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Synthesis, Magnetic, Spectral and Thermal Studies of Palladium(II) Complexes with some Potentially Bidentate Heterocyclic Nitrogen Donors

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Some palladium(II) complexes of the type [$PdLCl_2$] with bidentate heterocyclic nitrogen donors like prochloroperazine, trifluoroperazine and thioridazine have been synthesised and characterized by elemental analyses, molar conductance, magnetic susceptibility measurements, infra red and electronic spectral data. The conductometric measurements of these complexes in water, chloroform and DMF indicate their non-electrolyte nature. TG and DTA data show that these complexes are thermally stable upto 240°C and they decompose to yield pure palladium oxide. On the basis of the above data, square planar geometry has been suggested for these complexes.

INTRODUCTION

Prochloroperazine mesylate (PPM), trifluoroperazine dihydrochloride (TFP) and thioridazine hydrochloride (TH) are important phenothiazine derivatives containing bidentate heterocyclic nitrogen donor atoms. These phenothiazine derivatives have received increasing attention in recent years because of their potential coordinating nature and pharmacological properties. The chemical literature provides information on the complexation of some transition metals with such ligands[1,2]. The reaction between palladium(II) and these ligands have been spectrophotometrically investigated[3-5]. The present paper describes the syntheses and characterization of three complexes of palladium(II) with the above ligands.

EXPERIMENTAL

Prochloroperazine mesylate (May and Baker Ltd.), trifluoroperazine dihydrochloride (Smith, Kline and French Ltd.), and thioridazine hydrochloride (Sandoz Ltd., were received as gift samples from the respective pharmaceutical companies. Palladium(II) chloride (M/S Johnson Matthey Chemicals, London).

Preparation and analyses of complexes

50 Ml of 0.01M ethanolic solution of palladium(II) chloride was slowly added to 50 ml of 0.01M ethanolic solution of PPM, TFP and

TH separately. The ligands form complexes on heating the mixture on a water bath at 60–80°C for *ca.* 1/2 hr. The solid Pd(II) complexes were filtered, washed with ethanol and then with ether and were dried in vacuo. The melting points of the complexes were determined.

Elemental analyses were done by conventional methods[6]. Conductance measurements were made at 25°C on 10^{-4}M solutions of the complexes in water, chloroform and DMF for Pd(II)-PPM, Pd(II)-TFP and Pd(II)-TH, respectively. UV and visible spectra were recorded with 10^{-4}M solutions in water for Pd(II)-PPM complex, in chloroform for Pd(II)-TFP complex and in DMF for Pd(II)-TH complexes. IR spectra were recorded as Nujol mulls between NaCl discs (4000–600 cm^{-1}).

RESULTS AND DISCUSSION

Pd(II) forms a violet complex with PPM whereas TFP and TH ligands which are also bidentate ligands form reddish brown complexes of composition $[PdLCl_2]$, where L is the bidentate ligand. The results of the elemental analyses presented in Table 1 confirm this composition. All the

TABLE 1

ANALYTICAL DATA OF Pd(II) COMPLEXES OF PPM, TFP AND TH

Complex	Pd(II)-PPM	Pd(II)-TFP	Pd(II)-TH
1. Molecular formula	$Pd(C_{20}H_{24}N_3SCl)Cl_2$	$Pd(C_{21}H_{24}N_3SF_3)Cl_2$	$Pd(C_{21}H_{26}N_2S_2)Cl_2$
2. Colour	Violet	Reddish brown	Reddish brown
3. m.pt. (°C)	112–115°	173–175°	142–145°
4. Molar conductance (μs)	0.2	0.1	0.1
5. **Elemental analysis**			
C, Found (Calculated) %	43.55(43.57)	43.10(43.12)	46.0(46.04)
H, Found (Calculated) %	4.33(4.36)	4.10(4.11)	4.60(4.75)
N, Found (Calculated) %	7.60(7.62)	7.15(7.19)	5.10(5.12)
S, Found (Calculated) %	5.80(5.81)	5.5(5.47)	12.0 (11.69)
Cl, Found (Calculated) %	18.97(19.33)	12.44(12.14)	12.95(12.97)
Pd, Found (Calculated) %	19·54(19.31)	18.63(18.19)	19.33(19.44)

three complexes are amorphous. Pd(II)-PPM, Pd(II)-TFP and Pd(II)-TH melt at 112–115°, 173–175° and 142–145°C, respectively. They are all soluble in DMF, DMSO and acetonitrile. Pd(II)-PPM complex is soluble in water. Pd(II)-TFP and Pd(II)-TH complexes are slightly soluble in water, alcohol, methanol and acetone. Pd(II)-TFP is soluble in chloroform. All the three complexes are almost insoluble in benzene, carbon tetrachloride, ether and toluene.

The low molar conductance values (0.1–0.2 μS) indicate that all three complexes are non-electrolytes and practically no interchange reactions occur between the solvent and the dissolved complex.

Magnetic moment measurements of the new complexes confirmed the presence of palladium in +2 state. All the three complexes studied are found to be diamagnetic. This suggests a square planar arrangement of the ligand molecules around the central metal ion. Such a geometry is quite common for the palladium(II) complexes with d^8 configuration[7]. The ground state for the low spin d^8 system is $^1A_{1g} \rightarrow (=a_{1g}^2 \cdot eg^4 \cdot b_{2g}\ 2)^8$. The ligand field excited states are $^3A_{2g}$, $^1A_{2g}$ ($b_{2g} \rightarrow b_{1g}$), ^3E_g, ^1E_g($e_g \rightarrow b_{1g}$) and $^3B_{1g}$, $^1B_{1g}$ ($a_{1g} \rightarrow b_{1g}$). Therefore, three spin allowed and three spin forbidden transitions are expected. The UV and visible spectra of palladium(II) complexes are shown in Figs. 1 and 2. The more intense peak obtained at 255–270 nm may be assigned to $\pi \rightarrow \pi^*$ transition. The band around

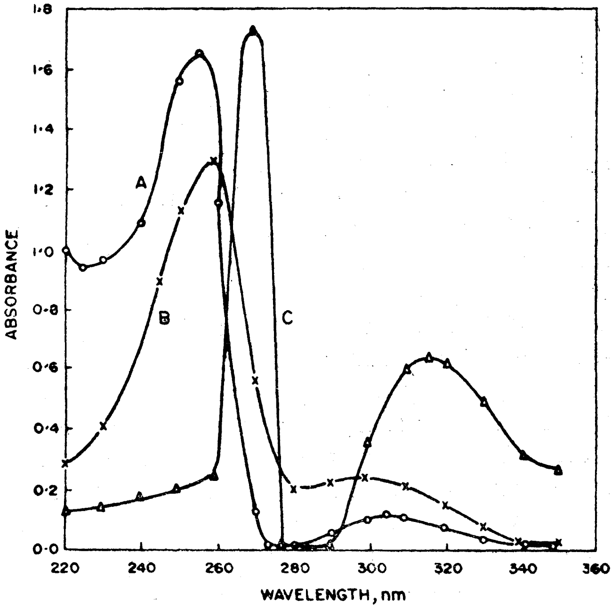


Fig. 1. UV spectra of Pd(II)-PPM (A), Pd(II)-TFP (B) and Pd(II)-TH (C)

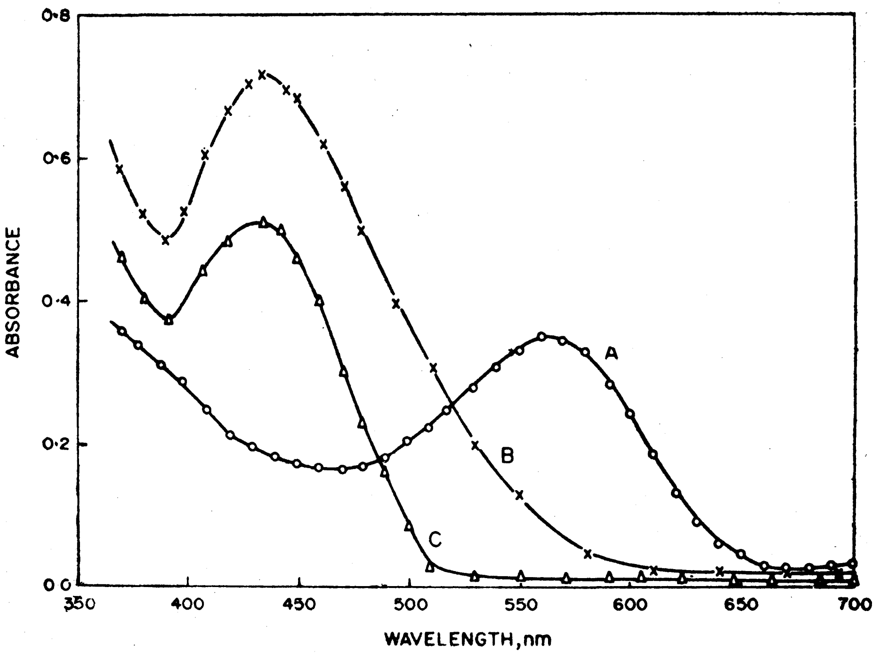


Fig. 2. Visible spectra of Pd(II)-PPM (A), Pd(II)-TFP (B) and Pd(II)-TH (C)

305–315 nm is due to n → π* transition. The intense peak at 435 nm in DMF solvent for Pd(II)-TH and Pd(II)-TFP arises out of the $^1A_{1g} \rightarrow {}^1B_{1g}$ transition. The single band at 565 nm exhibited by Pd(II)-PPM complex may also be due to $^1A_{1g} \rightarrow {}^1B_{1g}$ transition.

In all the three complexes, C-S stretching frequency appears in the same region (740–760 cm^{-1}) as in the free ligands, thus confirming that sulphur atom was not involved in the coordination. The stretching frequency of the heterocyclic nitrogen atom attached to the alkyl group in the ligands PPM, TFP and TH showed the band respectively at 2860–2940, 2950–3165 and 2890–2950 cm^{-1}. These bands are shifted by 10–20 cm^{-1} towards the higher frequency region in the IR spectra of all the three palladium(II) complexes. Thus suggesting that heterocyclic nitrogen atom attached to the alkyl group is the site of interaction. The stretching frequency of the tertiary nitrogen atom in the ligands (2300–2500 cm^{-1}) completely disappears in the IR spectra of the complexes; thereby indicating that the tertiary nitrogen is also the site of interaction. Therefore, the ligands coordinate to Pd(II) through their heterocyclic nitrogen atom and also the tertiary nitrogen atom in the side chain, thus exhibiting their bidentate nature.

The analysis of TG and DTA curves (Fig. 3) indicates that the complexes are generally stable upto 200–240°C. Afterwards oxidation of the organic substance begins. It has been found that concurrent with the decomposition and oxidation of the organic substance some volatilization reaction is also taking place. The final greenish black product obtained in each case has been chemically identified as pure palladium oxide.

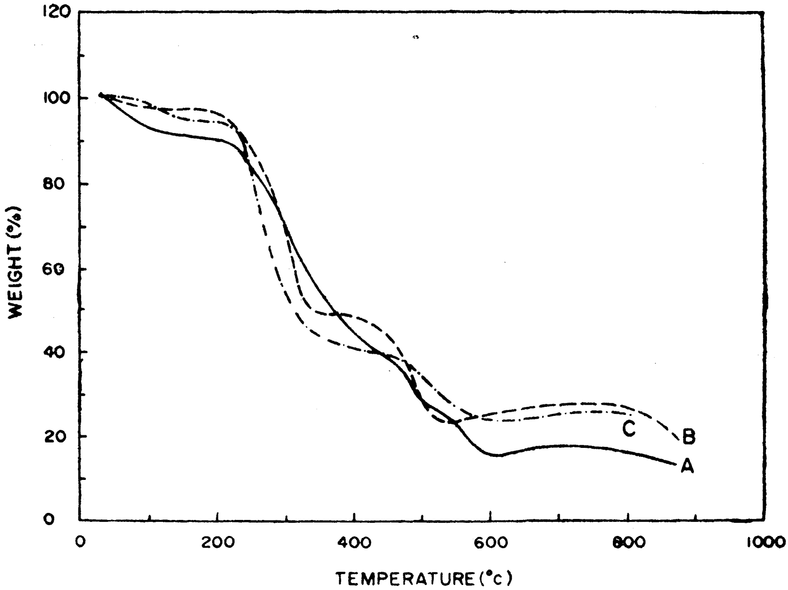
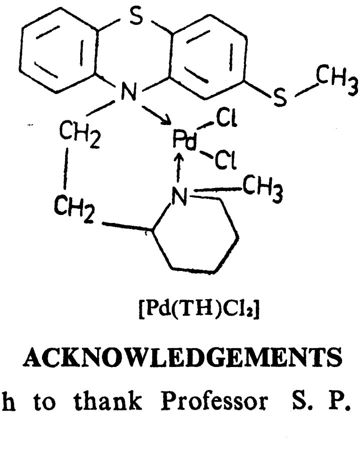


Fig. 3. TGA curves of Pd(II)-PPM(A). Pd(II)-TFP (B) and Pd(II)-TH (C)

In the light of the foregoing and usual divalency of palladium the following structure is proposed for the new complex $Pd(C_{21}H_{26}N_2S_2)Cl_2$.



$[Pd(TH)Cl_2]$

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REFERENCES

1. M. Tarasiewicz and H. Puzanowska Tarasiewicz, Phenothiazines and Structurally Related Drugs, Elsevier, pp. 145–148 (1980).
2. K. S. Ramachandra, *Ph. D. Thesis*, Mysore University (1987).
3. H. Sanke Gowda and P. G. Ramappa, *Fresenius Z. Anal. Chem.*, 275, 127 (1975).
4. H. Sanke Gowda and P. G. Ramappa, *J. Indian Chem. Soc.*, 52, 1123 (1975).
5. H. Sanke Gowda and P. G. Ramappa, *Indian J. Chem.*, 14A, 454 (1976).
6. A. I. Vogel, Textbook of Quantitative Inorganic Analysis, ELBS and Longman, p. 474 (1979).
7. F. R. Hartley, The Chemistry of Platinum and Palladium, Allied Science Publishers Ltd., London, p. 114 (1973).
8. G. W. Parshell, *Acc. Chem. Res.*, 3, 139 (1970).

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