Behaviour of Diamine-*af*-dibromo-dinitroplatinum(IV) Complexes and the Adduct *ac*-Dinitro-*bd*-bis(pyridine)platinum(II)–Boron Trifluoride in Acidic Solutions

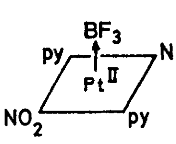
By **Derek Humphreys** and **Peter J. Staples,*** School of Chemistry, University of Bradford, Bradford BD7 1DP

Octahedral diamine-*af*-dibromo-dinitroplatinum(IV) complexes [diamine = *de*- and *ce*-bis(pyridine), *bc*-(2,2′-bipyridine), and *ce*-bis(triethylphosphine)] have been prepared from the corresponding square-planar platinum(II) complexes by oxidative addition with bromine. Kinetic studies of the replacement of the first nitro-group from the platinum(IV) complexes in aqueous sulphuric acid and sulphuric acid–acetic acid solutions show that the complexes are difficult to protonate, *i.e.* the protonated forms are very strong acids. The rate constant for the release of the first nitro-group has been measured and correlated with acidity function and other parameters. The mechanism of these reactions is discussed. Preliminary studies of the preparation and reactivity of a platinum(II) complex, in which an axial position is occupied by a boron trifluoride acceptor molecule, are also reported.

THE mechanisms of substitution of square-planar complexes are of considerable interest. In particular the role of orbitals in the ' axial positions ' has been widely discussed. Many of the postulated mechanisms[1] involve species in which these positions are occupied by solvent molecules, although the bonding is said to be ' weak '. The role of the solvent in acid-catalysed hydrolyses of octahedral complexes, *e.g.* those of cobalt(III), has been studied,[2] and it is of special interest in square-planar complexes because of the presence of the ' axial positions.' Thus one possible mechanism[3a] for acid-catalysed reactions of square-planar platinum(II) complexes is that the lone-pair in the axial ($5d_{z^2}$) position is protonated along with, or in preference to, the leaving group. A means of investigating this mechanism is to occupy or block one or both of the axial positions. In this study attempts were made to investigate a platinum(II) complex in which one ' axial position ' was occupied by boron trifluoride and platinum(IV) complexes in which both ' axial positions ' were occupied by bromide ligands.

RESULTS

The Adduct ac-*Dinitro*-bd-*bis*(*pyridine*)*platinum*(II)–*Boron Trifluoride*.—Attempts were made to prepare, isolate, and study the kinetic behaviour of the adduct *ac*-dinitro-*bd*-bis(pyridine)platinum(II)–boron trifluoride, (I). Analysis of isolated solids were much closer to that corresponding to a 2 : 1 (BF_3 : complex) adduct than to formula (I) (see Discussion section). Moreover kinetic studies of the replacement of a nitro-group were hampered by ' fluoroboron ' species liberated during the reaction which interfered with the nitritometric analysis used. Isolation of the products at early reaction times showed that the solids contained no fluorine. This is evidence that the boron trifluoride molecules are replaced very quickly, *i.e.* too rapidly for their effect on the reactivity and basicity of the nitro-group to be determined. In some runs reasonable first-order plots were obtained and the results were very similar to those expected for the square-planar precursor $[Pt(py)_2(NO_2)_2]$ (py = pyridine). In the solid state, the boron trifluoride adduct loses weight relatively slowly, *i.e. ca.* 5% in 2 days.



(I)

Diamine-af-*dibromo-dinitroplatinum*(IV) *Complexes* [*Diamine* = de- *and* ce-*Bis*(*pyridine*), bc-(2,2′-*Bipyridine*), *and* ce-*Bis*(*triethylphosphine*)].—In these complexes the axial positions are occupied by bromo-groups. It is to be noted that occupation of the *af* positions is accompanied by oxidation of platinum(II) to platinum(IV).† When the complexes were dissolved in aqueous sulphuric acid or sulphuric acid–acetic acid the nitro-groups were successively replaced, the rate of replacement of the first group being much faster than that of the second. The rate of reaction was first order in complex concentration and a plot of rate constant against acid concentration was a sigmoid curve; no maximum rate constants were observed under the conditions used (Tables 1 and 2). Highly acidic

TABLE 1

Pseudo-first-order rate constants for the replacement of a nitro-group by an H_2O group in diamine-*af*-dibromo-dinitroplatinum(IV) complexes in sulphuric acid at 25·0 °C

de-Bis(pyridine)		*bc*-(2,2′-Bipyridine)	
$[H_2SO_4]$ M	10^4k s^{-1}	$[H_2SO_4]$ M	10^4k s^{-1}
12·24	0·09	10·25	0·16
12·87	0·11	10·74	0·19
13·39	0·14	11·08	0·20
13·87	0·17	11·67	0·22
14·10	0·38	13·50	0·41
15·50	1·7	14·10	0·71
16·15	2·9	14·80	3·7
16·80	4·2	16·15	18
18·10	27	18·10	28
ce-Bis(pyridine)		*ce*-Bis(triethylphosphine)	
13·50	15	14·10	12
14·10	31	15·50	32
14·80	85	16·15	>100
		18·10	>200

---

† It has been assumed that the oxidative-addition reaction proceeds with retention of the configuration of the four original ligands in the square plane. Further work is in progress to elucidate this point.

[1] (*a*) F. Basolo and R. G. Pearson, ' Inorganic Reaction Mechanisms,' John Wiley, New York, 1967; (*b*) C. H. Langford and H. Gray, ' Ligand Substitution Processes,' W. A. Benjamin Inc., New York, 1965.

[2] P. J. Staples, *J. Chem. Soc.* (*A*), 1967, **45**; D. G. Lambert and J. G. Mason, *J. Amer. Chem. Soc.*, 1966, **88**, 1633.

[3] (*a*) K. A. Pilkington and P. J. Staples, *Inorg. Chem.*, 1968, **7**, 1421; (*b*) D. Humphreys and P. J. Staples, unpublished work.

media were required before any of the complexes displayed appreciable acid catalysis.

TABLE 2

Pseudo-first-order rate constants for the replacement of a nitro-group in diamine-*af*-dibromo-dinitroplatinum(IV) complexes in sulphuric acid–acetic acid at 25·0 °C

de-Bis(pyridine)		*bc*-(2,2′-Bipyridine)	
$[H_2SO_4]$ M	10^4k s^{-1}	$[H_2SO_4]$ M	10^4k s^{-1}
1·62	0·11	1·61	0·11
1·96	0·13	3·72	0·17
3·15	0·17	4·81	0·15
5·35	0·21	6·65	0·66
8·12	0·24	8·19	0·74
10·57	0·45	10·31	2·8
12·78	0·71	12·21	8·4
15·41	1·3	15·37	17
ce-Bis(pyridine)		*ce*-Bis(triethylphosphine)	
4·05	0·22	5·55	0·46
6·44	0·34	8·12	1·0
9·36	0·63	10·72	2·7
12·75	1·7	12·74	6·2
15·36	3·1	15·38	8·7

Before studying the reactions with acetic acid as solvent, the effects of (*a*) aqueous impurities, (*b*) sampling methods, (*c*) quenching methods, and (*d*) added sulphanilic acid on the run solvents, were examined. The main check was carried out using platinum(II) complexes.[3b] (*a*) If water was present as impurity in the acetic acid, the observed rate constants were considerably reduced. Thus water was carefully excluded. Reaction solvents were prepared in a nitrogen or argon atmosphere with the aid of siphoning devices. (*b*) Samples were removed under a nitrogen or argon atmosphere using siphoning devices. (*c*) As water had been shown to slow down the reaction, it was used as diluent, accompanied by rapid cooling. Acetic acid diluent gave similar results but the experimental difficulties were far greater. (*d*) Added sulphanilic acid had little effect on the observed rate constants.

At late reaction times, small amounts of bromine appeared in solutions of the reactants, presumably because of slow replacement of the bromo-groups; bromide ion would be rapidly oxidised to bromine under the relevant experimental conditions, *e.g.* 15M-sulphuric acid. The rate of appearance of bromine was measured and is very slow compared with the rate of removal of the first nitro-group (*ca.* 5% of a bromo-group is displaced during 7 half-lives of the replacement of the first nitro-ligand). Although the aquonitro-complex or its nitrosulphato-anation product were not isolated, they are fairly readily anated in aqueous solution and a diamine-*gf*-dibromochloronitroplatinum(IV) complex was isolated after the addition of sodium chloride; very little bromo-group had been replaced from the complex (see Experimental section).

Bailar *et al.*[4] prepared the complex *trans*-$[Pt(en)_2(OH)_2]^{2+}$ by oxidation of $[Pt(en)_2]^{2+}$ (en = ethylenediamine) with hydrogen peroxide. Attempts to prepare *af*-dihydroxo-analogues of for example the complexes *cis*-$[Pt(py)_2(NO_2)_2]$ or $[Pt(bipy)(NO_2)_2]$ (bipy = 2,2′-bipyridine) were unsuccessful as oxidation was accompanied by replacement of at least one nitro-group.

The reactions of many platinum(IV) complexes proceed by mechanisms involving (i) a redox path, catalysed by traces of platinum(II) species [5] and/or (ii) a photocatalytic path.[6] These possibilities appear unlikely in the systems studied here. Light had little effect on the rate constants, *i.e.* rate constants were the same, to within experimental error, for runs performed in clear and blackened vessels. Small amounts of corresponding platinum(II) complexes added to the reactant solutions ($Pt^{II} : Pt^{IV}$ = 0·05—0·10 : 1) also had little effect on the rate constants.

DISCUSSION

The Adduct ac-*Dinitro*-bd-*bis*(*pyridine*)*platinum*(II)–*Boron Trifluoride*.—The i.r. spectrum of the adduct shows B–F absorption frequencies characteristic of tetrahedrally bonded boron, *i.e.* at 1155 and 955 cm^{-1}. Shriver *et al.*[7] reported three absorption frequencies for tetrahedrally bonded boron in the complex $[Ir(CO)Cl(PPh_3)_2],2BF_3$ at 1138, 960, and 931 cm^{-1}; the latter was possibly masked in our investigation. An attempt to prepare a 1 : 1 adduct in the previous study was made but, although tensimetric titration indicated an ' end-point ' corresponding to such a species, the only species isolated had an analysis much closer to that for a 1 : 2 adduct. Our analyses are also much closer to that for a 1 : 2 adduct. The nature of the bonding of the second BF_3 molecule has been discussed,[7] but is not well understood. The reactivity of the BF_3 groups was too high to allow a study of their effect on the reactivity of the nitro-groups in the present study.

Diamine-af-*dibromo-dinitroplatinum*(IV) *Complexes* [*Diamine* = de- *and* ce-*Bis*(*pyridine*), bc-(2,2′-*Bipyridine*), *and* ce-*Bis*(*triethylphosphine*)].—These complexes have i.r. spectra which are extremely similar to those of the precursor square-planar platinum(II) complexes. Thus the addition of the two bromo-ligands accompanied by oxidation of platinum from the (II) to the (IV) state results in little alteration of the stretching and bending frequencies.

The main feature of the results obtained for the platinum(IV) complexes is that the complexes are extremely difficult to protonate, *i.e.* the protonated forms are very strong acids. Several dinitro-complexes of cobalt(III) are more readily protonated, despite the fact that the platinum complexes are uncharged. Such differences in behaviour of ligands attached to these metal ions are found in other systems; acid dissociation constants are compared in Table 3.

Some of the mechanisms feasible for square-planar complexes, *e.g.* those electrophilic catalysis, protonation of the lone-pair ($5d_{z^2}$), are ruled out for the complexes studied here. A redox pathway for acid-catalysed hydrolysis is also unlikely, since the addition of small quantities of the corresponding square-planar platinum(II) complexes to the reaction mixtures did not significantly affect the rate constants.

In aqueous solution, the results for the *bc*-(2,2′-bi-

---

[4] F. Basolo, J. C. Bailar, jun., and B. R. Tarr, *J. Amer. Chem. Soc.*, 1950, **72**, 2438.

[5] A. Syamal and R. C. Johnson, *Inorg. Chem.*, 1970, **9**, 265.

[6] C. Bartocci, F. Scandola, and V. Balzani, *J. Amer. Chem. Soc.*, 1969, **91**, 6948.

[7] R. N. Scott, D. F. Shriver, and L. Vaska, *J. Amer. Chem. Soc.*, 1968, **90**, 1079.

TABLE 3

Comparison of pK_a values for aquo-[a] and ammine-complexes[b] of the ions platinum(IV), cobalt(III), and rhodium(III)

Complex	pK_a (H_2O)	Complex	pK_a (NH_3)
$[Pt(NH_3)_5H_2O]^{4+}$	4	$[Pt(NH_3)_6]^{4+}$	7·2
$[Co(NH_3)_5H_2O]^{3+}$	6·6	$[Co(NH_3)_6]^{3+}$	14
$[Rh(NH_3)_5H_2O]^{3+}$	5·9	$[Rh(NH_3)_6]^{3+}$	14
$[Pt(en)_2(H_2O)_2]^{4+}$	Strong acid	$[Pt(en)_3]^{4+}$	5·5
cis-$[Co(en)_2(H_2O)_2]^{3+}$	6·1	$[Co(en)_3]^{3+}$	14
trans-$[Co(en)_2(H_2O)_2]^{3+}$	4·5	$[Rh(en)_3]^{3+}$	14
cis-$[Pt(NH_3)_2(H_2O)_2]^{2+}$	5·6	$[Pt(NH_3)_5Cl]^{3+}$	8·4
		cis-$[Pt(NH_3)_4Cl_2]^{2+}$	9·7
		trans-$[Pt(NH_3)_4Cl_2]^{2+}$	11·3

[a] J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, ' Stability Constants of Metal-ion Complexes,' Chem. Soc. Special Publ. No. 17, London, 1957. [b] R. G. Pearson and F. Basolo, *J. Amer. Chem. Soc.*, 1956, **78**, 4878; C. K. Jorgensen, *Acta Chem. Scand.*, 1956, **10**, 518; R. C. Johnson, F. Basolo, and R. G. Pearson, *J. Inorg. Nuclear Chem.*, 1962, **24**, 59.

TABLE 4

Parameters derived from kinetic results in aqueous solution at 25 °C

Platinum(IV) complex	w	Slope (log k/ $-H_0$)
af-Dibromo-*bc*-dinitro-*de*-bis(pyridine)	+0·2	0·95
af-Dibromo-*bc*-(2,2′-bipyridine)-*de*-dinitro	0·0	1·05
af-Dibromo-*bd*-dinitro-*ce*-bis(pyridine)	+0·1	1·1

pyridine) and *ce*-bis(pyridine) complexes suggest that, at lower-acid concentrations, hardly any protonated complex exists and a background reaction is observed. When treated by the methods of Bunnett[8] and of Zucker and Hammett,[9] these results favour a mechanism in which water is not involved in the transition state (Table 4). The mechanism postulated is an intramolecular reaction of the protonated substrate similar to that proposed by Jolly,[10] *i.e.* the rate-determining step involves synchronous bond-breaking (M–N) and bond-making (M–O) resulting in loss of a NO^+ ion and formation of a hydroxo-complex. However an unequivocal assignment cannot be made without a detailed isotopic study.

The results in acetic acid parallel those in water; a Bunnett-type analysis of the results was not possible as values for the activity of acetic acid in these solutions are not known. Expected differences between the two solvents, *e.g.* differences in reactivity due to different degrees of ion-pairing of the conjugate acid, were not apparent because only very low degrees of protonation were effected in both solvents.

EXPERIMENTAL

Preparations.— *Diamine-*af*-dibromo-dinitroplatinum*(IV) *complexes.* Square-planar platinum(II) complexes were prepared by literature methods[11] and then oxidised as follows. The platinum(II) precursor was suspended in water (25 ml) and the mixture placed on a steam-bath. Bromine was then added slowly, dropwise, and the mixture allowed to simmer for 15 min; during this period the excess of bromine evaporated. The solution was cooled, the bright yellow *product* filtered off, washed with alcohol and ether, and dried. As many platinum(IV) complexes are photosensitive, the products were stored in the absence of light. [*af*-Dibromo-*bc*-dinitro-*de*-bis(pyridine)platinum(IV), Found: C, 20·0; H, 1·60; Br, 26·0; N, 9·5. Calc.: C, 19·8; H, 1·65; Br, 26·4; N, 9·3. *af*-Dibromo-*bd*-dinitro-*ce*-bis(pyridine)platinum(IV), Found: C, 19·9; H, 1·9; Br, 26·3; N, 9·2. Calc.: C, 19·8; H, 1·65; Br, 26·4; N, 9·3. *af*-Dibromo-*bc*-(2,2′-bipyridine)-*de*-dinitroplatinum(IV), Found: C, 20·0; H, 1·6; Br, 26·5; N, 9·4. Calc.: C, 19·9; H, 1·4; Br, 26·3; N, 9·3. *af*-Dibromo-*bd*-dinitro-*ce*-bis(triethylphosphine)platinum(IV), Found: C, 21·2; H, 4·5; Br, 23·5; N, 4·0. Calc.: C, 21·1; H, 4·4; Br, 23·4; N, 4·1%].

The adduct ac-*dinitro*-bd-*bis(pyridine)platinum*(II)–*boron trifluoride.* The complex *cis*-$[Pt(py)_2(NO_2)_2]$ (0·3 g) was placed in a 100 ml beaker in a nitrogen atmosphere and boron trifluoride–ether added dropwise, the resulting mixture being stirred for 30 min. The surplus boron trifluoride–ether was allowed to evaporate and the grey *product* remaining was air-dried (yield 0·11 g) [Found: C, 21·0; H, 1·85; N, 9·8; F, 16·9. $C_{10}H_{10}B_2F_6N_4O_4Pt$ requires C, 20·65; H, 1·7; N, 9·6; F, 19·6% (see Discussion section)]. This procedure was not easily reproducible.

Sulphuric and acetic acids were prepared by a standard method.[3b] Only acetic acid which melted between 16·1 and 16·3 °C was used (a change in m.p. of 0·03 °C corresponds to 0·014% water present). The purified acetic acid was always completely transparent at wavelengths above 240 nm. Only sulphuric acid which froze between 10·35 and 10·37 °C was used.

I.r. spectra were carried out on KBr disc samples using a Perkin-Elmer 457 spectrophotometer.

Kinetic Measurements.—*Replacement of nitro-groups.* Aliquot portions of the reaction mixture were withdrawn at timed intervals and pipetted into Pyrex tubes which were already cooled in an acetone–solid carbon dioxide bath. After 1 or 2 min, the aliquot portions were diluted with several times their volume of water. At the end of a run, these were allowed to melt and the released ' nitrite ' estimated as described previously.[12]

Replacement of bromo-ligands. Aliquot portions of the reaction mixture were withdrawn, cooled, and diluted. Bromine present in the solutions was extracted with several portions of carbon tetrachloride and then estimated titrimetrically using potassium iodide and aqueous sodium thiosulphate solution.

Isolation of Products.—*Products of hydrolyses of the* af-*dibromo*-bc-*dinitro*-de-*bis(pyridine)*- *and* af-*dibromo*-bd-*dinitro*-ce-*bis(pyridine)-platinum*(IV) *complexes in aqueous sulphuric acid.* The complex (*ca.* 0·1 g) was dissolved in sulphuric acid (5 ml, 16·8M) at 25 °C and the reaction of removal of one nitro-group allowed to proceed for 7 half-lives. The solution was then cooled and carefully diluted to *ca.* 20 ml with water. As no precipitation occurred, potassium chloride was added and the solution was again cooled. A yellow *product* was filtered off, washed with

---

[8] J. F. Bunnett, *J. Amer. Chem. Soc.*, 1961, **83**, 4956.

[9] L. Zucker and L. P. Hammett, *J. Amer. Chem. Soc.*, 1939, **61**, 2791.

[10] A. D. Harris, R. Stewart, D. Hendrickson, and W. L. Jolly, *Inorg. Chem.*, 1967, **6**, 1052.

[11] P. J. Staples and A. Thompson, *J. Chem. Soc. (A)*, 1969, 1058.

[12] K. A. Pilkington and P. J. Staples, *J. Inorg. Nuclear Chem.*, 1967, **29**, 1029.

alcohol and ether, and dried (yield 0·04 g) (Found: C, 19·5; H, 1·9; Br, 25·1; Cl, 6·1; N, 6·7. $C_{10}H_{10}Br_2ClN_3O_2Pt$ requires C, 20·2; H, 1·7; Br, 26·8; Cl, 6·0; N, 7·1%).

Products of reaction of the adduct ac-*dinitro*-bd-*bis*-(*pyridine*)*platinum*(II)–*boron trifluoride*. The adduct (*ca.* 0·06 g) was dissolved in aqueous sulphuric acid (10 ml; 13·5M) at 25 °C and the reaction allowed to proceed; sets of such experiments were set up and run in parallel. At given times, *t*, the runs were quenched by cooling (acetone–solid carbon dioxide bath) and diluting to 50—60 ml with water. Solid potassium chloride was added and a cream or yellow precipitate was formed. This was filtered off, washed, and dried (yield 0·02—0·03 g). Products were analysed for C, H, Cl, F, and N; even at $t = 2$ and 5 min they contained virtually no fluorine and the analyses corresponded to mixtures of the complexes $[Pt(py)_2(NO_2)_2]$, $[Pt(py)_2NO_2Cl]$, and $[Pt(py)_2Cl_2]$, the proportions depending on the time of reaction. As many experiments as possible were undertaken at early reaction times. (The results are considered as evidence that the boron trifluoride molecules are displaced extremely quickly, *i.e.* before any appreciable amount of nitro-ligand is replaced.)

We thank Johnson, Matthey and Co., Ltd. for the loan of K_2PtCl_4 and the University of Bradford for a Research Scholarship (to D. H.).

[1/2260 *Received, 29th November,* 1971]