

SYNTHETIC AND THERMAL STUDIES OF POLYMERIC CHELATES OF SOME BIS-BIURETS WITH FIRST TRANSITION SERIES METALS

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Abstract

Some new coordination polymers have been synthesized by combining adipyl bis-biuret and azelyl bis-biuret with metals of first transition series *viz* Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). They were characterized by elemental analysis, infrared and reflectance spectral and magnetic studies. A detailed thermal study was carried out and thermal stability compared. The results obtained have been discussed.

Keywords: bis-biurets, polymeric chelates, transition series metals, thermal studies

Introduction

Thermal degradation study provides valuable information on the thermal behavior of chelate polymers. Since polymeric chelates are thermally resistant and have a large number of practical applications, it is useful to investigate various species formed due to polymer degradation and the effects of heat on such polymers, to establish their thermal stabilities. The basis of calculation of kinetic data from TG curves in most of the methods are based on the Arrhenius equation. Šesták [1] has compared experimental and analytical methods of analysis.

Recently some chelate polymers have been synthesized, characterized and their thermal stability studied [2, 3]. Some new Rh(II) polymeric chelates were also studied for their thermal stability and their kinetic parameters for thermal decomposition have been carried out [4]. Earlier some work has been done in our laboratory on biuret polymeric chelate [5]. The present paper describes a detailed study of the synthesis and thermal degradation of polymeric chelates of adipyl bis-biuret and azelyl bis-biuret with metals of first transition series *viz* Mn(II), Co(II), Ni(II), Cu(II) and Zn(II).

Experimental

Chemical

All the chemicals used were of AR grade

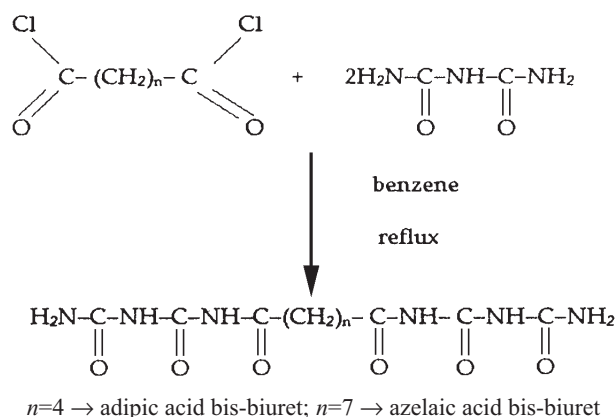
Instruments used

C, H and N were analysed on EA 1108 Elemental analyser Carlo Erba. FTIR were recorded on a Nicolet Magna IR 550 series 2, USA, using KBr pellet in the wavelength range, 400–4000 cm^{-1} at RSIC, Nagpur. Reflectance spectra was recorded on a single beam Karl Zeiss Jena, Specord M-400 spectrophotometer in the range 250–600 nm. Magnetic susceptibility of the polymeric chelates were determined by Gouy's method.

The non-isothermal TG measurement of coordination polymers were done at RSIC, Nagpur using Pt–PtRh thermocouple from 30 to 1000°C at a linear heating rate of 10°C min^{-1} in air. Mass loss was recorded continuously on the recorder.

Preparation of ligands

The ligands, adipyl bis-biuret and azelyl bis-biuret were synthesized by the condensation of biuret with the respective acid chlorides in aprotic medium.

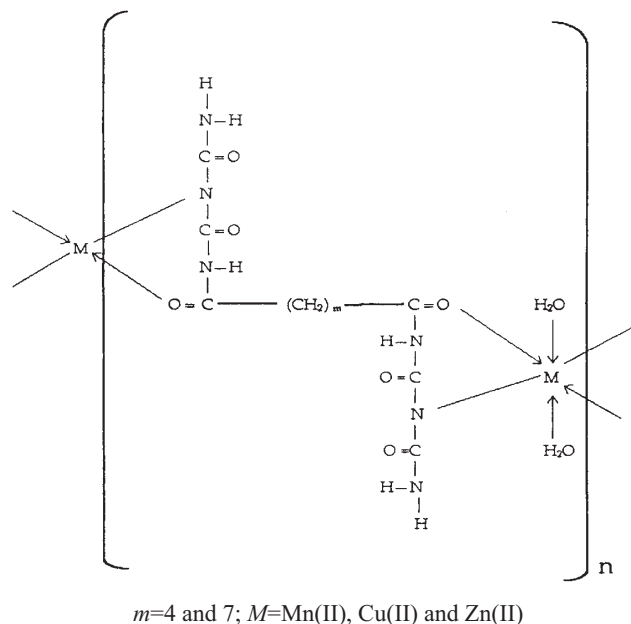


The ligands thus formed were recrystallized, dried and characterized by elemental analysis and IR spectral studies.

Preparation of coordination polymers

The coordination polymers were synthesized by the reaction between equimolar amounts of bis-ligands and metal acetates in minimum amount of DMF. The reaction mixture was heated in an oil bath at 120°C for 24 h. The following reaction produces the solid coordination polymers that were filtered and washed with hot DMF and al-

cohol to remove unreacted ligand and metal acetates. Then they were dried and characterized. Structures of polymers are given.



Results and discussions

The coordination polymers were analyzed for their elemental composition to propose the composition of polymeric units. TG studies indicated the nature of water present, whether lattice or coordinated.

Infrared spectral studies

The infrared spectrum of the ligand shows a broad peak in the region 3400 cm^{-1} which is attributed to $-\text{NH}_2$ group and which does not shift its position in the polymers indicating its non-participation in chelation. This band merges with another band due to lattice water in Co(II) polymeric chelate. A medium band in the region $2854\text{--}2880\text{ cm}^{-1}$ of the ligand is assigned to $-\text{NH}$ (imino) group [6]. In the polymeric chelate, it shows only a slight shifting towards the lower frequency region. This insignificant shift is due to the presence of other non-coordination $-\text{NH}$ groups present in the ligand. A careful examination of IR spectra however reveals that the intensity of $-\text{NH}$ bands in the polymeric chelates are reduced as compared to ligands, because only one $-\text{NH}$ group gives rise to $-\text{N}-\text{M}$ covalent band in the region.

The band in the region $1780\text{--}1550\text{ cm}^{-1}$ in ligands is attributed to $-\text{C}=\text{O}$ groups. It is shifted towards lower frequency region in the polymeric chelates. This indicates

the delocalisation of the electronic charge of $-C=O$ into the chelate ring. However, again due to the presence of non-chelated $-C=O$ groups, the effect is somewhat less prominent. A coordinate bond $-C=O \rightarrow M$ is expected to be formed which is further confirmed by the presence of a new band in the region $480-625 \text{ cm}^{-1}$ in the polymeric chelates which may be due to $O \rightarrow M$ band [7].

Table 1 Magnetic and electronic spectral data of polychelates

Polymer	Effective magnetic moment/B.M.	Electronic spectral absorbance/kk	Assignments	Stereochemistry
Mn-ADBB	6.35	23.80 15.62	$6A_1 \rightarrow 4E(G)$ C.T.	tetrahedral (h.s.)
Mn-AZBB	5.39	23.81 15.52	$6A_1 \rightarrow 4E(G)$ C.T.	tetrahedral (h.s.)
Co-ADBB	5.08	18.52 15.62	$4T_1 \rightarrow 4T_1 (P)$ $4T_1 \rightarrow 4A_2$	octahedral (h.s.)
Co-AZBB	4.42	18.52 15.15	$4T_1 \rightarrow 4T_1 (P)$ $4T_1 \rightarrow 4A_2$	octahedral (h.s.)
Ni-ADBB	4.83	23.81 13.51	$3A_2 \rightarrow 3T_1 (P)$ $3A_2 \rightarrow 3T_1 (F)$	octahedral (h.s.)
Ni-AZBB	3.46	20.83 17.86	$3A_2 \rightarrow 3T_1 (P)$ $3A_2 \rightarrow 3T_1 (F)$	octahedral (h.s.)
Cu-ADBB	2.10	22.73 14.29	C.T. $d_{xy}, d_{xz} \rightarrow dx^2 - dy^2$	sq. planar
Cu-AZBB	2.14	20.00 15.15	C.T. $d_{xy}, d_{xz} \rightarrow dx^2 - dy^2$	sq. planar
Zn-ADBB	diamagnetic	— —	— —	tetrahedral (h.s.)
Zn-AZBB	diamagnetic	— —	— —	tetrahedral (h.s.)

B.M. – Bohr Magnetron; kk – Kilokayser

Table 1 shows the results on effective magnetic and electronic spectral data on the basis of which the stereochemistry of the polymeric chelates are suggested [8–10].

Thermogravimetric analysis

In the present study, no sharp mass loss has been observed in the TG curves of the chelates indicating their polymeric nature. After the loss of lattice/coordinated water molecules, the polychelates gradually degrade. In case of two-step degradation, the first step is faster than the second step. This may be due to the fact that non-coordinated part of the ligand decomposes first, while the actually coordinated part decomposes later [11]. This step, in most cases, corresponds to the formation of stable metal oxide. Mostly higher oxides are formed [1, 2].

TG studies of ADBB polymeric chelates

The TG curve of a typical polymeric chelate of Mn(II)–ADBB is given in Fig. 1. The Mn(II), Cu(II) and Zn(II) polymeric chelates do not show the presence of lattice or coordinated water. The decomposition temperature range and half decomposition temperature of chelates are given in Table 2.

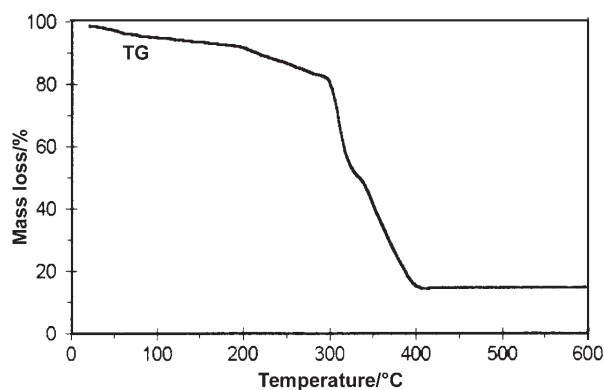


Fig. 1 TG curve of $[\text{Mn}(\text{ADBB})]_n$ coordination polymer

Table 2 Thermal data of ADBB and AZBB polymers

Polymer	Loss due to lattice water/%	Loss due to coordinated water/%	Loss due to decomp./%	Decomp. range/°C	Decomp. temp./°C
$[\text{Mn}(\text{ADBB})]_n$	–	–	85	200–400	310
$\{[\text{Co}(\text{ADBB})(\text{H}_2\text{O})_2](\text{H}_2\text{O})\}_n$	4.31 (4.21)	8.66 (8.43)	84	260–440	330
$[\text{Ni}(\text{ADBB})(\text{H}_2\text{O})_2]_n$	–	8.56 (8.44)	82	300–480	360
$[\text{Cu}(\text{ADBB})]_n$	–	–	82	220–460	330
$[\text{Zn}(\text{ADBB})]_n$	–	–	82	300–560	390
$[\text{Mn}(\text{AZBB})]_n$	–	–	50	200–390	270
$\{[\text{Co}(\text{AZBB})(\text{H}_2\text{O})_2](\text{H}_2\text{O})\}_n$	4.11 (3.98)	8.12 (7.95)	88	200–500	320
$[\text{Ni}(\text{AZBB})(\text{H}_2\text{O})_2]_n$	–	8.00 (7.94)	60	220–360	340
$[\text{Cu}(\text{AZBB})]_n$	–	–	76	220–480	380
$[\text{Zn}(\text{AZBB})]_n$	–	–	84	220–420	370

In case of Co(II) polymeric chelates, the curve shows mass loss corresponding to one molecule of lattice water and two molecules of coordinated water while Ni(II) coordination polymer shows an initial mass loss corresponding to two molecules of

coordinated water. The half decomposition temperatures and the decomposition range of the polymeric chelates are shown in Table 2.

TG studies of AZBB polymeric chelates

As an example, the TG curve of a typical Co(II)–AZBB chelate is shown in Fig. 2. The Mn(II), Cu(II) and Zn(II) polymeric chelates do not show presence of lattice or coordinated water. Co(II) polymeric chelate shows a mass loss between 80 and 130°C corresponding to one molecule of lattice water. After this there is another loss observed between 130 and 200°C, which is attributed to two molecules of coordinated water.

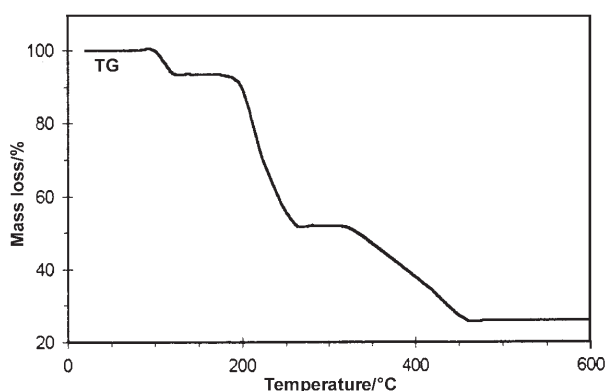


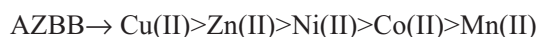
Fig. 2 TG curve of $\{[Co(AZBB)(H_2O)_2](H_2O)\}$ coordination polymer

In Ni(II) polymeric chelate however the loss corresponds to two molecules of coordinated water. The decomposition temperature ranges and the half decomposition temperatures are given in Table 2.

The lattice water molecules present in Co(II) polymers are lost below 150°C while coordinated water molecules are lost in the temperature range of 150–220°C in the coordination polymers of Ni(II) and Co(II). The presence of water molecules in these cases have also been supported by IR studies.

After the loss of lattice coordinated water molecules, the polychelates gradually degrade, the first step of degradation being fast compared to the second step. This may be due to the fact that non-coordinated part of ligand decomposes first while the actually coordinated part decomposes later.

The thermal stability of polymeric chelates were found to be in the order:



On the basis of spectral, magnetic and thermal studies, zinc polymers which show high thermal stability appear to have tetrahedral geometry. Co(II) and Ni(II) polymers however show octahedral geometry with two water molecules occupying

the trans position of the octahedra, Cu(II) polymers have the expected square planar geometry.

References

- 1 J. Šesták, *Talanta*, 13 (1966) 567.
- 2 K. Takaji, I. Tomita and T. Endo, *Macromolecules*, 30 (1997) 7386; *CA* 127 (1997) 346748.
- 3 A. Bajpai, S. Rai and U. D. N. Bajpai, *Polym. J.*, 29 (1997) 44; *CA* 126 (1997) 126137.
- 4 I. Rosca and D. Sibiescu, *Rev. Roum. Chim.*, 42 (1997) 615; *CA* 128 (1998) 175370.
- 5 N. Saxena and K. N. Munshi, *J. Thermal Anal.*, 37 (1991) 2259.
- 6 K. Aida, *J. Inorg. Nucl. Chem.*, 23 (1961) 155.
- 7 K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds', Wiley 1970.
- 8 A. B. P. Lever, 'Inorganic Electronic Spectroscopy', Elsevier 1965.
- 9 A. D. Liehr and C. Balhousen, *J. Ann. Phys.*, 7 (1969) 134.
- 10 B. N. Figgis and J. Lewis, *J. Prog. Inorg. Chem.*, 6 (1964) 37.
- 11 N. S. Bhave and V. N. Iyer, *J. Thermal Anal.*, 32 (1987) 1369.
- 12 E. Horowitz and J. P. Perros, *J. Research of National Bureau of Standards*, 69A, 1965, p. 1.