Inorganica Chimica Acta, 43 (1980) 113–119
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Platinum(II) Complexes Containing Amine Ligands;

S. HAGHIGHI, C. A. McAULIFFE

Department of Chemistry, University of Manchester, Institute of Science and Technology, Manchester M60 IQD, U.K.

W. E. HILL, H. H. KOHL and M. E. FRIEDMAN

Department of Chemistry, Auburn University, Auburn, Ala., 36830, U.S.A.

Received May 7, 1980

New Platinum(II) complexes of o- *and* p-*phenylenediamine, 2-aminopyridine, and 2,3- 3,4-, and 2,6-diaminopyridine have been prepared and characterized by a number of techniques. The complexes of 2-aminopyridine are of the general formula* $Pt(2\text{-}AmPy)_2X_2\cdot nH_2O$ *where X is Cl or I and n is 1 or 2. In these complexes only the ring nitrogen is coordinated. Complexes of the diaminopyridines have complex stoichiometries* $Pt_3L_2X_6\cdot 6H_2O$ *(L = 3,4 DamPy, X = Cl, I),* $Pt_2(2,3\text{-}DamPy)_3Cl_3OH$, $Pt_3L_4I_5OH$ *(L = 2,3 or 2,6 DamPy), and* $[Pt(2,6\text{-}DamPy)_3Cl_4]\cdot 4H_2O$ *which contain both ring nitrogen and* NH_2 *groups coordinated to the metal. The phenylenediamine complexes have the general formula* $PtLX_2$ *(L = OPDA, PPDA; X = Cl, I) where the amine groups are coordinated. The biological activity of these complexes are reported elsewhere.*

Introduction

The stimulus for the work reported here was the discovery by Rosenberg *et al.* in the late 1960s that *cis*-diamine complexes of platinum(II) and platinum(IV) are potent anti-tumor agents [1]. Further studies showed that small variations in the ligands in *e.g.* *cis*-PtL_2X_2 could produce large differences in anti-tumor activity, although these differences are quite random in nature and not necessarily related to amine structure [2–4]. Despite the obvious absence of structure/reactivity relationships work continues to find new agents and we report here our preparative and characterization studies on a range of platinum–amine complexes. Prior to animal studies we have already examined their activity towards Elinese hamster V79 cells [5], and their inhibitory

TABLE I. Colour, Decomposition Point and Analytical Results for Pt(II) Compounds.

Compound	Colour	C%[a]	H%	N%	Cl or I%	Pt%	H_2O%	Dec/°C
$[Pt(2\text{-}AmPy)_2Cl_2]\cdot H_2O$	green	25.8(25.4)	2.6(3.0)	12.2(11.9)	14.7(15.0)	40.9(41.3)	3.6(3.8)	285
$[Pt(2\text{-}AmPy)_2I_2]\cdot 2H_2O$	brown	17.6(17.8)	2.6(2.4)	8.9(8.3)	37.4(37.7)	28.1(29.0)	4.9(5.3)	269
$[Pt_3(3,4\text{-}DamPy)_2Cl_6]\cdot 6H_2O$	blue	10.5(10.7)	2.2(2.4)	7.7(7.5)	18.6(18.9)	52.4(52.0)	9.2(9.6)	170
$[Pt_3(3,4\text{-}DamPy)_2I_6]\cdot 6H_2O$	brown	7.3(7.2)	2.0(1.6)	4.8(5.0)	45.3(45.5)	34.6(35.0)	6.2(6.4)	180
$[Pt_2(2,3\text{-}DamPy)_3Cl_3(OH)]$	green	21.4(21.4)	2.5(2.6)	14.9(15.0)	13.4(12.6)	– (46.3)	1.6(2.0)	200
$[Pt_3(2,3\text{-}DamPy)_4I_5(OH)]\cdot H_2O$	green	14.3(14.2)	1.7(1.8)	9.8(9.9)	37.2(37.5)	34.3(34.7)	1.8(2.0)	220
$[Pt_2(2,6\text{-}DamPy)_3Cl_4]\cdot 4H_2O$	green	18.9(19.3)	2.6(3.1)	13.9(13.5)	14.9(15.2)	42.3(41.9)	6.7(7.0)	260
$[Pt_3(2,6\text{-}DamPy)_4I_5(OH)]\cdot H_2O$	brown	14.6(14.2)	1.8(1.8)	10.2(9.9)	37.7(37.5)	33.9(34.7)	1.4(1.6)	250
$[Pt(OPDA)Cl_2]$	grey	19.4(19.3)	1.9(2.0)	7.4(7.5)	18.5(18.9)	52.4(52.1)	– –	300
$[Pt(PPDA)Cl_2]$	brown	19.2(19.3)	2.0(2.0)	7.4(7.5)	18.8(18.9)	51.9(52.1)	– –	360
$[Pt(OPDA)I_2]$	brown	13.2(12.9)	1.4(1.4)	5.2(5.0)	45.2(45.6)	35.3(35.1)	– –	340
$[Pt(PPDA)I_2]$	yellowish brown	13.1(12.9)	1.5(1.4)	5.0(5.0)	45.1(45.6)	35.5(35.1)	– –	–

[a] Calculated values in parentheses.

TABLE II. Spectroscopic and Conductivity Data of Pt(II) Complexes.

Complex	Diffuse Reflectance 10^{-3} cm^{-1}	Λ_M (mhos cm^{-2} $mole^{-1}$)
$[Pt(2\text{-}AmPy)_2Cl_2]\cdot H_2O$	23.0 br.m 36.4 s	32
$[Pt(2\text{-}AmPy)_2I_2]\cdot 2H_2O$	23.2 m 35.7 s	24
$[Pt_3(3,4\text{-}DamPy)_2Cl_6]\cdot 6H_2O$	21.7 m 37.3 s	19
$[Pt_3(3,4\text{-}DamPy)_2I_6]\cdot 6H_2O$	21.3 m 37.2 s	21
$[Pt_2(2,3\text{-}DamPy)_3Cl_3(OH)]$	22.7 w 38.0 s	34
$[Pt_3(2,3\text{-}DamPy)_4I_5(OH)]\cdot H_2O$	21.5 m 37.5 s	40
$[Pt_2(2,6\text{-}DamPy)_3Cl_4]\cdot 4H_2O$	22.2 m 38.4 s	25
$[Pt_3(2,6\text{-}DamPy)_4I_5(OH)]\cdot H_2O$	22.0 m 37.6 s	31
$[Pt(OPDA)Cl_2]$	23.5 m 36.4 s	41
$[Pt(OPDA)I_2]$	23.2 m 37.0 s	33
$[Pt(PPDA)Cl_2]$	12.0 m 23.2 s 40.0 s	26
$[Pt(PPDA)I_2]$	12.3 m 22.9 sh 40.8 s	30

TABLE III. The Infrared Frequencies of the Platinum(II) Complexes with Aminopyridines.

Complex	Infrared Frequencies (cm^{-1})					
	ν(OH)	$\nu(NH_2)$	$\delta(NH_2)$	ν(C=N)	ν(C–N)	Others
$[Pt(2\text{-}AmPy)_2Cl_2]\cdot H_2O$	3500	3400, 3300	1630s	1620s	1265m	650, 460m
$[Pt(2\text{-}AmPy)_2I_2]\cdot H_2O$	3560br	3440s, 3306	1625	1615s	1270m	660br, 450
$[Pt_3(3,4\text{-}DamPy)_2Cl_6]\cdot 6H_2O$	3540	3300, 3210, 3160, 3050	1620	1610	1240	720
$[Pt_3(3,4\text{-}DamPy)_2I_6]\cdot 6H_2O$	3580br	3200s, 3160, 3100	1615	1600	1245	–
$[Pt_2(2,3\text{-}DamPy)_3Cl_3(OH)]$	3530	3420s, 3380, 3190m, 3030 3410	1630, 1610	1600, 1560	1270sh 1245w	740
$[Pt_3(2,3\text{-}DamPy)_4I_5(OH)]\cdot H_2O$	3520br 2480sh	3400s, 3300, 3140, 3060sh	1635, 1615	1605, 1570	1285, 1250	760
$[Pt_2(2,6\text{-}DamPy)_3Cl_4]\cdot 4H_2O$	3500br	3390, 3260s, 3120, 3040w	1635, 1620	1610, 1580 1560	1265, 1240	760, 700
$[Pt_3(2,6\text{-}DamPy)_4I_5(OH)]\cdot H_2O$	3550 3500	3400w, 3300, 3170, 3070	1640s, 1615sh	1600s 1560	1260, 1245	775, 720

effects on enzyme activity (α-chymotrypsin) [6], and DNA, RNA and protein synthesis in *E. Coli* [7]. The ligands used in this study were *o*-phenylenediamine (OPDA), *p*-phenylenediamine (PPDA), 2-aminopyridine (2-AmPy), and the disubstituted pyridines 2,3-, 3,4-, 2,6-diaminopyridine (2,3-DamPy, 3,4-DamPy, 2,6-DamPy, respectively).

Results and Discussion

2-Aminopyridine is of fundamental importance in pyridine chemistry, yet comparatively little use has been made of the base as a ligand. Generally the pyridine nitrogen atom of 2-aminopyridine coordinates to the metal ion [8, 9] although it has been claimed from IR spectra that the NH_2 groups of 2-aminopyridine and 2-amino-6-methylpyridine seem to be bound to the silver and copper(II) ions [10–12], it is also known that 2-aminopyridine-N-oxide acts as a monodentate ligand [13, 14]. There have been reports that 2-aminopyridine may function as a bidentate ligand [10, 15, 16], leading to the formation of cyclic compounds and in the case of 2-aminomethylpyridines to bridge compounds [17]. Complexes of stoichiometry $Fe(2\text{-}AmPy)_3Fe(CO)_8$ and $Pt(2\text{-}AmPy)Cl_2$ [16] have also been reported; the latter is probably dimeric.

When a slight excess of the ligand 2-aminopyridine is added with stirring to an aqueous solution

TABLE IV. The Far Infrared Frequencies of the Pt(II) Complexes.

Complex	ν(Pt–N)	ν(Pt–X)
$[Pt(2\text{-}AmPy)_2Cl_2]\cdot H_2O$	270 br	335 s, 320 s
$[Pt(2\text{-}AmPy)_2I_2]\cdot 2H_2O$	277 br	196 s, 190 sh
$[Pt_3(3,4\text{-}DamPy)_2Cl_6]\cdot 6H_2O$	560 br, 260 w	345, 330 s, 315 s 300 w
$[Pt_3(3,4\text{-}DamPy)_2I_6]\cdot 6H_2O$	550 br	200 s, 190 sh
$[Pt_2(2,3\text{-}DamPy)_3Cl_3(OH)]$		345 sh, 330 s
$[Pt_3(2,3\text{-}DamPy)_4I_5(OH)]\cdot H_2O$	540 br, 290 w	180 br
$[Pt_2(2,6\text{-}DamPy)_3Cl_4]\cdot 4H_2O$	530 br, 270 w	330 s,br
$[Pt_3(2,6\text{-}DamPy)_4I_5(OH)]\cdot H_2O$	270	
$[Pt(OPDA)Cl_2]$	560	324 s, 319 s
$[Pt(PPDA)Cl_2]$	565	315 br
$[Pt(OPDA)I_2]$	555	180 s, 176 sh
$[Pt(PPDA)I_2]$	550	182 s, 178 sh

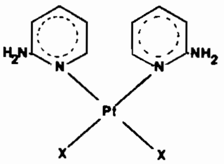


Fig. 1. *Cis*-$[Pt(2\text{-}AmPy)_2X_2]\cdot nH_2O$ (X = Cl, I, n = 1 or 2).

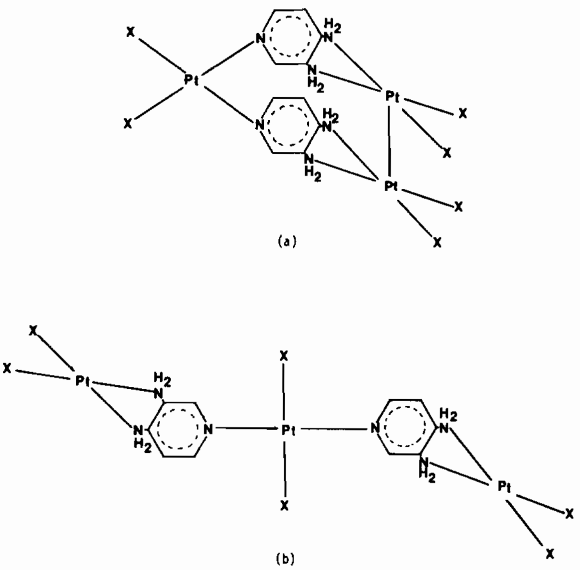


Fig. 2. Two possible structures for the complexes $[Pt_3(3,4\text{-}DamPy)_2Cl_6$ or $I_6]\cdot 6H_2O$.

of K_2PtCl_4 (Pt: ligand ratio 1:2.1) the complex $[Pt(2\text{-}AmPy)_2Cl_2]\cdot H_2O$ is precipitated. The corresponding iodo complex $[Pt(2\text{-}AmPy)_2I_2]\cdot H_2O$ is similarly obtained from K_2PtI_4. The complexes $[Pt(2\text{-}AmPy)_2X_2]\cdot nH_2O$ (X = Cl, I and n = 1, 2) react readily with silver nitrate to produce the species $[Pt(2AmPy)_2(H_2O)_2](NO_3)_2$ in solution. Addition of excess potassium or lithium iodide to the filtered solution and warming effects precipitation of the pure iodo complex. These complexes (Table I) are essentially non-electrolytes in dimethylformamide solution (Table II) and exhibit IR and electronic spectra characteristic of square-planar platinum(II) compounds, (Tables II–IV).

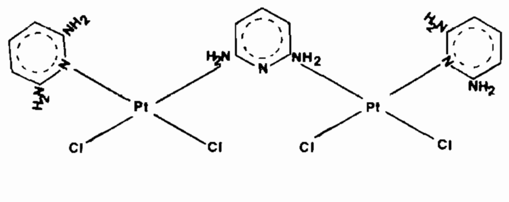
It has been reported that coordination of the amino group significantly shifts $\nu(NH_2)$ and $\delta(NH_2)$ bands [17]. We observe no significant difference in these bands on complexation of 2-AmPy. Similarly, there is a sharp difference in the infrared spectrum of free and coordinated pyridine [18, 23], and in the case of 2-AmPy free ligand is readily distinguished from bound ligand [16] by shifts of strong–medium bands (1574, 620, 420 cm^{-1}) to higher energy (1620, 650, 460 cm^{-1}, respectively). From Table III it can be seen that in $[Pt(2\text{-}AmPy)X_2]$ the ring nitrogen is coordinated.

The bands in the ν(Pt–N) region are difficult to assign since they are generally combination bands and not an isolated vibration of the Pt–N bond. Consequently the assignments are tentative and would be difficult to confirm without the use of isotope studies. The assignments have been made in accordance with previous results [18, 23, 30]. The frequency of ν(Pt–N) in the complexes $[Pt(2\text{-}AmPy)_2X_2]\cdot nH_2O$ (X = Cl or I; n = 1 or 2) is at ~270 cm^{-1} (Table IV). This frequency also decreases as the halogen increases in size in agreement with previous results [25, 28].

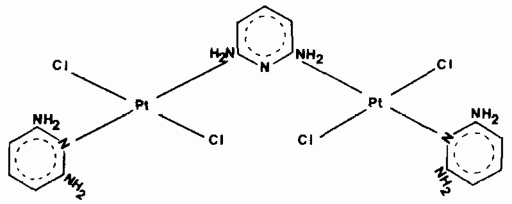
There are two possible stuctures and group theory predicts two bands due to ν(Pt–Cl) for the *cis* and one of each for the *trans* in C_{2v} and D_{2h} symmetry respectively [25]. The far infrared spectrum of

TABLE V. The Infrared Frequencies of the Platinum(II) Complexes with *o*- and *p*-Phenylenediamine.

Compound	$\nu(NH_2)$	$\delta(NH_2)$	ν(C–N)	Other bands
$[Pt(OPDA)Cl_2]$	3175s, 3125s, 3110sh, 3050m	1565s, 1550	1240s	1160s, 1150, 790s, 760m, 720s
$[Pt(PPDA)Cl_2]$	3180s, 3120m	1600	1240	1180s, br, 830s, 740, 720w
$[Pt(OPDA)I_2]$	3170s, 3075s, 3050w	1540s, 1500s	1235s	1150s, 1100m, 760s, 680s
$[Pt(PPDA)I_2]$	3200m, 3175w	1610m, 1570s, 1510s	1260m	1150br,s, 830s, 720m



cis



trans

Fig. 3. The possible *cis* and *trans* structures for the complex $[Pt_2(2,6\text{-DamPy})_3Cl_4]\cdot 4H_2O$.

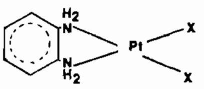


Fig. 4.

the complex $[Pt(2\text{-AmPy})_2Cl]\cdot H_2O$ contains two very strong bands at 335 cm^{-1} and 320 cm^{-1} due to asymmetric and symmetric Pt–Cl stretching vibrations for the (*cis*) C_{2v} isomer (Fig. 1), while in the complex $[Pt(2\text{-AmPy})_2I_2]\cdot 2H_2O$ a strong band and a shoulder are present at 196 and 190 cm^{-1} which are not present in the spectrum of corresponding chloro complex. This leads to a ν(Pt–I)/ν(Pt–Cl) ratio of 0.59, a value which is in agreement with other results.

The appearance of a broad band at ~3500 cm^{-1} supports the presence of water in the molecules of both complexes. This assignment is also confirmed by the thermogravimetric (TGA) data in Table I.

Diaminopyridine Complexes

These deeply coloured complexes are most interesting, especially in view of the current structural and biological interest in the so-called platinum blues [31, 34]. The preparations of these complexes are described in the Experimental section, and despite the apparently complex stoichiometry, we find that the preparative methods, analytical figures and spectroscopic data are entirely reproducible. The opinion we have formed as to their possible structures is open to interpretation. In some of the complexes all three potential donors are bound and in others not all are bound (Table III). Figures 2 and 3 give some indication of possible structures, but we are presently trying to obtain single crystals for a definitive conclusion as to the structure of these interesting materials.

Phenylenediamine Complexes

The complexes $[PtLX_2]$ (L = OPDA, PPDA; X = Cl, I) were prepared by reaction of a stoichiometric amount of the ligand and Pt(II) salt in water at room temperature (Table I). All of the complexes dissolve adequately in solvents such as dimethylformamide and dimethylsulfoxide (DMSO).

Infrared spectra (Table V) show only evidence for coordinated amine groups. The bands in the 565–530 cm^{-1} range are assigned to ν(Pt–N) (Table IV).

The far infrared spectrum of the chloride complex $[Pt(OPDA)Cl_2]$ shows two strong bands at 324 and 319 cm^{-1} (Table IV), which are absent in the spectrum of the corresponding iodide complex. The bands are assigned to platinum–chloride stretching frequencies and support the suggestion that this complex in the *cis* square planar configuration. The spectrum of the iodide complex has two bands at 180 and 176 cm^{-1}. In 10^{-3} molar dimethylformamide solution both complexes are essentially non-conducting, ruling out Magnus salt type structures $[PtL_2]$ $[PtX_4]$. It is highly likely that the complexes have structures as in Fig. 4.

The far infrared spectrum of the chloride complex $[Pt(PPDA)Cl_2]$ exhibits a broad band at 315 cm^{-1} which is absent in the spectrum of the corresponding iodide complex, with the latter complex

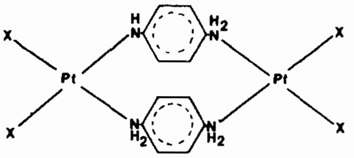


Fig. 5. The proposed structure for complexes [Pt(PPDA)X_2].

having a band and a shoulder at 182 and 175 cm^{-1}. Both of these complexes are non-electrolytes in DMF, but lack of sufficient solubility prevents molecular weight measurements.

Solid reflectance spectra (Table II) of the *ortho* ligand complexes show a strong band at ~37000 cm^{-1} and a medium intensity band at 23000 cm^{-1} whereas the *para* isomer complexes exhibit three bands at 40000, 23000 and 12000 cm^{-1}. The two bands of the *ortho* isomer complexes and the first two bands of the *para* isomer complexes are tentatively assigned to $'A_{1g} \rightarrow 'E_g$ and $'A_{1g} \rightarrow 'A_{2g}$ for square planar stereochemistry of C_{2v} symmetry.

On the basis of the IR spectra it is suggested that the structures of the [Pt(PPDA)X_2] complexes are dimers in which two ligands are briding two platinum atoms indicating in each case the ligand is behaving as a bidentate group, Fig. 5.

Experimental

Physical Measurements

Infrared Spectra

Routine infrared spectra were obtained in nujol and hexachlorobutadiene mulls in the range 4000–400 cm^{-1} on a Perkin Elmer Infracord 735 spectrophotometer between potassium bromide plates. Far infrared spectra (500–20) were obtained on a Beckman 720 M grating spectrophotometer fitted with a polyethylene disc (wedge shape). Full range (4000–200 cm^{-1}) spectra were obtained on a Perkin Elmer 621 on complexes as both nujol and hexachlorobutadiene mulls between caesium iodide plates.

Reflectance Spectra

Reflectance spectra were measured on a Beckman Acta M-4 spectrophotometer using magnesium oxide as dilutant and references; intensities are arbitrary. Due to the low solubility of the platinum(II) complexes solution electronic spectra were not obtained.

Conductivities

The conductivities of the platinum complexes were measured in dimethylformamide (DMF) solution with specific conductance 0.018 X 10^{-4} ohm^{-1} dm^{-1} at 21 °C on a Wheatstone bridge arrangement (Cambridge Instruments Ltd.) with a glass cell containing platinum electrodes acting as the fourth resistance. The calibration was carried out with standard potassium chloride solutions (0.1 *M* KCl) as described in the literature [35]. The calculated molar conductivities were compared with expected ranges obtained from the literature [36]. The expected ranges for complexes of different electrolyte types at about 10^{-3} *M* in DMF at 25 °C are:

Electrolyte	1:1	2:1	3:1	4:1
Molar conductivities (Λ_M)	65.90	130–170	200–240	300

Thermogravimetric Analysis (TGA).

Thermogravimetric analysis was carried out on a DuPont Model 950 thermobalance. The sample sizes were 15–20 mg; a furnace heating rate of 25 °C per minute was employed. The highest temperature attained was 500 °C. The TGA curves were recorded by a DuPont Model 900 Thermograph. The samples were studied in nitrogen furnace atmospheres. Decomposition points were also obtained by TGA.

Microanalyses

Carbon, hydrogen, nitrogen and halogen (Cl, I) analyses were preformed by the Microanalytical Services of the Chemistry Department at UMIST. Platinum(II) analyses were measured by atomic absorption methods.

Preparation of the Platinum(II) Complexes

All complexes were dried *in vacuo* at room temperature unless otherwise stated.

[Pt(2-AmPy)$_2$Cl$_2$]·H_2O

Potassium tetrachloroplatinate(II) (1.0377 g, 2.5 mmol) was dissolved in distilled water (20 cm^3), filtered and 2-aminopyridine(2-AmPy) (0.480 g, 5.1 mmol) was added. The mixture was stirred for 18 h after which time the green precipitate was filtered off and washed several times with water, ethanol and diethyl ether and dried. Yield 95%.

[Pt(2-AmPy)$_2$I$_2$]·H_2O

1). To a filtered solution of potassium tetrachloroplatinate(II) (1.0377 g, 2.5 mmol) in water (20 cm^3), lithium iodide (LiI·2H_2O; 1.78 g, 10.5 mmol) in water (10 cm^3) was added and the solution stirred for 15 minutes. 2-Aminopyridine (0.480 g, 5.1 mmol) in water was added (drop-wise) and stirred for 18 h until the product formed. The brown solid formed was filtered off, washed with water, ethanol and diethyl ether and dried. Yield 86%.

2). The $[Pt(2\text{-AmPy})_2Cl_2]\cdot H_2O$ was weighed (0.5021 g, 1 mmol) and suspended in water (20 cm^3). The slurry was treated with 2 equivalents of silver nitrate and stirred for 24 h protected from light. After addition of a few drops of 0.1 *M* hydrochloric acid to the filtered solution, the silver chloride formed was filtered off. To the filtrate which contained $[Pt(2\text{-AmPy})_2(H_2O)_2](NO_3)_2$, excess solid lithium iodide was added while heating gently on a hot plate until the product formed. The product was filtered off and washed with water, ethanol and diethyl ether. Yield 69%. By this method the pure iodo complex was obtained.

$[Pt_3(3,4\text{-DamPy})_2Cl_6]\cdot 6H_2O$

A solution of 3,4-diaminopyridine (0.1746 g, 1.6 mmol) in distilled water (20 cm^3) was added to a magnetically stirred filtered solution of potassium tetrachloroplatinate(II) (0.996 g, 2.4 mmol) in water, and stirring continued for *ca.* 24 h. A blue solid was formed. After refirgeration overnight, the solid was filtered and washed with water and diethyl ether and dried. Yield 75%.

$[Pt_3(3,4\text{-DamPy})_2I_6]\cdot 6H_2O$

Potassium tetrachloroplatinate(II) (0.996 g, 2.4 mmol) was dissolved in water (20 cm^3), filtered, and lithium iodide ($LiI\cdot 2H_2O$, 1.6647 g, 9.8 mmol) in water (10 cm^3) was added. The solution was stirred for 15 minutes. A solution of 3,4-diaminopyridine (0.1746 g, 1.6 mmol) in water (20 cm^3) was added drop-wise with gentle stirring over 15 minutes. The mixture was stirred for a further 24 h. The brown solid was filtered through a fine glass sinter, washed with warm water several times and dried. Yield 72%.

$[Pt_2(2,3\text{-DamPy})_3Cl_3(OH)]$

To a filtered solution of potassium tetrachloroplatinate(II) (0.996 g, 2.4 mmol) in water (20 cm^3) 2,4-diaminopyridine (0.3929 g, 3.6 mmol) in 20 ml water was added drop-wise with gentle stirring. After stirring for 24 h a greenish blue solid was formed and was filtered through a glass sinter, washed with cold water, ether and dried. The filtrate was still blue. After leaving overnight under refrigeration the colour changed to black (possibly platinum black). Another attempt to separate the soluble compound or compounds from the filtrate solution was unsuccessful. Yield 84%.

$[Pt_3(2,3\text{-DamPy})_4I_5(OH)]\cdot H_2O$

To a filtered solution of potassium tetrachloroplatinate(II) (0.996 g, 2.4 mmol) in water (20 cm^3), lithium iodide ($LiI\cdot 2H_2O$; 1.6647 g, 9.8 mmol) in 10 cm^3 water was added and the solution stirred for 15 minutes. 2,4-Diaminopyridine (0.3939 g, 3.6 mmol) in water (20 cm^3) was added and the solution stirred. A brown complex was formed at once. Stirring was continued for 2 h, after which the colour changed to bright green. After stirring for 24 h no further change was observed. The solid was filtered through a glass sinter, washed with water and diethyl ether and dried. Yield 64%. Attempts to prepare this complex in the ratio 3:4 (Pt: ligand) were unsuccessful.

$[Pt_2(2,6\text{-DamPy})_3Cl_4]\cdot H_2O$

Potassium tetrachloroplatinate(II) (0.996 g, 2.4 mmol) was dissolved in water (20 cm^3) and filtered. 2,6-Diaminopyridine (0.3929 g, 3.6 mmol) in 20 cm^3 of water was added drop-wise with stirring at 40 °C (water bath). A deep green solid formed after 3–4 h. The water bath was removed and the stirring continued at room temperature for a further 20 h. The product was filtered through a glass sinter and washed with warm (40 °C) and cold water and diethyl ether and dried. Yield 75%.

$[Pt_3(2,6\text{-DamPy})_4I_5(OH)]\cdot H_2O$

To a filtered solution of potassium tetrachloroplatinate(II) (0.006 g, 2.4 mmol) in water (20 cm^3), lithium iodide (1.6647 g, 9.8 mmol) in water (10 cm^3) was added and the solution stirred for 15 minutes. 2,6-Diaminopyridine (0.3929 g, 3.6 mmol) in 20 cm^3 water was added drop-wise similar to the preparation of the chloride complex of this ligand. The brown solid was filtered, washed with distilled water and diethyl ether and dried. Yield 53%.

$[Pt(OPDA)Cl_2]$

Potassium tetrachloroplatinate(II) (1.0377 g, 2.5 mmol) was dissolved in water (20 cm^3), filtered and *o*-phenylenediamine (0.2953 g, 2.5 mmol) in warm water (10 cm^3 at 40 °C) was added. The solution was stirred for 3 h. A grey solid formed, which was filtered through a fine glass sinter and washed with hot water (70–80 °C), ethanol, diethyl ether and dried. Yield 95%.

$[Pt(OPDA)I_2]$

To a filtered solution of potassium tetrachloroplatinate(II) (1.0377 g, 2.5 mmol) in 20 cm^3 water, lithium iodide ($LiI\cdot 2H_2O$; 1.78 g, 10.5 mmol) in water (10 cm^3) was added and the solution stirred for 15 minutes. *Ortho*-phenylenediamine (0.295 g, 2.5 mmol) in warm water (10 cm^3 at 40 °C) was added at once with gentle stirring. After one hour a brown solid was formed. The stirring was continued for *ca.* 4 h. The brown solid was filtered off, washed with hot water (70–80 °C) and ether and dried. Yield 72%.

$[Pt(PPDA)Cl_2]$ *and* $[Pt(PPDA)I_2]$

The methods of preparation of these complexes were analogous to those for the corresponding *ortho*-phenylenediamine complexes except that the periods of the stirring were *ca.* 18 h in both cases.

References

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

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

3 M. J. Cleare and J. D. Hoeschle, *Bioinorg. Chem., 2,* 187 (1973).

4 M. J. Cleare and J. D. Hoeschle, *Plat. Metals. Rev., 17,* 2 (1973).

5 S. Haghighi, C. A. McAuliffe, M. Fox and M. Friedman, *Chem. Biol. Interact.,* submitted for publication.

6 S. Haghighi, C. A. McAuliffe and P. Melius, *J. Inorg. Biochem.,* submitted for publication.

7 H. H. Kohl, S. Haghighi and C. A. McAuliffe, *Chem. Biol. Interact., 29,* 327 (1980).

8 R. Poddar and U. Agaruila, *J. Inorg. Nucl. Chem., 35,* 3769 (1973).

9 W. R. McWhinnie, *J. Inorg. Nucl. Chem., 27,* 1063 (1965).

10 W. R. McWhinnie, *J. Chem. Soc.,* 2959 (1964).

11 E. Uhlig and M. Masdler, *Z. Naturforsch., 20b,* 598 (1965).

12 E. Uhlig and M. Masdler, *Z. Anorg. Allgem. Chem., 338,* 199 (1965).

13 H. Sigel and H. Brintzinger, *Helv. Chim. Acta, 46,* 701 (1963).

14 H. Sigel and H. Brintzinger, *Helv. Chim. Acta, 46,* 712 (1963).

15 T. B. Kanunova and M. F. Frunze, *Russ. J. Inorg. Chem., 18,* 951 (1973).

16 W. R. McWhinnie, *Coord. Chem. Rev., 5,* 293 (1970).

17 D. Brodzki and G. Pannetier, *J. Organometal. Chem., 104,* 241 (1976).

18 N. S. Gill, R. H. Nuttall, D. E. Scaife and D. W. A. Sharp, *J. Inorg. Nucl. Chem., 18,* 79 (1961).

19 R. D. Gillard and G. Wilkinson, *J. Chem. Soc.,* 1224 (1964).

20 A. H. Norburg, E. A. Ryder and R. F. Williams, *J. Chem. Soc. (A),* 1439 (1967).

21 L. G. Hubert-Pfahzraf and J. G. Reiss, *J.Chem. Soc. Dalton,* 585 (1974).

22 H. G. Biedermann, E. Leeb and K. E. Schwarzhaus, *Z. Naturforsch., 29,* 371 (1974).

23 R. E. Yingst and B. E. Douglas, *Inorg. Chem., 3,* 1177 (1964).

24 A. D. Allen and T. Theophanides, *Can. J. Chem., 42,* 1551 (1964).

25 R. G. H. Clark and R. Williams, *Inorg. Chem., 4,* 350 (1965).

26 D. M. Adams, J. Chatt, J. Gerratt and R. D. Westland, *J. Chem. Soc.,* 734 (1964).

27 F. Herbelin, J. D. Herbelin, J. P. Mathieu and H. Poulet, *Spectrochim. Acta, 22,* 1515 (1966).

28 J. R. Durig, B. R. Mitchell, D. W. Sink, J. N. Willis and A. S. Wilson, *Spectrochim. Acta, 23A,* 1121 (1967).

29 A. H. Norburg and I. P. Sinha, *J. Inorg. Nucl. Chem., 35,* 1211 (1973).

30 D. M. Adams, 'Metal–Ligand and Related Vibrations', Arnold, London, p. 278 (1967).

31 J. P. Davidson, P. J. Faber, R. G. Fischer, S. Mansy, H. J. Peresic, B. Rosenberg and L. Van Camp, *Cancer Chemother. Rep., 59,* 287 (1975).

32 B. Rosenberg, *Cancer Chemother. Rep., 59,* 589 (1975).

33 J. K. Barton, H. N. Rabiowitz, D. J. Szalda and S. J. Lippard, *J. Am. Chem. Soc., 99,* 2827 (1977).

34 R. D. Gillard and G. Wilkinson, *J. Chem. Soc.,* 2835 (1964).

35 A. Findlay, 'Practical Physical Chemistry', Longmans, 8th ed., p. 209 (1969).

36 W. J. Geary, *Coord. Chem. Rev., 7,* 81 (1971).