

*Journal of Organometallic Chemistry*, 166 (1979) 241–249  
 © Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

**SYNTHESIS, CHARACTERISATION AND X-RAY STRUCTURE OF A FIVE-COORDINATE PLATINUM(II) CATIONIC COMPLEX, BIPYRIDINECHLORO(*o*-ISOPROPENYL-*N,N*-DIMETHYLANILINE)-PLATINUM(II) PERCHLORATE**

MERVYN K. COOPER \*, DARRYL W. YANIUK,  
*School of Chemistry, The University of Sydney, Sydney 2006 (Australia)*

and MARY McPARTLIN \*  
*Department of Chemistry, The Polytechnic of North London, London N7 8DB (Great Britain)*

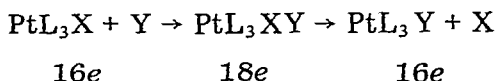
(Received August 15th, 1978)

**Summary**

Reaction of dichloro(*o*-isopropenyl-*N,N*-dimethylaniline)platinum(II), PtCl<sub>2</sub>(IMN), with 2,2'-bipyridine and sodium perchlorate gives the title compound [Pt(bipy)Cl(IMN)]ClO<sub>4</sub> (I). NMR, IR, and X-ray studies show that the cation in I is formally five coordinate both in solution and in the solid state. The X-ray structure of I has been determined using 693 diffractometer data with  $I/\sigma(I) \geq 2.0$ , and full matrix refinement has given an  $R$  of 0.068. Crystals of I are monoclinic, spacegroup  $P2_1/c$ ,  $a$  16.715(9),  $b$  10.278(6),  $c$  13.990(8) Å,  $\beta$  107.24°,  $Z = 4$ . The ligand arrangement about the platinum(II) atom of the cation is very distorted trigonal bipyramidal with the olefin and the bipyridine groups in the equatorial plane. The angle subtended at the platinum atom by the bipyridine donor atoms is only 77°. A 3c–4e bond, formed by overlap of an empty Pt<sup>II</sup>  $dsp^2$  orbital with the filled bipyridine nitrogen  $sp^2$  orbitals, is proposed, which allows the complex to be classified as obeying the 16e rule.

**Introduction**

Many reactions of square planar platinum(II) complexes proceed by an associative path involving five-coordinate intermediates.

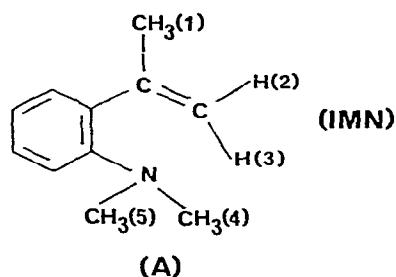


These reactions relate to the 16- and 18-electron rules and depend on the 18e

five-coordinate platinum(II) intermediate readily yielding the more stable 16e four coordinate product [1].

However, there is a small but increasing number of formally five-coordinate platinum(II) complexes, apparently with 18 valence electrons, which have unusual stability. For example the tridentate nitrogen donor ligand hydrotris-(pyrazolyl)borate gives very stable five-coordinate platinum(II) complexes [2]. The X-ray structural data for one of these, methyl[hydrotris(1-pyrazolylborato)]-hexafluorobut-2-yneplatinum(II), (II), has been compared with that of *trans*-chloromethylbis(trimethylarsine)hexafluorobut-2-yneplatinum(II), (III), a five-coordinate complex which readily undergoes "insertion" of the acetylene into the methyl-platinum bond [3]. The authors could not identify any abnormal structural features which would account for the difference in reactivity. A further example is the formation of the stable five-coordinate complexes Pt(C<sub>2</sub>H<sub>4</sub>)Cl<sub>2</sub>bis(hydrazone), although the coordinating ability of bis(hydrazone) ligands towards Pt<sup>II</sup> appears to be rather poor [4].

Reaction of dichloro(*o*-isopropenyl-*N,N*-dimethylaniline)platinum(II), PtCl<sub>2</sub>(IMN), with 2,2'-bipyridine (bipy) and sodium perchlorate gives a compound which analyses for [Pt(bipy)Cl(IMN)]ClO<sub>4</sub> (I).



This is the first stable cationic five-coordinate platinum(II) complex to be isolated and a preliminary account of the synthesis and X-ray structure analysis has appeared [5]. This work is now reported in full in relation to some of the factors which appear to influence the stability of five-coordinate platinum(II) complexes.

## Experimental

### Preparations

*o*-Isopropenylaniline was prepared from methyl anthranilate by the method of Atkinson and Simpson [6]. The aniline was methylated [7] to yield *o*-isopropenyl-*N,N*-dimethylaniline (A).

Dichloro-*o*-isopropenyl-*N,N*-dimethylanilineplatinum(II), Pt(IMN)Cl<sub>2</sub>, was prepared from Zeise's salt by a method similar to that reported [8] for the preparation of dichloro-*o*-vinyl-*N,N*-dimethylanilineplatinum(II) (Pt(IMN)Cl<sub>2</sub>, 80.7%; m.p. 227°C decomp. Found: C, 30.99; H, 3.44; N, 3.21, Cl, 16.9. C<sub>11</sub>H<sub>15</sub>NCl<sub>2</sub>Pt calcd.: C, 30.92; H, 3.54; N, 3.28; Cl, 16.6%). The IR spectrum showed bands at 340s and 307s cm<sup>-1</sup> attributable to the platinum-chlorine stretching vibrations.

Bipyridinechloro(*o*-isopropenyl-*N,N*-dimethylaniline)platinum(II), was made

by the reaction of  $\text{Pt}(\text{IMN})\text{Cl}_2$  with 2,2'-bipyridine.  $\text{Pt}(\text{IMN})\text{Cl}_2$  (0.43 g, 1.0 mmol) was dissolved in chloroform (20 ml) and an acetone solution (15 ml) of 2,2'-bipyridine (0.17 g, 1.1 mmol) and sodium perchlorate (0.13 g, 1.1 mmol) was added dropwise during a period of ten minutes. The resulting solution was stirred at room temperature for 2 h, after which it was filtered. The filtrate was evaporated to dryness at room temperature under reduced pressure and chloroform was added to the solid residue. An off-white solid was collected from a yellow-brown solution. This solid was recrystallised from acetone to give I as off-white crystals (0.35 g, 0.54 mmol, 54%). Found: C, 38.71; H, 3.60; N, 6.40; Cl, 11.1.  $\text{C}_{21}\text{H}_{23}\text{N}_3\text{Cl}_2\text{O}_4\text{Pt}$  calcd.: C, 38.96; H, 3.58; N, 6.49; Cl, 11.00%. The molar conductivity of the compound in nitrobenzene is  $18.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  indicating that it is a 1/1 electrolyte.

Crystals of I suitable for X-ray structure analysis were grown from acetone at  $-20^\circ\text{C}$ .

#### *Apparatus and techniques*

The NMR spectra of IMN,  $\text{Pt}(\text{IMN})\text{Cl}_2$  and  $[\text{Pt}(\text{bipy})\text{Cl}(\text{IMN})]\text{ClO}_4$  were recorded on a Varian HA 100 100 MHz spectrometer using  $\text{DMF-}d_7$  solutions with TMS as internal standard.

IR spectra of the complexes were recorded in Nujol mull on a Perkin-Elmer 457 grating IR spectrophotometer calibrated with polystyrene film and are believed to be accurate to  $\pm 2 \text{ cm}^{-1}$ .

Melting points were recorded in air on a Reichert hot stage melting point apparatus with a microscope, and are corrected.

Microanalyses were performed by the Australian Microanalytical Service, Division of Applied Organic Chemistry, CSIRO, University of Melbourne.

#### *Crystal data*

$\text{C}_{21}\text{Cl}_2\text{H}_{23}\text{N}_3\text{O}_4\text{Pt}$ , mol. wt. 647.43, monoclinic,  $a$  16.715(9),  $b$  10.278(6),  $c$  13.990(8) Å,  $\beta$  107.24°,  $V$  2295.5 Å<sup>3</sup>;  $Z$  4; Mo- $K_\alpha$  radiation,  $\lambda$  0.71069 Å,  $\mu(\text{Mo-}K_\alpha)$  66.9  $\text{cm}^{-1}$ . The spacegroup was unambiguously determined as  $P2_1/c$  from systematic absences in the diffraction data:  $h0l$ ,  $l = 2n + 1$ ;  $0k0$ ,  $k = 2n + 1$ .

#### *Intensity measurements*

Intensity measurements, in the  $\theta$ -range of 2–25° were made on a Philips PW1100 four-circle diffractometer using a  $\theta$ – $2\theta$  scan technique and Mo- $K_\alpha$  radiation from a graphite crystal monochromator. Weak reflections which gave  $I_t - 2\sqrt{I_t} \leq I_b$  on the first scan were omitted;  $I_t$  is the count rate at the maximum of the reflection peak and  $I_b$  is the mean count rate from two preliminary 5 second background measurements at the extremities of the scan. The background measuring time for each reflection was proportional to  $I_b/I_i$  where  $I_i$  is the mean count rate recorded in the first scan. Reflections for which the total count was less than 500 were scanned a second time. A constant scan speed of  $0.05^\circ \text{ s}^{-1}$  and a scan width of  $0.74^\circ$  were used. Three standard reflections were measured at intervals of 5 h during data collection and showed no significant variation in intensity.

Reflection intensities were calculated using a program written for the

TABLE 1  
 FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS FOR I WITH STANDARD DEVIATIONS IN PARENTHESES

(a) Fractional atomic coordinates and isotropic thermal parameters

Atom	x	y	z	$U(\text{\AA}^2)$	Atom	x	y	z	$U(\text{\AA}^2)$		
Independent atoms											
Pt	0.2044(2)	0.1293(3)	-0.1418(2)	a	O(1)	0.505(3)	0.154(6)	-0.094(4)	0.134(19)		
Cl(1)	0.1377(10)	0.2327(18)	-0.0386(12)	a	O(2)	0.605(3)	0.185(5)	-0.173(4)	0.135(20)		
N(1)	0.264(3)	0.036(4)	-0.232(3)	0.041(13)	O(3)	0.532(3)	0.352(7)	-0.158(4)	0.177(22)		
C(1)	0.140(3)	-0.051(6)	-0.122(4)	0.057(19)	O(4)	0.623(3)	0.253(6)	-0.008(4)	0.148(21)		
C(2)	0.108(3)	0.016(5)	-0.218(4)	0.048(18)	Atoms in a rigid group						
C(3)	0.018(4)	0.076(6)	-0.240(5)	0.086(26)	C(11)	0.206	-0.034	-0.309	0.062(20)		
C(4)	0.333(3)	-0.054(5)	-0.173(4)	0.063(20)	C(12)	0.229	-0.092	-0.386	0.087(24)		
C(5)	0.315(3)	0.123(6)	-0.278(3)	0.049(15)	C(13)	0.169	-0.153	-0.465	0.103(25)		
N(2)	0.224(2)	0.325(3)	-0.203(3)	0.022(12)	C(14)	0.086	-0.156	-0.465	0.122(28)		
C(21)	0.289(3)	0.392(4)	-0.138(3)	0.049(18)	C(15)	0.062	-0.099	-0.387	0.086(26)		
C(22)	0.302(3)	0.519(4)	-0.161(4)	0.088(24)	C(16)	0.122	-0.038	-0.309	0.048(18)		
C(23)	0.250(3)	0.570(6)	-0.250(4)	0.085(22)	(b) Anisotropic thermal parameters ( $\text{\AA}^2$ )						
C(24)	0.185(4)	0.506(6)	-0.318(5)	0.117(27)	Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
C(25)	0.170(4)	0.386(6)	-0.284(4)	0.104(24)	Pt	0.053(2)	0.039(2)	0.052(2)	0.003(3)	0.020(1)	0.002(3)
N(3)	0.315(3)	0.199(3)	-0.031(3)	0.046(15)	Cl(1)	0.088(14)	0.079(15)	0.075(14)	0.014(13)	0.028(11)	0.020(13)
C(31)	0.399(3)	0.323(4)	-0.046(3)	0.036(19)	Anisotropic temperature factor is in the form:						
C(32)	0.410(3)	0.372(6)	0.023(3)	0.090(21)	$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}kblb^*c^*)]$						
C(33)	0.461(4)	0.304(5)	0.103(4)	0.076(22)	exp						
C(34)	0.429(3)	0.183(5)	0.113(4)	0.067(21)	[ $-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}kblb^*c^*)]$						
C(35)	0.362(3)	0.123(6)	0.045(4)	0.065(18)	exp						
Cl(2)	0.569(1)	0.235(2)	-0.105(2)	0.087(6)	[ $-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}kblb^*c^*)]$						

<sup>a</sup> Anisotropic thermal parameters.

PW1100 diffractometer [9]. The variance of the intensity  $I$  was calculated as the sum of the variance due to counting statistics and  $(0.04 I)^2$  where the term in  $I^2$  was introduced to allow for other sources of error [10]. Corrections were made for Lorenz and polarisation factors but not absorption.

Equivalent reflections were averaged to give a total of 693 unique reflections with  $I/\sigma(I) \geq 2$ .

### *Structure solution and refinement*

The platinum and two chlorine atoms were located from Patterson synthesis. The other atom positions were obtained from difference Fourier syntheses. Due to poor diffraction by the only crystals that could be obtained there was a marked shortage of data and therefore the phenyl ring of the olefinic ligand was treated as a rigid group (C—C 1.395 Å) and the lengths of the three sets of chemically equivalent bonds in the bipyridine ligand were constrained to be equal to three extra free variables in the refinement. Full matrix refinement with anisotropic temperature factors for platinum and coordinated chlorine atoms gave an  $R$  of 0.073. Hydrogen atoms at calculated positions (C—H 1.08 Å) were introduced for the phenyl, methyl (treated as rigid pyramidal groups) and bipyridyl groups and were included in the final refinement cycles "riding" on the relevant atoms. The reflections were weighed as  $1/\sigma^2(F_0)$ , and the refinement converged to a final  $R$  of 0.068, with  $R_w = 0.063$  ( $R_w = w^{1/2}|F_0 - F_c|/w^{1/2}|F_0|$ ). The scattering factors used were those of Cromer and Mann [11] and corrections for the real and imaginary part of the anomalous dispersion were included. The computer programmes used were those of the SHELX system [12]. The final atomic coordinates and thermal parameters are given in Table 1. Bond lengths and angles are listed in Table 2.

A list of observed and calculated structure factors and details of least-squares planes are available from the authors on request (M.McP.).

## Results and discussion

That I is a five-coordinate cationic complex is indicated by the infrared and  $^1\text{H}$  NMR spectra. The single infrared Pt—Cl stretching frequency at  $335\text{ cm}^{-1}$  shows the presence of only one chloro ligand in the compound while the strong, broad absorption at ca.  $1100\text{ cm}^{-1}$  is ascribed to ionic perchlorate.

In the  $^1\text{H}$  NMR spectrum of I the protons of the bipyridine are downfield from their position in the free ligand (Table 3) and the coupling constants have both increased significantly. This indicates that both nitrogen atoms of the bipyridine are coordinated to the platinum\*.

The  $^1\text{H}$  NMR spectrum of I also provides evidence for coordination of both the nitrogen and olefin of IMN to the metal (Table 4). The proton resonances of the N-methyl groups, which appear as a single peak due to their equivalence in the free ligand, occur in the complex as separate peaks, each with sidebands arising from coupling between the  $^{195}\text{Pt}$  nucleus and the protons.

\* Similar conclusions, based on an increase in coupling constants between  $\alpha$  and  $\beta$  protons, have been drawn by B.G. McGrath (Ph.D. Thesis, University of Sydney, 1973) concerning the coordination of heterocyclic nitrogen ligands of Group VIA metal carbonyls.

TABLE 2  
BOND LENGTHS AND ANGLES IN I WITH STANDARD DEVIATIONS IN PARENTHESES

(a) Bond lengths (Å)		(b) Angles (°)	
<i>The cation</i>			
Pt—C(1)	2.33(2)	N(2)—C(21)	1.37(4)
Pt—N(1)	2.07(5)	N(2)—C(25)	1.37(4)
Pt—N(2)	2.25(4)	C(21)—C(22)	1.38(3)
Pt—N(3)	2.15(5)	C(22)—C(23)	1.38(3)
Pt—C(1)	2.20(8)	C(23)—C(24)	1.38(3)
Pt—C(2)	2.02(7)	C(24)—C(25)	1.38(3)
C(1)—C(2)	1.46(8)	N(3)—C(31)	1.37(4)
C(2)—C(3)	1.56(8)	N(3)—C(35)	1.37(4)
C(2)—C(16) <sup>a</sup>	1.47(8)	C(31)—C(32)	1.38(3)
		C(32)—C(33)	1.38(3)
N(1)—C(4)	1.51(7)	C(33)—C(34)	1.38(3)
N(1)—C(5)	1.50(7)	C(34)—C(35)	1.38(3)
N(1)—C(11) <sup>a</sup>	1.41(6)	C(21)—C(31)	1.48(9)
<i>The anion</i>			
Cl(2)—O(1)	1.39(7)	Cl(2)—O(3)	1.45(8)
Cl(2)—O(2)	1.38(6)	Cl(2)—O(4)	1.41(7)
<i>The cation</i>			
Cl(1)—Pt—N(1)	179(2)	Pt—N(2)—C(21)	112(3)
Cl(1)—Pt—N(2)	89(1)	Pt—N(2)—C(25)	125(5)
Cl(1)—Pt—N(3)	83(2)	C(21)—N(2)—C(25)	122(6)
Cl(1)—Pt—C(1)	88(2)	N(2)—C(21)—C(22)	118(4)
Cl(1)—Pt—C(2)	98(2)	N(2)—C(25)—C(24)	123(8)
N(1)—Pt—N(2)	92(2)	C(21)—C(22)—C(23)	118(6)
N(1)—Pt—N(3)	97(2)	C(22)—C(23)—C(24)	127(8)
N(1)—Pt—C(1)	92(2)	C(23)—C(24)—C(25)	112(9)
N(1)—Pt—C(2)	82(3)		
N(2)—Pt—N(3)	77(2)	Pt—N(3)—C(31)	115(4)
N(2)—Pt—C(1)	159(2)	Pt—N(3)—C(35)	123(4)
N(2)—Pt—C(2)	120(2)	C(31)—N(3)—C(35)	122(6)
N(3)—Pt—C(1)	123(2)	N(3)—C(31)—C(32)	118(4)
N(3)—Pt—C(2)	163(3)	N(3)—C(35)—C(34)	117(7)
C(1)—Pt—C(2)	40(2)	C(31)—C(32)—C(33)	125(6)
		C(32)—C(33)—C(34)	112(8)
		C(33)—C(34)—C(35)	126(8)
Pt—N(1)—C(4)	112(4)		
Pt—N(1)—C(5)	115(4)		
Pt—N(1)—C(11) <sup>a</sup>	110(4)	N(2)—C(21)—C(31)	118(3)
C(4)—N(1)—C(5)	100(5)	N(3)—C(31)—C(21)	118(3)
C(4)—N(1)—C(11) <sup>d</sup>	110(5)	C(22)—C(21)—C(31)	125(3)
C(5)—N(1)—C(11) <sup>d</sup>	110(5)	C(32)—C(31)—C(21)	125(3)
Pt—C(1)—C(2)	64(4)	C(3)—C(2)—C(16) <sup>a</sup>	112(6)
Pt—C(2)—C(1)	76(4)		
Pt—C(2)—C(3)	116(5)	N(1)—C(11)—C(16) <sup>a</sup>	119(3)
Pt—C(2)—C(16) <sup>a</sup>	111(4)	N(1)—C(11)—C(12) <sup>a</sup>	121(3)
C(1)—C(2)—C(3)	116(7)	C(2)—C(16)—C(11) <sup>a</sup>	114(3)
C(1)—C(2)—C(16) <sup>a</sup>	121(6)	C(2)—C(16)—C(15) <sup>a</sup>	126(3)
<i>The anion</i>			
O(1)—Cl(2)—O(2)	112(4)	O(2)—Cl(2)—O(3)	99(4)
O(1)—Cl(2)—O(3)	110(4)	O(2)—Cl(2)—O(4)	115(4)
O(1)—Cl(2)—O(4)	105(5)	O(3)—Cl(2)—O(4)	116(5)

<sup>a</sup> Estimated standard deviations do not include contributions from atoms in rigid groups.

TABLE 3  
<sup>1</sup>H CHEMICAL SHIFTS <sup>a</sup> AND INTERPROTON COUPLING CONSTANTS <sup>b</sup> FOR BIPYRIDINE

	Chemical shifts		Coupling constants	
	H(6)	H(6')	J(6, 5)	J(6', 5')
Free	8.73 <sup>c</sup>	8.73 <sup>c</sup>	4.8 <sup>c</sup>	4.8 <sup>c</sup>
Complexed in I	9.29	9.56	5.5	5.1

<sup>a</sup> Chemical shifts in ppm ( $\pm 0.01$  ppm) downfield from internal TMS.

<sup>b</sup> In Hz.

<sup>c</sup> Equivalent in the free ligands and arbitrarily assigned in the platinum(II) complexes.

A large upfield shift is observed for the olefinic protons 2 and 3 relative to their position in free IMN (A). This, together with their strong coupling to the <sup>195</sup>Pt nucleus, shows that the olefin group is coordinated to the platinum. Further evidence for olefin bonding is provided by the significant coupling between <sup>195</sup>Pt and the methyl of the isopropenyl group.

The platinum atom of the cation is formally five-coordinate with bonds to N(2) and N(3) of the bipyridine ligand, Cl(1), and the bidentate IMN ligand through N(1) and the olefin C(1)—C(2). The coordination of the platinum(II) atom may be described as distorted trigonal bipyramidal with the olefin and the bipyridyl nitrogen atoms N(2) and N(3) occupying the three equatorial sites.

The platinum carbon distances to the olefin are Pt—C(1), 2.20(8) and Pt—C(2), 2.02(7) Å; this difference may be caused by the steric requirements of the chelating ring of the IMN ligand but it is of low significance. In this ligand the phenyl ring and the nitrogen atom, N(1), are coplanar to within 0.03 Å. Due to its coordination to the metal the olefin group is twisted out of this plane so that the dihedral angle is 70° between the planes of C(16), C(1) and C(2), and of the phenyl ring and N(1).

The two Pt—N bond lengths to the bipyridine ligand are unequal being 2.15(5) and 2.25(4) Å. This difference is of low significance but may be related to the asymmetric bonding of the olefin group. The two rings of the bipyridine ligand are each planar to within 0.1 Å; the dihedral angle between the least squares planes through these rings is 3.74° which is similar to the angles observed

TABLE 4  
<sup>1</sup>H CHEMICAL SHIFTS <sup>a</sup> AND <sup>195</sup>Pt—<sup>1</sup>H COUPLING CONSTANTS <sup>b</sup> FOR IMN (A)

	IMN <sup>c</sup>	PtCl <sub>2</sub> (IMN) <sup>c</sup>	[Pt(bipy)Cl(IMN)]ClO <sub>4</sub> (I) <sup>c</sup>
H(1)	2.13	2.24(32.2)	1.96(37.2)
H(2)	5.06	5.03(70.1)	4.10(63.2)
H(3)	5.12	4.30(75.7)	3.08(70.4)
H(4)	2.56	3.45(32.0)	2.80(28.2)
H(5)	2.56	3.47(29.7)	3.33(29.8)

<sup>a</sup> Chemical shifts in ppm ( $\pm 0.01$  ppm) downfield from internal TMS. <sup>b</sup>  $J(^{195}\text{Pt}-\text{H})$  coupling constants in Hz ( $\pm 0.02$  Hz), in parentheses. <sup>c</sup> Solvent DMF-*d*<sub>7</sub>, proton numbering as above (A).

in other mono-bipyridine metal complexes [13].

As a result of the small bite of the bipyridyl ligand the N(2)—Pt—N(3) angle in I is only  $77^\circ$ , very small compared to the ideal value of  $120^\circ$  for five coordination using  $dsp^3$  hybrid orbitals. The factors which cause some five-coordinate platinum(II) compounds to exhibit unusual stability are not well understood but it may be significant that, like I, most compounds of this type contain a ligand of very small bite and consequently their trigonal bipyramidal coordination geometry is very distorted. In fact the structure of the methyl hydrotris(1-pyrazolylborato) complex II [3] seems to provide some evidence that such complexes prefer ligands of small bite in equatorial sites. To approach ideal trigonal bipyramidal coordination it would have been possible for the equatorial N—Pt—N angle in II to open out to at least  $88^\circ$  as angles as large as this have been observed in other tridentate pyrazolylborate complexes [14], but instead the observed value of this angle is  $83.1(1)^\circ$  which is one of the smallest N—M—N angles observed for this ligand. In fact the pyrazolyl limbs spanning the axial to equatorial sites have larger N—Pt—N angles of  $86.4(2)^\circ$ .

In discussing the structure of I it is significant that the midpoint of the olefin, N(1), Cl(1), and the midpoint of the bipyridyl N(2) and N(3) donors are coplanar to within  $0.03 \text{ \AA}$ . Thus the expected direction of a  $dsp^2$  orbital from the platinum(II) atom bisects a line joining the bipyridyl donor atoms, so that it overlaps both filled  $sp^2$  orbitals of the bipyridine nitrogens (Fig. 2). This allows a description of the bonding in terms of three-centred, four-electron bonding; in such a bond one pair of electrons from the nitrogen donors would be in a bonding molecular orbital and the other pair in a non-bonding orbital of predominantly ligand character [15]. Thus the platinum(II) atom would effectively be obeying the  $16e$  rule which dominates platinum(II) chemistry.

This approach to the platinum(II)—bipyridine bonding, if applied in other complexes, would be consistent with the apparent preference of most five-coordinate complexes for ligands of small bite in equatorial sites of distorted trigonal bipyramidal coordination geometries. The stability of  $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2\text{bis}(\text{hydrazone})$  (IV) which was mentioned earlier [4], may be due to  $3c-4e$  bonding between

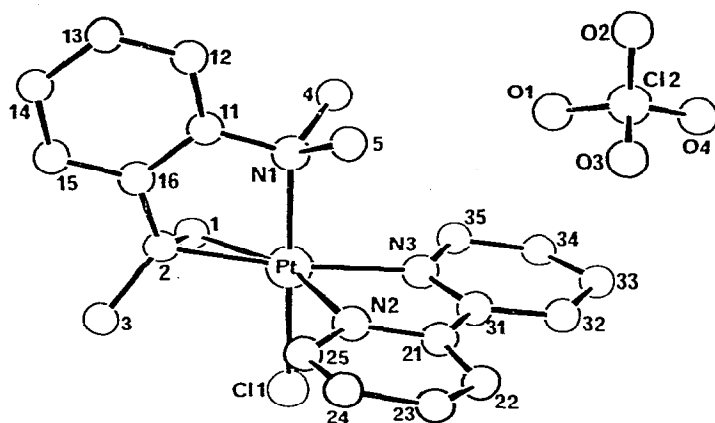


Fig. 1. The structure of  $[\text{Pt}(\text{bipy})\text{Cl}(\text{IMN})][\text{ClO}_4]$  (I).



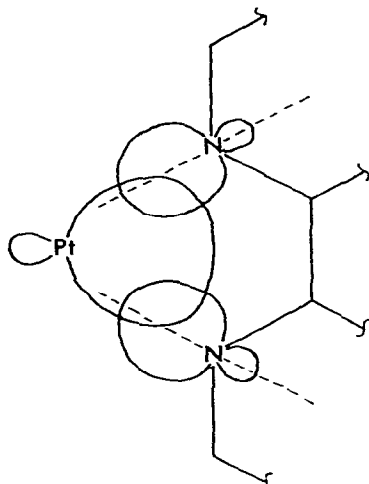


Fig. 2. A schematic representation of orbital overlap in the platinum(II)-bipyridine bonds.

the donor nitrogen atoms of the bis(hydrazone) and the platinum(II) atom; the N—Pt—N angle in this compound is  $72^\circ$ . The lower reactivity of II with an equatorial N—Pt—N of  $83.1^\circ$  compared to III with the larger equatorial As—Pt—As angle of  $104.2^\circ$  [3] may also be related to this type of bonding in II.

## References

- 1 C.A. Tolman, *Chem. Soc. Rev.*, 3 (1972) 337.
- 2 L.E. Manzer, *Inorg. Chem.*, 15 (1976) 2354.
- 3 B.W. Davies and N.C. Payne, *Inorg. Chem.*, 13 (1974) 1843.
- 4 L. Maresca, G. Natile, M. Calligaris, P. Delise and L. Randaccio, *J. Chem. Soc. Dalton*, (1976) 2386.
- 5 M.K. Cooper, D.W. Yaniuk, M. McPartlin and J.G. Shaw, *J. Organometal. Chem.*, 131 (1977) C33.
- 6 C.M. Atkinson and J.C.E. Simpson, *J. Chem. Soc.*, (1948) 808.
- 7 M.G. Seeley, R.E. Yates and C.R. Noller, *J. Amer. Chem. Soc.*, 73 (1951) 772.
- 8 M.K. Cooper, N.J. Hair and D.W. Yaniuk, *J. Organometal. Chem.*, 150 (1978) 157.
- 9 J. Hornstra and B. Stubbe, PW1100 Processing Program, Philips Research Laboratories, Eindhoven, The Netherlands, 1972.
- 10 P.W. Corfield, R.J. Doedens and J.A. Ibers, *Inorg. Chem.*, 6 (1967) 197.
- 11 D. Cromer and J. Mann, *Acta Cryst.*, A, 24 (1968) 321.
- 12 G. Sheldrick, "SHEL76", University of Cambridge.
- 13 E.D. McKenzie, *Coord. Chem. Rev.*, 6 (1971) 187.
- 14 F.A. Cotton, B.A. Frenz and A. Shaver, *Inorg. Chim. Acta*, 7 (1973) 161.
- 15 F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 3rd edit., Interscience Publ., New York, 1972, p. 109.