The Crystal Structure of Potassium [3,6-Dimethyloct-4-yne-3,6-dioltrichloroplatinate(II)], K{Cl₃Pt^II[(C₂H₅)(CH₃)C(OH)–C≡C–C(OH)(CH₃)(C₂H₅)]}

By R. J. Dubey*

Department of Chemistry, University of Quebec, Montreal, Canada

The crystal structure of the title compound has been determined from X-ray intensity data collected on a four-circle diffractometer with a θ–2θ scan and graphite-monochromated Mo $K\alpha$ radiation ($2\theta = 62°$). The crystals are monoclinic, space group $P2_1/c$ (C_{2h}^5, No. 14), $Z=4$, with $a=10\cdot721(10)$, $b=9\cdot592(7)$, $c=16\cdot440(8)$ Å and $\beta=103\cdot19(6)°$. Crystal densities are $\varrho_m=1\cdot95$ and $\varrho_c=2\cdot06$ g cm^{-3}. The structure was solved by the heavy-atom technique and refined by least-squares procedures to a final value of $R=0\cdot084$ and $R_w=0\cdot095$, based on the 2291 observed reflexions with $I>3\sigma(I)$. The acetylenic bond is perpendicular to the plane of platinum coordination. The Pt–Cl distance *trans* to the triple bond is longer [$2\cdot322(7)$ Å] than the *cis* Pt–Cl distances of $2\cdot304(6)$, $2\cdot293(6)$ Å. Other important bond distances are Pt–C(1)$=2\cdot127(25)$, Pt–C(6)$=2\cdot153(22)$, and C≡C$=1\cdot23(3)$ Å. Deformation from linearity occurs in the C–C–C angles [$157\cdot4(24)$ $161\cdot6(25)°$]. The C–Pt–C angle is $33\cdot41(88)°$ and the molecules in the crystal are joined by electrostatic forces to the K$^+$ ion.

Introduction

This investigation is a part of the study of metal–alkyne complexes which have the general formula Pt[R₁R₂C(OH)–C≡C–C(OH)R₁R₂]₂. In a previous paper (Dubey, 1975) the crystal structure of Pt[(C₂H₅)₂C(OH) –C≡C–C(OH) (C₂H₅)₂]₂ has been studied (where R₁ and R₂ groups are the same). The present structure was undertaken to determine the geometry of the molecule where R₁ is different from R₂.

Experimental

Yellow prismatic crystals elongated along the *a* axis were obtained by crystallization of the compound from acetone solution at 0°. The crystal density measured by flotation is in good agreement with the calculated value. The space group $P2_1/c$ was deduced from the systematic absences for $h0l$, $l=2n+1$, and $0k0$, $k=2n+1$, together with the $2/m$ Laue symmetry observed photographically. Precise lattice parameters were obtained from a least-squares refinement of the 2θ, ω, χ and φ angles of 15 well centred reflexions on a Syntex PĪ automatic diffractometer using graphite-monochromated (take-off angle of 12°) Mo $K\alpha$ radiation. The crystal selected for X-ray intensity measurement was approximately $0\cdot5 \times 0\cdot3 \times 0\cdot3$ mm (the long axis parallel to the φ axis). Intensity data were collected ($2\theta \le 62°$) at room temperature with the $\theta/2\theta$ scan mode and the reflexions were scanned at between 1° and 24° min^{-1} depending upon the peak intensity. The intensities of two standard reflexions, recorded after every 25 measurements to monitor the crystal stability, re-

mained essentially constant throughout the data collection. Out of 5234 measured intensities, 2291 were observed on the basis of $I>3\sigma(I)$.

A standard deviation was assigned to each reflexion according to the formula:

$$\sigma(I)=[S+\{(B_1+B_2)/\alpha^2\}]^{1/2} \times \text{scan rate}$$

where S is the total counts collected during the scan, B_1 and B_2 are the number of counts collected for each background, and α is the ratio of scan time to total background time. The raw intensities were corrected for Lorentz and polarization factors and absorption corrections were applied according to the procedure described by Ahmed (1970). The corrected intensities were placed on an approximate absolute scale obtained from a Wilson plot. A summary of crystallographic data is given in Table 1.

Table 1. *Crystallographic data*

C₁₀H₁₈O₂Cl₃KPt, F.W. 510·8

Monoclinic, $P2_1/c$
$a=10\cdot721$ (10) Å
$b=9\cdot592$ (7)
$c=16\cdot440$ (8)
$\beta=103\cdot19$ (6)°
$V=1646\cdot12 \pm 2\cdot22$ Å³
ϱ obs. $=1\cdot95$ g cm^{-3}
ϱ cal. $=2\cdot06$
$Z=4$
μ(Mo $K\alpha$)$=96\cdot8$ cm^{-1}
λ(Mo $K\alpha$)$=0\cdot71069$ Å
$|F_{000}|=968$

Structure determination and refinement

The structure was solved with the heavy-atom method. All computations required in the structure determination were performed on a CDC 6000 computer using

* Present address: Department of Chemistry–Biology, University of Quebec (Trois-Rivières), C.P. 500, Trois Rivières G9A 5H7, P. Quebec, Canada.

the X-RAY 72 system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The coordinates, isotropic temperature factors and scale factor were refined by full-matrix least-squares procedures. All least-squares calculations were carried out on F, with $CRYLSQ$, the function minimized being $\sum w(|F_o|-|F_c|)^2$, and the weights were derived from the counting statistics. In the calculation of the structure factors the atomic scattering factors for Pt, K^+, Cl, O and C were taken from *International Tables for X-ray Crystallography* (1968). The effects of anomalous dispersion were included, and the values of $\Delta f'$ and $\Delta f''$ for Pt, K and Cl were taken from Cromer & Liberman (1970). The structure converged to an R of 0·14, were $R=(\sum||F_o|-|F_c||)/\sum|F_o|$. The introduction of anisotropic thermal parameters for all non-hydrogen atoms followed by four cycles of full-matrix least-squares refinement gave the final values of $R=0.084$ and $R_w=0.095$ $(R_w=[\sum w(|F_o|-|F_c|)^2/\sum wF_o^2]^{1/2})$. The estimated

standard deviation in a reflexion of unit weight, $\{[\sum w(|F_o|-|F_c|)^2]/(m-s)\}^{1/2}$, is 1·01. The number of observations, m, is equal to 2291 reflexions and $s=155$, the number of parameters refined. In the final cycle of least squares, all shifts were less than 1% of their e.s.d.'s. The final difference Fourier map showed no significant features. Hydrogen atoms were not located. The largest residual maxima and minima were ±1.3 e Å^{-3} in the vicinity of the Pt atom. The final positional and thermal parameters are given in Table 2. The estimated standard deviations of the atomic parameters are given in parentheses and refer to the least significant digit in the parameter.*

Table 2. *Fractional coordinates and thermal parameters* ($\times 10^3$) *with e.s.d.'s in parentheses*

The anisotropic temperature parameters are of the form:

$$T=\exp[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23})].$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt†	0·0606 (1)	0·2493 (1)	0·3546 (0)	467 (4)	430 (4)	353 (3)	−43 (5)	126 (2)	−10 (5)
K^+	−0·0003 (6)	0·6585 (5)	0·4218 (4)	79 (4)	51 (3)	50 (3)	−6 (3)	18 (3)	5 (2)
Cl(1)	0·1873 (6)	0·3859 (6)	0·4560 (4)	59 (3)	59 (3)	56 (3)	−10 (3)	10 (3)	−17 (3)
Cl(2)	−0·0660 (6)	0·1129 (7)	0·2542 (3)	62 (3)	65 (3)	41 (3)	−13 (3)	6 (2)	−6 (3)
Cl(3)	−0·1227 (6)	0·3543 (7)	0·3788 (4)	52 (3)	64 (3)	65 (4)	3 (3)	21 (3)	−6 (3)
O(1)	0·1793 (17)	0·3252 (18)	0·1817 (10)	66 (11)	70 (11)	44 (8)	−4 (9)	13 (8)	8 (8)
O(2)	0·1168 (20)	−0·1155 (19)	0·3750 (12)	97 (14)	67 (11)	68 (11)	−34 (11)	33 (11)	−4 (9)
C(1)	0·2268 (22)	0·1975 (23)	0·3109 (13)	51 (13)	50 (10)	37 (10)	−10 (10)	3 (9)	−7 (9)
C(2)	0·2840 (24)	0·2747 (23)	0·2502 (18)	55 (13)	49 (15)	82 (17)	−3 (10)	35 (13)	13 (11)
C(3)	0·3585 (25)	0·3955 (31)	0·2875 (17)	54 (15)	90 (19)	62 (16)	−27 (15)	3 (12)	11 (15)
C(4)	0·4763 (33)	0·3574 (46)	0·3590 (26)	71 (22)	141 (34)	122 (30)	−6 (23)	25 (22)	30 (28)
C(5)	0·3539 (31)	0·1643 (33)	0·2048 (24)	98 (23)	88 (20)	143 (30)	17 (18)	105 (24)	5 (20)
C(6)	0·2145 (19)	0·1032 (23)	0·3592 (15)	33 (10)	48 (11)	67 (14)	−5 (9)	20 (10)	−10 (10)
C(7)	0·2353 (23)	−0·0277 (26)	0·4081 (15)	47 (13)	59 (14)	58 (14)	2 (11)	−5 (11)	8 (11)
C(8)	0·3490 (40)	−0·0982 (38)	0·3873 (27)	113 (31)	86 (24)	139 (34)	41 (22)	6 (26)	25 (23)
C(9)	0·3662 (48)	−0·2461 (42)	0·4291 (35)	134 (37)	103 (29)	181 (47)	58 (28)	29 (34)	28 (30)
C(10)	0·2411 (38)	0·0003 (34)	0·5021 (17)	152 (35)	94 (22)	38 (14)	12 (24)	−16 (17)	7 (14)

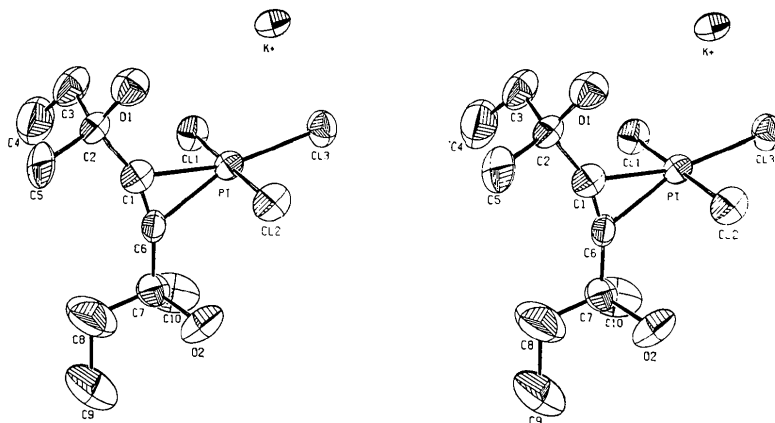† Thermal parameters of the platinum atom are multiplied by 10^4.

Fig. 1. Stereoscopic view of the molecule.

Description and discussion of the structure

Fig. 1 shows a stereoscopic view of the molecule drawn by the *ORTEP* program (Johnson, 1970). The interatomic distances and angles are given in Tables 3 and 4 respectively. The centre of the C–C triple bond and three Cl atoms form a square-planar environment about the central Pt atom. The Pt–C bond lengths are equal and the plane of the C≡C bond is perpendicular to the plane of Pt, Cl(1), Cl(2), and Cl(3). The equation of the least-squares plane and the atomic deviations are listed in Table 5. C(1) is -0.55 Å below and C(6) 0.66 Å above the plane. A coordination diagram of the Pt atom is shown in Fig. 2. The C(1)≡C(6) line makes an angle of 5° with the plane of Pt coordination. The Cl–Pt–Cl angles have the usual values of 90 or 180°. The Pt–Cl bond lengths *cis* to the C–C triple bond are, 2·304 (6) and 2·293 (6) Å; however, the *trans* Pt–Cl distance of 2·322 (7) Å is not significantly different from the other values to give a conclusive *trans* effect. In the structure of Zeise's salt, $K[Cl_3Pt(C_2H_4)]H_2O$, the Pt–Cl distance *trans* to the olefin ligand is 2·327 (5) Å, while a mean Pt–Cl distance of 2·305 (9) Å was determined for the other two Pt–Cl bonds. The Pt–Cl distances observed in this structure are comparable to that found in Zeise's salt (Jarvis, Kilbourn & Owston, 1971).
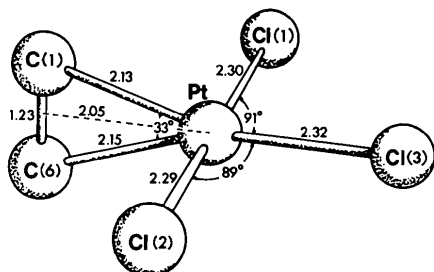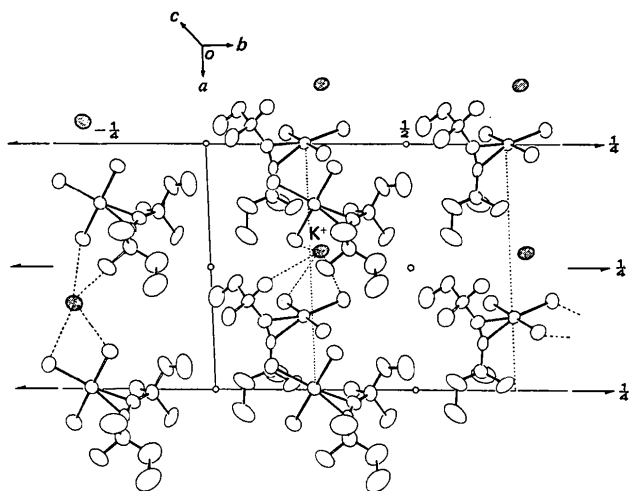

Fig. 2. Coordination of the platinum atom.

Fig. 3. Molecular packing seen along c. Potassium ion coordination is shown by dotted lines.

Table 3. *Bond lengths (Å) and their e.s.d.'s (in parentheses)*

Symmetry code

(i)	$x, 1+y, z$
(ii)	$-x, \frac{1}{2}+y, \frac{1}{2}-z$
(iii)	$-x, 1-y, 1-z$

Pt—Cl(1)	2·304 (6)	C(6)–C(7)	1·48 (3)
Pt—Cl(2)	2·293 (6)	C(7)–O(2)	1·52 (3)
Pt—Cl(3)	2·322 (7)	C(7)–C(8)	1·50 (5)
Pt—C(1)	2·127 (25)	C(7)–C(10)	1·56 (4)
Pt—C(6)	2·153 (22)	C(8)–C(9)	1·57 (6)
C(1)–C(6)	1·23 (3)	K⋯O(2^i)	2·70 (2)
C(1)–C(2)	1·48 (4)	K⋯O(1^{ii})	2·77 (2)
C(2)–O(1)	1·48 (3)	K⋯Cl(1)	3·27 (1)
C(2)–C(3)	1·46 (4)	K⋯Cl(3)	3·21 (1)
C(2)–C(5)	1·58 (5)	K⋯Cl(1^{iii})	3·18 (1)
C(3)–C(4)	1·56 (4)	K⋯Cl(3^{iii})	3·25 (1)
		K⋯Cl(2^{ii})	3·16 (1)

Table 4. *Bond angles (°) with their e.s.d.'s in parentheses*

Cl(1)–Pt—Cl(2)	179·72 (24)
Cl(1)–Pt—Cl(3)	90·69 (22)
Cl(3)–Pt—Cl(2)	89·18 (23)
C(1)–Pt—C(6)	33·41 (88)
Pt—C(1)–C(2)	128·1 (16)
Pt—C(6)–C(7)	126·2 (18)
C(1)–Pt—Cl(3)	165·09 (61)
C(6)–Pt—Cl(3)	161·48 (68)
C(1)–Pt—Cl(1)	88·62 (58)
C(1)–Pt—Cl(2)	91·57 (58)
C(6)–Pt—Cl(1)	91·40 (58)
C(6)–Pt—Cl(2)	88·65 (58)
C(2)–C(1)–C(6)	157·4 (24)
C(7)–C(6)–C(1)	161·6 (25)
C(1)–C(2)–O(1)	108·5 (20)
C(1)–C(2)–C(3)	112·5 (23)
C(1)–C(2)–C(5)	107·2 (21)
C(5)–C(2)–O(1)	102·7 (21)
C(3)–C(2)–O(1)	108·0 (18)
C(3)–C(2)–C(5)	117·2 (24)
C(2)–C(3)–C(4)	113·7 (26)
C(6)–C(7)–O(2)	105·4 (17)
C(6)–C(7)–C(8)	106·8 (25)
C(6)–C(7)–C(10)	111·1 (22)
O(2)–C(7)–C(10)	107·0 (23)
O(2)–C(7)–C(8)	109·0 (22)
C(8)–C(7)–C(10)	116·9 (25)
C(7)–C(8)–C(9)	109·2 (37)

Torsion angle

C(2)–C(1)–C(6)–C(7)	139·01

Table 5. *Least-squares plane and atomic deviations from the plane*

The plane was calculated according to the method of Schomaker, Waser, Marsh & Bergman (1959). The equation of the plane is expressed in direct space as $Px + Qy + Rz = S$, where x, y, z are fractional coordinates relative to crystallographic axes.

Plane through atoms: Pt, Cl(1), Cl(2) and Cl(3).

Equation: $-2·263x - 6·643y + 11·833z = 2·406$

Atomic deviations (Å)

Pt	$-0·0033$	Cl(3)	0·0000
Cl(1)	0·0017	C(1)*	$-0·5527$
Cl(2)	0·0017	C(6)*	0·6728

* Denotes atoms not included in the least-squares fit.

The prominent feature of the crystal structure (Fig. 3) is the geometry of the acetylene coordination. In this structure the angular distortions of C–C–C angles from linearity are 18° and 23° and the acetylenic bond length is 1·23 (3) Å and thus it would appear that the acetylenic bond distance is twice the C–C triple-bond radius of 0·603 Å (Pauling, 1960, p. 224). The acetylenic C atoms C(1) and C(6) subtend an angle of 33 (1)° at the Pt atom, and this compares well with the values given by Manojlović-Muir, Muir & Ibers (1969) and Davies & Payne (1974). The Pt–C distances to C(1) and C(6) are 2·127 (25) and 2·153 (22) Å, respectively, and are almost equal within 3σ. The geometry, bond lengths and angles of C≡C and Pt–C interactions in the present structure compare well with those of the *trans* [PtCl$_2$(Bu^{t}C≡CBu^t) (MeC$_6$H$_4$NH$_2$)] complex (Davies, Hewertson, Mais, Owston & Patel, 1970). The molecules in the crystal are stabilized by electrostatic forces from the K ion. Each of the K ions is coordinated to five Cl and to two O atoms. Seven nearest neighbours for the K ion have also been reported by Pauling (1960, p. 546) and for K$_3$(H$_2$C$_6$H$_3$) (HC$_6$O$_6$H$_3$).2H$_2$O (Carrell, 1973) and K$_3$HP$_2$O$_7$.3H$_2$O (Dumas, Galigné & Falgueirettes, 1973). The K$^+$ environment is given in Table 3 with K$^+$···O distances ranging from 2·70 to 2·77 Å and K$^+$···Cl, 3·16 to 3·27 Å. A mechanism of bonding for the complexes of acetylenes with Pt^{II} was proposed by Chatt, Guy & Duncanson (1961) and by Chatt, Guy, Duncanson & Thompson (1963), according to whom the metal–acetylene bond consists of a σ- and π-interaction type. Donation of electrons from π-bonding molecular orbitals of the acetylene to empty metal *p* or *d* orbitals occurs, forming a σ bond. This is accompanied by 'back-bonding' from filled metal d_π–p_π hybrid orbitals to π* antibonding orbitals on the acetylene ligand (Cotton & Wilkinson, 1972). The present structure fits this theory.

References

AHMED, F. R. (1970). *Crystallographic Computing*, pp. 255–294. Copenhagen: Munksgaard.

CARRELL, H. L. (1973). *Acta Cryst.* B**29**, 2082–2088.

CHATT, J., GUY, R. G. & DUNCANSON, L. A. (1961). *J. Chem. Soc.* pp. 827–834.

CHATT, J., GUY, R. G., DUNCANSON, L. A. & THOMPSON, D. T. (1963). *J. Chem. Soc.* pp. 5170–5183.

COTTON, F. A. & WILKINSON, G. (1972). *Advanced Inorganic Chemistry*, 3rd ed., p. 730. New York: Interscience.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

DAVIES, B. W. & PAYNE, N. C. (1974). *Inorg. Chem.* **13**, 1848–1853.

DAVIES, G. R., HEWERSTON, W., MAIS, R. H. B., OWSTON, P. G. & PATEL, C. G. (1970). *J. Chem. Soc. (A),* pp. 1873–1877.

DUBEY, R. J. (1975). *Acta Cryst.* B**31**, 1860–1864.

DUMAS, Y., GALIGNÉ, J. L. & FALGUEIRETTES, J. (1973). *Acta Cryst.* B**29**, 1623–1630.

International Tables for X-ray Crystallography (1968). Vol. III, 2nd ed., pp. 202–216. Birmingham: Kynoch Press.

JARVIS, J. A. J., KILBOURN, B. T. & OWSTON, P. G. (1971). *Acta Cryst.* B**27**, 366–372.

JOHNSON, C. K. (1970). *ORTEP.* Oak Ridge National Laboratory Report ORNL-3794 (2nd rev.).

MANOJLOVIĆ-MUIR, R., MUIR, K. W. & IBERS, J. A. (1969). *Discuss. Faraday Soc.* **47**, 84–92.

PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.

SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600–604.

STEWART, J. M., KRUGER, G., AMMON, H., DICKINSON, C. H. & HALL, S. R. (1972). *X-RAY 72 Program System.* Technical Report TR-192, Computer Center, Univ. of Maryland, College Park, Maryland, U.S.A.