

Mixed Ligand Alkaline Earth Metal Complexes

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Mixed Ligand complexes of magnesium and calcium with some chelating organic acids, viz., salicylaldehyde, salicylic acid, anthranilic acid or 8-hydroxy quinoline as primary ligands and vanilline as secondary ligand, have been synthesised and characterised.

INTRODUCTION

Magnesium and calcium are biologically important metals.¹ Their coordination chemistry in the mixed ligand environment would be helpful to unravel their mode of transport and storage in biological kingdom. Banerjee *et. al.*,²⁻⁵ have synthesised a number of alkaline earth metal complexes and studied their mode of bonding. Presently, we have synthesised and characterised some mixed ligand complexes of magnesium and calcium of general formula, $[MLL']$, where $M = \text{Mg(II)}$ or Ca(II) , $L =$ deprotonated salicylaldehyde (salH); salicylic acid (salA), anthranilic acid (anth) or 8-hydroxy quinoline (8Hq) and $L' =$ deprotonated vanilline (Van).

EXPERIMENTAL

Mg/Ca salts of different organic acids were prepared by the interaction of metal hydroxide and organic acid in 1:2 mole ratio in acetone medium and were found to be of ML_2 composition by elemental analysis.

The mixed complexes were prepared by the interaction of a suspension of magnesium or calcium salt of primary ligands in acetone with the secondary ligand, vanilline, in 1:1 mole ratio. The reaction mixtures were refluxed with constant stirring on hot plate magnetic stirrer for 1 h. The resulting solutions were then cooled, where upon, the compounds separated. They were then filtered, washed with the solvent and dried at 100°C.

RESULT AND DISCUSSION

The complexes have been found to be stable when stored under dry conditions. The colour, melting or decomposition temperature and analytical results of complexes are mentioned in Table-1.

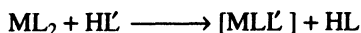
Melting/decomposition temperature of the complexes have been found to be higher than that of the secondary ligand, suggesting the genuinity of the compounds.

TABLE-I
 ANALYTICAL DATA OF Mg(II) AND Ca(II) COMPLEXES

S.No.	Compound	Colour	Melting/ decomposition temperature (°C)	Analysis % Found (Calcd)			
				M	C	H	N
1.	[H. Van]	White	81 (m)	— (22.30)	22.10 (22.30)	4.20 (4.60)	7.6 (7.8)
2.	[Mg (Sal H)Van]	Light Yellow	266 (d)	8.01 (8.09)	61.20 (60.80)	(4.23) (4.05)	— —
3.	[Mg (Sal A)Van]	White	288 (d)	7.28 (7.69)	57.92 (57.69)	4.02 (3.84)	— —
4.	Mg (8 Hq)Van]	Light Yellow	275 (d)	7.23 (7.52)	64.16 (63.94)	4.21 (4.07)	4.25 (4.38)
5.	[Mg (anth)Van]	Light Pink	284 (d)	7.32 (7.71)	57.26 (57.87)	4.73 (4.18)	4.18 (4.50)
6.	[Ca (SalH)Van]	Light Brown	210 (d)	12.43 (12.83)	58.44 (57.69)	3.92 (3.52)	— —
7.	[Ca (SalA)Van]	Grey	266 (d)	11.68 (12.19)	54.36 (54.88)	3.88 (3.65)	— —
8.	[Ca (8 Hq)Van]	Light Brown	270 (d)	11.52 (11.94)	60.62 (60.62)	3.96 (3.88)	3.98 (4.17)
9.	[Ca (anth)Van]	Light Brown	280 (d)	12.14 (12.23)	55.32 (55.04)	4.12 (3.98)	4.46 (4.28)

m—melted, d—decomposed

Analytical results suggest a 1 : 1 : 1 mole ratio among metal, primary ligand and secondary ligand, indicating following scheme of reaction



M = Mg(II) or Ca(II) HL = primary ligand, HL' = secondary ligand.

Infrared Studies: Selected infrared bands of ligand and complexes are mentioned in Table-2. In the infrared spectra of vanilline, a weak band at 3530 cm^{-1} is observed. This may be assigned to $\nu(\text{OH})$ band. In the spectra of mixed ligand complexes, this band has been found to be absent, suggesting deprotonation of OH of vanilline, on complexation. The $\nu(\text{OCH}_3)$ band of vanilline spotted out at 1040 cm^{-1} , has been found to undergo a red shift by 10–20 wave number in complexes. This suggest coordination of vanilline through $-\text{OCH}_3$ group.

The $\nu(\text{C}=\text{O})$ of vanilline, occurring at 1260 cm^{-1} , also undergoes a low frequency shift by 20–30 cm^{-1} upon complexation. This further supports involvement of $-\text{OCH}_3$ in coordination to the metal. The $\nu(\text{CHO})$ of vanilline, spotted at 1650 cm^{-1} , remains mostly undisturbed in the mixed complexes suggesting that CHO group is not involved in coordination.

In the spectra of mixed complexes with anthranilate as primary ligand, the $\nu(\text{N}=\text{H})$ appears as two bands in the region $3400\text{--}3140\text{ cm}^{-1}$, this split of $\nu(\text{N}=\text{H})$ suggest that the $-\text{NH}_2$ of anthranilate moiety is coordinated to the metal. The $\nu(\text{CHO})$ band of complexes with salicylaldehyde as primary ligand could not be pinpointed as the secondary ligand, too, contains the $-\text{CHO}$ group. With salicylate as primary ligand, the complexes showed $\nu(\text{OH})$ as doubly split

bands in the region 3480–3400 cm^{-1} . This split suggest the coordination of —OH of salicylate moiety to the metal.

TABLE-2
SELECTED IR BANDS (cm^{-1}) OF Mg(II) AND Ca(II) COMPLEXES

S.No.	Compound	$\nu(\text{OH})$	$\nu(\text{OCH}_3)$	$\nu(\text{C—O})$	$\nu(\text{CHO})$	Bands due to primary ligand		
						$\nu(\text{N—H})$	$\nu(\text{CHO})$	$\nu(\text{OH})$
1.	H Van	3530	1040	1260	1650	—	—	—
2.	[Mg (Sal H)Van]	—	1020	1230	1640	—	Obscured	
3.	[Mg (Sal A)Van]	—	1025	1240	1650	—	—	3400 3480
4.	[Mg (anth)Van]	—	1020	1230	1640	3140 3310	—	—
5.	[Mg (8 Hq)Van]	—	1020	1225	1650	—	—	—
6.	[Ca (Sal H)Van]	—	1020	1225	1630	—	Obscured	
7.	[Ca (Sal A)Van]	—	1020	1240	1650	—	—	3420 3470
8.	[Ca (anth)Van]	—	1020	1240	1650	3180 3400	—	—
9.	[Ca (8 Hq)Van]	—	1020	1225	1640	—	—	—

Thus, both primary and secondary ligands form chelate rings with the metal, which perhaps, is the driving force for the formation and stabilisation of these mixed complexes.

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