

## Preparation and Characterisation of Some New Polymeric Chelates of Transition Metal Ions

I.M. SARIN, H.D. JUNEJA and K.N. MUNSHI\*

*Department of Chemistry*

*PGTD Campus, Nagpur University, Nagpur-440 010, India*

Polymeric complexes of 4,4'-bis-mercaptoacetamide diphenyl (BMAD), 4,4'-bis-mercaptoacetamide-3,3'-dimethyl diphenyl (BMADD) and 4,4'-bis-mercaptoacetonamide-3,3'-dimethyl diphenyl (BBMPDD) have been synthesised by the interaction of these ligands with transition metal ions, viz., Mn(II), Co(II), Ni(II), Cu(II) and Zn(II), under suitable experimental conditions. The extent of interaction of metal to ligand has been established as  $[ML]_n$  in case of Mn(II), Cu(II) and Zn(II) polymers whereas  $[ML(H_2O)_2]_n$  in case of Co(II) and Ni(II) polymers. The composition was established on the basis of elemental analysis while electronic spectra, magnetic moment, infrared spectral studies and thermogravimetric analysis have been used for the structural aspects of the chelates. Thermal studies of these polymeric chelates indicate their stability up to 380–440°C. All these polymeric chelates were found to be amorphous and insoluble in almost all organic solvents which indicates their high polymeric nature.

### INTRODUCTION

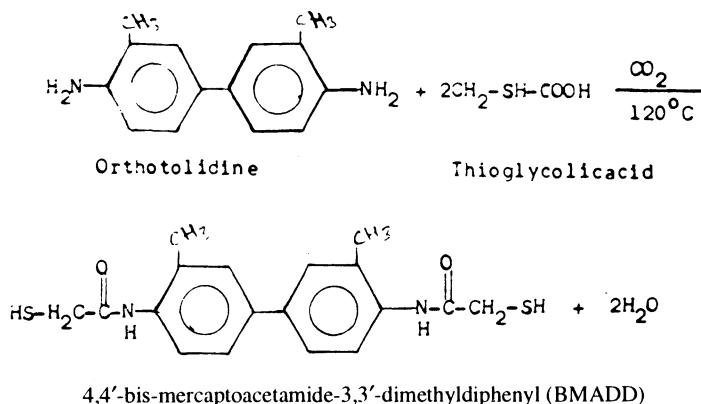
Polymeric complexes of bis-mercapto ligands containing nitrogen and sulphur as donor atoms show the formation of stable five or six-membered ring with transition metal ions. These chelates have been synthesised and characterised on the basis of elemental analysis, infrared spectra, electronic spectra, magnetic and thermal studies.

### EXPERIMENTAL

All chemicals used as starting material were of pure quality and the solvents which were used were distilled twice.

A single beam Karl-Zeiss-2p-spectrophotometer was used for recording reflectance spectra of the compounds. Magnesium carbonate was used as a reference material. The infrared spectra of the ligands and polymeric complexes were recorded on Perkin-Elmer 983 in the range of 4000–200  $\text{cm}^{-1}$  using KBr pellets. Magnetic susceptibility of the chelates was studied by Gouy's method using  $\text{Hg}[\text{Co}(\text{CNS})_4]$  as a reference substance. Thermogravimetric analysis was done





### Synthesis of Coordination Polymers

The hot solutions of metal acetates (0.1 M) and bis ligands (0.1 M) were mixed in a beaker which was then kept for digestion (at about 80°C) on water bath for about 30 minutes. The products so obtained were filtered and washed a number of times with dimethyl formamide (DMF) and then with absolute alcohol to remove unreacted ligand and metal acetates. These products were found to be insoluble in almost all organic solvents. The color, physical appearance and elemental analysis of ligands and polymeric complexes are given in Table-1.

## RESULTS AND DISCUSSION

### Spectral and Magnetic Studies of the Coordination Polymers

*Mn(II)-MBAD, BMADD and BBMPDD polymers:* Band appearing at 20.83 kK in Mn(II)-BMAD and 23.25 kK in case of BMADD-Mn(II) polymeric complexes are assigned to  ${}^6\text{A}_1 \rightarrow {}^4\text{E}(\text{G})$  transition. While in case of Mn(II)-BBMPDD the band appearing at 18.86 kK is assigned due to charge transfer in a tetrahedral field. Magnetic moment values of these polymers, indicating the presence of five unpaired electrons, support the tetrahedral geometry.

*Co(II)-BMAD, BMADD and BBMPDD polymers:* Magnetic moment values of these Co(II)-polymers favour the octahedral geometry which is strongly supported by electronic spectra, showing band at 18.86 kK in case of Co(II)-BMAD and 23.80 kK in case of Co(II)-BMADD and 16.16 kK in case of Co(II)-BBMPDD which are assigned to  ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$  transition in octahedral environment.

*Ni(II)-BMAD, BMADD and BBMPDD polymers:* Ni(II)-BMAD polymeric complex exhibits bands at 20.83 kK and 17.54 kK which is assigned to  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$  transition. While in case of Ni(II)-BMADD and Ni-BBMPDD the band appears at 16.66 kK and 17.54 kK respectively which is assigned to  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$  transition in octahedral field. The magnetic moment values of these Ni(II)-polymers also favour the geometry of octahedral complexes.

Electronic spectra of Cu(II) BMAD and BMADD complexes indicate the presence of sharp bands at 20.00 kK and 19.23 kK which is assigned to charge transfer while in case of Cu-BBMPDD the band appearing at 16.66 kK is assigned

to  $d_u^2$ ,  $d_x^2 \rightarrow d_{x^2-y^2}$  transition in square-planar environment. The magnetic moment values indicate the presence of one unpaired electron.

TABLE-I  
COLOUR, PHYSICAL APPEARANCE AND ELEMENTAL ANALYSIS OF LIGANDS  
AND POLYMERIC COMPLEXES

S. No.	Name of species (Colour)	Elemental analysis %, Found (Calcd.)					Decomposition Temperature (°C)
		C	H	N	S	M	
1.	BMAD (white)	56.19 (57.84)	4.95 (4.82)	8.91 (8.55)	20.12 (19.28)	— —	286
2.	BMADD (white)	60.95 (60.07)	5.91 (5.55)	7.88 (7.75)	18.12 (17.78)	— —	288
3.	BBMPDD (white)	62.34 (61.86)	6.51 (6.18)	6.36 (6.85)	17.15 (16.59)	— —	261
4.	{[Mn(BMAD)]H <sub>2</sub> O} <sub>n</sub> (yellowish white)	48.86 (47.45)	4.12 (3.45)	7.46 (6.91)	16.36 (15.59)	13.41 (13.54)	390
5.	[Co(BMAD)(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub> (dark pink)	45.74 (44.97)	4.35 (3.29)	7.41 (6.59)	16.49 (15.06)	15.12 (13.82)	433
6.	[Ni(BMAD)(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub> (dark green)	45.78 (44.97)	4.12 (3.29)	7.41 (6.59)	16.84 (15.06)	14.13 (13.82)	420
7.	{[Cu(BMAD)]H <sub>2</sub> O} <sub>n</sub> (light green)	46.84 (46.64)	4.37 (3.41)	7.12 (6.81)	15.94 (15.54)	15.24 (15.44)	390
8.	[Zn(BMAD)] <sub>n</sub> (dirty white)	48.48 (49.58)	4.76 (5.09)	6.88 (7.08)	16.62 (16.19)	17.11 (16.45)	380
9.	{[Mn(BMADD)]H <sub>2</sub> O} <sub>n</sub> (yellow)	50.95 (50.13)	4.95 (4.17)	6.84 (6.49)	15.25 (14.85)	12.88 (12.74)	360
10.	[Co(BMADD)(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub> (light brown)	48.24 (47.71)	4.16 (3.71)	6.27 (6.18)	14.85 (14.13)	12.91 (12.96)	410
11.	[Ni(BMADD)(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub> (dark green)	48.14 (47.71)	4.05 (3.97)	6.67 (6.18)	14.76 (14.13)	12.93 (12.96)	325
12.	{[Cu(BMADD)]H <sub>2</sub> O} <sub>n</sub> (green)	50.09 (49.13)	4.27 (4.09)	6.56 (6.36)	15.23 (14.55)	15.01 (14.46)	320
13.	[Zn(BMADD)] <sub>n</sub> (yellowish white)	51.75 (51.03)	4.46 (4.72)	6.62 (6.58)	15.65 (15.12)	16.05 (15.28)	440
14.	{[Mn(BBMPDD)H <sub>2</sub> O]H <sub>2</sub> O} <sub>n</sub> (ash colour)	53.15 (52.29)	5.44 (4.79)	6.36 (6.10)	15.00 (13.94)	11.96 (12.34)	420
15.	[Co(BBMPDD)(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub> (dark brown)	50.01 (49.92)	4.92 (4.57)	6.21 (5.82)	14.28 (13.31)	13.45 (12.21)	440
16.	[Ni(BBMPDD)](H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub> (dark green)	51.05 (49.92)	5.34 (4.57)	6.31 (5.82)	14.35 (13.31)	13.85 (12.21)	345
17.	{[Cu(BBMPDD)]H <sub>2</sub> O} <sub>n</sub> (green colour)	52.25 (51.32)	5.41 (4.72)	6.38 (5.98)	14.85 (13.68)	14.92 (13.59)	390
18.	[Zn(BBMPDD)] <sub>n</sub> (white)	53.69 (53.18)	5.39 (5.31)	6.41 (6.08)	14.52 (14.18)	19.28 (18.15)	418

*Infrared Spectra:* Sharp band present in the region  $3307\text{ cm}^{-1}$  in case of BMAD and at  $3253\text{ cm}^{-1}$  in case of BMADD and at  $3284\text{ cm}^{-1}$  in BBMPDD ligand is due to the presence of stretching vibration of  $\text{—NH}$  group<sup>1</sup>. The band appearing in the region of  $1690\text{—}1600\text{ cm}^{-1}$  may be assigned to  $\text{C=O}$  stretching vibration<sup>2</sup>. In case of BMAD, BMADD and BBMPDD a sharp band is observed in the region  $1450\text{—}1400\text{ cm}^{-1}$  which may be assigned to  $\text{—S—CH}_2$  band. A medium band in the region of  $2575\text{—}2500\text{ cm}^{-1}$  is observed in these ligands because of the  $\text{S—H}$  stretching frequency whereas a medium band in the range between  $1350\text{—}1250\text{ cm}^{-1}$  may be assigned due to  $\text{C—N}$  group frequency.

The infrared spectra of the polymers show lowering of  $\text{C—N}$  group frequency of the bis-ligands after the formation of polymeric complexes by donating lone pair of electrons of nitrogen to the metal atom. However, disappearance of  $\text{S—H}$  stretching frequency in the region of  $2575\text{—}2500\text{ cm}^{-1}$  in case of these polymeric complexes clearly indicates that the formation of polymeric complexes with metal ion takes place by the replacement of the protons of the thio group. This fact is also supported by the increase in  $\text{—S—CH}_2$  stretching frequency in the polymers<sup>3</sup>.

A sharp band which appears in the region of  $680\text{ to }660\text{ cm}^{-1}$  may be assigned to  $\text{M—N}$  stretching vibration<sup>5</sup> while weak band appearing in the region of  $500\text{ to }300\text{ cm}^{-1}$  is assigned to  $\text{M—S}$  stretching vibration in polymers<sup>6-8</sup>.

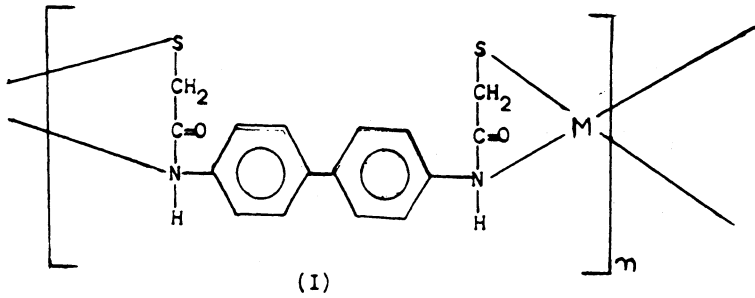
The free  $\text{H—O—H}$  stretching vibration of water<sup>9</sup> are generally observed in the range of  $3500\text{—}3200\text{ cm}^{-1}$ . However, in  $\text{Mn(II)}$  and  $\text{Cu(II)}$  polymers this peak has been found to be merged with  $\text{N—H}$  band and appears as a broad band in this region. Medium band appearing in the region  $820\text{—}760\text{ cm}^{-1}$  in case of  $\text{Co(II)}$  and  $\text{Ni(II)}$  polymers is due to the presence of water of coordination<sup>10</sup>.

*Thermogravimetric analysis:* It was carried out by maintaining heating rate of about  $5^\circ\text{C/minute}$  with the help of temperature control devices. The temperature from which polymers start decomposing to the temperature at which it forms a stable metal oxide is termed as decomposition range. The decomposition temperature was determined by half decomposition curve method.

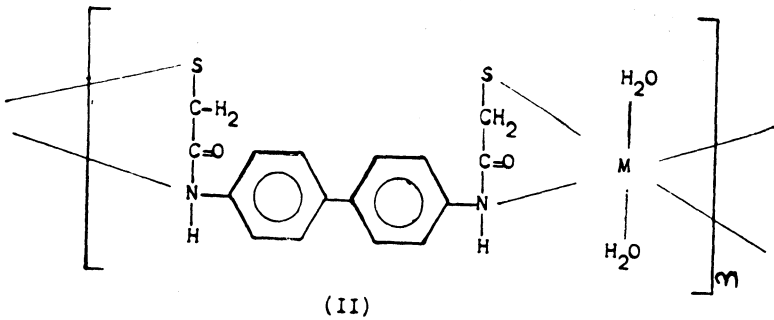
The decomposition temperature of polymeric complexes of BMAD, BMADD and BBMPDD are given in Table-1.

### **Proposed structures of polymeric complexes of BMAD, BMADD and BBMPDD ligands**

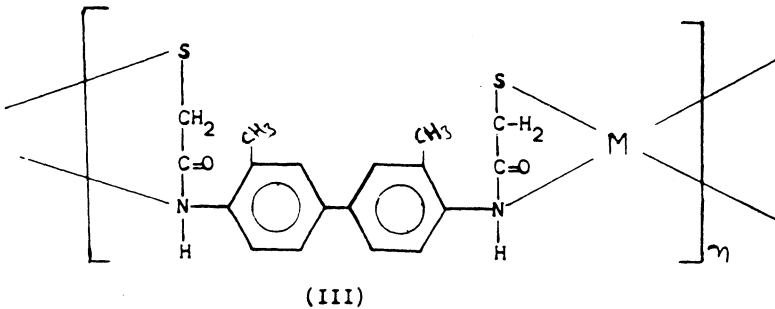
On the basis of the results obtained from elemental analysis, infrared spectra, magnetic studies and thermogravimetric studies the tentative structures proposed for all the polymeric complexes are given below. Structure I is proposed for  $\text{Mn(II)}$ ,  $\text{Cu(II)}$  and  $\text{Zn(II)}$  BMAD polymers and Structure II for  $\text{Co(II)}$  and  $\text{Ni(II)}$  BMAD polymers, whereas structures III, IV, V and VI are proposed for BMADD and BBMPDD polymers respectively.



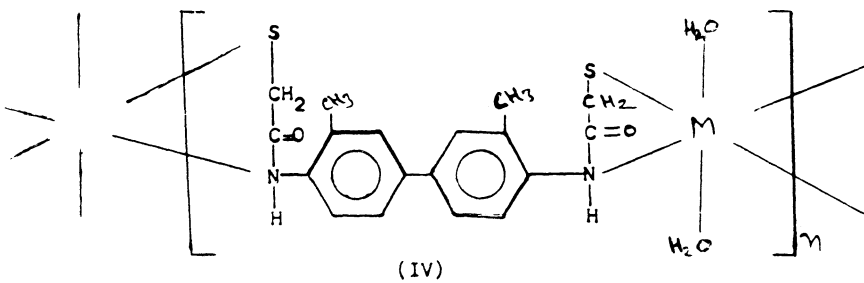
M = Mn(II), Cu(II) and Zn(II)



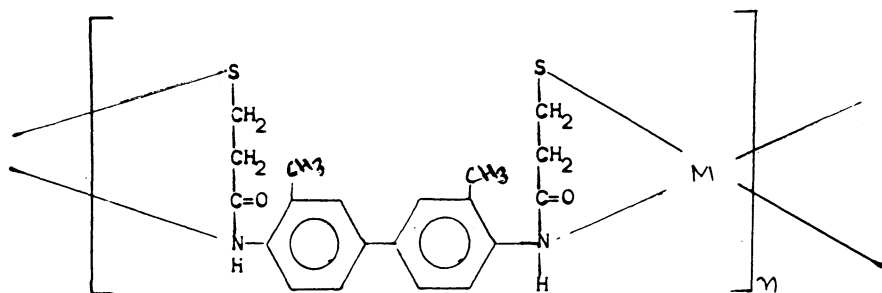
M = Co(II) and Ni(II)



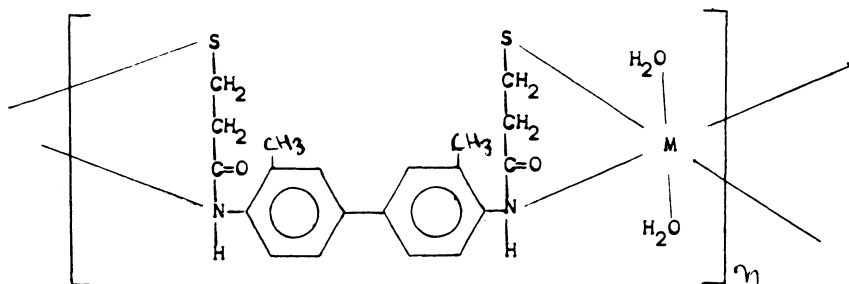
M = Mn(II), Cu(II) and Zn(II) BMADD polymers



M = Co(II), and Ni(II) BMADD polymers



M = Mn(II), Cu(II) and Zn(II) BBMPDD polymers



M = Co(II) and Ni(II) BBMPDD polymers

### REFERENCES

1. R.J. Dyer, Applications of Absorption Spectroscopy of Organic Compounds, p. 37 (1978).
2. N.L. Alport, W.E. Keiser and H.A. Szymanski, I.R. Theory and Practice of Infra-red Spectroscopy, p. 268 (1963).
3. N.B. Colthup, L.H. Daly and S.S. Wiberly, Introduction to I.R. and Raman Spectroscopy Academic Press, New York, p. 306 (1964).
4. R.J. Dyer, Applications of Absorption Spectroscopy of Organic Compounds, p. 38 (1978).
5. K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley-Interscience (1970).
6. D.M. Adams and J.B. Cornoli, *J. Chem. Soc.*, 1299 (1968).
7. Kaguo-Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, p. 167 (1970).
8. *Ibid.*, p. 166.
9. F.W. Moore and M.L. Larsen, *Inorg. Chem.*, **6**, 998 (1967).
10. K.W. Bagnall, D. Brown and D.G. Holah, *J. Chem. Soc.*, 1149 (1968).

(Received: 26 April 1997; Accepted: 20 October 1997)

AJC- 1368