

**SYNTHESIS AND CHARACTERISATION OF SOME MIXED LIGAND COMPLEXES OF THALLIUM (I) METAL**

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Received for publication: July 17, 2014; Revised: August 21, 2014; Accepted: September 07, 2014

Abstract: The present investigation has been undertaken to examine complex formation by thallium (I) derivatives of 2-nitro phenol (ONP), 2,4-dinitrophenol (DNP), 2,4,6-trinitrophenol (TNP), 1-nitroso-2-naphthol (1N2N), 8-hydroxyquinoline (8HQ), and 2-aminobenzoic acid (OABA) with thioacetamide. They have general formula $[ML(L')_2]$, where M = Tl (I), L = deprotonated ONP, DNP, TNP, 8-HQ, 1N2N and OABA and L' = thioacetamide. Thioacetamide is ambidentate ligand and can donate through sulfur or nitrogen or both. The preparation of mixed ligand complex with the thallium (I) salt of o-nitrophenol and 2, 4-dinitrophenol with the thioacetamide (TAD) was unsuccessful.

Key Words: 2, 4, 6-trinitrophenol (TNP), 1-nitroso-2-naphthol (1N2N), 8-hydroxyquinoline (8HQ), and 2-aminobenzoic acid (OABA), thioacetamide

INTRODUCTION

Metal complexes of sulfur ligands have received much attention during the recent years because of their versatile use as antifungal and antibacterial agents. Complexes of nitrogen and sulfur containing ligands are the subject of much interest in current research. Ligands containing nitrogen and sulfur donor atoms represent two donor sites for coordination. Thus, the coordination behaviors of such ligands are quite interesting. They can coordinate the central atom in three different manners: (a) Through nitrogen atoms, (b) Through sulfur atoms, or (c) Through both sulfur and nitrogen atoms, simultaneously.

Not much work has been done on thioacetamide and N-substituted thioacetamide as complexing agents, although these ligands are isoelectronic with thiourea. Mostly the physical studies have been limited to their crystallographic properties¹⁻⁴.

MATERIALS AND METHODS

The chemicals used are products of across and Sigma-Aldrich Ltd. All mixed ligand complexes of thallium were obtained in many steps. In first step potassium salt of all organic acid were prepared. After that, thallium salts of all organic acid were prepared by ligand substitution method. Thereafter thioacetamide was added to the suspension of thallium salts of all organic acid in absolute ethanol in 1:2 mole ratios. The whole mass was refluxed with constant stirring on hot plate with magnetic stirrer for two hours at 50°C. On cooling at room temperature, it was filtered, washed with absolute ethanol, and dried in an air oven at 80°C. After analysis it was found that:

1. Analysis of [Tl (TNP) (TAD)₂]:

The analytical result of the complex was found to contain: C, 21.13; H, 3.01; O, 18.04; N, 11.43; S, 11.85; Tl, 34.96%

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The complex $[C_{10}H_{12}N_5O_7S_2Tl]$ required C, 20.62; H, 2.06; O, 19.24; N, 12.07; S, 10.99; Tl, 35.05 %

2. Analysis of [Tl (8HQ) (TAD)₂]:

The analytical result of the complex was found to contain: C, 31.33; H, 3.21; N, 8.43; O, 3.21; S, 12.85; Tl, 40.96 %

The complex $[C_{13}H_{16}N_3OS_2Tl]$ required: C, 31.13; H, 3.27; N, 8.34; O, 3.24; S, 12.76; Tl, 40.24 %

IR v: 3387 vw, 2940 w, 1623.5 m, 1547 m, 1426.9 w, 929.1 w, 762 670.6 vs, 622.9 vw, 464.1 vw.

3. Analysis of [Tl (1N2N) (TAD)₂]:

The analytical result of the complex was found to contain: C, 31.94; H, 3.04; N, 7.91; O, 6.04; S, 12.17; Tl, 38.78 %

The complex $[C_{14}H_{16}N_3O_2S_2Tl]$ required: C, 31.78; H, 2.99; N, 7.52; O, 5.94; S, 12.07; Tl, 38.23 %

IR v: 3446.1 s br with spike, 2977.5 w, 1648 m, 1520 m, 1424.6 w, 928.7 w, 760, 670.7 vs.

4. Analysis of [Tl (OABA) (TAD)₂]:

The analytical result of the complex was found to contain: C, 26.94; H, 3.27; N, 8.57; O, 6.53; S, 13.06; Tl, 41.63 %

The complex $[C_{11}H_{16}N_3O_2S_2Tl]$ required: C, 26.78; H, 3.42; N, 8.46; O, 6.44; S, 12.96; Tl, 41.26 %

IR v: 3424 vs b with spike, 2946 w 1640.5 m br, 1519.7 w br, 1424.7 w, 928.9 w, 758, 670.8 vs, 491.4 vw.

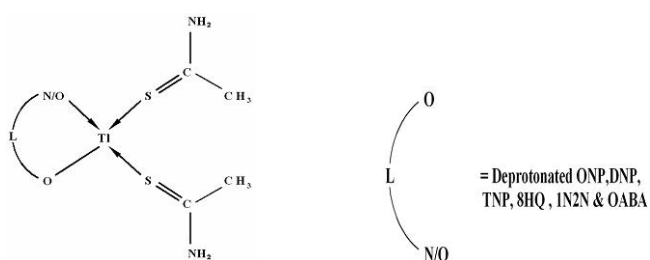
a- assymmetric, s-symmetric, sb-strong broad, w-weak, wb-weak broad, d-doublet, m-medium, sh-shoulder



RESULTS

On the basis of elemental analysis, the molecular formula of the mixed ligand complexes of Tl(I) metal chelates of 2,4,6-trinitrophenol; 1-nitroso-2-naphthol; 8-hydroxyquinoline; 2-aminobenzoic acid with thioacetamide is found to be $[ML(L')_2]$, (where M = Tl (I), L = deprotonated ONP, DNP, TNP, 8-HQ, 1N2N and OABA and L' = thioacetamide).

Their IR data suggest that the Tl (I) is bonded through sulfur atom of thiocarbonyl group and organic acids are bidentate in metal complexes. So, based on all the factual information as well as analytical data, the probable structure of the complexes is as such



DISCUSSION

Organic compounds containing a thioamide moiety (H-N-C=S) have been studied by several workers^{5,6-8}, and it has been suggested that all such compounds give rise to four thioamide bands in their IR spectra. Thioamide band I, band II, band III, and band IV, generally appeared in the range of 1550 cm^{-1} , 1250 cm^{-1} , 900-1000 cm^{-1} , and 750-850 cm^{-1} respectively. All these were mixed bands and have had contributions from (δ N-H + δ C-H + ν C=N + ν C=C), (δ N-H + δ C-H + ν C=N + ν C=S), (ν C=N + ν C=S), and (ν C=S), respectively.

It has been reported that for monodentate sulfur ligands, band IV, (ν C=S), has been used as diagnostic of metal ligand bonding⁹⁻¹⁶. Metal sulfur bonding resulted in red shift of about 50 cm^{-1} in the thioamide band IV, and metal nitrogen bonding generally results in either no shift or blue shift of the order 30-40 cm^{-1} in this band. A red shift of the order of about 100 cm^{-1} in the thioamide band IV, is an identification of a bridging system. However, not much work has been done on sulfur and nitrogen containing ligands (having a thioamide group) to establish the nature of bonding in the complexes. Although many authors agreed that, the position of thioamide band IV on complexation is very useful to indicate whether bonding has taken place through metal nitrogen or through metal sulfur. Practically little attention has been paid towards the shift in all the four-thioamide bands of the ligand on complexation with metal ions. It also remained to be established as to how the four thioamide bands are affected when coordination

occurred only through sulfur or only through nitrogen¹⁷ or through both nitrogen and sulfur atoms.

The IR spectra of thioacetamide have been studied by several investigators¹⁸⁻²³ and the assignments of some vibration band have been reported. In IR spectra the band at 3290 cm^{-1} were assigned to NH_2 asymmetric stretching. The band at 3165 cm^{-1} has been assigned to NH_2 symmetric stretching. The bands at 2945 cm^{-1} have been assigned to CH_3 asymmetric stretching. The band at 1648 cm^{-1} has been assigned to NH_2 bending vibration.

The band at 1478 cm^{-1} has been assigned to CH_3 asymmetric deformation. The band at 1393 cm^{-1} has been assigned due to ν C-N stretching. The band at 1364 cm^{-1} has been attributed to CH_3 symmetric deformation. The band at 1306 cm^{-1} has been due to skeleton vibration and NH_2 rocking. A band at 1030 cm^{-1} has been assigned to NH_2 rocking and CH_3 rocking. A band at 975 cm^{-1} has been assigned due to combination of C-C stretching, CH_3 rocking and C=S stretching. A band at 718 cm^{-1} was due to combination of C=S stretching and C-C stretching. A band at 709 cm^{-1} was due to NH_2 wagging and NH_2 twisting. A band at 517 cm^{-1} was due to π C-C bond.

A band at 471 cm^{-1} and 460 cm^{-1} was due to NCS deformation. A band at 375 cm^{-1} has been observed due to C-C deformation. Some combination bands were also observed at 2860 cm^{-1} and 2670 cm^{-1} .

The IR spectrum of mixed ligand complexes of Tl (I) chelates with thioacetamide has following characteristics. A broad band in the range 3400 cm^{-1} is due to weak hydrogen bonding. A band at 3290 cm^{-1} and 3165 cm^{-1} in the ligand thioacetamide due to asymmetric and symmetric NH_2 stretching respectively. There has been negative shift of 8-25 cm^{-1} in the NH_2 bending of the ligand, except in $[\text{Tl}(\text{8HQ})(\text{TAD})_2]$ complex. The ligand thioacetamide display thioamide band III at 975 cm^{-1} and thioamide band IV at 748 cm^{-1} . Thioamide band IV due to C=S stretching in ligand thioacetamide was observed at 758-765 cm^{-1} in the mixed ligand complexes. The shift of ν (C=S) indicated localised (C=S) double bond character on bonding. The shift can be explained as co-ordination through sulfur atom of thioacetamide ligand to Tl metal. There is also small increase in the band at 460 cm^{-1} of the ligand due to NCS deformation, which is consistent with the fact reported by Kutzelnigg and Mecke²³, that the band was shifted by 29 cm^{-1} towards a lower frequency on the formation of complexes with metal atoms.

Thioacetamide is white crystalline powder having the melting point 110-113 $^{\circ}$ C. It is soluble in water, ethanol, acetone etc. but it's all mixed ligand

complexes are colored. Complexes are almost insoluble or slightly soluble in polar solvents. Thus conductivities measurements are not possible in these complexes. The magnetic susceptibility of Tl (I) mixed ligand complexes were determined at room temperature by Gouy method. It was found that almost all complexes are diamagnetic as expected.

ACKNOWLEDGMENT

The authors pay their sincere gratitude to Department of Chemistry, Patna Science College and Department of Chemistry, Patna University, Patna, for providing lab facilities. The authors would also like to thank CSIR-Central Drug Research Institute Lucknow for the elemental analysis and Infra-red spectroscopy.

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Source of support: Nil

Conflict of interest: None Declared