

Mixed Ligand Complexes of Thallium (I) Metal Chelates of Deprotonated ONP, DNP, TNP, 1N2N, 8HQ with Propylenediamine.

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ABSTRACT: A series of new ligand complexes of thallium (I) metal chelates of some organic acids, such as o-nitro phenol (ONP), 2,4- dinitrophenol (DNP), 2,4,6- trinitrophenol (TNP), 8-hydroxyquinoline (8HQ) and 1-nitroso-2-naphthol with propylenediamine as nitrogen donor ligands. Co-ordination sites in this ligand is only nitrogen atoms. It acts as a bidentate ligand.

Keywords- Thallium (I) metal chelate, Mixed ligand complex, Propylenediamine, Infrared spectra, Electronic absorption spectra.

I. INTRODUCTION

Coordination ability of Propylenediamine has been well documented with transition metals¹, rare earth metals², alkaline earth metals³ and alkalis metals⁴⁻⁵. In this communication we have synthesized and characterized a number of mixed ligand complexes of thallium (I) metal chelates of some organic acids with propylenediamine. They have general formula MLL^1 , where M = Tl (I), L = deprotonated ONP, TNP, 8HQ or 1N2N and L^1 = propylenediamine. The structure of the complexes have been characterized by elemental analysis, molecular conductivities, infrared spectra. Low values of molar conductivities of these complexes show they have complex nature.

Experimental

Thallium (I) chloride, propylenediamine, Potassium hydroxide (KOH), o-nitrophenol (ONP), 2,4- dinitrophenol (DNP), 2,4,6-trinitrophenol (TNP), 8-hydroxyquinoline (8HQ) and 1-nitroso-2-naphthol (1N 2N) of AnalaR Grade were used.

1. Preparation of alkali metal salt:

Preparation of potassium salt of o-nitrophenol (KONP): 139 mg. (0.001 mole) of o-nitrophenol

was taken in a dry conical flask and dissolved in limited amount of absolute ethanol. Now 56 mg. (0.001 mole) of KOH was added to it and refluxed for an hour with constant stirring on hot plate of magnetic stirrer at 50°C-60°C for about one hour. On cooling the content, orange yellow precipitate was obtained. It was filtered, washed with absolute ethanol and dried in an electric oven at 80°C.

2. Preparation of Thallium (I) metal salts:-

Preparation of thallium (I) salt of o-nitrophenol (ONP): 177 mg. (0.001 mole) of KONP was taken in aqueous medium in a conical flask and 239 mg. (0.001 mole) TlCl was added. The Whole mass was refluxed with constant stirring on hot plate of magnetic stirrer for one hour at 60°C-70°C. The content were cooled to give yellow precipitate. It was filtered, washed with absolute ethanol and dried in an electric oven at 80°C Yield -316 mg (95%) TL (ONP):-

Found:- 'C' = 20.93, H = 1.08, N = 13.86, Tl = 59.52% $C_6H_4NO_3$ Tl required:

C- 21.05, H-1.16, N-14.03. TL- 59.64%

3. Preparation of mixed ligand complexes:-

To a suspension of 342 mg. (0.001 mole), Tl (ONP) in absolute ethanol, 74 mg. (0.001 mole) propylenediamine (Pn) was added. When mixture was heated whole mass went into the solution. The solution was refluxed with constant stirring on hot plate of magnetic stirrer for two hours and cooled to give brick red solid adduct. It was filtered, washed with the solvent and dried at 100°C, Yield-349 mg (84%).

Tl(ONP)-Found:- C-25.89, H-3.25, N-9.91, Tl- 48.85%

$C_9H_{14}N_3O_3$ TL required : C-25.96, H-3.36, N- 10.09, Tl-49.03%

II. RESULT AND DISCUSSION

Some physical properties of the ligand (L¹) and the new mixed ligand complexes (MLL¹) are listed.

Table-1

Compound	Colour	M.p/B.p Decomp/trans Temp (°C)	Conductivity
Propylenediamine	Colourless	116.5 b	-
Tl (ONP) pn	Brick red	>300	12.1
Tl (DNP) Pn	Cream	220 md	10.5
Tl (ONP) pn	Yellow	295 d	8.5
Tl (8HQ) pn	Yellow	264 md	10.1
Tl (1N2N) pn	Greenish yellow	220 md	13.5

The mixed ligand complexes are generally coloured. They are appreciably soluble in polar solvent⁸ like methanol, DMF etc, Partly soluble in non-polar solvent namely chloroform, benzene, toluene etc. The complexes are stable under dry conditions.

The mixed ligand complexes of propylenediamine and thallium (I) metal chelates of some organic acids are characteristic- colour. They are appreciably soluble in most polar solvents like methanol, DMF etc. but they are partly soluble in non-polar solvents namely chloroform benzene, toluene etc. The complexes are found to be stable under dry conditions, e-g over anhydrous calcium chloride. They showed no change in stoichiometry or physical properties even after a long period but the complexes are unstable in moist air in presence of which they appear to decompose giving discolour solids of intermediate composition.

Table-1. It is appeared that all the complexes are fairly stable upto 300°C and undergoes transformation at a temperature higher than boiling

point of second ligand indicating thereby greater stability.

Molar conductance:

Molar conductance of all these complexes were measured in DMF at 31°C at a concentration of 10⁻³M. A value of about 35-40 ohm⁻¹ cm² mol⁻¹ appears characteristics of 1:1 electrolyte¹. Whereas ideally molar conductivity of a neutral complex should be zero. Low values (8.5-13.5 ohm⁻¹ cm² mol⁻¹) of molar conductivities of these complexes are due to slight ionization in the solvent. These values of molar conductivities indicate them to be covalent nature.

Integrated spectra:

Infrared spectra of the ligand (Propylenediamine) and its mixed ligand thallium (I) complexes⁴ were recorded in KBr phase between 4000-400cm⁻¹ with the help of FTIR spectrophotometer Shimadze 820/pc. Selected absorption bands are listed in

Table – 1.2 Pertinent TR data for ligand (Propylene diamine) & its mixed ligand thallioms (I) complexes

Compound	Selected infrared absorption bands (in cm ⁻¹)				
	ν_{N-H}	Asym δ_{N-H}	Sym δ_{N-H}	Rocking NH ₂	Far Infrared ν_{M-N}
Propylenediamine	3400	1600	1100	210	-
Tl (ONP) Pn	3446	1650,1593	1056,1006	892,790	670,610,520
Tl (DNP) Pn	3428	1650, 1599	1099	890,790	674,495
Tl (TNP) Pn	3435, 3082	1631,1563	1157,1077	796	544,519,485
Tl (8HQ) Pn	3237	1595,1578,1497	1100,1065	817, 785	648,585, 486
Tl (1N2N) Pn	3395	1622,1594,1552	1153, 839	875, 839	622,570,494

A comprehensive study of the infrared spectra of complexes of thallium (I) metal chelates of some organic acids with propylenediamine show that different NH₂ vibrations are present in the complexes. Through in some cases the vibrations of

organic acid salts of thallium (I) metal, overlap the-NH₂ vibrations but in most of the NH₂ vibrations can be located. A comparison of the spectra of the acid salt and complexes formed by propylenediamine,

points that these are extra peaks due to propylenediamine molecule.

The two N-H stretching vibrations appear as broad or medium peaks between 3400-3300 cm^{-1} . These bands are very much affected in the complexes. This appear between 3446-3237 cm^{-1} with increased intensity in the complexes, thereby suggesting that the decrease in bond order of N-H on complexation. This shifts is in conformity with the coordination through N-H as there has been electron drain from nitrogen of propylenediamine to the thallium (I)

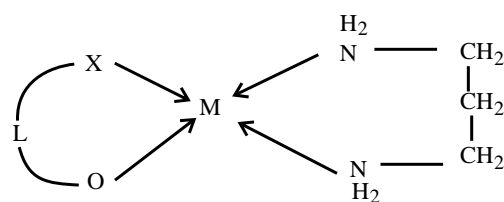
As we have discussed above lower symmetry⁹ of cis-isomer will split the NH_2 band at 1600 cm^{-1} (asymmetric mode) and $\sim 100\text{cm}^{-1}$ (symmetric mode). One or two bands have been observed in the region 1650-1473 cm^{-1} in the complexes of thallium (I) metal salts of some organic acids with propylenediamine. The complexes also show one or two bands between 1157-100 cm^{-1} region. These shifting indicates coordination of thallium (I) metal through nitrogen atom of NH_2 of second ligand (Pn)

Further the NH_2 rocking at 810 cm^{-1} shifted to higher frequency region 890-785 cm^{-1} in all these complexly also suggestive of coordination of thallium (I) metal through nitrogen atom of NH_2 group of propylenediamine.

The band in the region 520-485 cm^{-1} in the spectra of all mixed legand thallium (I) complexes may be assigned to M-O band frequency, while medium bands in the regions 674-544 cm^{-1} is assigned to M-N band frequency¹⁰. These bands are not present to ligand (Propylenediamine). The assignments are based on the assumption that since oxygen atom is more electronegative than nitrogen, the M-O band tends to be more ionic then M-N band. Consequently M-O vibrations are expected to appear at lower frequencies. The above data confirm the co-ordinations of oxygen atoms of O-H (phenolic) group and nitrogen atom of -NO (in case of 1N2N) or -NO₂ (in case of ONP, DNP & TNP) Pyridine ring (in case of 8HQ) to thallium (2) metal in all the mixed ligand complexes.

Structure and Bonding

On the basis of elemental analysis, the molecular formula of the mixed ligand Tl(I) complexes with propylenediamine is found it be MLL^1 , where M = Tl(I), L = deprotonated ONP, DNP, TNP, 8HQ or 1N2N and L^1 = propylenediamine (Pn). From infrared spectral studies, probable structure for all these complexes are suggested fig.-1



(X = O or N)

Figure -1

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