COMPLEXES OF DIVALENT PLATINUM WITH DIPHENYLPHOSPHINEACETIC ACID*

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Received July 2nd, 1980

Diphenylphosphineacetic acid (HA) acts as a monodentate P-donor towards divalent platinum; the anion acts as a bidentate P,O-donor. Three types of complexes have been prepared, $PtX_2(HA)_2$, $PtXA(HA)$ and PtA_2 ($X = Cl$, Br, I, SCN), whose formation is determined primarily by the type of X, the acidity of the medium and the polarity of the solvent. It follows from electronic, nfrared and ^{31}P-NMR spectra that all the prepared complexes are *cis*-square planar in structure.

The chemistry of phosphine complexes of divalent platinum is quite extensive. Simple phosphine ligands with phosphorus as the only type of donor atom yield several types of complexes[1,2], which are known as both *cis*- and *trans*-isomers. Far less information is available on complexes of "hybrid" phosphine ligands, which, in addition to phosphorus, contain other donor atoms of the hard type (primarily oxygen). The lability of the bond to the hard donor atoms leads to the potential importance of these complexes in homogeneous catalysis[3]; another moreover, introduction of a hydrophilic group into the ligand molecule affects the solubility of the complexes, leading to the possibility of studying phosphine coordination chemistry in aqueous solutions, which is a region having so far been studied very little.

The previous works in this series were devoted to studying complexes of divalent nickel[4] and palladium[5-7] with diphenylphosphineacetic acid (HA) as a simple hybrid ligand; two types of coordination were demonstrated: monodentate through phosphorus alone and chelating through phosphorus and oxygen. The stepwise formation of $PtClA(HA)$ and PtA_2 with uncertain structure is mentioned in connection with study of the complexes of phosphineacetate esters[8], indicating the unusual variability of ligand bonding. This work contains a detailed study of the effects determining coordination of diphenylphosphineacetic acid to divalent platinum as the last member of the given homologous series of metal ions.

EXPERIMENTAL

Diphenylphosphineacetic acid was prepared by a modification[4] of the procedure by Issleib and Thomas[9]. Chloroplatinic acid (Safina, Vestec) served for the synthesis of the following

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* Part XVII in the series Compounds Structurally Related to Complexones; Part XVI: This Journal *45*, 2049 (1980).

complexes of divalent platinum[10–12]: K_2PtCl_4, K_2PtBr_4, *cis*-$PtCl_2(C_6H_5CN)_2$, *cis*-$PtBr_2(C_6H_5CN)_2$. The other chemicals were the *p.a.* substances from Lachema, Merck and IBJ (Poland). Solvents were purified by standard procedures.

The instruments and measuring methods have already been described[4]. The $^{31}P\{^1H\}$-NMR spectra were measured at 80·8941 MHz on a Varian XL-200 instrument using 85% H_3PO_4 as an external standard. The deuterated solvents employed ensured external deuterium lock of the instrument. Upfield chemical shifts are defined as positive.

Platinum[13] and phosphorus[14] were determined colorimetrically after mineralization of the sample with a mixture of nitric and perchloric acids. The halide content was determined by the Schöniger method and carbon, hydrogen and nitrogen by elemental microanalysis. Acid hydrogens were determined by titration with sodium hydroxide in 80% aqueous dioxan medium with indication using a glass electrode.

Complex Preparation

All the products were dried at 80°C/100 Pa to a constant weight.

$PtCl_2(HA)_2$, $PtBr_2(HA)_2$: A solution of 2 mmol HA in 10 ml toluene was slowly added with intense stirring to a solution of 1 mmol *cis*-$PtX_2(C_6H_5CN)_2$ (X = Cl, Br) in 50 ml toluene. After stirring for 1 h, the crystalline precipitate was washed with toluene. The yield was 85—95%. During attempted recrystallization, the complex was converted to PtXA (HA).

$PtI_2(HA)_2$, $Pt(SCN)_2(HA)_2$: First 2·2 mmol HA in 2 ml acetic acid and then a saturated aqueous solution of 4 mmol KX (X = I, SCN) were added to a solution containing 1mmol K_2PtCl_4 in 5 ml warm water. The precipitate was washed with water and recrystallized from acetic acid. The yield was 70—90%.

PtClA(HA), PtBrA(HA): A solution containing 2·2 mmol HA in 5 ml acetic acid was added to a solution of 1 mmol K_2PtCl_4 in 5 ml warm water and the mixture was heated under reflux for 1 h. In preparation of the bromo complex, a saturated aqueous solution of 4 mmol KBr was added after 1/2 h. After cooling, the precipitated product was washed with water and recrystallized from acetic acid. The yield was 70—90%.

PtIA(HA); $PtI_2(HA)_2$ was stirred at room temperature for 1 h with an excess of a 70 vol.% aqueous acetone; the filtered product was washed with acetone. The yield was 75%. The completeness of the reaction was controlled by alkalimetric determination of the eliminated hydrogen iodide in the filtrate.

Pt(SCN)A(HA): Equimolar amounts of PtClA(HA) and KSCN were heated under reflux with 80% acetic acid until all components dissolved. The product was crystallized by adding water to turbidity and slow cooling. The product was washed with water, ethanol and ether. The yield was 50%.

Attempts to recrystallize the latter two complexes led to partial disproportionation to $PtX_2.(HA)_2$ and PtA_2.

PtA_2: A solution of 1 mmol K_2PtCl_4 in 15 ml water was added to a solution of 2 mmol NaA in 10 ml water containing a small amount of HA (pH 5·5—6). The suspension of pinkish precipitate was heated for a short time to loss of colour, washed with water and recrystallized from aqueous ethanol. The yield was 65%.

RESULTS AND DISCUSSION

A number of factors are important in the formation of the complexes of divalent platinum with HA, The kinetic *trans*-effect[15], seems to be of most importance, followed by the type of donor atom, by conditions for dissociation of the carboxyl group (chelate effect, acidity of the medium) and also by the solvent polarity. In the synthesis of the individual complexes, these effects often operate in opposite directions, so that it is not possible to find a general preparation procedure for the individual types of complexes. In this respect platinum complexes are clearly different from those of palladium the *trans*-arrangement of whose eliminated the critical factor, *i.e.* the *trans*-effect of phosphorus atoms. This difference already indicates the probable *cis*-configuration of platinum(II) complexes, unambiguously confirmed by their further properties.

The complexes prepared are crystalline substances, which are diamagnetic, stable in the air and soluble in polar organic solvents to give nonconducting solutions. The analytical data and some other properties are given in Table I. Diagnostically signifi-

TABLE I
Analytical Data and Other Properties

Compound M.w.	Colour	Calc./Found, %						M.p., °C
		Pt	P	C	H	X(N)	H^+	
$PtCl_2(HA)_2$	yellowish	25·88	8·21	44·60	3·48	9·40	0·27	221–224
754·0		25·34	7·80	46·02	3·59	9·66	0·31	(dec.)
$PtBr_2(HA)_2.0{\cdot}5\ C_7H_8$	light yellow	23·15	7·35	40·39	3·28	18·96	0·24	252–255
842·9		24·40	7·69	41·17	3·38	17·43	0·25	
$PtI_2(HA)_2$	orange	20·83	6·61	35·90	2·80	27·09	0·22	261–262
936·9		20·43	6·24	35·87	3·02	26·51	0·23	(dec.)
$Pt(SCN)_2(HA)_2$	yellowish	24·41	7·75	45·09	3·28	3·51	0·25	222–225
799·2		23·75	7·29	42·42	3·39	3·40	0·28	(dec.)
PtClA(HA)	white	27·19	8·63	46·87	3·51	4·94	0·14	235–238
717·6		26·03	8·12	46·55	3·70	6·11	0·14	(dec.)
PtBrA(HA)	white	25·60	8·13	44·13	3·31	10·49	0·13	235–238
762·0		25·21	8·14	43·88	3·41	10·76	0·13	(dec.)
PtIA(HA)	light yellow	24·12	7·66	41·57	3·11	15·69	0·13	142–145
809·0		24·80	7·96	41·63	3·21	15·56	0·12	(dec.)
Pt(SCN)A(HA)	white	26·36	8·37	47·06	3·40	1·89	0·14	213–218
740·2		26·03	8·66	45·26	3·35	1·96	0·18	
PtA_2	white	28·64	9·09	49·38	3·55	—	—	280–285
681·1		28·29	9·63	49·40	3·52	—	—	(dec.)

cant bands in the IR spectra are given in Table II; the ν_{as}(COO) region is especially important, permitting immediate determination of the type of complex formed. Table III gives the electronic spectra whose parameters were found by Gaussian analysis[16]. The $^{31}P\{^1H\}$-NMR spectra are given in Table IV. The complexes were also studied by powder X-ray diffraction and it was found that PtClA(HA) and PtBrA(HA) are isostructural; the powder patterns of the other complexes are different. No similarity with palladium complexes was observed.

The commonest type of phosphine complex of divalent platinum is represented by the $PtX_2(HA)_2$ series. While the diiodide and bis(thiocyanate) are formed directly from the components because of the predominating effect of the affinity of platinum for iodide and thiocyanate (S-bonded), the *trans*-effect of phosphorus is decisive in chloride and bromide complexes, leading to chelating of one ligand molecule. Coordina-

TABLE II

Selected Infrared Spectral Bands

Compound	ν(C=O)	ν_{as}(COO) cm^{-1}	ν(Pt—X) (ν(Pt—S))	ν(Pt—P)
$PtCl_2(HA)_2$	1 717 vs		249 m 272 w	315 s 344 vs
$PtBr_2(HA)_2.0{\cdot}5\ C_7H_8$	1 717 vs		[a] 219 vs	328 s
$PtI_2(HA)_2$	1 717 vs		[a]	314 s
$Pt(SCN)_2(HA)_2$[b]	1 717 vs 1 739 vs		270 vw 280 w	320 b, w
PtClA(HA)	1 730 s	1 620 vs	280 vw	315 vs 361 s
PtBrA(HA)	1 730 s	1 620 vs 1 600 sh	210 s	319 s 356 vs
PtIA(HA)	1 754 m	1 627 vs	[a]	325 w, b 360 s
Pt(SCN)A(HA)[c]	1 733 s	1 615 vs	[d]	307 m 395 vs
PtA_2		1 670 vs		325 s 364 s

[a] Below 200 cm^{-1}; [b] $\nu(C{\equiv}N)$ 2130 vs; [c] $\nu(C{\equiv}N)$ 2119 vs; [d] masked by ligand bands.

TABLE III

Electronic Spectra $\nu_{max} \cdot 10^3$ cm^{-1} (ε_{max}); A tetrahydrofuran solution, B diffusion reflectance

Compound		Ligand field bands		Charge transfer bands		Other
		Singlet →triplet	Singlet →singlet	Pt-X	Pt-P	
$PtCl_2(HA)_2$	A	23·3 (8·7)	31·2 (835)	36·0 (20 100)	38·9 (5 610)	>44 (>25 000)
	B	23·8 sh	31·1 sh	36·0		41·7
$PtBr_2(HA)_2.0{\cdot}5\ C_7H_8$	A		28·1 (183)	33·9 (9 200)	38·9 (11 900)	>46 (>40 000)
	B	23·7 sh	29·4	33·7	37·3	41·3
$PtI_2(HA)_2$	A		26·2 (703)[a]	32·4 (2 210)	37·6 (18 000)	>45 (>70 000)
	B	21·2	28·7	32·1	35·3	41·3
$Pt(SCN)_2(HA)_2$	A		29·8 (890)	33·3 (3 220)	37·9 (17 200)	>45 (>38 000)
	B		26·3	31·9	36·4	40·5 sh
PtClA(HA)	A		31·6 (686)	36·1 (1 590)	37·3 (8 280)	>44 (>46 000)
	B		31·4	36·1		43·1
PtBrA (HA)	A		33·4 (89)	31·3 (505)	38·2 (4 010)	>44 (>33 000)
	B		35·3	30·7	37·2	41·7
PtIA(HA)	A			30·9 (2 860)	37·2 (3 100)	>41 (>29 000)
	B		25·9 sh	31·0	37·4	41·1
Pt(SCN)A(HA)	A			33·1 (3 520)	37·2 (1 770)	>45 (>67 000)
	B			32·3	37·0	41·8
PtA_2	A			33·3[b] (1 100)	38·5 (1 160)	>42 (>32 000)
	B			33·0	38·5[c]	42·0

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[a] Additional band 28·9 (2 070), [b] Pt-O, [c] additional band 36·1.

tion of oxygen cannot be prevented even by a large excess of Cl^- or Br^- ions. Thus the dichloro and dibromo complexes were prepared indirectly from $PtX_2(C_6H_5CN)_2$ by substitution of benzonitrile by diphenylphosphineacetic acid, whose dissociation is suppressed by using toluene as a solvent of low polarity. The dihalogeno complexes contain undissociated HA molecules, coordinated through phosphorus alone, and both in the solid state and in solution are *cis*-square planar, in contrast to their palladium analogues. This structural assignment has been confirmed by electronic and infrared spectra (two vibrations ν(Pt–X) and two ν(Pt–P) (ref.[17])) and especially by the NMR spectra: the coupling constants of ^1J(Pt, P) unambiguously correspond[18] to the *cis*-isomers. Thiocyanate is coordinated through the sulphur atom[19].

The second type of complex, PtXA(HA) is specific for divalent platinum. It is formed under conditions favourable for partial dissociation and subsequent coordination of one carboxyl group, *i.e.* especially at higher solvent polarities. The chloride and bromide are formed directly from the components as mentioned above, the thiocyanate by substitution from the chloride and iodide by elimination of hydrogen iodide of the diiodide. The presence of dissociated and undissociated carboxyls

TABLE IV
$^{31}P\{^1H\}$-NMR Spectra

Compound	Solvent	δ, ppm	^1J(Pt, P), Hz
$PtCl_2(HA)_2$	DMSO	−3·02	3 793
$PtBr_2(HA)_2$	DMSO	−2·65	3 750
$PtI_2(HA)_2$	THF	−2·20	3 712
$Pt(SCN)_2(HA)_2$	THF	−5·28	3 240
PtClA(HA)	DMSO	−1·33	3 507
		5·49	3 723
PtBrA(HA)	DMSO	−2·79	3 483
		7·02	3 686
PtIA(HA)	DMSO	−3·17	3 329
		9·29	3 645
Pt(SCN)A(HA)	THF	4·72	3 467
		6·69	3 650
PtA_2	AcOH/H_2O	8·80	3 525
HA	DMSO	17·90	—
NaA	H_2O	18·43	—

in a ratio of 1 : 1 is apparent from the infrared spectra, as for the S-bonding of the thiocyanates. The NMR spectra clearly demonstrate the presence of two nonequivalent phosphorus atoms and also confirm the *cis*-configuration of these complexes on the basis of their coupling constants. The proposed structure was confirmed by X-ray crystal structure determination[20].

The third type of complex is the bis-chelated compound, PtA_2. This compound seems to be the most stable of the whole studied system of complexes. It is readily formed from the components in neutral aqueous solution and can also be obtained from the two previous types of complexes: either by complete neutralization of the halide, *e.g.* using a silver salt, or by elimination of both acid hydrogens, *e.g.* by sodium acetate. The infrared spectra indicate a high degree of covalence[21] of the COO–Pt bond and the NMR spectra confirm the *cis* configuration. The platinum(II) complex, PtA_2, thus has the same molecular structure as the palladium(II) complex but powder patterns indicate that the crystal structures are different.

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Translated by M. Štuliková.