Equilibria in Complex Compounds of N-Heterocyclic Molecules. Part IV.[1] Complexes of Platinum(II) in Basic Solution

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We report: (*i*) reversible spectroscopic changes (electronic and n.m.r.) as a function of pH in solutions containing complex ions of platinum(II) with two 2,2′-bipyridyls or 1,10-phenanthrolines; (*ii*) lack of proton exchange in the solution of $[Pt(phen)_2]^{2+}$; (*iii*) similar spectroscopic changes, but lack of proton exchange, in 5-nitrophenanthroline; and (*iv*) the isolation from basic solutions of substances of composition $Pt(phen)_2(OH)X$ (X = Br or Cl). These findings are interpreted in terms of an equilibrium of the co-ordinated N-heterocycle with solvent. This involves reaction at the carbon atom adjacent to the ring nitrogen.

AN earlier summary[1] gave reasons for linking those reactivities of N-heterocycles which are enhanced by quaternization to the similar reactivities of the heterocycles when bound to a metal ion. This paper reports results on the reaction with hydroxide ion of bis(2,2′-bipyridyl)platinum(II), bis(1,10-phenanthroline)platinum(II), and some of their analogues, and offers new experimental support to the suggestion that nucleophilic attack on complexes of N-heterocyclic molecules may occur through intermediates with nucleophiles linked to carbon atoms of the ligand. A preliminary report[2] of a few results on co-ordinated bipyridyls has appeared.

RESULTS

Bis(1,10-*phenanthroline*)*platinum*(II).—A neutral aqueous solution of $[Pt(phen)_2]Cl_2$, treated with base, showed a marked change of electronic spectrum (Figure 1). This was complete within the time of mixing and reversible on rapid acidification. The apparent pK_a is *ca.* 11.5, determined from plots of optical absorption at various wavelengths against pH. The magnetic resonance of the protons in the ligand also showed reversible changes on addition of base (Figure 2). The greatest effect on the spectrum is the apparent disappearance of the signals arising from the 2 and 4 protons (and, of course, 9 and 7). However, no chemical exchange of C–H for deuterium occurred in alkaline heavy water (*i.e.* there is no carbanionic conjugate base involved). The original proton resonance spectrum in acid solution was fully recovered on acidifying the alkaline solution.

After a time, which depended on the concentrations of reagents, dark precipitates formed in the basic solutions. These insoluble solid substances have the composition $Pt(phen)_2(OH)Cl$ and $Pt(phen)_2(OH)Br$, depending on whether the chloride or bromide of $[Pt(phen)_2]^{2+}$ was used. The analysis for halide is particularly critical in distinguishing the products from possible hydrates of $[Pt(phen)_2]X_2$. The preparations were reproducible.

The chief differences between the i.r. spectra of $[Pt(phen)_2]X_2$ and $[Pt(phen)(phen{\cdot}OH)]X$ (collected in Table 1) occur between 1 600 and 1 400 cm^{-1}, and at *ca.* 1 000—1 100 cm^{-1}. The spectra of the new species are richer, and clearly defined new bands occurred at 1 553 (X = Cl) and 1 555 (X = Br), at *ca.* 1 080, and at 831 (Cl) and 829 cm^{-1} (Br). The spectra of $[Pt(phen)(phen{\cdot}OH)]Cl$ and of $[Pt(phen)(phen{\cdot}OH)]Br$ are mutually superposable,

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[1] Part III, R. D. Gillard, *Co-ordination Chem. Rev.*, 1975, **16**, 67.

[2] R. D. Gillard and J. R. Lyons, *J.C.S. Chem. Comm.*, 1973, 546.

but quite distinct from those of $[Pt(phen)_2]Cl_2{\cdot}3H_2O$ and of $[Pt(phen)_2]Br_2$, which are mutually different.

A very concentrated aqueous solution of $[Pt(phen)_2]Cl_2$ showed no spectroscopic (electronic or magnetic resonance) change on treatment with lithium chloride (*ca.* 5 mol dm^{-3}) so we rule out five-co-ordination.

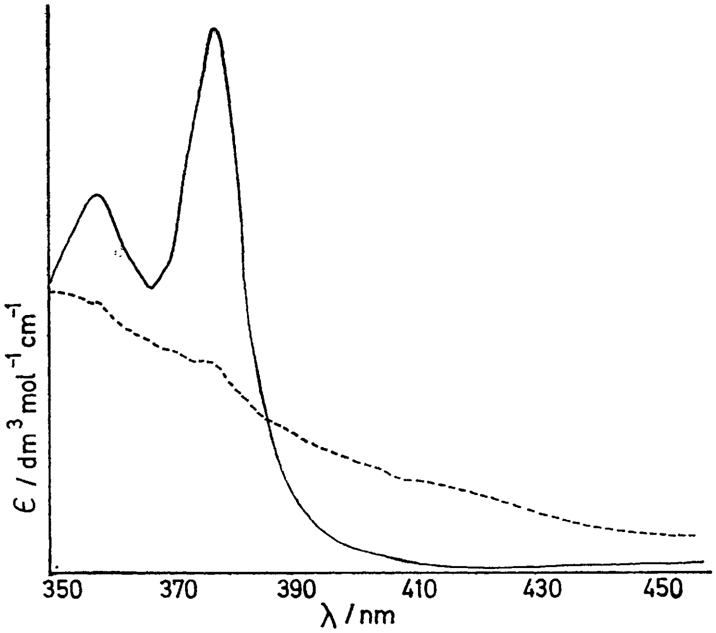

FIGURE 1 Electronic spectra of $[Pt(phen)_2]Cl_2$ in neutral or acidic aqueous solution (——), actually run at pH 5.80, and in alkaline solution (– – – –), run at pH 12.95

Bis(2,2′-*bipyridyl*) *Complexes of Platinum*(II).—The electronic spectrum of a neutral aqueous solution containing salts of $[Pt(bipy)_2]^{2+}$ undergoes a large change [2] on addition of sodium hydroxide (*cf.* Figure 1 of ref. 2). This change is complete within the time of mixing and fully reversed by acidification. The apparent p*K* was determined as 9.0 ± 0.2 from plots of optical density (at several wavelengths between 240 and 325 nm) against pH. Similar changes were observed for bis(5,5′-dimethyl-2,2′-bipyridyl)-platinum(II) (p*K* 9.5 ± 0.3) and for bis(5,5′-dimethyl-2,2′-bipyridyl)palladium(II) (p*K* 8.20 ± 0.3). However, the ions diammine(2,2′-bipyridyl)platinum(II), (2,2′-bipyridyl)-dipyridineplatinum(II), and tetrapyridineplatinum(II) showed no such obvious effect.

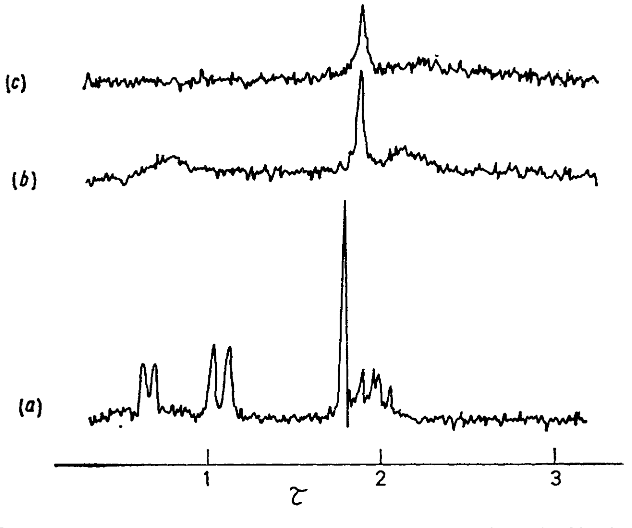

FIGURE 2 Proton resonance spectrum of $[Pt(phen)_3]Cl_2$ in neutral solution of pD 7.2 (*a*) and successive spectra in alkaline solution corresponding to pD 9.5 [(*b*) and (*c*)] [scan time 300 s (1 000 Hz)$^{-1}$]

The change in the electronic spectrum is matched by a change (*cf.* Figure 2 of ref. 2) in the ^1H n.m.r. spectrum, which was assigned [3] by reference to the spectra of the methyl-substituted bipyridyls. The resonances due to the aromatic protons were all slightly shifted on treatment with base, but that of $H^{6(6')}$ was most seriously affected. (Loss of intensity was accompanied by the appearance of a new resonance at high field.) The ^1H n.m.r. spectrum of $[Pt(5,5'\text{-}Me_2bipy)_2]^{2+}$ in neutral water included a single signal arising from the protons of the methyl group, whereas that of the derived species in alkaline solution showed at least three signals, arising from the inequivalence of the methyl groups. The n.m.r. changes were fully reversible and thus there is no specific hydrogen exchange of any of the aromatic protons with the deuterons of the solvent.

The electronic spectra of alkaline solutions of the platinum complex ions were constant for at least 1 h at room temperature. We recorded proton resonance spectra for $Pt(bipy)(OH)_2$ and its conjugate acids at various pH, and there is no coincidence with values for $[Pt(bipy)_2]^{2+}$, so we rule out hydrolysis. Crystallization of weakly basic solutions of $[Pt(bipy)_2]X_2$ gave solids with i.r. spectrum and microanalyses (for C, H, N) the same as those for the 'parent' complex. However, in a single experiment, which we have so far been unable to repeat, brown needles of $[Pt(bipy)_2][ClO_4]_2{\cdot}H_2O$ isolated at pH 9 gave a different

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[3] E. Bielli, P. M. Gidney, R. D. Gillard, and B. T. Heaton, *J.C.S. Dalton*, 1974, 2133.

i.r. spectrum and *X*-ray powder photograph, but identical analytical composition and electronic spectrum, to samples crystallized at pH 6—7; it is possible that the needles were contaminated with a decomposition product of similar composition.

No deuterium exchange was detected (by i.r. or Raman spectroscopy) in samples of $[Pt(bipy)_2]X_2$ isolated from alkaline D_2O. The palladium complex $[Pd(5,5'\text{-}Me_2bipy)_2]^{2+}$ is unstable in basic solution; the electronic spectrum slowly changed (to a significant extent after 30 min at room temperature) and crystallization gave an impure product of hydrolysis containing only one 5,5′-dimethyl-2,2′-bipyridyl ligand per metal atom. Bis(1,10-phenanthroline)palladium(II) ion decomposes under alkaline conditions without showing reversible changes in the electronic spectrum.

TABLE 1

Infrared spectra (cm^{-1}) of $[Pt(phen)_2]X_2$ (X = Cl or Br) and derivatives in Nujol

$[Pt(phen)_2]Cl_2\cdot3H_2O$	$[Pt(phen)_2(OH)]Cl\cdot1.5H_2O$	$[Pt(phen)_2]Br_2$	$[Pt(phen)_2(OH)]Br$
3 450 (sh)			
3 350s, b	broad band between 3 500 and 3 100		broad band centred at *ca.* 3 400
3 090w			
3 040w			
	1 655 (sh), b		1 660 (sh), b
1 629	1 631w		1 630w
1 604w	1 605s		1 606s
		1 599vw	
1 582m	1 582s	1 587vw 1 580w	1 582m
	1 562 (sh)		
	1 553s, b		1 555m, b
	1 547 (sh)		
	1 540 (sh)		
1 518s			
1 507 (sh)	1 505s, (sh)	1 506 (sh)	1 504m
	1 493s, b	1 490w, b *	1 495 (sh)
			1 470w *
			1 460w *
1 439 (sh)			1 438 (sh) *
1 434vs	1 430s	1 435s	1 428s
		1 430 (sh)	
1 413w	1 411w	1 412vw	1 410w
		1 402vw	
	1 340vw		
1 320vw	1 320w	1 326vw	1 318w
1 265vw	1 280m, b	1 248vw	1 270vw
1 224w	1 226m	1 228m	1 225w
	1 220 (sh)		
1 205vw		1 207vw	
	1 194m	1 198m	1 192w
	1 180 (sh)		
1 150w		1 150vw	
1 139vw		1 140vw	
	1 132m, b		1 132b
		1 114vw	
	1 092 (sh)		1 090w
	1 083 (sh)		1 082w
	1 076m		1 073w
	1 060 (sh)		1 060vw
1 049w	1 042w	1 042w	1 040vw
		1 032w	
1 014vw	1 019w		1 018vw
		1 001w	
	924w	935vw	924w
881w	879m	880w	875w
857vs		860vs	
	849s	850vs	846m
837vw	831vs		829s
	810 (sh)		
786 (sh)		788vw	
780w	779s	776s	775w
	745 (sh)		
	737 (sh)		
723 (sh)	725s		
710s	711vs	709vs	709s
	653w	657vw	650w
	644		
		531w	
		444w	

* In C_4Cl_6.

5-Nitrophenanthroline.—Samples of 5-nitrophenanthroline were suspended in alkaline deuterium oxide at room temperature at pD ⩾ 11 for periods of up to 5 h and then recovered. In no case was evidence of exchange observed, using i.r., Raman, and ^{1}H n.m.r. spectroscopy. In hot alkali, there is a remarkable reaction of 5-nitrophenanthroline or its metal complexes giving ammonia in good yield, which we discuss elsewhere.

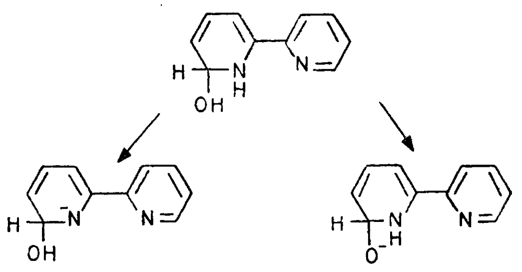
DISCUSSION

The behaviour of the bis complexes in basic solution could stem from several causes. (*i*) Opening of a chelate ring by rupture of a metal–nitrogen bond. Attack by hydroxide ion at Pt^{II} or at Pd^{II} is slow, and while it causes gradual hydrolysis of the complexes it is unlikely to be responsible for the rapid changes of the spectra.* Further, if unidentate bipyridyl groups were present in alkaline solution, addition of acid would lead to competitive protonation of the unco-ordinated nitrogen and not exclusively to the observed ring closure. Coupling between the platinum and the H^6 proton is observed in the n.m.r. spectra of neutral solutions of $[Pt(bipy)_2]^{2+}$, but not in alkaline solutions, where the quality of the spectra is not so good. However, the n.m.r. spectra of $[Pt(bipy)(OH)_2]$ at various pH do not coincide with our alkaline spectra of $[Pt(bipy)_2]^{2+}$.

(*ii*) Attack by hydroxide ion at the metal to give a five-co-ordinate complex. The spectroscopic changes are apparently specific for hydroxide ion: neither chloride nor cyanide ions produce shifts of this type. Furthermore the changes in the electronic spectrum produced by hydroxide ion do not resemble those produced by halide ions in $Pd(2,9\text{-}Me_2phen)_2X,Y\cdot nH_2O$ (X, Y = halide). Complexes of this type have been assigned[4] a five-co-ordinate structure in the solid state on the basis of a shift of the absorption maximum to longer wavelengths relative to solutions in polar solvents. Effects similar to those we observe may be in operation.

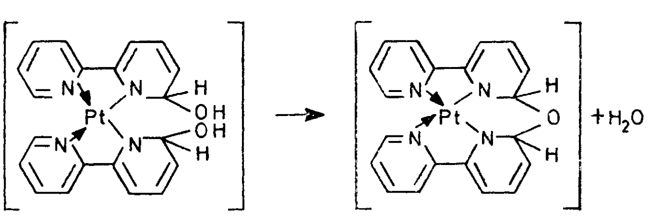
(*iii*) Formation of a conjugate base by abstraction of a proton from co-ordinated phenanthrolines or bipyridyls. This possibility, suggested to account for the pH dependence of the spectrum of $5\text{-}NO_2phen$ and its iron(II) complex, is ruled out by the lack of exchange in alkaline D_2O.

(*iv*) The most likely explanation, attack by hydroxide ion on the aromatic ring at $C^{6(6')}$ of bipy or $C^{2(9)}$ of phen. The carbon atom becomes more nearly tetrahedral and the altered stereochemistry may offer relief from steric strain,[5] although it is worth noting that not all apparently unstrained bipyridyl ligands are planar. Loss of some aromatic character is accompanied by formation of a carbon–oxygen bond. The factors involved are similar to those relevant to the formation of covalently bonded hydrates[6] at the carbon–nitrogen double bond of polyazanaphthalenes, and have been discussed at length.[1] Indeed it is possible to formulate the change as addition of water followed by deprotonation in one of two possible ways (of which, certainly in metal complexes, the N-acid seems more reasonable). Either process would lead to the observed effects, which may be



summarized as: (*a*) changes in the resonance of the H^6 proton relative to those of H^3, H^4, and H^5; (*b*) changes in the electronic spectrum due to loss of aromatic character in one of the pyridine rings; (*c*) inequivalence of substituents at the 5 and 5′ positions; (*d*) absence of C–H exchange; and (*e*) decrease of the overall cationic charge by one unit.

We have not considered one extension of such nucleophilic attack at C^2, the ether formation (common enough in pseudo-base chemistry) shown (which would probably need to be intramolecular on steric grounds). While this is certainly a possible species, it would be uncharged, and our isolated solids have ratios of counter ion : Pt of 1 : 1. Although, in such a kinetically labile system as this, the nature of an isolated product need not necessarily be related to the dominant components in solution, the isolation of monohalides indicates the presence of singly charged cationic complexes of platinum.



Exactly why we should find it easiest to isolate the products of nucleophilic attack for the strained complexes, $[PtL_2]^{2+}$, it is not easy to say. We envisage the attack by hydroxide on complexes of co-ordinated N-heterocycles as proceeding *via* the intermediate conjugate base (CB) shown in the example. Presumably, if $k_{\text{intra.}}$ is very large, CB will never exist in quantities large enough for ready observation, let alone isolation. (Probably the case[1] for substitution into $[FeL_3]^{2+}$ by $[OH]^-$, and for reduction by $[OH]^-$ of $[ML_3]^{3+}$.) However, if for some reason $k_{\text{intra.}}$ is close to zero, then CB will be isolable.

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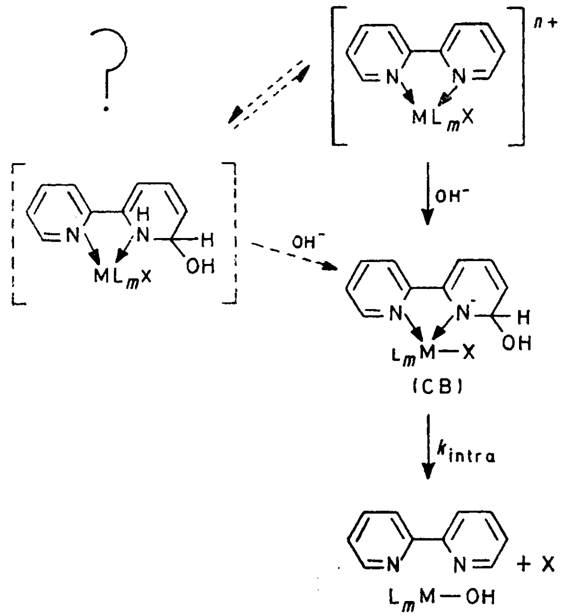
* The magnetic resonance observations are inconsistent with hydrolysis. The recent proposals by Nord (*Acta Chem. Scand.*, 1975, **A29**, 270) that all the observed changes arise from hydrolysis ignore most of the published evidence.

[4] R. A. Plowman and L. F. Power, *Austral. J. Chem.*, 1971, **24**, 303.

[5] E. D. McKenzie, *Co-ordination Chem. Rev.*, 1971, **6**, 187.

[6] A. Albert, *Angew. Chem. Internat. Edn.*, 1967, **6**, 919.



As was pointed out some years ago, the *trans*-bis(ligand) structure leads[5,7] to marked steric repulsion between *ortho* substituents of the ligands. In this light, the very existence (and remarkable stability) of the present *trans* complexes, $[ML_2]^{2+}$, is surprising. (As is that of several other species, *e.g.* 1,10-phenanthroline di-*N*-oxide, although this was characterized[8] only as its picrate and the work could not[9] be repeated.) Although the steric compression for totally planar systems $[ML_2]^{2+}$ is real, relaxation may be more facile than is commonly supposed. For example, even the bipyridyl ligands in bis(2,2′-bipyridyl)nitritocopper(II) nitrate are[10] distorted,* although there is no severe steric compression of the *trans*-bis kind. Similarly,[11] the so-called 4,5-dimethyl-1,8-phenanthrolines show optical activity. It may be that the relief of steric strain by saturation at the 2-position gives (in the present complexes and a few others) an intermediate conjugate base whose subsequent reactions are sufficiently slow for it to be non-labile.

TABLE 2

Analytical results (%)

Compound	Found					Calc.				
	C	H	N	X[a]	Pt	C	H	N	X	Pt
5-NO_2phen[b]	64.0	3.1	18.7			64.0	3.1	15.7		
$[Pt(bipy)_2][NO_3]_2 \cdot H_2O$	36.6	3.1	12.9			37.0	2.8	12.9		
$[Pt(bipy)_2][ClO_4]_2$	33.8	2.8	7.8			34.0	2.3	7.9		
$[Pt(5,5'\text{-}Me_2bipy)_2][NO_3]_2 \cdot 2H_2O$	39.5	3.0	11.2			39.8	3.9	11.6		
$[Pd(5,5'\text{-}Me_2bipy)_2][NO_3]_2 \cdot 2H_2O$	45.9	4.3	13.2			45.4	4.5	13.2		
$[Pt(phen)_2]Cl_2 \cdot 3H_2O$	42.5	2.95	7.8			42.35	3.2	8.2		
	42.2	3.1	7.9							
$[Pt(phen)_2][ClO_4]_2$	37.8	2.0	7.4			38.2	2.1	7.4		
$[Pt(phen)_2][CF_3SO_3]_2$	37.1	1.8	6.6			36.6	1.9	6.6		
	35.9	1.6	6.4							
$[Pt(phen)_2]Br_2$	40.2	2.5	7.7			40.3	2.2	7.8	22.35	
c	40.1	2.4	7.7	22.0						
$[Pt(phen)(phen \cdot OH)]Cl \cdot 1.5H_2O$[d]	45.2	2.5	8.5	6.0		45.4	3.15	8.8	5.6	30.7
	44.3	3.0	8.6	5.9	30.6					
$[Pt(phen)(phen \cdot OH)]Br$	42.3	2.7	8.0	10.5						
	43.9	2.9	8.5	11.2	29.8	44.2	2.6	8.6	12.2	29.9
$[Pt(bipy)Cl_2]$					45.8[e]					46.2

[a] X = halogen. [b] Prepared following G. F. Smith and F. W. Cagle, *J. Org. Chem.*, 1947, **12**, 781, and recrystallized from methylated spirit. [c] After recrystallization from hot water. [d] A short-period *X*-ray powder photograph of this substance gave two strong lines at *d* spacings of 2.84 and 3.08 Å. [e] This analysis on a known complex served as a check of the method.

Several earlier proton-resonance findings are reminiscent of ours. For example, Miller and Prince[12] observed that for various $[M(phen)_x]^{n+}$ complexes large alterations in resonance position occur for the 2 and 9 protons, much more pronounced than those for the signal of any other proton. This they attributed to an interaction between the metal and these non-bonded hydrogens. However, it seems likely that covalent hydration is responsible in those cases also, the shifted signal observed for C^2–H being a time average of the signal for the parent unsolvated C^2–H(aromatic) and that for the solvated $C^2H(OH)$, a more nearly alicyclic situation.

EXPERIMENTAL

Analyses are collected in Table 2.

Preparation of Complexes.—Complexes of the type[13] $[PtCl_2L]$ (L = 2,2′-bipyridyl or 5,5′-dimethyl-2,2′-bipyridyl) were converted into $[PtL_2]^{2+}$ by heating under reflux with an excess of 2,2′-bipyridyl (or 5,5′-dimethyl-2,2′-bipyridyl) in aqueous ethanol. The complexes were isolated as the nitrate or perchlorate and extracted at least

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* While each pyridine ring is planar, the two such rings in each bipyridyl are skewed by *ca.* 11°.

[7] H. M. Irving and D. H. Mather, *J. Chem. Soc.*, 1962, 5222 and refs. therein.

[8] F. Linster and R. L. Evans, *J. Amer. Chem. Soc.*, 1946, **68**, 403.

[9] G. Marker and F. H. Case, *J. Amer. Chem. Soc.*, 1958, **80**, 2745.

[10] I. M. Proctor and F. S. Stephens, *J. Chem. Soc. (A)*, 1969, 1248.

[11] W. Theilacker and F. Baxmann, *Annalen*, 1953, **581**, 117.

[12] J. D. Miller and R. H. Prince, *J. Chem. Soc.*, 1965, 3185.

[13] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1934, 965.

twice with either benzene or toluene to remove free ligand. The complexes $[Pd(5,5'\text{-}Me_2bipy)_2][NO_3]_2\cdot 2H_2O$ and $[Pd(phen)_2][NO_3]_2$ were prepared by the methods described by Livingstone,[14] and similarly extracted with toluene.

The following i.r. spectra were recorded in Nujol mulls: $[Pt(bipy)_2][ClO_4]_2$ 3 125w 3 090w, 1 610vs, 1 565w, 1 503m, 1 425 (sh), 1 325w, 1 317m, 1 267m, 1 248m, 1 235 (sh), 1 172m, 1 166m, 1 100—1 050vs,br, 1 040m, 1 023m, 993w, 969m, 930m, 908m, 890m, 814m, 778vs, 765 (sh), 752m, 722s, 655w, 648m, 622vs, 560w, and 432m; $[Pt(5,5'\text{-}Me_2bipy)_2][NO_3]_2\cdot 2H_2O$ 3 490m, 3 420m, 1 610m, 1 585m, 1 340s, 1 315s, 1 235w, 1 148m, 1 060m, 1 045w, 860m, 850m, 825m, 820w, 760w, 720m, 520w, and 440w; and $[Pd(5,5'\text{-}Me_2bipy)_2][NO_3]_2\cdot 2H_2O$ 3 450br, 1 740w, 1 605s, 1 585s, 1 510s, 1 250m, 1 235m, 1 165m, 1 145s, 1 060s, 1 005m, 895w, 850vs, 825m, 715s, 655w, 505m, and 430m cm^{-1}.

Salts of Bis(1,10-*phenanthroline*)*platinum*(II).—Attempts to adapt the standard methods were unsuccessful and the complex was finally obtained by a method kindly suggested by Professor R. A. Plowman, to whom we are indebted for his permission to describe it (*cf.* M. Parsons, M.Sc. Thesis, University of Queensland, 1954).

Yellow acicular *cis*-$[PtCl_2(NH_3)_2]$ (167 mg, 0.556 mmol) was dissolved in hot water and a three-fold excess of 1,10-phenanthroline hydrate (also dissolved in hot water) was added. The mixture was set to reflux for 3.5 h, and the yellow solution so obtained was reduced to a small volume. Phenanthroline was removed by filtration, a few drops of hydrochloric acid (0.1 mol dm^{-3}) were added to the filtrate, and finally acetone was added dropwise. This gave a pale yellow flaky precipitate, which was collected and recrystallized from the minimum of water with acetone. The final product was collected, washed carefully with ethanol, then with diethyl ether, and dried in a desiccator, yield 75%.

The yellow bromide was obtained by anion exchange (Zerolit FFIP, Br^- form), and the white perchlorate and yellow trifluoromethanesulphonate by adding respectively $Na[ClO_4]$ and barium trifluoromethanesulphonate to a solution of the chloride. The perchlorate is insoluble in water, the trifluoromethanesulphonate sparingly soluble, and the bromide is soluble in water (it can be recrystallized from hot water) and ethanol. The chloride trihydrate is very soluble in water, much more so that the bromide (and is soluble in ethanol): hydrolysis is very slow.

An attempt to make $[Pt(phen)_2][NO_3]_2$ by adding sodium nitrate to aqueous $[Pt(phen)_2]Cl_2$ gave a solid which analyzed reasonably well, but was a mixture of yellow-green and pink components. Analysis for platinum was by ignition to metallic platinum, and keeping red hot for 0.5 h.

The Reaction $[Pt(phen)_2]X_2 + [OH]^- \longrightarrow [Pt(phen)(phen\cdot OH)]X\cdot nH_2O + X^-$.—On adding a few drops of aqueous potassium hydroxide (5 mol dm^{-3}) to a concentrated solution of $[Pt(phen)_2]Cl_2\cdot 3H_2O$ (*e.g.* 50 mg) in water (0.6 cm^3) a sudden change from yellow to dark green occurred, and a dark greenish black precipitate was formed. (Exactly similar behaviour occurred in the absence of oxygen.) The precipitate was collected, washed with a little ice-water, ice-cold ethanol, and diethyl ether, and dried *in vacuo*. The solid is soluble in water, to give a greenish yellow solution with pH 8.2. The bromide, on similar treatment, gave an almost black product.

5-*Nitrophenanthroline: Proton Exchange*.—Each experiment used 5-nitro-1,10-phenanthroline (0.045 g) and the other constituents were as listed.

(*a*) Deuterium oxide (2.5 cm^3), containing Na[OH] (0.006 25 g) and methanol (0.5 cm^3). After 3 d at room temperature the solution was made strongly basic (Na[OH]), and the precipitate was separated, washed with water, and dried at room temperature. The i.r. spectrum indicated (partial) decomposition.

(*b*) Deuterium oxide (13 cm^3), 1 drop of 4N Na[OH]; measured 'pH' 11.3. The slurry was stirred at room temperature for 95 min and the solvent removed by rotary evaporation at 30 °C. There was no change in the C–H and C–D regions of the Raman spectrum.

(*c*) Repeat of experiment (*b*) but stirred for 5 h at room temperature. The solid was separated (using a bench centrifuge), washed twice with water, and recrystallized from ethanol. The proton n.m.r. spectrum was unchanged from that of the starting material.

(*d*) As experiments (*b*) and (*c*), but with the addition of ethanol (1 cm^3) and 4N Na[OH] (two drops). The slurry was stirred for 2.5 h at room temperature, centrifuged, washed twice with water (the final washings were neutral to litmus), and dried in air. The proton n.m.r. spectrum was identical with that of untreated 5-nitrophenanthroline.

This work was started at the University of Kent. We thank the Royal Society European Programme for support (to E. B.), Drs. A. W. Addison and P. M. Gidney for providing samples of some compounds, and Dr. J. R. Lyons for some preliminary experiments on the complexes with 2,2'-bipyridyl.

[5/2357 *Received, 3rd December*, 1975]

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[14] S. E. Livingstone, *J. Proc. Roy. Soc. New South Wales*, **1952**, **86**, 32; *ibid.*, 1951, **85**, 151.