

Mixed Ligand Complexes of Alkali Metal Salts of Organic Acids with *o*-Amino Thiophenol

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Complexes of the type ML·HL' have been synthesised and characterised, where M = Li, Na or K, HL' = *o*-amino thiophenol, L = deprotonated *o*-nitro phenol, 2,4-dinitrophenol, 1-nitroso-2-naphthol and 8-hydroxy quinoline. All the complexes have been found to be four-coordinated in which ligand *o*-amino thiophenol is coordinated through N-atom of amino group and S-atom of the thiol group forming five-membered stable chelation.

INTRODUCTION

o-Amino thiophenol (OATP) is a very common and useful mordant dye and dye intermediate. Transition metal complexes with systems containing both nitrogen and sulphur donors have been reported¹⁻⁷. The present paper deals with the synthesis and characterization of complexes of alkali metal salts of 1-nitroso-2-naphthol (1N-2N); 8-hydroxy quinoline (8HQ), *o*-nitrophenol (ONP) and 2,4-dinitro phenol (2,4-DNP) with *o*-amino thiophenol, having as coordination sites nitrogen and sulphur atoms.

EXPERIMENTAL

1-Nitroso-2-naphthol, 8-hydroxy quinoline, *o*-nitrophenol and 2,4-dinitrophenol of AnalaR grade were taken. *o*-Amino thiophenol of E.M. grade was distilled at 23°C and when cooled, its needle-like crystals (m.p. = 26°C) were obtained.

Preparation of alkali metal salts: 1 : 1 Stoichiometric amount of organic acid (1N-2N, 8HQ, ONP or 2,4-DNP) and alkali metal hydroxide was refluxed in ethanolic medium with constant stirring, which on cooling precipitated out coloured crystals of respective alkali metal salts. The precipitated salts were filtered, washed with ethanol and dried in an electric oven at 80°C.

Preparation of the mixed ligand complexes: 1 : 1 Stoichiometric amount of alkali metal salt of organic acid and *o*-amino thiophenol was refluxed in absolute alcohol with constant stirring for 1.5 h in nitrogen atmosphere. The solution was concentrated and cooled when the coloured complex precipitated out. It was filtered, washed with the solvent and finally dried in an electric oven at 80°C.

RESULTS AND DISCUSSION

Some physical properties of the ligand *o*-amino thiophenol and its mixed ligand complexes are listed in Table-1.

TABLE-1

Compound (Colour)	m.p./decomp/ trans. temp. (°C)	Conductivity*	Analysis %, found (calcd.)			
			C	H	N	M
<i>o</i> -amino thiophenol (OATP) (Colourless)	26	-	-	-	-	-
Li·1N2N·OATP (Deep brown)	230 t	2.2	64.20 (63.15)	4.32 (4.27)	9.25 (9.21)	2.08 (2.30)
Na·1N2N·OATP (Deep brown)	218 t	4.4	59.25 (60.00)	4.10 (4.06)	9.25 (8.75)	6.90 (7.18)
K·1N2N·OATP (Deep brown)	190 t	6.8	55.85 (57.14)	3.90 (3.86)	8.10 (8.33)	10.85 (11.60)
Li·8HQ·OATP (Deep brown)	250 d	3.5	65.82 (65.21)	4.75 (4.71)	9.80 (10.14)	2.50 (2.53)
Na·8HQ·OATP (Deep brown)	225 t	5.6	60.75 (61.64)	4.50 (4.45)	9.28 (9.58)	6.95 (7.87)
K·8HQ·OATP (Deep brown)	210 d	7.2	57.60 (58.44)	4.30 (4.22)	8.90 (9.09)	11.95 (12.66)
Li·ONP·OATP (Yellowish brown)	220 d	4.5	54.20 (53.35)	4.15 (4.07)	10.40 (10.37)	2.50 (2.59)
Na·ONP·OATP (Yellowish brown)	205 d	5.6	48.70 (50.34)	3.90 (3.84)	9.25 (9.97)	7.50 (8.04)
K·ONP·OATP (Yellowish brown)	195 d	7.5	46.50 (47.68)	3.68 (3.64)	8.98 (9.27)	12.50 (12.91)
Na·DNP·OATP (Yellowish brown)	240 d	5.5	41.85 (43.50)	3.10 (3.02)	12.45 (12.68)	6.75 (6.94)
K·DNP·OATP (Yellowish brown)	215 d	7.2	39.95 (41.49)	2.90 (2.88)	11.80 (12.10)	10.90 (11.23)

*Molar conductivity $\text{ohm}^{-1} \text{mol}^{-1} \text{cm}^2$ of 10^{-3} M solution in methanol.

All the mixed ligand complexes of alkali metal salts of organic acids with *o*-amino thiophenol have been found to be either deep brown or yellowish brown coloured and stable in dry condition. They are soluble in polar solvent, *e.g.*, DMF, MeOH, EtOH, but insoluble in non-polar solvents, *e.g.*, CCl_4 , diethyl ether. From the results it was evident that all these complexes undergo a transformation or decomposition at temperatures which are considerably higher than the melting point of the second ligand, indicating greater thermal stability. Molar conductivities of all the complexes are measured in MeOH at 25°C at a concentration of 10^{-3} M. A value of about $35\text{--}40 \text{ ohm}^{-1} \text{mol}^{-1} \text{cm}^2$ correspond to 1 : 1 electrolyte⁹. From the result, it is evident that the molar conductivities of none of the complexes approach either ideal or 1 : 1 electrolyte. However, the

significantly low values of molar conductivities of these complexes suggest them to be covalent in nature. K- complexes of *o*-amino thiophenol are relatively high values of molar conductivity than that of Li and Na-metal complexes, suggest that they have undergone partial dissociation in the solvent used.

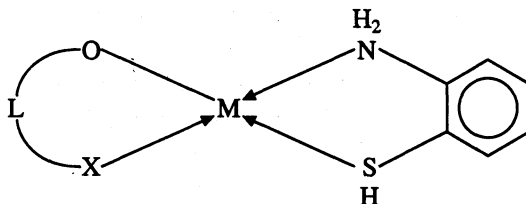
Infrared Spectra

Infrared spectra of ligand *o*-amino thiophenol (OATP) and its mixed ligand complexes have been recorded in region 4000–650 cm^{-1} in KBr phase with the help of spectrophotometer. Pertinent IR data for ligand (OATP) and its mixed ligand complexes are listed in Table-2. It is well known that *o*-amino thiophenol acts as chelating ligand towards transition metal ions, coordinating both through the —NH_2 and the —SH groups¹⁰⁻¹¹. The ligand, *o*-amino thiophenol has two strong absorption bands at 3400 cm^{-1} and 3300 cm^{-1} respectively. For this reason a well defined trend in the NH_2 frequency is not observable for their transition metal complexes, although there is a general lowering of the absorption bands. Similar shift of the absorption range of NH has been observed in the mixed ligand complexes of alkali metals, which might be due to coordination of —NH_2 group to the alkali metals. The medium intensity of the —NH_2 bending vibration occurring at 1610 cm^{-1} in *o*-amino thiophenol has also shifted down by 10 cm^{-1} and the other band appearing in the region 1580–1560 cm^{-1} is due to the presence of different functional group, present in the first ligand. The spectra of the mixed ligand complexes differ from that of the acid metal salts and the second ligand, *i.e.*, *o*-amino thiophenol. While the spectra of the ligand contain a moderately medium absorption band at 2550 cm^{-1} , the region of S—H vibration frequency, this band has shifted down by 70–40 cm^{-1} in the alkali metal complexes, indicating thereby that coordination has taken place through S-atom of —SH group.

TABLE-2
KEY IR ABSORPTION BANDS (cm^{-1}) OF METAL COMPLEXES

Compounds	$\nu(\text{N—H})$	$\nu(\text{S—H})$	$\nu(\text{NH}_2)$
OATP	3400 s, 3300 m	2550 m	1610 s,
Li-8HQ-OATP	3380 m, 3280 m	2510 w	1600 m, 1570 m
Na-8HQ-OATP	3350 m, 3280 m	2500 m	1600 s, 1570 sh
K-8HQ-OATP	3350 m, 3275 m	2510 m	1600 s, 1575 m
Li-1N2N-OATP	3360 m, 3270 m	2500 w	1600 m, 1580 m
Na-1N2N-OATP	3380 m, 3280 m	2510 m	1600 s, 1570 m
K-1N2N-OATP	3380 m, 3290 m	2570 w	1600 s, 1575 m
Li-ONP-OATP	3390 m, 3300 m	2490 m	1600 s, 1580 m
Na-ONP-OATP	3380 m, 3290 m	2480 m	1605 s, 1575 sh
K-ONP-OATP	3380 m, 3280 m	2500 m	1600 m, 1570 m
K-DNP-OATP	3380 s, 3290 m	2510 m	1600 s, 1560 m

Based on the gained results, the structural formula for these complexes can be produced and schematically given as below:



where $M = \text{Li, Na or K}$ and $X = \text{O or N}$

REFERENCES

1. G.N. Watt and J.F. Knifton, *Inorg. Chem.*, **7**, 1443 (1968).
2. W. Hieber and A. Schockig, *Z. Anorg. Allgem. Chem.*, **226**, 209 (1936).
3. W. Hieber and R. Bruck, *Nature Wissenschaften*, **36**, 312 (1949).
4. S.E. Livingstone, *J. Chem. Soc.*, 437, 1042 (1956).
5. E.J. Olszewaski and M.J. Albinak, *J. Inorg. Nucl. Chem.*, **27**, 1431 (1965).
6. W. Hieber and R. Bruck, *Z. Anorg. Allgem. Chem.*, **13**, 269 (1952).
7. R.I. Stiefel, J.H. Waters, E. Billigs and H.B. Gray, *J. Am. Chem. Soc.*, **87**, 3016 (1965).
8. A. Syamal and B.K. Gupta, *Rev. Chem. Miner*, **20**, 123 (1983).
9. A.K. Banerjee, A.J. Layton, R.S. Nyholm and M.R. Truter, *Nature*, **5134**, 1147 (1968).
10. S.E. Livingstone and John D. Nolan, *Inorg. Chem.*, **7**, 1443 (1968).
11. V.S. Korobkov, I.V. Kuzin and E.P. Artamonov, *Akad. Nauk. SSSR, Sibirsk. Otd.*, 161 (1964).

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