Complexes of Platinum(II) with 2,2′-Bipyrimidine: The Effect of Hydrogen Bonding on Intermetallic Interactions

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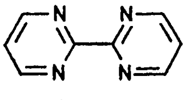
Platinum(II) complexes with 2,2′-bipyrimidine, $[PtX_2(bipym)]$ (X = CN, Cl, or SCN; $X_2 = C_2O_4$), $[Pt(bipym)_2][PtX_4]$ (X = Cl or CN), and $[Pt_2(NH_3)_4(bipym)][NO_3]_4$, have been synthesised and characterised. Intense absorption bands in the visible region assigned to metal–metal interactions are related to strong hydrogen bonding involving the unco-ordinated heterocyclic nitrogen atoms.

ALTHOUGH both 1 : 1 and 2 : 1 complexes of platinum(II) with 2,2′-bipyridine (bipy) have been well studied,[1,2] no detailed report has been made of analogous complexes with 2,2′-bipyrimidine (bipym). A $[PtCl_2(bipym)]$ complex has been mentioned recently;[3] no data or properties, however, are given. 2,2′-Bipyrimidine is potentially interesting for two reasons. It may act as a doubly bidentate bridging ligand forming oligonuclear complexes, but, when acting in terminal fashion, has two unco-ordinated imine nitrogen atoms available for hydrogen bonding. Since recent studies imply that hydrogen bonding between successive layers may play an important role in shortening interplanar spacings in columnar 'one-dimensional' platinum(II) complexes,[4-6] it is important to test ligands which may enhance this effect in attempting to design further systems.



RESULTS AND DISCUSSION

The 1 : 1 *Complexes*.—*(2,2′-Bipyrimidine)dicyanoplatinum*(II). The analogous 2,2′-bipyridine complex is known in two forms. The yellow monohydrate is converted into the red anhydrous form on heating or on washing with non-aqueous solvents.[1]

Prolonged reflux of $[Pt(CN)_4]^{2-}$ solutions in 1 mol dm^{-3} sulphuric acid in the presence of excess of 2,2′-bipyrimidine gives pale yellow crystals of $[Pt(CN)_2(bipym)]\cdot H_2O$. Rapid cooling of the solution yields a purple crystalline fibrous mass of $[Pt(CN)_2(bipym)]\cdot 1.5H_2O$. Both forms are stable in air and sparingly soluble in boiling water to give a very pale yellow solution. Recrystallisation invariably produces a mixture of both forms, fast cooling slightly favouring the purple, slow cooling the yellow hydrate.

Crystals of the monohydrate are monoclinic (a = 7.04, b = 17.77, c = 4.47 Å, β = 99.75°, space group Pc or $P2/c$). We have not succeeded in growing crystals of the purple form owing to their extremely fast growth in one direction. Recrystallisation from dimethylformamide (dmf) yields red needles of $[Pt(CN)_2(bipym)]\cdot$dmf which rapidly darken on exposure to water or moist air, probably owing to formation of a surface layer of the purple hydrate.

The i.r. spectra of the hydrates (Figure 1, Table 1) differ significantly only in the ν(OH) region where the yellow monohydrate exhibits two strong sharp bands at 3 555 and 3 510 cm^{-1}, characteristic of non-hydrogen-bonded lattice water. The purple hydrate, however, exhibits only one band in this region at 3 533 cm^{-1} together with four broader absorptions shifted to lower wavenumbers, characteristic of moderately strongly hydrogen-bonded water molecules. That the cyanide ligands do not participate in this hydrogen bonding to any significant extent is indicated by the similarity of the spectra of the hydrates in the ν(CN) region (Figure 2). The frequencies and relative intensities of the two main bands (as required for C_{2v} symmetry) remain unchanged in the presence of hydrogen bonding and a negligible broadening in their half-widths of only one wavenumber is noticed, whereas strongly hydrogen-bonded cyanide groups generally give rise to broadened absorptions at considerably higher (*ca.* 30—60 cm^{-1}) frequency.[7]

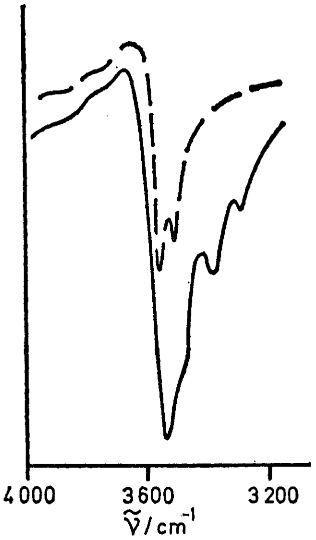


FIGURE 1 O–H Stretching vibration of $[Pt(CN)_2(bipym)]\cdot H_2O$ (— — —) and $[Pt(CN)_2(bipym)]\cdot 1.5H_2O$ (——)

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

[2] W. A. Little and R. Lorentz, *Inorg. Chim. Acta*, 1976, **18**, 273.

[3] U. T. Mueller-Westerhoff, *Adv. Chem. Ser.*, 1976, **150**, 31.

[4] J. M. Williams, J. L. Petersen, H. M. Gerdes, and S. W. Peterson, *Phys. Rev. Letters*, 1974, **33**, 1079.

[5] J. M. Williams, K. D. Keefer, D. M. Washecheck, and N. P. Enright, *Inorg. Chem.*, 1976, **15**, 2446.

[6] J. S. Miller and A. J. Epstein, *Progr. Inorg. Chem.*, 1976, **20**, 1.

[7] D. F. Evans, D. Jones, and G. Wilkinson, *J. Chem. Soc.*, 1964, 3164.

TABLE 1

Infrared spectra (600—4 000 cm^{-1}) of 2,2′-bipyrimidineplatinum(II) complexes as Nujol mulls

	ν(OH) + δ(HOH)	2,2′-Bipyrimidine modes	Others
$[Pt(CN)_2(bipym)]\cdot H_2O$ *	3 550ms, 3 510ms, 1 637s 1 600m	3 102w, 3 038w, 3 072s, 3 065w, 3 058 (sh), 1 582vs, 1 558m, 1 550m, 1 410vs, 1 250w, 1 225w, 1 215 (sh), 1 115w, 1 107m, 1 094w, 1 078w, 1 039w, 1 029m, 838w, 823ms, 812 (sh), 788w, 747s, 695mw, 673ms, 645w	2 146.7ms, 2 139vw, 2 135.7s [ν(CN)]
$[Pt(CN)_2(bipym)]\cdot 1.5H_2O$	3 533s, 3 480 (sh), 3 380m, 3 290w, 1 663w, 1 638ms, 1 623 (sh)	1 580vs, 1 550s, 1 409vs, 1 029m, 824ms, 748s, 673ms	2 210w, 2 150.3 (sh), 2 147.3s, 2 138.5w, 2 135.8s [ν(CN)]
$[PtCl_2(bipym)]$		1 583s, 1 555m, 1 404s, 1 027m, 816m, 737s, 675m	
$[PtCl_2(bipym)]\cdot 0.5H_2O$	3 520m,br, 3 460 (sh), 1 652m, 1 643m	1 583s, 1 553m, 1 404s, 1 028m, 817m, 737s, 674m	
$[Pt(SCN)_2(bipym)]$		1 582s, 1 548s, 1 403s, 1 033s, 809s, 738vs, 674s	2 100vs,br [ν(CN)]
$[Pt(C_2O_4)(bipym)]$		1 582s, 1 551m, 1 401vs, 1 034m, 808s, 745s, 679ms	1 714vs, 1 704vs, 1 683s, 1 664s [ν(CO)]
$[Pt(bipym)_2][PtCl_4]\cdot 2.5H_2O$	3 490m,br, 3 250vbr, 1 694m, 1 650s	1 583s, 1 552ms, 1 410s, 1 405s, 1 028m, 836m, 817m, 741s, 738s, 675ms	
$[Pt(bipym)_2][Pt(CN)_4]\cdot 2.5H_2O$	3 420s,vbr, 3 260br, 1 702s, 1 658s	1 586vs, 1 554ms, 1 411s, 1 032m, 821m, 742s, 678m	2 195m, 2 150 (sh), 2 130s [ν(CN)]
$[(H_3N)_2Pt(bipym)Pt(NH_3)_2][NO_3]_4\cdot 4H_2O$	3 420m, br, 1 645m	1 594m, 1 560 (sh), 1 403s, 824m	3 140s,br [ν(NH)], 1 370vs,br [δ(HNH)]

* Spectrum reported in full. All weak bands omitted for the remaining species.

A broad weak absorption is found at *ca.* 2 210 cm^{-1} for the purple hydrate, but is probably due to partial hydrolysis to hydrated $Pt(CN)_2$ during recrystallisation, this being more difficult to remove from the less crystalline purple form. Other minor ν(CN) splittings noted may be attributed to crystal effects.

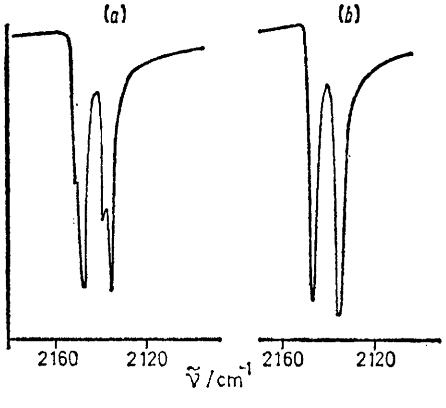

FIGURE 2 C–N Stretching vibration of $[Pt(CN)_2(bipym)]\cdot H_2O$ (*b*) and $[Pt(CN)_2(bipym)]\cdot 1.5H_2O$ (*a*)

Owing to the extremely low solubility of the complexes in most solvents their electronic spectra could not be recorded throughout the visible and u.v. region. Solution spectra at >280 nm have been measured for a few cases using dimethyl sulphoxide as solvent (Table 2). Poly(vinyl alcohol) foils have been used to record the visible spectra of solid complexes. Identical results were obtained using Nujol mulls. Only the purple hydrate shows an absorption band at long wavelength; the absorption maximum occurs at 600 nm (Figure 3 and Table 3).

TABLE 2

Solution spectra of bipyrimidineplatinum(II) complexes (band maxima in nm, absorption coefficient in dm^3 mol^{-1} cm^{-1} given in parentheses)

Complex	Solvent
$[PtCl_2(bipym)]$	dmso 380 (2 × 10^3), 394 (2.1 × 10^3)
$[Pt(bipym)_2]^{2+}$	dmso 370 (2.5 × 10^3), 395 (2.3 × 10^3), 480 (5.8 × 10^2)
$[(H_3N)_2Pt(bipym)Pt(NH_3)_2]^{4+}$	Water 250 (sh), 410 (sh)

TABLE 3

Low-energy bands (in nm) of bipyrimidineplatinum(II) complexes

Complex	
$[Pt(CN)_2(bipym)]\cdot 1.5H_2O$	600
$[PtCl_2(bipym)]\cdot 0.5H_2O$	700
$[Pt(bipym)_2][Pt(CN)_4]\cdot 2.5H_2O$	450 (sh), 580
$[Pt(bipym)_2][PtCl_4]\cdot 2.5H_2O$	550 (sh), 690

That some of the water present in $[Pt(CN)_2(bipym)]\cdot 1.5H_2O$ is playing a different role to that in the yellow $[Pt(CN)_2(bipym)]\cdot H_2O$ and $[Pt(CN)_2(bipy)]\cdot H_2O$ [1] species is obvious from these results. That it may be acting to decrease the separation between successive complexes in a linear column of $[Pt(CN)_2(bipym)]$ units (thus enhancing metal–metal interactions) is an attractive proposition tacitly supported by the strongly one-dimensional growth of the purple microcrystals and the intense low-energy absorption at 600 nm. In the absence of single-crystal data, however, such a conclusion must remain tentative.

(2,2′-*Bipyrimidine*)*dichloroplatinum*(II). Once again, two forms of the bipy analogue are known: one yellow, one red, both anhydrous.[1]

Slow addition of an aqueous bipyrimidine solution to hot aqueous $K_2[PtCl_4]$ precipitates dark green $[PtCl_2(bipym)]\cdot0.5H_2O$, which, when washed with acetone or ethanol or dried at 100 °C, yields the orange anhydrate irreversibly. Both are only very sparingly soluble in hot water. Recrystallisation from dmf yields long, red, dichroic crystals of $[PtCl_2(bipym)]\cdot$dmf. These lose dmf rapidly in air, and darken immediately when washed with water, probably owing to formation of a surface layer of the green hydrate.

The only significant differences between the i.r. spectra of the three forms are the occurrence of strong absorptions due to water or dmf. The extreme broadness of the ν(OH) bands again suggests the presence of hydrogen bonding in the hydrate.

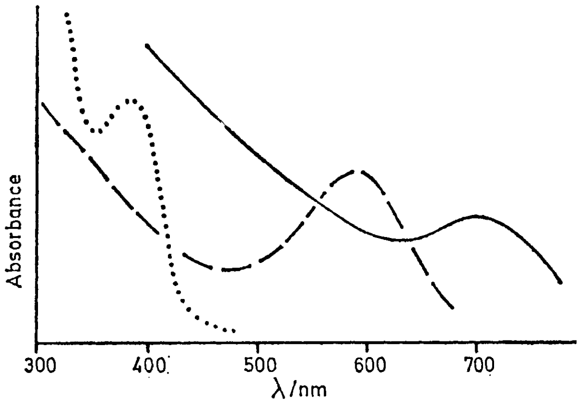

FIGURE 3 Electronic spectra of $[Pt(bipym)_2]^{2+}$ in dmso (· · · ·), $[Pt(CN)_2(bipym)]\cdot1.5H_2O$ (— — —), and $[Pt(bipym)_2][PtCl_4]\cdot2.5H_2O$ (——)

As found for the purple cyano-complex, the visible spectrum of the green hydrate is dominated by a low-energy absorption at 700 nm, this being the main difference from the spectra in solution and of the other crystalline forms (Table 3). Such low-energy bands have been assigned to charge-transfer interactions within the platinum spine of columnar square-planar units.[8] It seems, therefore, that these interactions are considerably intensified by the hydrogen bonding present in the hydrates of the cyano- and chloro-complexes.

Other 1 : 1 *complexes*. Yellow $[Pt(SCN)_2(bipym)]$ and brown $[Pt(C_2O_4)(bipym)]$ have also been prepared and characterised, each having apparently only the one form. The strong i.r. absorption at 856 cm^{-1} for the thiocyanato-complex, assigned to the ν(C–S) modes, is indicative of *S*-co-ordination.

Apart from absorption due to other ligands or to lattice water or dmf, the i.r. spectra of all the 1 : 1 bipym complexes are very similar. The strong pattern of absorptions at *ca.* 1 580, 1 550, 1 400—1 410, 1 030, 810—825, 740, and 675 cm^{-1} may thus be taken as being typical of a terminal bipyrimidineplatinum(II) group.

Worth noting is the large volume of recent work on reactions involving heterocyclic rings when co-ordinated to transition-metal ions, the most relevant being the evidence for covalent hydration of the bipy ring in solutions of $[Pt(CN)_2(bipy)]$ [9] (no direct evidence having been produced for a similar solid-state conversion). That covalent hydration plays no part in the different hydration states of the bipym complexes studied here is clearly shown by the effective invariance of the characteristic bipyrimidine i.r.-absorption pattern found for these complexes in the solid state, whereas strong perturbations indeed may reasonably be expected should the water add across a N=C bond. Similar arguments exclude the possibility of solid-state Reissert-type complexes [10] with cyanide added in the 3 position. Furthermore, these species in solution exhibit no temperature-dependent colour change, akin to that observed for the $[Pt(CN)_2(bipy)]$ system.[9] We conclude that, in all the reactions and measurements described here, the bipyrimidine entity remains intact.

The 1 : 2 *Complex Cation*.—Prolonged reflux of an aqueous suspension of $[PtCl_2(bipym)]$ in the presence of excess of bipyrimidine gives a red solution containing the $[Pt(bipym)_2]^{2+}$ ion. Addition of an aqueous solution of the appropriate anion produces intensely coloured precipitates of $[Pt(bipym)_2][PtCl_4]\cdot2.5H_2O$ (green) and $[Pt(bipym)_2][Pt(CN)_4]\cdot2.5H_2O$ (purple) which may be considered as analogues of Magnus' Green Salt $[Pt(NH_3)_4][PtCl_4]$. All these salts are insoluble in water or organic solvents.

The i.r. spectra of the two salts show absorptions characteristic of terminal bipym co-ordination and of moderately strongly hydrogen-bonded water. The spectrum of the $[Pt(CN)_4]^{2-}$ salt has a strong ν(CN) band at 2 130 cm^{-1}, with an additional moderately strong absorption at 2 190 cm^{-1}, attributed to participation of some of the cyanide groups in this hydrogen bonding.

As found previously for other analogues of $[Pt(NH_3)_4][PtCl_4]$, the main feature of the visible spectra is a strong band at long wavelength (Figure 3). The value of 580 nm for the $[Pt(CN)_4]^{2-}$ salt compares with 485 nm for the same salt of $[Pt(bipy)_2]^{2+}$.[2]

Bridged Species.—2,2′-Bipyrimidine has been found reluctant to form a doubly bidentate bridge between two platinum(II) ions. That this may be for steric reasons is indicated by the structure of $[PtCl_2(bipy)]$,[11] which shows a co-ordinated N · · · N ' bite ' of 2.55 Å, giving rise to a C(6) · · · C(6′) bite of 3.00 Å.

Reflux of an aqueous solution of the $[Pt(NH_3)_2(OH_2)_2]^{2+}$ ion with the stoicheiometric amount of bipyrimidine leads to the formation of a brown solution containing the $[(H_3N)_2Pt(bipym)Pt(NH_3)_2]^{4+}$ ion, which has been isolated as the nitrate and perchlorate salts. These are very soluble in water, but difficult to recrystallise, readily forming oils. In the presence of moderately

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[8] T. W. Thomas and A. E. Underhill, *Chem. Soc. Rev.*, 1972, **1**, 99.

[9] R. D. Gillard, L. A. P. Kane-Maguire, and P. A. Williams, *Transition Metal Chem.*, 1976, **1**, 247.

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

[11] R. S. Osborn and D. Rogers, *J.C.S. Dalton*, 1974, 1002.

strong potential ligands, decomposition quickly sets in.

The i.r. pattern of the bridging bipyrimidine is quite different from that found for the terminal ligand. The absorptions are weaker and somewhat broader, the main features occurring at *ca.* 1 590, 1 560, 1 405—1 425, and 830—840 cm^{-1} (Table 1). Particularly noticeable is the disappearance of the intense absorption at 740 and 675 cm^{-1}.

EXPERIMENTAL

Analytical data are given in Table 4. 2,2′-Bipyrimidine was prepared according to a published procedure [12] and purchased from Lancaster Synthesis Ltd. Purification of the ligand was accomplished by vacuum sublimation.

TABLE 4

Analytical data (%) for 2,2′-bipyrimidineplatinum(II) complexes

Complex	Found C	Found H	Found N	Found Cl or S	Calc. C	Calc. H	Calc. N	Calc. Cl or S
$[Pt(CN)_2(bipym)]\cdot H_2O$	28.4	2.0	19.8		28.4	1.9	19.9	
$[Pt(CN)_2(bipym)]\cdot 1.5H_2O$	27.7	1.9	19.3		27.8	2.1	19.4	
$[Pt(CN)_2(bipym)]\cdot dmf$	32.7	2.7	20.6		32.6	2.7	20.5	
$[PtCl_2(bipym)]$	22.8	1.4	13.6	16.6	22.7	1.4	13.6	16.7
$[PtCl_2(bipym)]\cdot 0.5H_2O$	22.2	1.5	12.9	16.0	22.2	1.6	12.9	16.4
$[PtCl_2(bipym)]\cdot dmf$	26.8	2.5	14.2	14.3	26.6	2.6	14.1	14.3
$[Pt(SCN)_2(bipym)]$	25.4	1.4	17.7	13.3	25.6	1.3	17.9	13.6
$[Pt(C_2O_4)(bipym)]$	27.6	1.8	12.7		27.2	1.4	12.7	
$[Pt(bipym)_2][PtCl_4]\cdot 2.5H_2O$	21.5	1.7	12.5	15.8	21.5	1.9	12.5	15.9
$[Pt(bipym)_2][Pt(CN)_4]\cdot 2.5H_2O$	28.2	2.0	19.5		28.1	2.0	19.6	
$[(H_3N)_2Pt(bipym)Pt(NH_3)_2][NO_3]_4\cdot 4H_2O$	10.1	2.5	17.9		10.3	2.8	17.9	

(2,2′-*Bipyrimidine*)*dicyanoplatinum*(II) *Monohydrate*, $[Pt(CN)_2(bipym)]\cdot H_2O$.—The salt $K_2[Pt(CN)_4]\cdot 3H_2O$ (3 g) was dissolved in 1 mol dm^{-3} sulphuric acid (20 cm^3) and heated under reflux with 2,2′-bipyrimidine (2 g) for 6 h. The yellow crystals were filtered off while hot, washed with cold water, and recrystallised from boiling water by slow (48 h) cooling to room temperature.

(2,2′-*Bipyrimidine*)*dicyanoplatinum*(II) *Sesquihydrate*, $[Pt(CN)_2(bipym)]\cdot 1.5H_2O$.—A saturated solution of the monohydrate in boiling water was filtered and cooled rapidly to room temperature and left to stand for 20 min. The voluminous purple precipitate was filtered off and washed with ice-cold water.

(2,2′-*Bipyrimidine*)*dicyanoplatinum*(II)–NN-*Dimethylformamide* (1/1), $[Pt(CN)_2(bipym)]\cdot dmf$.—A saturated solution of $[Pt(CN)_2(bipym)]$ in dmf at 100 °C was filtered rapidly and allowed to cool slowly to 0 °C. The red crystals were filtered off, washed with ice-cold dmf, and dried in a current of dry air.

(2,2′-*Bipyrimidine*)*dichloroplatinum*(II) *Hemihydrate*, $[PtCl_2(bipym)]\cdot 0.5H_2O$.—To a hot (*ca.* 50 °C) solution of $[NH_4]_2[PtCl_4]$ (0.4 g) in water (50 cm^3) was added, dropwise, a concentrated aqueous solution of bipym (0.17 g) over a period of 5 min. The dark green precipitate was filtered off, washed with water, and dried in air.

(2,2′-*Bipyrimidine*)*dichloroplatinum*(II), $[PtCl_2(bipym)]$.—The orange anhydrous complex was prepared by drying the hemihydrate either at 100 °C for several hours, or by refluxing in 95% ethanol for *ca.* 1 h.

(2,2′-*Bipyrimidine*)*dichloroplatinum*(II)–NN-*Dimethylformamide* (1/1), $[PtCl_2(bipym)]\cdot dmf$.—This complex was made similarly to its dicyano-analogue.

(2,2′-*Bipyrimidine*)*dithiocyanatoplatinum*(II), $[Pt(SCN)_2(bipym)]$.—2,2′-Bipyrimidine (0.16 g) was stirred in solution with $K_2[Pt(SCN)_4]$ (0.5 g) in water (25 cm^3) at 60 °C for 30 min. The yellow precipitate was filtered off when cold, washed with water, recrystallised from dmf, and dried in air.

(2,2′-*Bipyrimidine*)*oxalatoplatinum*(II), $[Pt(C_2O_4)(bipym)]$.—A solution of $K_2[Pt(C_2O_4)_2]\cdot 2H_2O$ (0.5 g) in water (50 cm^3) was heated under reflux with bipym (0.4 g) for 6 h. The brown crystals were filtered off when cold and washed with water.

Bis(2,2′-*bipyrimidine*)*platinum*(II) *Tetrachloroplatinate*(II) *Hydrate*, $[Pt(bipym)_2][PtCl_4]\cdot 2.5H_2O$.—The complex $[PtCl_2(bipym)]$ (1.0 g) was heated under reflux with bipym (1.5 g) in water (100 cm^3) for 3 h. The red solution was filtered when cold and an aqueous solution of $[NH_4]_2[PtCl_4]$ (0.88 g) was added. The green precipitate was filtered off, washed with water and methanol, and dried in air. The hydrated $[Pt(CN)_4]^{2-}$ salt was prepared similarly.

μ-2,2′-*Bipyrimidine-bis*[*diammineplatinum*(II)] *Tetranitrate Tetrahydrate*, $[(H_3N)_2Pt(bipym)Pt(NH_3)_2][NO_3]_4\cdot 4H_2O$.—The complex *cis*-$[PtCl_2(NH_3)_2]$ (1.0 g) was heated under reflux with a solution of $Ag[NO_3]$ (1.132 g) in water (50 cm^3) in the dark. The solution was filtered while hot and the residue was washed with water. The filtrate and washings were centrifuged for 1 h at high speed then decanted. 2,2′-Bipyrimidine (0.263 g) was added and the solution evaporated to dryness on a steam-bath. The residue was extracted with water and filtered. The brown filtrate was again evaporated to dryness and the product washed with methanol and dried in air. The perchlorate salt was made similarly.

Infrared spectra were recorded from 4 000 to 600 cm^{-1} on a Perkin-Elmer 580 instrument as Nujol mulls between potassium bromide plates; electronic spectra as Nujol mulls between quartz plates and poly(vinyl alcohol) foils, and solution spectra in quartz cells, were obtained on a Cary 17 spectrophotometer. Analyses were by the microanalytical laboratory of Ciba-Geigy, Basle.

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[12] D. D. Bly and M. G. Mellon, *J. Org. Chem.*, 1962, **27**, 2945.