

## Palladium(II) Complexes of Thiosemicarbazones of 2-Furfuraldehyde & Thiophene-2-carboxaldehyde

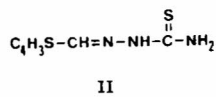
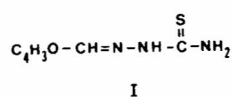
K MUKKANTI, K B PANDEYA & R P SINGH\*

Chemistry Department,  
University of Delhi, Delhi 110 007

Received 14 March 1985; revised and accepted 3 October 1985

Palladium(II) complexes of the type  $PdL_2X_2$  ( $L=2$ -furfuraldehyde thiosemicarbazone, FATA-H; thiophene-2-carboxaldehyde thiosemicarbazone, TATS-H; and  $X=Cl^-$ ,  $Br^-$ ,  $I^-$  and  $\frac{1}{2}SO_4^{2-}$ ) and  $PdL'_2$  ( $L'=FATS$ ;  $TATS$ ) have been synthesised. The complexes have been characterised on the basis of their elemental analyses and physicochemical techniques. The complexes behave as 1:2 electrolytes and their room temperature magnetic moments indicate the absence of unpaired electrons. Electronic spectral data indicate square planar geometry around the metal ion. IR spectral data reveal bidentate chelating nature of both the ligands.

Metal complexes of thiosemicarbazides and thiosemicarbazones have recently drawn special attention due to their activity against small pox, viral diseases and certain kinds of tumour<sup>1-3</sup>. In continuation of our work in this area<sup>4,5</sup>, we report herein the synthesis and characterisation of palladium(II) complexes of thiosemicarbazones(I) and (II) of 2-furfuraldehyde and thiophene-2-carboxaldehyde, respectively.



The ligands were synthesised by the method reported earlier<sup>4</sup>. Palladium bromide was prepared from  $PdCl_2$  by repeated evaporation of a solution of  $PdCl_2$  in concentrated  $HBr$ . The product was heated at  $200^\circ C$  to constant weight.  $PdI_2$  was prepared by the known procedure<sup>7</sup>.

*Preparation of complexes:*  $PdL_2X_2$  ( $L=I$  or  $II$ ;  $X=Cl^-$ ,  $Br^-$  or  $I^-$ )

Solution of  $PdX_2$  (0.01 mol) and the ligand (0.02 mol) in ethanol containing a few drops of concentrated  $HX$ , were mixed and refluxed for 1 hr. The precipitate obtained was filtered, washed with ethanol and dried *in vacuo* over  $P_2O_5$ .

$PdL'X'_2$  ( $L'=I$  or  $II$ ;  $X'=NO_3^-$  or  $\frac{1}{2}SO_4^{2-}$ ) (ref. 8)

These complexes were prepared by adding palladium chloride solution to a solution of ligand ( $M:L$  in 1:2 ratio) in dil.  $HNO_3$  or  $H_2SO_4$  (2*N*). The contents were refluxed for 1 hr, the precipitate filtered and dried *in vacuo* over  $P_2O_5$ .

$PdL'_2$  ( $L'=FATS$  or  $TATS$ ) (ref. 9)

An ethanolic solution (20 ml; 0.02 *M*) of  $PdCl_2$  was added to an ethanolic solution (0.02 *M*) of ligand in the molar ratio of 1:2. Aqueous  $NH_4OH$  (1.0 *M*) was added to the above mixture dropwise until the solution was weakly alkaline. The mixture was refluxed for 1 hr, filtered, the precipitate washed and dried *in vacuo* over  $P_2O_5$ .

The analytical data given in Table 1, indicate 1:2 stoichiometry for  $Pd(II)$  complexes. Palladium was estimated gravimetrically by precipitation with dimethylglyoxime in acid<sup>10</sup>. The molar conductances of  $10^{-3} M$  solution of  $ML_2X_2$  type complexes in methanol lie in the range of 210-245  $\text{ohm}^{-1} \text{mol}^{-1} \text{cm}^2$ , indicating that these complexes behave as 1:2 electrolytes<sup>11</sup>. The complexes are diamagnetic as expected for square planar  $d^8$ -metal complexes. The electronic spectra of palladium(II) complexes are indicative of square planar<sup>12</sup> geometry. Three  $d-d$  spin allowed transitions are expected. Accordingly, the complexes show bands around 18,000, 21,000 and 25,000  $\text{cm}^{-1}$ , which may be assigned to the transitions  $^1A_{1g} \rightarrow ^1A_{2g}$ ,  $^1A_{1g} \rightarrow ^1B_{1g}$ ,  $^1A_{1g} \rightarrow ^1E_g$ , respectively. The single electron parameters  $\Delta_1$ ,  $\Delta_2$  and  $\Delta_3$ , calculated using the equations suggested by Gray and Ballhausen<sup>13</sup> lie in the ranges 24690-26370; 6000-8000 and 2000-4000  $\text{cm}^{-1}$  respectively. The  $\nu_2/\nu_1$  values lie in the range of 1.14 to 1.27. The values obtained are in close agreement with those reported earlier<sup>14,15</sup>.

The infrared spectra of the free ligands display bands around 3400 and 3100  $\text{cm}^{-1}$  assignable to  $\nu_{as} NH_2$  and  $\nu_s NH_2$  respectively. The band around 1600  $\text{cm}^{-1}$  in the free ligands due to  $\nu C=N$  moves to lower frequencies ( $\Delta\nu=15-20 \text{ cm}^{-1}$ ) in metal complexes, suggesting coordination through azomethine nitrogen. Further, a medium band (1045  $\text{cm}^{-1}$  for I and 1030  $\text{cm}^{-1}$  for II), assignable to  $\nu N-N$  is shifted to higher frequencies in the spectra of the metal complexes. A similar increase, but of much greater magnitude, is observed for  $\nu N-N$  (1090-1080  $\text{cm}^{-1}$ ) of hydrazine on coordination to a metal ion<sup>16</sup>. The absence of bands in the region 2750-2600  $\text{cm}^{-1}$  in the free ligands indicates absence of  $S-H$  grouping in the free ligands<sup>17</sup>. The  $\nu C=S$  in the ligands I and II appear at 840  $\text{cm}^{-1}$  and 835  $\text{cm}^{-1}$ , respectively. These bands shift by about 90  $\text{cm}^{-1}$  to lower frequencies on complex formation. This band is largely  $\nu C=S$ , and the major shift on complexation indicates considerable change in a bond order and the formation of a metal-sulphur bond. The bands around 1240-1290 ( $\nu CN + \nu CS$ ) and around 1160-1172 and 1000  $\text{cm}^{-1}$  ( $\delta NH_2 + \beta NH_2$ ) are only

Table I – Characterization Data of Palladium(II) Complexes

Complex*	Colour	m.p. (°C)	Found (Calc) %			
			Pd	C	H	N
Pd(FATS-H) <sub>2</sub> Cl <sub>2</sub>	Orange yellow	272	20.52 (20.63)	28.06 (27.95)	2.74 (2.73)	16.30 (16.29)
Pd(FATS-H) <sub>2</sub> Br <sub>2</sub>	Light orange	275	17.72 (17.59)	23.75 (23.84)	2.31 (2.33)	13.92 (13.90)
Pd(FATS-H) <sub>2</sub> I <sub>2</sub>	Black	277	15.20 (15.23)	20.53 (20.63)	2.00 (2.02)	12.13 (12.03)
Pd(FATS-H) <sub>2</sub> SO <sub>4</sub>	Yellow (light)	265	19.82 (19.67)	26.84 (26.44)	2.62 (2.61)	15.58 (15.54)
Pd(FATS) <sub>2</sub>	Yellowish green	270	24.30 (24.03)	32.70 (32.55)	2.73 (2.73)	18.79 (18.98)
Pd(TATS-H) <sub>2</sub> Cl <sub>2</sub>	Orange	265	19.58 (19.42)	26.39 (26.31)	2.58 (2.58)	15.15 (15.34)
Pd(TATS-H) <sub>2</sub> Br <sub>2</sub>	Brown	280	16.54 (16.71)	22.65 (22.63)	2.20 (2.22)	13.29 (13.20)
Pd(TATS-H) <sub>2</sub> I <sub>2</sub>	Black	260	14.72 (14.56)	19.69 (19.72)	1.95 (1.93)	11.65 (11.50)
Pd(TATS-H) <sub>2</sub> SO <sub>4</sub>	Light green	274	18.39 (18.57)	25.18 (25.13)	2.44 (2.46)	14.69 (14.67)
Pd(TATS) <sub>2</sub>	Light yellow	275	23.34 (23.39)	31.65 (31.68)	2.65 (2.66)	18.42 (18.42)

\* FATS-H = Thiosemicarbazone of 2-furfuraldehyde; TATS-H = thiosemicarbazone of thiophene-2-carboxaldehyde

slightly affected by complex formation<sup>19</sup>. But a very important feature of the IR spectra of the ML<sub>2</sub> complexes is the appearance of a strong band in the region 955-960 cm<sup>-1</sup>. This is most likely the νN-N, due to elongation of N<sup>2</sup>-N<sup>3</sup> bond and a charge localisation on the C-N<sup>2</sup> bond<sup>20</sup>. In conclusion, we may suggest that FATS-H and TATA-H act as bidentate ligands in all the cases. The important resonance structures generate a positive charge on ring sulphur and this may account for the non-participation of thiophene sulphur in coordination<sup>21</sup>.

## References

- Orlova N, Aksenova V A, Sclidovkin V A, Bogdanova N S & Perskin G N, *Russ pharm Toxicol*, (1968) 348.
- Baver D J, Vincent L S, Kempe C H & Downie A W, *Lancet*, **20** (1963) 494.
- Petering H G, Buskik H H & Underwood G E, *Cancer Res*, **64** (1964) 367.
- Mukkanti K, Pandeya K B & Singh R P, *Indian J Chem*, **21A** (1982) 641.
- Mukkanti K, *Synthesis & characterisation of some transition metal complexes of 2-furfuraldehyde thiosemicarbazone and thiophene-2-carboxaldehyde thiosemicarbazone*, Ph.D. Thesis, Delhi University, Delhi, 1984.
- Sah P T & Daniels T C, *React Trav chim Pays-Bas Belg*, **69** (1950) 1545.
- Hartley F R, *The chemistry of platinum and palladium* (Applied Science Publishers, London) 1973, 178.
- Banerjee A K & Ghosh S P, *J Indian chem Soc*, **51** (1974) 720.
- Chandra S, *Syn React Inorg Met-Org Chem*, **13** (1983) 89.
- Vogel A I, *A text book of quantitative inorganic analysis* (Longmans Green, ELBS, London), 1961, 512.
- Jones M M, *Elementary coordination chemistry* (Prentice Hall, Englewood Cliffs, New Jersey) 1964, 254.
- Goggin P L, Goodfellow R J & Reed F J S, *J chem Soc Dalton Trans*, (1972) 1298.
- Gray H B & Ballhausen C J, *J Am chem Soc*, **85** (1963) 1368.
- Gajendragad M R & Aggarwala U C, *J inorg nucl Chem*, **37** (1975) 2429.
- Dwivedi J S & Aggarwala U C, *Indian J Chem*, **10** (1972) 657.
- Wiles D M & Suprunchuk T, *Can J Chem*, **47** (1969) 1087.
- Poddar S N & Saha N J, *J Indian chem Soc*, **52** (1975) 57.
- Mashima M, *Bull chem Soc Japan*, **37** (1964) 974.
- Sahni S K, Gupta R P, Sangal S K & Rana V B, *J Indian chem Soc*, **54** (1977) 200.
- Chandra S, Pandeya K B & Singh R P, *Indian J Chem*, **18A** (1979) 476.
- Burman S & Satyanarayaya D N, *Indian J Chem*, **20A** (1981) 57.