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# Alkali Metal Complexes: Mixed Ligand Complexes of Some Organic Compounds of Alkali Metals with 4-Isonitroso-1-Phenyl-3-Methyl-5-Pyrazolone

D. PRAKASH*, B. KUMAR and O.P. GUPTA
*Department of Chemistry*
*Patna University, Patna-800 005, India*

Mixed ligand complexes of alkali metal salts of *o*-nitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol, 1-nitroso-2-naphthol, 8-hydroxyquinoline, salicylic acid, acetylacetone and *o*-aminobenzoic acid with 4-isonitroso-, phenyl-3-methyl-5-pyrazolone have been synthesised and characterised on the basis of elemental analysis, conductivity measurement and IR spectral data.

## INTRODUCTION

Complexing behaviour of 4-isonitroso-1-phenyl-3-methyl-5-pyrazolone has been well documented with transition metals[1–5] as well as with alkali metals[6]. We have here extended the investigation to synthesise the mixed ligand complexes of alkali metals having the general formula $ML \cdot HL'$, where M = Li, Na or K, L = deprotonated *o*-nitrophenol (ONP), 2,4-dinitrophenol (DNP), 2,4,6-trinitrophenol (TNP), 1-nitroso-2-naphthol (1N2N), 8-hydroxyquinoline (8HQ), acetylacetone (AcAc), salicylic acid (SalA) and *o*-aminobenzoic acid (OABA) and HL′ = 4-isonitroso-1-phenyl-3-methyl-5-pyrazolone (INPMP).

## EXPERIMENTAL

### Preparation of ligand

4-Isonitroso-1-phenyl-3-methyl-5-pyrazolone (INPMP) was prepared by the method of L. Knoor[7].

### Preparation of alkali metal salts of various organic compounds

1-Nitroso-2-naphthol, *o*-nitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol, 8-hydroxyquinoline, acetylacetone, salicylic acid and *o*-aminobenzoic acid of analaR grade were taken and made to react with alkali metal hydroxides mainly of Li, Na and K in an ethanolic medium to produce their respective salts.

### Preparation of the complexes

1 : 1 Stoichiometric amount of alkali metal salts of ONP, DNP, TNP, 1N2N, 8HQ, SalA, AcAc or OABA and INPMP were used in absolute ethanolic medium with constant stirring and heating, which on concentration and cooling of the solution led to the separation of coloured adducts of respective complexes. The precipitates were filtered, washed with absolute ethanol and dried in an electric oven at 80°C.

## RESULTS AND DISCUSSION

Some physical properties of second ligand INPMP and its mixed ligand alkali metal complexes are listed in Table 1.

TABLE 1

| Compound/Colour | M.pt./decomp/ trans./temp. (°C) | Analysis % (Found/Calcd.) | | | |
|---|---|---|---|---|---|
| | | C | H | N | M |
| INPMP | 157 m | 59.10 | 4.42 | 20.65 | — |
| (Orange) | | (59.11) | (4.43) | (20.69) | |
| Li(IN2N)INPMP | 130 d | 61.25 | 3.96 | 14.50 | 1.78 |
| (Yellowish green) | | (61.83) | (3.93) | (14.66) | (1.83) |
| Na(IN2N)INPMP | 190 d | 58.82 | 3.80 | 13.68 | 5.42 |
| (Brown) | | (60.30) | (3.77) | (14.07) | (5.70) |
| K(IN2N)INPMP | 230 d | 55.98 | 3.68 | 13.20 | 9.20 |
| (Yellowish brown) | | (57.97) | (3.62) | (13.53) | (9.42) |
| Li(8HQ)INPMP | 190 d | 65.28 | 4.28 | 15.00 | 1.70 |
| (Greenish yellow) | | (64.41) | (4.54) | (15.65) | (1.98) |
| Na(8HQ)INPMP | 190 d | 59.88 | 4.15 | 14.80 | 5.98 |
| (Yellow) | | (61.62) | (4.05) | (15.13) | (6.22) |
| Na(SalA)INPMP | 96 t | 54.58 | 3.90 | 10.95 | 6.25 |
| (Deep orange) | | (56.20) | (3.86) | (11.57) | (6.34) |
| Li(AcAc)INPMP | 175 t | 60.15 | 5.25 | 14.20 | 1.95 |
| (Dirty yellow) | | (58.25) | (5.18) | (13.50) | (2.26) |
| Na(AcAc)INPMP | 208 d | 53.80 | 4.96 | 12.50 | 6.80 |
| (Yellowish orange) | | (55.38) | (4.92) | (12.92) | (7.08) |
| Li(OABA)INPMP | 200 d | 58.81 | 4.24 | 16.15 | 1.87 |
| (Dirty yellow) | | (58.96) | (4.38) | (16.18) | (2.02) |
| Na(OABA)INPMP | 180 t | 56.20 | 4.16 | 14.98 | 6.20 |
| (Deep orange) | | (56.35) | (4.14) | (15.47) | (6.35) |
| Na(ONP)INPMP | 210 d | 50.68 | 3.60 | 14.90 | 6.25 |
| (Orange yellow) | | (52.75) | (3.57) | (15.38) | (6.32) |
| Na(DNP)INPMP | 235 d | 48.25 | 3.10 | 18.20 | 5.10 |
| (Light brown) | | (46.94) | (2.98) | (17.14) | (5.62) |
| K(DNP)INPMP | 230 d | 46.80 | 3.00 | 16.50 | 8.90 |
| (Yellow) | | (45.18) | (2.82) | (16.47) | (9.17) |
| K(TNP)INPMP | 212 d | 40.28 | 2.38 | 16.90 | 8.25 |
| (Yellow) | | (40.85) | (2.34) | (17.87) | (8.30) |

Almost all the alkali metal mixed ligand complexes of INPMP have been found to be coloured and stable to dry air but stability decreased on exposure to moisture leading ultimately to hydrolysis; hence all the salts and complexes made were kept in a desiccator over solid anhydrous calcium chloride.

From the result it was evident that almost all complexes except Na(SalA) INPMP and Li(1N2N)INPMP undergo a transformation at temperature which are considerably higher than the melting point of the ligands, indicating their greater thermal stability. Most of the complexes have been found to be soluble in polar solvents such as methanol and ethanol but are insoluble in nonpolar solvents such as benzene, ether etc. and get decomposed when dissolved in aqueous medium;

even the ligand too was found to be insoluble in water. Ease of complexation and the quantum of yield was found to increase with increase in radius of the alkali metal ion *i.e.*, $Li^+ < Na^+ < K^+$.

Molar conductivities were measured in DMF at 23°C at a concentration $10^{-3}$ M. A value of about 35–40 $ohm^{-1}$ $cm^{-2}$ $mole^{-1}$ appears and characteristics of 1 : 1 electrolyte[8], whereas ideally molar conductivity of a neutral complex should be zero. From the result, it is evident that the molar conductivity values of none of the complexes approach either ideal or 1 : 1 electrolyte. However, significantly low values of molar conductivity of the mixed ligand complexes of Li and Na with INPMP could seem to indicate that they are non-electrolyte, while the slightly higher values for the K-complexes suggest that they have undergone partial dissociation in the solvent used. As the complexes of INPMP with alkali metal salts of salicylic acid and 8-hydroxyquinoline are only partly soluble in common solvents including DMP and MeOH, their molar conductivities could not be measured.

Table 2 shows the pertinent IR data for ligand (INPMP) and its mixed ligand alkali-metal complexes.

TABLE 2

PERTINENT IR DATA ($cm^{-1}$) FOR LIGAND (INPMP) AND ITS MIXED LIGAND ALKALI METAL COMPLEXES

| Compound | O–H/O–H . . O | C=O | C=N–OH | C=N(ring) | N–O |
|---|---|---|---|---|---|
| INPMP | 3280–3180 br,<br>2850 br | 1720 s | 1620 m | 1595 s | 1045 s |
| Li(1N2N)INPMP | 3380 m, 2500 br | 1710 s | 1650 w | 1590 m | 1055 m |
| Na(1N2N)INPMP | 2600–2500 br,<br>1900–1800 br | 1700 m | 1650 s | 1590 m | 1060 s |
| K(1N2N)INPMP | 2500 br, 1900 br | 1710 s | 1660 s | 1595 m | 1055 m |
| Li(8HQ)INPMP | 2600–2500 br | 1690 m | 1655 m | 1595 m | 1030 m |
| Na(8HQ)INPMP | 2800 br, 2600–2500 br | 1700 m | 1650 m | 1590 m | 1060 s |
| Na(SalA)INPMP | 2800 br, 1950–1850 br | 1700 s | 1650 w | 1595 s | 1055 m |
| Li(AcAc)INPMP | 2500 br, 1900–1800 br | 1700 sh | 1650 s | 1590 m | 1055 m |
| Na(AcAc)INPMP | 1950–1850 br | 1690 m | 1650 m | 1595 s | 1060 s |
| Li(OABA)INPMP | 3490 m, 3380 m,<br>2500 br | 1700 sh | 1660 s,<br>1610 sh | 1590 s | 1050 m |
| Na(OABA)INPMP | 3480 m, 3350 m,<br>2600–2500 br | 1690 m | 1650 s,<br>1610 m | 1590 m | 1050 m |
| Na(ONP)INPMP | 2800 m, 1900 br | 1700 m | 1610 m | 1595 m | 1040 s |
| Na(DNP)INPMP | 2700–2500 br,<br>1950–1850 br | 1690 s | 1630 m | 1600 s | 1050 m,<br>1020 s |
| K(DNP)INPMP | 2600 br, 1950 br | 1710 s | 1650 s | 1595 m | 1055 m |
| K(TNP)INPMP | 3100 br, 2850 br | 1705 s | 1630 s | 1595 w | 1040 s |

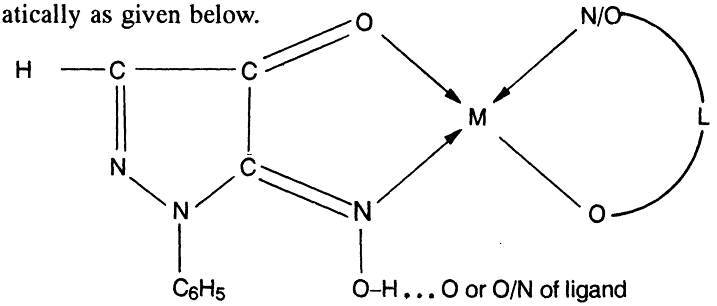
br = broad, s = strong, sh = shoulder, m = medium, w = weak

The study of IR spectra of the ligand (INPMP) shows the broad ν(O–H) stretching frequency at 3280–3180 and 2850 $cm^{-1}$, which indicates the presence of intramolecular hydrogen bonding involving isonitroso (oximino) hydrogen atom and the carbonyl oxygen atom of the ligand.

In the mixed ligand alkali-metal complexes of INPMP, broad ν(O–H) stretching frequency is observed at 2800–2500 $cm^{-1}$ and 1900–1800 $cm^{-1}$, except in case of K(TNP)INPMP, in which medium absorption band at 3100–2800 $cm^{-1}$ is seen, which indicates the weaker hydrogen bonding in the complex due to its bulky nature.

The IR spectra of the ligand (INPMP) shows characteristic absorption at 1720 $cm^{-1}$, 1620 $cm^{-1}$, 1595 $cm^{-1}$ and 1045 $cm^{-1}$, which may be assigned to $\nu(C{=}O)$, $\nu(C{=}N{-}OH)$, $\nu(C{=}N)$ (ring) and $\nu(N{-}O)$ modes respectively. In the mixed ligand complexes, shifting of the $\nu(C{=}O)$ and $\nu(C{=}N)$ stretching frequency by 10–30 $cm^{-1}$ and 10–40 $cm^{-1}$ respectively are suggestive of coordination through carbonyl oxygen atom and nitrogen atom of the oximino group. Addition bands along with $\nu(C{=}N)$ stretching frequency at 1620 $cm^{-1}$ region are probably due to the presence of primary ligand. The higher shifting of $\nu(N{-}O)$ absorption band by 5–15 $cm^{-1}$ implies that the double bond character of the NO linkage increases on complexation and also suggests the coordination through nitrogen atom of the oximino group in the complex. $\nu(C{=}N)$ (ring) absorption band at 1595 $cm^{-1}$ is almost not affected due to non-participation in complexation.

The probable structure on the basis of above studies can be produced and schematically as given below.



where M = Li, Na or K, $L\left\langle {}^{O}_{N/O} \right.$ = deprotonate ONP, DNP, TNP, 1N2N, 8HQ, OABA, SalA and AcAc.

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## REFERENCES

1. M.C. Patel, J.R. Shah and R.P. Patel, *J. Prakt. Chem.*, **314**, 181 (1972).
2. S.K. Das, J.R. Shah and R.P. Patel, *J. Indian Chem. Soc.*, **50**, 228 (1973).
3. N.B. Das, A. Nayak, B.B. Mahapatra and A.S. Mitra, *J. Indian. Chem. Soc.*, **58**, 337 (1981).
4. Yu. A. Darydovskaya, Yu. I. Vainshtein, I.S. Markovich, S.L. Zelichenok and V.M. Dziomke, *Zh. Anal. Khim. (Russ.)*, **28**, 590 (1973).
5. R.K. Agarwal and K. Arora, *Synth. React. Inorg. Met-org. Chem.*, **23**, 653 (1993).
6. O.L. Brady and M.D. Porter, *J. Chem. Soc.*, 840 (1933).
7. L. Knoor, *Ann.*, **238**, 158, 185 (1987).
8. A.K. Banerjee, A.J. Layton, R.S. Nyholm and M.R. Truter, *Nature*, **5134**, 1147 (1968)

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