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Condensation Polymerization of *Bis*-(Salicylaldehydo) Metal(II) with Diamines

P. L. Maurya, B. V. Agarwala and Arun K. Dey*

Chemical Laboratories, University of Allahabad, Allahabad-211 002, India

Summary

Condensation of bis-(salicylaldehydo) metal(II) (metal = Be, Zn and Cd) and diamines (1,4-diaminobenzene or 4,4'-diaminodiphenyl) yield polymeric complexes which have been investigated for their characteristics, composition, structure, thermal stability and polymeric nature. The stable, powdery solids obtained by refluxing 1:1 bis-(salicylaldehydo) metal-chelate (in DMF) and the diamine (ethanolic) have the composition $-(ML)-_n$ and are insoluble in common organic solvents. I.R. study indicates that salicylaldehyde molecule is bonded to the metal ion through the oxygen atoms of phenolic and aldehydic groups in bis-(salicylaldehydo) metal-chelates. On interaction with the diamines, the polymeric complexes are formed, the nitrogen atoms of the amino groups replacing the aldehydic oxygens. The terminal nitrogens of the diamine, bridge two bis-(salicylaldehydo) metal-chelates, and the polymeric chain grows in a similar manner. The complexes obtained from 4,4'-diaminodiphenyl are thermally more stable than those from 1,4-diaminobenzene. The order of thermal stability of the polymers is : Be $\backsim$ Zn > Cd.

Introduction

Polymerization reactions of monomeric metal-chelates with one another through tne reacting groups of the ligands have been studied by BAILES and CALVIN 1947, and MARVEL et al 1960. Polymeric Schiff base complexes have also been synthesized by the interaction of coordinated metal(II) salicylaldehyde with methylenedianiline (DRINKARD and CHAKRAVARTY 1960).

Here, polymeric metal-complexes have been synthesized by the condensation of bis-(salicylaldehydo) metal(II) (metal = Be, Zn and Cd) with 1,4-diamino-

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* For correspondence

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benzene (DBA) or 4,4'-diaminodiphenyl (DADP), and their compositions, structures and thermal stabilities are described.

Experimental

Salicylaldehyde (BDH AnalaR), and 1,4-diaminobenzene and 4,4'-diaminodiphenyl (Chempure) were used. Metal salts and solvents employed were as reported earlier (DEY et al 1979).

An aqueous-ethanolic solution of 0.01 mole of the metal salt, [containing 1.77 g of $BeSO_4.4H_2O$, 2.19 g of $Zn(CH_3COO)_2.2H_2O$ or 2.66 g of $Cd(CH_3COO)_2.2H_2O$] was mixed with 0.02 mole salicylaldehyde (2.18 ml in 25 ml ethanol) (metal : salicylaldehyde = 1:2). The mixture was stirred for half an hour and then refluxed over a water bath for 2-3 h as necessary, and the separated bis-(salicylaldehydo) metal(II)-chelate [M(II)-SAL] was filtered, washed with ether and dried, and analyzed for metal, carbon and hydrogen (Table 1).

The metal-chelate was dissolved in hot DMF and mixed with an equimolecular amount of an ethanolic solution of the diamine. The mixture was refluxed over a water bath for 1-2 h as necessary, and left overnight. The precipitated polymeric complex was filtered, washed with ethanol, DMF and ether, and dried in vacuum. The yield is ca 80% in all the cases.

The compounds are air stable, powdery and insoluble in water and in common organic solvents. Colour of the complexes are given in Table 1.

The I.R. spectra of the complexes were recorded on a Beckman Infrared Spectrophotometer in the range of 4000 - 400 cm^{-1} using KBr pellets. Thermogravimetric analysis data were obtained from an assembly with a heating rate of 10^{o} min^{-1} upto 800^{o}in air.

Results and Discussion

The analytical data of the complexes (Table 1) are in accordance with the formula $-(ML)_n$ [where M = Be(II), Zn(II), Cd(II); and L = $C_{20}H_{14}N_2O_2$(A) or $C_{26}H_{18}N_2O_2$(B)].

I.R. spectrum of salicylaldehyde shows the absorption bands (wave numbers in cm^{-1}) at 3500 and 1660 due to O-H and aldehydic C=O stretching vibrations, respectively (BELLAMY 1954). The spectra of bis-(salicylaldehydo) metal(II)-chelates [the spectra of Be(II) complexes are shown in fig. 1] do not exhibit any band near 3500 indicating that the hydrogen of the O-H group

TABLE 1

Colour and analytical data of the Complexes

Complex	Colour	Elemental Analyses (%)			
		Found (calc.)			
		Metal	C	H	N
Be(II)SAL	White	3.34	66.78	3.92	...
		(3.58)	(66.93)	(3.98)	...
Zn(II)SAL	White	21.02	54.69	3.18	...
		(21.17)	(54.72)	(3.25)	...
Cd(II)SAL	White	31.52	47.37	2.81	...
		(31.63)	(47.45)	(2.82)	...
$[Be(II)A]_n$	Yellow	2.04	73.42	3.92	7.56
		(2.78)	(74.30)	(4.33)	(8.67)
$[Zn(II)A]_n$	Reddish	17.05	64.63	4.33	7.62
		(17.15)	(63.32)	(3.69)	(7.38)
$[Cd(II)A]_n$	Yellow	21.36	57.18	3.04	7.81
		(22.03)	(56.28)	(3.28)	(6.56)
$[Be(II)B]_n$	Light	1.85	77.84	5.04	7.96
	yellow	(2.55)	(78.19)	(4.51)	(7.01)
$[Zn(II)B]_n$	Greenish	13.14	67.55	4.25	7.16
	yellow	(14.35)	(68.51)	(3.95)	(6.15)
$[Cd(II)B]_n$	Light	20.86	63.44	3.96	6.43
	green	(22.37)	(62.10)	(3.58)	(5.57)

of salicylaldehyde gets dissociated on complexation, leading to the formation of M-O bond. The band at ca 1625 appearing in the complexes is due to the coordinated aldehydic C=O group. The shifting of the frequency to lower side on chelation is because of the increased mass of metal attached to the oxygen, as well as to a weakening of the carbon-oxygen linkage. The spectra of DAB and DADP show the absorption bands near 3400, which may be assigned to NH_2 stretching vibrations (COLTHUP et al 1975). The bands at 1625 and 3400 disappear in the spectra of the Schiff base complexes (table 2), and new bands near 1560 and 1600 in the Schiff base complexes of DAB, and DADP respectively, are due to the formation of -C=N bond. The bands in the range of 630-570 and 480 - 430 due to M-O and M-N stretching vibrations, further confirm the formation of metal-oxygen and metal -nitrogen linkages in the Schiff base complexes (UENO and MARTELL 1956).

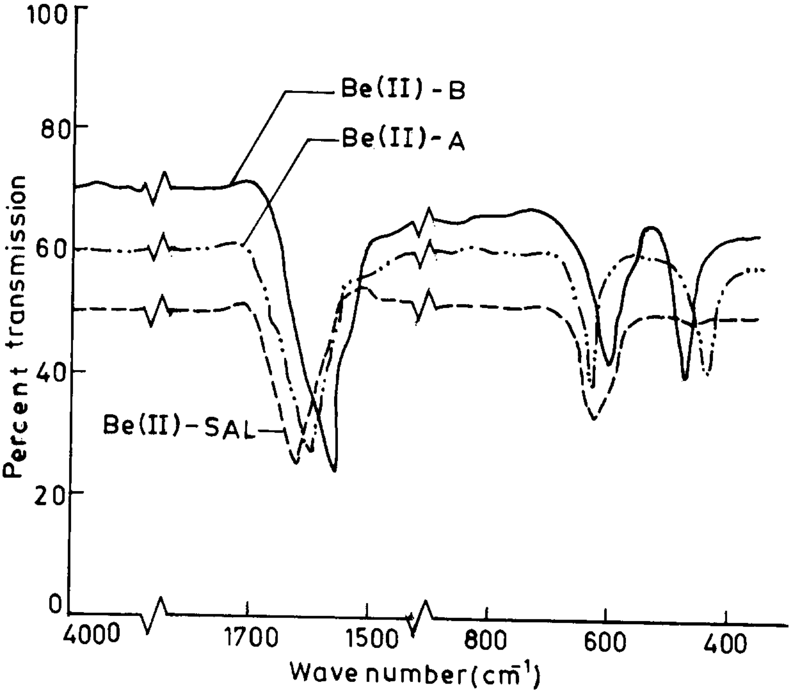


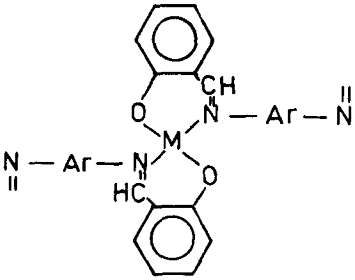
Fig. 1 - Infrared Spectra of Be(II)-complexes

TABLE 2

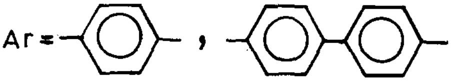
I.R. spectra of the Complexes

Complexes with A			Complexes with B			Assignment
Be(II)	Zn(II)	Cd(II)	Be(II)	Zn(II)	Cd(II)	
1560	1560	1600	1590	1600	1600	νC=N
590	580	570	635	640	630	νM-O
440	430	440	480	480	470	νM-N

The two terminal nitrogens of DAB or DADP group act as bridging unit between the two bis-(salicylaldehydo) metal(II)-chelate, and the polymeric chain grows as indicated (I) :



I. M = Be(II), Zn(II), Cd(II)



The pyrolysis curves are shown in fig. 2, wherefrom the percentage loss in weights may be obtained.

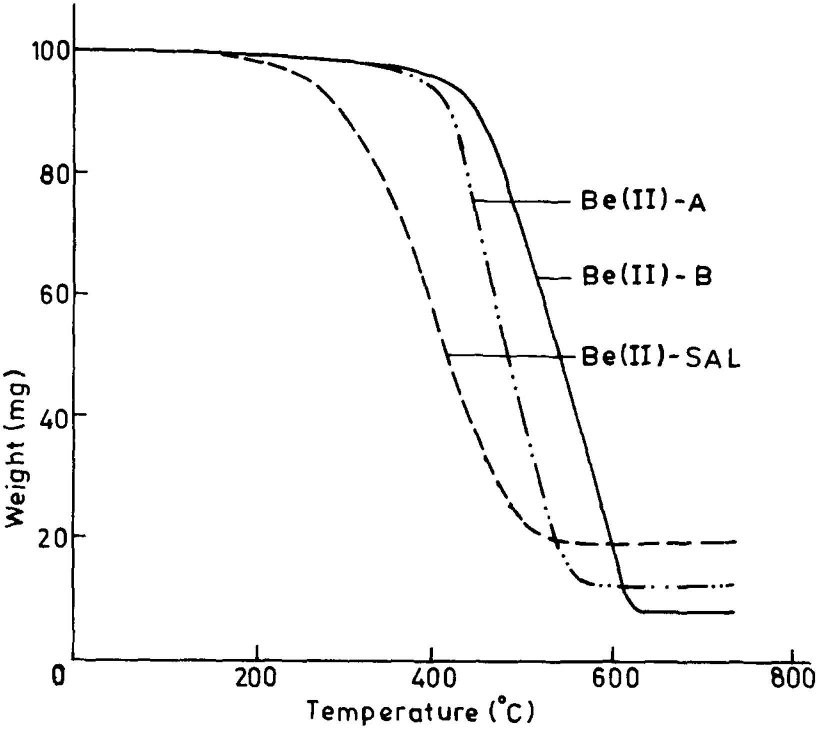


Fig. 2 - Pyrolysis curves of Be(II)-complexes

The initial loss in weights on heating, indicates the gradual decomposition of the complexes. The abrupt change in weight on further heating, shows the decomposition of the ligand, and the final product being the oxide. The decomposition of M(II)-A and M(II)-B commence at higher temperatures when compared to M(II)-SAL. This is an indication of the polymeric nature of the Schiff base complexes. The temperatures of the commencement and the completion of decomposition are given in Table 3.

TABLE 3

Thermal decomposition of the Complexes

Complex	Temperature °C		Final Loss in Weight (%)	
	Commencement of Decomposition	Completion of Decomposition	Observed	Theoretical (for oxide formation)
Be(II)SAL	280	540	...	...
Zn(II)SAL	280	560	...	...
Cd(II)SAL	260	520	...	...
Be(II)A	400	560	87.45	89.26
Zn(II)A	400	600	77.02	78.54
Cd(II)A	340	600	72.59	69.88
Be(II)B	420	640	91.67	93.73
Zn(II)B	420	680	85.29	82.12
Cd(II)B	360	640	73.33	74.44

The order of thermal stability is Be $\sim$ Zn $>$ Cd for both the series of the polymers. Polymers derived from DAB are thermally more stable than those from DADP. The increase is presumably due to greater delocalization of the electrons from the metal atoms into the aromatic π-system.

The geometry of the ligand, composition, and insolubility of the complexes as well as their high thermal stability, indicate the polymeric nature of the complexes (DEY et al 1978, 1979a, 1979b, 1980).

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