

PALLADIUM(II) COMPLEXES OF DIPHENYLPHOSPHINEACETIC ACID*

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Palladium(II) forms the following types of complexes with diphenylphosphineacetic acid (HA): *trans*-square planar $\text{PdX}_2(\text{HA})_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{S-bonded SCN}$) and *trans*-planar, halide (thiocyanate) bridged dimers $\text{Pd}_2\text{X}_4(\text{HA})_2$, both containing HA as a monodentate P-donor. In neutral solutions, the extremely stable square planar complex PdA_2 ($\beta_2 > 10^{39}$) is formed with bidentate A^- ligands. The results are based on preparative work together with electronic and IR spectral, conductance, molecular weight and magnetic data.

As a typical soft cation, palladium(II) forms a number of complexes with monodentate tertiary phosphines. The complexes belong to the following two basic structural types¹⁻³: monomeric square planar $\text{PdX}_2(\text{PR}_3)_2$ (X represents a monodentate ligand, frequently halide) which are mostly *trans*. The second type includes *trans*-square planar $\text{Pd}_2\text{X}_4(\text{PR}_3)_2$ dimers with X-bridges and *trans* arrangement of the terminal phosphines. These complexes are interesting theoretically, especially the contribution of σ and π palladium-phosphorus bonding, and also find practical use in homogeneous catalysis².

In a previous paper of this series⁴ we studied the coordinating properties of diphenylphosphineacetic acid (abbreviated as HA), as the simplest representative of carboxyphosphines of the $\text{Ph}_{3-n}\text{P}(\text{CH}_2\text{COOH})_n$, type, with nickel(II) cation which has comparable affinity for both donor atoms of the ligand. This work was carried out to study complexes of HA with palladium(II) which, as a typical soft metal ion, has much lower affinity for the carboxyl oxygen.

EXPERIMENTAL

Chemicals

Diphenylphosphineacetic acid was prepared according to the literature⁴. The palladium(II) chloride solution (Safina, Vestec) was analyzed and found to be 2·29M- H_2PdCl_4 . The chloro-

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complexes K_2PdCl_4 and Na_2PdCl_4 were prepared by neutralization of this solution followed by crystallization from water. The Na_2PdBr_4 and $K_2Pd(SCN)_4$ complexes were prepared by conversion of the chloro complexes with NaBr and KSCN, respectively, in absolute ethanol followed by filtration of the alkali chloride and crystallization. Other chemicals were *p.a.* products (Lachema and Merck). Solvents were purified using standard methods. Spectrograde tetrahydrofuran and methanol were fractionated in a stream of nitrogen and the fractions not absorbing at $\lambda \geq 230$ nm were used.

Apparatus

The instruments and measuring methods used are described in a previous paper⁴. Molecular weights were determined by vapour-pressure osmometry in tetrahydrofuran using a Perkin-Elmer-Hitachi 115 instrument.

Analytical Methods

After a wet mineralization of the samples with a nitric-perchloric acid mixture, palladium was determined either by EDTA-titration⁵ or photometrically⁶ and phosphorus photometrically⁷. Halogens were determined after combustion of the samples according to the method of Schöniger and the thiocyanate content was found through nitrogen determination by the Dumas method.

Preparation of the Complexes $PdX_2(HA)_2$ ($X = Cl, Br, I, SCN$)

Method 1: 4 mmol of M_2PdX_4 dissolved in 2 ml water (for Br and I prepared *in situ* from Na_2PdCl_4 and an excess of NaX; the suspension of PdI_2 in NaI formed required stirring for several hours in the subsequent reaction) were mixed with a solution of 8 mmol of HA in 20 ml of acetic acid. The products separated overnight and were washed with water, recrystallized from acetic acid and dried at room temperature. Yields varied from 55 to 85%.

Method 2: a solution of 4 mmol of $PdCl_2(HA)_2$ in 20 ml of ethanol was prepared by mixing stoichiometric amounts of H_2PdCl_4 and HA. To this solution were added 16 mmol of NaX ($X = Br, I, SCN$) dissolved in 10 ml of ethanol. The products which crystallized out after several hours were isolated as previously with yields of 60 to 75%.

The two methods yielded identical products. Method 2 is far more convenient for the synthesis of the iodo complex.

$Pd_2X_4(HA)_2$

5 mmol of pulverized $PdX_2(HA)_2$ and 5 mmol of M_2PdX_4 (for I a suspension of PdI_2 in 2 NaI) were dissolved under reflux in 100 ml of ethanol. After evaporation to dryness, the crude products were washed with water, crystallized from ethanol and dried at room temperature. Yields were 30–65%.

PdA_2

In a nitrogen atmosphere a solution of 5 mmol of NaA in 20 ml of water was acidified to $pH < 7$ by addition of a small amount of HA (to prevent palladium(II) from being reduced to the metal). The white precipitate formed on the addition of a solution of 2.5 mmol of K_2PdCl_4 in 20 ml of water was separated, washed with water and crystallized from 50% ethanol. After drying in the air the yield was 68%.

RESULTS

The palladium(II) complexes with HA are light yellow to deep reddish-brown crystalline diamagnetic substances, stable in the air, insoluble in water and soluble in polar organic solvents to give non-conducting solutions. The results of analysis and other properties are given in Table I. Diagnostically significant bands of the IR spectra are given in Table II and the electronic spectra are summarized and assigned in Table III.

The thermodynamic stability of PdA₂ was qualitatively estimated from spectrophotometric measurements in the system

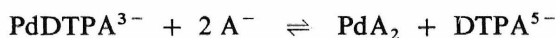


TABLE I
Analytical Data and Properties of the Complexes Prepared

Compound	Colour	Calculated/Found				M.p. ^a , °C
		M.w.	% Pd	% P	% X(N)	
PdCl ₂ (HA) ₂	yellow	665.8	15.98	9.30	10.65	201—203
		652	15.89	9.03	10.98	
PdBr ₂ (HA) ₂	orange	754.8	14.10	8.20	21.18	219—221
		771	14.37	8.20	21.08	
PdI ₂ (HA) ₂	red	848.7	12.54	7.30	29.91	210—213
		829	12.51	7.45	29.15	
Pd(SCN) ₂ (HA) ₂	yellow	711.0	14.96	8.71	3.94	179—181
		708	15.01	8.80	4.01	
Pd ₂ Cl ₄ (HA) ₂	red-brown	843.1	25.24	7.35	16.82	203—206
		870	25.15	7.18	16.66	
Pd ₂ Br ₄ (HA) ₂	dark red	1 022.4	20.84	6.07	31.31	236—238
		1 075	21.31	6.03	31.68	
Pd ₂ I ₄ (HA) ₂ ·C ₂ H ₅ OH ^b	red-brown	1 256.5	16.94	4.93	40.40	231—232
		1 201	17.00	4.84	40.19	
Pd ₂ (SCN) ₄ (HA) ₂ · 2 C ₂ H ₅ OH	orange-red	1 027.3	20.72	6.03	5.46	194—196
		930	20.85	6.71	5.19	
PdA ₂	light yellow	592.4	17.95	10.45		218—220
		614	18.40	10.73		

^a Capillary; ^b desolvation at 150°C without lattice change; weight loss calc.: 3.67%, found: 3.75%;

^c desolvation at 170°C with lattice change; weight loss calc.: 9.00%, found: 10.42%.

(H₅DTPA = diethylenetriaminepentaacetic acid). After equilibration, the absorbance of solutions containing various amounts of H₅DTPA, HA and Pd(ClO₄)₂ (ref.^{8,9}) in an acetate buffer of pH 5.5 was measured in the near UV region where the molar absorption coefficients of PdDTPA³⁻ and PdA₂ differ considerably ($\epsilon_{325} = 1450$ (ref.¹⁰) and 3560, respectively). Within experimental error (1%), the formation of PdA₂ was found to be complete at all reagent ratios including $c_{\text{DTPA}} = 5c_{\text{A}} = 10c_{\text{Pd}} = 0.01\text{M}$. As $\beta_{\text{PdDTPA}} = 10^{29.7}$ (ref.¹⁰) it follows that the stability constant of PdA₂ must be higher than 10^{39} .

Other methods tested for the determination of the stability constant have been found unsuitable: the Pd²⁺-A⁻-SCN⁻ system yields mixed complexes, the polarographic reduction of PdA₂ is irreversible and a palladium metal electrode is poisoned in the presence of phosphines (see also⁹).

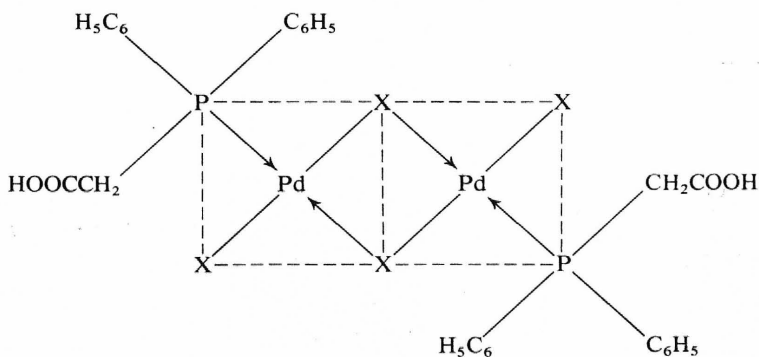
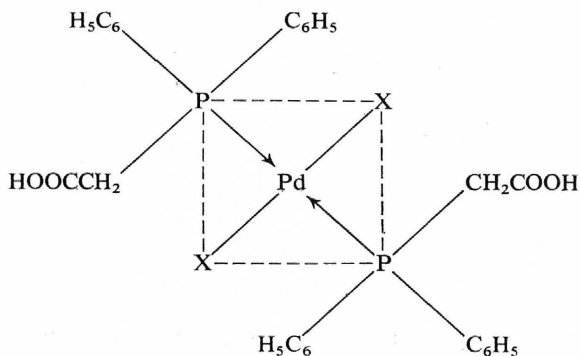
TABLE II
Selected Bands of the IR Spectra of the Complexes in Nujol Mulls

Compound	$\nu_{\text{as}}(\text{COO})$	$\nu_{\text{s}}(\text{COO})$	(C—P)	$\nu(\text{Pd—X})$			$\nu(\text{Pd—P})$
				<i>a</i>	<i>b</i>	<i>c</i>	
PdCl ₂ (HA) ₂	1 690 vs	1 290 s	517 m 490 m	360 m	—	—	220 w
PdBr ₂ (HA) ₂	1 702 vs	1 295 s	508 m 478 m	276 m	—	—	226 w
PdI ₂ (HA) ₂	1 705 vs	1 305 s	505 s 477 m	209 m	—	—	228 w
Pd(SCN) ₂ (HA) ₂	1 739 vs	1 227 m	507 s 480 s	2 140 vs ^d	665 w ^e	318 m ^f	219 w
Pd ₂ Cl ₄ (HA) ₂	1 730 s	1 300 m	515 w 490 w	357 m	261 m	300 w	215 vw
Pd ₂ Br ₄ (HA) ₂	1 710 vs	1 300 s	428 s 416 sh	280 s	229 w	213 vs ^g	213 vs ^g
Pd ₂ I ₄ (HA) ₂ ·C ₂ H ₅ OH	1 710 s	1 288 s	415 m	207 s ^g	<i>i</i>	<i>i</i>	207 s ^g
Pd ₂ (SCN) ₄ (HA) ₂ · ·2 C ₂ H ₅ OH ^h	1 720 vs	1 297 s	462 m 435 m	2 138 s ^d 2 173 s	<i>j</i>	299 m ^f 260 w ^k	210 w
PdA ₂	1 650 vs	1 295 vs	492 s 447 w	—	—	—	222 w

^a Terminal; ^b bridging, trans to P; ^c bridging, trans to X; ^d $\nu(\text{C}\equiv\text{N})$; ^e $\nu(\text{C—S})$; ^f $\nu(\text{Pd—S})$; ^g overlapping; ^h C₂H₅OH bands at 3 350 m (OH), 2 980 w (CH₃), 1 050 m (CO); ⁱ below 200 cm⁻¹; ^j overlapped by HA bands; ^k $\nu(\text{Pd—N})$.

DISCUSSION

The molecular structure of palladium(II) diphenylphosphineacetate complexes follows clearly from the experimental material. The $\text{PdX}_2(\text{HA})_2$ and $\text{Pd}_2\text{X}_4(\text{HA})_2$ complexes are formed under conditions where the HA molecule is undissociated. As follows from the IR spectra, ($\nu_{\text{as}}(\text{COOH})$ around 1700 cm^{-1}) the undissociated HA molecule coordinates through the phosphorus atom alone, as a typical monodentate tertiary phosphine: the spectra contain a new band attributable to $\nu(\text{Pd}-\text{P})$ at 220 cm^{-1} and the $\nu(\text{P}-\text{C})$ region exhibits splitting. The coordination sphere of palladium is completed by halide or thiocyanate anions in the usual square-planar arrangement¹¹⁻¹⁵.



The coordination of halides is also reflected in the IR spectra where palladium-halogen stretching vibrations were identified: in accordance with local D_{2h} symmetry¹⁶, the spectra of the monomeric complexes exhibit only one $\nu(\text{Pd}-\text{X})$ band, similarly to the nickel(II) analogues⁴. The spectrum of the dimeric chloro complex exhibits all the three IR active $\text{Pd}-\text{X}$ stretching modes belonging to local C_{2h} symmetry^{12,16,17}; the spectra of dimeric bromo and iodo complexes are less clear as the $\nu(\text{Pd}-\text{X})$

TABLE III

The Electronic Spectra of the Complexes

Band parameters obtained by Gaussian deconvolution⁸ are given in $10^3 \text{ cm}^{-1} (\epsilon_M)$

Compound	$^1A_{1g} \rightarrow ^3E_g$	$^1A_{1g} \rightarrow ^1A_{2g}$
PdCl ₂ (HA) ₂	<i>a</i>	25.75 (657)
	<i>b</i>	24.4 25.9
PdBr ₂ (HA) ₂	<i>a</i>	21.64 (24)
	<i>b</i>	20.4 23.9
PdI ₂ (HA) ₂	<i>a</i>	17.79 (41)
	<i>b</i>	21.23 (252) 22.0
Pd(SCN) ₂ (HA) ₂	<i>a</i>	22.87 (432)
	<i>b</i>	21.9 22.7
Pd ₂ Cl ₄ (HA) ₂	<i>a</i>	24.84 (413)
	<i>b</i>	19.4 25.4
Pd ₂ Br ₄ (HA) ₂	<i>a</i>	22.23 (258)
	<i>b</i>	17.9 22.7
Pd ₂ I ₄ (HA) ₂ ·C ₂ H ₅ OH	<i>a</i>	16.94 (356)
	<i>b</i>	15.1 16.7
Pd ₂ (SCN) ₄ (HA) ₂ ·2 C ₂ H ₅ OH	<i>a</i>	16.64 (51)
	<i>b</i>	22.10 (428) 22.2
PdA ₂	<i>a</i>	29.67 (1 620)
	<i>b</i>	30.3

bands coincide with the ligand maxima or are outside the measuring range. Nevertheless, the structural type of both monomeric and dimeric halogen complexes is independent of the type of halogen, as the powder patterns obtained are similar; the PdBr₂(HA)₂ and PdI₂(HA)₂ complexes are isostructural. Analogously, the *d-d* transition energies in the electronic spectra correspond to the position of X in the spectrochemical series, indicating the absence of structural anomalies.

The spectral data are also useful in determining the thiocyanate-coordination mode. In the monomeric Pd(SCN)₂(HA)₂ complex, both thiocyanates are S-bonded, as the $\nu(\text{C}\equiv\text{N})$ and $\nu(\text{C}-\text{S})$ bands at 2140 and 665 cm^{-1} , respectively, correspond¹⁸ to Pd—S—C≡N coordination; in addition, only one (Pd—S) band¹⁹ at 318 cm^{-1} is present in the palladium-ligand stretching vibration region and thus the thiocyanates are *trans*-bonded; the *d-d* transition energies are consistent with the spec-

TABLE III
(Continued)

${}^1A_{1g} \rightarrow {}^1E_g$	$p\sigma(P) \rightarrow Pd$	$p\pi(X) \rightarrow Pd$	$p\sigma(X) \rightarrow Pd$
	30.03 (20 900)	34.40 (4 590)	
	29.55	34.7	
	27.96 (11 500)	33.68 (10 500)	
	28.0	32.4	
23.94 (3 320)	27.41 (3 380)	31.53 (13 900)	
24.1	27.3		
	28.03 (6 030)	32.80 (13 100)	
		32.6	
	26.71 (2 230)	36.00 (15 200)	>41
		35.8	
	25.19 (3 170)	32.15 (10 800)	37.52 (38 600)
	26.3	29.4	37.0
20.71 (4 540)	25.44 (11 000)	29.60 (29 800)	34.41 (20 800)
20.8	24.4	30.3	
	26.29 (2 630)	31.19 (27 600)	36.45 (7 960)
	26.3	31.3	
	31.82 (3 030)		
	32.0		

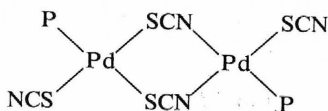
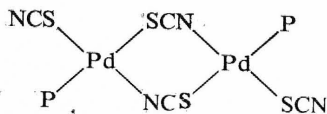
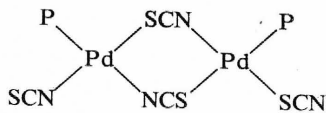
^a Tetrahydrofuran solution (PdA₂ in methanol); ^b diffuse reflectance.

trochemical series only for S-bonded thiocyanates. From the electronic point of view, the presence of Pd—SCN bonding in phosphine complexes is somewhat anomalous considering the usual σ and π distribution character in coordination bonds^{18,20}.

The diphenylphosphineacetate complex differs from the analogous triphenylphosphine complex²¹, which has been shown to involve SCN coordination through nitrogen. However, a very slight modification of the phosphine structure has been shown in a number of cases to cause a change in the type of thiocyanate coordination. The reasons for this behaviour have not been unambiguously elucidated.

In the dimeric Pd₂(SCN)₄(HA₂) complex, two types of thiocyanate bonding are evident from the splitting of the $\nu(C\equiv N)$ band into two maxima of equal intensity. Their positions indicate the presence of two terminal and two bridging (2173 cm⁻¹) thiocyanate groups in the complex molecule^{18,22}.

The bridging groups bound to one central nitrogen atom have an appropriate effect on the energy of the $d-d$ transitions, which exhibit a marked shift to higher wavenumbers in agreement with the position of N-coordinated thiocyanate in the spectrochemical series. The proposed arrangement involves, of course, three possible isomers:



As the attempted isolation of the isomers failed, one of the forms seems to be favoured energetically in the solid state and in solution.

Similarly to the Ni(II) complexes⁴, a second, completely different ligand bonding appears when the carboxyl is dissociated. In neutral aqueous solutions, an extremely stable, square planar PdA_2 complex containing two chelating A^- ions is formed. The strongly covalent carboxyl^{2,3} bond is reflected in the position of the $\nu_{\text{as}}(\text{COO})$ band at 1650 cm^{-1} as well as in the marked blue shift of the spin-allowed bands. The position of the bidentate A^- ion in the spectrochemical series is consistent with the parameters obtained⁴ from the spectrum of the nickel(II) complex. The coordination sphere of the nickel(II) complex (with the same composition) is, however, closer to a tetrahedral arrangement with a triplet ground state, which may be connected with the smaller radius of the Ni^{2+} ion. As a consequence of the high affinity of palladium for phosphorus, the thermodynamic stabilities of the NiA_2 and PdA_2 complexes are quite different; the diphenylphosphineacetate anion is one of the strongest chelating agents for palladium(II) known.

Note added in proof: Recently, Shaw and coworkers²⁴ prepared the complex PdA_2 using a different synthetic path.

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