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Mixed Ligand Complexes of Magnesium and Calcium with Anilic Acids as Secondary Ligands

T.V.R.K. RAO* and R.P. YADAV
Department of Chemistry,
Purnea College, Purnea–854 301, India.

Mixed ligand complexes of magnesium and calcium with some chelating organic acids, *e.g.*, salicylaldehyde, salicylic acid or anthranilic acid as primary ligands and some anilic acids *viz.*, 1–phenyl phthalanilic acid or 1–*p*–tolyl phthalanilic acid as secondary ligand have been synthesised and characterised.

INTRODUCTION

Banerjee *et. al.*[1–4] have synthesised and characterised a large number of alkali and alkaline earth metal complexes with different lignads. Anilic acids are interesting chelating polydentate ligands. They have earlier been used as complexones for transition metals[5,6]. Analytical, bio-chemical and industrial applications of anilic acids has also been stressed earlier[7–11]. Presently, we have synthesised and characterised some mixed ligand complexes of general formula [MLL′], where M = Mg or Ca, L = deprotonated salicylaldehyde (salH), salicylic acid (salA) or anthranilic acid (anth) and L′ = deprotonated 1–phenyl phthalanilic acid (PHTH), 1–*p*–tolyl phthalanilic acid (TLTH).

RESULTS AND DISCUSSION

Complexes have been found to be stable under dry condition. Physical and analytical data are shown in Table 1. Since metal salts of primary ligands have been reacted with the secondary ligand to get the mixed complexes and the analytical data suggest a 1:1:1 mole ratio among the metal, primary ligand and secondary ligand, the following scheme of reaction is indicated.

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

Where, M = Mg or Ca;

HL = Primary ligand; HL′ = Secondary ligand

Infrared spectra of anilic acid complexes of transition metals has been studied earlier[6]. The main bands studied are ν_{NH} and ν_{CO}. In the IR spectra of phthalanilic acid, ν_{NH} appears at 3340 cm^{-1}, which on complexation found to split into two bands, one band showing up at *ca.* 3400 cm^{-1} and the other one showing down at *ca.* 3200 cm^{-1}, suggesting coordination through NH of secondary amide group. The ν_{CO} of anilic acid, identified at 1720 cm^{-1}, remains mostly unaffected in the spectra of complexes, suggesting that CO of secondary amide group is not coordinated to the metal.

TABLE 1
ANALYTICAL AND PHYSICAL DATA OF Mg AND Ca COMPLEXES

Compound/Colour	Decomp. temp (°C)	Analysis % found/ (Calcd.)			
		Mg/Ca	C	H	N
HPHTH = HL (White)	155		70.12 (69.70)	4.92 (4.56)	5.16 (5.81)
[Mg (sal A). L] (Dirty white)	288	5.54 (5.98)	62.93 (62.84)	3.82 (3.74)	3.11 (3.49)
[Mg (anth). L] (Grey)	290	5.86 (6.00)	63.26 (63.00)	4.23 (4.00)	6.82 (7.00)
[Ca (SalH).L] (Light orange)	270	9.63 (9.97)	62.92 (62.84)	3.82 (3.47)	3.16 (3.49)
[Ca (anth). L] (Violet)	298	9.33 (9.61)	61.21 (60.05)	3.96 (3.84)	6.01 (6.73)
HTLTH = HL′ (White)	152	— —	71.17 (70.59)	5.32 (5.10)	5.23 (5.49)
[Mg (sal H).L′] (Light yellow)	302	5.82 (6.01)	66.42 (66.16)	4.43 (4.29)	3.11 (3.50)
[Mg (anth).L′] (Grey)	304	5.73 (5.80)	63.52 (63.70)	4.16 (4.14)	6.41 (6.76)
[Ca (Sal A).L′] (Light yellow)	250	9.21 (9.28)	61.63 (61.21)	3.82 (3.94)	3.06 (3.25)
[Ca (anth).L′] (Violet)	305	9.18 (9.27)	61.73 (61.39)	4.48 (4.12)	6.36 (6.51)

In case of 1-*p*-tolyl phthalanilc acid, the band at 3340 cm^{-1} (ν_{NH}) splits into two bands (*ca.* 3400 and 3200 cm^{-1}) in its complexes, suggesting coordination through NH of CONH group. The ν_{CO} (1720 cm^{-1}) remains mostly unaffacted on complexation, suggesting that CO group is not coordinated to metal ion.

In the mixed complexes with anthranilic acid as primary ligand the IR spectra contains additional bands in the region 3000–3500 cm^{-1}. These extra bands invariably appear at *ca.* 3300 and 3100 cm^{-1}. These split bands are most likely due to the coordinated NH_2 of anthranilate moiety. In mixed complexes with salicyladehyde as primary ligand, the ν_{CHO} appears as split up bands at 1660 and 1670 cm^{-1}, suggesting coordination through CHO of salicylaldehyde moiety. In case of mixed complex with salicylic acid as primary ligand, the ν_{OH} of salicylate gets obscured by the ν_{NH} of anilic acid. However additional humps at *ca.* 2600 and 2700 cm^{-1} in the spectra of these complexes suggest an associated nature of OH group of salicylate.

Thus, both the primary and the secondary ligands form chelate rings with the metal. This may be an important factor in the formation and stabilization of these mixed ligand complexes.

On the basis of foregoing studies, the structure of the mixed ligand complexes may be represented as;

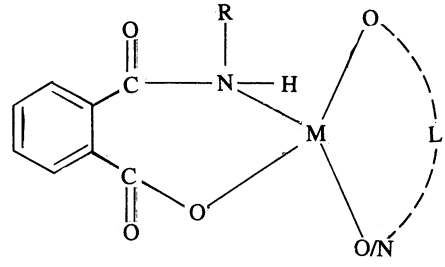

Fig. 1

EXPERIMENTAL

Mg/Ca salts of different organic acids 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.

The anilic acids were prepared by the interaction of phthalic anhydride (2.96 g) in benzene with aniline (1.023 ml) or *p*-toluidine (2.14 g). The reaction mixtures were stirred on a magnetic stirrer for 1 h. The white compounds separated were filtered, washed with benzene and dried at 100°C.

Mixed complexes were prepared by the general method of intraction of suspension of magnesium or calcium salts or primary ligand in acetone with the secondary ligand (anilic acid) in 1:1 mole ratio. The mixtures were refluxed with stirring on a hot plate for 1h and the resulting solids were filtered and washed with the solvent and dried (100°C).

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