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Mixed Ligand Complexes of Magnesium and Calcium

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Mixed ligand complexs of magnesium and calcium with some chelating organic acids, *vez,* *o*-nitrophenol, salicylaldehyde, salicylic acid, anthranilic acid or 8-hydroxy quinoline as primary ligands and schiff hase, salicylidene anthranilic acid as secondary ligand, have been synthesised and characterised.

INTRODUCTION

Studies in mixed ligand complexes of magnesium and calcium would be interesting which throw light on the mode of storage and transport of these macronutrient metal ions in the biological kingdom. Banerjee *et al.*[1–4] have synthesised a number of mixed ligand alkaline earth metal complexes with a view to understand more about the bioinorganic chemistry of these metal ions. Presently, we have synthesised and characterised some mixed ligand complexes of magnesium and calcium of general formula [MLL′], where M = Mg or Ca, L = deprotonated *o*-nitrophenol (ONP), salicylaldehyde (SalH), salicylic acid (SalA), anthranilic acid (Anth), or 8-hydroxy quinoline (8Hq), and L′ = unideprotonated salicylidene anthranilic acid (salanth).

EXPERIMENTAL

Mg/Ca salts of different organic acid were prepared by the interaction of metal hydroxide and organic acids in 1 : 2 mole ratio in acetone medium and were found to be of ML_2 composition by elemental analysis. Salicylidene anthranilic acid was prepared by suspending 5.480 g of anthranilic acid in approximately 50 mL absolute ethanol and adding 4.2 mL salicylaldehyde to it. The reaction minture was stirred over a magnetic stirrer for about 1 h. The compound separated was filtered, washed with a little ethanol and dried at 100°C.

Mixed complexes were prepared by the general method of interaction of a suspension of magnesium or calcium salts of primary ligand in abs. ethanol with the secondary ligand, salicylidene anthranilic acid in 1:1 mole ratio. The reaction mixtures were refluxed with constant stirring on hot plate magnetic stirrer for 1 h. The compounds formed were filtered, washed with the solvent and dried at 100°C.

RESULTS AND DISCUSSION

The complexes have been found to be stable when stored under dry conditions.

The colour, melting/decomposition temperature and analytical results of the complexes are mentioned in Table-1.

TABLE-1
PHYSICO-CHEMICAL DATA OF Mg AND Ca COMPLEXES

Compound	Colour	Melting/ Decomposion temperature	Analysis, Found (Calcd)%			
			Mg/Ca	C	H	N
Salanth = HL′	Yellow	180 (m)	—	70.11 (69.70)	5.06 (4.58)	5.30 (5.80)
[Mg(ONP)·L′]	Brownish yellow	210 (d)	5.46 (5.97)	60.01 (59.70)	3.82 (3.48)	6.33 (6.96)
[Mg(SalH)·L′]	Yellow	220 (d)	6.18 (6.23)	65.82 (65.45)	3.91 (3.89)	3.72 (3.63)
[Mg(8Hq)·L′]	Light yellow	300 (d)	5.53 (5.88)	68.02 (67.64)	3.54 (3.92)	6.58 (6.86)
[Mg(Anth)·L′]	Light yellow	230 (d)	5.81 (6.00)	62.84 (63.00)	4.11 (4.00)	6.73 (7.00)
[Mg(SalA)·L′]	Yellow	230 (d)	5.66 (5.98)	62.43 (62.84)	3.82 (3.74)	3.35 (3.49)
[Ca(ONP)·L′]	Yellow	285 (d)	9.28 (9.56)	57.62 (57.41)	3.27 (3.34)	6.52 (6.69)
[Ca(SalH)·L′]	Light yellow	300 (d)	9.57 (9.97)	62.92 (62.84)	3.64 (3.74)	4.02 (3.49)
[Ca(Anth)·L′]	Yellow	290 (d)	9.53 (9.61)	60.67 (60.57)	3.56 (3.84)	6.68 (6.73)
[Ca(SalA)·L′]	Yellow	290 (d)	9.48 (9.59)	60.62 (60.43)	3.71 (3.59)	3.26 (3.35)

Melting/decomposition temperatures of the complexes have been found to be higher than that of the secondary ligand, suggesting that the complexes are genuine compounds and not the mixtures of reactants.

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

$ML_2 + HL' \rightarrow [MLL'] + HL$

Infrared studies

In the infrared spectra of salicylidene anthranilic acid, a medium band at 1615 cm^{-1} may be assigned to $\nu(CH{=}N)$. This band splits into two and shows down at 1600–1580 and 1615–1605 cm^{-1} in the mixed complexes, suggesting the co-ordination of azomethine group to the metal.

The $\nu(OH)$ does not show up in its usual position in the spectra of Schiff base but shows as weak bands at 2720 and 2340 cm^{-1} indicating the involvement of OH in hydrogen bonding. In the spectra of mixed complexes, $\nu(OH)$ shows as weak broad bands at *ca.* 3400, 3120 and 2340 cm^{-1}. This indicates that most likely hydrogen bonding in the ligand breaks during complexation and the OH group coordinats to the metal.

The $\nu(C{=}O)$ of COOH group of ligand shows at 1680 cm^{-1} as a weak and broad band. In case of complexes this band disappears and a new band appears at *ca.* 1565 cm^{-1}, which may be assigned to $\nu_{asym}(COO^-)$, this is suggestive of deprotonation of COOH group and coordination of COO^- in the complexes.

In the spectra of mixed complexes with *o*-nitrophenol as primary ligand, the $\nu_{asym}(NO_2)$ shows at 1555 cm^{-1} indicating coordination of NO_2 group to the metal. In case of complexes with salicylaldehyde as primary ligand the ν(CHO) band shows at 1640–1630 cm^{-1} region indicating coordination of CHO group in the complexes. In complexes with anthranilic acid as the primary ligand, the ν(NH) of anthranilate moiety shows at 3320 cm^{-1}. This indicates the involvement of NH_2 group in coordination to the metal. Pin pointing of ν(OH) of salicylate moiety in complexes with salicylic acid as primary ligand is not possible since the secondary ligand too contains OH group.

Thus it is seen that both the primary and the secondary ligand form chelate rings with the metal in the mixed complexes, which perhaps is the reason for the formation and stabilisation of these mixed complexes of alkaline earth metal.

Selected infrared bands of ligand and complexes are recorded in Table-2.

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

Compound	Bands due to secondary ligand				Bands due to primary ligand		
	ν(CH=N)	ν(C=O)	ν(OH)	$\nu_{asym}(COO^-)$	ν(NH)	$\nu(NO_2)$	ν(CHO)
Salanth = HL′	1615 (m)	1680 (w)	3400 (br)	—	—	—	—
[Mg(ONP)·L]	1605 1590	—	3400 3090	1570	—	1555	—
[Mg(SalH)·L]	1605 1590	—	3340 3140	1565	—	—	1640
[Mg(8Hq)·L]	1605 1580	—	3320 3160	1570	—	—	—
[Mg(Anth)·L]	1615 1600	—	3140	1565	3320	—	—
[Mg(SalA)·L]	1610 1600	—	3400 3130	1570	—	—	—
[Ca(ONP)·L]	1615 1600	—	3400 3020	1565	—	1555	—
[Ca(SalH)·L]	1615 1600	—	3400 3060	1565	—	—	1630
[Ca(Anth)·L]	1610 1600	—	3400 3120	1565	3320	—	—
[Ca(SalA)·L]	1610 1600	—	3400 3120	1565	—	—	—

From analytical and infrared studies the tentative structure proposed for the mixed complexes is shown in Fig. 1.

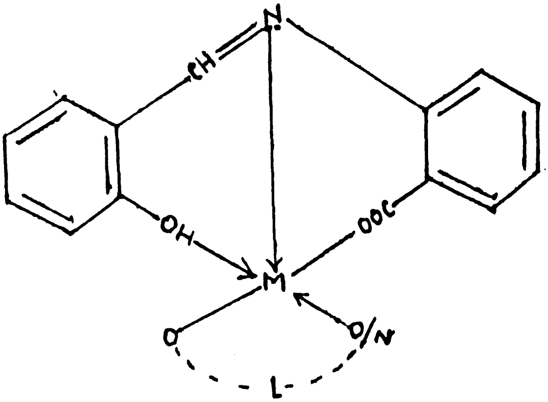

Fig. 1
M = Mg or Ca; L = Deprotonated primary ligand

REFERENCES

1. A.K. Banerjee, Sailendra K. Singh, Monojit K. Ghosh and S.K. Roy. *J. Indian Chem. Soc.*, **62**, 269 (1985).
2. A.K. Banerjee, Basabi Mahapatra, Dharambir Prasad and S.K. Roy, *J. Indian. Chem. Soc.*, **62**, 552 (1985).
3. A.K. Banerjee, Basabi Mahapatra and S.K. Roy, *J. Indian Chem. Soc.*, **62**, 778 (1985).
4. A.K. Banerjee, T.V. R.K. Rao and S.K. Roy, *J. Indian Chem. Soc.*, **63**, 480 (1986).

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