

## Mixed Ligand Complexes of Alkaline Earth Metal Salts of Some Organic Acids with Isonitroso-*p*-methyl Acetophenone

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In the present work, the authors report the complexing behaviour of isonitroso-*p*-methyl acetophenone with various alkaline earth metal salts of the organic acids.

### INTRODUCTION

Coordinating ability of isonitroso acetophenone and its *p*-methyl derivative with transition metal<sup>1,2</sup> and alkali metals<sup>3-6</sup> have been extensively studied. In the present communication we report the complexing behaviour of isonitroso-*p*-methyl acetophenone with various alkaline earth metal salts of the organic acids, having general formula  $ML_2 \cdot HL'$ , where M = Mg, Ca, Sr or Ba; L = deprotonated *o*-nitrophenol, 1-nitroso-2-naphthol, 8-hydroxy quinoline, *o*-amino benzoic acid and  $HL'$  = isonitroso-*p*-methyl acetophenone.

### EXPERIMENTAL

**Preparation of Ligand:** The ligand, isonitroso-*p*-methyl acetophenone was prepared by the method of Pechmann and Muller<sup>7</sup>.

**Preparation of the complexes:** Equimolar proportion of alkaline earth metal salts of the organic acids *e.g.*, *o*-nitrophenol, (ONP), 1-nitroso-2-naphthol (IN2N), 8-hydroxy quinoline (8HQ), *o*-amino benzoic acid (OABA) and isonitroso-*p*-methyl acetophenone were taken in absolute ethanol and refluxed for 2–3 h on a hot plate magnetic stirrer at 80°C. The solution was concentrated and cooled. Precipitates obtained were filtered, washed with absolute ethanol and dried in an electric oven at 80°C.

### RESULTS AND DISCUSSION

The colours, decomposition/transition temperatures as well as analytical data of these complexes are listed in Table-1. Almost all the complexes were found to be coloured and stable in dry air but stability decreased on exposure to moisture leading ultimately to decomposition; so they are kept in a desiccator over  $CaCl_2$ . The complexes are insoluble in most of the organic solvents such as methanol, ethanol, chloroform, ether, etc., but soluble in DMF. The melting points or decomposition temperatures of the complexes are higher than the secondary ligand ( $HL'$ ), which suggest the greater thermal stability of the complexes.

Molar conductivities of all the complexes were measured in DMF at 25°C at a concentration  $10^{-3}$  M. A value of *ca.* 35–40  $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$  corresponds to 1 : 1 electrolyte. From the results (Table-1), it is evident that the molar conductivity values of some of the complexes approach either ideal or 1 : 1 electrolyte<sup>8</sup>. However, fairly low values of molar conductivities of these complexes suggest that they are covalent compounds.

TABLE-1

Compounds	Colour	m.p./decomp./ trans.temp. (°C)	Conducti- vity	Analysis % (Found/Calcd.)			
				C	H	N	M
INPMAP (HL')	White	129md	—	65.90 (66.20)	5.20 (5.50)	8.20 (8.50)	—
Mg(ONP) <sub>2</sub> HL'	Yellow	280d	5.9	54.28 (54.28)	3.51 (3.67)	8.98 (9.07)	4.98 (5.18)
Ca(ONP) <sub>2</sub> HL'	Yellow	265d	6.6	51.89 (52.60)	2.89 (3.54)	8.02 (8.76)	7.98 (8.35)
Sr(ONP) <sub>2</sub> HL'	Yellow	270d	6.5	47.18 (47.90)	2.88 (3.23)	7.11 (7.98)	15.87 (16.93)
Ba(ONP) <sub>2</sub> HL'	Orange Yellow	245d	6.9	42.89 (43.75)	2.85 (2.95)	6.53 (7.29)	23.42 (23.78)
Mg(1N2N) <sub>2</sub> HL'	Light Yellow	283d	6.2	64.98 (65.53)	3.82 (3.95)	7.28 (7.90)	4.21 (4.51)
Ca(1N2N) <sub>2</sub> HL'	Yellow	181d	6.8	63.18 (63.61)	3.25 (3.83)	7.20 (7.60)	6.91 (7.31)
Sr(1N2N) <sub>2</sub> HL'	Light Green	200d	6.8	58.12 (58.58)	2.98 (3.53)	6.28 (7.07)	13.98 (14.64)
Ba(1N2N) <sub>2</sub> HL'	Green	285d	7.1	53.84 (54.03)	3.01 (3.26)	5.97 (6.52)	20.94 (21.27)
Mg(8HQ) <sub>2</sub> HL'	Light Green	228d	6.1	62.81 (63.21)	4.10 (4.42)	8.16 (8.84)	4.65 (5.05)
Ca(8HQ) <sub>2</sub> HL'	Brown	200d	6.5	65.24 (65.98)	3.89 (4.27)	7.98 (8.55)	7.82 (8.14)
Sr(8HQ) <sub>2</sub> HL'	Brown	220d	6.9	60.00 (60.22)	3.28 (3.90)	7.11 (7.80)	18.85 (16.17)
Ca(8HQ) <sub>2</sub> HL'	Chocolate	192d	7.3	54.78 (55.10)	3.21 (3.57)	6.89 (7.14)	22.78 (23.29)
Mg(OABA) <sub>2</sub> HL'	Brown	300d	5.8	59.89 (60.13)	4.11 (4.57)	8.89 (9.15)	4.89 (5.22)
Ca(OABA) <sub>2</sub> HL'	White	300d	6.9	52.11 (52.97)	3.89 (4.03)	7.58 (8.06)	15.89 (16.50)
Sr(OABA) <sub>2</sub> HL'	Dirty White	300d	7.5	47.88 (48.25)	3.21 (3.67)	6.67 (7.34)	23.02 (23.95)
Ba(OABA) <sub>2</sub> HL'	White	185d	6.8	52.35 (52.67)	3.21 (3.62)	6.87 (2.67)	23.02 (16.60)

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

Infrared spectra of the ligand and its complexes have been recorded in region 4000–650  $\text{cm}^{-1}$  in Nujol mulls or KBr disc with the help of Perkin Elmer spectrophotometer, model 257. Table-2 shows the pertinent IR data for the ligand, isonitroso-*p*-methyl acetophenone and its mixed ligand complexes with alkaline earth metal salts of some organic acids.

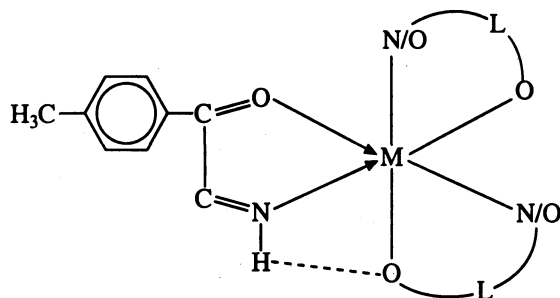
TABLE-2

Compounds	$\nu(\text{O—H})$	$\nu(\text{C—O})$	$\nu(\text{C=N})$	$\nu(\text{N—O})$
INPMAP	3300–3200br	1650s	1600s	980s
Mg(ONP) <sub>2</sub> -INPMAP	2800–2600br	1590sh	1578s	1000s
Ba(ONP) <sub>2</sub> -INPMAP	3400–3200br	1590sh	1580s	1000s
Mg(8HQ) <sub>2</sub> -INPMAP	3300br	1590sh	1570s	1010s
Ba(8HQ) <sub>2</sub> -INPMAP	3200br	1590s	1575w	1010br
Ca(1N2N) <sub>2</sub> -INPMAP	3400br	1610m	1590m	1020s
Ba(1N2N) <sub>2</sub> -INPMAP	3300br	1590s	1565sh	1000s
Mg(OABA) <sub>2</sub> -INPMAP	3400–3200br	1590sh	1578m	1000br
Ba(OABA) <sub>2</sub> -INPMAP	3400–3200br	1600m	1582s	1010m

s = strong, m = medium, br = broad, sh = shoulder, w = weak

The spectra of ligand isonitroso-*p*-methyl acetophenone shows multiple medium broad absorption bands over a wide range (3300–3200  $\text{cm}^{-1}$  and 2800–2600  $\text{cm}^{-1}$ ). The presence of absorption features in this region points out the presence of strong intramolecular hydrogen bonding involving oximino hydrogen atom and the carbonyl oxygen atom of the ligand. Shifting of broad absorption bands in the region 3300–1800  $\text{cm}^{-1}$  of the ligand (HL') to 3400–3200  $\text{cm}^{-1}$  in its mixed ligand complexes suggests that there is hydrogen bonding. None of these mixed ligand complexes showed anomalous broad absorption band between 1100–700  $\text{cm}^{-1}$  characteristic of acid salt structure with very short O...H—O (*ca.* 2.7 Å). The IR spectrum of the ligand shows characteristic absorption at 1650  $\text{cm}^{-1}$ , 1600  $\text{cm}^{-1}$  and 980  $\text{cm}^{-1}$ , which may be assigned to  $\nu(\text{C=O})$ ,  $\nu(\text{C=N})$  and  $\nu(\text{N—O})$  modes respectively. In all the complexes shifting by 50–60  $\text{cm}^{-1}$  in the region 1650  $\text{cm}^{-1}$  was found which suggests the coordination of metal ion through oxygen atom of C=O group of ligands. Some of the complexes also showed another band in this region which may be attributed to the presence of groups like —COOH, NO<sub>2</sub>, NH<sub>2</sub> bending etc. in the various alkaline earth metal anions of organic acids. Shifting to the lower frequency by 10–25  $\text{cm}^{-1}$  in the region 1600  $\text{cm}^{-1}$  (for  $\nu(\text{C=N})$  stretching) and shifting to the higher frequency by 20–30  $\text{cm}^{-1}$  in the region 980  $\text{cm}^{-1}$  suggest the coordination through nitrogen atom of (N—OH) group in the complexes. Shifting of  $\nu(\text{N—O})$  group towards higher frequency also implies the double bond character of the (N—O) group linkage.

**Structure and bonding:** The probable structures on the basis of elemental analysis, conductivity measurement and IR spectral studies can be produced schematically as such:



where M = Mg, Ca, Sr or Ba:  $\begin{matrix} \text{N/O} \\ \text{L} = \text{deprotonated ONP, 1N2N,} \\ \text{O} \quad \quad \quad \text{8HQ, OABA} \end{matrix}$

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