

## Mixed ligand complexes of alkaline earth metals: Part XII. Mg(II), Ca(II), Sr(II) and Ba(II) complexes with 5-chlorosalicylaldehyde and salicylaldehyde or hydroxyaromatic ketones

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The reactions of alkaline earth metal chlorides with 5-chlorosalicylaldehyde and salicylaldehyde, 2-hydroxyacetophenone or 2-hydroxypropiophenone have been carried out in 1 : 1 : 1 mole ratio and the mixed ligand complexes of the type  $MLL'(H_2O)_2$  (where M = Mg(II), Ca(II), Sr(II) and Ba(II), HL = 5-chlorosalicylaldehyde and HL' = salicylaldehyde, 2-hydroxyacetophenone or 2-hydroxypropiophenone) have been isolated. These complexes were characterized by TLC, conductance measurements, IR and <sup>1</sup>H-NMR spectra.

*Keywords:* mixed ligand complexes, alkaline earth metals.

### INTRODUCTION

ML<sub>2</sub> type complexes of alkaline earth metals with aromatic aldehydes and ketones have been widely studied. Pfeiffer *et al.*<sup>1</sup> synthesized  $M(\text{sal})_2(H_2O)_2$  [where M = Mg(II) and Ca(II) and salH = salicylaldehyde]. Kumov and coworkers<sup>2</sup> synthesized complexes of the type  $M(\text{hnp})_2$  [where M = Mg(II), Ca(II), Sr(II), Ba(II) and hnpH = 2-hydroxy-1-naphthaldehyde] and their use in gravimetric and volumetric semimicro determinations was studied by Gusev *et al.*<sup>3</sup> Clarke and coworkers<sup>4</sup> carried out solution studies on  $Mg(\text{sal})_2(H_2O)_2$  and reported its formation constant and Wendlandt *et al.*<sup>5</sup> carried out TGA and DTA studies on the same complex. Similar complexes of alkaline earth metals with 2-hydroxyacetophenone and 2-hydroxypropiophenone have been reported from these laboratories.<sup>6</sup>

Reports on mixed ligand complexes of these metals are very scanty<sup>7,8</sup> as until recently there was no obvious necessity for interest in such studies. However, in the recent years complexation studies of these metal ions have been undertaken following the recognition of various important roles of these metal ions in biological systems. Earlier,  $MLL'(H_2O)_2$  type of mixed ligand complex with salicylaldehyde, 2-hydroxy-1-naphthaldehyde, 2-hydro-

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xyacetophenone, 2-hydroxypropiophenone, 2-hydroxybenzophenone and  $\beta$ -diketones have been synthesized in our laboratories<sup>9-16</sup> and their mass spectral studies were also reported.<sup>17,18</sup>

However, such mixed ligand complexes with substituted salicylaldehydes have not been studied so far. In the present paper mixed ligand complexes of substituted salicylaldehydes of the type  $MLL'(H_2O)_2$  [where  $M = Mg(II), Ca(II), Sr(II)$  and  $Ba(II)$ ,  $HL = 5$ -chlorosalicylaldehyde (5-clsalH) and  $HL' =$  salicylaldehyde (salH), 2-hydroxyacetophenone (hapH) or 2-hydroxypropiophenone (hppH)] are described.

## EXPERIMENTAL

### Materials.

Salicylaldehyde (Merck), 2-hydroxyacetophenone (John Baker) and 2-hydroxypropiophenone (Fluka) were purified by distillation before use. 5-Chlorosalicylaldehyde was purified by recrystallization from ethanol.  $MgCl_2 \cdot 6H_2O$  (Glaxo),  $CaCl_2 \cdot 2H_2O$  (Merck),  $SrCl_2 \cdot 6H_2O$  (Glaxo) and  $BaCl_2 \cdot 2H_2O$  (Glaxo) were of AR grade.

### Synthesis of mixed ligand complexes of $Mg(II)$ , $Ca(II)$ , $Sr(II)$ and $Ba(II)$

The mixed ligand complexes were synthesized by the reactions of ethanolic solutions of metal chlorides with two different carbonyl compounds in a 1 : 1 : 1 mole ratio by raising the pH to  $\approx 6-6.5$  with a 5 % aqueous sodium hydroxide solution and stirring the solution on a magnetic stirrer at 50–60 °C. The pH was measured with the aid of pH paper and stirring was continued for ninety minutes. The solid that separated was filtered and dried *in vacuo*.

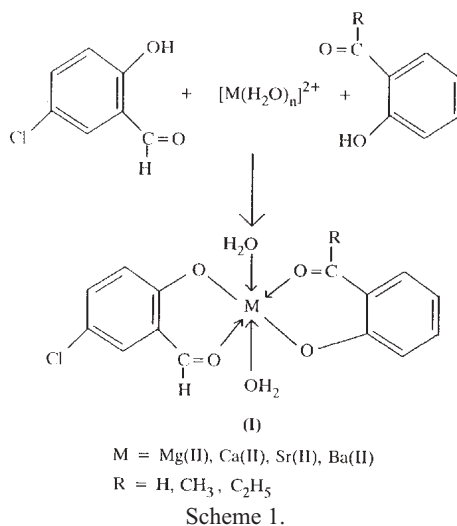
### Analytical methods

Magnesium, calcium and strontium were determined volumetrically by EDTA and barium was determined gravimetrically as barium sulphate. Carbon and hydrogen were determined on a Coleman C, H Analyser Model-33. A Systronic Direct Reading conductivity Meter 304 was used to measure the conductance at room temperature in methanol using a glass cell with a cell constant of  $1.0 \text{ cm}^{-1}$ . The infrared spectra were recorded in the region  $4000-200 \text{ cm}^{-1}$  using a Nicolet Magna-550 FT IR spectrometer as KBr pellets. The  $^1H$ -NMR spectra were recorded in DMSO- $d_6$  on a Jeol FX 90 Q FT NMR spectrometer at 90 MHz using TMS as the internal standard.

## RESULTS AND DISCUSSION

The 1 : 1 : 1 molar reactions (Scheme 1) of metal chlorides with 5-chlorosalicylaldehyde and carbonyl compounds (salicylaldehyde, 2-hydroxyacetophenone or 2-hydroxypropiophenone) result in the formation of mixed ligand complexes (I).

These mixed ligand complexes are yellow solids, insoluble in water, carbon tetrachloride and chloroform but soluble in methanol and DMSO. The characteristics and analyses of the complexes are recorded in Table I. The conductances of the complexes are very low, indicating their non-electrolytic nature. Thus, the metal atom in these mixed ligand complexes is hexacoordinated and the probable geometry is octahedral. The crystal structures of  $Mg(acac)_2(H_2O)_2$ ,<sup>19</sup>  $[Ca(acac)_2(H_2O)_2] \cdot H_2O$ ,<sup>20</sup>  $Mg(dbzm)_2(DMF)_2$ ,<sup>21</sup>  $Ca(dbzm)_2(EtOH)_{1/2}$ ,<sup>22</sup> and  $Sr(dbzm)_2(Me_2CO)_{1/2}$ ,<sup>23</sup> have been reported and octahedral geometry for the metal ions was confirmed.



#### Thin layer chromatography

TLC of the mixed ligand complexes was performed along with their corresponding bis-complexes on silica gel G using benzene–petroleum ether (1:1) as solvent and iodine vapour as the spray reagent. All the mixed ligand complexes showed single spots with  $R_f$  values intermediate between the two corresponding symmetrical bis-complexes, confirming that these are mixed ligand complexes and not mixtures of the corresponding bis-complexes.

#### Infrared spectra

In the IR spectra of the mixed ligand complexes, the weak to medium intensity bands observed in the complexes in the region  $400\text{--}500\text{ cm}^{-1}$ , which were absent in the free ligands, may be attributed to  $\nu_{\text{M-O}}$  vibrations. The coordination of water molecules to the metal atom was confirmed by the appearance of weak or medium intensity absorption bands in the region  $220\text{--}300\text{ cm}^{-1}$  due to metal coordinated OH stretching.

The mixed ligand complexes exhibit strong absorption bands in the region  $1600\text{--}1675\text{ cm}^{-1}$  which may be assigned to coordinated C=O groups. Bands in the region  $1500\text{--}1580\text{ cm}^{-1}$  may be assigned to C=C stretching modes. In the mixed ligand complexes of bromosalicylaldehyde,  $\nu_{\text{C=O}}$  is observed at  $1600\text{ cm}^{-1}$ , whereas in the complexes of chlorosalicylaldehyde this band appears at  $1650\text{ cm}^{-1}$ . The appearance of the  $\nu_{\text{C=O}}$  band of chlorosalicylaldehyde at a higher wave number than that of bromosalicylaldehyde may be due to the higher electronegativity of the chlorine atom compared to the bromine atom.

In the absence of any electron withdrawing group, the  $\nu_{\text{C=O}}$  frequencies of free salicylaldehyde, 2-hydroxyacetophenone and 2-hydroxypropiophenone have been reported at  $1660$ ,  $1650$  and  $1640\text{ cm}^{-1}$ , respectively. These bands shift to lower wave numbers on chelation with metal ions.<sup>24</sup> In copper, nickel and cobalt complexes, these bands have been re-

ported to appear in the region 1605–1625  $\text{cm}^{-1}$ . Banerjee *et al.*<sup>25</sup> reported the  $\nu_{\text{C=O}}$  band in free salicylaldehyde at 1700  $\text{cm}^{-1}$ , which is shifted to lower frequencies in magnesium complexes, *e.g.*, at 1630  $\text{cm}^{-1}$  in  $\text{Mg}(\text{sal})_2(\text{H}_2\text{O})_2$ . Thus, the shifting of  $\nu_{\text{C=O}}$  to lower wave numbers in the mixed ligand complexes of the alkaline earth metals studied during the present investigations, supports the coordination of C = O group to the metal atom.

TABLE I. Analyses and characteristics of the mixed ligand complexes of Mg(II), Ca(II), Sr(II) and Ba(II)

S. No.	Complex	Colour and decomposition temp. ( $^{\circ}\text{C}$ )	Yield (%)	Analysis (%)			
				C Found (Calc.)	H Found (Calc.)	Cl Found (Calc.)	Metal Found (Calc.)
1	$[\text{Mg}(5\text{-Clisal})(\text{sal})(\text{H}_2\text{O})_2]$	Yellow 210	39	50.01 (49.89)	4.01 (3.89)	10.55 (10.53)	7.28 (7.22)
2	$[\text{Mg}(5\text{-Clisal})(\text{hap})(\text{H}_2\text{O})_2]$	Yellow 210	50	51.32 (51.29)	4.36 (4.31)	10.17 (10.12)	7.01 (6.39)
3	$[\text{Mg}(5\text{-Clisal})(\text{hpp})(\text{H}_2\text{O})_2]$	Yellow 280	42	52.60 (52.61)	4.80 (4.70)	9.80 (9.73)	6.71 (6.66)
4	$[\text{Ca}(5\text{-Clisal})(\text{sal})(\text{H}_2\text{O})_2]$	Yellow 185	79	47.64 (47.66)	3.77 (3.71)	10.05 (10.06)	11.32 (11.36)
5	$[\text{Ca}(5\text{-Clisal})(\text{hap})(\text{H}_2\text{O})_2]$	Yellow 230	41	49.00 (49.09)	4.09 (4.12)	9.70 (9.68)	10.95 (10.93)
6	$[\text{Ca}(5\text{-Clisal})(\text{hpp})(\text{H}_2\text{O})_2]$	Yellow 260	45	50.48 (50.43)	4.55 (4.50)	9.37 (9.32)	10.58 (10.53)
7	$[\text{Sr}(5\text{-Clisal})(\text{sal})(\text{H}_2\text{O})_2]$	Yellow 150-160	70	41.98 (42.00)	3.30 (3.27)	8.88 (8.87)	21.90 (21.88)
8	$[\text{Sr}(5\text{-Clisal})(\text{hap})(\text{H}_2\text{O})_2]$	Yellow 180	69	43.42 (43.45)	3.62 (3.63)	8.56 (8.57)	21.19 (21.15)
9	$[\text{Sr}(5\text{-Clisal})(\text{hpp})(\text{H}_2\text{O})_2]$	Yellow 140-160	48	44.85 (44.83)	4.01 (4.00)	8.30 (8.29)	20.45 (20.46)
10	$[\text{Ba}(5\text{-Clisal})(\text{sal})(\text{H}_2\text{O})_2]$	Yellow 120-130	72	37.30 (37.36)	2.97 (2.91)	7.90 (7.89)	30.65 (30.51)
11	$[\text{Ba}(5\text{-Clisal})(\text{hap})(\text{H}_2\text{O})_2]$	Yellow 200	66	38.71 (38.80)	3.25 (3.26)	7.68 (7.65)	29.71 (29.60)
12	$[\text{Ba}(5\text{-Clisal})(\text{hpp})(\text{H}_2\text{O})_2]$	Yellow 220	68	40.15 (40.17)	3.55 (3.58)	7.40 (7.43)	28.89 (28.73)

#### Nuclear magnetic resonance spectra

The  $^1\text{H}$ -NMR spectra of the mixed ligand complexes were recorded in  $\text{DMSO-d}_6$  at 90 MHz. The aromatic protons appear at  $\delta$  6.0–8.0 ppm as complex multiplets. In free 5-chlorosalicylaldehyde, the aldehydic CH proton gives a signal at  $\delta$  10.34 ppm which is shifted upfield in the mixed ligand complexes. This confirms the coordination of the C = O group of the aldehyde to the metal atom.

Free 2-hydroxypropiophenone exhibits a triplet at  $\delta$  1.13 ppm and a quartet at  $\delta$  2.93 ppm due to  $\text{CH}_3$  and  $\text{CH}_2$  protons, respectively. In the mixed ligand complexes.

The CH<sub>3</sub> and CH<sub>2</sub> protons show a slight upfield shift indicating that the oxygen of the C = O group is weakly coordinated to the metal atom.

The OH proton peak of free 2-hydroxypropiophenone at  $\delta$  12.4 ppm disappears in the mixed ligand complexes confirming the binding of metal to the phenolic oxygen of these ligands through replacement of the hydrogen of the OH group.

### ИЗВОД

#### КОМПЛЕКСИ ЗЕМНОАЛКАЛНИХ МЕТАЛА СА МЕШОВИТИМ ЛИГАНДИМА. ДЕО XII. КОМПЛЕКСИ Mg(II), Ca(II), Sr(II) И Ba(II) СА 5-ХЛОРОСАЛИЦИЛАЛДЕХИДОМ И САЛИЦИЛАЛДЕХИДОМ ИЛИ ХИДРОКСИАРОМАТИЧНИМ КЕТОНИМА

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Проучаване су реакције земноалкалних хлорида са 5-хлоросалицилалдехидом и салицилалдехидом, 2-хидроксиацетофеноном или 2-хидроксипропиофеноном у молским односима 1:1:1 при чему су добијени комплекси са мешовитим лигандима типа MLL'(H<sub>2</sub>O)<sub>2</sub> (овде је M = Mg(II), Ca(II), Sr(II) или Ba(II), HL = 5-хлоросалицилалдехид, а HL' = салицилалдехид, 2-хидроксиацетофенон или 2-хидроксипропиофенон). Ови комплекси су карактерисани помоћу TLC, мерењем проводљивости, као и помоћу IR и <sup>1</sup>H-NMR спектра.

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