCN)₂. TG curve of [Fe(III)-(OH)(Ni(II)- MADTCB)₂]_n 4H₂O

polynuclear chelate also shows three step decomposition. Four hydrated water molecule losses below 125⁰C. After dehydration, organic part of the polymer undergoes decomposition in second step and sulphide of the corresponding metal may formed. In final step thermogram shows some rise in weight may be due to formation of metal sulphate. (Fe₂SO₄)₃/NiSO₄) residue left at 725⁰C is 50.00%. [Co(II)-(Ni(II)- MADTCB)₂]_n H₂O poly nuclear chelate shows single stage decomposition. Residue left at 725⁰C is 52.00% which may indicate the formation of polysulphide of Co(II) and Ni(II). (NiS_{2.5}, CoS_{2.5})⁽²⁴⁾

Thermogram of [Ni(II)-(Ni(II)- MADTCB)₂]_n 4H₂O polynuclear chelate degrade below 100⁰C correspond to four mole of hydrated molecules. After this there is no loss upto 300⁰C indicates the formation of stable dehydrated species. After this, degradation occur upto 500⁰C. In final stage inflation in the curve occur upto 725⁰C. Residue left at last is 40% which may corresponds to NiS. Dehydration of [Cu(II)-(Ni(II)- MADTCB)₂]_n 4H₂O polynuclear chelate takes place below 125⁰C as single stage process, corresponds to four hydrated water molecules. There is a slight inflation in the curve near 150⁰C and rapid degradation occur upto 325⁰C leading to the formation of metal sulphide at 450⁰C. Beyond 450⁰C thermogram shows gain in weight suggests the formation of metal sulphate from metal sulphide. [Zn(II)-(Ni(II)- MADTCB)₂]_n 3H₂O thermogram losses three water molecules of hydration below 100⁰C. Then there is no mass loss upto 325⁰C. Beyond this gradual mass loss upto 500⁰C is followed by rapid inflation at 525⁰C. After 525⁰C thermogram shows gradual increase in mass upto 600⁰C and then again curve shows gradual mass loss beyond 625⁰C. Nature of this type of decomposition is indicative of the process

Metal sulphide → Metal sulphate → Metal oxide

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' -(Ni(II)- MADTCB)₂]_n xH₂O Polynuclear Chelates.

Sr No	Coordination Polymers	Activation Energy (KCal/mole)	
		Temperature range	Room Temp. - 150 ⁰ C
1	[Ni(II)- MADTCB) ₂ 4H ₂ O	7.369	5.490
2	[VO(IV)-(Ni(II)- MADTCB) ₂] _n 3H ₂ O	--	--
3	[Mn(II)-(Ni(II)- MADTCB) ₂] _n 4H ₂ O	7.747	4.606
4	[Fe(III)-(OH)(Ni(II)- MADTCB) ₂] _n 4H ₂ O	7.367	3.067
5	[Co(II)-(Ni(II)- MADTCB) ₂] _n H ₂ O	3.011	4.564
6	[Ni(II)-(Ni(II)- MADTCB) ₂] _n 4H ₂ O	7.7947	4.564
7	[Cu(II)-(Ni(II)- MADTCB) ₂] _n 4H ₂ O	5.862	6.408
8	[Zn(II)-(Ni(II)- MADTCB) ₂] _n 3H ₂ O	13.156	3.490

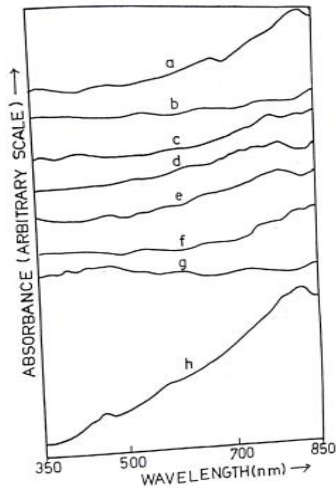
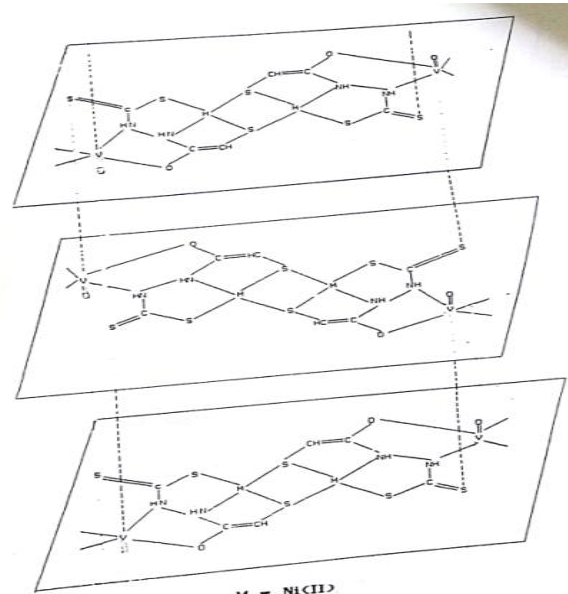


FIG. 1 - DIFFUSE REFLECTANCE SPECTRA OF
 a = [Ni(II)-MADTCB]₂·4H₂O, b = [VO(IV)-C(Ni(II)-MADTCB)₂]_n·3H₂O,
 c = [Mn(II)-C(Ni(II)-MADTCB)₂]_n·4H₂O, d = [Fe(III)-C(OH)(Ni(II)-MADTCB)₂]_n·4H₂O,
 e = [Ni(II)-C(Ni(II)-MADTCB)₂]_n·4H₂O, f = [Ni(II)-C(Ni(II)-MADTCB)₂]_n·4H₂O,
 g = [Co(II)-C(Ni(II)-MADTCB)₂]_n·4H₂O, h = [Zn(II)-C(Ni(II)-MADTCB)₂]_n·3H₂O,
 i = [Cu(II)-C(Ni(II)-MADTCB)₂]_n·4H₂O.



[Fig. 4] M = Ni(II)

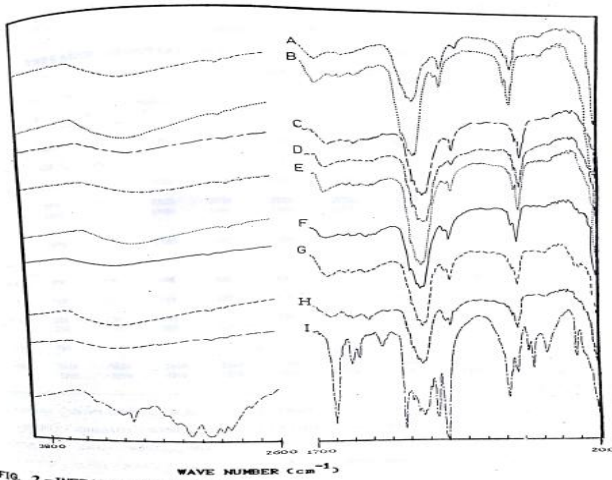
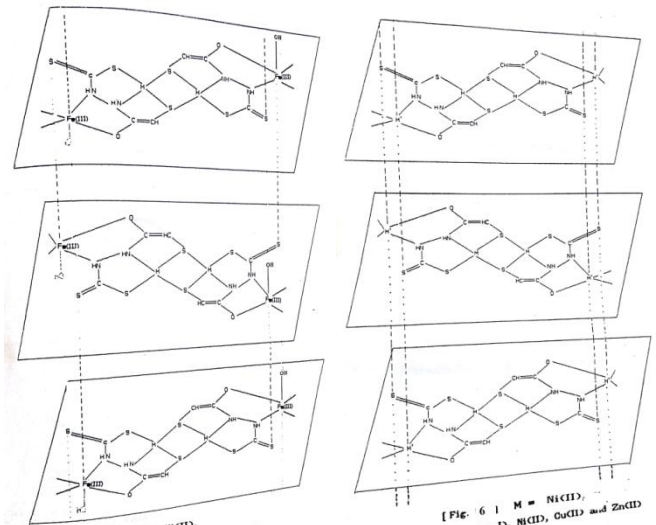


FIG. 2 - INFRARED SPECTRA OF
 A = [VO(IV)-C(Ni(II)-MADTCB)₂]_n·3H₂O, B = [Mn(II)-C(Ni(II)-MADTCB)₂]_n·4H₂O,
 C = [Fe(III)-C(OH)(Ni(II)-MADTCB)₂]_n·4H₂O, D = [Co(II)-C(Ni(II)-MADTCB)₂]_n·4H₂O,
 E = [Ni(II)-C(Ni(II)-MADTCB)₂]_n·4H₂O, F = [Ni(II)-C(Ni(II)-MADTCB)₂]_n·4H₂O,
 G = [Zn(II)-C(Ni(II)-MADTCB)₂]_n·3H₂O, H = [Ni(II)-C(Ni(II)-MADTCB)₂]_n·4H₂O,
 I = [Ni(II)-C(Ni(II)-MADTCB)₂]_n·4H₂O.



[Fig. 5.] M = Ni(II),

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

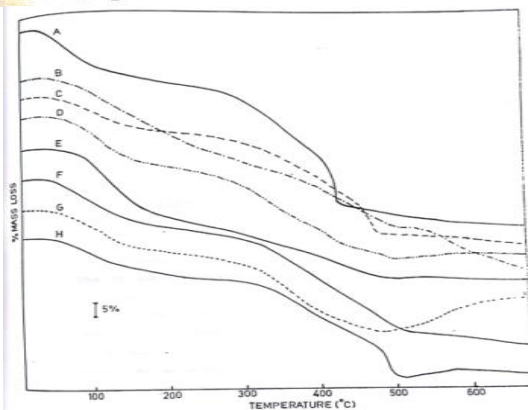


FIG. 3 - THERMOGRAVIMETRIC ANALYSIS OF
 A = [Ni(II)-MADTCB]₂·4H₂O, B = [VO(IV)-C(Ni(II)-MADTCB)₂]_n·3H₂O,
 C = [Mn(II)-C(Ni(II)-MADTCB)₂]_n·4H₂O, D = [Fe(III)-C(OH)(Ni(II)-MADTCB)₂]_n·4H₂O,
 E = [Ni(II)-C(Ni(II)-MADTCB)₂]_n·4H₂O, F = [Ni(II)-C(Ni(II)-MADTCB)₂]_n·4H₂O,
 G = [Zn(II)-C(Ni(II)-MADTCB)₂]_n·3H₂O, H = [Ni(II)-C(Ni(II)-MADTCB)₂]_n·4H₂O,
 i = [Cu(II)-C(Ni(II)-MADTCB)₂]_n·4H₂O.

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The tentative structure for polymers is as follows.

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