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MIXED LIGAND COMPLEXES OF Tl(I) METAL SALTS OF SOME ORGANIC ACIDS WITH PROPYLENEDIAMINE

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Some new mixed ligand Tl(I) complexes of propylenediamine(pn) have been synthesized and characterized on the basis of physico-chemical analyses. The infrared spectral data indicate that the coordinaton of the ligand(pn) with Tl(I) metal salts of organic acids through nitrogen atoms of -NH_2 groups.

KEYWORDS : Mixed ligand complexes, Propylenediamine, Thallium(I) metal salt, Infrared spectra.

INTRODUCTION

Propylenediamine is an important bidentate cheating ligand. Its complexes with alkali metals and some transition metals have well established [1-6]' In this communication, we have a number of mixed ligand Tl(I) complexes of general formula ML.HL', where M = Tl(I); L = deprotonated o-nitrophenol (ONP), 2, 4-dinitrophenol (DNP), 2, 4, 6-trinitro-phenol (TNP), 1-nitroso-2-naphthol (1N2N) or 8-hydroxyquinoline (8HQ); HL' = propylene-diamine(pn).

EXPERIMENTAL

O-nitrophenol (ONP), 2, 4-dinitrophenol (DNP), 2, 4, 6-trinitrophenol (TNP), 1-nitroso-2-naphthol (1N2N) or 8-hydroxyquinoline (8HQ) and propylenediamine(pn) of AnalaR grade were used as such.

Preparation of Tl(I) metal salts :

Organic acid and sodium hydroxide were taken in 1 : 1 molar ratio in 95% ethanol, and refluxed on hot plate with constant stirring at 80°C for about one hour. The solution was concentrated and cooled, when the sodium salt of organic acid precipitated out. It was filtered, washed with 95% ethanol and then dried in an electric oven at 100°C.

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Again sodium salt of organic acid was dissolved in 95% ethanol and an alcoholic solution of TlCl were mixed in 1 : 1 molar ratio. The mixture was refluxed on hot plate of magnetic stirrer at 60 – 70°C for about half an hour, when coloured precipitate of Tl(I) metal salt of organic acid was obtained. It was filtered, washed with 95% ethanol and then dried in an electric oven at 100°C.

Preparation of Mixed ligand complexes :

To a suspension of Tl(I) metal chelate of organic acid(ML) in absolute alcohol second ligand (propylenediamine) was added in 1 : 1 mole ratio. The mixture was refluxed on magnetic hot plate with constant stirring at 80°C for about two hours. On cooling the resulting solution, the characteristic colour adduct got separated. It was filtered, washed with absolute ethanol and then dried in an electric oven at 100°C.

RESULTS & DISCUSSION

Some physical properties of the ligand (propylenediamine) and the mixed ligand complexes (ML.HL′) obtained are listed in Table 1.

Table 1

Compound	Colour	M.P./Decomp./ Trans. Temp. (°C)	Molar Conductance	Analysis % found/(calcd.)			
				C	H	N	M
Propylenediamine (pn)	Colourless	119.5b	---	---	---	---	
Tl(ONP).pn	Yellowish green	245d	8.4	25.78 (26.00)	3.01 (3.13)	9.85 (10.11)	48.95 (49.20)
Tl(DNP).pn	Bright orange	268d	9.9	23.32 (23.46)	2.45 (2.61)	12.01 (12.16)	44.23 (44.40)
Tl(TNP).pn	Yellowish orange	275d	10.6	21.19 (21.37)	2.05 (2.18)	13.68 (13.85)	40.27 (40.44)
Tl(1N2N).pn	Brown	288d	9.3	35.84 (35.99)	3.35 (3.46)	9.51 (9.69)	46.86 (47.16)
Tl(8HQ).pn	Yellow	262md	10.2	34.55 (34.71)	3.26 (3.34)	9.20 (9.34)	45.31 (45.48)

Propylenediamine(pn) is a colourless liquid which is insoluble in cold water but soluble in ethanol, benzene, acetone etc. The mixed ligand complexes are generally characteristic coloured. They are appreciably soluble in polar solvents like methanol, ethanol, partly soluble in DMF, pyridine, acetone etc; but sparingly soluble in non-polar solvents like chloroform, n-hexane, benzene, dioxane etc.

Molar Conductance : Molar conductance of all the compounds were measured in methanol at 30°C at a concentration of 10^{-3} M. The values are given in Table 1. The value of about 35 – 40 ohm^{-1} cm^{2} mole [1] is characteristic of 1 : 1 electrolyte [7] whereas ideally molar conductance of neutral compound should be zero. However, significantly low values (8.4 - 10.6) of molar conductance of the compounds indicate them to be covalent nature.

Infrared Spectra : Infrared spectra of ligand, propylenediamine(pn) and its mixed ligand complexes were recorded in KBr phase between 4000 - 450 cm^{-1} with the help of JASCO-FTIR spectrophotometer model - 5300. Selected absorption bands are listed in Table 2.

An examination of the infrared spectra of mixed ligand complexes of Tl(I) metal salts of some organic acids with second ligand(pn) show that different NH_2 vibrations are present the complexes, Though in some cases, vibrations of the Tl(I) metal salts of organic acids overlap the $–NH_2$ vibrations, but most of the $-NH_2$ vibrations, can be located. A comparative study of the spectra of the Tl(I) metal salts and the complexes, points that there are extra peaks due to the propylene molecule.

Table 2. Pertinent IR data for ligand (propylenediamine) & its mixed ligand Tl(I) complexes

Compound	υ_{N-H}	**δasymN-H**	**δsymN-H**	**Rocking NH_2**	$\upsilon_{M-O/M-N}$
Propylenediamine (pn)	3400	1600	1100	810	---
Tl(ONP).pn	3254	1597	1142, 1102	878	630, 548
Tl(DNP).pn	3410	1564	1161	838	544, 520, 470
Tl(TNP).pn	3336	1600	1161, 1103	837, 811	621
Tl(1N2N).pn	3398	1602	1176, 1114	871	647, 576, 545, 456
Tl(8HQ).pn	3408	1596, 1563	1173, 1104	861	670, 647, 598, 558, 435

The N-H stretching vibration appears as broad band at 3400 cm^{-1}. This band is shifted between 3410 - 3254 cm^{-1} in the complexes, thereby suggesting that there has been decrease in the bond order of N-H, and hence coordination through the N-H as there has been electron drain from the nitrogen of second ligand(pn) to the Tl(I) metal.

As we have discussed above, lower symmetry of cis isomer will split the NH_2 band at nearly 1600 cm^{-1} (asymmetric mode) and 1100 cm^{-1} (symmetric mode). One or two bands have been observed in the complexes in the region 1602 - 1563 cm^{-1}. The complexes also show one or two bands in the region 1176 - 1102 cm^{-1}. These shifting indicate coordination of Tl(I) metal through nitrogen atom of $- NH_2$ groups of second ligand(pn).

Further the NH_2 rocking at 810 cm^{-1} shifted to higher frequency region 878 - 811 cm^{-1} in all these complexes also suggest coordination of Tl(I) metal through nitrogen atom of $- NH_2$ group of second ligand(pn).

The band in the region 520 - 435 cm^{-1} in the spectra of all mixed ligand Tl(I) complexes may be assigned to M - O band frequency while medium bands in the region 670 - 545 cm^{-1} assigned to M - N band frequency [8]. These assignments are based on the assumption [9] that since oxygen is more electronegative than nitrogen, the M – O bond tends to be more ionic than the M – N bond. Consequently M – O vibrations are expected to appear at lower frequencies. The above data confirm the coordination of oxygen atom of O – H (phenolic) group and nitrogen atom of –NO(1N2N)/$-NO_2$(ONP, DNP or TNP)/ pyridine ring (in case 8HQ) of first ligand, *i.e.*, organic acid to Tl(I) metal ion in all the complexes.

Electronic Spectra : Electronic spectra were recorded on Systronic Double Beam UV-VIS spectrophotometer - 2201 in methanol. The bands observed in electronic spectra of ligand (propylenediamine) and the mixed ligand Tl(I) complexes are given in Table 3.

The electronic absorption bands of the mixed ligand Tl(I) complexes are observed in the region 226 - 262 nm, which indicate π-π^* transition in the complexes. The mixed ligand complexes also show charge transfer bands in the region 329 - 390 nm.

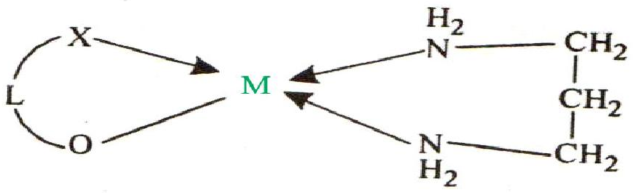
The shift in position of π-π^* and charge transfer bands of the ligand in the complexes show that there is a π-interaction between metal and ligand orbitals.

Table 3. Major diffuse reflectance bands(in nm) for mixed ligand Tl(I) complexes with propylenediamine(pn)

Compound	Diffuse reflectance (in nm)
Tl(ONP).pn	262
Tl(DNP).pn	390, 347, 330, 238
Tl(TNP).pn	390, 246
Tl(1N2N).pn	371, 329, 246, 232
Tl(8HQ).pn	258, 226

STRUCTURE & BONDING

On the basis of quantitative analysis and spectral data the probable structures of the complexes are shown in Fig. 1.



(Fig. 1)

where L = Deprotonated ONP, DNP, TNP, 8HQ or 1N2N; X = O or N

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