# Spectroscopic Studies on some Compounds (including Dimorphic Solids) of Platinum(II) with 2,2′-Bipyridyl and Its Analogues

By **E. Bielli**,† **P. M. Gidney**, **R. D. Gillard**,* and **B. T. Heaton**, Inorganic Chemical Laboratories, University of Kent at Canterbury, Canterbury, Kent.

The structure and spectroscopic properties of the red form of $[Pt(bipy)Cl_2]$ (bipy = 2,2′-bipyridyl) are discussed. Some novel cases of dimorphism are reported. Preparation of the new complexes $[Pt(LL)Cl_2]$ (LL = 6,6′-$Me_2$-bipy, 5,5′-$Me_2$bipy, 4,4′-$Me_2$bipy), $[Pt(LL)_2]^{2+}$ (LL = 5,5′-$Me_2$bipy, 4,4′-$Me_2$bipy), $[Pt(bipy)(py)_2]^{2+}$, $[Pt(bipy)(NO_3)(OH)]$, and $[Pt(bipy)(H_2O)(OH)]^+$ (py = pyridine) are described and $^1H$ n.m.r. assignments of $[Pt(bipy)(OH)_2]$ and $[Pt(bipy)_2]^{2+}$ have been made by comparison with the corresponding methyl-substituted 2,2′-bipyridyl derivatives. At pH *ca.* 6, the 220 MHz $^1H$ m.r. spectrum of $[Pt(bipy)_2]^{2+}$ is consistent with a square planar or tetrahedrally distorted structure.

THE complex compounds of palladium(II) and platinum(II) occupied a central position in the development of co-ordination chemistry, and much of their behaviour had been clearly charted by the end of the 1930's. The discovery[1] that even the simplest such compounds, *e.g. cis*-$[Pt(NH_3)_2Cl_2]$, may interfere specifically with cell-division (and the consequent possibility of development in the therapy of cancer) has revived interest in them.

Particular effort attaches to the means whereby such complexes may bind, link, or otherwise alter biopolymers. One suggestion involved physical interaction through hydrogen bonding between the intact dichloro-complex and the biopolymer, perhaps giving an ordered structure of platinum atoms. This suggestion[2a] was based on the known hydrogen-bonding propensity of *cis*-$[Pt(NH_3)_2Cl_2]$,[2b] which forms a red black crystalline 1 : 1 adduct with sulphuric acid, held together by hydrogen bonds, and with Pt–Pt of 3·45 Å, and implicit in the formation[2c] of other black di-ammine platinum(II) complexes.

In considering such theories of interactions between intact platinum(II) complexes and biopolymers, the detailed mode of operation of 'residual affinity' is at issue. Such effects are most easily found in solid-state adducts, solvates, and polymorphs, since the alternative interactions responsible for holding together the almost iso-ergonic lattices are of exactly the type envisaged in interactions of monomeric complex compounds with biopolymers.

Isomers of composition $[ML_2X_2]$ (M = Pd or Pt, L = a nitrogenous ligand such as $NH_3$, py, $\frac{1}{2}$ bipy, *etc.*, X = Br or Cl: *cf.* Table 1) may be divided into (i) ionisation isomers, *e.g.* $[ML_4][MX_4]$, $[ML_3X][MLX_3]$, $[ML_4][MLX_3]_2$, and $[ML_3X]_2[MX_4]$; (ii) monomeric (*cis*- and *trans*-geometric) isomers. Apparent isomerism may also arise from (iii) mixed crystal formation by two quite distinct compounds; thus, the so-called '$\gamma$-$[Pt(NH_3)_2Cl_2]$,' despite its individual *X*-ray powder picture,[3] was shown[4] to arise by co-crystallizing about 20% of the *cis*- with the *trans*-isomer, or (iv) twinning, as found[5] with a novel red crystalline form of *trans*-$[Pd(NH_3)_2Cl_2]$ and *trans*-$[Pd(NH_3)_2I_2]$.

TABLE 1

Some cases of dimorphism (yellow and red)[b] in non-electrolytes of the stoicheiometry $[ML_2X_2]$

| M | $L_2$ | X | Ref. |
|---|---|---|---|
| Pd | $2NH_3$ | Cl | 5 |
| | $2NH_3$ | I | 5 |
| Pt | $2NH_3$ | Br | 13 |
| | $NH_3$,py | Cl | *c* |
| | Bipy | Cl[a] | 10 |
| | $2(PPh_3)$ | I | *d* |
| | $2(OPPh_3)$ | I | *d* |

[a] It is probable that the red compound (Found: C, 30·95; H, 2·3; Pt, 43·3%) made[9] by treating yellow $[Pt(bipy)Cl_2]$ with an excess of 2,2′-bipyridyl in molten phenol was in fact the red dimorph (Calc. C, 28·4; H, 1·9; Pt, 46·2%). [b] P. E. Fanwick and D. S. Martin (*Inorg. Chem.*, 1973, **12**, 24) have shown that the red form of Cossa's salt (normally yellow) described by S. M. Jørgensen (*Z. anorg. Chem.*, 1900, **24**, 153) is not a dimorph, but contains some platinum(IV). [c] H. D. K. Drew, *J. Chem. Soc.*, 1932, 1013. [d] L. Malatesta and C. Cariello, *J. Chem. Soc.*, 1958, 2323.

Dimorphism is known among ionic compounds of type (i): $[Pt(NH_3)_4][PtCl_4]$ exists as the well-known green Magnus' salt and a red modification, discovered[6] by Jørgensen and Sorensen.‡ There is also apparent dimorphism associated with changes of solvation, as in the case[7,8] $[Pt(bipy)_2]I_2,2H_2O$ (red) $\rightleftharpoons$ $[Pt(bipy)_2]I_2$ (black) + $2H_2O$.

---

* *Present address:* Dept. of Chemistry, University College, P.O. Box 78, Cardiff, CF1 1XL.

† On leave from Istituto di Chimica Generale ed Inorganica, Universita di Milano.

‡ Morgan and Burstall obtained[7] a brown compound, supposedly a form of $[Pt(bipy)_2][PtCl_4]$ (required: C, 28·4; H, 1·9; N, 6·6; Cl, 16·8%) by boiling an aqueous solution of $K_2[PtCl_4]$ with 2,2′-bipyridyl. Although an attempt to repeat their preparation gave a brown product (Found: C, 25·2; H, 2·2; N, 5·9; Cl, 17·0%), this had an i.r. absorption at 3500 $cm^{-1}$ and was, from its *X*-ray powder photograph, a mixture of yellow $[Pt(bipy)_2][PtCl_4]$ and yellow $[Pt(bipy)Cl_2]$ (A); other lines were unidentified. However, we once obtained a nicely crystalline brown form of $[Pt(bipy)_2][ClO_4]_2$, discussed later as (H).

[1] B. Rosenberg, *Platinum Metals Rev.*, 1971, **15**, 42.

[2] (*a*) R. D. Gillard, Contribution at Conference on Platinum and Cancer Chemotherapy, Michigan State Univ., East Lansing, Sept., 1970; (*b*) R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 1964, 2835; (*c*) K. A. Jensen, *Z. anorg. Chem.*, 1936, **229**, 250.

[3] H. D. K. Drew, F. W. Pinkard, W. Wardlaw, and E. G. Cox, *J. Chem. Soc.*, 1932, 988.

[4] F. Rosenblatt and A. Schleede, *Chem. Ber.*, 1933, **66**, 472.

[5] F. G. Mann, D. Crowfoot, D. C. Gattiker, and N. Wooster, *J. Chem. Soc.*, 1935, 1642.

[6] S. M. Jørgensen and S. P. L. Sorensen, *Z. anorg. Chem.*, 1906, **48**, 441.

[7] G. T. Morgan and F. H. Burstall, 'Inorganic Chemistry: A Survey of Modern Developments,' Heffers, Cambridge, 1936, p. 251.

[8] S. E. Livingstone and B. Wheelahan, *Austral. J. Chem.*, 1964, **17**, 219.

Complexes of 2,2′-bipyridyl (bipy) and 1,10-phenanthroline (phen) with platinum(II) were first prepared[9,10] in the 1930's. We have re-examined and extended some of that work. Here, we describe a few types of dimorphism in complexes of platinum(II) and report the properties of the red form[10] of $[Pt(bipy)Cl_2]$ (its *X*-ray crystal structure being discussed in a following paper),[11] some novel cases of dimorphism in $Pt(LL)X_2$ and the nature of the ion $[Pt(bipy)_2]^{2+}$ (in particular its $^1$H n.m.r. spectrum). To help with $^1$H n.m.r. assignments, complexes containing methyl-substituted 2,2-bipyridyls have been made, and some new complexes (from various acidifications of $[Pt(bipy)(OH)_2]$) are also described.

*Red Dichloro-2,2′-bipyridylplatinum*(II).—Two modifications of $[Pt(bipy)Cl_2]$ are known, one, (A), yellow, the other, (B), red. We find that they are both diamagnetic. As Morgan and Burstall said[7] in 1936, it was ' uncertain whether the two compounds are isomeric or whether they are dimorphous varieties of the same chemical entity.' Yellow is the colour expected for a *cis*-$[PtN_2Cl_2]$ chromophore, and (A) is thought to have a simple monomeric square structure. (The mass spectrum of ' $[Pt(bipy)Cl_2]$ ' —almost certainly yellow (A): (B) is not easy to come by —was recently reported[12] and shows the molecular ion.) The nature of (B) was less clear: * the details of the structure have emerged from a study[11] by *X*-ray diffraction; monomeric *cis*-$[Pt(bipy)Cl_2]$ molecules are arranged in a columnar structure with an inter-planar distance of 340 pm.

The original preparation of (B) involved[10] reaction of $[Pt(bipy)(en)]^{2+}$ with hot hydrochloric acid (12M).† We find that the reaction of either $[Pt(bipy)(py)_2]^{2+}$ or $[Pt(bipy)(NH_3)_2]^{2+}$ with hot hydrochloric acid (12M) also gives (B) whereas $[Pt(bipy)_2]^{2+}$ gives (A). Morgan and Burstall also found[4] that recrystallisation of (A) from hot pyridine gave (B). Since the chloride ligands in $[Pt(bipy)Cl_2]$ are readily replaced by pyridine (see Experimental section), this preparation probably involves the reaction of $[Pt(bipy)(py)_2]^{2+}$ with chloride and is thus similar to the above preparative routes to (B), which all involve the displacement of nitrogenous ligands by chloride. Attempts to prepare red forms of the related complexes $[Pt(bipy)X_2]$ (X = Br, I), $[Pt(phen)Cl_2]$, and $[Pd(bipy)Cl_2]$ were unsuccessful.‡

The electronic reflectance spectra of (A) and (B) (Table 2) are very similar except for the appearance of a band at 520 nm in (B). The acicular crystals of B exhibit marked dichroism, appearing deep red when the electric vector of the light is parallel to the *c*-axis (needle-axis) and yellow when it is perpendicular. The 520 nm band, which causes the red colour of (B), is polarised along the needle axis, that is, perpendicular to the molecular planes. Similar behaviour[15-18] is found in crystals of the bisdimethylglyoximato-complexes of nickel(II), palladium(II), and platinum(II), and in green $[Pt(NH_3)_4][PtCl_4]$, which also contain[19-22] square-planar molecules stacked in columns. However, dichroic properties of this type cannot[23] be taken as conclusive evidence for a columnar structure.

TABLE 2

Visible and u.v. absorption spectra for platinum(II) complexes with 2,2′-bipyridyl: $\lambda_{max.}$ (nm) and $\varepsilon$ ($cm^{-1}$ l $mol^{-1}$)

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Yellow $[Pt(bipy)Cl_2]$ (A)[a] | | 478w | | 446vw, sh | 391s | 345sh | 323s | 312sh | | | |
| Red $[Pt(bipy)Cl_2]$ (B)[a] | 520m, br | 478w | 458w, sh | 444w, sh | 393s | 345m, br | 325s | 313sh | | | |
| (A)[b] or (B)[b] | | 476<br>(50) | 450<br>(100) | | 398<br>(3,100) | 377sh<br>(2,000) | 324<br>(5,200) | 312<br>(5,200) | 285<br>(18,000) | 275sh<br>(15,000) | 255<br>(11,000) |
| $[Pt(bipy)(OH)_2],3H_2O$[c] | | | | | | 375<br>(2,900) | 322<br>(7,400) | 309<br>(6,500) | | 271<br>(19,000) | 249<br>(12,000) |
| $[Pt(bipy)(H_2O)(OH)]^+$[d] | | | | | | 350sh<br>(1,800) | 319<br>(12,300) | 306<br>(9,600) | | | 247<br>(19,000) |
| $[Pt(bipy)(NO_3)_2],2H_2O$[e] | | | | | | 350sh<br>(6,000) | 320<br>(21,000) | 312sh<br>(19,000) | | | 240<br>(33,000) |

w = weak, m = medium, s = strong, sh = shoulder, br = broad, v = very.

[a] Reflectance spectrum. [b] The spectra are identical in chloroform solution: removal of solvent from either solution gives (A). This spectrum (in $CHCl_3$) was reported by L. A. Rossiello and C. Furlani, *Ricerca sci.*, 1965, **8**, 1416. [c] In aqueous sodium hydroxide solution (pH 8). [d] A solution of $[Pt(bipy)(OH)_2],3H_2O$ in aqueous perchloric acid (pH 4). [e] In aqueous solution, equilibrated with carbon dioxide (pH *ca.* 6). No significant change occurs when perchloric acid is added to give pH 1.

The far-i.r. spectrum of (A), as expected, shows two strong bands due to the symmetric and asymmetric

---

* Its mass spectrum also shows the molecule ion.

† en = ethane-1,2-diamine.

‡ However, red and yellow *cis*-$[Pt(NH_3)_2Br_2]$ have recently been discussed:[13] the red form may have a columnar structure like (B), or this system may resemble that of $[Pd(NH_3)_2Cl_2]$, which was shown[14] to exist as a yellow monomer and a red isomer, $[Pd(NH_3)_4][PdCl_4]$.

[9] F. Rosenblatt and A. Schleede, *Annalen*, 1933, **505**, 51.

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

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

[12] P. Haake and S. H. Mastin, *J. Amer. Chem. Soc.*, 1971, **93**, 6823.

[13] V. A. Palkin, N. N. Kuz'mina, V. E. Gorbunov, and O. N. Evstaf'eva, *Zhur. neorg. Khim.*, 1972, **17**, 556 (*Russ. J. Inorg. Chem.*, 1972, **17**, 290).

[14] H. D. K. Drew, F. W. Pinkard, G. H. Preston, and W. Wardlaw, *J. Chem. Soc.*, 1932, 1895.

[15] S. Yamada and R. Tsuchida, *J. Amer. Chem. Soc.*, 1953, **75**, 6351.

[16] C. V. Banks and D. W. Barnum, *J. Amer. Chem. Soc.*, 1958, **80**, 4767.

[17] S. Yamada, *J. Amer. Chem. Soc.*, 1951, **73**, 1579.

[18] P. Day, A. F. Orchard, A. J. Thomson, and R. J. P. Williams, *J. Chem. Phys.*, 1965, **42**, 1973.

[19] L. E. Godycki and R. E. Rundle, *Acta. Cryst.*, 1953, **6**, 487.

[20] D. E. Williams, G. Wohlauer, and R. E. Rundle, *J. Amer. Chem. Soc.*, 1959, **81**, 755.

[21] E. Frasson, C. Panattoni, and R. Zannetti, *Acta. Cryst.*, 1959, **12**, 1027

[22] M. Atoji, J. W. Richardson, and R. E. Rundle, *J. Amer. Chem. Soc.*, 1957, **79**, 3017.

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

metal–chlorine stretching modes which have been variously reported at[24] 357, 350 and[25] 351, 338 cm$^{-1}$. We favour the latter values since we find two strong bands at 348 and 335 cm$^{-1}$ which we assign to $\nu$(Pt–Cl). Our spectrum was calibrated against water vapour and the constant difference between our values and Walton's[25] may arise simply from an error in calibration. We find no evidence for a strong band in the region 357 cm$^{-1}$ as recently reported.[24] $[Pd(bipy)Cl_2]$, Isomorphous with (A), also shows two strong bands at 355 and 343 cm$^{-1}$. However, the far-i.r. spectrum of (B), instead of having two absorptions in the metal–chlorine stretching region, shows only one strong band at 335 cm$^{-1}$ and is thus similar to that[26] of *cis*-$[Pt(NH_3)_2Cl_2]$, which also shows only one band due to $\nu$(Pt–Cl).

The isomeric complex salt, $[Pt(bipy)_2][PtCl_4]$, is clearly distinguished from (A) and (B) by comparing their far-i.r. spectra. The position of $\nu$(Pt–Cl) in the tetrachloroplatinate(II) anion is known to depend on the cation and for salts with $Rb^+$, $Cs^+$, and $[Pt(NH_3)_4]^{2+}$ is found[27] at 320, 316, and 310 cm$^{-1}$ respectively. The complex, $[Pt(bipy)_2][PtCl_4]$, shows a strong band at 313 cm$^{-1}$ due to $\nu$(Pt–Cl) and neither (A) nor (B) show bands in this region.

The i.r. spectra (4000—400 cm$^{-1}$, Table I) * of (A) and (B) are distinctly different: they are also different from the i.r. spectrum of the related complex, $[Pt(bipy)Br_2]$, which rather surprisingly is not isomorphous (*cf.* Table II) with (A). This is to be contrasted with polymorphism in *cis*-$[Rh(phen)_2X_2]X, xH_2O$ ($X = Cl$ or Br), which has[28] little effect on the i.r. spectrum (4000—400 cm$^{-1}$). The i.r. spectra of (A) and of $[Pd(bipy)Cl_2]$ are almost identical in this region.

*Some Novel Dichroisms.*—Rosenblatt and Schleede mentioned[3] that dicyano-2,2′-bipyridyl-platinum(II) could be obtained in a yellow or a red form depending on conditions. We have verified this, using the displacement (1) at room temperature. The product is yellow

$$[Pt(bipy)(en)][ClO_4]_2 + 2KCN \longrightarrow [Pt(bipy)(CN)_2] + 2KClO_4 + en \quad (1)$$

(C), but slowly becomes red (D) when left in dry air, or more rapidly on washing with any solvent other than water, or on heating, either alone, or suspended in water. In the last case, the red form obtained reverts to yellow on cooling. The change of colour in the solid state is reversible. The i.r. spectra of (C) and (D) are similar but

$$\underset{\text{yellow (C)}}{[Pt(bipy)(CN)_2]H_2O} \rightleftharpoons \underset{\text{red (D)}}{[Pt(bipy)(CN)_2]} + H_2O$$

distinct (see Table I). In particular, in the $-C{\equiv}N$ stretching region, although both forms have a doublet at 2140, 2131, the relative intensities ($I$) differ. For (C), $2140(I) < 2131(I)$, whereas for (D), $2140(I) > 2131(I)$. Apart from bands arising from water, there are few other distinctions. [The absorption at 1170 cm$^{-1}$ is more intense for (D) than for (C).] The $X$-ray powder photographs are, however, clearly different (Table II).

A similar dependence of colour on the vapour pressure of water is shown in the new isomeric salt $[Pt(bipy)_2][Pt(CN)_4]$, made by double decomposition. Again, the water-dependent equilibrium is reversible. The i.r.

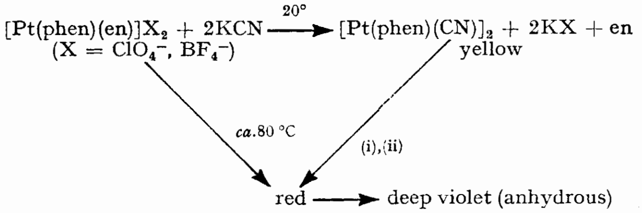
$$\underset{\text{yellow (E)}}{[Pt(bipy)_2][Pt(CN)_4],xH_2O} \rightleftharpoons \underset{\text{red (F)}}{[Pt(bipy)_2][Pt(CN)_4]} + xH_2O$$

(from analytical compositions, $3 < x < 4$)

spectra in the CN stretching region distinguish (E) (with a single band at 2135 cm$^{-1}$) and (F) (with a doublet at 2123, 2115) from each other and from (C) and (D).

Apparent dimorphism also occurred in the salt $[Pt(bipy)_2][ClO_4]_2$. This, crystallized from neutral solution, is yellow (G) but on one occasion crystallization from alkaline solution gave beautiful light-brown crystals, (H), which also have the stoicheiometry $[Pt(bipy)_2][ClO_4]_2$. Although, so far, attempts at repetition have failed, (H) is almost certainly a genuine dimorph of (G). They are not isomorphous (Table III), and their i.r. spectra differ. While neither shows absorption due to O–H, and both have, in the region where absorption occurs due to perchlorate, the bands of the ionic form only, the brown (H) shows a distinct splitting of the band occurring at 778 cm$^{-1}$ in yellow (G) (out-of-plane CH bending).

Apparent polymorphs of varying colours also exist for the new compound dicyano-1,10-phenanthrolineplatinum(II), whose preparation and interconversions are given in the Scheme. The anhydrous deep violet form shows 2 absorptions in the C≡N stretching region at 2139 and 2128 cm$^{-1}$.



(i) Dry in air (ii) Anhydrous organic solvents

All these colour changes are strongly reminiscent of those observed (particularly with protic acids) by Schilt for his compounds[29] such as $[Fe(phen)_2(CN)_2]$, where

---

* Tables I, II, and III are deposited as a Supplementary publication (SUP No. 21100, 16 pp.). See Notice to Authors No. 7, *J.C.S. Dalton*, 1973, Index issue for details of the Supplementary publication scheme.

[24] J. S. Strukl and J. L. Walter, *Spectrochim. Acta.*, 1971, **27A**, 223.

[25] R. A. Walton, *Canad. J. Chem.*, 1966, **44**, 1480.

[26] D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J. Chem. Soc.*, 1964, 734.

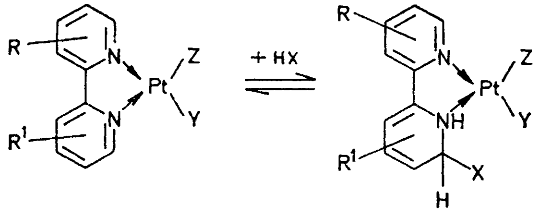
[27] D. M. Adams, 'Metal–Ligand and Related Vibrations,' 1967, p. 60.

[28] J. G. Gibson and E. D. McKenzie, *J. Chem. Soc.* (*A*), 1969, 2637.

[29] A. A. Schilt, *J. Amer. Chem. Soc.*, 1962, **82**, 3000; 1962, **82**, 5779; 1963, **85**, 904.

there is some evidence for equilibria involving protonation of the cyano-groups. In a similar way, we find that, at room temperature, with the vapours of HF, $H_2O$, $H_2S$ (but not HCl or $NH_3$), the red-form (D) of $[Pt(bipy)(CN)_2]$ becomes yellow, the rate of conversion being HF (apparently instantaneous) $\gg H_2O > H_2S$. With liquids, water brings about the colour change rapidly, hydrogen chloride in a few minutes, and liquid ammonia not at all.

All these processes are reversible. Further work is planned on these novel apparent dimorphisms, with particular attention to the possibility of equilibria involving covalent addition of water or hydrogen cyanide to the pyridine rings, as shown in (2) and as we found earlier[30] for $[Pt(bipy)_2]^{2+}$ and some analogues.



(2)

*Some New Complexes of Platinum*(II) *containing* 2,2′-*Bipyridyl or Substituted* 2,2′-*Bipyridyl*.—While studying the reversible spectroscopic changes of $[Pt(bipy)_2]^{2+}$ with pH, discussed elsewhere, it became necessary to prepare $[Pt(bipy)(OH)_2]$, so that it could be eliminated as a possible product. Treatment of $[Pt(bipy)Cl_2]$ with aqueous sodium hydroxide, followed by removal of chloride and concentration (at pH *ca*. 14) gives $[Pt(bipy)(OH)_2],3H_2O$ as orange-yellow crystals. This dihydroxo-complex has not previously been isolated although it had been prepared in solution.[4,31]

The electronic spectrum of an alkaline solution of $[Pt(bipy)(OH)_2]$ shows large changes upon acidification; the spectrum then depends on the acid used. Thus hydrochloric and nitric acids give (at pH *ca*. 1) the dichloro- and dinitrato-complex respectively. The latter complex, previously obtained[4] by Morgan and Burstall, shows strong broad bands in the i.r. spectrum at 1530, 1285, 1270, and 960 $cm^{-1}$, characteristic[32] of nitrate co-ordinated to a metal; ionic nitrate shows[33] strong absorptions at *ca*. 1400 and 830 $cm^{-1}$. Acidification (to pH *ca*. 4) of the dihydroxo-complex with nitric acid gives the new complex, $[Pt(bipy)(NO_3)(OH)]$. Treatment of the dihydroxo-complex with tetrafluoroboric acid (to pH *ca*. 2) results in the formation of $[Pt(bipy)(H_2O)(OH)][BF_4]$ whereas addition of perchloric acid (to give pH *ca*. 1) gives a product which appears to be a mixture of salts of the diaqua- and hydroxo-aqua-complexes. The i.r. spectrum of the latter product shows none of the bands characteristic[34,35] of co-ordinated perchlorate groups.

These results suggest that $[Pt(bipy)(OH_2)_2]^{2+}$ is a strong acid. The analogous $[Pd(phen)(OH_2)_2]^{2+}$ has recently been prepared[36] although its $pK_a$ is not yet available.

Acidification of $[Pt(bipy)(OH)_2]$ with perchloric or tetrafluoroboric acid to pH *ca*. 2 produces changes in the electronic spectrum due to the equilibrium (2). The

$$[Pt(bipy)(OH)_2] \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} [Pt(bipy)(OH_2)(OH)]^+ \quad (2)$$

lowest-energy band undergoes quite large shifts to higher energy and it may be that this band, like that[37] of $[Pt(bipy)Cl_2]$, is due to a metal to 2,2′-bipyridyl charge-transfer (MLCT) transition. Further support for this assignment comes from the similar behaviour observed[29] for $[FeL_2(CN)_2]$ (L = bipy or phen), where the lowest-energy absorption band, which is also thought to arise from a MLCT transition, moves to higher energy in acid due to the formation[38] of protonated species such as $[FeL_2(CNH)_2]^{2+}$. A new alternative explanation is given elsewhere of the changes among the species present in solutions of complexes of *N*-heterocyclic ligands in protic media.

In order to make unambiguous $^1H$ n.m.r. assignments, we have also prepared 4,4′-dimethyl-2,2′-bipyridyl and 5,5′-dimethyl-2,2′-bipyridyl complexes of the type $[Pt(LL)Cl_2]$, $[Pt(LL)(OH)_2]$, and $[Pt(LL)_2]^{2+}$ (LL = 4,4′-$Me_2$bipy or 5,5′-$Me_2$bipy), by procedures similar to those used for the preparation of the parent 2,2′-bipyridyl derivatives.

The reaction of potassium chloroplatinate(II) in solution with 6,6′-dimethyl-2,2′-bipyridyl gives $[Pt(6,6'\text{-}Me_2bipy)Cl_2]$ in very low yield only. Similar difficulties were experienced in preparing[39] the related complex with 2,9-dimethyl-1,10-phenanthroline (dmp). In both cases, steric hindrance between the chloride and the *o*-methyl substituents is expected and support for this idea comes from a recent *X*-ray structural determination[40] of $[Pd(2,9\text{-}Me_2phen)(NO_2)_2]$ which shows considerable steric interaction between the nitro- and methyl groups.

$^1$*H N.m.r. Spectra*.—The $^1H$ n.m.r. spectra of $[Pt(bipy)(OH)_2]$ and $[Pt(bipy)_2]^{2+}$ have been assigned by comparison with the spectra of the corresponding dimethyl-substituted 2,2′-bipyridyl derivatives (see Table 3), and, where the complex was sufficiently soluble, the assignment of the low-field resonance to $H^6$ was verified by the observation of $^{195}Pt$ coupling (*ca*. 28—30 Hz). The

---

[30] R. D. Gillard and J. R. Lyons, *J.C.S. Chem. Comm.*, 1973, 583.

[31] J. L. Burmeister and M. Y. Al-Janabi, *Inorg. Chem.*, 1965, **4**, 962.

[32] C. C. Addison, N. Logan, S. C. Wallwork, and C. D. Garner, *Quart. Rev.*, 1971, **25**, 289.

[33] K. Nakamoto, 'Infrared Spectra of Inorganic and Co-ordination Compounds,' 1963, p. 92.

[34] J. Peone and L. Vaska, *Angew. Chem. Internat. Edn.*, 1971, **10**, 511.

[35] B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 1961, 3091.

[36] L. Rasmussen and C. K. Jørgensen, *Inorg. Chim. Acta.*, 1969, **3**, 547.

[37] P. M. Gidney, R. D. Gillard, and B. T. Heaton, *J.C.S. Dalton*, 1973, 132.

[38] N. K. Hamer and L. E. Orgel, *Nature*, 1961, **190**, 439.

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

[40] L. F. Power, *Inorg. and Nuclear Chem. Letters*, 1970, **6**, 791.

ordering of the resonances is the same as that found for $[Ni(bipy)Et_2]$ [41-43] ($\gamma H^6 < H^3 \approx H^4 < H^5$).

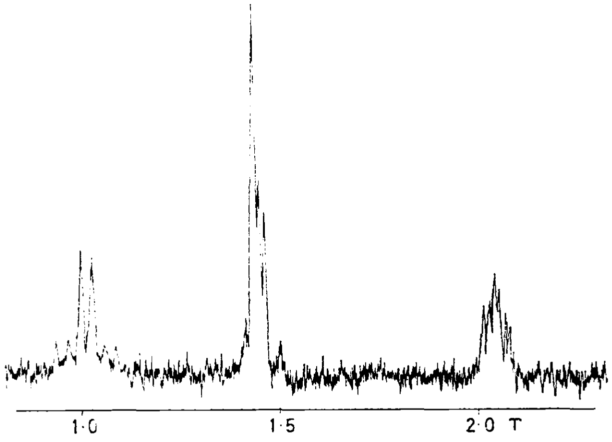


FIGURE 1 The proton magnetic resonance spectrum of $[Pt(bipy)_2]Cl_2$ in heavy water at pD 6, measured at 100 MHz

The resonances due to $H^3$ and $H^4$ in $[Pt(5,5'\text{-}Me_2bipy)(OH)_2]$ appear as an AB pattern at 100 MHz. However, it seems probable that their chemical shifts are correctly assigned in Table 3, since introduction of alkyl substituents into bipy generally results in a shift of all the other resonances to higher field; the alternative assignment would result in $H^3$ being at lower field than in $[Pt(bipy)(OH)_2]$.

The $^1H$ n.m.r. spectrum of $[Pt(4,4'\text{-}Me_2bipy)_2]^{2+}$ exhibits simple first-order pattern, although it should be noted that all the aromatic resonances have experienced a considerable downfield shift compared with $[Pt(4,4'\text{-}Me_2bipy)(OH)_2]$ due to the increased withdrawal of electronic charge. In aqueous solution (pH $\leqslant$ 7), similar shifts are observed for $[Pt(bipy)_2]^{2+}$ and $[Pt(5,5'\text{-}Me_2bipy)_2]^{2+}$, but since $H^3$ and $H^4$ have very similar chemical shifts and are strongly coupled the 100 MHz $^1H$ n.m.r. spectra of both these complexes are 'deceptively simple.' The 100 MHz spectrum of $[Pt(bipy)_2]^{2+}$ is shown in Figure 1 together with the 220 MHz spectrum (Figure 2), which enables a complete analysis to be made [44] (see Table 3). The $^1H$ n.m.r. results obtained for bis(2,2'-bipyridyl)platinum(II) complexes are thus consistent with a square-planar or tetrahedrally distorted configuration. However, it seems probable that, in keeping with *X*-ray results [45] on $[Pd(bipy)_2](NO_3)_2,H_2O$ *, the latter configuration is also involved in solution since $H^3$ experiences a larger downfield shift than any of the other resonances on going from $[Pt(LL)(OH)_2]$ to $[Pt(LL)_2]^{2+}$ (LL = bipy or $4,4'\text{-}Me_2bipy$): this is consistent with increased van der Waals interaction between $H^3$ and $H^{3'}$ due [46] to deviation from a coplanar arrangement of the ligand.

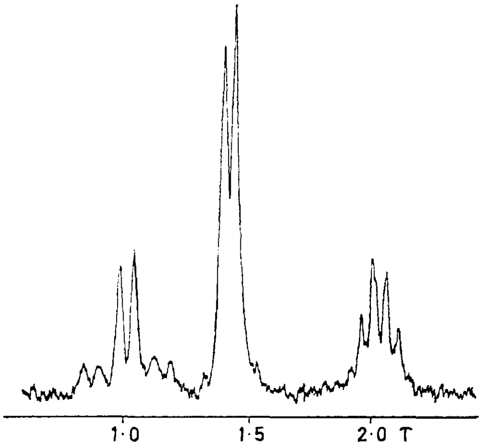


FIGURE 2 As Figure 1, measured at 220 MHz

TABLE 3

$^1H$ N.m.r. chemical shift (τ) and coupling constants (Hz) for 2,2'-bipyridyl complexes of platinum(II) in $D_2O$

| Compound | MHz | $H^3$ | $H^4$ | $H^5$ | $H^6$ | $J_{34}$ | $J_{45}$ | $J_{56}$ | $J_{Pt-H(6)}$ |
|---|---|---|---|---|---|---|---|---|---|
| $[Pt(bipy)(OH)_2]$ | 220 | 2·21d | 2·02dd | 2·59dd | 1·55d | 6 | 8 | 5 | |
| $[Pt(4,4'\text{-}Me_2bipy)(OH)_2]$ | 100 | 2·51s | 7·42s | 2·80d | 1·84d | 0 | 0 | 5·5 | |
| $[Pt(5,5'\text{-}Me_2bipy)(OH)_2]$ | 100 | 2·40 * | 2·17 * | 7·36s | 1·77s | 8 | 0 | 0 | 34·2 |
| $[Pt(bipy)_2Cl_2]$ | 220 | 1·42c | 1·44c | 2·04c | 1·01d | 8·0 | 8·87 [a] | 6·5 | 28·0 [c] |
| $[Pt(4,4'\text{-}Me_2bipy)_2Cl_2]$ | 60 | 1·69s | 7·28s | 2·31d | 1·36d | 0 | 0 | 6 | |
| $[Pt(5,5'\text{-}Me_2bipy)_2Cl_2]$ | 100 | *ca.* 1·69s | | 7·41s | 1·28s | *b* | 0 | 0 | 30·0 |

* Probable assignment, but see text.

[a] Analysis of the spectrum gives $J_{35} + J_{45} = 9{\cdot}5$ Hz: $J_{35} = 0{\cdot}63$. [b] Deceptively simple spectrum which was not analysed. [c] Measured at 100 MHz. s = singlet; d = doublet; c = complex.

## EXPERIMENTAL

*Instruments*.—Electronic spectra of solutions were measured using 1 cm matched silica cells in a Unicam SP800B or Hitachi Perkin-Elmer 124 Spectrophotometer. Reflectance spectra of solids, suitably diluted with magnesium oxide, were obtained using a Unicam SP890 diffuse reflectance attachment. I.r. spectra were taken on solid samples, as Nujol, KEL-F No. 3, or hexachlorobutadiene mulls between KBr or CsI plates with a Perkin-Elmer 457, 337, or 225 Spectrometer, and far-i.r. spectra in Polythene discs using an R.I.I.C. Fourier Transform Interferometer (FS-720),

---

* Although this is *not* isomorphous with our sample of $[Pt(bipy)_2][NO_3]_2,H_2O$, obtained from solution at pH 6 (see Table III).

[41] T. Saito, Y. Uchida, A. Misono, A. Yamamoto, K. Morifugi, and S. Ikeda, *J. Amer. Chem. Soc.*, 1966, **88**, 5198.

[42] H. Günther and S. Castellano, *Z. Naturforsch.*, 1968, **23b**, 1113.

[43] T. Saito, M. Araki, Y. Uchida, and A. Misono, *J. Phys. Chem.*, 1967, 71, 2370.

[44] R. J. Abraham, 'The Analysis of High Resolution N.M.R. Spectra,' Elsevier, 1971, pp. 76—81.

[45] P. C. Chieh, *J.C.S. Dalton*, 1972, 1643.

[46] S. Castellano and H. Günther, *J. Phys. Chem.*, 1967, **71**, 2368.

fitted with an FTS-100-7a computer. $^1H$ n.m.r. spectra were determined at 60, 100, and 220 MHz using, respectively, a Perkin-Elmer R10 instrument, a JEOL spectrometer, and a Varian HR220 spectrometer, operated by I.C.I. Ltd. *X*-Ray powder photographs were taken using a Phillips Debye-Scherrer powder camera, type PW 1024/10. Conductances of solutions were measured with a Phillips conductance bridge (PR 9500). Elemental analyses are given in Table 4. I.r. and other spectra not quoted in this report are in the thesis of P. M. Gidney (University of Kent, 1972).

*Ligands.*—The convenient method [47] of Badger and Sasse (refluxing a substituted pyridine over Raney nickel in a Soxhlet tube) gave, from 150 ml of β-picoline, 30 g (first crop from EtOH) with m.p. 116—117° and 2 n.m.r. peaks in the methyl region (? 3,3′-$Me_2$bipy impurity), followed by a second crop (30 g) of 5,5′-$Me_2$bipy, m.p. 115—116 °C (lit.,[48] 114—115 °C) with only one methyl resonance. From 150 ml of α-picoline, after 2 recrystallisations of the product from $H_2O$–EtOH, the same method gave 1·6 g of 6,6′-$Me_2$bipy, m.p. 86—89 °C (lit.,[47] 88—90 °C) with $^1H$ n.m.r. (in $CCl_4$) at $-CH_3$ 7·32, $H_5$ 2·84, $H_4$ 2·27, and $H_3$ 1·57 (proton resonances of the other *n,n′*-$Me_2$bipy's are known[48]).

TABLE 4

Analytical results for 2,2′-bipyridyl and substituted 2,2′-bipyridyl platinum(II) complexes

| | Found (%) | | | | Required (%) | | | |
|---|---|---|---|---|---|---|---|---|
| Compound | C | H | N | Cl | C | H | N | Cl |
| (A) Yellow [Pt(bipy)$Cl_2$] | 28·9 | 1·8 | 6·6 | 16·8 | 28·4 | 1·9 | 6·6 | 16·8 |
| (B) Red [Pt(bipy)$Cl_2$] | 27·8 | 1·9 | 6·6 | 16·8 | 28·4 | 1·9 | 6·6 | 16·8 |
| (C) Yellow [Pt(bipy)$(CN)_2$],$H_2O$ | 34·4 | 1·64 [a] | 13·3 | | 34·2 | 1·90 | 13·3 | |
| (D) Red [Pt(bipy)$(CN)_2$] | 35·3 | 1·84 | 13·7 | | 35·7 | 1·98 | 13·9 | |
| (E) Yellow [Pt$(bipy)_2$][Pt$(CN)_4$],$x$$H_2O$ | 33·0 | 2·22 [a] | 12·65 | | | | | |
| : $x = 2$ | | | | | 34·2 | 2·38 | 13·3 | |
| : $x = 3$ | | | | | 33·5 | 2·55 | 13·0 | |
| : $x = 4$ | | | | | 32·8 | 2·73 | 12·75 | |
| (F) Red [Pt$(bipy)_2$][Pt$(CN)_4$] | 35·5 | 1·77 | 13·4 | | 35·7 | 1·98 | 13·9 | |
| [Pt(phen)$(CN)_2$] (violet) | 38·8 | 2·03 | 12·8 | | 39·3 | 1·87 | 13·1 | |
| [Pt(6,6′-$Me_2$bipy)$Cl_2$] | 31·2 | 2·6 | 6·0 | | 31·8 | 2·7 | 6·2 | |
| [Pt(5,5′-$Me_2$bipy)$Cl_2$] | 31·9 | 2·9 | 6·1 | | 31·8 | 2·7 | 6·2 | |
| [Pt(4,4′-$Me_2$bipy)$Cl_2$] | 32·0 | 2·6 | 6·2 | | 31·8 | 2·7 | 6·2 | |
| [Pt(bipy)$(OH)_2$],3$H_2O$ | 26·9 | 3·2 | 6·1 | 0·0 | 27·3 | 3·6 | 6·4 | |
| [Pt(5,5′-$Me_2$bipy)$(OH)_2$],3$H_2O$ | 30·5 | 4·1 | 5·9 | | 30·8 | 3·9 | 6·0 | |
| [Pt(4,4′-$Me_2$bipy)$(OH)_2$],2$H_2O$ | 31·7 | 4·1 | 6·0 | | 32·0 | 3·6 | 6·2 | |
| [Pt(bipy)$(py)_2$][$ClO_4$]$_2$ [b] | 34·0 | 3·1 | 7·4 | | 33·9 | 2·5 | 7·9 | |
| [Pt(bipy)$(NO_3)_2$] | 24·8 | 2·1 | 11·3 | | 25·3 | 1·7 | 11·8 | |
| [Pt(bipy)$(NO_3)$(OH)] | 27·3 | 2·1 | 9·4 | | 27·3 | 2·1 | 9·6 | |
| [Pt(bipy)$(H_2O)_2$][$ClO_4$]$_2$ | 20·2 | 2·1 | 4·9 | | 20·5 | 2·0 | 4·8 | |
| [Pt(bipy)$(H_2O)$(OH)][$BF_4$] [c] | 25·1 | 1·9 | 5·7 | | 25·4 | 2·3 | 5·9 | |
| [Pt$(bipy)_2$]$(NO_3)_2$,$H_2O$ | 36·6 | 2·9 | 13·4 | | 37·0 | 2·8 | 12·9 | |
| [Pt(5,5′-$Me_2$bipy)$_2$]$(NO_3)_2$,0·5$H_2O$ | 41·3 | 3·5 | 12·3 | | 41·4 | 3·6 | 12·1 | |
| [Pt(4,4′-$Me_2$bipy)$_2$]$(NO_3)_2$,3$H_2O$ | 38·5 | 3·2 | 11·0 | | 38·9 | 4·1 | 11·3 | |
| [Pt$(bipy)_2$][$ClO_4$]$_2$ | 33·6 | 2·3 | 7·9 | | 34·0 | 2·3 | 7·9 | |
| [Pt$(bipy)_2$][Pt$Cl_4$] | 28·8 | 1·8 | 6·6 | 16·8 | 28·4 | 1·9 | 6·6 | 16·8 |
| [Pt$(bipy)_2$]$S_2O_6$,2$H_2O$ | 34·0 | 2·8 | 8·3 | | 34·2 | 2·9 | 8·0 | |

[a] The rather low hydrogen figure arises from the easy loss of the water in this form. [b] Conductivity ($\Omega^{-1}$ cm$^2$ mol$^{-1}$) of *ca.* $10^{-3}$M-nitromethane solution was 164. [c] Conductivity 78.

*Preparation of Red and Yellow Modifications of* [Pt(bipy)$Cl_2$]. *Yellow Isomer* (A).—This complex was prepared by the method [10] of Morgan and Burstall. Occasionally, when left in the open laboratory, parts of the surface became very slowly (*ca.* 1—2 weeks) bright red.

*Red Isomer* (B).—This complex was prepared by treating [Pt(bipy)(en)]$Cl_2$,2$H_2O$ with vigorously boiling HCl (12M), as described [10] by Morgan and Burstall. The product is obtained as an orange-red microcrystalline precipitate. Larger crystals (for the *X*-ray structural determination described [11] by Professor Rogers and Miss Osborn) were obtained as follows. A solution of yellow [Pt(bipy)$Cl_2$] (0·05 g) in warm pyridine (*ca.* 10 ml) was slowly evaporated from an open beaker on a water-bath at 55 °C to *ca.* 2·5 ml. At this stage addition of carbon tetrachloride (30 ml) produced an immediate precipitate of the red isomer. The red crystals were filtered off, washed with carbon tetrachloride, and air-dried. The method is not particularly reproducible, since a mixture of red and yellow forms may be obtained. In such cases, the red crystals may usually be separated manually.

In connection with the apparently common mode of formation of all known samples of the red form (B) (*i.e.* by displacing ligands L from [Pt(bipy)$L_2$]$^{2+}$ with chloride, L being ½ en, $NH_3$, or py) the spectrum of the solution of (A) in pyridine at 20 °C is relevant. Fresh, it shows λ 397, 378sh, 352 nm; after 4 min, it had λ 350(sh) nm, suggesting that the displacement of one and perhaps two chloride ligands occurs readily.

Similar evaporations of solutions in pyridine of a number of compounds analogous to (A) gave only the original yellow forms (for [Pt(bipy)$Br_2$], [Pt(bipy)$I_2$], [Pt(phen)$Cl_2$], [Pd(bipy)$Cl_2$], [Pt(2,9-$Me_2$phen)$Cl_2$], [Pt(5,5′-$Me_2$bipy)$Cl_2$], and [Pt(4,4′-Mephen)$Cl_2$]).

[Pt(bipy)(en)][$ClO_4$]$_2$. A suspension of [Pt(bipy)$Cl_2$] in water with a very slight excess of ethylenediamine was kept at 50 °C for 18 h. Sodium perchlorate was added, when the desired product crystallised. The chloride salt's dihydrate had been made by Morgan and Burstall [10] and also in this work, and the α-bromocamphor sulphonate by Rosenblatt and Schleede.[9]

[Pt(bipy)$(CN)_2$]. A solution of [Pt(bipy)(en)][$ClO_4$]$_2$ (0·477 mmol) in cold water (50 ml) was treated with the

---

[47] G. M. Badger and W. H. F. Sasse, *J. Chem. Soc.*, 1956, 616.

[48] Y. McL. Spotswood and C. I. Tanzer, *Austral. J. Chem.*, 1967, **20**, 1227.

stoicheiometric quantity of KCN. During 1 day, yellow $[Pt(bipy)(CN)_2],xH_2O$ slowly precipitates. This was collected, washed with water, and dried in the air, when it remained yellow (in very dry air, (C) $\longrightarrow$ (D) at room temperature, slowly), yield 68%. On drying in the oven it became red * and if the heated solid was cooled in a desiccator it remained red. The red form (D) reverts to the original yellow form (C), as shown by i.r. spectroscopy, on addition of water (even in humid air, this change occurs slowly). Heavy water also restores the original colour. Both forms are insoluble in the organic solvents tried (which of course did convert yellow to red by removal of water), almost insoluble in water (although Rosenblatt and Schleede spoke [9] of recrystallizing from copious hot water), but dissolved in aqueous pyridine or DMSO. Recrystallization from hot anhydrous $Me_2SO$ gave red needles, but from hot aqueous pyridine gave yellow needles. The red needles (from $Me_2SO$) keep their shape on treatment with water (when they become yellow). On adding acetone, the resulting yellow needles instantly become red, but as the solvent evaporates the residual water in it suffices to turn them yellow again.

$[Pt(bipy)_2][Pt(CN)_4]$. $K_2[Pt(CN)_4]$ (0·045 g; 0·15 mmol) dissolved in water was treated with a solution in aqueous $Me_2SO$ of $[Pt(bipy)_2][ClO_4]_2$ at room temperature, giving a yellow precipitate which was washed with water and dried in air (it remained yellow). Yield *ca.* 80 mg. On drying this yellow form (E) in the oven, it gave the red form (F), a deeper red than (D).

$[Pt(bipy)_2][ClO_4]_2$. The 'normal' form (G) was made following Morgan and Burstall[10] and Livingstone and Wheelahan [8] by treating the neutral filtered product {*i.e.* $[Pt(bipy)_2]Cl_2$} of dissolving $[Pt(bipy)Cl_2]$ (0·1 g) in a solution in water (100 ml) of 2,2′-bipyridyl (0·12 g) with sodium perchlorate (0·1 g) in water. This perchlorate (0·05 g) was dissolved in warm water, the pH adjusted to 10 with aqueous sodium hydroxide, and, after a day, light-brown glistening crystals of the form (H) had *on one occasion only* been deposited.

$[Pt(phen)(CN)_2]$. A stoicheiometric amount of potassium cyanide was added to a solution of $Pt(phen)(en)X_2$ ($X = BF_4^-$ or $ClO_4^-$) at room temperature. A flaky *yellow* fine precipitate at once formed. This was collected, washed with water and alcohol (when it became red), and dried in air to a violet anhydrous form, which dissolves only in $Me_2SO$ and remains violet in contact with water; yield *ca.* 85%. This violet form showed i.r. absorption (in $cm^{-1}$) at: 2139s, 2128s, 1635vw, 1626vw, 1607m, 1580m, 1522s, 1437vs,sh, 1420m,sh, 1420m,sh, 1305vw,bd, 1230vw, 1215vw, 1204vw, 1150m, 1113vw, 880w, 856vs, 788m, 747vw, 723sh, 717vs, 570vw, 517w, 458w, and 440w.

*Preparation of Complexes of the Type* $[Pt(LL)Cl_2]$ (LL = 4,4′-$Me_2$bipy, 5,5′-$Me_2$bipy, 6,6′-$Me_2$bipy).—Addition of a solution of the ligand (0·11 g) in 1M-hydrochloric acid (5 ml) to a solution of $K_2[PtCl_4]$ (0·25 g) in water (20 ml) followed by heating for 2 h produced a fluffy yellow precipitate which was collected, air dried, and recrystallised from dichloromethane to give the complex in *ca.* 80% (LL = 4,4′-$Me_2$bipy, 5,5′-$Me_2$bipy) and 10% (LL = 6,6′-$Me_2$bipy) yield.

*Preparation of Complexes of the Type* $[Pt(LL)(OH)_2]$ (LL = bipy, 4,4′-$Me_2$bipy, 5,5′-$Me_2$bipy).—$[Pt(LL)Cl_2]$ (0·15 g) was suspended in water (50 ml) and treated with a solution of sodium hydroxide (0·1 g) either in water (when LL = bipy) or in ethanol (when LL = 4,4′-$Me_2$bipy or 5,5′-$Me_2$bipy). Boiling this suspension for *ca.* 30 min resulted in dissolution and this solution was cooled and then passed down an anion-exchange column in the hydroxide form. The yellow eluant was concentrated to *ca.* 5 ml whereupon yellow-orange needles were formed. The product was filtered off and dried in a vacuum desiccator over conc. $H_2SO_4$.

*Di-aqua-2,2′-bipyridylplatinum*(II) *Perchlorate*, $[Pt(bipy)(H_2O)_2][ClO_4]_2$.—Addition of conc. $HClO_4$ (1 ml) to a solution of $[Pt(bipy)(OH)_2]$ (0·1 g) in water (10 ml) gave, after 24 h, a yellow precipitate of the product.

*2,2′-Bipyridylhydroxonitratoplatinum*(II), $[Pt(bipy)(OH)(NO_3)]$.—$[Pt(bipy)(OH)_2],3H_2O$ (0·15 g) was dissolved in water (20 ml) and the pH adjusted to *ca.* 4 with 4N-$HNO_3$ whereupon an orange-yellow precipitate of the product slowly formed.

*Aqua-2,2′-bipyridylhydroxoplatinum*(II) *Tetrafluoroborate*, $[Pt(bipy)(OH)(H_2O)][BF_4]$.—$[Pt(bipy)(OH)_2],3H_2O$ (0·15 g) was dissolved in water (20 ml) and the pH adjusted to *ca.* 2 with tetrafluoroboric acid whereupon an orange-yellow precipitate of the product slowly formed.

*2,2′-Bipyridyldinitratoplatinum*(II), $[Pt(bipy)(NO_3)_2]$.—This complex was prepared following the procedure used for the preparation of $[Pt(bipy)(OH)(NO_3)]$ except that the pH was adjusted to *ca.* 1.

*2,2′-Bipyridylbis(pyridine)platinum*(II) *Perchlorate*, $[Pt(bipy)(py)_2][ClO_4]_2$.—A suspension of $[Pt(bipy)Cl_2]$ (0·1 g) in 5 : 1 aqueous pyridine (12 ml) was warmed on a water-bath to give a pale yellow solution which on addition of sodium perchlorate gave pale yellow crystals of the product.

*Preparation of Complexes of the Type* $[Pt(LL)_2]X_2$ (LL = bipy, 4,4′-$Me_2$bipy, 5,5′-$Me_2$bipy; $X = Cl^-, I^-, ClO_4^-, NO_3^-, \frac{1}{2}S_2O_6^{2-}, \frac{1}{2}PtCl_4^{2-}$).—The cation $[Pt(LL)_2]^{2+}$ was prepared by a procedure analogous to that described for the preparation of $[Pt(bipy)_2]^{2+}$. Treatment of an aqueous solution containing $[Pt(LL)_2]Cl_2$ with the appropriate anion resulted in immediate precipitation of the desired salt. The salts with the counter ions $[ClO_4]^-$ and $[PtCl_4]^{2-}$ are discussed in detail above. $[Pt(LL)_2]Cl_2$ is unstable in solution at 25 °C and readily gives $[Pt(LL)Cl_2]$ and free ligand. However, such complexes can be prepared by pouring an aqueous solution (20 ml) containing $[Pt(bipy)_2][NO_3]_2,H_2O$ (0·1 g) down an anion-exchange column in the chloride form. The eluant was evaporated at 1·0 mmHg pressure and 10 °C until crystallization occurred. The solutions of $[Pt(LL)_2]Cl_2$ used for $^1H$ n.m.r. studies were obtained by adding to the above liquor $D_2O$ (10 ml) followed by evaporation as above to *ca.* 1 ml. This procedure was repeated and the $^1H$ n.m.r. spectrum of the filtrate was recorded immediately.

We are grateful for an M.R.C. studentship (to P. M. G.) and for a Royal Society European Fellowship (E. B.). The platinum was supplied by Johnson Matthey and Co. Ltd., whom we thank for their kind co-operation. We wish to thank Professor D. Rogers and Dr. Ruth Osborn of Imperial College for undertaking and keeping us *au fait* with their most useful parallel study [11] of the crystal structure of red $[Pt(bipy)Cl_2]$.

[4/323 *Received*, 19*th February*, 1974]

---

* A measurement of specific heat as a function of temperature gave no discontinuity in the range 15–100 °C, though the change (C) $\longrightarrow$ (D) occurred. 0·1117 g of (C) after 24 h in the oven had lost 0·0071 g of water (0·393 mmol) leaving 0·1046 g of red (D) (0·277 mmol). This value of $x \simeq 1$ in yellow $[Pt(bipy)(CN)_2],xH_2O$ is supported by the elemental analyses.