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Synthesis, Spectral and Antimicrobial Studies of Hg(II), Pd(II) and Pt(II) Complexes with 2-Thiopicoline anilide

YOGENDRA JHA* and L.K. MISHRA
Department of Chemistry, C.M. Science College, Darbhanga-846 004, India

Complexes of mercury(II), platinum(II) and palladium(II) with the 2-thiopicoline anilide have been prepared and characterized by elemental analysis, magnetic and electronic spectral studies. The square planner geometry to all the palladium(II) and platinum(II) complexes and tetrahedral geometry to the mercury(II) complexes have been suggested. 2-Thiopicoline anilide and its palladium(II) complexes were found to show antimicrobial activity towards the growth of the *Subtilis* and *Micrococcus* sp.

Key Words: Synthesis, Antimicrobial studies, Transition metal complexes thioamide ligands.

INTRODUCTION

Metal complexes of β-diketone as well as thio compounds have been widely used in coordination chemistry due to their versatility and antimicrobial activity[1-3] for the first chelate ring the coordinating atom of is pyridyl nitrogen and the second coordinating atom is sulphur of thioamide group. To explore the effect of potential coordinating ability of thioamide adjacent to 2-pyridyl group the synthesis, characterization and biological activity of 2-thiopicoline anilide (Fig. 1) and its Pd(II), Pt(II) and Hg(II) complexes are reported in this paper.

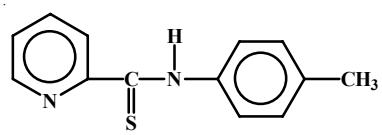

Fig. 1. 2-Thiopicoline anilide

EXPERIMENTAL

All the organic solvents and metal salts used were of AnalaR grade. The solvent ethanol and methanol were distilled by standard procedures before use. The ligand used in this work was prepared and characterized by elemental analysis. The metal and sulphur estimations were carried out by standard methods[4-6] and nitrogen by Kjeldahl method. The conductance was measured in DMF a DMSO solvent on an

Elico CM-82 conductivity bridge. The magnetic susceptibility measurements at room temperature were made in Gouy's balance. The IR spectra were recorded on Perkin-Elmer-137 instrument in Nujol Mull/KBr pellets. ^{1}H NMR spectra were recorded on an Bruker WP 80 SY spectrometer and electron spin resonance spectra complexes in polycrystalline state were recorded on varian E-4x band ESR spectrometer using DPPH free radical as 'g' marker (g = 2.0027) at room temperature.

Synthesis of 2-thiopicoline anilide: 2-Thiopicoline anilide was prepared under the reaction of Willgerdot.

2-Methyl pyridine and *p*-methyl aniline are distilled with pure sulphur. *p*-Methyl aniline (distilled 100 mL), 2-methyl pyridine (distilled 50 mL) and sulphur (powder 50 g) were mixed in a 500 mL flask fitted with water reflux condenser. The mixture was refluxed at 145 to 150 ºC. The mixture was left overnight. The solid red crystals obtained, were filtered and recrystallized twice with ethanol. The deep yellow compound was obtained. It was dried in vacuum. The ligand is highly soluble in methanol, acetone, *etc*. The melting point of the product was found to be 105 ºC (m.f. $C_{13}H_{12}N_2S$). Analysis: Found in %, C (68.41), H (5.26), N (12.26), S (14.02) requires in % C (68.42), H (5.27), N (12.28), S (14.03).

Synthesis of mercury complex: Mercuric acetate (0.02 M) solution is aqueous ethanol (30 mL) was treated with ligand (0.01 M) solution in acetone (30 mL) and refluxed slowly on a steam bath for 0.5 h. The yellow granular precipitate was filtered, washed with excess of water and finally with ethanol and then dried in a dessicator over $CaCl_2$.

Complex of palladium: One per cent aqueous solution of palladium chloride (0.02 M) solution with a few drops of dil. HCl (pH 3-4) in aqueous ethanol (30 mL) was treated with ligand (0.01 M) solution in acetone (30 mL) and refluxed slowly on a steam bath for 45 min. A chocolate brown precipitate separated out. It was filtered, washed with water and ethanol and then dried in a vacuum over fused $CaCl_2$.

Platinum complex: One per cent platinum(II) chloride (H_2PtCl_4) (0.02 M) solution in aqueous ethanol (30 mL) was treated with ligand (0.01 M) solution in acetone (30 mL) and refluxed slowly on a steam bath for 0.5 h. The yellow precipitate was filtered, washed with excess of water and finally with ethanol and then dried in a desicator over $CaCl_2$.

RESULTS AND DISCUSSION

The complexes prepared are stable at room temperature and are non-hygroscopic. The complexes are freely soluble in DMF and DMSO. The analytical data, motor conductance values and colours of the complexes have been presented in Table-1. The low conductance values of the complexes indicate that all complexes are non-electrolytic in nature, which implies that the new ligand deprotonate during complexation. The analytical data of all the new complexes (Table-1) agree well with the proposed molecular formulae.

TABLE-1

Complex	Colour	Elemental analysis (%): Found (Calcd.)			λ_m [b] (o_C)	μ_{eff} (BM)
		Metal	Nitrogen	Sulphur		
$[Hg(L)_2]\cdot H_2O$	Yellow	29.71 (29.73)	8.31 (8.32)	9.47 (9.50)	8	D[c]
$[Pt(L)_2]\cdot H_2O$	Yellow	29.13 (29.14)	8.36 (8.37)	9.55 (9.57)	8	D[c]
$[Pd(L)_2]\cdot H_2O$	Chocolate brown	18.26 (18.27)	9.66 (9.67)	11.02 (11.04)	7	D[c]

[b]Molar conductance (Ω^{-1} cm^2 mol^{-1}); [c]Diamagnetic.

2-Thiopicoline anilide complexes of Hg(II), Pd(II) and Pt(II) showed broad bands when compared to ligands in the region of 3600-3200 cm^{-1}. The absence of 780 cm^{-1} band in the 2-thiopicoline anilide complexes of Hg(II), Pd(II) and Pt(II) indicates the presence of lattice water[7-9]. The bands due to pyridine ring ν(C=N) made at 1620-1600 cm^{-1} for the free ligands are shifted to lower frequency by 20-30 cm^{-1} in all the complexes. This indicates the coordination of pyridine ring nitrogen to the metal ion in the complexes Hg(II), Pt(II) and Pd(II)[10,11]. The additional band observed in these complexes at about 510 cm^{-1} assignable ν(M-N ring) further supports the involvement of pyridine ring. The thioamide band of the free ligand observed at 1295 cm^{-1} is located almost at the same position in the complexes. The second thioamide band of free ligand at 965 cm^{-1} has a larger contribution of ν(C-N) and a little contribution of ν(C-N) vibration splits into two or three weak bands in all the complexes.

The third thioamide band observed at 785 cm^{-1} in free ligand shifts to lower frequencies by (125 ± 20) cm^{-1} in the complex, indicating the bonding of thiol (C-S) sulphur to the atoms[12,13]. The new bands near (345 ± 12) cm^{-1} and (385 ± 20) cm^{-1} in the complexes are attributed to ν(M-S) and ν(M-N) vibration[14,15], respectively.

The PMR spectral data of the ligand and its Pd(II), Pt(II) and Hg(II) complexes are recorded. The relatively small down field shift of 0.05-0.15 δ observed in the signal of amide proton (4.3-5.2 δ) of the complexes, compared to their ligands indicates the non-involvement of the amide nitrogen to the metal ion[16] in all the Pd(II), Pt(II) and Hg(II) complexes.

The magnetic susceptibility of the complexes were made at room temperature on a Gouy balance. Magnetic moments of the complexes of Hg(II) presented in Table-1 indicates that all these complexes are weak field complex supporting the tetrahedral geometry. Palladium(II) and platinum(II) complexes were found to be diamagnetic supporting square planar geometry.

The cup diffusion method[17] was used to study the antimicrobial activity of the ligand 2-thiopicoline anilide and its complexes $[Pd(L)_2]\cdot H_2O$. The test organisms were *B. subtilis* (gram negative bacteria) and *Micrococcus* sp. (gram positive bacteria). The activity of the compounds against the bacteria was compared with that of two standard antibiotics penicillin and streptomycin. The free ligand and its complexes (200 mL of 10 mg mL^{-1} DMSO) were found to show microbial activity towards the growth of the bacteria. The complex of Pd(II) was found to be more active than the free ligand (*B. subtilis* 1.2 cm for 2-thiopicoline anilide and 2.3 cm for palladium(II)

complex, *Micrococcus* sp: 1.7 cm for ligand and 2.0 cm for palladium(II) complex. The growth of inhibition of the complexes when compared to the free ligand may be attributed to the deprotonation of the ligand and its chelation around the central metal ion. Palladium(II) complexes exhibit lower activity against *B. subtilis* and *Micrococcus* sp. than penicillin (22.3, 31.8 cm) and streptomycin (24.4, 35.7 cm).

Square planar geometry has been tentatively proposed to the palladium(II) and platinum(II) complexes and mercury(II) complex has tetrahedral geometry (Fig. 2). 2-Thiopicoline anilide and its palladium(II) complex (200 mL of 10 mg mL^{-1} DMSO) was found to show antimicrobial activity towards the growth of the *B. subtilis* and *Micrococcus* sp.

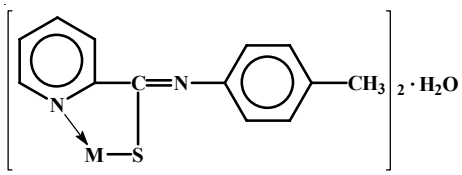

Fig. 2.

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