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Palladium(II) Chelates of 1,1-Dimethyl-3-(4-methyl-2-thiazolyl)thiourea and Related Thioureas

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Pd(II) chelates of 1,1-dimethyl-3-(4-methyl-2-thiazolyl)thiourea and related *N*-(2-thiazolyl)-thioureas were prepared and their molecular structures were determined by means of spectroscopic, thermochemical, and X-ray crystallographic measurements, in order to establish the identity of the colored substances in the spectrophotometric determination of Pd(II) with the thiazolylthioureas. The results indicated that Pd(II) formed 1 : 2 chelates with the thiazolylthioureas and that the ligands were bidentate and coordinated through the thiourea sulfur and thiazole nitrogen atoms. The geometry of Pd(II) coordination was roughly square-planar and the configuration of the two thiazolylthiourea molecules was *cis*.

Keywords——palladium(II); metal chelate; *N*-(2-thiazolyl)thiourea; 1,1-dimethyl-3-(4-methyl-2-thiazolyl)thiourea; thermogravimetric curve; differential scanning calorimetric curve; X-ray crystallography

In the previous papers,[2)] we reported that 1,1-dimethyl-3-(4-methyl-2-thiazolyl)thiourea (**1**) and related *N*-(2-thiazolyl)thioureas are potentially useful chelating agents which can be used as reagents for spectrophotometric determination of metal ions. Facile and sensitive methods for the determination of Pd(II) with 1,1-dimethyl-3-(4-methyl-5-nitro-2-thiazolyl)thiourea (**3**)[2b)] and 1,1-dimethyl-3-(4-*p*-nitrophenyl-5-nitro-2-thiazolyl)thiourea (**5**)[2c)] were proposed.

A knowledge of the structures of the colored substances is necessary for further development of the chelating ligands in this series. 1,1-Dimethyl-3-(2-thiazolyl)thioureas form yellow chelates with Pd(II); these chelates can be extracted into organic solvents such as chloroform, and they were identified as the colored substances involved in the spectroscopic analysis.[2,3)] It has been shown that the thiazolylthioureas are bidentate ligands; they coordinate through the thiourea sulfur and thiazole nitrogen, and form 1 : 2 Pd(II) chelates.[2-6)]

Though the square-planar geometry has been assumed for Pd(II) coordination, the coordination configuration of the two ligands was not known. In order to determine the molecular structures of the metal chelates, we prepared several Pd(II) chelates of this series of ligands and determined their crystal structures by means of X-ray crystallography. The present paper describes the results of the X-ray crystallographic studies as well as other physicochemical studies on the Pd(II) chelates. The *cis* configuration was established for the two ligands.

Experimental

N-(2-Thiazolyl)thioureas were prepared according to the methods described in the previous papers.[2,4-7)] A

JEOL JMS-D100 mass spectrometer, a JEOL JNM-NH 100 NMR spectrometer [100 MHz], a Shimadzu UV-200 s double-beam spectrometer and a Hitachi EPI-G3 infrared (IR) spectrometer were used throughout the present study. The thermogravimetric (TG) and the differential scanning calorimetric (DSC) curves were recorded on a Rigakudenki model 8085Dl thermal analyzer at a heating rate of 5°C/min.

Pd(II) Chelate of Compound 1 (Pd-1)——An aqueous solution of $PdCl_2$ was added to an MeOH solution of compound **1** and the mixture was shaken for 30 min. The mixture was further shaken for 30 min after the addition of $CHCl_3$. The $CHCl_3$ layer was separated, washed with 1 N NaOH and water, dried over $MgSO_4$, and then evaporated to dryness. The residue was purified through chromatography on a silica gel column with acetone–$CHCl_3$ as an eluent.

Pd(II) Chelate of Compound 3 (Pd-3)——Compound **3** was dissolved in a $CHCl_3$ solution of dichlorobis(benzonitrile) Pd(II). The mixture was shaken for 1 h, then 1 N NaOH was added. The whole was shaken for 30 min, then the $CHCl_3$ layer was separated, dried with $MgSO_4$, and evaporated to dryness. The residue was purified by recrystallization from $CHCl_3$–EtOH.

The Pd(II) chelates of 1,1-dimethyl-3-(4-phenyl-2-thiazolyl)thiourea (**2**) (Pd-**2**), 1,1-dimethyl-3-(4-*p*-nitrophenyl-2-thiazolyl)thiourea (**4**) (Pd-**4**), compound **5** (Pd-**5**), and 1,1-diethyl-3-(4-methyl-5-nitro-2-thiazolyl)thiourea (**6**) (Pd-**6**) were prepared analogously. The analytical and spectroscopic data for the Pd(II) chelates are listed in Tables I and II, respectively.

X-Ray Diffraction Study——X-Ray diffraction analysis was carried out for Pd-**1**, Pd-**2** and Pd-**3**, which are the most useful chelates for spectrophotometric analysis. The lattice parameters and intensity data were collected on a Philips PW 1100 diffractometer using graphite-monochromated MoK_α radiation. The crystal data and the process of structure determination are summarized in Table III.[8]

The crystal structures were determined by the heavy atom method and refined by least-squares calculations with block-diagonal matrix approximations.[9] In Pd-**1** and Pd-**3**, disordered solvent molecules were located on the difference electron-density map with the help of model building. The solvent content was consistent with the results of elemental and thermal analyses.

Results and Discussion

Spectroscopic Studies

Six Pd(II) chelates were prepared, and their properties are listed in Tables I and II. The

TABLE I. Analytical Data for Pd(III) Chelates

	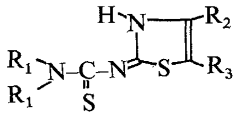				Pd-Chelates	Analysis (%) Calcd (Found)				
Symbol of ligand	R_1	R_2	R_3	Symbol of Pd-chelate	Formula mp (°C) (Recryst. solvent)	C	H	N	S	Cl
1	CH_3	CH_3	H	Pd-**1**	$C_{15}H_{21}N_6S_4PdCl_3$	28.76	3.38	13.42	20.47	16.98
					294—295	(28.92	3.41	13.31	20.35	16.98)
					$CHCl_3$–EtOH					
2	CH_3	Ph	H	Pd-**2**	$C_{24}H_{24}N_6S_4Pd$	45.67	3.83	13.31		0
					286—289	(45.60	3.67	13.21		0)
					$CHCl_3$–EtOH					
3	CH_3	CH_3	NO_2	Pd-**3**	$C_{15}H_{19}N_8O_4S_4PdCl_3$	25.15	2.67	15.64	17.90	14.85
					269—271	(25.11	2.57	15.57	17.94	14.74)
					$CHCl_3$–EtOH					
4	CH_3	Ph-NO_2 (*p*)	H	Pd-**4**	$C_{24}H_{22}N_8O_4S_4Pd$	39.97	3.08	15.54		
					>300	(39.66	3.13	15.04)		
					Dioxane–H_2O					
5	CH_3	Ph-NO_2 (*p*)	NO_2	Pd-**5**	$C_{24}H_{20}N_{10}O_8S_4Pd$	35.54	2.49	17.27		
					>300	(35.49	2.41	16.81)		
					Dioxane–H_2O					
6	C_2H_5	CH_3	NO_2	Pd-**6**	$C_{18}H_{26}N_8O_4S_4Pd$	33.10	4.01	17.16		
					232—235	(33.15	4.03	17.41)		
					Dioxane–H_2O					

TABLE II. Physicochemical Data for Pd(II) Chelates

Compds.	UV $\lambda_{\max}^{\mathrm{CHCl_3}}$ nm[a] (ε)		IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}[b]		MS m/e (RI, %)	^{1}H-NMR (CDCl$_3$) δ (ppm)[d]
			1600—1300			
Pd-1	380 sh	4.5 × 10^3	1550 sh	1394 vs	507 (16, M$^+$), 306 (11, (M$^+$ −ligand))	1.92 (4-CH$_3$, 3H × 2)
	328	18.1	1525 sh	1359 vs	200 (60, (ligand−H))	6.27 (5-H, 1H × 2)
	285	25.4	1513 sh	1300 vs	88 (base, (CH$_3$)$_2$N$^+$CS))	3.30 (($\underline{\mathrm{CH_3}}$)$_2$N, 6H × 2)
			1487 vs			
			1411 m			
Pd-2	380	5.6	1515 s	1389 vs	631 (8, M$^+$), 368 (12, (M$^+$−ligand))	—[e]
	338	15.9	1481 vs	1360 s	262 (91, (ligand−H))	
	288	30.1	1445 s	1330 m	88 (base, (CH$_3$)$_2$N$^+$CS)	
			1410 s			
Pd-3	413	43.7	1545 sh	1393 vs	596 (2, M$^+$), 552 (7, (M$^+$ −(CH$_3$)$_2$N)	2.48 (4-CH$_3$, 3H × 2)
	350 sh	13.7	1535 m	1335 vs	550 (7, (M$^+$ −NO$_2$), 245 (13, (ligand−H))	3.31, 3.45 ($\underline{\mathrm{CH_3}}$)$_2$N
	300	12.5	1500 sh	1300 vs	213 (7, (ligand−SH)), 88 (base, (CH$_3$)$_2$N$^+$CS)	
	260 sh	30.8	1481 s		72 (16)	
Pd-4	375.5 sh	17.4	1597 vs	1387 vs	—[c]	—
	339	23.6	1532 sh	1350 sh		
	290	33.4	1515 sh	1344 vs		
	260 sh	35.8	1487 vs	1319 m		
			1403 vs			
Pd-5	430	25.1	1600 w	1392 vs	—	—
	310 sh	21.0	1545 sh	1348 vs		
	275 sh	33.5	1520 s	1330 vs		
			1490 vs	1306 vs		
			1480 sh			
Pd-6	415.5	47.3	1538 s	1378 s	653 (3, M$^+$), 607 (8, (M$^+$ −NO$_2$)	2.48 (4-CH$_3$, 3H × 2)
	345 sh	13.6	1495 s	1337 s	241 (12, (ligand−H)), 88 (71), 72 (base)	1.29 (($\underline{\mathrm{CH_3}}CH_2$)$_2$N, 6H × 2)
	360 sh	13.0	1470 s	1303 s		3.40—4.20 ((CH$_3$$\underline{\mathrm{CH_2}}$)$_2$N, 4H × 2)
	260	30.3	1455 sh			
			1429 s			

a) sh, shoulder. *b*) vs, very strong; s, strong; m, medium; w, weak; sh, shoulder. *c*) Not measurable. *d*) Internal standard: tetramethylsilane (TMS). *e*) Practically insoluble.

Table III. Crystal Data and the Process of Structure Determination[8)]

Compd.	Pd-1	Pd-2	Pd-3
Solvate	Chloroform	None	Chloroform
Formula	$(C_7H_{10}N_3S_2)_2Pd \cdot CHCl_3$	$(C_{12}H_{12}N_3S_2)_2Pd$	$(C_7H_9N_4O_2S_2)_2Pd \cdot CHCl_3$
Formula weight	626.4	631.2	716.4
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/a$	$C2/c$
Z	4	4	4
Crystallographic symmetry imposed on chelate (site sym. at Pd)			
chloroform	2 Cl(1) on $\bar{1}$	1	2 Diad through Cl(1) and the center line of Cl_3 triangle
Radiation	MoK_α monochromated by a graphite plate		
a (Å)	18.817 (9)	17.248 (9)	18.246 (9)
b (Å)	11.975 (6)	19.535 (9)	18.086 (9)
c (Å)	11.596 (6)	7.691 (4)	8.124 (4)
β (°)	109.11 (5)	91.91 (5)	94.92 (5)
U (Å^3)	2469	2590	2671
D_{calc} (g cm^{-3})	1.685	1.619	1.782
μ for MoK_α (cm^{-1})	14.1	10.4	13.2
Crystal size (mm)	0.04 × 0.07 × 0.3	0.06 × 0.07 × 0.1	0.1 × 0.1 × 0.3
Scan speed (°θ/min)	6	4	4
2θ range (°)	6—50	6—50	6—50
No of reflections			
Theoretical	2230	4617	2705
Observed above 2σ (I)	1596	3683	2215
No of independent atoms	17	35	19
H atoms		No H atoms located	
Final R	0.070	0.047	0.055
Distribution nature of chloroform	Two 1/2 weight molecules related by $\bar{1}$, Cl(1) lies on $\bar{1}$		Two 1/2 weight molecules related by 2, Cl(1) lies on 2

results of elemental analysis and mass spectroscopy showed that the thiazolylthioureas formed 1 : 2 chelates with Pd(II). Figure 1 shows the mass spectrum of Pd-**3** and the assignments of ion peaks. The peaks at m/e 596 and 598 correspond to the 1 : 2 chelate molecules of ^{106}Pd and ^{108}Pd. The spectrum at m/e 245 and lower was the same as that of the ligand. Analogous spectra were obtained with the other Pd(II) chelates (Table II).

The IR spectra of the ligands showed bands at the 3200 and 1570 cm^{-1} regions which are assignable to stretching and deformation vibrations of the N–H bond, respectively. These bands were absent in the spectra of the Pd(II) chelates, suggesting that the hydrogen atom was lost upon chelation.

In the proton magnetic resonance spectra, higher field shifts accompanying Pd(II) chelation were noted for the signals of 4-thiazolylmethyl hydrogens. For example, these were 2.20 and 1.92 ppm in **1** and Pd-**1**, respectively.

Thermal Study

To determine the composition of the crystals for X-ray crystallographic study, the crystals were analyzed by means of TG and DSC techniques. Crystals of Pd-**1**, Pd-**2**, and Pd-**3** for the studies were obtained by recrystallization from chloroform–ethanol. The TG and DSC

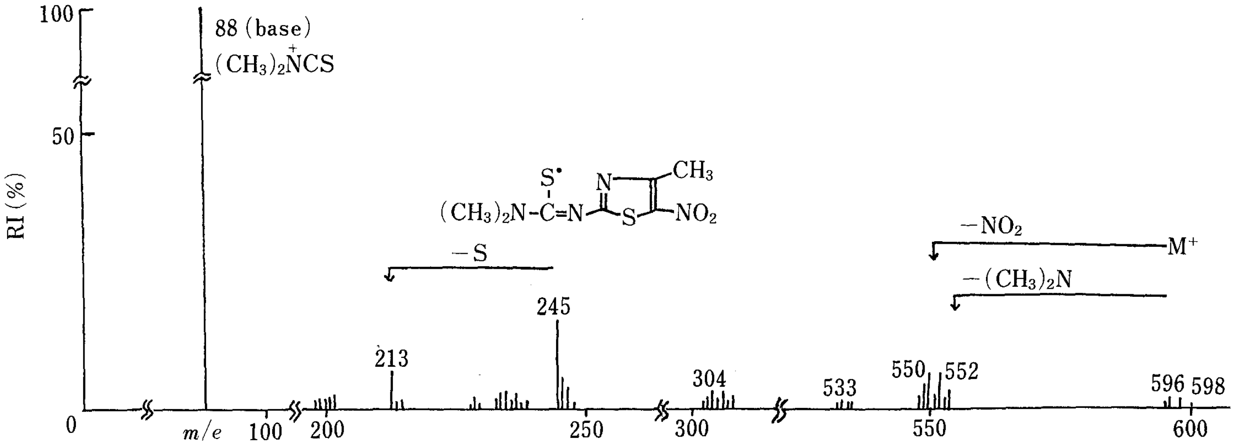

Fig. 1. Mass Spectra of the Chelate Pd-3

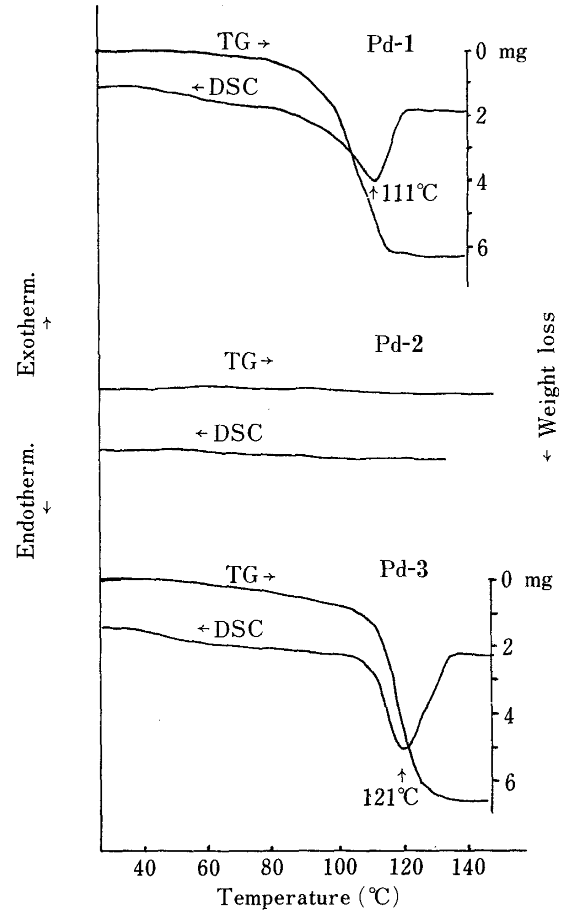

Fig. 2. The Thermogravimetric (TG) and Differential Scanning Calorimetric (DSC) Curves of the Pd(II) Chelates

Heating rate, 5 °C/min; DSC range, 4 mcal/s. Amount of sample: Pd-**1**, 31.51 mg; Pd-**2**, 20.66 mg; Pd-**3**, 33.11 mg.

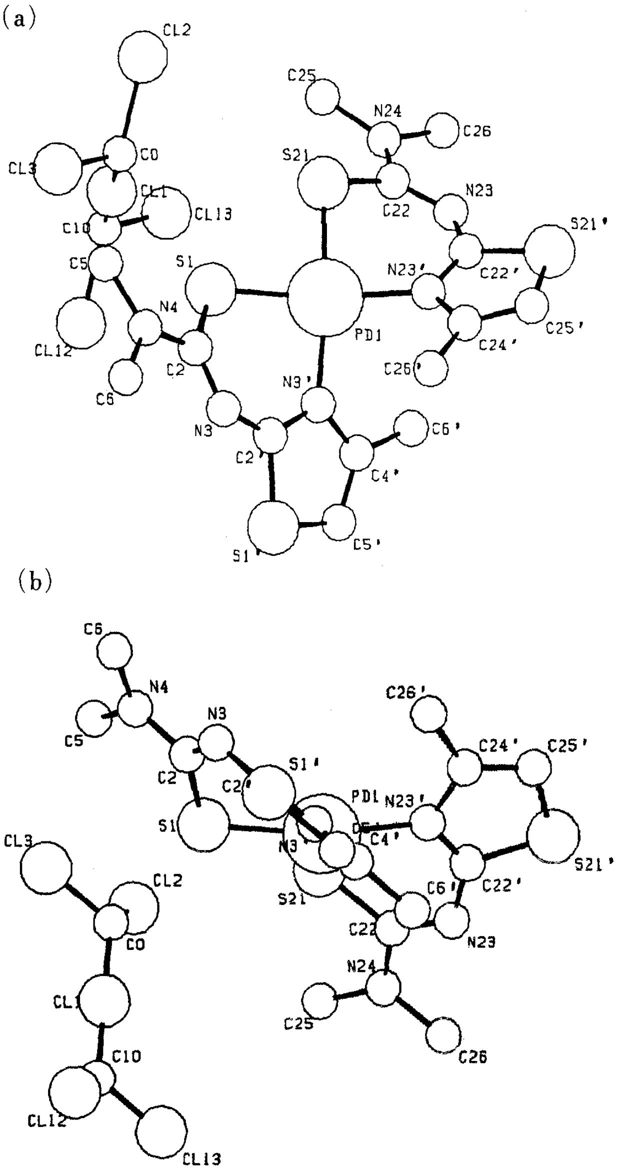

Fig. 3. Molecular Structure of Chelate Pd-**1**, with the Crystallization Solvent Molecule

Drawn by using the PLUTO program.[11] For details, see the text.

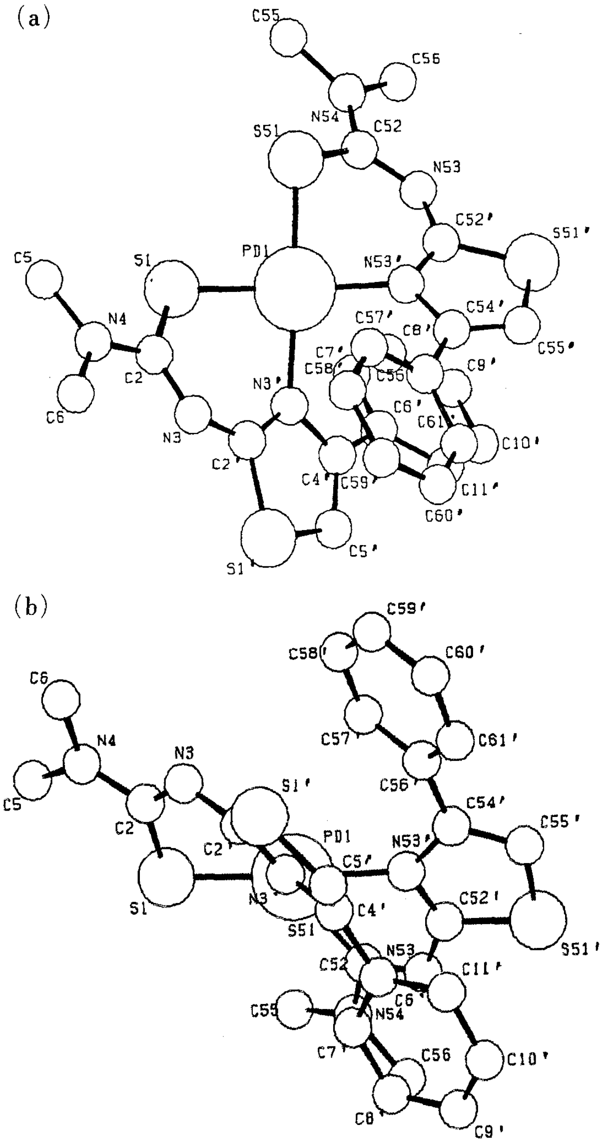

Fig. 4. Molecular Structure of the Chelate Pd-**2**

Drawn by using the PLUTO program.[11] For details, see the text.

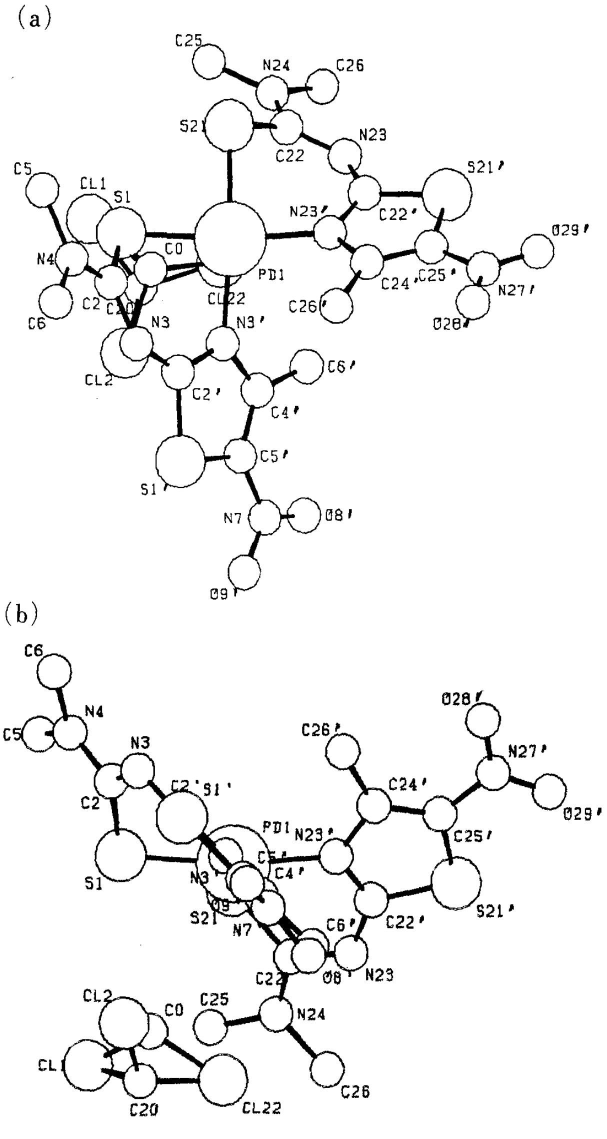

Fig. 5. Molecular Structure of the Chelate Pd-**3** with the Crystallization Solvent Molecule

Drawn by using the PLUTO program.[11] For details, see the text.

curves of the three Pd(II) chelates are shown in Fig. 2. Chelate Pd(II)-**2** was thermally stable in the range of 40—140 °C.

The TG curves of chelates Pd-**1** and Pd-**3** showed a decrease of weight corresponding to the liberation of a molecule of chloroform at 111 °C and at 121 °C, respectively. The values of the energy of liberation calculated from the DSC data were 34.9 and 35.0 kJ mol^{-1} for Pd-**1** and Pd-**3**, respectively. The values are slightly higher than the enthalpy of evaporation of chloroform at 760 Torr, 29.4 kJ mol^{-1}.[10] The differences reflect the energy of inclusion of the chloroform molecule in crystals of the Pd(II) chelates. The crystals were fragile and were disintegrated by grinding with loss of the chloroform molecule, as determined by the powder X-ray diffraction method.

X-Ray Crystallographic Study

A summary of the bond lengths and angles among the three Pd(II) chelates is given in Tables IV and V. Each chelate molecule has two ligands, but in Pd-**1** and Pd-**3**, the two ligands are related by a diad axis. Therefore, only one independent ligand molecule is

Table IV. Variation of the Bond Lengths in the Four Different Kinds of Liganded Groups, One in Each Pd-**1** and Pd-**3** and Two in Pd-**2**

Bond length	Range (Å)	Max. deviation ($\times 10^3$ Å)	Mean of four (Å)	e.s.d. ($\times 10^3$ Å)	Observed s.d. ($\times 10^3$ Å)
Pd-S(1)	2.274—2.287	13	2.279	2	3
Pd-N(3′)	2.051—2.070	19	2.058	6	4
S(1)-C(2)	1.752—1.771	19	1.761	9	4
C(2)-N(3)	1.304—1.337	33	1.322	10	7
C(2)-N(4)	1.333—1.377	44	1.355	11	9
N(4)-C(5)	1.453—1.487	34	1.470	12	7
N(4)-C(6)	1.480—1.489	9	1.485	12	2
N(3)-C(2′)	1.325—1.342	17	1.335	10	4
S(1′)-C(2′)	1.729—1.736	7	1.733	8	2
S(1′)-C(5′)	1.709—1.723	14	1.719	9	3
C(2′)-N(3′)	1.326—1.351	25	1.336	10	6
N(3′)-C(4′)	1.377—1.405	28	1.396	10	6
C(4′)-C(5′)	1.355—1.368	13	1.363	11	3

e.s.d., estimated standard deviation.

Table V. Variation of the Bond Angles in the Four Different Kinds of Liganded Groups, One in Each Pd-**1** and Pd-**3** and Two in Pd-**2**

Bond angle	Range (°)	Max. deviation	Mean of four (°)	e.s.d. ($\times 10°$)	Observed s.d. ($\times 10°$)
S(1)-Pd-N(3′)	87.5—89.5	2.0	88.5	2	6
S(1)-Pd-S(1)[a]	86.7—90.6	3.9	88.1	1	12
N(3′)-Pd-N(3′)[a]	94.5—97.3	2.8	96.2	3	9
S(1)[a]-Pd-N(3′)[a]	87.6—89.5	1.9	88.5	2	5
Pd-S(1)-C(2)	98.1—101.4	3.3	100.3	3	8
Pd-N(3′)-C(2′)	119.8—122.9	3.1	121.0	5	7
S(1)-C(2)-N(3)	125.5—127.7	2.2	126.9	6	5
C(2)-N(3)-C(2′)	122.5—123.2	0.7	122.9	7	2
N(3)-C(2′)-N(3′)	129.9—131.4	1.5	130.9	7	3
S(1)-C(2)-N(4)	115.5—117.4	1.9	116.3	6	5
C(2)-N(4)-C(5)	122.8—123.8	1.0	123.5	8	2
C(2)-N(4)-C(6)	118.2—119.3	1.1	118.9	8	3
C(5)-N(4)-C(6)	116.7—118.6	1.9	117.4	8	4
N(3)-C(2)-N(4)	116.2—116.9	0.7	116.7	7	2
N(3)-C(2′)-S(1′)	116.5—117.5	1.0	117.0	6	2
S(1′)-C(2′)-N(3′)	111.7—112.5	0.8	112.1	6	2
C(2′)-N(3′)-C(4′)	112.3—113.7	1.4	112.9	6	3
N(3′)-C(4′)-C(5′)	111.3—114.4	3.1	113.1	7	7
N(3′)-C(4′)-C(6′)	120.6—121.7	1.1	121.1	7	2
C(4′)-C(5′)-S(1′)	109.8—113.6	3.8	111.3	6	8
C(5′)-C(4′)-C(6′)	123.8—127.8	4.0	125.6	7	8
C(5′)-S(1′)-C(2′)	88.7—91.3	2.6	90.5	4	6

[a] They are related by the crystallographic symmetry of the complex in Pd-**1** and Pd-**3** (*e.g.* S21 *vs.* S1). In Pd-**2**, they belong to another ligand molecule coordinated to the same Pd (*e.g.* S51 *vs.* S1).

contained in these chelates, while in Pd-**2**, there are two independent ligand molecules giving in total four ligand structures to be compared in the present study. Tables IV and V list the ranges of variation of the bond lengths and angles, maximum deviations of the values, mean values and standard deviations estimated from the e.s.d's of the atomic parameters and those

Table VI. Planarity and Dihedral Angles of the Planar Groups

	Pd-1	Pd-2		Pd-3
Least-squares plane of the thiourea group				
Through atoms S(1), C(2), N(4) and N(3)				
Mean deviation of the atoms from the plane (Å)	±0.005	±0.002	±0.003	±0.008
Deviation of Pd from the plane (Å)	1.380	1.150	1.337	1.647
Least-squares plane of the thiazole group				
Through atoms S(1′), C(2′), N(3′), C(4′) and C(5′)				
Mean deviation of the atoms from the plane (Å)	±0.003	±0.009	±0.011	±0.009
Deviation of Pd from the plane (Å)	0.154	−0.452	0.404	0.041
Dihedral angle between				
Thiourea and thiazole groups (°)	31.8	23.4	23.5	32.7
Thiazole and phenyl groups (°)	—	33.7	33.4	—
Thiazole and nitro groups (°)	—	—	—	6.3

Table VII. Coordination Geometry of S(1) and N(3′)

	Pd-1	Pd-2		Pd-3
Thiourea group				
<[C(2)–S(1)–Pd]	101.4 (4)°	127.7 (5)°	100.1 (2)°	98.1 (2)°
τ[N(3)–C(2)–S(1)–Pd]	−39.9 (11)	−31.7 (3)	−37.4 (2)	−50.0 (2)
τ[N(4)–C(2)–S(1)–Pd]	142.8 (8)	149.3 (2)	144.1 (2)	134.6 (1)
Thiazole group				
<[C(2′)–N(3′)–Pd]	122.9 (7)	120.3 (4)	119.8 (4)	120.8 (3)
<[C(4′)–N(3′)–Pd]	124.4 (7)	125.5 (4)	127.2 (4)	125.3 (3)
<[C(4′)–N(3′)–C(2′)]	112.4 (9)	113.2 (6)	112.3 (5)	113.7 (4)
τ[S(1′)–C(2′)–N(3′)–Pd]	175.0 (3)	−165.4 (2)	−166.7 (2)	178.7 (2)
τ[C(5′)–C(4′)–N(3′)–Pd]	−174.5 (6)	164.8 (3)	166.8 (3)	−177.8 (1)

actually observed for the four ligand molecules. It is clear that the disagreements of the values are within the limits of experimental error.

Figures (a) 3, 4 and 5 show plans of the molecular structures projected on the plane defined by two vectors, one being S(1) to N(3′) of the other ligand coordinating to Pd(II) at the *trans* position to S(1) and the second being the S(1) to N(3′) vector in the same ligand. Figures (b) are another projection drawn by rotating the molecules in (a) through 90° about the horizontal axis. It can be seen that the ligands coordinate to Pd(II) through the sulfur atom of thiourea and the nitrogen atom of the thiazole ring. The geometry of Pd(II) coordination is roughly square-planar with *cis* configuration of the two thiazolylthiourea ligands.

For the purpose of discussion, the ligand molecule may be divided into at least two parts. The planarity and dihedral angles between the planar groups are shown in Table VI. Pd(II) lies nearly on the plane of the thiazole group but deviates significantly from the thiourea plane. This deviation may be accounted for by the twist of the S(1)–Pd(II) bond about S(1)=C(2) as shown in Table VII. A similar twist has commonly been observed in thiourea chelates. The phenyl groups in Pd-**2** are not coplanar with the thiazole plane, while the nitro group in Pd-**3** is almost coplanar. The results are consistent with the previous proposals.[2c)]

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References and Notes

1) Deceased September 6th, 1983.
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