

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

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A number of mixed ligand Tl(I) complexes having general formula ML_2HL , where $M = Tl(I)$; $L =$ deprotonated o-nitrophenol (ONP), 2, 4-dinitrophenol (DNP), 2, 4, 6-trinitrophenol (TNP), 1-nitroso-2-naphthol (1N2N) or 8-hydroxyquinoline(8HQ); $HL =$ ethylenediamine (en) have been synthesized. On the basis of various physico-chemical investigations, it has been found that ethylenediamine behaves as bidentate ligand coordinating through nitrogen atoms of $-NH_2$ group.

KEY WORDS : Mixed ligand complexes, Ethylenediamine, Thallium (I) metal salt and Infrared spectra.

INTRODUCTION

Ethylenediamine is an important bidentate chelating ligand. It forms more stable five membered ring with metal ions. Werner *et al* [1] have prepared complexes of ethylenediamine with Co, Ni, Ag, Cu etc. by substituting NH_2 of metal amines. Prakash *et al* [2, 3] have synthesized a number of Au (III), Co (III) etc. complexes with ethylenediamine. The metal complexes of Zn (II) and Cd (II) with ethylenediamine containing two or three chelated ligands have been reported by Block *et al* [4, 5]. Recently, Kumar *et al* [6] have studied mixed ligand complexes of alkali metal salts of picolinic acid, quinaldinic acid and their N-oxides with ethylenediamine. In continuation, we report the synthesis of mixed ligand complexes of Tl (I) metal salts of some organic acids with ethylenediamine.

EXPERIMENTAL

O-nitrophenol (ONP), 2, 4-dinitrophenol (DNP), 2, 4, 6-trinitrophenol (TNP), 1-nitroso-2-naphthol (1N2N) or 8-hydroxyquinoline (8HQ) and ethylenediamine 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 $80^\circ C$ 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 $100^\circ C$.

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 (ethylenediamine) 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 (ethylenediamine) 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
Ethylenediamine (en)	Colourless	116.5b	---	---	---	---	
Tl(ONP).en	Greenish yellow	>300	10.2	23.78 (23.86)	2.91 (2.98)	10.35 (10.44)	50.65 (50.79)
Tl(DNP).en	Deep yellow	275d	9.5	21.32 (21.46)	2.40 (2.46)	12.41 (12.52)	45.33 (45.68)
Tl(TNP).en	Deep yellow	265d	8.0	12.39 (12.50)	1.95 (2.03)	14.08 (14.22)	41.37 (41.51)
Tl(1N2N).en	Light brown	298d	10.5	32.24 (32.32)	3.35 (3.43)	10.11 (10.28)	49.86 (50.03)
Tl(8HQ).en	Light yellow	262d	6.2	32.85 (33.00)	3.06 (3.21)	9.50 (9.62)	46.71 (46.84)

Ethylenediamine is a colourless liquid, insoluble in cold water but soluble in hot water, ethanol and ether. It is steam volatile. The mixed ligand complexes are of characteristic colours. They are appreciably soluble in polar solvents like methanol, ethanol, partly soluble in DMF, pyridine, acetone etc; but they are sparingly soluble in non-polar solvents, namely, chloroform, n-hexane, benzene dioxane etc.

Molar Conductance : Molar conductance of all the compounds were measured in methanol at 33°C at a concentration of 10^{-3} M. The values are given in Table 1. The value of about $35 - 40 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ is characteristic of 1 : 1 electrolyte [7] whereas ideally molar conductance of neutral compound should be zero. However, significantly low values (6.2 – 10.5) of molar conductance of the compounds indicate them to be covalent nature.

Infrared Spectra : Infrared spectra of the ligand (ethylenediamine) and its mixed ligand Tl(I) 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.

Table 2. Pertinent IR data for ligand(ethylenediamine) and its mixed ligand Tl (I) complexes

Compound	$\nu_{\text{N-H}}$	$\delta_{\text{asym N-H}}$	$\delta_{\text{sym N-H}}$	Rocking NH_2	$\nu_{\text{M-O/M-N}}$
Ethylenediamine (en)	3377, 3316	1600	1100	810	---
Tl(ONP).en	3468	1648, 1610, 1549	1148, 1140	848, 814	654, 568, 532, 455
Tl(DNP).en	3425	1625, 1590, 1565	1160	820	668, 546, 521
Tl(TNP).en	3551, 3375	1604, 1566	1135	837	635, 585, 530, 471
Tl(1N2N).en	3465	1639, 1610, 1560	1155, 1140	820	637, 585, 476
Tl(8HQ).en	3423	1610	1170, 1114	826	649, 560, 546, 455

In metal amine complexes. The four principle regions of absorptions are nearly 3300, 1600, 1100 and 800 cm^{-1} . These have been assigned to the N-H stretching mode [8] the asymmetric deformation, the symmetric deformation and the NH_2 rocking mode [9] respectively.

In present work, we have found that all the principal regions of absorption 3377 and 3316 cm^{-1} (stretching mode of $\nu_{\text{N-H}}$), 1600 cm^{-1} (asymmetric deformation of $\delta_{\text{N-H}}$) and 800 cm^{-1} (rocking NH_2) are present in the ligand (en).

The one N-H vibration appears as broad peak between 3551-3423 cm^{-1} . The 3377 and 3316 cm^{-1} bands of ethylenediamine are very much affected in the complexes. These appear between 3451-3423 cm^{-1} with increased intensity in the complexes, thereby suggesting that there has been decrease in the bond order of N-H on complexation. The higher shifting of bands are in conformity with the coordination through the N-H as there has been electron drain from the nitrogen of ethylenediamine to the Tl (I) metal.

Taking into consideration that lower symmetry of cis isomer will give rise to multiplicity in the nearly 1600 cm^{-1} (asym $\delta_{\text{N-H}}$) and 1100 cm^{-1} (sym $\delta_{\text{N-H}}$), it is observed that these complexes give relatively simple spectra. Two or three bands have been observed between 1648 -1549 cm^{-1} . Extra bands are due to presence of - NO_2 , - NH_2 , - NO of first ligand (*i.e.*, organic acids), very much overlap with other ligand vibration. These complexes also show one or two peaks between 1170-1114 cm^{-1} .

Further the NH_2 rocking at 810 cm^{-1} shifted to higher frequency region 848-814 cm^{-1} in all these complexes also suggestive of coordination of Tl (I) metal through nitrogen atom of - NH_2 group of the ligand.

The band in the region 521 - 455 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 668-530 cm^{-1} assigned to M - N band frequency [8, 9]. The above data confirm the coordination of oxygen atom of phenolic group and nitrogen atom of - $\text{NO}/-\text{NO}_2$ of first ligand, *i.e.*, organic acid to Tl(I) metal ion in all the mixed ligand 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 (ethylenediamine) 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 236 - 250 nm, which indicate $\pi-\pi^*$ transition in the complexes. The mixed ligand complexes also show charge transfer bands in the region 328 - 390 nm.

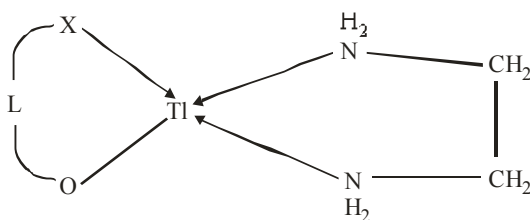
The shift in position of $\pi-\pi^*$ and charge transfer bands of the ligand in the complexes show that there is a π -interaction between metal and ligand orbitals.

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

Compound	Diffuse reflectance (in nm)
Tl (ONP).en	353, 250, 236
Tl (DNP).en	390, 351, 339, 240
Tl (TNP).en	371, 328, 248
Tl (1N2N).en	358, 373, 233
Tl (8HQ).en	364, 269, 251

STRUCTURE & BONDING

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



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

(Fig. 1)

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