Polymer Bulletin 23, 51–56 (1990)

Polymer Bulletin

Coordination polymers of Zn(II) and N,N'-bis (carboxymethyl) dithiooxamide

A sulphur-oxygen coordinated product

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SUMMARY

Coordination polymers were synthesized using N,N'-Bis (carboxymethyl) dithiooxamide (NN'CMDTO) and Zinc(II) salts. The complexes were characterized by elemental analyses, IR spectral studies, TGA and viscosity measurements. In the proposed structures the ligand was supposed to be coordinated to metal through sulphur and oxygen.

INTRODUCTION

In a programme of synthesizing thermally resistant polymeric complexes of S and N containing ligands we have chosen dithiooxamide and its various substitutes which generally form S,N or S,S coordinated complexes with metal ions (1-5). For the first time we observed that a substitute of dithiooxamide, viz. N,N'-Bis (carboxymethyl) dithiooxamide behaves as S,O coordinating ligand with zinc(II) salts to form polymeric complexes. Present communication reports the synthesis and the characterization with elemental analysis, IR spectra, thermogravimetry and viscosity measurements.

EXPERIMENTAL PART

Materials : All the chemicals were of A.R. grade and were used as such.

Synthesis of Ligand : The ligand NN'CMDTO was prepared by the reported method (6).

Preparation of Complexes : The complexes were prepared using 1:2 ligand to metal salt mole ratio. The ligand was dissolved in DMF-ethanol (equal volumes) mixture and metal salts were dissolved in minimum quantity of water. The solutions were warmed, mixed and then refluxed over a steam bath for about 12 hours. Complexes were obtained as pale coloured powders, which were filtered, washed with solvent mixture and ethanol and finally dried over P_2O_5. The metal salts used were hydrated zinc chloride, acetate and sulphate.

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Measurements : C,H,N analyses were carried out with a Carloerba elemental analyser. The metal content was determined by decomposing the complexes with conc. HNO_3 and titrating against EDTA. The IR spectra were recorded over the 4000-200 cm^{-1} range on a Perkin-Elmer spectro photometer using CsI pellets. Thermogravimetric analysis was carried out on a Perkin-Elmer Thermal Analyser in air at the heating rate of 15°C/min.
Viscosity Measurements : A 0.2 mM solution of ligand was prepared in 1:1 DMF-ethanol mixture, its flow time (i.e.T_0) through a capillary viscometer was recorded.

RESULTS AND DISCUSSION

Although we have employed different metal salts, viz. zinc sulphate, zinc acetate and zinc chloride for the preparation of complexes it was found that anions do not appear in the final structure of complexes. The role of anions appears only to affect the yield of complex formation. Under identical conditions zinc acetate gives the highest yield(79%), zinc chloride the lowest(42%) and the yield of polymeric complex is moderate with zinc sulphate(67%).

Analytical data (Table 1) are in accordance with the 2:1 metal to ligand mole ratio for the complexes. Slight variation in the compositions of A,B, and C (the complexes prepared with acetate, sulphate and chloride respectively) may be due to their polymeric nature. Similar observations were made in the case of nickel(II) complexes(7). The complex is insoluble in common organic solvents but dissolves in aqueous NaOH or KOH probably due to presence of acidic hydrogen.

Table 1 : Analytical Data - Found/(Calcd.)

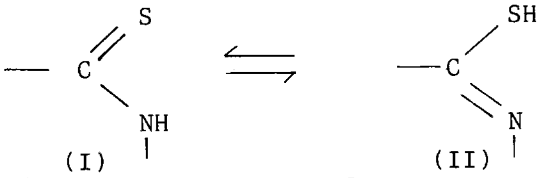
COMPOUND	C%	H%	N%	S%	Zn%
NN'CMDTO	30.01 (30.25)	3.38 (3.36)	11.59 (11.79)	27.30 (26.80)	-
$Zn_2L.2H_2O$(A)	18.18 (17.92)	1.98 (1.99)	6.26 (6.90)	-	32.45 (32.33)
$Zn_2L.2H_2O$(B)	18.75 (17.92)	2.10 (1.99)	6.88 (6.90)	-	31.64 (32.33)
$Zn_2L.2H_2O$(C)	18.81 (17.92)	2.47 (1.99)	6.42 (6.90)	-	32.07 (32.33)

Important IR bands and their assignments are given in Table 2.The IR spectrum of ligand is compared with the spectra of complexes to illucidate the nature of coordination. In the earlier reports dithiooxamide has been shown to S,S or S,N coordinated ligand (1-5), whereas in the present investigation with substituted dithiooxamide our observation is contrary to this.The band due to ν C=0 which is observed in the spectrum of ligand at 1720 cm^{-1} appears as a broad and very strong band at 1620 cm^{-1} in the spectra of complexes. The lowering of this

Table 2

NN'CMDTO	Polymer(A)	Polymer(B)	Polymer(C)	Assignments
3160s	3340vb	3320vb	3340vb	νNH and νOH
3040w	3140sh	3140sh	3140sh	
1720s	1610s	1610s	1610s	νC=O, δNH, δOH,
1510m	1570sb	1570sb	1575sb	νC=N
1440m	1430s	1435s	1440s	NCS group
1390m	1390s	1380s	1385s	vibrations
1360m		1360m	1360sh	
1090s	1090s	1090s	1090s	ν C-O
870s	850s	840s	850s	ν C=S
	450m	450m	450m	ring vibrations
	360m	360m	360m	ν Zn-S

band by 100 cm^{-1} on coordination indicates bonding through oxygen.Broadening of this band may be due to merger of absorption associated with uncoordinated C=O groups present in the end units of the ligand in the polymeric complexes. Further the band in 1510 cm^{-1} region may be assigned to δNH and νCN.On complex formation this band shifted towards higher wavenumber side which may be due to increase in C=N character. This observation suggests the absence of coordination through N,as we know that on coordination through N this band either remains unchanged or is shifted towards lower wavenumber (9).In dithiooxamides the thioamide groups exist in tautomeric equilibrium. Salt linkage with sulphur is proposed in the complexes under study.



-----eq. 1

This salt linkage will shift the equilibrium (eq.1) towards right side and therefore the cntribution of structure II will be more in the complexes.This observation is reflected in the IR spectra of complexes. This further explains the greatly reduced intensity of νNH band observed in the range 3120-3300 cm^{-1}. In the proposed structure (fig.1),the repeat unit of the coordination polymer contains C=N group and NH band is absent, and the little absorption from νNH may be due to end units of coordination polymer, where NH group is present. The band at 870 cm^{-1} in the spectrum of ligand has main contribution of νC=S of thioamide group, on coordination it shifts by 20-30 cm^{-1} and is

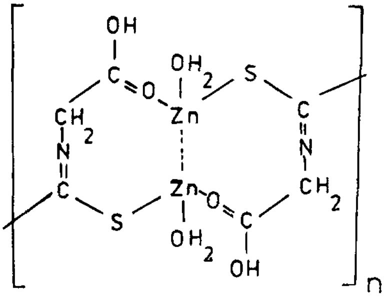


Fig. 1

observed at 840-850 cm^{-1} in the spectra of complexes, which supports coordination of metal through sulphur. In far-infrared spectra of complexes a band observed at 360 cm^{-1} is assigned for ν Zn-S (9). Thus on the basis of IR spectral studies it is concluded that coordination has been taken place through sulphur and oxygen (fig.1). Zn-Zn bonding has been propsed to satisfy the coordination number of zinc(II) as in the case of copper(II) complexes (10).

It is observed that the complexes decompose before melting. Oxidative thermogravimetric analysis (fig.2) has been done, by heating complexes upto 900°C, to study the thermal stability of all the complexes. The first major weight loss is observed between 190-240°C range which corresponds to the calculated percentage weight loss for two water molecules (8.9%). The highest rate of weight loss (about 0.0026 mg/s) was

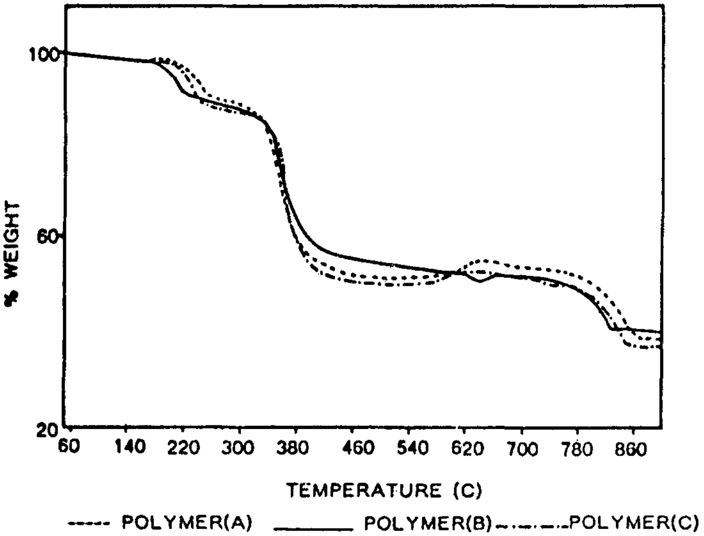


Fig. 2

observed at ∿360°C. This can be considered as the onset of decomposition of ligand molecule. In the structure assigned to the coordination polymer two $-CH_2-COOH$ groups contribute 29.3% to the repeat unit and the sample undergoes about 30% weight loss in between 320-400°C. Therefore the weight loss between this temperature range may be due to loss of carboxymethyl fragment.

On the basis of physical properties such as high thermal stability, low solubility, variable composition (in A,B and C) and IR spectral studies the polymeric structure (fig.1) assigned to the coordination complex is supported.

To further confirm the polymeric nature of complexes viscosity measurements were done. Zinc sulphate (0.4mM) was dissolved in ligand solution and flow time was recorded (i.e.T_1). The flow time at 20°C was measured after every 24 hours. A constant value was observed after about 100 hours. Relative viscosity at zero time was calculated as $\eta_0 = T_1/T_0$. Similar calculations were done for each value of T_2, T_3--- etc. A graph was ploted for relative viscosity vs time of reaction as shown in figure 3. This increase in viscosity is indicative of the polymeric nature of complexes.

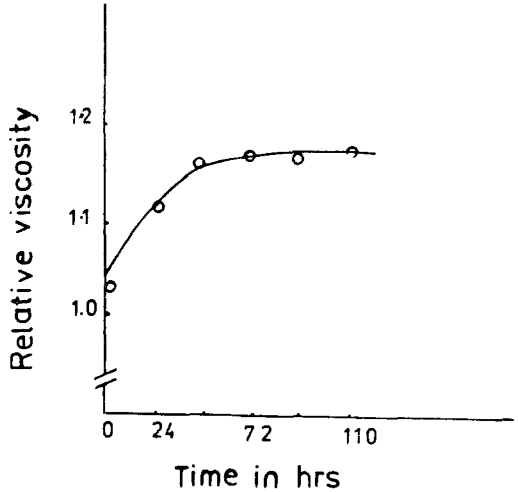


Fig. 3

Acknowledgement

The authors are thankful to Indian Space Research Organization, Department of Space, Govt. of India for financial assistance.

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Accepted November 7, 1989 C