

## Synthesis, Spectral and Thermal Studies of Mixed Ligand Complexes of $\text{Cd}^{2+}$ , $\text{Zn}^{2+}$ and $\text{Cu}^{2+}$ with Succinic, Phthalic and Anthranilic Acid

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**Abstract:** Mixed ligand complexes of zinc, cadmium and copper with phthalic, succinic and anthranilic acid have been synthesized. The complexes have been characterized on the basis of analytical data, thermogravimetric studies, IR and NMR. IR spectral studies suggest that bidentate chelating behavior of succinic and phthalic and anthranilic acid in its complexes.

**Keywords:** Mixed ligand complex, Zinc, Cadmium, Copper, Succinic acid, Phthalic acid, Anthranilic acid

### Introduction

The formation of mixed ligand complexes in solution with aspartic acid or glutamic acid as a primary ligand has been potentiometrically studied<sup>1</sup>. Some mixed ligand complexes formed with glycine, nitrilotriacetic acid or histidine as primary ligand and adenine, guanine, uracil, thymine or hippuric acid as secondary ligand have also been studied<sup>2-4</sup> mixed ligand copper complexes of hippuric acid and nitriloacetic acid have been studied<sup>5</sup>. This paper describes the synthesis, spectral and thermal studies of mixed ligand complexes of  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  with succinic, phthalic and anthranilic acid.

### Experimental

All the chemicals used in this study were obtained from E. Merck. The complexes were analyzed for metal using standard literature procedure<sup>6</sup>. Carbon, hydrogen, nitrogen and oxygen were determined microanalytically (Table 1). Thermogravimetric studies of the complexes was also carried out at the heating rate 10 °C/min. Infra red spectra were recorded on Perkin Elmer FTIR spectrophotometer in the range 450-4000  $\text{cm}^{-1}$  in KBr disc. NMR spectra were recorded on NMR spectrophotometer.

#### *Synthesis of the complexes*

Solution of acids were obtained by mixing acid and equivalent of sodium hydroxide. The solution of  $\text{ZnSO}_4$ ,  $\text{CdCl}_2$  and  $\text{CuSO}_4$  were prepared in equivalent of hydrochloric acid to

suppress hydrolysis. To prepare metal complexes the two ligand and metal were mixed in a 1:1:1 molar ratio at room temperature, the solution then concentrated and allow to crystallize. The product was then filtered, wash first with distill water and then with ethyl alcohol and dried in desiccators.

**Table 1.** Analytical data of mixed ligand complexes

Complex	Color	% Found (Calcd)				
		Zn/Cd/Cu	C	H	N	O
Na <sub>2</sub> [Zn(succinic)(phthalic)]	Colorless	17.10 (17.14)	37.0 (37.7)	2.1 (2.09)	-	33.50 (33.56)
Na[Zn(succinic)(anthranilic)]	Colorless	19.20 (19.21)	38.80 (38.77)	2.90 (2.93)	4.10 (4.11)	28.0 (28.2)
Na <sub>2</sub> [Cd(succinic)(phthalic)]	Colorless	25.60 (25.64)	32.80 (32.84)	1.83 (1.82)	-	29.10 (29.11)
Na[Cd(succinic)(anthranilic)]	Colorless	26.94 (26.93)	31.90 (31.62)	2.40 (2.39)	3.36 (3.35)	22.93 (22.90)
Na <sub>2</sub> [Cu(succinic)(phthalic)]2H <sub>2</sub> O	Bluish	12.40 (12.42)	28.20 (28.15)	2.30 (2.34)	-	31.30 (31.27)
Na[Cu(succinic)(anthranilic)]	Bluish	18.80 (18.76)	53.10 (53.16)	3.00 (2.95)	4.2 (4.135)	28.30 (28.35)
Na[Cu(phthalic)(anthranilic)]H <sub>2</sub> O	Bluish	15.90 (15.70)	44.50 (44.49)	2.95 (2.96)	3.45 (3.46)	27.70 (27.68)

## Results and Discussion

The analytical data and stoichiometries of the complexes reveal the formation of mixed ligand complexes of Zn(II), Cd(II) and Cu(II) ions with acids. The complexes were almost insoluble in water and common organic solvents such as DMF and DMSO, while copper complexes were soluble in ethanol. Thermogravimetric data reveals that the decomposition temperature for complexes lie in the range 63.62 °C to 700 °C.

### IR studies

Succinic, phthalic and anthranilic acid show the characteristic broad absorption band for the -COOH group at 2500-3000 cm<sup>-1</sup>, which vanishes in metal complexes. Instead asym(COO<sup>-</sup>) and sym(COO<sup>-</sup>) frequencies were observed at 1553.9-1623.6 cm<sup>-1</sup> and 1380.2-1434.5 cm<sup>-1</sup> respectively<sup>7</sup> (Table 2) lower stretching frequencies 3122.8 -3299 cm<sup>-1</sup> for NH<sub>2</sub> suggest N of NH<sub>2</sub> group involved in co-ordination, stretching frequencies at 3275.7-3456.6 cm<sup>-1</sup> assigned for lattice water which was confirmed by thermogravimetric data. The band in the region 482.6 - 482.8 cm<sup>-1</sup> and 514.5- 518.6 cm<sup>-1</sup> assigned to  $\nu$  M-N and  $\nu$  M-O<sup>8</sup> respectively (Table 2).

**Table 2.** Spectral data of metal complexes

Complex	IR cm <sup>-1</sup>						NMR( $\delta$ )	
	-OH	NH <sub>2</sub>	COO <sup>-</sup> Asym	COO <sup>-</sup> Sym	M-O	M-N	ArH	NH <sub>2</sub>
Na <sub>2</sub> [Zn(succinic)(phthalic)]	-	-	1596.9	1406.6	514.5	-	6.5-8.0	-
Na[Zn(succinic)(anthranilic)]	-	3299.6	1594.8	1407.5	515	-	6-8	4.73
Na <sub>2</sub> [Cd(succinic)(phthalic)]	-	1558.7	1406.5	-	-	-	7-8	-
Na[Cd(succinic)(anthranilic)]	-	3290.6	1590.7	1402.1	515.7	-	6.43-7.80	3.3-5
Na <sub>2</sub> [Cu(succinic)(phthalic)]2H <sub>2</sub> O	3456.6	1623.6	1435.5	-	-	-	-	-
Na[Cu(succinic)(anthranilic)]	-	3276.1	1554.1	1380.2	518.6	482.8	7.50-8.30	5.75
Na[Cu(phthalic)(anthranilic)]H <sub>2</sub> O	3275.7	3122.8	1553.9	1381.2	518.4	482.6	8.1	3.34

### NMR studies

In free acid for –COOH proton was expected to appear around 10 (10.5 to 12) ppm could not be observed in complexes. The signal due to proton was at 6 to 8 ppm placed far from site of coordination occur mainly through –COOH and –NH<sub>2</sub> group of acid (Table 2).

### Thermal analysis

Decomposition temperature of Na<sub>2</sub>[Cu(succinic)(phthalic)]<sub>2</sub>H<sub>2</sub>O and Na[Cu(phthalic)(anthranilic)]H<sub>2</sub>O complexes were 63.62-70.94 °C and 60.3-90.55 °C respectively. Suggest the presence of lattice water while Na[Cu(succinic)(anthranilic)] decomposes at 251.35 °C (Table 3).

Decomposition of the complexes Na<sub>2</sub>[Zn(succinic)(phthalic)] Na[Cu(phthalic)(anthranilic)] and Na [Cd (succinic) (anthranilic)] started at 315.79 °C, 327.65 °C, 335.36 °C, 249.97 °C respectively. The decomposition product of all complexes was metal oxide<sup>9</sup>. (ZnO, CdO and CuO) (Table 3).

**Table 3.** Thermal characteristics of the complex

Complex	Total Wt for Tg mg	Decomposition Temperature for Water, °C	Water loss Found (Calcd)%	Decomposition Temperature, °C	Decomposition Product Above 700 °C
Na <sub>2</sub> [Zn(succinic)(phthalic)]	6.86	-	-	315.9-348.45 434.87-484.15	ZnO
Na[Zn(succinic)(anthranilic)]	6.90	-	-	327.65-347.81 439.16-484.19 683-745.99	ZnO
Na <sub>2</sub> [Cd(succinic)(phthalic)]	14.22	-	-	335.36-342.42 452.87-476.83	CdO
Na[Cd(succinic)(anthranilic)]	4.35	-	-	249.97-294.99 612.61-685.69	CdO
Na <sub>2</sub> [Cu(succinic)(phthalic)] <sub>2</sub> H <sub>2</sub> O	2.71	63.62-70.94	5.78 (7.04)	-	CuO
Na[Cu(succinic)(anthranilic)]	6.48	-	-	251.36-257.86	CuO
Na[Cu(phthalic)(anthranilic)]H <sub>2</sub> O	8.99	60.03-90.55	5.73 (4.45)	28780-304.99	CuO

### Conclusion

Based on stiochiometries, thermogravimetric and spectrochemical studies and diamagnetic characteristics of complexes reveals that tetrahedral structure have been proposed for zinc and cadmium complexes while square planner structure have been assigned for copper complexes.

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