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Synthesis, Spectral and Thermal Characterization of The Complexes of Palladium(II), Platinum(II) and Mercury(II) with 2-Thioquinaldine Anilide

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The complexes of palladium(II), platinum(II) and mercury(II) with 2-thio quinaldine anilide have been prepared and characterized by elemental analysis, magnetic and electronic spectral studies. The studies suggest square planner geometry to all the palladium(II) and platinum(II) complexes and tetrahedral geometry to the mercury(II) complexes with ligand in which nitrogen and sulphur are as donor atoms.

Key Words: Pd^{2+}, Pt^{2+}, Hg^{2+}, Complexes, 2-Thioquinaldine anilide.

INTRODUCTION

Compounds containing > C = N and -NH-C- groups find wide application in biological, pharmaceutical and analytical system. It has attracted the attention of the chemists to synthesize the coordination compounds of transition metal ions with the ligand containing >C=N and -NH-C- to study. The structure, antifungal, antibacterial and physiological activity of the ligand and their metal complexes have been reported[1-3]. The involvement of carbonyl group in the chelation depends upon the second donor at the correct spacing for the formation of a stable chelate ring[4]. Wiersema and Windle[5] have reported that salicylamide coordinates through the nitrogen of the anilide group compounds containing >C=N and -NH-C- groups and find wide applications in biological, pharmaceutical and analytical systems.

In view of the growing interest of thio amide ligand and their complexes in this work presentation the synthesis and characterization of 2-thioquinaldine anilide (**I**) and its complexes with Pd(II), Pt(II) and Hg(II) ions are reported.

EXPERIMENTAL

Preparation of ligand: 2-Thioquinaldine anilide was prepared under the reaction of Willgerodt. Aniline (50 mL), quinaldine (25 mL) and sulphur (powder 25 mg) were mixed in a 200 mL flask fitted with water reflux condenser. The mixture was refluxed at 160 ºC for 6 h on a sandbath. The reaction mixture was left over night. The solid red crystals obtained were filtered and recrystallized twice with ethanol. The deep yellow compound was obtained. It was dried in vacuum. The melting point of the desired product was found to be 110 ºC (decomposition) as reported method[6].

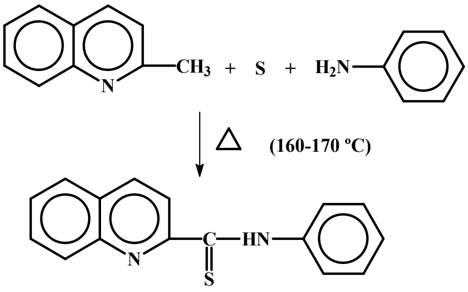

Fig. 1.

m.f. $C_{16}H_{12}N_2S$; Found (%): C (72.71), H (4.53), S(10.61), N (12.13); Calcd. (%) C (72.72), H(4.54), S(10.62), N (12.14); Yield 1.74 g (82 %).

Preparation of complexes:

Preparation of Pd-complex: Aqueous solution of $PdCl_2$ (1 %) containing a few drops of dilute HCl (pH 3-4) was added to an equimolar amount of the ligand solution in acetone. The resulting mixture was digested on a steam bath for 0.5 h when a chocolate brown precipitate separated out. It was filtered, washed with water and ethanol and then dried in vacuum over fused $CaCl_2$.

Preparation of Pt-complex: Platinum(II) chloride (H_2PtCl_4) (1 %) in water was treated with equimolar amount of ligand solution in alcoholic-acetone mixture. The reaction mixture was digested on a steam bath for 0.5 h. The yellow precipitate separated, was filtered off, washed thoroughly with water and finally with aqueous ethanol and then dried in vacuum over fused $CaCl_2$.

Preparation of Hg-complex: Mercuric acetate (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 granular precipitate was filtered, washed with excess of water and finally with ethanol and then dried in vacuum over fused $CaCl_2$.

The metal and sulphur estimations were carried out by standard methods[7,8] and nitrogen by Kjeldahl method. The conductance was measured in DMSO 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 a 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.

RESULTS AND DISCUSSION

The elemental analysis shows all the bivalent metals form complexes $[M(L)_2]\cdot nH_2O$ [M = Hg(II), Pt(II) and Pd(II), n = 1, or 2] are neutral and are dark coloured amorphous substances are sparingly soluble in common organic solvents but quite soluble in

DMF on warming. The measurements of electrical conductivity of the complexes (Table-1) indicates their non-ionic character. The solubility of metal complexes suggest that they are mono-nuclear in nature.

TABLE-1
ELEMENTAL ANALYSIS, MOLAR CONDUCTANCE VALUES AND MAGNETIC MOMENT OF THE COMPLEXES

m.f. (colour)	Elemental analysis %: Found (calcd.)			Λ (ohm^{-1} mol^{-1} cm^{2})
	M	N	S	
$Hg(C_{16}H_{11}N_2S)_2$ (Dirty yellow)	26.25 (26.45)	7.30 (7.50)	8.42 (8.56)	8.0
$Pd(C_{16}H_{11}N_2S)$ (Chocolate brown)	16.35 (16.39)	8.61 (8.66)	9.84 (9.88)	5.0
$Pt(C_{16}H_{11}N_2S)$ (Yellow)	26.39 (26.45)	7.57 (7.62)	8.66 (8.69)	7.0

The hydrated complexes slowly lose water molecules on heating below 100 ºC, indicating that they are uncoordinated and weakly held up in crystal lattices. As expected the complexes of bivalent mercury, platinum and palladium have been found to be diamagnetic supporting Pt(II) and Pd(II) are four coordinated square planar (dsp^2) and Hg(II) is four coordinated tetrahedral sp^3 structure.

The electronic spectra of complexes display ligand absorptions and strong charge transfer transition below 450 nm.

The IR spectra of the complexes indicate the mode of linkage of ligand to the metal atoms. The complexes exhibit very weak (or weak and broad) bands at (3205 ± 10) and (3045 ± 10) cm^{-1} attributable to ν_{as}(N-H) and ν_s(N-H) vibrations[9,10], respectively. The hydrated complexes display a weak and broad band near (3450 ± 5) cm^{-1} indicating the presence of associated water molecules in the complexes. The IR spectra of Hg(II) complex, $[Hg(L)_2]_2 \cdot H_2O$ exhibits. The splitting of ν(C=N) vibration into two bands in which one (C=N) stretching band is located almost at the original position (1600 ± 5) cm^{-1} and the other at lower frequency (1590 ± 5) cm^{-1} indicating that one of the hydrazone (C=N) groups in free and not involved in coordination Hg(II) complex exhibits medium to strong bands at 1560 and 1492 cm^{-1} attributable to benzene ring ν(C=C), ν(C=N) and δ(N-H) vibrations[11].

The second thioamide band of the free ligand observed at 1290 cm^{-1} is located almost at the same position in the complexes. The third thio amide band of true ligand at 960 cm^{-1} has a larger contribution of ν(C-N) and a little contribution of ν(C-S) vibration splits into two or three weak bands in all the complexes.

The fourth thioamide band observed at 780 cm^{-1} in free ligand shifts to lower frequencies by (120 ± 15) cm^{-1} in the complex indicating the bonding of thiol (C-S) sulphur to the atoms[12,13] the new bands near (340 ± 10) cm^{-1} and (380 ± 15) in the complexes are attributed to ν(M-S) and ν(M-N) vibration[14,15], respectively.

On the basis of foregoing discussion it is concluded that ligand is bidentate. The probable structure is suggested for the complexes is shown below.

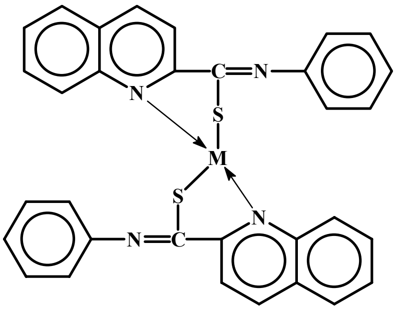

Fig. 2.
(where M = Pt(II) and Pd(II) & n = 1, M = Hg(II), n = 2, L-H = $C_{16}H_{11}N_2S$-H)

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