

Synthetic and Structural Studies of Some Coordination Polymers

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Abstract : *Coordination Polymers of VO(IV), Mn(II), Fe(III), Co(II), Ni(II), and Zn(II) were prepared by using Ligand MAAN derived from 1,5 Bis (mercapto acetamido) naphthelene and mercapto acetic acid. They have been characterized on the basis of elemental, thermal, spectral data Mossbauer, XRD .*

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 [MAAN] 1,5 Bis- (mercaptoacetamido) naphthelene, derived from diamino naphthelene and 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 diamino naphthelene (25 g, 0.15 mole) was dissolved in benzene (400 ml) and mercaptoacetic acid (22.10 ml, 0.03 mole) was added to it. The mixture was refluxed for two hours. The reaction mixture was cooled to room temperature and product was filtered and dried. Product was crystallized from benzene. m.p. 85° 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.

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

Compound	M	C	H	N	S
MAAN	54.3(54.9)	4.35(4.57)	8.90(9.15)	20.75(20.91)
[VO(IV)-MAAN] _n 4H ₂ O	13.85(12.60)	45.60(41.58)	2.40(3.25)	7.60(6.90)	17.39(15.84)
[Mn(II)-MAAN] _n 2H ₂ O	15.45(14.05)	47.19(43.03)	2.52(3.50)	7.86(7.15)	17.92(16.50)
[Fe(III)-MAAN] _n 3H ₂ O	15.68(14.05)	44.70(43.03)	2.52(3.50)	7.84(7.15)	17.92(16.50)
[Co(II)-MAAN] _n 4H ₂ O	15.68(14.15)	44.70(44.03)	2.52(2.32)	7.84(7.67)	17.92(17.51)
[Ni(II)-MAAN] _n 4H ₂ O	16.38(17.05)	46.66(42.41)	2.50(2.30)	7.70(7.51)	17.77(17.56)
[Zn(II)-MAAN] _n 2H ₂ O	17.75(17.35)	45.90(44.85)	2.45(2.30)	7.65(7.56)	17.48(16.98)

-C-O-H vibration frequency of MAAN exhibits a broad band around 3230 cm⁻¹ which is known to be lowered due to intra and inter molecular hydrogen bonding [1,2]. -N-H shows band at 2950 cm⁻¹ 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⁻¹ suggest -S-H stretching vibration [3]. This band disappears after formation of coordination polymers. Band observed at 680 cm⁻¹ 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⁻¹. C=O band with well defined shoulder at 1660 and 1620 cm⁻¹ in the ligands. In the chelate shoulder disappear and frequency of the band shifted to lower region indicates wide delocalization of electronic charge. [4,5] All coordination polymers display a very broad bands in the range 3100-3600 cm⁻¹ 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⁻¹ [6,7] and M-S in 310-350 cm⁻¹. In VO(IV) chelate frequency observed at 1030 cm⁻¹ is due to asymmetric stretching vibration [8]

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

Table 2 Magnetic and Spectral Data of [M(II)-MAAN]_n

Sr No	Coordination Polymers	μ_{eff} e. B.M.	Absorption nm	Bands kK	Assignment	Suggested Geometry	References
1	[VO(IV)-MAAN] _n H ₂ O	1.80	850 770 540 400	11.76 13.0 18.5 25.00	${}^3B_2 - {}^3E$ ${}^3B_2 - {}^3B_1$ ${}^3B_2 - {}^3A_1$	Octahedral geometry	8
2	[Mn(II)-MAAN] _n H ₂ O	6.23	833 400	12.00 25.00	${}^6A_{1g} - {}^4T_{1g}(4G)$ ${}^6A_{1g} - {}^4E_g(4D)$	Octahedral geometry	9 10
3	[Fe(III)-MAAN] _n 2H ₂ O	6.10	865 525 430	11.62 20.00 23.00	${}^6A_{1g} - {}^4T_{1g}$ ${}^6A_{1g} - {}^4T_{2g}$ ${}^6A_{1g} - {}^4T_{2g}$	Octahedral geometry	11 12
4	[Co(II)-MAAN] _n H ₂ O	5.38	833 440	12.00 22.72	${}^4T_{1g}(F)$ ${}^4T_{1g}(P)$ ${}^4T_{1g}(F)$ ${}^4T_{2g}(F)$	Octahedral geometry	12, 13 14
5	[Ni(II)-MAAN] _n H ₂ O	2.95	870 600 400	11.50 16.66 25.00	${}^3A_{2g} - {}^3T_{2g}(F)$ ${}^3A_{2g} - {}^3T_{1g}(F)$ ${}^3A_{2g} - {}^3T_{1g}(P)$	Octahedral geometry	15

Mössbauer study of [Fe(III)-MAAN]_n 2H₂O polymer shows well resolved doublet. Isomer shift (δ) value found to be 6.2mm s⁻¹. Five 3 d electron are equally populated. Therefore, no valancy contribution should be expected for quadrupole splitting. In case of perfect cubic symmetry no quadrupole 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 ΔE_Q 0.87.

X-ray diffraction pattern of [Co(II)-MAAN]_n H₂O and [Ni(II)-MAAN]_n H₂O 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 [Co(II)-MAAN]_n

a= 27.091

b= 34.287

c= 7.756

n	2 Θ Obs.	2 Θ Cal.	H	K	L	d Obs.
1	6.59	6.54	2	0	0	13.412
2	11.41	11.41	0	0	1	7.756
3	12.15	12.15	1	1	1	7.284
4	13.80	13.80	0	3	1	6.418
5	17.41	17.41	4	0	1	5.094
6	22.31	22.30	6	4	0	3.986
7	31.49	31.49	1	12	0	2.841
8	36.33	36.29	1	12	0	2.841
9	36.33	36.29	0	4	3	2.473
10	37.95	37.98	5	13	0	2.371
11	47.33	47.32	8	14	1	1.921
12	55.04	55.05	7	18	1	1.668
13	68.91	68.91	13	19	0	1.363
14	78.21	78.21	6	27	0	1.222

Table 4 X- ray Diffraction Data of [Ni(II)-MAAN]_n

a= 35.626

b= 20.820

c= 5.605

n	2 Θ Obs.	2 Θ Cal.	H	K	L	d Obs.
1	16.38	16.38	0	1	1	5.412
2	17.50	17.50	3	0	1	5.069
3	20.37	20.37	0	3	1	4.360
4	22.23	22.22	6	1	1	3.999
5	26.43	26.44	10	2	0	3.372
6	34.38	30.40	1	6	1	2.942
7	37.85	34.84	2	8	0	2.574
8	37.10	37.07	13	4	0	2.424
9	46.43	46.44	12	3	2	1.956
10	52.47	52.49	16	0	2	1.744
11	54.28	54.29	9	0	3	1.690
12	63.63	63.66	17	7	2	1.462
13	89.03	89.03	7	11	14	1.100

Thermogravimetric study of [M-(II)-MAAN]_n polymers shown in **Fig-3**. In [VO(IV)-MAAN]_n.4H₂O polymer undergoes degradation in two steps. Initially polymer undergoes dehydration by losing four hydrated molecules below 125 °C. After 125 °C gradual mass losses is observed followed by rapid decrease in weight in the range 375 °C – 425 °C. Residue formed at this stage corresponds to vanadyl sulphide which further undergoes oxidation. During the oxidation of sulphide to vanadyl sulphate increase in weight is observed beyond 550 °C.

[Mn(II)-MAAN]_n.2H₂O polymer loss below 100 °C two hydrated molecules and free part of ligand. This hydrated species is stable upto 375 °C. After 375 °C sudden loss in weight is observed. Residue obtained at 600 °C may be of Mn(SCN)₂. [Fe(III)-MAAN]_n.3H₂O TG curve shows loss of

three hydrated molecule below 100°C . After this dehydration polymer undergo rapid degradation upto 275°C . Residue obtained in the final step may be of $\text{Fe}_2(\text{SO}_4)_3$. **[Co(III)-MAAN] $_n$.H $_2$ O** polymer shows loss of one molecule of water of hydration below 100°C . After this continuous mass loss upto 525°C . Beyond this increase in weight is observed. Increase in weight may be due to the oxidation of metal sulphide to metal sulphate. Residue may be the mixture of $\text{Co}(\text{SCN})_2 + \text{CoS}$.

[Ni(II)-MAAN] $_n$.H $_2$ O from TG curve polymer start degradation around 100°C . After 100°C rapid mass losses observed. Beyond 200°C to 325°C rate of mass loss is gradual. Near 325°C inflection in mass loss is observed. Residue obtained at 725°C may be of $\text{Ni}(\text{SCN})_2 + \text{NiS}$. Thermogram of **[Zn(II)-MAAN] $_n$.2H $_2$ O** polychelate indicate loss of two hydrated water molecule below 100°C . After this temperature polymer losses its mass gradually upto 400°C . Followed by sudden decrease in mass. Residue at 600°C may be of $\text{Zn}(\text{SCN})_2 + \text{ZnS} + \text{ZnSO}_4$.

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-(II)-MAAN] $_n$.xH $_2$ O Coordination Polymers

Sr No	Coordination Polymers	Activation Energy (KCal/mole)	
		Temperature range	
		150 $^{\circ}\text{C}$ – 450 $^{\circ}\text{C}$	Room Temp. – 150 $^{\circ}\text{C}$
1	[VO(IV)-MAAN] $_n$.4H $_2$ O	13.180	3.860
2	[Mn(II)-MAAN] $_n$.2H $_2$ O	5.418	2.763
3	[Fe(III)-MAAN] $_n$.3H $_2$ O	5.117	2.763
4	[Co(III)-MAAN] $_n$.H $_2$ O	9.673	4.763
5	[Ni(II)-MAAN] $_n$.H $_2$ O	11.843	8.980
6	[Zn(II)-MAAN] $_n$.2H $_2$ O	7.537	3.684

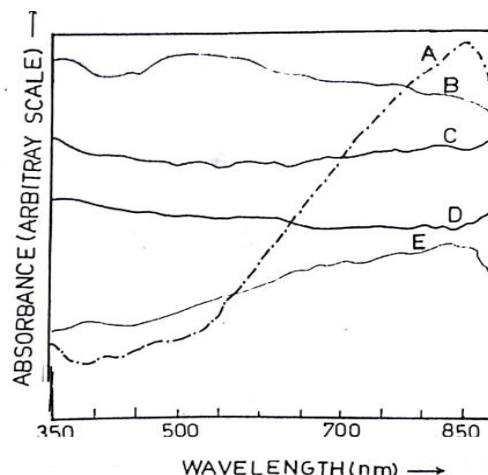


FIG. 1 - DIFFUSE REFLECTANCE SPECTRA OF
A = [Fe(III)-COHD MAAN] $_n$.3H $_2$ O, B = [VO(IV)-MAAN] $_n$.4H $_2$ O,
C = [Co(III)-MAAN] $_n$.H $_2$ O, D = [Ni(II)-MAAN] $_n$.H $_2$ O,
E = [Mn(II)-MAAN] $_n$.2H $_2$ O, I

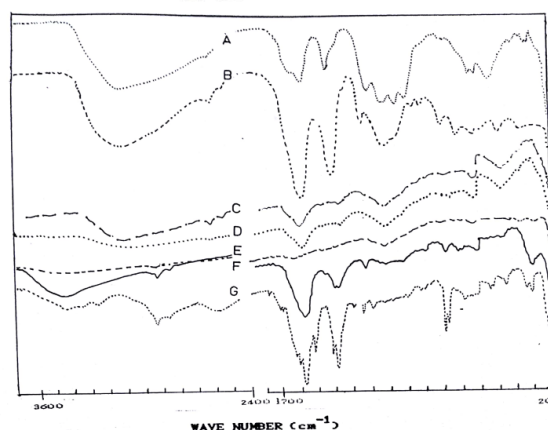


FIG. 2 - INFRARED SPECTRA OF
A = [VO(IV)-MAAN] $_n$.4H $_2$ O, B = [Mn(II)-MAAN] $_n$.2H $_2$ O,
C = [Fe(III)-COHD MAAN] $_n$.3H $_2$ O, D = [Co(III)-MAAN] $_n$.4H $_2$ O,
E = [Ni(II)-MAAN] $_n$.H $_2$ O, F = [Zn(II)-MAAN] $_n$.2H $_2$ O, G = MAAN.

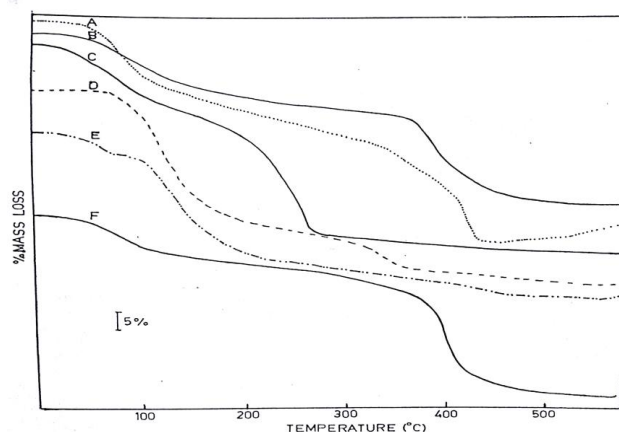


FIG. 3 - THERMOGRAVIMETRIC ANALYSIS OF
A = [VO(IV)-MAAN] $_n$.4H $_2$ O, B = [Mn(II)-MAAN] $_n$.2H $_2$ O,
C = [Fe(III)-COHD MAAN] $_n$.3H $_2$ O, D = [Ni(II)-MAAN] $_n$.4H $_2$ O,
E = [Co(III)-MAAN] $_n$.4H $_2$ O, F = [Zn(II)-MAAN] $_n$.2H $_2$ O.

The tentative structure for polymers is as follows.

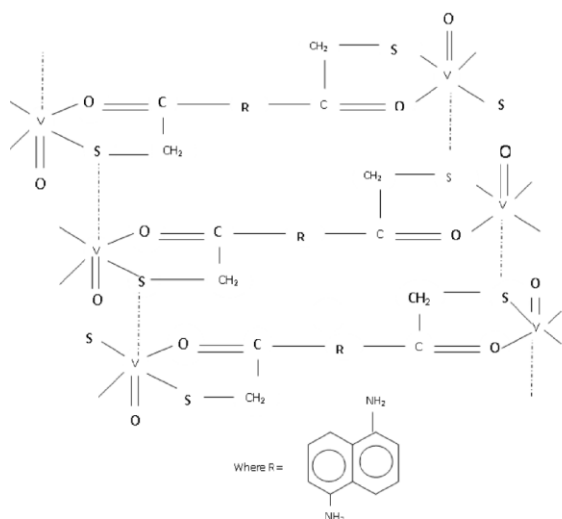


Fig. 4

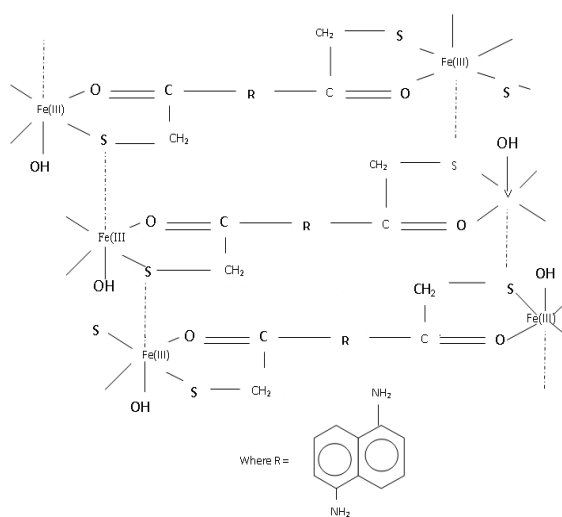


Fig 5

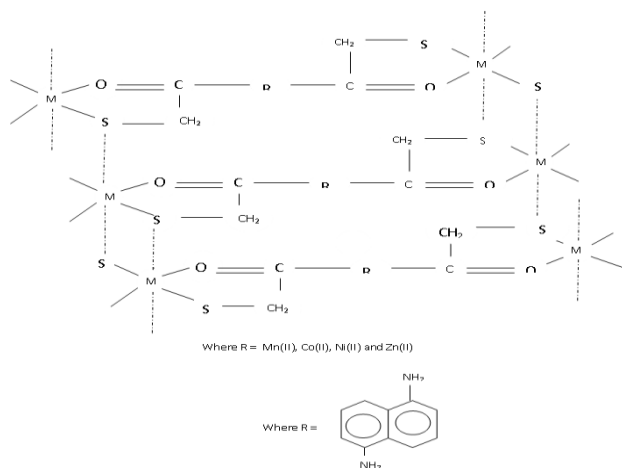


Fig.6

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