

## Synthesis and characterisation of some mixed ligand complexes of thallium (I) metal with isonitrosoethylmethyl ketone

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Received: 21.10.2021; accepted: 21.10.2021; published online: 30.12.2021

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 Isonitrosoethylmethyl Ketone. They have general formula  $[ML(HL')]$ , where  $M = Tl(I)$ ,  $L =$  deprotonated ONP, DNP, TNP, 8-HQ, 1N2N and OABA and  $L' =$  Isonitrosoethylmethyl Ketone. Isonitrosoethylmethyl Ketone is ambidentate ligand and can donate through oxygen or nitrogen or both. The preparation of mixed ligand complex with the thallium (I) salt of 2,4-dinitrophenol and 2,4,6-trinitrophenol with the Isonitrosoethylmethyl Ketone (INEMK) have very low yield.

**Key words:** 2-nitrophenol (ONP), 1-nitroso-2-naphthol (1N2N), 8-hydroxyquinoline (8HQ), and 2-aminobenzoic acid (OABA), Isonitrosoethylmethyl Ketone (INEMK).

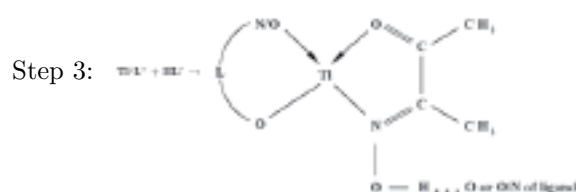
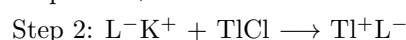
### 1. Introduction

Synthesis of complexes containing two different ligands is of great interest for coordination chemists due to their enhanced stability than single ligand complexes. Most of these works have been done with the transition metal<sup>1-4, 37-39</sup>, rare earth, and alkali metals<sup>5-21</sup>. Thallium salts and complexes have been widely used in analytical laboratories, as powerful bacteriocides, and efficient catalyst in organic reactions. Literature survey<sup>22-32</sup> revealed that Tl(I) either received very little attention or have neglected towards its coordination behaviour. This paper describes the synthesis and characterization of mixed ligand thallium (I) complexes with some organic acids and isonitrosoethylmethyl ketone. The latter ligands have been specifically chosen to clarify the nature of the linkage of the ambidentate isonitroso group.

### 2. Experimental

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. The next step was to prepare ligand Isonitrosoethylmethyl ketone by the method described by Semon et. al.<sup>33</sup>. Thereafter isonitrosoethylmethyl ketone was added to the suspension of thallium salts of all

organic acid in absolute ethanol in 1 : 1 mole ratio. The whole mass was refluxed slowly with constant stirring on hot plate with magnetic stirrer for two hours at 50 °C. On cooling at room temperature, obtained precipitate was filtered, washed with absolute ethanol, and dried in an air oven at 80 °C.



After analysis it was found that:

#### I. Analysis of [Tl(ONP) INEMK]:

The analytical result of the complex was found to contain:

On analysis it was found to contain: C, 27.08; H, 2.48; O, 18.08; N, 6.32; Tl, 46.05%.

The complex  $[C_{10}H_{11}N_2O_5Tl]$  required: C, 27.00; H, 2.02; O, 18.23; N, 6.73; Tl, 46.03%.

Colour: Light Pink

IR  $\nu$  : 3369.4 s, 1633.5 m, 1620 m, 1521.4 m & b, 1218 s, 1047.2 m, 928.6 m, 761.3 s, 671 m, 504 s, 488 s.

#### II. Analysis of [Tl(DNP) INEMK]:

The analytical result of the complex was found to contain:

On analysis it was found to contain: C, 24.56; H, 2.05; O, 22.95; N, 8.62; Tl, 41.09%.

The complex  $[C_{10}H_{10}N_3O_7Tl]$  required: C, 24.82; H, 2.95; O, 22.30; N, 8.11; Tl, 41.80%.

Colour: Red

IR  $\nu$  : 3278.7 s, 1633.5 m, 1521.4 m & b, 1215.6 s, 1047.2 m, 928.6 m, 756.8 m, 670 m, 557.1 s, 496 mb.

### III. Analysis of [Tl(TNP) INEMK]:

The analytical result of the complex was found to contain:

On analysis it was found to contain: C, 22.51; H, 1.65; O, 27.02; N, 10.51; Tl, 38.22%.

The complex  $[C_{10}H_9N_4O_9Tl]$  required: C, 22.17; H, 1.58; O, 26.46; N, 11.07; Tl, 37.32%.

Colour: Brown Red

IR  $\nu$  : 3177.7 m, 1620 m, 1521.4 m & b, 1215.9 s, 1047.2 m, 928.6 m, 761.6 s, 670 m, 514.4 m, 514 s.

### IV. Analysis of [Tl(8-HQ) INEMK]:

The analytical result of the complex was found to contain:

On analysis it was found to contain: C, 34.79; H, 2.89; O, 10.68; N, 6.32; Tl, 45.06%.

The complex  $[C_{13}H_{13}N_2O_3Tl]$  required: C, 34.28; H, 2.37; O, 10.37; N, 6.64; Tl, 45.34%.

Colour: Light Brownish Cream

IR  $\nu$  : 3300–3200 sb, 1670 m, 1580 m, 1216.2 s, 1010 s, 761.4 vs, 670 s, 488 m.

### V. Analysis of [Tl(1N2N) INEMK]:

The analytical result of the complex was found to contain:

On analysis it was found to contain: C, 35.22; H, 2.79; O, 13.28; N, 6.02; Tl, 43.00%.

The complex  $[C_{14}H_{13}N_2O_4Tl]$  required: C, 35.02; H, 2.72; O, 14.22; N, 5.87; Tl, 42.76%.

Colour: Yellowish Brown

IR  $\nu$  : 3448.3 sb, 1620.8 m, 1545.2 m, 1216.1 s, 1045.9 s, 928.9 s, 760.1 vs, 670.7 s, 623.9 m, 570.5 m, 504 m.

### VI. Analysis of [Tl(OABA) INEMK]:

The analytical result of the complex was found to contain:

On analysis it was found to contain: C, 29.93; H, 2.95; O, 14.51; N, 6.35; Tl, 46.26%.

The complex  $[C_{11}H_{13}N_2O_4Tl]$  required: C, 29.48; H, 2.42; O, 14.46; N, 6.76; Tl, 46.00%.

Colour: Light Pink

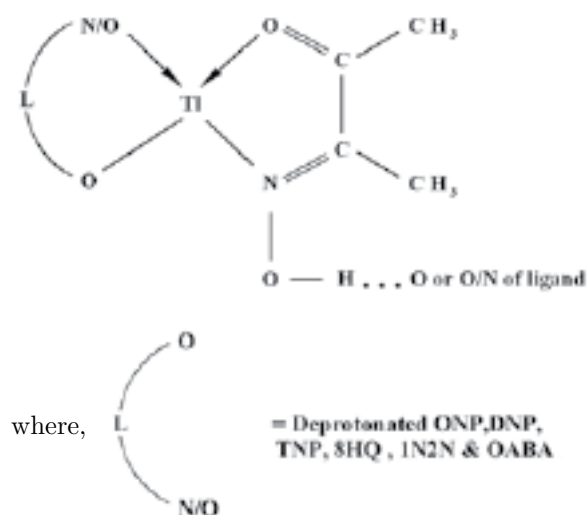
IR  $\nu$  : 3391 sb, 1649.2 vs, 1519.6 m, 1216.6 s, 1045.8 m, 929 s, 764 s, 670.6 m, 504 s, 480 m.

Note: s-strong, sb-strong broad, wb-weak broad, d-doublet, m-medium, b-broad, vw-very weak

## 3. Result and discussion

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

Their IR data suggest that the Tl (I) metal is coordinated through oxygen atom of carbonyl group as well as the nitrogen atom of the oximino group. So, based on all the factual information as well as analytical data, the probable structure of the complexes is as such shown in Figure.



### 3.1 IR Spectra

Infrared spectra of the ligand (Isonitrosoethylmethyl ketone) and its mixed ligand Thallium(I) complexes were recorded in KBr disc between 4000–500  $cm^{-1}$  with the help of FTIR Spectrophotometer PERKIN ELMER X (: 4 scans 4.0  $cm^{-1}$ ). The spectra of isonitrosoethylmethyl ketone shows 143 multiple medium broad absorption band in the range 3300–3200  $cm^{-1}$ . The presence of absorption features in this region points out the presence of intramolecular hydrogen bonding involving isonitroso hydrogen atom and the carbonyl oxygen atom of the ligand. The infrared spectrum of the ligand shows characteristic absorption at 1670  $cm^{-1}$ , 1580  $cm^{-1}$  and 1010  $cm^{-1}$  which may be assigned to carboxyl  $\nu C=O$ , aldimine  $\nu C=N$  and  $\nu N-O$ , modes of IR vibrations respectively.

The absorption band at  $1580\text{ cm}^{-1}$  of the ligand has been assigned to the stretching  $\nu\text{C}=\text{N}$  absorption either disappear or towards lower frequency by  $38\text{--}60\text{ cm}^{-1}$  with few exception. This shift towards lower frequency is due to weakening of  $\text{C}=\text{N}$  bond strength. This feature suggests the coordination of the ligand with thallium metal through imine nitrogen atom.

The bands at  $1670$  due to  $\nu\text{C}=\text{O}$  vibrations are observed in the spectra of the ligands but either it disappear or there is negative shift In the mixed ligand thallium (I) complexes with appearance of  $\nu\text{C}-\text{O}$  bands, supports coordination of oxygen<sup>30</sup>.

Further the entire mixed ligand complexes exhibit a presence of very strong band at  $1216\text{--}1217\text{ cm}^{-1}$  which is characteristic of coupled isonitroso N-bonded  $\nu\text{N}-\text{O}$ . The IR data therefore clearly indicate that the isonitroso group coordinates through its nitrogen<sup>34</sup>.

The presence of a very strong absorption band at  $767\text{ cm}^{-1}$  in ligand is due to aromatic C-H out of plane bending of monosubstituted benzene whereas in mixed ligand complexes either its presence may be due to same reason or due to orthodisubstituted benzene as well as the quinoline ring in deprotonated salt of Tl with organic acid. The band  $680\text{ cm}^{-1}$  and between  $670\text{--}465\text{ cm}^{-1}$  is due to aromatic ring deformation band in them or  $\text{C}=\text{C}$  deformation band of the ring compound deformation vibration of phenyl and other substituents.

The band in the region  $521\text{--}455\text{ cm}^{-1}$  in the spectra of all mixed ligand Tl (I) complexes may be assigned to Tl-O band frequency while medium bands in the region  $668\text{--}530\text{ cm}^{-1}$  assigned to Tl-N band frequency<sup>32, 35-36</sup>. 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.

### 3.2 Electronic Spectra

Electronic spectra were recorded on Systronic Double Beam UVVIS spectrophotometer-2201 in ethanol. The electronic spectra of the mixed ligand Tl(I) complexes show bands at the region  $233\text{--}302\text{ nm}$  which indicates  $\pi-\pi^*$  transition in the complexes. Most of the mixed ligand complexes also show a charge transfer bands in the region  $328\text{--}386\text{ nm}$ . The shift in position of  $\pi-\pi^*$  transition and charge transfer bands in the mixed ligand Tl(I) complexes show that there is a  $\pi$ -interaction between metal and ligand orbitals<sup>3, 30, 32, 37</sup>.

### 3.3 Conductivity Measurements

Isoethylmethyl ketone ligand is a white shiny powder having the melting point  $76.5\text{ }^\circ\text{C}$ . It is soluble in ethanol and its all mixed ligand complexes are coloured. Molar conductance of all the compounds was measured in DMF at  $30\text{ }^\circ\text{C}$  at a conc. of  $10^{-3}\text{ M}$ . The value of about  $35\text{--}40\text{ ohm}^{-1}\text{ mol}^{-1}\text{ cm}^2$  should be observed which a characteristic of 1 : 1 electrolyte was whereas ideally molar conductance of a neutral compound should be zero. However, significantly low values (7.0-9.2) of molar conductance of the compounds indicate that ligand molecules are bonded to metal atom and no free ionic ligand molecule is present in complexes.

### 3.4 Magnetic Susceptibility

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.

## 4. Conclusion

The ligands L and L/H coordinate in 1 : 1, metal : ligand ratio as monobasic bidentate. The analytical and spectral studies suggest structures shown in figure in results part. Based on the above studies it is clear that Tl (I) metal is coordinated through oxygen atom of carbonyl group as well as the nitrogen atom of the oximino group in the molecule, capable of chelation to form five membered ring for requisite stabilization of adducts.

### Acknowledgement

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.

### References

- [1] V. J. Babar, B. J. Desai and V. M. Shinde: *Ind. Chem. Soc.* 60 (9) (1983).
- [2] K. K. Banerji, P. Nath and G. V. Bakore : *Bulletin of the chemical society of japan* vol. 43 (1970) 2027-2029.
- [3] A. Sreekantan, N. S. Dixit and C.C. Patel, *J. Inorg. Nucl Chem.* Vol. 42, pp. 483-487 (1980).
- [4] S. V. Salvi, P. H. Umadikar, M. R. Patil, P. M. Dhadhke and N. V. Bhatt: *SpectrochimActa*, Part B, 39B (8), (1984) 965-8 (Eng).
- [5] A. K. Banerjee, A. J. Layton, R. S. Nyholm and M. R. Truter: *J. Chem. soc. A*, 292 (1970) 1894.
- [6] Dharm Prakash and S. P. Singh : *Polyhedron*, 7 (1988) 1.

- [7] A. K. Banerjee, A. J. Layton, R. S. Nyholm and M. R. Truter: *J. Chem. soc. A*, 292, (1970) 1894.
- [8] Dharm Prakash and S. P. Singh : *Polyhedron*, 3, (1984) 243.
- [9] A. K. Banerjee, Dharm Prakash, S. K. Roy and P. Kejriwal: *J. Ind. Chem. soc.* 53, (1976) 524.
- [10] A. K. Banerjee, Dharm Prakash and S. K. Roy: *Ibid*, 53, (1976) 458.
- [11] A. K. Banerjee, Dharm Prakash, P. Kejriwal and S. K. Roy: *Ibid*, 55, (1978) 1308.
- [12] A. K. Banerjee, Dharm Prakash and S. K. Roy: *Ibid*, 53, (1976) 465.
- [13] Dharm Prakash and S. P. Singh: *Ibid*, 60, (1983) 695.
- [14] *Idem*: *Ibid*, 62, (1985) 424.
- [15] A. K. Banerjee and Dharm Prakash: *Ibid*, 58, (1981) 1102.
- [16] T. K. Sinha and S. K. Roy: *J. Ind. Chem. soc.* 58, (1981) 1008.
- [17] O. P. Gupta: Ph.D. Thesis, P. U. (1996).
- [18] Birendra Kumar: Ph.D. Thesis, P. U. (1992).
- [19] Jai Ram Prasad Singh: Ph.D. Thesis, P. U. (1996).
- [20] Rajneesh Kumar: Ph.D. Thesis, P. U. (1992).
- [21] Kwaskowska, E. and Ziolkowski, J. J., *Trans. Met. Chem.*, 8(2), 103 (1983).
- [22] Allan, J. R., Geddes, W. C., Hindle, C. S. and Lowe, A. J., *Plastics Rubber & Composites Processing & Appls.*, 16(2), 91 (1991).
- [23] Smith G., Kennard, C. H. L. and Byriel, K. A., *Aust. J. Chem.*, 52(4), 325 (1999).
- [24] Ivlieva, V. I., Gridasova, R. K., Zaitsev, B. E. and Ezhov, A. I., *Russ. J. Coord. Chem.*, 27(1), 70 (2001).
- [25] Ros, M. G. A., Metwally, S. M., El Gamel, M. M. and Abd El Haleem, S. M., *Bull. Korean Chem. Soc.*, 22(7), 663 (2001).
- [26] Ivlieva, V. I., Zaitsev, B. E., Ezhov, A. I. and Gridasova, R. K., *Russ. J. Coord. Chem.*, 27(1), 70 (2001).
- [27] Ros, T. G., Lee, M. K. V. D., Dillen, A. J. V, Geus, J. W. and Koningsbergeran, D. C., *J. Mol. Catalysis*, 186(1-2), 13 (2002).
- [28] Humphrey, S. M., Redshawi, C., Holmes, K. E and Elsegood, M. R. J., *Inorg. Chim. Acta.*, 358(1), 222 (2005).
- [29] Soares-Santos, P. C. R., Sa, R. A., Trindade, T. and Carlos, L. D., *J. Alloys. Compds.* 451(1-2) 575, (2008).
- [30] M. K. Saini, Monika Swami, N. Fahmiy, Kusum-jain and R. V. Singh, *Journal of Coordination Chemistry* Vol. 62, No. 24, 3986-3996 (2009).
- [31] Ashok kr. Gupta, Mehendi Imam, Sanjay kr. Srivastawa, Chhote Lal Barai, *ActaCienciaIndica*, Vol. XL C, No. 1, 19 (2014).
- [32] M. Mishra, A K gupta, Salinipriya, Birendrakumar: *actacienciaindica*, vol. Xlii c, no. 1, 01 (2016).
- [33] W. L. Semon and V. R. Domerill: *J. Am. Chem. Soc.* 47, 2038 (1925).
- [34] M. J. Lacey, C. G. Macdonald, J. S. Shannon and P. J. Collin, *Aust. J. chem.* 23, 2279 (1970).
- [35] Shyamal, A. and Singhal, O. P., *Trans. Met. Chem.*, 4, 179 (1995).
- [36] Condrate, R. A. and Nakamoto, K., *J. Chem. Phys.*, 42, 2590 (1965).
- [37] Nitin H. K., Shridhar S. J, Sajid H. S, Sushma J. T., Dinkar J. A: *Orient J Chem* 2016; 32(6). Available from: <http://www.orientjchem.org/?p=25851>
- [38] Asha kumari and H. P. Yadav, *ActaCienciaIndica*, Vol. XLVI-C, No. 1, 1 (2020).
- [39] MD. Ashrafuzzaman. Et. al., *J. Chil. Chem. Soc.* vol. 66, no. 3 Concepción set (2021). <http://dx.doi.org/10.4067/S0717-97072021000305295>