centroids of the Cp rings are 2.388 [6] Å from the Y atoms, but the Cp planes are not perpendicular to the Y—Cp vectors. Y—C(Cp ring) distances range from 2.585 (5) to 2.817 (6) Å, with the C atoms closest to the Si bridge being closest to Y. This effect is caused by the bridging Si atom; it 'pinches' the Cp rings together and the Y atom can no longer fit between them perfectly. This effect is also seen in the angle between the two Cp planes: this is 113 (4)°, whereas the Cp1—Y—Cp2 angle is 122.3°. {The Cp(C)—Si1—Cp(C) angle is 99.3 [3]°.} Other distances in the Y molecule are normal: Y—Cl 2.627 [12], Si—C 1.863 [12], C—C (Cp rings) 1.422 [17] Å. In each molecule there is a strain evidenced by two normal C(Cp)—Si—CH$_3$ angles of 108.4 [4]° and a third larger angle of 117.0[10]°, to the methyl C atom near the other Cp ring. This strain appears in all four independent Cp rings and reflects a steric crowding between the —Si(CH$_3$)$_3$ group and the rest of the molecule: from the affected CH$_3$ group, C—C distances are 3.81 [4] Å to a methyl C atom on the Si bridge (C1 or C2), 4.02 [5] Å to a methyl C atom on the ^{t}Bu group of the opposite bridge and only 3.68 [3] Å to a Cp C atom in the opposite Cp ring. The 'radius' of a —CH$_3$ group is taken as 2.0 Å; thus the first contact is 0.09 Å short while the second is at just the van der Waals distance. The 3.68 Å contact is short enough to imply the severe strain of bending a C—Si—C bond by 8° or so.

The Li(thf)$_2^+$ group is joined to the two Cl atoms of the Y molecule, with Li—Cl distances averaging 2.371 [25] Å, almost exactly the sum of the crystal radii for Li$^+$ and Cl$^-$ and shorter than the Li—C distance (2.57 Å) in LiCl (Wells, 1962). Coordination about the Li$^+$ atom is approximately tetrahedral (Fig. 1), with normal Li—O distances {1.92 [2] Å}. The thf molecules have large apparent thermal motions, indicating a moderate disorder.

This work has been supported by the USDOE Office of Basic Energy Sciences (Grant No. DE-FG03-85ER113431) and by Exxon Chemicals Americas.

References

Cromer, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 149–151. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 99–101. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Duchamp, D. J. (1964). CRYM crystallographic computing system. Am. Crystallogr. Assoc. Meet., Bozeman, Montana. Paper B14, p. 29.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.

Piers, W. E., Shapiro, P. J., Bunel, E. E. & Bercaw, J. E. (1990). *Synlett*, **2**, 74–84.

Roll, W., Brintzinger, H. H., Rieger, B. & Zolk, R. (1990). *Angew. Chem. Int. Ed. Engl.* **29**, 279–280.

Wells, A. F. (1962). *Structural Inorganic Chemistry*, 3rd edition, p. 357. Oxford Univ. Press.

Wiesenfeldt, H., Reinmuth, A., Barsties, E., Evertz, K. & Brintzinger, H. H. (1989). *J. Organomet. Chem.* **369**, 359–370.

Acta Cryst. (1992). C**48**, 1776–1778

A Bis(pyrazolyl)(bipyridyl)platinum Complex

By William P. Schaefer, William B. Connick, Vincent M. Miskowski and Harry B. Gray

Division of Chemistry and Chemical Engineering and The Beckman Institute, Mail Code* 139-74,
California Institute of Technology, Pasadena, California 91125, *USA*

(*Received* 26 *December* 1991; *accepted* 11 *February* 1992)

Abstract. (4,4′-Dimethyl-2,2′-bipyridyl)bis(3,5-dimethylpyrazolium)platinum(II) 0.5-tetrahydrofuran solvate monohydrate, [Pt(C$_5$H$_7$N$_2$)$_2$(C$_{12}$H$_{12}$N$_2$)].0.5C$_4$H$_8$O.H$_2$O, M_r = 623.65, monoclinic, $P2_1/n$, a = 8.625 (2), b = 20.593 (8), c = 14.451 (4) Å, β = 90.32 (2)°, V = 2566.7 (14) Å^3, Z = 4, D_x = 1.61 g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, μ = 55.50 cm^{-1}, F(000) = 1232, room temperature, R = 0.0387 for 2874 reflections with $F_o^2 > 3\sigma(F_o^2)$. The square-planar Pt complex has normal Pt—N(bipyridyl) bonds [2.009 (8) Å] and slightly short Pt—N(pyrazolyl) bonds [1.983 (7) Å]. The ligand molecules have normal distances and angles; the planes of the pyrazolyl ligands are twisted by about

---

* Contribution No. 8555.

0108-2701/92/101776-03$06.00

60° to the bipyridyl–Pt plane, with the closest contacts between the pyrazolyls being ~3.3 Å (C14···N5 and C19···N3).

Introduction. In the course of our work on platinum(II) pyrazolyl bridged dimers, we have prepared a series of bis(pyrazolyl)(bipyridyl)platinum(II) monomers. These complexes have emissive states of MLCT or π–π^* character, depending on the substituents on the pyrazole ring. Here we report the structure of (4,4′-dimethyl-2,2′-bipyridyl)bis(3,5-dimethylpyrazolium)platinum(II), a derivative synthesized according to the literature method for the unmethylated analog (Minghetti, Banditelli & Bonati, 1979).

Experimental. A yellow needle, 0.07 × 0.07 × 0.36 mm, crystal was used for data collection on a CAD-4 diffractometer with ω scans. 25 reflections with $14 < 2\theta < 16°$ were used for determination of the unit cell. An absorption correction based on ψ scans of six reflections, with relative transmissions from 0.882 to 1.000, was applied to the data collected: $(\sin\theta/\lambda)_{\max} = 0.59$ Å^{-1}; h from −10 to 10, k from −24 to 24, l from 0 to 17. Three standard reflections (204, $2\bar{5}\bar{2}$, $2\bar{3}3$) showed no variations greater than those predicted by counting statistics. 9834 reflections were measured, of which 4501 were independent; goodness of fit for merging 4368 multiples was 0.974; $R_{\text{merge}} = 0.041$ for 3377 duplicates. All reflections were used in solution and refinement of the structure. The Pt atom was located from a Patterson map, while the remaining heavy atoms were found by successive structure factor–Fourier calculations. F^2 values were used in the least-squares refinement. H atoms were positioned by calculation (C—H = 0.95 Å) and not refined. Coordinates and anisotropic displacement parameters of all atoms in the Pt molecule and the water O atom, plus a scale factor were refined. For 3933 reflections with $F_o^2 > 0$, R (on F) = 0.062, wR (on F^2) = 0.0078; S = 1.49 for 271 parameters and 4501 reflections. Weights were taken as $1/\sigma^2(F_o^2)$; variances $[\sigma^2(F_o^2)]$ were derived from counting statistics plus an additional term, $(0.014I)^2$; variances of the merged data by propagation of e.s.d. plus another additional term, $(0.014\bar{I})^2$. $(\Delta/\sigma)_{\max} = 0.01$. The final difference map showed one peak of 2.2 e Å^{-3}, 1.8 Å from C18 and C19, with the next highest of 1.4 e Å^{-3} near the Pt atom; the largest negative peak, −1.9 e Å^{-3}, was near C23 of the disordered thf. Atomic scattering factors and dispersion corrections were taken from Cromer & Waber (1974) and Cromer (1974). Computer programs used were those of the *CRYM* crystallographic computing system (Duchamp, 1964) and *ORTEP* (Johnson, 1976). Final refined parameters of the atoms are listed in Table 1.* The tetrahydrofuran molecule is located near a center of symmetry and its parameters could not be refined; an idealized thf molecule was positioned based on difference maps.

Table 1. *Final refined positional parameters* (× 10^4) *and equivalent isotropic displacement parameters* (Å^2 × 10^4)

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Pt	2451 (.4)	1366 (.2).	3618 (.3)	372 (1)
N1	1470 (8)	1091 (3)	4821 (5)	396 (18)
C1	540 (10)	1446 (5)	5346 (7)	491 (24)
C2	−19 (11)	1231 (5)	6192 (7)	579 (29)
C3	380 (11)	620 (5)	6506 (7)	519 (29)
C4	−198 (14)	363 (6)	7413 (8)	818 (38)
C5	1326 (11)	243 (4)	5948 (7)	486 (25)
C6	1867 (9)	480 (4)	5124 (7)	393 (22)
C7	2904 (9)	129 (4)	4492 (7)	412 (24)
C8	3346 (11)	−506 (4)	4646 (7)	495 (25)
C9	4327 (11)	−804 (5)	4013 (8)	537 (27)
C10	4760 (14)	−1510 (5)	4131 (9)	810 (39)
C11	4858 (11)	−452 (5)	3263 (8)	539 (27)
C12	4342 (11)	194 (5)	3147 (7)	488 (25)
N2	3379 (8)	481 (3)	3747 (5)	384 (18)
N3	1428 (8)	2224 (3)	3584 (5)	396 (19)
C13	2057 (10)	2817 (4)	3578 (7)	445 (24)
C14	3747 (11)	2936 (5)	3683 (8)	615 (29)
C15	872 (12)	3267 (5)	3496 (7)	567 (28)
C16	−471 (10)	2901 (5)	3445 (7)	501 (26)
C17	−2140 (12)	3126 (5)	3354 (8)	735 (34)
N4	−161 (8)	2272 (4)	3502 (5)	454 (21)
N5	3488 (8)	1581 (3)	2430 (5)	413 (19)
C18	2854 (11)	1740 (5)	1615 (7)	487 (26)
C19	1160 (12)	1696 (6)	1420 (8)	709 (34)
C20	4045 (12)	1901 (5)	1020 (7)	589 (30)
C21	5428 (11)	1837 (5)	1529 (7)	498 (26)
C22	7058 (12)	1937 (6)	1233 (8)	805 (38)
N6	5087 (8)	1639 (4)	2389 (6)	489 (21)
W1	7648 (8)	1255 (3)	3509 (6)	901 (23)

We collected data for this compound with a crystal that had $\beta = 90.14°$, solved and refined the structure, but large peaks in the difference map and distorted geometry in pyrazolyl ligand 2 caused us to conclude that our crystal was bad. The results reported here are based on data from a crystal that showed no sign of any twinning or deformity; still, the large positive peak in the difference map is near where the worst one was for the first crystal.

Discussion. A drawing of the molecule including the numbering system is shown in Fig. 1, and Table 2 gives distances and angles in the molecule. The packing is shown in Fig. 2. The Pt—N distances to the bipyridyl N atoms are equal at 2.009 (13) Å, and to the pyrazolyl N atoms at 1.983 (11) Å. Distances and angles in the ligand atoms are normal, with C—CH_3 bonds being a little short, especially in the pyrazolyl

---

* Lists of assigned H-atom parameters, anisotropic displacement parameters, complete distances and angles, and observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55183 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0621]

ligands [C18—C19 = 1.449 (14) Å is the shortest]. The pyrazolyl ligands are twisted out of the Pt–bipyridyl plane by 64 (3)° each. This orientation is comparable to other *cis*-bis(nitrogen heterocycle) platinum(II) systems {41.7° for *cis*-[Pt(*N*-methylimidazole)$_2$Cl$_2$] (Graves, Hodgson, van Kralingen & Reedijk, 1978), and 55.3 and 73.2° for *cis*-[Pt(pyrazole)$_2$Cl$_2$] (Cinellu, Stoccoro, Minghetti, Bandini, Banditelli & Bovio, 1989)}. There are short distances between N3 and C19 [3.32 (1) Å] and N5 and C14 [3.33 (1) Å]. The H atoms on C14 and C19 show up as two sets of three H atoms each in the plane where they are expected, but none of them points toward the close N atom. The water molecule is 2.82 (1) Å from N4, indicating a hydrogen bond between them; there are also contacts between the water molecule and C5 and C8 in a different molecule [3.30 (1) and 3.20 (1) Å]. The Pt—O(water) distance [4.492 (7) Å] and all other intermolecular distances are at van der Waals distances or greater.

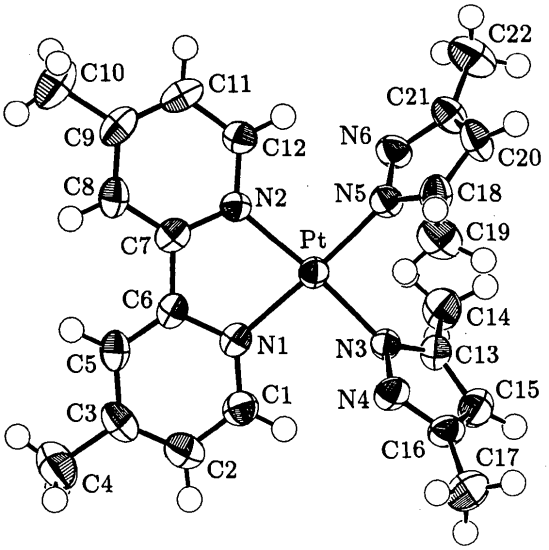

Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the molecule showing the numbering system. Heavy atoms are shown as 50% probability ellipsoids, H atoms as spheres of arbitrary size.

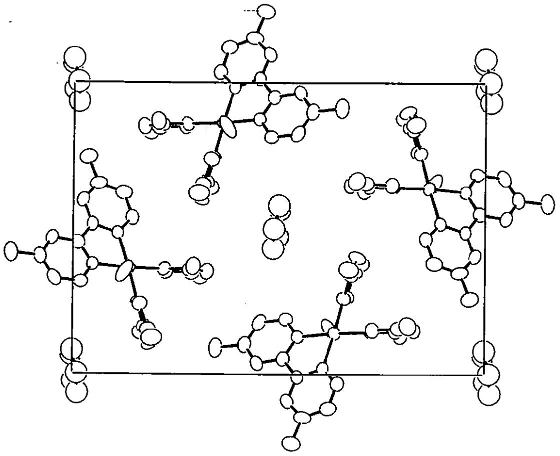

Fig. 2. An *ORTEP*II (Johnson, 1976) projection down the *a* axis, with 50% probability ellipsoids. The contents of one unit cell (not including H atoms) are shown, plus three additional thf molecules. Only one molecular orientation is shown at each thf site.

Table 2. *Distances* (Å) *and angles* (°)

Pt—N1	2.018 (7)	C11—C12	1.412 (14)
Pt—N2	2.000 (7)	C12—N2	1.341 (12)
Pt—N3	1.975 (7)	N3—C13	1.337 (11)
Pt—N5	1.990 (7)	N3—N4	1.379 (10)
N1—C1	1.327 (12)	C13—C14	1.485 (13)
N1—C6	1.376 (11)	C13—C15	1.384 (13)
C1—C2	1.389 (14)	C15—C16	1.383 (14)
C2—C3	1.381 (14)	C16—C17	1.517 (15)
C3—C4	1.501 (15)	C16—N4	1.326 (12)
C3—C5	1.388 (14)	N5—C18	1.338 (12)
C5—C6	1.371 (13)	N5—N6	1.386 (10)
C6—C7	1.471 (12)	C18—C19	1.489 (14)
C7—C8	1.379 (13)	C18—C20	1.383 (14)
C7—N2	1.363 (11)	C20—C21	1.404 (14)
C8—C9	1.391 (14)	C21—C22	1.486 (15)
C9—C10	1.512 (15)	C21—N6	1.342 (12)
C9—C11	1.384 (14)		

N1—Pt—N2	80.4 (3)	C11—C9—C10	120.7 (9)
N1—Pt—N3	94.8 (3)	C12—C11—C9	118.8 (9)
N1—Pt—N5	176.2 (3)	N2—C12—C11	122.2 (8)
N2—Pt—N3	175.2 (3)	C12—N2—C7	117.9 (7)
N2—Pt—N5	95.8 (3)	N4—N3—C13	109.7 (7)
N3—Pt—N5	89.0 (3)	C14—C13—N3	123.2 (8)
C6—N1—C1	118.2 (7)	C15—C13—N3	108.2 (8)
C2—C1—N1	122.8 (9)	C15—C13—C14	128.6 (9)
C3—C2—C1	119.6 (9)	C16—C15—C13	105.0 (9)
C4—C3—C2	121.7 (9)	C17—C16—C15	129.2 (9)
C5—C3—C2	117.7 (9)	N4—C16—C15	111.2 (8)
C5—C3—C4	120.7 (9)	N4—C16—C17	119.6 (8)
C6—C5—C3	120.7 (9)	C16—N4—N3	105.9 (7)
C5—C6—N1	121.1 (8)	N6—N5—C18	110.0 (7)
C7—C6—N1	113.8 (7)	C19—C18—N5	123.2 (8)
C7—C6—C5	125.2 (8)	C20—C18—N5	107.7 (8)
C8—C7—C6	122.3 (8)	C20—C18—C19	128.9 (9)
N2—C7—C6	114.6 (7)	C21—C20—C18	106.5 (9)
N2—C7—C8	123.2 (8)	C22—C21—C20	129.7 (9)
C9—C8—C7	118.7 (9)	N6—C21—C20	108.9 (8)
C10—C9—C8	120.1 (9)	N6—C21—C22	121.4 (9)
C11—C9—C8	119.3 (9)	C21—N6—N5	106.8 (7)

This research was supported by the Office of Naval Research.

References

Cinellu, M. A., Stoccoro, S., Minghetti, G., Bandini, A. L., Banditelli, G. & Bovio, B. (1989). *J. Org. Chem.* **372**, 311–325.

Cromer, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 149–151. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 99–101. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Duchamp, D. J. (1964). *CRYM* crystallographic computing system. Am. Crystallogr. Assoc. Meet., Bozeman, Montana. Paper B14, p. 29.

Graves, B. J., Hodgson, D. J., van Kralingen, C. G. & Reedijk, J. (1978). *Inorg. Chem.* **17**, 3007–3011.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-3794, third revision. Oak Ridge National Laboratory, Tennessee, USA.

Minghetti, G., Banditelli, G. & Bonati, F. (1979). *J. Chem. Soc. Dalton Trans.* pp. 1851–1856.