

**MIXED LIGAND COMPLEXES OF ALKALINE EARTH METALS.
PART II. Sr(II) AND Ba(II) COMPLEXES WITH SALICYLALDEHYDE,
o-HYDROXYACETOPHENONE AND 2,4-PENTANEDIONE**

R. N. PRASAD, MITHLESH JINDAL and R. P. SHARMA

Department of Chemistry, University of Rajasthan, Jaipur 302004, India.

ABSTRACT

Reactions of chlorides or freshly prepared hydroxides of strontium(II) and barium(II) with a 1:1 mixture of two carbonyl compounds in ethanol have resulted in the formation of mixed ligand complexes of the type, $[MLL'(H_2O)_2]$ (where M = Sr(II) or Ba(II) and HL and HL' are salicylaldehyde, o-hydroxyacetophenone or 2,4-pentanedione). These complexes have been characterized by elemental analyses, TLC, TGA and IR spectra.

INTRODUCTION

THE coordination chemistry of alkali and alkaline earth metal ions remained neglected for a long due to their weaker complexing ability. It is only during the last fifteen years that due to their biological importance¹⁻⁴ complexes of these metal ions with conventional⁵⁻⁹ and macrocyclic¹⁰⁻¹² ligands have been studied. Mixed ligand complexes of transition metal ions have been extensively studied¹³⁻¹⁵ due to their biological^{16,17} and analytical¹⁸ importance. However the reports on such type of complexes of alkali and alkaline earth metals are very scanty¹⁹⁻²². In view of the biological relevance of the complexes of lower symmetry work on mixed ligand complexes of these metal ions has been started. We have earlier reported such complexes of Mg(II) and Ca(II) with salicylaldehyde, o-hydroxyacetophenone and 2,4-pentanedione²³ and

in the present paper similar complexes of Sr(II) and Ba(II) are described.

EXPERIMENTAL

Materials and methods:

Salicylaldehyde (E. Merck), o-hydroxyacetophenone (John Baker), 2,4-pentanedione (IDPL) and ethanol were purified by distillation before use. $SrCl_2 \cdot 6H_2O$ and $BaCl_2 \cdot 2H_2O$ were of AR grade.

Synthesis of mixed ligand complexes:

To the aqueous ethanolic (1:1) solution of strontium or barium chloride an ethanolic solution of the two carbonyl compounds, salicylaldehyde, o-hydroxyacetophenone or 2,4-pentanedione (1:1:1 molar ratio) was added. The pH of the reaction mixture was raised

Table 1 Characteristics, yields and analyses of mixed ligand complexes of Sr(II) and Ba(II)

Complex	Physical characteristics	Yield (%)	Analyses			IR bands		
			C Found (Calcd)	H Found (Calcd.)	M Found (Calcd.)	$\nu_{C=O}$	ν_{M-O}	ν_{O-H}
$[Sr(H_2O)_2(sal)(hap)]^\circ$	Yellow solid decomposed at 172°C	67	47.44 (47.42)	4.37 (4.25)	23.30 (23.06)	1650s	470w	230w 260w
$[Sr(H_2O)_2(sal)(acac)]^\circ$	Yellow solid decomposed at 207°C	72	42.12 (41.91)	4.37 (4.69)	25.50 (25.48)	1650s	465w	240w 280w
$[Sr(H_2O)_2(hap)(acac)]^\circ$	Light yellow solid decomposed at 188°C	60	43.71 (43.63)	5.16 (5.07)	24.60 (24.48)	1640s	440w	240w 250w
$[Ba(H_2O)_2(sal)(hap)]^\circ$	Yellow solid decomposed at 300°C	70	42.09 (41.93)	3.87 (3.75)	32.05 (31.97)	1635s	465w	240m 290m
$[Ba(H_2O)_2(sal)(acac)]^\circ$	Yellow solid m.p. 245°C	68	36.50 (36.62)	4.12 (4.10)	34.91 (34.89)	1630s	470w	250m 280m

s = strong, m = medium, w = weak.

to ~ 8.5 by adding ammonia solution (1:4) drop by drop with constant stirring. The crystalline solid obtained was filtered, washed with ethanol and dried *in vacuo*.

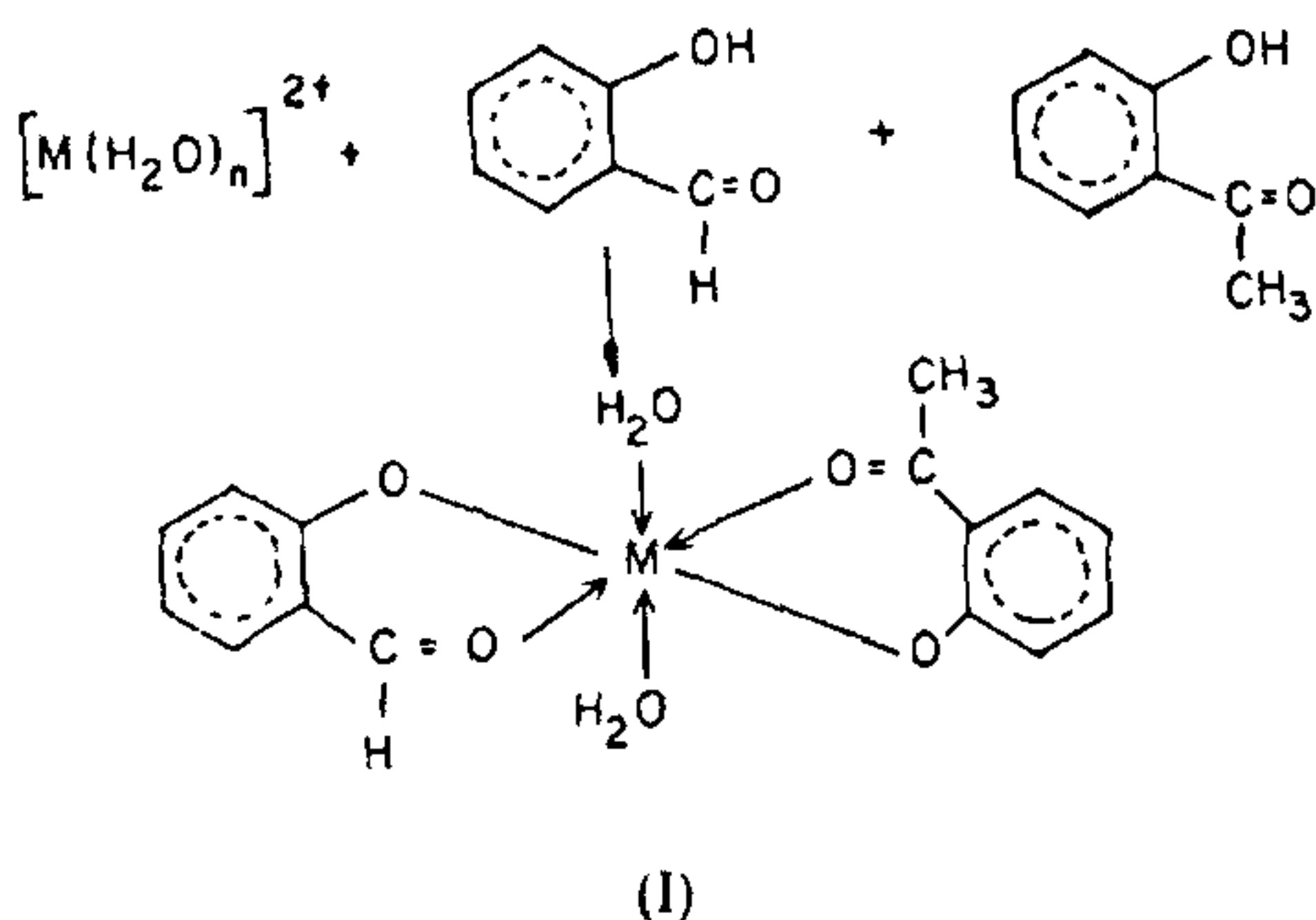
The mixed ligand complexes of strontium were recrystallized from methanol and analyzed. Complexes of barium decomposed on heating in methanol and hence could not be recrystallized. However, the mixed derivative of barium with *o*-hydroxyacetophenone and 2,4-pentanedione could not be synthesized. The analyses of the mixed complexes are recorded in table 1.

Analytical methods:

Strontium was determined by atomic absorption spectrophotometer and barium was determined gravimetrically as barium sulphate. Carbon and hydrogen were analyzed on a Coleman C,H-Analyser Model 33. IR spectra were recorded as nujol mulls and as KBr pellets in the region, $4000-200\text{ cm}^{-1}$ on a Perkin-Elmer 577 grating infrared spectrophotometer.

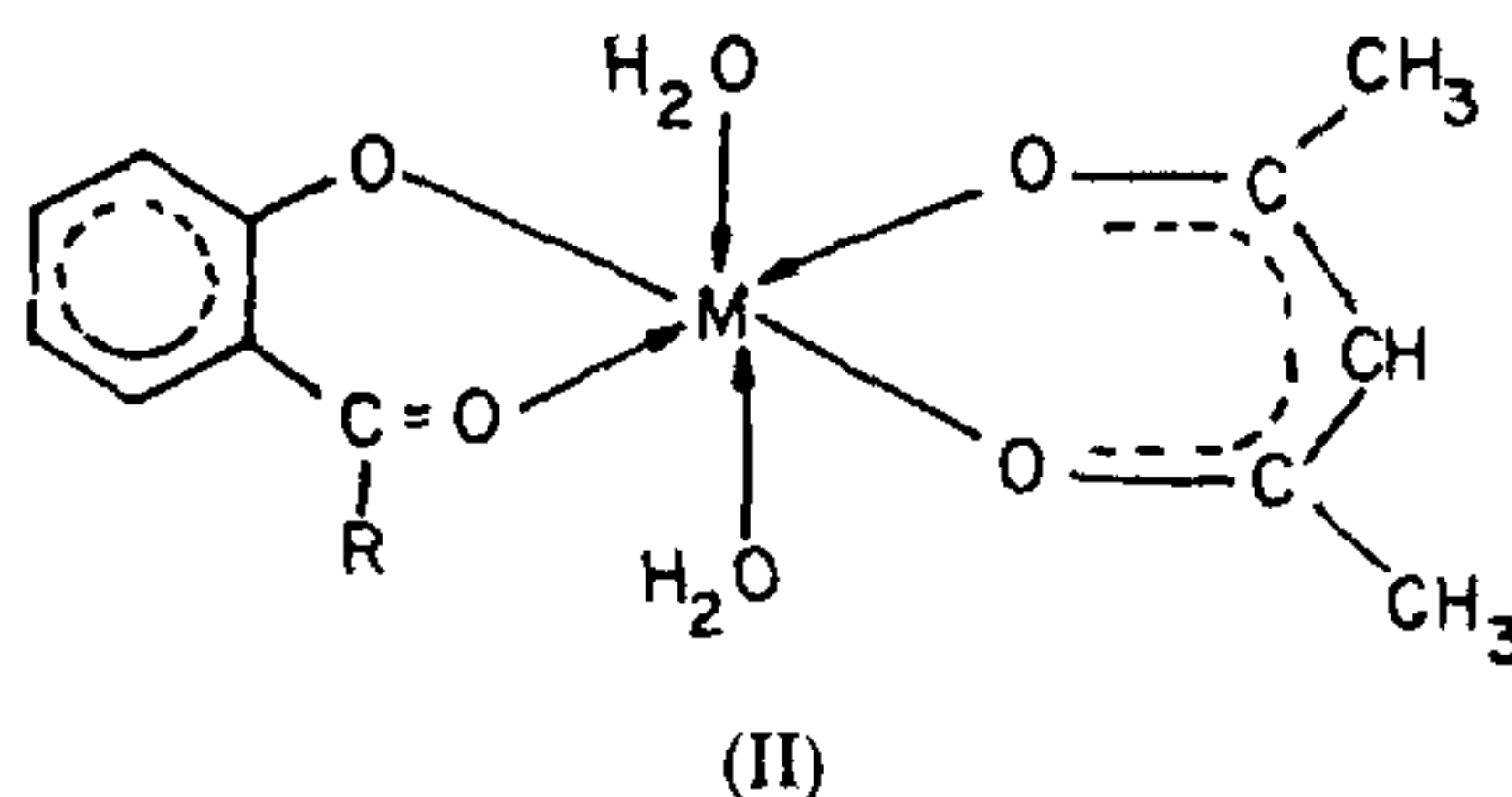
RESULTS AND DISCUSSION

The reaction of the metal ions with salicylaldehyde and *o*-hydroxyacetophenone in 1:1:1 molar ratio proceeds according to the following scheme:



Where $M = \text{Sr(II)}$ or Ba(II)

Similarly, 1:1 mixture of 2,4-pentanedione with salicylaldehyde or *o*-hydroxyacetophenone reacts with the metal ions to give the mixed ligand complexes(II).



Where $M = \text{Sr(II)}$, $R = \text{H}$ or CH_3
 $M = \text{Ba(II)}$, $R = \text{H}$

All the mixed ligand complexes are stable solids, insoluble in water and soluble in organic solvents, like chloroform and methanol.

The TLC of the mixed ligand complexes on silica gel G using chloroform-ether (3:1) mixture as a solvent showed a single spot having R_f value intermediate of the two corresponding symmetrical bis-complexes. This indicates that they are mixed complexes rather than a mixture of the corresponding bis-complexes.

IR spectra of the mixed ligand complexes show weak bands in the region, $200-300\text{ cm}^{-1}$ which may be due to metal coordinated OH stretching. Appearance of a broad absorption at ~ 1650 in complexes 1,2,4 and 5 and a split band in complex 3 indicates the presence of coordinated $>\text{C}=\text{O}$ groups. Bands in the region, $440-470\text{ cm}^{-1}$ may be assigned to $\nu_{\text{M-O}}$. The characteristic IR bands are recorded in table 1.

The presence of two coordinated water molecules in

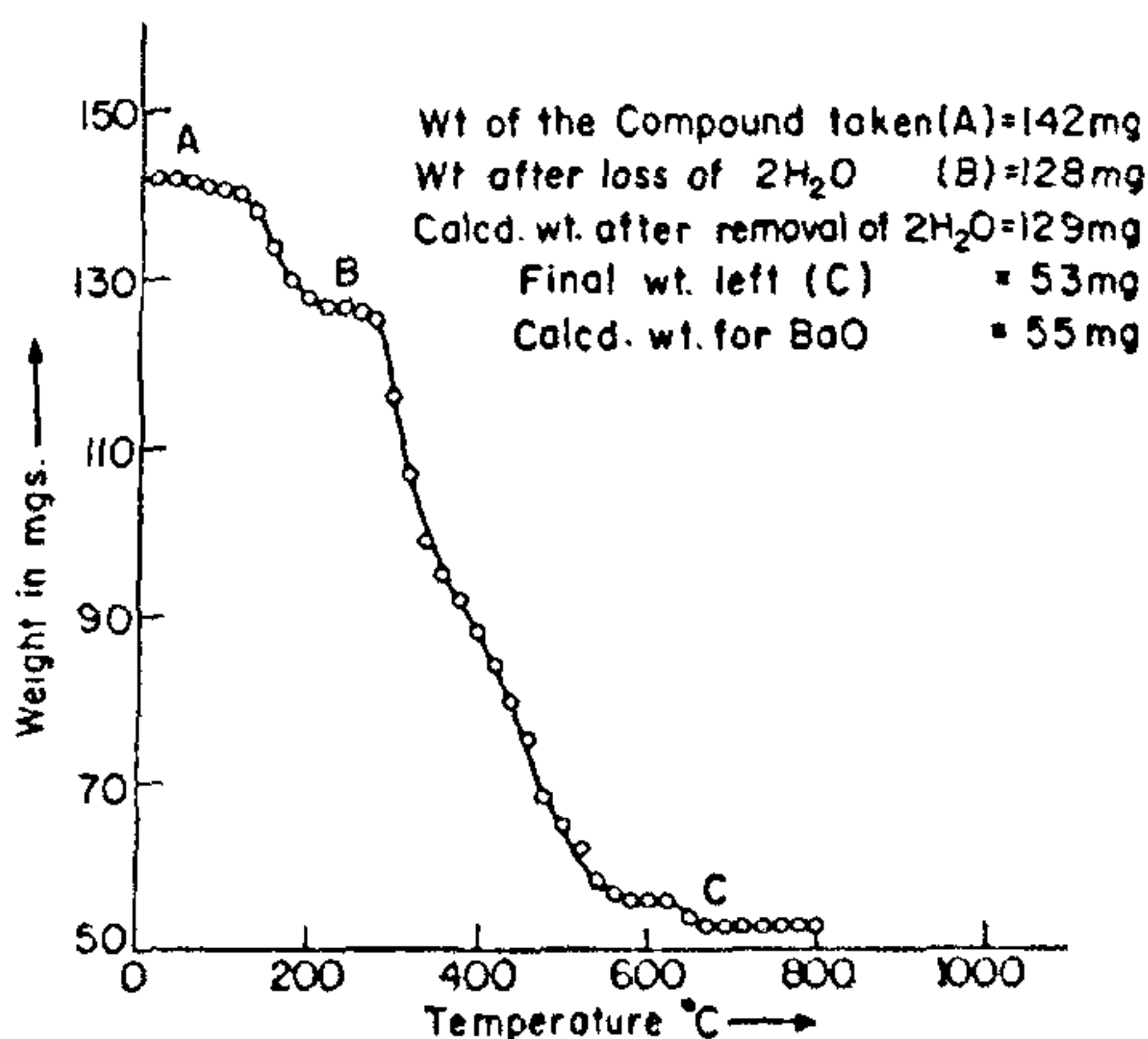


Figure 1. Thermogram of (salicylaldehydato)(2,4-pentanedionato) diaquobarium (II) ($\text{BaC}_{12}\text{H}_{12}\text{O}_4 \cdot 2\text{H}_2\text{O}$)

these complexes is supported by thermogravimetric analysis. Thermogram of the complex, (salicylaldehyde) (2,4-pentanedionato) diaquobarium(II) is shown in figure 1. After the loss of two water molecules the weight of the compound remains constant for a while (B), thereafter, a continuous loss in weight is observed and finally it gets converted to BaO at 660 C(C).

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ANNOUNCEMENT

XII ANNUAL SYMPOSIUM OF THE INDIAN BIOPHYSICAL SOCIETY

The Indian Biophysical Society (IBS) will be holding its XII IBS Symposium at Mysore University, Mysore on Sunday December 23 and Monday December 24, 1984. This Symposium will immediately follow the International Symposium on Biomolecular Structure that would be held the previous week at Bangalore. The dates are so arranged as to benefit from the participants of the International Symposium in Bangalore and to aid the delegates to plan their visit such that they can attend both the meetings and thus optimise the time and effort.

The broad theme of the XII IBS Symposium will be "Structure, Assembly and Function of Biomolecules". The format of the Symposium will be invited lectures, poster presentations and poster discussion sessions, in much the same way as in the previous year. We invite contributions and participation from all interested scientists in this Symposium.

Kindly contact the Convener of the XII IBS Symposium, Dr C J M D'Souza, Department of Biochemistry, Mysore University, Manasagangotri, Mysore 570 006, for further information and circulars.