

## Mixed Ligand Complexes of Pb(II) Chelates of Some Organic Acids with Picolinic Acid-N-Oxide and Quinaldinic Acid-N-Oxide

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The mixed ligand complexes of the type  $ML_2 \cdot HL'$ , where  $M = Pb$ ,  $HL' =$  picolinic acid-N-oxide,  $HH = o$ -nitrophenol(ONP), 2,4-dinitrophenol (DNP) and 2,4,6-trinitrophenol (TNP) have been synthesised and characterised by physical measurements. IR spectral data show that hydrogen bonding in these complexes is a dominant factor for their stability.

### INTRODUCTION

Transition metals, rare earth metals, alkaline earth metals as well as alkali metal complexes with picolinic acid-N-oxide and quinaldinic acid-N-oxide have been well investigated earlier<sup>1-8</sup>. In this communication, we have taken the picolinic acid N-oxide and quinaldinic acid N-oxide to investigate the coordination behaviour towards Pb(II) metal salt and also to study whether it is more selective in comparison to the picolinic acid or quinaldinic acid complexes.

### EXPERIMENTAL

*o*-Nitrophenol (ONP), 2,4-dinitrophenol (DNP) and 2,4,6-trinitrophenol (TNP) of AnalaR grade were taken and made to react with lead acetate in 95% ethanol to produce their respective complexes. Picolinic acid-N-oxide and quinaldinic acid-N-oxide are prepared by the method of Diels *et al.*<sup>9</sup>

**Preparation of the Complexes:** To the suspension of lead chelate of organic acid (ONP, DNP or TNP) in absolute ethanol, ligand (HPicO or HQuinO) was added in 1 : 1 mole ratio. The resulting suspension was refluxed with continuous stirring on a hot plate for about 2-3 h and cooled. The precipitate of mixed ligand complexes was obtained which was filtered, washed with absolute ethanol and finally dried at 80°C in an electric oven.

### RESULTS AND DISCUSSION

Some physical properties of the second ligand (HPicO) and the mixed ligand complexes  $ML_2 \cdot HL'$  obtained are listed in Table-1.

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TABLE-1  
PHYSICAL CHARACTERISTICS OF LIGANDS AND THEIR LEAD(II) COMPLEXES

Compound	Colour	m.p./Decomp./ trans. temp. (°C)	Found (Calcd.) %			
			C	H	N	Pb
HPicO	Light yellow	159–161 m	51.75 (51.80)	3.68 (3.60)	10.45 (10.07)	–
Pb(ONP) <sub>2</sub> ·HPicO	Light yellow	> 275 t	34.52 (34.72)	2.20 (2.09)	6.60 (6.70)	32.98 (33.27)
Pb(DNP) <sub>2</sub> ·HPicO	Pale yellow	270 d	30.02 (30.33)	1.82 (1.54)	9.16 (9.83)	28.62 (29.07)
Pb(TNP) <sub>2</sub> ·HPicO	Deep yellow	280 t	22.21 (26.93)	1.25 (1.12)	12.01 (12.21)	24.86 (25.80)
HQuinO	Light yellow	168–170 d	63.68 (63.49)	3.82 (3.70)	7.38 (7.40)	–
Pb(ONP) <sub>2</sub> ·HQuinO	Yellowish brown	280 d	38.98 (39.28)	2.27 (2.23)	6.01 (6.25)	30.15 (30.80)
Pb(DNP) <sub>2</sub> ·HQuinO	Light yellow	280 d	33.98 (34.64)	1.90 (1.70)	8.98 (9.18)	27.00 (27.16)
Pb(TNP) <sub>2</sub> ·HQuinO	Orange yellow	265 t	30.12 (30.98)	1.37 (1.29)	11.25 (11.50)	24.01 (24.29)

TABLE-2  
KEY INFRARED BANDS (cm<sup>-1</sup>) OF LIGANDS AND THEIR LEAD(II) COMPLEXES

Compound	Selected IR absorption bands (cm <sup>-1</sup> )			
HPicO	2800–1850 br	1720 s 1295 s	1680 s 1267 s	1620 s 847 s
Pb(ONP) <sub>2</sub> ·HPicO	3380 br, 3040 wbr	1670 w 1280 m	1630 sh 1255 s	1585 s 820 s
Pb(DNP) <sub>2</sub> ·HPicO	3400 br, 3190 wbr	1660 w 1280 m	1650 w 1255 s	1590 s 820 s
Pb(TNP) <sub>2</sub> ·HPicO	3400 br, 3030 s	1670 w 1270 s	1630 sh 1240 w	1595 m 810 s
HQuinO	2800–1900 br	1680 br	1610 m	1300 m, 1280 m
Pb(ONP) <sub>2</sub> ·HQuinO	3460–3200 br	3020 w	1630 sh	1535 s, 1240 s 1210 w
Pb(DNP) <sub>2</sub> ·HQuinO	3400–3340 br	3060 m	1630 sh	1585 s, 1250 s 1210 w
Pb(TNP) <sub>2</sub> ·HQuinO	3490–3340 br	3060 m	1610 sh	1585 m, 1260 s 1210 w

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

The ligand and mixed ligand complexes are generally coloured. They are insoluble in non-polar solvents, *viz.*, ether etc., but are partly soluble in polar solvents, *viz.*, benzene, ethanol etc. Almost all the compounds are stable under dry conditions. The transition or decomposition temperature of these complexes is much higher than the melting point of the ligand itself, indicating thereby greater thermal stability.

Infrared measurements for the ligands and their mixed ligand complexes with Pb(II) metal were made between 4000–650  $\text{cm}^{-1}$  in KBr phase. The broad band in the range 2800–1900  $\text{cm}^{-1}$  in the spectrum of second ligand (HPicO or HQinO) indicates that in the solid state, it contains a strong hydrogen bonding possibly of the symmetrical type probably resulting in the dimer<sup>10</sup>.

In the spectra of the complexes, these multiple bands have disappeared. However, the spectra of all complexes exhibit new broad band of medium to strong intensity in the region 3400–3030  $\text{cm}^{-1}$  (in HPicO) or 3490–3200  $\text{cm}^{-1}$  (in HQinO). These bands could be assigned to O—H...O/N...H—O absorption and suggest hydrogen bonding to be a dominant factor in stabilising these complexes. None of these mixed ligand complexes show anomalous broad absorption band between 1100–700  $\text{cm}^{-1}$ . The 1680  $\text{cm}^{-1}$  band that occurs in the spectrum of the ligand may be attributed to asymmetric vibration of the —COOH group. On complexation this band gives a negative shift 50–70  $\text{cm}^{-1}$ . The 1620–1610  $\text{cm}^{-1}$  band of medium intensity present in the ligand may be assigned to CC + CN absorptions. In complexes, this band has either remained or lowered in wave number.

### Structure and Bonding

On the basis of elemental analysis and IR spectral data, the following structure of the mixed ligand complexes may be proposed (Fig. 1 and 2).

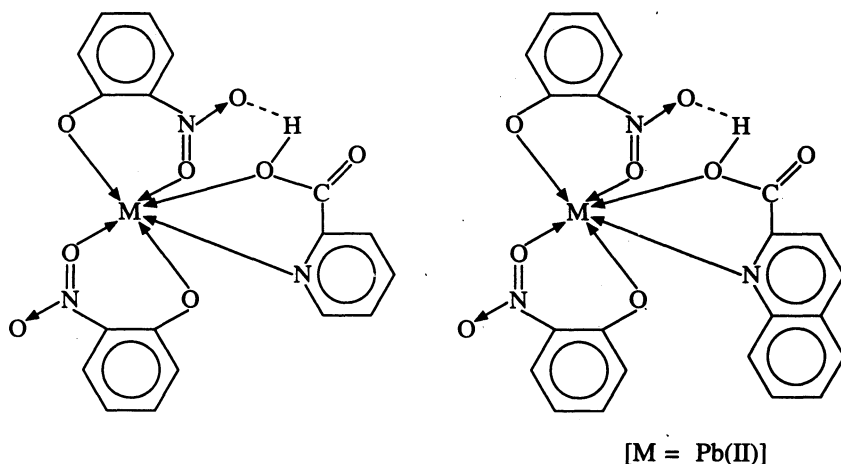


Fig. 1

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