

## The Cyanobis(1,10-phenanthroline)platinum(II) Complex in Aqueous Solution and as the Crystalline Nitrate. Nuclear Magnetic Resonance Measurements and Crystal-structure Determination

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The bis(1,10-phenanthroline)platinum(II) cation rapidly adds cyanide in aqueous solution forming the cyanobis(1,10-phenanthroline)platinum(II) ion, which from  $^{13}\text{C}$  n.m.r. spectra has been shown to contain five-co-ordinated platinum both in water and in nitromethane solution. The crystals of cyanobis(1,10-phenanthroline)platinum(II) nitrate are triclinic, space group  $P\bar{1}$ , with  $Z = 2$  and unit-cell dimensions  $a = 15.616(11)$ ,  $b = 7.264(6)$ ,  $c = 10.564(7)$  Å,  $\alpha = 102.81(4)$ ,  $\beta = 80.90(4)$ , and  $\gamma = 96.47(4)^\circ$ . The structure has been determined by the heavy-atom method from diffractometer data and refined to  $R = 0.031$  for 3 562 independent reflections. Three nitrogen atoms from the phenanthroline groups and the carbon atom from the cyanide form an approximately square-planar configuration about the platinum; Pt-N(1) 2.062(5), Pt-N(2) 2.007(5), Pt-N(3) 2.053(5), and Pt-C(25) 1.931(6) Å. The remaining nitrogen atom of the phenanthroline groups is at the apex of a square pyramid, Pt-N(4) 2.761(5) Å. In aqueous solution  $\text{OH}^-$  and  $\text{SH}^-$  appear to react analogously with the bis(1,10-phenanthroline)-platinum(II) ion. The cyano-complex is stable in solution and reacts only slowly with other nucleophiles (e.g. excess of  $\text{CN}^-$ ,  $\text{OH}^-$ , and halide ions).

DURING the last six years numerous reactions between various nucleophiles and complexes containing 1,10-phenanthroline or 2,2'-bipyridine † have been interpreted as involving nucleophilic attack on the ligand molecule rather than the usual attack on the metal centre.<sup>1-6</sup> In some cases ‡ similar species have been postulated as reactive intermediates in order to explain anomalous kinetic phenomena,<sup>7-10</sup> but in general the so-called 'Gillard pseudo-base mechanism' has been invoked in cases where  $\text{OH}^-$  and  $\text{CN}^-$  are the nucleophiles. A large amount of experimental data has been produced purporting to support this model,<sup>4</sup> although in some cases alternative mechanisms have been preferred.<sup>11,12</sup> In particular, the postulate of a pseudo-base as a long-lived intermediate in the reaction of aqueous  $[\text{PtL}_2]^{2+}$  with  $\text{OH}^-$  as stated by Gillard and co-workers<sup>1,2</sup> has been challenged by Nord,<sup>13</sup> who investigated the kinetics of the  $[\text{Pt}(\text{bipy})_2]^{2+} + \text{OH}^-$  reaction and showed that the results were in agreement with the formation of a five-co-ordinate species as the intermediate in the hydrolysis reaction, thus following the scheme of an associative mechanism which is that generally accepted for substitution reactions in platinum(II) complexes.<sup>14</sup>

In the present work we show that  $[\text{Pt}(\text{phen})_2]^{2+}$  in water rapidly adds cyanide forming the  $[\text{Pt}(\text{phen})_2(\text{CN})]^+$  ion which is proved to be five-co-ordinate § both in solution and in the solid nitrate. From the many spectral similarities we conclude that the rapid reactions of the  $[\text{Pt}(\text{phen})_2]^{2+}$  ion with  $\text{OH}^-$  and  $\text{SH}^-$  also lead to formation of species containing five-co-ordinate  $\text{Pt}^{\text{II}}$ .

### RESULTS

Figure 1 is typical of a conductometric titration of an aqueous solution of  $[\text{Pt}(\text{phen})_2]\text{Cl}_2$  with aqueous  $\text{K}[\text{CN}]$ . The conductivity changes observed after each addition of cyanide are rapid and the values remain constant with time.

† 1,10-Phenanthroline and 2,2'-bipyridine ligands are abbreviated to phen and bipy respectively, and collectively as L.

‡ The reduction of  $[\text{ML}_3]^{3+}$  ( $M = \text{Fe}, \text{Ru}, \text{or Os}$ ) by  $\text{OH}^-$  in water, for example (refs. 7-10).

The  $\Delta$  curve indicates that a 1 : 1 reaction is taking place. A parallel pH recording showed that at the equivalence point the solution is neutral so the concentration of free cyanide is low. Beyond the equivalence point, addition of cyanide is accompanied by an increase in pH and  $\Delta$ , indicating the presence of free  $\text{CN}^-$  in the solution. During

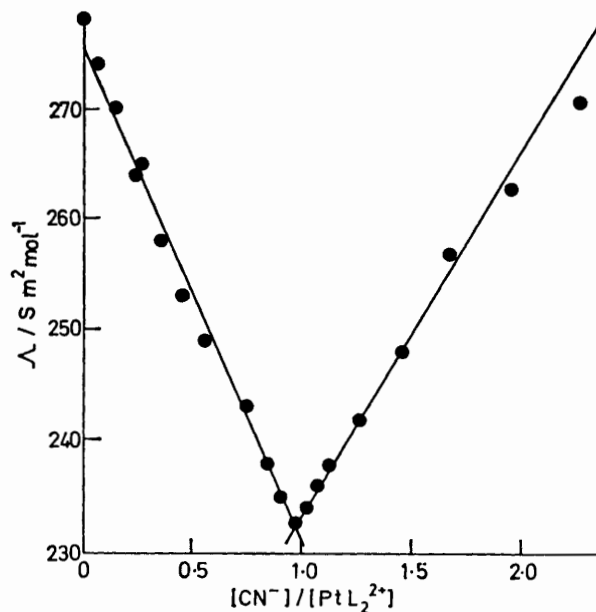


FIGURE 1 Conductometric titration of  $[\text{Pt}(\text{phen})_2]\text{Cl}_2$  ( $15.0 \text{ cm}^3$ ,  $8.90 \times 10^{-4} \text{ mol dm}^{-3}$ ) in water with aqueous  $\text{K}[\text{CN}]$  ( $3.00 \times 10^{-3} \text{ mol dm}^{-3}$ )

the latter part of the titration a slow precipitation of  $\text{Pt}(\text{phen})(\text{CN})_2$  was also observed.

The u.v. spectra of mixtures of  $\text{Pt}(\text{phen})_2\text{Cl}_2$  and  $\text{K}[\text{CN}]$  in water at varying mol ratios are shown in Figure 2. When this ratio is less than 1 : 1, isosbestic points are observed. The spectrum of the 1 : 1 mixture is identical to that of

§ One of the Pt-N bonds in the solid compound is 35% longer than the others. However, we shall use the term five-co-ordinate as referring to the number of ligating atoms in the co-ordination sphere without regard to the strength of the individual bonds.

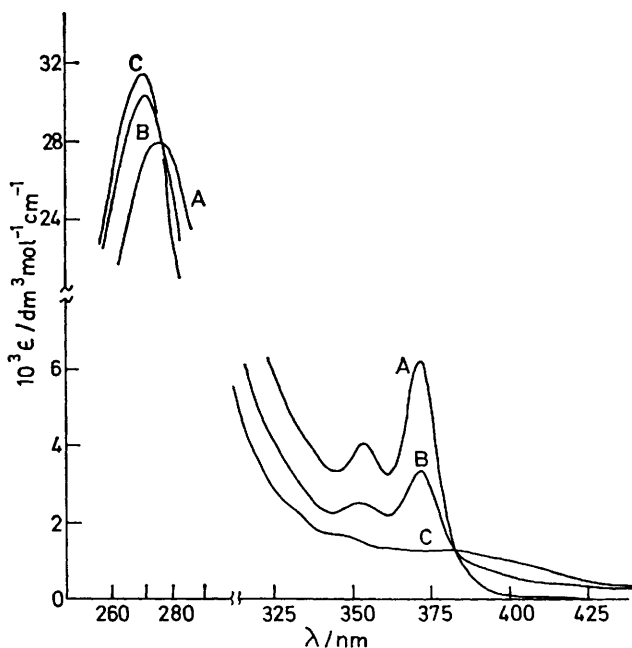
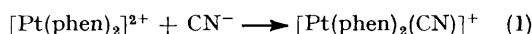
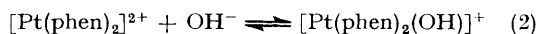


FIGURE 2 Ultraviolet spectra of  $\text{Pt(phen)}_2(\text{ClO}_4)_2$  ( $8.90 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ) in water with added cyanide ion. Mol ratios of  $\text{CN}^-$ :  $\text{Pt}^{\text{II}}$  are A, 0:1; B, 0.56:1; C, 1.00:1 and greater

dissolved  $[\text{Pt(phen)}_2(\text{CN})][\text{ClO}_4]$  prepared by the procedure given below. Addition of an excess of cyanide does not produce immediate changes in the spectrum of the 1:1 mixture. This indicates that, within experimental error, reaction (1) goes to completion. On this basis the equilibrium constant of reaction (1) must be greater than  $10^6$   $\text{dm}^3$   $\text{mol}^{-1}$ .



It is of interest to compare these spectra with those of mixtures of  $[\text{Pt(phen)}_2]^{2+}$  and hydroxide (Figure 3). The spectra of the two systems are quite similar with isosbestic points at the same wavelengths. This may suggest that an addition reaction similar to process (1) is taking place in mixtures of  $[\text{Pt(phen)}_2]^{2+}$  and  $\text{OH}^-$ . From the spectral data the equilibrium constant for the addition reaction (2) is  $10^2$   $\text{dm}^3$   $\text{mol}^{-1}$ , in agreement with the published value.<sup>2</sup>



The proton-decoupled  $^{13}\text{C}$  n.m.r. spectral data of the complexes are given in Table 1 and Figure 4. The  $^{195}\text{Pt}$ - and  $^{13}\text{C}$ -coupling gives rise to doublet satellites of intensity corresponding to the natural abundance of  $^{195}\text{Pt}$  (34%).

These satellites are easily observed in spectra (b) and (c) (see Figure 4) surrounding the signals of the  $\text{C}^2, \text{C}^9$  and the  $\text{C}^3, \text{C}^8$  atoms of the phenanthroline and surrounding the CN resonance in spectra (a) and (c). This confirms that  $\text{CN}^-$  in  $[\text{Pt(phen)}_2(\text{CN})]^+$  is bound to platinum and not to a carbon atom of the ligand. Since 95%  $^{13}\text{C}$  was used in experiments, the above conclusion is further supported by the lack of  $^{13}\text{C}$ - $^{13}\text{C}$  couplings in the spectra of  $[\text{Pt(phen)}_2(\text{CN})]^+$ . Because of the long nuclear relaxation time of the cyanide carbon the spectra have been recorded in solutions to which chromium(III) was added. This gives rise to the line broadening of the cyanide part of spectrum (b). Since addi-

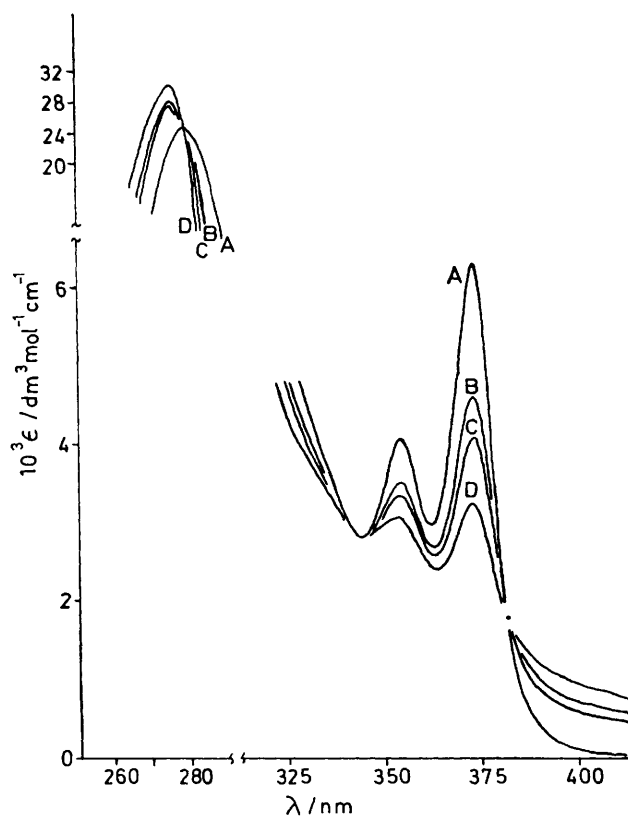


FIGURE 3 Ultraviolet spectra of  $\text{Pt(phen)}_2(\text{ClO}_4)_2$  ( $8.9 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ) in water with added hydroxide ion. Mol ratios of  $\text{OH}^-$ :  $\text{Pt}^{\text{II}}$  are A, 0:1; B, 5.62:1; C, 11.2:1; D, 20.2:1

tion of chromium(III) salts to the aqueous solutions of  $[\text{Pt(phen)}_2(\text{CN})]\text{Cl}$  leads to precipitation this spectrum has been recorded without  $\text{Cr}^{\text{III}}$ , so the  $\text{CN}^-$  resonances are not visible.

The phenanthroline signals of the spectra of  $[\text{Pt(phen)}_2]^{2+}$  and  $[\text{Pt(phen)}_2(\text{CN})]^+$  are very similar and the differences in

TABLE 1

Carbon-13 n.m.r. data: <sup>a</sup> chemical shifts <sup>b</sup> with Pt-C coupling constants <sup>c</sup> in parentheses

Sample	$\text{C}^2, \text{C}^9$	$\text{C}^{11}, \text{C}^{12}$	$\text{C}^4, \text{C}^7$	$\text{C}^{13}, \text{C}^{14}$	$\text{C}^5, \text{C}^6$	$\text{C}^3, \text{C}^8$	CN
(1) $\text{K}_2[\text{Pt}(\text{CN})_4]$ in water							125.8 (1 029.3)
(2) $[\text{Pt(phen)}_2]\text{Cl}_2$ in water	151.7 (33.2)	145.6	142.6	130.8	129.0	126.8 (38.1)	
(3) $[\text{Pt(phen)}_2(\text{CN})][\text{ClO}_4]$ in $\text{CH}_3\text{NO}_2-(\text{CH}_3)_2\text{CO}$	153.5 (30.3)	145.8 (19.5)	141.2	132.6 (16.6)	129.4	127.2 (32.9)	108.6 (1 516.6)
(4) $[\text{Pt(phen)}_2(\text{CN})]\text{Cl}$ in water	152.2 (30.3)	144.5 (19.0)	140.5	131.5 (15.6)	128.5	126.4 (32.2)	
(5) Phen in water	157.9	152.6	145.2	136.9	134.6	131.8	

<sup>a</sup> Carbon atoms numbered according to the structure given in Figure 3. <sup>b</sup> In p.p.m. relative to  $\text{SiMe}_4$ . <sup>c</sup> In Hz.

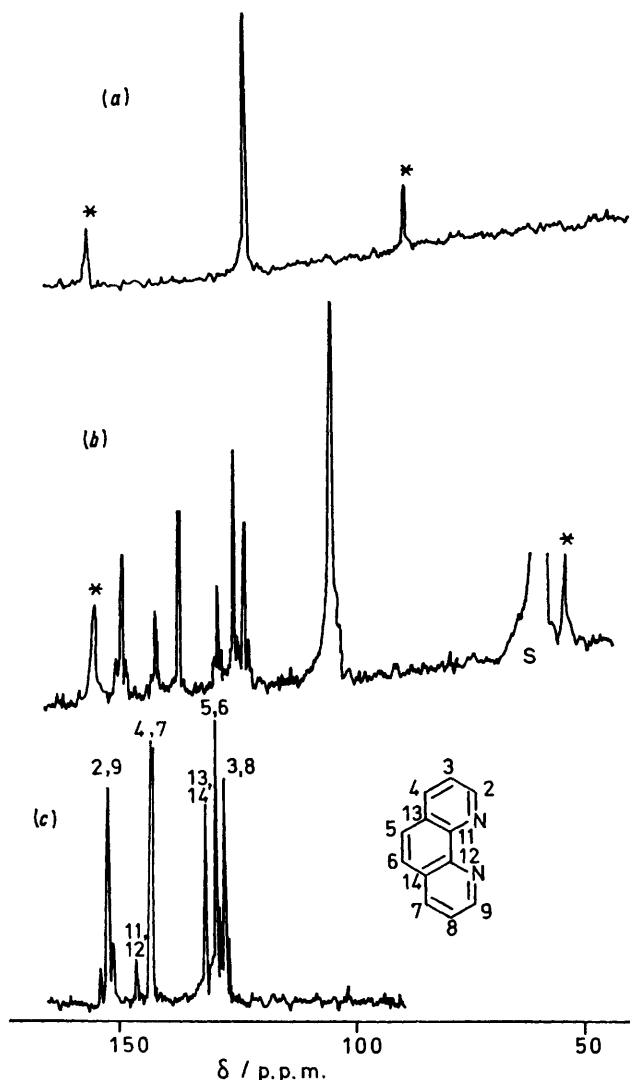


FIGURE 4 The  $^{13}\text{C}$  n.m.r. spectra of (a)  $[\text{Pt}(\text{CN})_4]^{2-}$  [sample (1)], (b)  $[\text{Pt}(\text{phen})_2(\text{CN})]^+$  [sample (3)], and (c)  $[\text{Pt}(\text{phen})_2]^{2+}$  [sample (2)]. Satellites of the cyanide signal are indicated by an asterisk, S is a solvent line

chemical shift are of the same magnitude as the solvent dependence of the signals (spectra, Figures 3 and 4). The spectra of the complexes are, however, significantly different from the spectrum of the free ligand in water (see Table 1). The proton n.m.r. spectra of the two complexes in water are also considerably different with differences in chemical shifts of *ca.* 0.5 p.p.m. for the  $\text{H}^2, \text{H}^9$  protons and *ca.* 0.3 p.p.m. for the others (see Table 2).

No difference between the two phenanthroline molecules can be observed in any of the spectra and both halves of each chelate molecule give identical signals.

**X-Ray Structure.**—The cation  $[\text{Pt}(\text{phen})_2(\text{CN})]^+$  has, in the solid state, a square-pyramidal structure (Figure 5). One of the phenanthroline nitrogens [N(4)] occupies the apical position. The corresponding phenanthroline mole-

\* The value of 2.78 Å given for  $\text{Pd}(\text{NO}_3)_2(\text{Me}_2\text{phen})$  seems to be a misprint, the original reference gives 2.73 Å ( $\text{Me}_2\text{phen} = 2,9$ -dimethyl-1,10-phenanthroline).

† We thank the referees for pointing this out.

Sample	$\text{H}^2, \text{H}^9$	$\text{H}^4, \text{H}^7$	$\text{H}^5, \text{H}^6$	$\text{H}^3, \text{H}^8$
(2)	9.41	8.99	8.23	8.16
	9.32	8.85		8.08
(4)	(30) <sup>b</sup>			8.03
	8.89	8.70	7.94	7.86
	8.81	8.56		7.78
				7.73
				7.64

<sup>a</sup> In p.p.m. relative to  $\text{SiMe}_4$ . <sup>b</sup>  $\text{Pt}-^1\text{H}$  coupling constant in Hz.

cule is rotated so that the angle between the planes through the two phenanthroline groups is  $104^\circ$ . The Pt is displaced 0.069 Å, towards N(4), out of the plane defined by N(1), N(2), N(3), and C(25). The Pt-N(4) distance (2.761 Å) is scarcely shorter than that of Pt-C(11) (2.86 Å) and Pt-C(12) (2.87 Å). The mean length of the other Pt-N bonds is 2.04 Å, Pt-C(25) being 1.93 Å. The main difference between the phenanthroline groups is in the length of the bite. In the phenanthroline molecule in the plane the distance N(1) ··· N(2) is 2.66(1) Å, which lies in the range 2.63–2.73 Å, \* quoted for 20 phenanthrolines by Frenz and Ibers.<sup>15</sup>

The N(3) ··· N(4) distance is 2.81(1) compared with 2.724 in phenanthroline<sup>16</sup> and 2.767 Å for the free phenanthroline<sup>17</sup> in  $[\text{Cu}\{\text{SC}(\text{NH}_2)_2\}(\text{phen})]\text{I}\cdot\text{phen}$ .

In  $[\text{PtCl}(\text{phen})(\text{PEt}_3)_2]^+$ , where the phenanthroline is bound similarly to the N(3)-N(4) group in  $[\text{Pt}(\text{phen})_2(\text{CN})][\text{NO}_3]$ ,<sup>18</sup> Pt-N lengths are 2.14(2) and 2.84(2) respectively and N ··· N is 2.85 Å. The shortening of the N ··· N distances leads to changes in angles, the biggest changes being for N(1)-C(12)-C(11), from 120 to  $116.5^\circ$ , and for C(3)-C(4)-C(5), from 122.5 to  $125.5^\circ$  (mean values for equivalent angles are given). There does not seem to be any significant difference between the two halves of the apical ligand.

The cations pack in such a way that the non-apical phenanthrolines form stacks parallel to *b* with the distances between the planes through the rings being 3.5 and 3.4 Å.

The distance between the planes through the apical ligands is 3.4 Å.

## DISCUSSION

In the solid state the cation possesses no elements of symmetry. This raises the question of whether this structure persists in aqueous solution, since the n.m.r. spectra only show signals corresponding to phenanthroline molecules in which both halves are equivalent on the n.m.r. time scale. From these data one cannot exclude the possibility that the non-equivalent parts of the ligands may give rise to n.m.r. signals of almost identical frequency but since the resolution in this experiment is about ten times better than the magnitude of the observed solvent dependence this is unlikely.

A better explanation perhaps is to assume that the ion in solution rapidly changes its geometry. Because  $^{195}\text{Pt}$  satellites are observed rapid dissociation processes do not take place † and the best explanation is probably to assume that the ion in solution is fluxional. Such behaviour has frequently been observed for species of five-co-ordinate structure<sup>19</sup> and has also been postulated

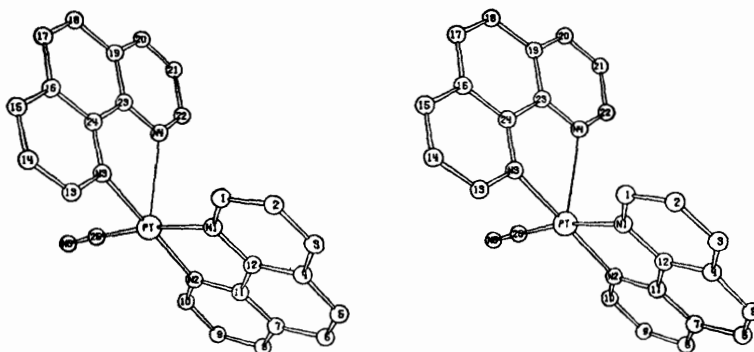


FIGURE 5 Stereoscopic view of the cation  $[\text{Pt}(\text{phen})_2(\text{CN})]^+$ .

The carbon atoms are numbered without the chemical symbol

in the discussion of ligand-catalyzed isomerization reactions.<sup>20,21</sup> By adopting the model of trigonal pseudorotation<sup>22</sup> we can show (Figure 6) that the structure observed in the X-ray experiment can be transformed into structures where all four nitrogen atoms of the phenanthroline molecules are in identical positions relative to the platinum atom and the cyanide group. This can occur without passing through a structure in which the phenanthroline molecules lie in the plane and the cyanide at the apex. This structure is presumably very unlikely because of mutual interaction between the  $\text{H}^2, \text{H}^9$  protons of the two ligands. If this process is assumed to occur rapidly compared to the n.m.r. frequency this would account for the spectra observed.

We believe that the steric interaction of the  $\text{H}^2, \text{H}^9$  protons of the ligands precludes a strictly planar configuration of the bis(phenanthroline) complex and that this property plays an important part in the observed affinity for five-co-ordination. In a recent report anomalous kinetic data have been reported<sup>23</sup> for the reactions of  $[\text{Pt}(\text{terpy})\text{Cl}]^+$  (terpy = 2,2':6',2''-terpyridyl) and the formation of a stable five-co-ordinate intermediate has again been proposed. The chloro-terpyridine complex is probably distorted in the same way as the analogous palladium complex,<sup>24</sup> where the angles between the ligating atoms deviate considerably from  $90^\circ$ .

Neither the  $^{13}\text{C}$  nor the  $^1\text{H}$  n.m.r. data give any evidence for the postulated addition products, with the

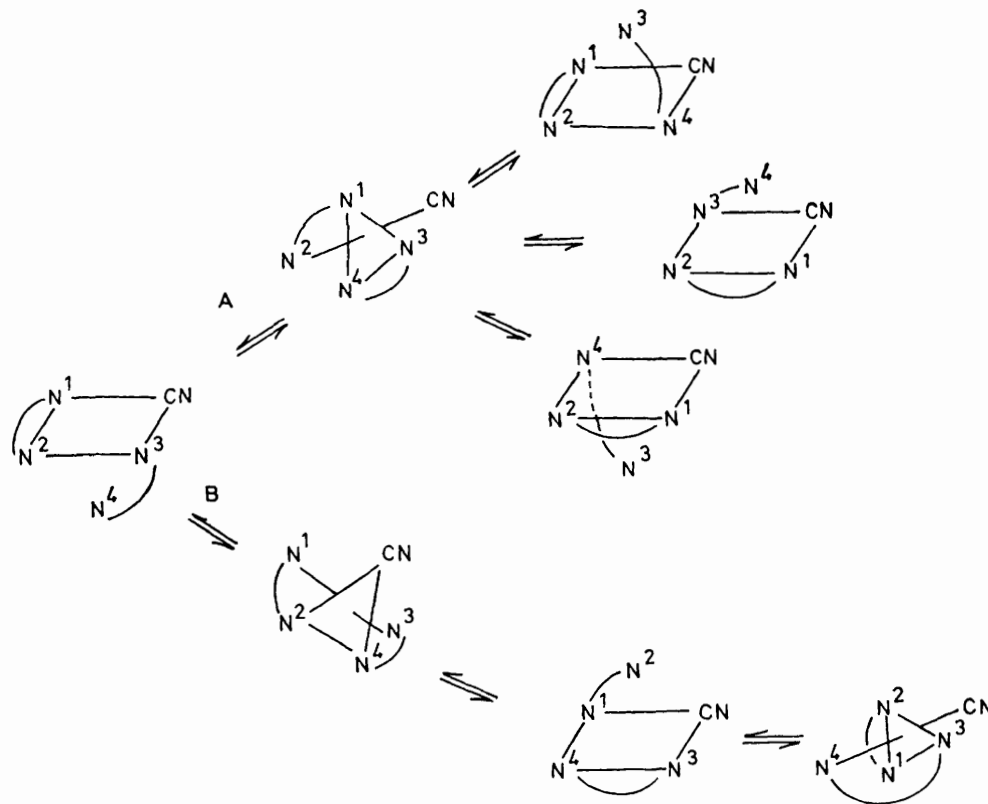


FIGURE 6 A possible mechanism for the pseudorotation of the  $[\text{Pt}(\text{phen})_2(\text{CN})]^+$  ion. The two phenanthroline molecules are shown as  $\text{N}^1\text{—N}^2$  and  $\text{N}^3\text{—N}^4$ . The Pt atom has been omitted for clarity. Part A shows the pseudorotation around the  $\text{N}^2\text{—CN}$  axis. Part B shows the pseudorotation around the  $\text{N}^1\text{—N}^3$  axis followed by a pseudorotation using one of the new axes formed by the first process (the  $\text{N}^4\text{—CN}$  axis)

formation of covalent bonds to the aromatic ligands, which earlier workers<sup>1-4</sup> have based upon observations of small changes in the <sup>1</sup>H n.m.r. spectra alone. The reaction of CN<sup>-</sup> with [Pt(phen)<sub>2</sub>]<sup>2+</sup> conforms to known patterns. No novel mechanisms or structures are required either in solution or in the solid state.

#### EXPERIMENTAL

*Preparation of Compounds.*—The compound [Pt(phen)<sub>2</sub>]-Cl<sub>2</sub> was prepared and purified by the method described in ref. 1. The white perchlorate and the pale yellow nitrate were made from a solution of the chloride in water by precipitation with Na[ClO<sub>4</sub>] or Na[NO<sub>3</sub>].

*Salts of Cyanobis(1,10-phenanthroline)platinum(II).*—A precise stoichiometric amount of a solution of K[CN] (ca. 0.1 mol dm<sup>-3</sup>) in water was added dropwise and with rapid stirring to a solution of [Pt(phen)<sub>2</sub>]Cl<sub>2</sub> (ca. 0.01 mol dm<sup>-3</sup>) in water. A large local excess of cyanide leads to the form-

TABLE 3  
Fractional atomic co-ordinates

Atom	x	y	z
Pt	0.217 89(1)	0.143 87(3)	-0.068 53(2)
N(1)	0.144 6(4)	0.169 1(7)	-0.209 1(5)
N(2)	0.106 9(3)	0.209 1(7)	0.049 8(5)
N(3)	0.325 4(3)	0.061 7(8)	-0.199 6(5)
N(4)	0.340 5(3)	0.447 4(7)	-0.078 6(5)
N(5)	0.302 9(4)	0.081 7(9)	0.161 9(6)
C(1)	0.164 7(5)	0.144 2(10)	-0.336 8(7)
C(2)	0.102 7(6)	0.163 2(11)	-0.415 6(7)
C(3)	0.020 0(5)	0.204 6(11)	-0.363 9(8)
C(4)	-0.003 9(5)	0.228 8(9)	-0.227 2(7)
C(5)	-0.088 1(5)	0.276 2(11)	-0.159 8(9)
C(6)	-0.106 0(5)	0.301 1(10)	-0.028 6(9)
C(7)	-0.042 2(4)	0.280 1(8)	0.049 7(7)
C(8)	-0.056 6(5)	0.304 2(10)	0.185 8(7)
C(9)	0.010 6(5)	0.281 3(10)	0.249 4(7)
C(10)	0.090 6(4)	0.236 3(9)	0.180 4(6)
C(11)	0.040 2(4)	0.232 3(8)	-0.014 7(6)
C(12)	0.060 2(4)	0.209 1(8)	-0.154 0(6)
C(13)	0.319 6(5)	-0.121 6(9)	-0.264 0(6)
C(14)	0.389 6(5)	-0.207 0(10)	-0.345 0(7)
C(15)	0.468 0(5)	-0.105 6(11)	-0.360 2(6)
C(16)	0.475 6(4)	0.086 3(10)	-0.297 8(6)
C(17)	0.556 0(5)	0.201 7(12)	-0.315 6(6)
C(18)	0.563 4(4)	0.387 2(12)	-0.259 2(7)
C(19)	0.490 8(4)	0.476 4(10)	-0.178 9(6)
C(20)	0.497 0(5)	0.665 8(10)	-0.113 8(7)
C(21)	0.428 4(5)	0.742 7(10)	-0.033 5(7)
C(22)	0.350 5(5)	0.627 8(10)	-0.018 0(7)
C(23)	0.410 2(4)	0.368 8(9)	-0.156 3(6)
C(24)	0.402 3(4)	0.170 4(9)	-0.218 1(5)
C(25)	0.272 8(4)	0.107 1(9)	0.074 5(6)
N(6)	0.810 6(5)	0.406 2(10)	0.524 4(7)
O(1)	0.777 1(5)	0.455 8(9)	0.439 6(7)
O(2)	0.790 7(7)	0.477 7(14)	0.637 7(8)
O(3)	0.857 0(6)	0.280 3(13)	0.488 6(8)
O(4)	0.327 4(4)	0.226 2(10)	0.444 1(6)
H(1)	0.222 1	0.111 1	-0.376 5
H(2)	0.118 4	0.148 8	-0.507 5
H(3)	-0.020 3	0.216 7	-0.418 3
H(5)	-0.132 5	0.288 2	-0.206 2
H(6)	-0.162 3	0.334 4	0.011 7
H(8)	-0.111 5	0.333 5	0.231 4
H(9)	0.001 9	0.299 4	0.342 6
H(10)	0.136 2	0.220 9	0.226 1
H(13)	0.265 5	-0.194 9	-0.254 2
H(14)	0.384 0	-0.336 1	-0.388 5
H(15)	0.516 5	-0.163 1	-0.412 8
H(17)	0.605 1	0.146 4	-0.367 2
H(18)	0.616 7	0.458 0	-0.275 2
H(20)	0.549 3	0.743 0	-0.127 6
H(21)	0.432 8	0.871 1	0.012 7
H(22)	0.302 0	0.681 4	0.039 1

TABLE 4

Bond distances (Å) and angles (°) with estimated standard deviations in parentheses

(a) Distances			
Pt-N(1)	2.062(5)	C(3)-C(4)	1.409(10)
Pt-N(2)	2.007(5)	C(7)-C(8)	1.395(9)
Pt-N(3)	2.053(5)	C(15)-C(16)	1.404(10)
Pt-N(4)	2.761(5)	C(19)-C(20)	1.395(10)
Pt-C(25)	1.931(6)	C(4)-C(5)	1.434(10)
N(1)-C(1)	1.312(8)	C(6)-C(7)	1.430(10)
N(2)-C(10)	1.337(8)	C(16)-C(17)	1.439(10)
N(3)-C(13)	1.354(8)	C(18)-C(19)	1.430(9)
N(4)-C(22)	1.329(8)	C(5)-C(6)	1.346(11)
N(1)-C(12)	1.390(8)	C(17)-C(18)	1.347(10)
N(2)-C(11)	1.375(8)	C(4)-C(12)	1.394(9)
N(3)-C(24)	1.373(8)	C(7)-C(11)	1.400(8)
N(4)-C(23)	1.355(8)	C(16)-C(24)	1.420(8)
C(1)-C(2)	1.409(10)	C(19)-C(23)	1.420(8)
C(9)-C(10)	1.377(9)	C(11)-C(12)	1.431(8)
C(13)-C(14)	1.391(9)	C(23)-C(24)	1.445(9)
C(21)-C(22)	1.404(9)	C(25)-N(5)	1.158(8)
C(2)-C(3)	1.359(11)	N(6)-O(1)	1.240(8)
C(8)-C(9)	1.377(10)	N(6)-O(2)	1.201(9)
C(14)-C(15)	1.361(10)	N(6)-O(3)	1.189(8)
C(20)-C(21)	1.349(10)		
(b) Angles			
N(1)-Pt-N(2)	81.7(2)	C(17)-C(18)-C(19)	120.6(6)
N(1)-Pt-N(3)	95.0(2)	C(3)-C(4)-C(12)	117.0(7)
N(1)-Pt-N(4)	101.0(2)	C(8)-C(7)-C(11)	117.7(6)
N(1)-Pt-C(25)	172.6(2)	C(15)-C(16)-C(24)	119.8(6)
N(2)-Pt-N(3)	175.3(2)	C(20)-C(19)-C(23)	117.6(6)
N(2)-Pt-N(4)	114.2(2)	C(5)-C(4)-C(12)	118.7(6)
N(2)-Pt-C(25)	92.2(2)	C(6)-C(7)-C(11)	117.9(6)
N(3)-Pt-N(4)	69.7(2)	C(17)-C(16)-C(24)	119.0(6)
N(3)-Pt-C(25)	90.8(2)	C(18)-C(19)-C(23)	120.0(6)
Pt-C(25)-N(5)	177.6(6)	C(4)-C(12)-N(1)	123.3(6)
Pt-N(1)-C(1)	130.2(5)	C(7)-C(11)-N(2)	123.3(6)
Pt-N(2)-C(10)	128.9(4)	C(16)-C(24)-N(3)	119.6(6)
Pt-N(3)-C(13)	114.9(4)	C(19)-C(23)-N(4)	121.8(6)
Pt-N(4)-C(22)	137.6(5)	C(12)-N(1)-C(1)	118.4(5)
Pt-N(1)-C(12)	111.3(4)	C(11)-N(2)-C(10)	117.0(5)
Pt-N(2)-C(11)	114.1(4)	C(24)-N(3)-C(13)	119.1(5)
Pt-N(3)-C(24)	125.8(4)	C(23)-N(4)-C(22)	118.0(5)
Pt-N(4)-C(23)	103.7(5)	N(1)-C(1)-C(2)	120.7(7)
C(1)-C(2)-C(3)	122.0(7)	N(2)-C(10)-C(9)	122.6(6)
C(8)-C(9)-C(10)	120.9(6)	N(3)-C(13)-C(14)	122.6(6)
C(13)-C(14)-C(15)	119.7(6)	N(4)-C(22)-C(21)	123.7(6)
C(20)-C(21)-C(22)	118.3(6)	C(4)-C(12)-C(11)	119.8(5)
C(2)-C(3)-C(4)	118.6(6)	C(7)-C(11)-C(12)	120.7(6)
C(7)-C(8)-C(9)	118.6(6)	C(16)-C(24)-C(23)	119.4(5)
C(14)-C(15)-C(16)	119.1(6)	C(19)-C(23)-C(24)	119.2(6)
C(19)-C(20)-C(21)	120.6(6)	N(1)-C(12)-C(11)	116.9(5)
C(3)-C(4)-C(5)	124.3(6)	N(2)-C(11)-C(12)	116.0(5)
C(6)-C(7)-C(8)	124.4(6)	N(3)-C(24)-C(23)	121.0(5)
C(15)-C(16)-C(17)	121.2(6)	N(4)-C(23)-C(24)	119.1(5)
C(18)-C(19)-C(20)	122.2(6)	O(1)-N(6)-O(2)	119.2(8)
C(4)-C(5)-C(6)	121.2(6)	O(1)-N(6)-O(3)	117.3(7)
C(5)-C(6)-C(7)	121.7(6)	O(2)-N(6)-O(3)	123.4(9)
C(16)-C(17)-C(18)	121.8(6)		

ation of Pt(phen)(CN)<sub>2</sub> and must be avoided. The lemon-yellow nitrate or perchlorate was isolated after precipitation with Na[NO<sub>3</sub>] or Na[ClO<sub>4</sub>] {Found for the perchlorate: C, 43.4; H, 2.40; Cl, 5.25; N, 10.05; Pt, 28.15%. Calc. for [Pt(phen)<sub>2</sub>(CN)][ClO<sub>4</sub>]·0.5H<sub>2</sub>O: C, 43.5; H, 2.50; Cl, 5.15; N, 10.15; Pt, 28.3%}.

*pH and Conductivity Measurements.*—These were made with a CDM 3 conductivity meter with CDC 4 electrodes and a PHM 64 pH meter with GK 2301 C combined glass-calomel electrode, all from Radiometer, Copenhagen. All solutions were saturated with N<sub>2</sub>.

*Spectroscopic Measurements.*—Ultraviolet spectra were recorded on a Beckman Acta III spectrometer and n.m.r. spectra on a JEOL FX-60 Fourier-transform spectrometer.

The samples used were prepared in the following way.

**Sample (1).** The salt  $K_2[Pt(CN)_4]$  (ca. 30 mg) was dissolved in  $D_2O$  (ca. 1.8 cm<sup>3</sup>) and hydrated chromium(III) chloride (30 mg) was added. The spectrum was recorded during 16 h.

**Sample (2).** The compound  $[Pt(phen)_2]Cl_2$  (ca. 30 mg) was dissolved in  $D_2O$  (2 cm<sup>3</sup>). The spectrum was recorded during 16 h.

**Sample (3).** Acetone–nitromethane (1 : 4) was saturated with  $[Pt(phen)_2(CN)]_2[ClO_4]$ , and  $[Cr(acac)_3]$  (acac = acetylacetonate) was added (30 mg per cm<sup>3</sup>). The spectrum was recorded during 16 h.

**Sample (4).** The compound  $[Pt(phen)_2]Cl_2$  (30 mg) was dissolved in  $D_2O$  (0.8 cm<sup>3</sup>) and the equivalent amount of  $K[CN]$  dissolved in  $D_2O$  (1 cm<sup>3</sup>) was added dropwise and with rapid stirring. Experiments with addition of chromium chloride led to precipitation and so the spectrum was recorded during 16 h without addition of  $Cr^{III}$ .

**Sample (5).** Water was saturated with phenanthroline at ca. 80 °C, and the spectrum recorded at this temperature.

The <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra were recorded subsequently with the same instrument.

All solutions used for n.m.r. measurements were analysed by their u.v. spectra which were identical to the spectra of the dissolved crystalline samples. The assignments of the <sup>13</sup>C peaks were checked by comparison with spectra of the methyl-substituted phenanthrolines and were in agreement with theoretical calculations of Rosenberger *et al.*<sup>25</sup>

**X-Ray Investigation.**—The crystal used was grown from an aqueous solution of the nitrate by slow evaporation. Crystals thus obtained gave Hagg–Guinier diagrams that were identical with those of the original sample.

**Crystal Data.**— $C_{25}H_{14}N_6O_4Pt$ ,  $M = 657.5$ , Triclinic,  $a = 15.616(11)$ ,  $b = 7.264(6)$ ,  $c = 10.564(7)$  Å,  $\alpha = 102.81(4)$ ,  $\beta = 80.90(4)$ ,  $\gamma = 96.47(4)^\circ$ ,  $U = 1150$  Å<sup>3</sup>,  $D_c = 1.90$  g cm<sup>-3</sup>,  $Z = 2$ ,  $F(000) = 732$ , Mo- $K_\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu = 62.1$  cm<sup>-1</sup>, space group  $P\bar{1}$  ( $C_1$ ). The compound crystallizes as pale yellow laths elongated along  $b$  and terminated by {001} or by {010}; the most prominent faces are {100}.

**Crystallographic Measurements.**—A crystal  $0.05 \times 0.55 \times 0.32$  mm was mounted on a Picker FACS-1 diffractometer. Unit-cell dimensions were determined from the setting angles for 20 reflections and intensities were measured out to  $2\theta = 45^\circ$  with monochromatic Mo- $K_\alpha$  radiation. Data were collected using the  $\omega$ - $2\theta$  step scanning technique with a step length of  $0.04^\circ$  and a scan width of  $3.0 + 0.692 \tan \theta$ . A total of 4056 independent reflections were measured of which 3562 had  $I > 3\sigma(I)$  according to counting statistics. The intensities were corrected for absorption, the transmission factors ranging from 19 to 73%.

**Structure Analysis.**—The position of the Pt was determined from a Patterson synthesis. A difference map showed the phenanthroline groups, the nitrate ion, and a water molecule. Least-squares refinement of atomic co-ordinates, with anisotropic thermal parameters for Pt, C, N, and O, a scale factor, and an isotropic extinction factor,  $g$ , gave  $R = 0.031$  and  $R' = 0.038$  for 312 parameters and 3562 reflections. Positions of the H atoms of the phenanthroline groups were obtained from a difference map at  $R = 0.044$ . These were included in the final calculations but were not refined. The value for  $g$  was  $1.2(2) \times 10^{-7}$  with  $l$ , the mean pathlength, assumed to be unity. Atomic co-ordinates are given in

\* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

Table 3 and bond lengths and angles in Table 4. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22719 (18 pp.).\*

Calculations were carried out on a CYBER 173 computer with the following programs: data processing, PROFILE, DATAP, and DSORTH, State University of New York at Buffalo; full-matrix least-squares refinement, LINUS;<sup>26</sup> distances and angles, ORFFE;<sup>27</sup> drawings, ORTEP.<sup>28</sup> Atomic scattering factors were taken from ref. 29 for Pt, ref. 30 for C, N, and O, and ref. 31 for H. Corrections were made for the anomalous dispersion of Pt.<sup>32</sup>

We thank Dr. G. Nord, the University of Copenhagen, for bringing ref. 1 to our notice.

[9/730 Received, 11th May, 1979]

#### REFERENCES

- R. D. Gillard and J. R. Lyons, *J.C.S. Chem. Comm.*, 1973, 585.
- E. Bielli, R. D. Gillard, and D. W. James, *J.C.S. Dalton*, 1976, 1837.
- R. D. Gillard, L. A. P. Kane-Maguire, and P. A. Williams, *Transition Metal Chem.*, 1976, 1, 247.
- K. H. Al-Obaidi, R. D. Gillard, L. A. P. Kane-Maguire, and P. A. Williams, *Transition Metal Chem.*, 1977, 2, 64, and refs. therein.
- J. Burgess and R. I. Haines, *J.C.S. Dalton*, 1978, 1447.
- J. Burgess, A. J. Duffield, and R. I. Haines, *Transition Metal Chem.*, 1977, 2, 276.
- G. Nord and O. Wernberg, *J.C.S. Dalton*, 1972, 866.
- G. Nord and O. Wernberg, *J.C.S. Dalton*, 1975, 845.
- G. Nord, *Inorg. Chem.*, 1976, 15, 1921.
- C. Creutz and N. Sutin, *Proc. Nat. Acad. Sci. U.S.A.*, 1975, 72, 2858.
- M. A. Jamieson, N. Serpone, and V. Balzani, *Inorg. Chem.*, 1978, 17, 2432.
- M. Matestri, F. Bolletta, N. Serpone, and V. Balzani, *Inorg. Chem.*, 1976, 15, 2048.
- G. Nord, *Acta Chem. Scand.*, 1975, A29, 270.
- F. Basolo and G. Pearson, 'Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967.
- B. A. Frenz and J. A. Ibers, *Int. Rev. Sci.: Phys. Chem. Ser. One*, 1972, 11, 33.
- S. Nishigaki, H. Yoshioka, and K. Nakasatu, *Acta Cryst.*, 1978, B34, 875.
- S. R. Hall, D. L. Kepert, C. L. Raston, and A. H. White, *Austral. J. Chem.*, 1977, 30, 1955.
- G. W. Bushnell, K. R. Dixon, and M. A. Khan, *Canad. J. Chem.*, 1974, 52, 1367.
- E. L. Muetterties and R. A. Schunn, *Quart. Rev.*, 1966, 20, 245.
- P. Haake and R. M. Pfeiffer, *J. Amer. Chem. Soc.*, 1970, 92, 4996.
- W. J. Louw, *Inorg. Chem.*, 1977, 16, 2147.
- D. R. Eaton, *J. Amer. Chem. Soc.*, 1968, 90, 4272.
- R. J. Mureinik and M. Bidani, *Inorg. Chem. Acta*, 1978, 29, 37.
- G. M. Intille, C. E. Pfluger, and W. A. Baker, jun., *J. Cryst. Mol. Struct.*, 1973, 3, 47.
- H. Rosenberger, M. Pettig, K. Madeja, T. Pehk, and E. Lippmaa, *Org. Magn. Reson.*, 1970, 2, 329.
- P. Coppens and W. C. Hamilton, *Acta Cryst.*, 1970, A26, 71.
- W. R. Busing, K. O. Martin, and H. A. Levy, ORFFE, Oak Ridge National Laboratory, Report ORNL-TM-306, 1964.
- C. K. Johnson, ORTEP, Oak Ridge National Laboratory, Report ORNL-3794, 1965.
- 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, p. 92.
- D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, A24, 321.
- R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, 42, 3175.
- D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, 53, 1891.