Inorganica Chimica Acta, 34 (1979) 81–86
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Ligating Properties of Model Bioheterocyclics.
III. Synthesis and Characterization of the Palladium(II) and Platinum(II) Complexes with 3,6-Disubstituted-2,7-dihydro-1,4,5-thiadiazepine Derivatives

S. S. SANDHU, S. S. TANDON and H. SINGH

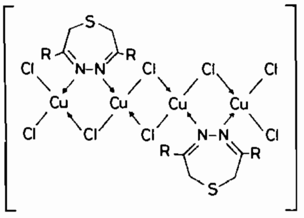
Department of Chemistry, Guru Nanak Dev University, Amritsar, India 143005

Received September 15, 1978

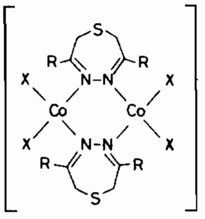
Palladium(II) and platinum(II) halides with 3,6-disubstituted-2,7-dihydro-1,4,5-thiadiazepine derivatives (L) form complexes of general formula, [$MX_2 \cdot L'$] (L' = monohydrazone, VII). During the formation of these complexes, the thiadiazepine ring underwent hydrolytic cleavage at the carbon–nitrogen double bond, the nitrogen of which is involved in coordination with the metal ions. These complexes have also been obtained from monohydrazones of 2,2''-thiodiacetophenones. These are diamagnetic and non-electrolytes. From their ir, n.m.r., electronic spectra, T.G.A., D.T.A., magnetic susceptibility and conductivity measurements, these complexes have been assigned a square planar structure.

Introduction

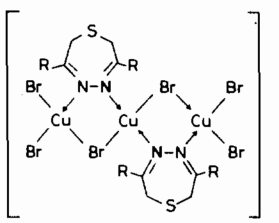
Recently we have reported [1, 2] that the coordinating behaviour of 3,6-disubstituted-2,7-dihydro-1,4,5-thiadiazepine ligands (L) depends upon the nature of metal ions. With copper(II) chloride and copper(II) bromide, these ligands (L) form tetranuclear dimeric(I) and trinuclear monomeric complexes(II) of stoichiometries 2:1 and 3:2 respectively, where bridging through the thiadiazepine ring and halide ions takes place, whereas cobalt(II) halides react with these ligands (L) to form dimeric complexes(III) in which bridging takes place only through thiadiazepine ring. Zinc(II) and cadmium(II) halides with these ligands(L) form monomeric tetrahedral complexes(IV), in which the coordination is through sulphur and one of the two nitrogen atoms. The thiadiazepine ring undergoes a conformational change so as to bring nitrogen and sulphur atoms closer for coordination to metal ion.



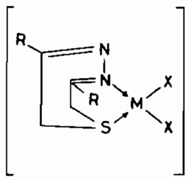
I



III



II



IV

The discovery of antitumor activity [3–8] among platinum and palladium complexes has stimulated a new interest in the complexes of these metal ions. Hence in order to investigate the coordinating behaviour of these ligands (L) towards platinum and palladium and procure such complexes for biological screening, we have studied the complexation of 1,4,5-thiadiazepine ligands (L) with palladium(II) and platinum(II) halides.

Experimental

Material

All the chemicals used were of analar grade. Palladium(II) bromide was obtained from palladium(II) chloride and hydrobromic acid. 3,6-Disubstituted-2,7-dihydro-1,4,5-thiadiazepine derivatives (L) were synthesized by the method reported earlier [9] and are denoted as L-I (V, R = C_6H_5); L-2 (V, R = C_6H_5-CH_3(p); L-3 (V, R = C_6H_4Cl(p) and L-4(V, R = C_6-H_4CCH_3(p). Monohydrazones (L'; VII, R = C_6H_5, $C_6H_4CH_3$(p) were prepared by the reported method [24] and are denoted as L'-I (VII, R = C_6H_5); L'-2-(VII, R = $C_6H_4CH_3$(p); L'-3(VII, R = C_6H_4Cl(p) and L'-4(VII, R = $C_6H_4OCH_3$(p).

TABLE I. The Colour, Decomposition Temperature, Analytical and NMR Data for Pd(II) and Pt(II) Complexes.

S. No.	Complex	Colour	Decomposition temp. (°C)	Analytical data						NMR Data[a], chemical shift in δ (ppm)
					M	C	H	N	S	
1.	$[PdCl_2L'\text{-}1]$	Yellow	172–173	F[b]	22.90	42.22	3.36	5.75	–	7.95–7.42 (m, 10H aromatic) 4.82 (s, broadened, 2H, NH_2, exchanged with D_2O) 3.68–3.45 (m, 4H, CH_2)
				C	23.00	41.70	3.45	6.07		
2.	$[PdCl_2L'\text{-}2]$	Yellow	187–188	F	21.88	43.64	4.39	5.43	–	
				C	21.68	44.17	4.10	5.72	–	–
3.	$[PdCl_2L'\text{-}3]$	Yellow	218–220	F	19.89	36.62	2.93	–	5.90	AB quartet centred at 7.82 (4H, aromatic) AB quartet centred at 7.50 (4H, aromatic) 4.62 (s, broadened, 2H, NH_2 exchanged with D_2O) 3.70–3.42 (m, 4H, CH_2)
				C	20.0	36.23	2.64	–	6.03	
4.	$[PdCl_2L'\text{-}4]$	yellow	203–204	F	19.87	41.16	3.77	4.82	–	AB quartet centred at 7.80 (4H, aromatic) AB quartet centred at 6.92 (4H, aromatic) 4.56 (s, broadened, 2H, NH_2 exchanged with D_2O)
				C	20.35	41.45	3.84	5.36	–	
5.	$[PdBr_2L'\text{-}1]$	Dark brown	220–225	F	19.09	34.90	2.90	5.09	–	
				C	18.65	34.78	3.08	4.85	–	–
6.	$[PdBr_2L'\text{-}2]$	Dark brown	197–198	F	17.96	37.71	3.59	4.58	–	
				C	18.34	37.37	3.46	4.84	–	–
7.	$[PdBr_2L'\text{-}3]$	Dark yellow	212–214	F	16.84	30.86	2.42	4.36	4.98	–
				C	17.12	31.02	2.26	4.52	5.17	–
8.	$[PdBr_2L'\text{-}4]$	Dark brown	>200	F	16.87	35.20	3.36	4.21	5.50	–
				C	17.38	35.41	3.28	4.59	5.25	–
9.	$[PtCl_2L'\text{-}1]$	Dark brown	>200	F	35.21	34.82	2.87	4.86	–	
				C	35.46	34.91	2.91	5.09	–	
10.	$[PtCl_2L'\text{-}2]$	Grey	170–175	F	33.94	36.94	2.39	4.38	–	
				C	33.73	37.37	3.45	4.85	–	
11.	$[PtCl_2L'\text{-}3]$	Dark brown	160–165	F	32.04	31.75	2.17	–	5.46	
				C	32.44	31.02	2.26	–	5.16	
12.	$[PtCl_2L'\text{-}4]$	Dark brown	185–190	F	32.13	35.00	3.24	–	5.03	
				C	32.00	35.41	3.28	–	5.24	

[a] The n.m.r. spectrum of the monohydrazone (L', VII, R = C_6H_5) showed the signals at δ 8.0–7.30 (m, 10H, aromatic): 6.01 2H, NH_2 exchanged with D_2O); 3.87 (s, 2H, CH_2) and 3.75 (s, 2H, CH_2). [b] F = found, C = calculated.

Preparation of Complexes

Palladium(II) chloride complexes

Palladium(II) chloride (0.01 mol) was dissolved in 25 ml of ethanol or methanol containing a few drops of concentrated hydrochloric acid (AR) and the ligands (L, 0.01 mol) were dissolved in tetrahydrofuran (50 ml). The two solutions were mixed, and the reaction mixtures were refluxed for 1–1.5 hours when yellow coloured compounds started separating. Subsequently, the reaction mixtures were refluxed for 15–30 minutes more and were allowed to cool slowly. The complexes formed were filtered from the dark brown mother liquor, washed repeatedly with methanol, tetrahydrofuran and dried under vacuum at 60 °C. Using this method, the complex with L-1 (V, R = C_6H_5) was not formed. In this case, the reaction mixture was cooled at 0 °C for 6–8 hours, when the yellow complex separated out.

Palladium(II) bromide complexes

To a solution of palladium(II) bromide (0.01 mol) in ethanol (25 ml) containing a few drops of hydrobromic acid was added a solution of the ligand (L) (0.01 mol) in tetrahydrofuran (50 ml). The reaction mixtures were refluxed on a water bath for 15–30 minutes and dark yellow complexes were separated in case of L-2 and L-3. The complexes formed in the case of L-1 and L-4 were separated by adding petroleum ether to the reaction mixtures. These complexes were filtered, washed with methanol and tetrahydrofuran and dried under vacuum at 60 °C.

Platinum(II) chloride complexes

A solution of chloroplatinic acid (0.01 mol) in methanol (20 ml) was refluxed for about 20 minutes and the ligand (L, 0.01 mol) dissolved in tetrahydrofuran (50 ml) was added. The reaction mixtures were refluxed on a water bath for 2–3 hours and dark brown solutions were obtained. These were concentrated to half of their volumes under reduced pressure and the complexes were separated by adding petroleum ether (40–60 °C). These were filtered, washed with methanol, benzene and dried under vacuum at 60 °C.

Palladium (II) chloride complexes will monohydrazone (L′, VII, R = C_6H_5)

A mixture of monohydrazone (VII, R = C_6H_5) (0.01 mol) dissolved in tetrahydrofuran (50 ml) and palladium(II) chloride (0.01 mol) in ethanol (20 ml) containing a few drops of concentrated hydrochloric acid (AR) was kept at 0 °C for 4–5 hours and the yellow coloured complex which separated was filtered and washed with tetrahydrofuran and methanol. It was found to be identical (m.p., i.r.) with the complex obtained from ligand L-1 and palladium(II) chloride.

Hydrolysis of 1,4,5-Thiadiazepine Derivatives (V) to 2,2″-Thiodiacetophenones (VI)

3,6-Disubstituted-2,7-dihydro-1,4,5-thiadiazepine (V, R = C_6H_5) (100 mg) was dissolved in tetrahydrofuran (25 ml) and a few drops of hydrochloric acid were added to it. The reaction mixture was refluxed on a water bath for five minutes and was extracted with chloroform. The extract was dried over anhydrous sodium sulphate and a solid compound was obtained after removing the solvent. It was found to be 2,2″-thiodiacetophenone (VI, R = C_6H_5) (tlc, m.p.). Similarly V (R = $C_6H_4CH_3$(p); C_6H_4Cl(p) and $C_6H_4OCH_3$(p)) were hydrolysed to corresponding VI, (R = $C_6H_4CH_3$(p)), C_6H_4Cl(p), and C_6H_3-OCH_3(p) respectively.

Analysis

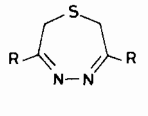
Palladium and platinum were estimated gravimetrically. Carbon, hydrogen, nitrogen and sulphur were analysed by the Australian Microanalytical Service, Melbourne (Table I).

Physical Measurements

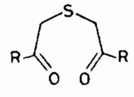
These were carried out as already described [1, 2].

Results and Discussion

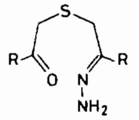
The reactions of palladium(II) chloride, platinum(II) chloride and palladium(II) bromide with 3,6-disubstituted-2,7-dihydro-1,4,5-thiadiazepine derivatives (L-1 to L-4), in the presence of the respective acid in order to solubilize the metal ions, form the complexes which analyse for the general molecular formula [$MX_2 \cdot L'$]. Their i.r. spectra exhibit weak to medium intensity absorption bands in the range 3340–3050 cm^{-1} and a very strong band in the range 1690–1670 cm^{-1}. Both these absorption bands are neither present in the i.r. spectra of thiadiazepine ligands (L) nor in those of their complexes with copper(II), cobalt(II), zinc(II) and cadmium(II) [1, 2]. These bands have been assigned to –NH_2 and $\rangle$CO stretching modes respectively. In the formation of these complexes (MX_2L'), elements of only one molecule of water have been added. Hence, under the acidic reaction conditions only one of the carbon–nitrogen double bonds of the ligand has been cleaved. Ordinarily, the thiadiazepines (V) undergo hydrolytic cleavage to 2,2″-thiodiacetophenones (VI) by addition of two molecules of water. However, in the course of complex formation at no stage of the reaction could the formation of 2,2″-thiodiacetophenones be detected by TLC. Hence for the formation of [MX_2L'] possessing $\rangle$CO and –NH_2 groups (i.r., n.m.r.), the complexation precedes the hydrolytic cleavage of one $\rangle$C=N bond, the nitrogen of which is involved in the coordination with the metal ion. It has been visualized that platinum(II) and palladium(II) initially coordinate at S and one N atom to form (VIII) which through the attack of water at the electrophilic carbon (C6) opens up to furnish IX. An alternate synthesis of IX (R = C_6H_5) from palladium(II) chloride and monohydrazone VII (R = C_6H_5) further confirms this structure as is discussed later on.



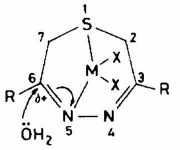
V



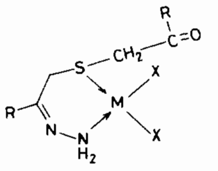
VI



VII



VIII



IX

These complexes in the solid state are fairly stable to air and moisture but somewhat unstable in solution. They are insoluble in ethanol, methanol, benzene, tetrahydrofuran and have very poor solubilities in chloroform, acetone, nitrobenzene and nitromethane but are fairly soluble in dimethylformamide and dimethylsulphoxide. The low conductivity values

TABLE II. The Molecular Formulae, Conductivity Measurements, DTA and TGA Data for Pd(II) and Pt(II) Complexes.

S. No.	Complex	Molecular Formulae	Molar[a] Conductance (cm^2 ohm^{-1} mol^{-1})	DTA Temp. Range °C (peak temp. °C)	TGA		
					Loss %	at temp. °C	Loss due to
1.	[PdCl$_2$L'-1]	$C_{16}H_{16}N_2SOPdCl_2$	16.05	145–230b[e]	17.5	(160–240)	$H_2O + S + N_2$
				240–320 (265)[e]	76.4	(400)	L' + Cl_2
2.	[PdCl$_2$L'-2]	$C_{18}H_{20}N_2SOPdCl_2$	12.61	80–145 (135)[e]	5.2	(100–140)	1.5 H_2O
				145–230 (185,	7.2	(180–200)	S
				200)[e]	6.0	(210–220)	N_2
					78.0	(560)	L' + Cl_2
3.	[PdCl$_2$L'-3]	$C_{16}H_{14}N_2SOPdCl_4$	14.30	225–318	15.0	(220–240)	$H_2O + S + N_2$
				(290)[e]	76.5	(580)	L' + Cl_2
4.	[PdCl$_2$L'-4]	$C_{18}H_{20}N_2SO_3PdCl_2$	12.80	80–150 (140)[e]	17.7	(100–220)	$H_2O + S + N_2$
				150–230 (205)[e]	78.5	(560)	L' + Cl_2
				230–295 (250)[e]			
5.	[PdBr$_2$L'-1]	$C_{16}H_{16}N_2SOPdBr_2$	16.6	170–370b[e]	80.5	(80–380)	L' + Br_2
6.	[PdBr$_2$L'-2]	$C_{18}H_{20}N_2SOPdBr_2$	13.6	145–475	14.8	(160–240)	$H_2O + S + N_2$
				(300)b[e]	81.8	(460)	L' + Br_2
7.	[PdBr$_2$L'-3]	$C_{16}H_{14}N_2SOPdCl_2Br_2$	12.8	170–250 (200)[e]	8.2	(180–240)	$H_2O + S$
				250–440b[e]	82.6	(440)	L' + Br_2
8.	[PdBr$_2$L'-4]	$C_{18}H_{20}N_2SO_3PdBr_2$	15.7	110–380b[e]	81.3	(120–360)	L' + Br_2
9.	[PtCl$_2$L'-1]	$C_{16}H_{16}N_2SOPtCl_2$	15.1	140–260b[e]	65.2	(420–240)	$H_2O + S + N_2$
				260–400 (290)[e]	63.8	(420)	L' + Cl_2
10.	[PtCl$_2$L'-2]	$C_{18}H_{20}N_2SOPtCl_2$	20.0	115–160 (140)[e]	3.5	(120–160)	H_2O
				215–260 (240)[e]	10.5	(180–280)	$S + N_2$
				365–400 (385)[e]	64.5	(400)	L' + Cl_2
11.	[PtCl$_2$L'-3]	$C_{16}H_{14}N_2SOPtCl_4$	17.8	190–370b[e]	66.7	(180–400)	L' + Cl_2
12.	[PtCl$_2$L'-4]	$C_{18}H_{20}N_2SO_3PtCl_2$	16.00	80–225 (195)[e]	1.5	(100–120)	0.5 H_2O
				225–305 (240)[e]	3.0	3.0 (140–180)	H_2O
					9.8	(200–240)	$S + N_2$
					65.5	(400)	L' + Cl_2

[a] Molar conductance has been determined in dimethylformamide (10^{-3} *M*) solution. [b] Broad. [e] Endothermic.

(Table II) (below 20 ohm^{-1} cm^2 mol^{-1}) for these complexes in dimethylformamide at 20 °C show that they behave as non-electrolytes [10]. These complexes decompose into black masses in the temperature range 160–225 °C.

The magnetic susceptibilities of these complexes measured at room temperature (15 ± 3 °C) indicate them to be diamagnetic and support a square planar structure IX for these complexes.

The solid state electronic spectra of palladium(II) and platinum(II) complexes show the main bands in the ranges 29410–27780, 26316–23810, 25000 22220 and 21275–16660 cm^{-1}. In case of platinum(II) complexes, two additional bands appear in the range 21275–16660 cm^{-1}. Of the four main bands, the first very intense band in the range 29410–27780 cm^{-1} is due to the internal ligand transitions [11] which occur at 27780 cm^{-1} for the uncomplexed ligands. In analogy with the reported data [12], both the strong bands in the ranges 26316–23816 and 25000–22220 cm^{-1} have been assigned to L → M and M → L charge transfer transitions respectively. The bands in the range 21275–16660 cm^{-1} may be assigned to the $A_{1g} \rightarrow B_{1g}$ transition in square planar palladium(II) and platinum(II) complexes [13].

In the infrared spectra of the ligand (L', VII), the bands due to $-NH_2$ stretching appear at 3420 and 3250 cm^{-1}. In the complexes of palladium(II) and platinum(II) (Table III), these bands are shifted to lower frequencies and appear in the range 3340–3050 cm^{-1}. This negative shift of 100–200 cm^{-1} indicates coordination of ligand (L') through $-NH_2$ [14, 15]. A very strong band in the range 1690–1670 cm^{-1} in all these complexes appears nearly at the same

TABLE III. The Electronic Spectra, Far I.r. and I.r. Data for Pd(II) and Pt(II) Complexes.[a]

S. No.	Complex	Electronic spectra (cm^{-1})	ν(N–H) (cm^{-1})	ν(C=O) (cm^{-1})	ν(M–X) (cm^{-1})	ν(M–S) (cm^{-1})	ν(M–N) (cm^{-1})	Other Main Bands (cm^{-1})
1.	[PdCl$_2$L'-1]	29410vs, 26316vs 25000s, 17240 w	3150m	1690vs	325w	365m	470vs 505w	1600s, 1582m, 1320m, 1285m, 1190s, 997s, 980s, 875m, 760vs, 740sh
2.	[PdCl$_2$L'-2]	29410vs, 26316vs, 24390m, 20830sh, 17240w	3100w	1685vs	312s 332m	350m	460sh 475vs	1610vs, 1580sh, 1340s, 1300vs, 1200s, 1180s, 1120m, 100m, 982s, 947s, 872m, 835vs, 805s, 780vs
3.	[PdCl$_2$L'-3]	27780vs, 26316s, 25000s, 17240w	3240m	1685vs	315w, 335vs	352w	460sh 472vs	1595s, 1580m, 1207s, 1195m, 1102s, 1095m, 995s, 835vs, 795s
4.	[PdCl$_2$L'-4]	29410s, 26316vs, 25000s, 23810s, 18518sh	3260m, 3050m	1680vs	320m, 340w	385w	490sh 502vs	1600vs, 1520vs, 1345s, 1305s, 1260s, 1205s, 1025vs, 1005m, 985vs, 825vs, 803m, 777s
5.	[PdBr$_2$L'-1]	28570vs, 24390sh, 22220vs, 20020s, 18180s, 16660m	3100w	1680s	285m	380w	470vs	1610m, 1585sh, 1325m, 1288s, 1188s, 975m, 878s, 775s
6.	[PdBr$_2$L'-2]	28570vs, 24390s, 23260s	3100m	1685s	250w 270m	370m	468sh 510vs	1615s, 1580w, 1300m, 1185m, 1065m, 990m, 838m, 810w, 795w
7.	[PdBr$_2$L'-3]	28850b,vs, 22990b	3200m	1678s	250w 260w	370w	480vs	1595s, 1575sh, 1332m, 1202m, 1100s, 1015s, 990s, 835vs, 792m
8.	[PdBr$_2$L'-4]	27780s, 23810sh, 22220vs, 20870sh, 18180sh	3240m	1670s	–	380w	500vs	1605s, 1388m, 1205m, 1015vs, 820vs, 800vs, 750m
9.	[PtCl$_2$L'-1]	28570s, 24340s, 23260m, 21275s, 19608s, 17240vs	3250m	1680vs	325s	368w	480vs	1605s, 1585sh, 1315m, 1295m, 1185s, 1003s, 975s, 870m, 750vs
10.	[PtCl$_2$L'-2]	28570s, 24390m, 22727sh, 21275s, 19230vs, 17095vs	3240bw	1685vs	295m, 340w	380w	470sh 505vs	1610vs, 1325w, 1295m, 1180s, 810vs
11.	[PtCl$_2$L'-3]	28570s, 27030sh, 24340s, 21275s, 19680s, 18180bw	3260m 3190w	1685s	335s	–	460sh 500w	1595vs, 1495m, 1315m, 1290m, 1197m, 1100vs, 1013s, 988m, 820vs
12.	[PtCl$_2$L'-4]	29000s, 27030sh, 25000m, 24340sh, 21275sh, 20440m, 18180bw	3340bw 3200bw	1670m	325s	–	470vs	1595vs, 1552sh, 1303m, 1265vs, 1176vs, 1023s, 990m, 840s, 830s, 720s

[a] vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, b = broad.

position as in the uncomplexed monohydrazones (VII), indicating lack of coordination by carbonyl group with the metal ions. The $>$C=N stretching in the region 1600–1580 cm^{-1} does not show any significant change on complex formation indicating no participation of $>$C=N in coordination to the metal ions [16]. The other absorption bands in the region 1600–700 cm^{-1} in these complexes appear nearly at the same positions as in the spectra of VII, but are at positions different from those of the bands of thiadiazepine ligands (V).

In the far i.r. region, the absorption bands in the range 340–295 cm^{-1} (Table III) have been assigned tentatively to the M–Cl stretching modes on the basis of reported data for square planar complexes of palladium(II) and platinum(II) [16, 17, 19]. The absorption frequencies in the range 285–250 cm^{-1} have tentatively been assigned to Pd–Br stretching modes. A weak to medium intensity band in the region 380–352 cm^{-1} is possibly due to the M–S stretching frequency in square planar complexes [11, 17–19]. A very strong band in the region

510–460 cm^{-1} has tentatively been assigned to the M–N stretching mode [11]. Hence the i.r. spectral data supports the proposed structure (IX) for these complexes in which the ligands (L′) form a six-membered chelate ring with the metal ions.

In the ^{1}H n.m.r. spectra of palladium(II) complexes in deuterated dimethylsulphoxide, NH_2 hydrogens appear upfield (100–125 Hz) as compared with those of the free monohydrazones (VII). In analogy with a similar upfield shift of the NH_2 hydrogen signal in a nickel(II) complex of an amine [20] and of olefinic carbon signals in c.m.r. spectra of platinum(II) complexes of olefins [21], these results have also been attributed to the non-bonding magnetic anisotropy effects associated with heavy metal ions [21] and/or the back donation [22] from metal to ligand which increases the electron density on the nitrogen atom, causing the upfield shift. In the downfield region, the *para* substituted phenyl hydrogens form two distinct AB quartets (4H each) as compared with only one AB quartet (8H) in case of thiadiazepines [9] indicating the non-equivalence of the two phenyl groups in these complexes in comparison to their equivalence in the parent thiadiazepine ring. The ^{1}H n.m.r. spectra of platinum(II) complexes could not be studied due to their insufficient solubilities.

Thermogravimetric and differential thermal analysis data (Table II) indicate that the weight loss in different complexes occurs at different temperature ranges. The first stage of decomposition in some of the complexes sets in at ~100 °C and is complete at ~200 °C. The weight loss in this temperature range corresponds to the loss of one water molecule from the complexes which is correborated by DTA as a strong endothermic peak in the temperature range 140–195 °C (peak temperature) appears. It clearly shows that the water lost is not the occluded water but is lost from the complexes after cyclization of the coordinated monohydrazone to form the thiadiazepine ring. In the DTA curves, another endothermic peak is recorded in the temperature range 200–260 °C, corresponding to the loss of one sulphur atom from the complexes [1, 2]. It is significant to note that the sulphur is lost from these complexes at relatively higher temperature than that from the parent ligands which further indicates that the coordination of the ligands to the metal atoms has taken place through the sulphur atom [23]. The decomposition in the complexes with L-2 and L-4 occurs stepwise with the loss of H_2O, S and N_2 respectively, but complexes obtained from L-1 and L-4 decompose continuously without giving any conclusive information.

These studies on the complexes of palladium(II) and platinum(II) with 3,6-disubstituted-2,7-dihydro-1,4,5-thiadiazepine derivatives (L) support a square planar geometry and structure IX, in which the thiadiazepine ring of the ligands (L) is cleaved by hydrolysis of one of the two carbon–nitrogen double bonds after complexation and the coordination occurs via sulphur and nitrogen atoms (NH_2).

Acknowledgement

We thank UGC, New Delhi for providing financial assistance during these investigations.

References

1 S. S. Sandhu, S. S. Tandon and H. Singh, *J. Inorg. Nucl. Chem.*, in press.

2 S. S. Sandhu, S. S. Tandon and H. Singh, *J. Inorg. Nucl. Chem.*, in press.

3 B. Rosenberg, L. Van Camp, J. E. Trosko and V. N. Mansour, *Nature (London), 222,* 385 (1969).

4 B. Rosenberg and L. Van Camp, *Cancer Res., 30,* 1799 (1970).

5 A. J. Thomson, R. J. P. Williams and S. Reslova, *Structure and Bonding, 11,* 1 (1972).

6 M. J. Cleare and J. D. Hoeschele, *Platinum Metal. Rev., 17,* 2 (1973).

7 T. A. Cannors, M. Jones, W. C. J. Ross, P. D. Braddock, A. R. Khokhar and M. L. Tobe, *Chem. Biol. Interactions, 5,* 415 (1972).

8 (a) J. Dehand, J. Jordanov and J. P. Beck, *Chem. Biol. Interactions, 11,* 605 (1975).
(b) A. B. Callear, I. Fleming, R. H. Ottewill, S. G. Warren and R. H. Prince, *Chemistry and Industry, 6,* 234 (1977).

9 S. S. Sandhu, S. S. Tandon and H. Singh, *Indian, J. Chem., 15B,* 664 (1977).

10 M. R. Udupa, and M. Padmanabhan, *Inorg. Chim. Acta, 13,* 239 (1975).

11 K. Nag and D. S. Joardar, *Inorg. Chim. Acta, 14,* 133 (1975).

12 S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams and H. B. Gray, *J. Am. Chem. Soc., 86,* 4594 (1964).

13 H. B. Gray and C. J. Ballhausen, *J. Am. Chem. Soc., 85,* 260 (1963).

14 I. S. Ahuja, *J. Inorg. Nucl. Chem., 29,* 2091 (1967).

15 I. S. Ahuja and P. Rastogi, *Inorg. Nucl. Chem. Lett., 5,* 255 (1969).

16 N. Sonoda and T. Tanaka, *Inorg. Chim. Acta, 12,* 261 (1975).

17 S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, V. A. Pickles, and J. S. Shannon, *Aust. J. Chem., 18,* 673 (1965).

18 J. R. Allkins, and P. J. Hendra, *J. Chem. Soc. A,* 1325 (1967).

19 B. Singh and R. K. Mehra, *Indian, J. Chem., 13,* 1194 (1975).

20 R. J. Fitzgerald and R. S. Drago, *J. Am. Chem. Soc., 89,* 2879 (1967).

21 D. G. Coper and J. Powell, *Inorg. Chem., 15,* 1959 (1976).

22 C. A. Tolman, A. D. English and L. E. Manzer, *Inorg. Chem., 14,* 2353 (1975).

23 S. S. Sandhu, S. S. Tandon and H. Singh, unpublished results.

24 E. Cuthbertson, A. D. U. Hardy and D. D. Mac Nicol, *J. Chem. Soc. Perkin I,* 254 (1975).