Crystal Structure of the Red Form of 2,2′-Bipyridyldichloroplatinum(II)

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The crystal structure of the red form of [(2,2′-bipyridyl)$PtCl_2$] has been determined from *X*-ray diffractometer data. Crystals are orthorhombic, space group *Cmcm*, with a = 17·666(2), b = 9·086(1), c = 6·803(1) Å, Z = 4. The structure was derived from 554 intensities, by Patterson and Fourier methods, and refined by least squares to R 0·024. The structure comprises layers of monomeric molecules lying parallel to (001) and separated by 3·40 Å. The platinum atoms are nearly superimposed and are separated by 3·45 Å. There is marked pleochroism, the maximum absorption of the broad line at 520 nm occurring when the electric vector is parallel to the strings of platinum atoms.

Unit-cell parameters for the yellow form are a = 15·93, b = 7·22, c = 18·38 Å; space group *Pbca*, Z = 8.

Two polymorphic forms of 2,2′-bipyridyldichloroplatinum(II), $Pt(bipy)Cl_2$, are known, a yellow form (A) and a red form (B). The latter, which is obtained from boiling concentrated hydrochloric acid,[1] exists only in the solid state and reverts to (A) in solution. Details of the preparation, chemical properties, and spectra have been described by Gillard and Gidney [2] who also reported the two powder patterns. In early correspondence they suggested that the chemical and spectroscopic observations for the red form were consistent with either a polymeric structure or a simple stacking of monomers. We have determined the unit cell and space group for both forms, and report the detailed structure of the red form. It is monomeric with all molecules lying parallel to the (001) plane and with the platinum atoms almost superimposed and separated by 3·45 Å.

EXPERIMENTAL

Unit-cell parameters were determined photographically for the yellow form, and by means of a diffractometer for the red form.

Crystal Data.—$C_{10}H_8Cl_2N_2Pt$, M = 422·19. Yellow form (A): Orthorhombic, a = 15·93, b = 7·22, c = 18·38 Å, U = 2114 Å^3, D_c = 2·65 g cm^{-3}, Z = 8. Space group *Pbca* uniquely from Laue symmetry and systematic absences. Powder pattern [2] shows the structure to be isomorphous with that of $Pd(bipy)Cl_2$.

Red form (B): Orthorhombic, a = 17·666(2), b = 9·086(1), c = 6·803(1) Å, U = 1092 Å^3, D_c = 2·56 g cm^{-3}, Z = 4. $F(000)$ = 776, $\mu(\text{Cu-}K_\alpha)$ = 292 cm^{-1}. Space group *Cmcm* (No. 63), $Cmc2_1$, or *C2cm* (variants of Nos. 36 and 40 respectively) from systematic absences: hkl when $h + k = 2n + 1$, $h0l$ when $l = 2n + 1$. *Cmcm* was established by the structure solution. See ref. 2 for powder pattern. The crystals were needles, bounded by {110}, which showed marked pleochroism (red-orange), the maximum absorption occurring when the electric vector was parallel to the needle axis c. The specimen used was selected for its uniformity of cross-section and, taking advantage of the good cleavage on (001), it was cut to approximately equant proportions. It was mounted on a Siemens single-crystal diffractometer with c parallel to the ϕ axis, and its dimensions were measured for use when applying an absorption correction.

Intensity data were collected by the five-value technique [3] with copper-K_α radiation, to θ 70°. Within the unique volume of reciprocal space 569 distinct reflections were measured of which 15 having $I < 2·58\ \sigma(I)$ were classed unobserved.[3] Intensity data were processed in the usual way [3] and a three-dimensional Patterson computed. This showed clearly that the molecules occupied special positions of $m2m$ symmetry, with the molecular planes parallel to (001) at intervals of $c/2$, the diad running through the platinum atom and parallel to b. Only space group *Cmcm* has special positions of this sort, but both $Cmc2_1$ and *C2cm* have special positions of symmetry m so that, if the departure from $m2m$ symmetry were small, the Patterson for these two space groups would have looked very similar. The Patterson therefore, only eliminated the special posi-

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[1] P. M. Gidney, Ph.D. Thesis, University of Kent, 1972.

[2] E. Bielli, R. D. Gillard, P. M. Gidney, and B. T. Heaton, *J.C.S. Dalton*, submitted for publication.

[3] P. G. H. Troughton, *Siemens Review*, 4th Special Issue *X*-Ray and Electron Microscopy News, 1970, **37**, 22—32; F. H. Allen, D. Rogers, and P. G. H. Troughton, *Acta Cryst.*, 1971, **B27**, 1325.

tions on the diads of *C2cm*. For simplicity, solution and refinement were started in *Cmcm* and proved successful.

The Harker section ($w = 0$) contained among other things four conspicuously strong images of the molecule, each due to bringing a platinum atom to the origin of the Patterson. They occurred in two centrosymmetric pairs centred on 0,0,0 and ½,½,0 respectively, and each pair was readily separated into its component images. The y co-ordinate of the Pt atom was obtained from the Harker section $w = \frac{1}{2}$. It was possible, therefore, to insert all the non-hydrogen atoms in the first electron-density map, which then formed the basis for full-matrix least-squares refinement. Four cycles of isotropic refinement using ORFLS[4] gave R 0·109.

Intensities were then corrected for absorption,[5] and all non-hydrogen atoms were refined anisotropically to R 0·054. The ΔF map at this stage gave no clear indication of hydrogen atom positions, so ' ideal ' hydrogen co-ordinates were calculated using BONDLA[4] and assuming C–H 1·075 Å. Hydrogen atoms at these positions were given isotropic temperature factors and included in the next stages of refinement, but as their thermal parameters did not converge satisfactorily they were all fixed at B 4·0 Å^2 for the later cycles of refinement. The platinum form factors were corrected for dispersion, by use of a program by D. J. Williams for centrosymmetric structures, and values of $\Delta f'$ and $\Delta f''$ from ref. 6. Examination of the ΔF values led to the exclusion of seventeen terms which had apparently suffered extinction. Otherwise, no weighting scheme was deemed necessary. After further cycles of ORFLS, R was 0·024, and bond lengths and valence angles were calculated. As hydrogen atoms H(2) and H(3) had moved to quite improbable positions, they were resited and a few more cycles were run. The only appreciable shifts were for a few hydrogen atoms, but these gave no significant overall improvement, and, as the hydrogen atoms are not of particular importance in this structure, computing was stopped. Calculated hydrogen atom co-ordinates are listed in Table 1, together with final atomic co-ordinates for non-hydrogen atoms, with their standard deviations. Bond lengths and valence angles are in Tables 2 and 3, and shorter intermolecular contacts in Table 4. Observed and calculated structure factors (including those for the seventeen terms affected by extinction) are compared in Supplementary Publication No. SUP 20953 (6 pp.),* which also contains the anisotropic temperature factors for the non-hydrogen atoms.

A final ΔF map showed no value of $\Delta\rho > 0{\cdot}4$ e Å^{-3} except for small regions near the platinum atoms where values from $-1{\cdot}6$ to $0{\cdot}9$ e Å^{-3} occurred. The shape of these was generally rather similar to that resulting from inadequate anisotropic refinement, but there seem to be unusual anisotropy problems with the electron distribution in platinum atoms; we have recently observed similar effects in other thoroughly refined structures containing platinum.

TABLE 1

Fractional atomic co-ordinates ($\times 10^5$), with standard deviations, derived from full-matrix least-squares refinement, in parentheses

Atom	x	y	z
Pt	0	−3102(4)	25000
Cl	9143(13)	−21223(22)	25000
N	7251(36)	13811(71)	25000
C(1)	4284(44)	27229(87)	25000
C(2)	8458(63)	39918(106)	25000
C(3)	16265(69)	38680(120)	25000
C(4)	19522(57)	24790(139)	25000
C(5)	14961(48)	12676(111)	25000

Calculated fractional atomic co-ordinates ($\times 10^3$) for hydrogen atoms *

H(2)	59	510	250
H(3)	200	484	250
H(4)	258	237	250
H(5)	179	18	250

* Numbered according to the carbon atom to which each is bound.

TABLE 2

Bond lengths (Å), with calculated standard deviations in parentheses

Pt–Cl	2·306(2)	C(3)–C(4)	1·39(2)
Pt–N	2·001(6)	C(4)–C(5)	1·36(2)
N–C(1)	1·33(1)	C(5)–N	1·37(1)
C(1)–C(2)	1·37(1)	C(1)–C(1′)	1·51(3) *
C(2)–C(3)	1·38(2)		

* Estimated standard deviation.

TABLE 3

Valence angles (°). The standard deviation for all angles is *ca.* 1°

Cl–Pt–Cl′	88
Cl–Pt–N	96
N–Pt–N′	80
Pt–N–C(1)	117
N–C(1)–C(1′)	113
N–C(1)–C(2)	124
C(1)–C(2)–C(3)	118
C(2)–C(3)–C(4)	119
C(3)–C(4)–C(5)	119
C(4)–C(5)–N	122
C(5)–N–C(1)	118

TABLE 4

Intermolecular distances (Å) from the atoms of one molecule to those of the molecule immediately above or below it

Cl · · · N	3·48
Cl · · · C(1)	3·55
Cl · · · C(5)	3·64
Pt · · · Pt	3·45
Separation of molecular planes	3·40

DISCUSSION OF THE STRUCTURE

The structure (Figures 1 and 2) is unequivocally shown to be the second of the two alternatives mentioned earlier, *viz.*, a simple stacked arrangement of monomers, separated by 3·40 Å. During the course of this work further chemical evidence emerged in favour of this structure.[1] The platinum co-ordination is essentially

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are sent as full size copies).

[4] ' *X*-Ray '63 ' Program System for *X*-Ray Crystallography, J. M. Stewart, University of Maryland, Technical Report TR 646.

[5] P. G. H. Troughton, ICABS, absorption correction program for the University of London ATLAS Computer, based on program by P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Cryst.*, 1965, **18**, 1035.

[6] ' International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1965.

square planar and the Pt–Cl and Pt–N distances [2·306(2) and 2·001(6) Å] are similar to values given for such bonds in other compounds.[7-10] The bond lengths in the bipyridyl unit agree closely with corresponding values reported for 2-hydroxypyridinium chloride,[11] the standard deviations being *ca.* 0·01 Å in both studies.

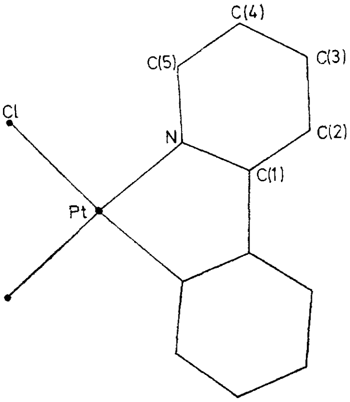

FIGURE 1 Numbering scheme used. Atoms in the lower mirrored half of the molecule are denoted by primes

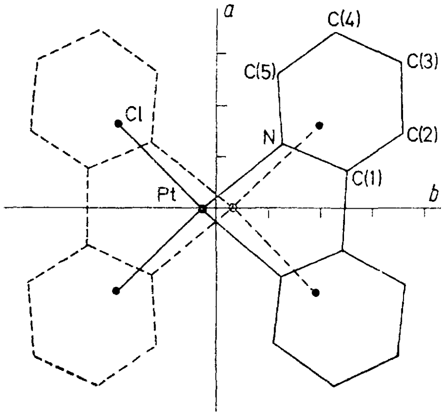

FIGURE 2 View along the *c* axis showing the superimposition of molecules in one stack

The manner in which the molecules overlie one another in the [001] projection is shown in Figure 2, which shows that the platinum atoms are nearly superimposed. They are separated by 3·45 Å and the Pt · · · Pt vector is inclined to the *c* axis at only 4·7°. The distances between the chlorine atoms and the nearest atoms in the adjacent aromatic rings are: Cl–N 3·48, Cl–C(1) 3·55, Cl–C(5) 3·64 Å; none of these is shorter than the expected van der Waals contact distance. The need to maintain these minimal clearances seems to have prevented the exact superimposition of the platinum atoms, since any movement of the molecules in their own plane to reduce the lateral displacement of platinum atoms would be resisted by the shortening of four of the six contacts of each chlorine. This is an inefficient mode of packing compared with the yellow polymorph as it is 3·2% less dense.

In complexes of this type, consisting of monomeric units stacked so that there is a continuous chain of metal atoms throughout the structure, there is frequently a metal–metal interaction which gives rise to pleochroism and to characteristic spectral properties. The latter have been comprehensively reviewed.[12] Most of the values reported for the Pt · · · Pt distance lie in the range 3·09—3·40 Å, whereas we find 3·45 Å. However, the colourless compound, $Sr[Pt(CN)_4],5H_2O$,[13] has a Pt · · · Pt separation of 3·60 Å and there is spectroscopic evidence for a weak metal–metal interaction. Gillard and Gidney [2] have shown that for $Pt(bipy)Cl_2$ the visible and u.v. reflectance spectra of the yellow and red forms differ only in the occurrence for the red form of an extra line at 520 nm which is polarised, having its maximum absorption when the *E* vector is parallel to the *c* axis and thus to the Pt · · · Pt chains.

The structure of the yellow form of this compound is currently under study in this laboratory.

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[11] S. A. Mason, J. C. B. White, and A. Woodlock, *Tetrahedron Letters*, 1969, 5219.

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

[13] K. Krogmann and D. Stephan, *Z. anorg. Chem.*, 1968, **362**, 290; see also ref. 12, pp. 110 and 111.