BAUR, W. H. & KHAN, A. A. (1971). *Acta Cryst.* **B27**, 2133–2139.

BRENNER, P., ENGEL, G. & WONDRATSCHEK, H. (1970). *Z. Kristallogr.* **131**, 206–212.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.

ENGEL, G. (1968). *Z. anorg. allgem. Chem.* **362**, 273–280.

ENGEL, G. (1970). *Z. anorg. allgem. Chem.* **378**, 49–61.

ENGEL, G. & KLEE, W. E. (1972). *J. Solid-State Chem.* **5**, 28–34.

HENDRICKS, S. B., JEFFERSON, M. E. & MOSLEY, V. M. (1932). *Z. Kristallogr.* **81**, 352–369.

*International Tables for X-ray Crystallography* (1959). Vol. II. Birmingham: Kynoch Press.

*International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.

JAMES, R. W. (1950). *The Optical Principles of the Diffraction of X-rays*, p. 181. London: Bell.

KLEE, W. E. (1970). *Z. Kristallogr.* **131**, 95–102.

KLEE, W. E. (1972). *Zur Kenntnis der Schwingungsspektren von Substanzen mit Apatitstruktur.* Habilitationsschrift, Universität Karlsruhe.

KLEE, W. E. & ENGEL, G. (1970). *J. Inorg. Nucl. Chem.* **32**, 1837–1843.

KLEMENT, R. & HASELBECK, H. (1965). *Z. anorg. allgem. Chem.* **336**, 113–128.

KREIDLER, E. R. & HUMMEL, F. A. (1970). *Amer. Min.* **55**, 170–184.

LARSON, A. C. (1965). *Acta Cryst.* **23**, 664–665.

MACKIE, P. E., ELLIOTT, J. C. & YOUNG, R. A. (1972). *Acta Cryst.* **B28**, 1840–1848.

MEIER, W. M. & VILLIGER, H. (1969). *Z. Kristallogr.* **129**, 411–423.

NÁRAY-SZABÓ, S. (1930). *Z. Kristallogr.* **75**, 387–398.

PRENER, J. S. (1967). *J. Electrochem. Soc.* **114**, 77–83.

PRENER, J. S. (1971). *J. Solid-State Chem.* **3**, 49–55.

PRETZSCH, J. (1972). Diplomarbeit im Fach Physik, Universität Karlsruhe.

SCHWARZENBACH, D. (1972). *Helv. Chim. Acta*, **55**, 2990–3004.

SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* **B25**, 925–946.

STEWART, J. M., KUNDELL, F. A. & BALDWIN, T. C. (1970). The X-RAY System of Crystallographic Programs, Univ. of Maryland, College Park, Maryland.

STRÄHLE, J. & BÄRNIGHAUSEN, H. (1968). *Z. anorg. allgem. Chem.* **357**, 325–337.

SUDARSANAN, K., MACKIE, P. E. & YOUNG, R. A. (1972). *Mat. Res. Bull.* **7**, 1331–1338.

SUDARSANAN, K. & YOUNG, R. A. (1969). *Acta Cryst.* **B25**, 1534–1543.

SUDARSANAN, K. & YOUNG, R. A. (1972). *Acta Cryst.* **B28**, 3668–3670.

SUDARSANAN, K. & YOUNG, R. A. (1974). *Acta Cryst.* **B30**, 1381–1386.

SUDARSANAN, K., YOUNG, R. A. & DONNAY, J. H. (1973). *Acta Cryst.* **B29**, 808–814.

TILLMANNS, E., GEBERT, W. & BAUR, W. H. (1973). *J. Solid-State Chem.* **7**, 69–84.

WEITZ, G. (1971). *Neues Jb. Miner. Mh.* pp. 223–227.

YOUNG, R. A. & ELLIOTT, J. C. (1966). *Arch. Oral Biol.* **11**, 699–707.

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# The Crystal and Molecular Structure of Bis-[(3,6-diethyl-4-octyne-3,6-diol)]platinum(0), $Pt[(C_2H_5)_2C(OH)C{\equiv}CC(OH)(C_2H_5)_2]_2$

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Crystals of bis-[(3,6-diethyl-4-octyne-3,6-diol)]platinum(0), $Pt[(C_2H_5)_2C(OH)C{\equiv}CC(OH)(C_2H_5)_2]_2$, are monoclinic, space group $C2/c$ ($C_{2h}^6$) with four molecules in a unit cell of dimensions $a = 21{\cdot}751$ (5), $b = 9{\cdot}275$ (6), $c = 17{\cdot}079$ (9) Å and $\beta = 129{\cdot}54$ (4)°. X-ray diffracted intensities were measured on a four-circle diffractometer using $\theta$–$2\theta$ scans and graphite-monochromatized Mo $K\alpha$ radiation. The structure was solved by the heavy-atom method. Full-matrix least-squares refinement gave a final $R$ of 0·074, and $R_w$ of 0·075 based on the 2695 reflexions with $I > 3\sigma(I)$. The crystal structure is composed of molecules lying on the twofold (crystallographic) axis through the Pt atom. The prominent feature of the molecular geometry is that the two acetylenic groups bonded to the central Pt atom are 180° apart and perpendicular to each other. The bond distances are 2·066 (11), 2·043 (11) Å for Pt–C, 1·35 (3), 1·36 (2) Å for C≡C, and 1·95, 1·93 Å for Pt ⊥C≡C. Each molecule is stabilized by four OH···O hydrogen bonds.

## Introduction

The title compound was prepared by Rochon & Theophanides (1972) during a study of platinum–acetylenic ligands (ac). The structural assignment for the $Pt(ac)_2$ complex, where (ac) = $R_1R_2C(OH)–C{\equiv}C–C(OH)R_1R_2$ and $R_1 = R_2 =$ ethylenic groups, was accomplished by means of infrared, e.s.r. and n.m.r. experiments. The structure determination was undertaken to confirm this assignment by the X-ray diffraction method.

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## Experimental

Colourless single crystals of the compound suitable for X-ray diffraction work were grown from dimethylformamide solution by slow evaporation at room temperature. Most of the crystals thus obtained were disordered or twinned. The crystal density was measured by flotation in a mixture of $CCl_4$ and methanol. Laue and precession photographs showed monoclinic symmetry ($2/m$). The systematic absences, *hkl* absent for $h+k=2n+1$, $h0l$ absent for $l=2n+1$ ($h=2n+1$), and $0k0$ absent for $k=2n+1$, indicated either space group *Cc* or *C*2/*c*. The latter was confirmed by refinement. The choice of the unit cell corresponds to the setting in *International Tables for X-ray Crystallography* (1969), however, another cell can be transformed with $\beta$ nearer to 90°.

Accurate unit-cell parameters were obtained by least-squares refinement of the angular settings, $2\theta$, $\omega$, $\chi$ and $\varphi$ using 15 well centred reflexions measured on a Syntex $P\bar{1}$ automatic diffractometer with graphite-monochromatized (take-off angle of 12°) Mo $K\alpha$ radiation ($\lambda=0.71069$ Å). A summary of the crystal data is given in Table 1.

Table 1. *Crystallographic data*

| | | | |
|---|---|---|---|
| System | Monoclinic | $a=$ | $21.751\pm0.005$ Å |
| Space group | *C*2/*c* (No. 15) | $b=$ | $9.275\pm0.006$ |
| Molecular formula | $C_{24}H_{44}O_4Pt$ | $c=$ | $17.079\pm0.009$ |
| F.W. | 591·09 | $\beta=$ | $129.54\pm0.04$° |
| $V$ | $2656.94\pm3.44$ Å$^3$ | $\mu$(Mo $K\alpha$) | 55·78 cm$^{-1}$ |
| $\varrho_{\text{cal}}$ | 1·48 g cm$^{-3}$ | $\lvert F_{000}\rvert$ | 1192 |
| $\varrho_{\text{obs}}$ | 1·46 g cm$^{-3}$ | $\lambda$(Mo $K\alpha$) | 0·71069 Å |
| $Z$ | 4 | | |

The crystal selected for X-ray intensity measurements was approximately of dimensions: 0·4 × 0·2 × 0·5 mm. It was mounted in a random orientation on the Syntex $P\bar{1}$ four-circle diffractometer and the orientation matrix was determined. Data were collected using the $\theta$–$2\theta$ scan mode ($2\theta_{\text{max}}=60°$), and the reflexions were scanned at a variable scan speed from 1–24° min$^{-1}$ depending upon the peak intensity. The intensities of the two standard reflexions, recorded after every 25 measurements to monitor the crystal stability and alignment, indicated that there was no sign of crystal deterioration and its intensity remained almost constant throughout the data collection.

Out of 3768 measured intensities 2695 were observed

Table 2. *Fractional coordinates and thermal parameters* ($\times10^3$) *with e.s.d.'s in parentheses*

The anisotropic temperature parameters are of the form:

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

| | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Pt† | 0 | 0·1252 (1) | $\frac{1}{4}$ | 526 (3) | 161 (3) | 324 (3) | 0 | 266 (2) | 0 |
| O(1) | −0·0112 (7) | 0·5529 (10) | 0·3502 (10) | 65 (6) | 19 (4) | 89 (8) | −5 (4) | 44 (6) | −23 (4) |
| O(2) | 0·1096 (7) | −0·3022 (10) | 0·3466 (10) | 59 (6) | 28 (4) | 79 (7) | 9 (4) | 44 (6) | 2 (4) |
| C(1) | −0·0034 (9) | 0·3357 (10) | 0·2867 (11) | 61 (8) | 1 (3) | 60 (8) | −5 (4) | 40 (7) | −5 (4) |
| C(2) | −0·0126 (11) | 0·3999 (13) | 0·3595 (14) | 67 (9) | 23 (6) | 73 (9) | −0 (5) | 42 (8) | −8 (6) |
| C(3) | −0·0952 (15) | 0·3590 (19) | 0·3264 (15) | 141 (16) | 42 (8) | 84 (11) | 1 (10) | 97 (12) | −0 (8) |
| C(4) | −0·1695 (14) | 0·3917 (23) | 0·2115 (31) | 64 (11) | 47 (12) | 227 (29) | −11 (10) | 55 (16) | 17 (17) |
| C(5) | 0·0529 (12) | 0·3489 (19) | 0·4682 (13) | 94 (12) | 56 (10) | 51 (8) | 6 (9) | 52 (9) | 6 (7) |
| C(6) | 0·1367 (17) | 0·3841 (31) | 0·5046 (25) | 87 (14) | 69 (13) | 111 (17) | 12 (14) | −4 (12) | −11 (15) |
| C(7) | 0·0401 (8) | −0·0825 (12) | 0·2886 (8) | 65 (7) | 23 (5) | 19 (4) | 7 (5) | 27 (5) | 6 (3) |
| C(8) | 0·1182 (9) | −0·1499 (12) | 0·3527 (11) | 51 (7) | 23 (5) | 54 (7) | 13 (5) | 30 (6) | 24 (5) |
| C(9) | 0·1624 (11) | −0·1012 (20) | 0·4622 (13) | 57 (9) | 58 (10) | 49 (8) | −0 (8) | 18 (7) | 4 (7) |
| C(10) | 0·1217 (16) | −0·1318 (19) | 0·5150 (14) | 137 (15) | 36 (7) | 58 (9) | −8 (11) | 51 (10) | 7 (9) |
| C(11) | 0·1711 (11) | −0·1043 (15) | 0·3290 (17) | 71 (10) | 29 (7) | 103 (12) | 4 (7) | 57 (10) | 17 (8) |
| C(12) | 0·1331 (15) | −0·1415 (24) | 0·2131 (17) | 132 (16) | 74 (12) | 98 (12) | −5 (13) | 102 (13) | 4 (12) |

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

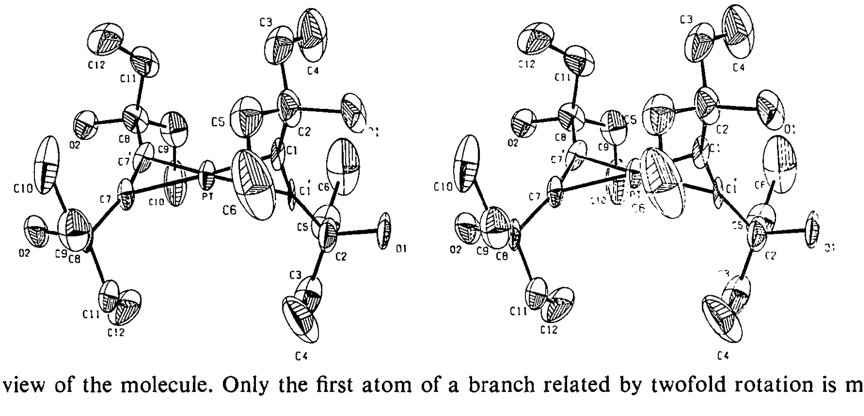

Fig. 1. Stereoscopic view of the molecule. Only the first atom of a branch related by twofold rotation is marked with a prime.

with $I>3\sigma(I)$. The standard deviation was assigned to each reflexion according to 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 numbers of counts collected for each background, and $\alpha$ is the ratio of scan time to total background time. Lorentz and polarization factors were applied to the data and the absorption corrections were made according to the procedure described by Ahmed (1970). From a Wilson plot the corrected intensities were placed on an approximate absolute scale.

## Determination and refinement of the structure

There are four molecules in the unit cell. If the space group were $C2/c$, the molecule would be constrained to lie either on the twofold axis or on the centre of symmetry with half the molecule per asymmetric unit. An examination of the statistical distribution of intensities indicated the centrosymmetric space group. A three-dimensional Patterson function was computed to determine the coordinates of the heavy atom. The Pt atom was found to lie on the special position 0, 0·125, $\frac{1}{4}$. A subsequent Fourier synthesis showed the remaining non-hydrogen atoms. A structure-factor calculation with all non-hydrogen atoms produced an $R$ index of 0·23, where $R=\sum||F_o|-|F_c||/\sum|F_o|$). All calculations used in the structure determination were performed on a CDC 6000 computer with the X-RAY 72 system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

The structure was refined by least-squares procedures using the *CRYLSQ* program and the function minimized was $\sum w(|F_o|-|F_c|)^2$, based on $F_o$, and $w=1$ during the first part of the refinement. Three cycles of full-matrix least-squares refinement of the scale, positional and isotropic thermal parameters of the non-hydrogen atoms reduced $R$ to 0·125. Atomic scattering factors used throughout the refinement were taken from *International Tables for X-ray Crystallography* (1968) for neutral Pt, C and O atoms. A correction of anomalous dispersion was made for the Pt atom. The values of Dauben & Templeton (1959) were used for $\Delta f'$ and $\Delta f''$. In the subsequent refinement the reflexions were given weight $w=1/[\sigma(F_o)]^2$, where $\sigma(F_o)$ was derived from the counting statistics. Four cycles of full-matrix least-squares refinement of the scale, positional and anisotropic thermal parameters gave a final $R$ of 0·074. The final weighted reliability index $R_w=[\sum w(|F_o|-|F_c|)^2/\sum wF_o^2]^{1/2}$ is 0·075. The estimated standard deviation of an observation of unit weight $S=[\sum w(|F_o|-|F_c|)^2/(m-s)]^{1/2}=0·97$, where $m=2695$ reflexions with $I>3\sigma(I)$ and $s=130$ parameters. Reflexions with $I<3\sigma(I)$ were excluded from all calculations. The final difference Fourier map showed no significant features. The largest residual electron-

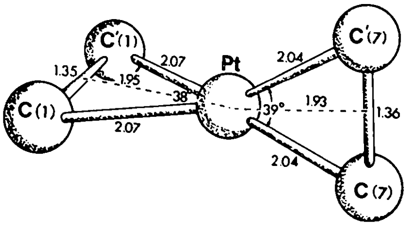

Fig. 2. Coordination of the platinum atom.

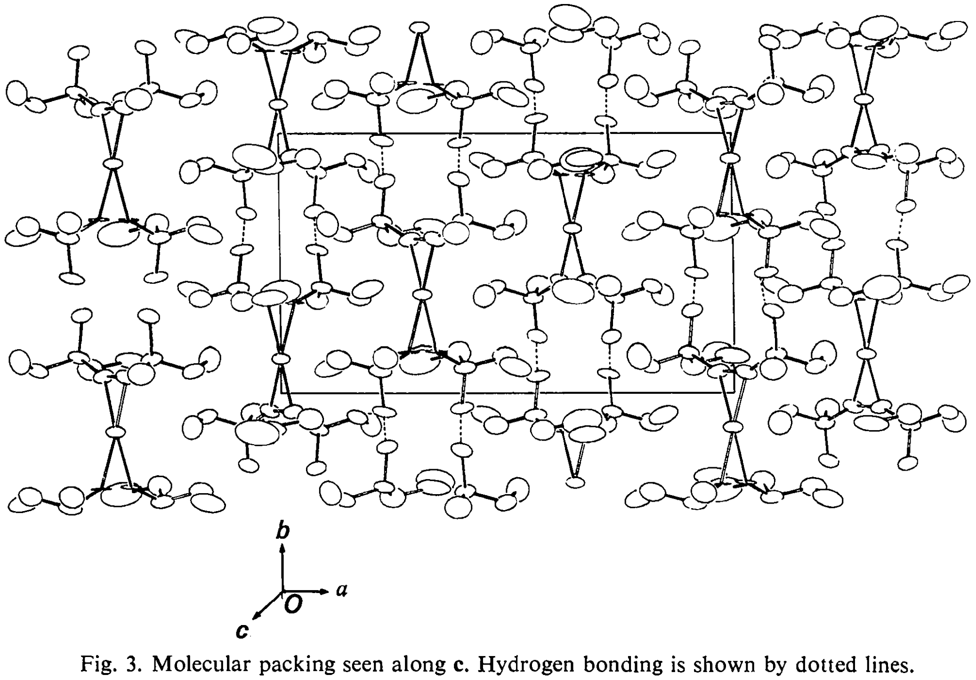

Fig. 3. Molecular packing seen along **c**. Hydrogen bonding is shown by dotted lines.

density maxima and minima were = 1·3 e Å$^{-3}$. The average shift/error was 0·01 in the final cycle of the refinement. Hydrogen atoms were not located. In order to confirm the choice of the centrosymmetric group to be correct, an attempt was made to refine the structure in the *Cc* space group which resulted in the conventional *R* of 0·13. The positional and thermal parameters are listed in Table 2.* The estimated standard deviations are given in parentheses and refer to the least significant digit in the parameter.

## Results and discussion

Fig. 1 shows a stereoscopic view of the molecule drawn by the *ORTEP* program (Johnson, 1970). The bond lengths and bond angles are listed in Table 3 and Table 4 respectively. The basic structural unit consists of two $[(C_2H_5)_2C(OH)C{\equiv}CC(OH)(C_2H_5)_2]$ groups bonded through a central platinum atom. The molecule lies on the twofold rotation axis of the space group *C*2/*c*. The centre of gravity of the molecule lies on the central platinum atom and the two (ac) groups are oriented in such a way that they are 180° apart and approximately perpendicular to each other. The crystal structure analysis confirms the orientation of the acetylenic ligand and the structural model proposed by the spectroscopic method.

Table 3. *Bond lengths* (Å) *and their standard deviations*

| | | | |
|---|---|---|---|
| Pt—C(1) | 2·066 (11) | C(2)—C(5) | 1·53 (2) |
| Pt—C(7) | 2·043 (11) | C(3)—C(4) | 1·59 (4) |
| | | C(5)—C(6) | 1·54 (5) |
| C(1)–C(1′)* | 1·35 (3) | | |
| C(7)–C(7′)* | 1·36 (2) | C(7)—C(8) | 1·45 (2) |
| | | C(8)—O(2) | 1·42 (2) |
| C(1)–C(2) | 1·50 (3) | C(8)—C(9) | 1·53 (3) |
| C(2)–O(1) | 1·43 (2) | C(8)—C(11) | 1·50 (4) |
| C(2)–C(3) | 1·55 (4) | C(9)—C(10) | 1·64 (5) |
| | | C(11)–C(12) | 1·62 (4) |

* Symmetry operation: $-x,y,\frac{1}{2}-z$.

The platinum coordination has noteworthy features. The $Pt(ac)_2$ molecule is a dialkyne–metal complex in which the platinum atom is coordinated to two acetylenic groups of the ligand molecules. A coordination diagram around the platinum atom is illustrated in Fig. 2. The interatomic distances between Pt–C atoms found in this structure are almost equal within 3$\sigma$ and compare well with those reported in similar structures by Manojlović-Muir, Muir & Ibers (1969). The Pt–C(1) and Pt–C(7) distances are 2·066 (11) and 2·043 (11) Å respectively. The most interesting feature of the structure, however, is the geometry of the coordinated acetylene. The acetylenic triple-bond lengths are C(1)–C(1′) = 1·35 (3) and C(7)–C(7′) = 1·36 (2) Å. The observed C≡C distance, however, is longer than the average value, 1·203 (3) Å, quoted for a series of triple bonds in simple alkynes (*International Tables for X-ray Crystallography*, 1968) at the 3$\sigma$ level. The C–M–C angles vary from 36 to 48° (Davies & Payne, 1974). In the present case, the angles C(1)–Pt–C(1′) and C(7)–Pt–C(7′) are 38·21 (85) and 38·95 (46)° respectively. The C–C–C angles are 157 (1) and 153 (1)°. This angular distortion from linearity and the increase in the triple-bond distances are due to the removal of electrons from the bonding $\pi$-orbitals of the acetylenes ($\sigma$-type symmetry) and placing of electrons (back-bonding) into the antibonding $\pi^*$ orbital of the acetylenes (Cotton & Wilkinson, 1972).

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

| | |
|---|---|
| C(1)–Pt—C(1′)* | 38·21 (85) |
| C(7)–Pt—C(7′)* | 38·95 (46) |
| C(7)–Pt—C(1) | 152·07 (48) |
| Pt—C(1)—C(2) | 132·4 (12) |
| C(2)–C(1)—C(1′)* | 156·6 (11) |
| C(1)–C(2)—C(3) | 109·6 (14) |
| C(1)–C(2)—C(5) | 111·8 (17) |
| C(1)–C(2)—O(1) | 106·1 (19) |
| O(1)–C(2)—C(5) | 111·9 (12) |
| O(1)–C(2)—C(3) | 107·7 (15) |
| C(3)–C(2)—C(5) | 109·5 (21) |
| C(2)–C(3)—C(4) | 115·8 (27) |
| C(2)–C(5)—C(6) | 111·8 (24) |
| Pt—C(7)—C(8) | 134·8 (9) |
| C(8)–C(7)—C(7′)* | 153·3 (11) |
| C(7)–C(8)—C(9) | 108·6 (16) |
| C(7)–C(8)—C(11) | 113·8 (14) |
| C(7)–C(8)—O(2) | 109·7 (11) |
| O(2)–C(8)—C(9) | 109·6 (14) |
| O(2)–C(8)—C(11) | 110·3 (17) |
| C(9)–C(8)—C(11) | 104·7 (15) |
| C(8)–C(9)—C(10) | 118·8 (15) |
| C(8)–C(11)–C(12) | 112·6 (16) |
| Torsion angles | |
| C(2)–C(1)–C(1′)*–C(2′)* | 133·29 |
| C(8)–C(7)–C(7′)*–C(8′)* | 128·97 |

* Symmetry operation: $-x,y,\frac{1}{2}-z$.

The dihedral angle between the planes defined by C(1), Pt, C(1′), and C(7), Pt, C(7′) atoms is 86°. The geometry of the remaining atoms of the molecule is comparable with that found in the structures containing similar groups. The prominent feature revealed by an X-ray structure analysis is that the two alkylene bond lengths are found to be significantly lengthened and they are mutually perpendicular to each other.

### *Hydrogen bonds and intermolecular packing*

The molecular packing arrangement along **c** is illustrated in Fig. 3. As can be seen from the diagram, the structure consists of layers of $Pt(ac)_2$ molecules approximately perpendicular to **b** and stabilized by a network of OH···O hydrogen bonds. Although no attempt was made to locate the hydrogen atoms from

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30912 (21 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

the Fourier map, the presence of four OH···O bonds can be inferred from a consideration of interatomic distances. Each molecule is hydrogen-bonded to four neighbours.

| | | |
|---|---|---|
| $O(1)\cdots O(2^{i})$ | 2·99 (3) Å | $[O(2^{i})$: $x,\ 1+y,\ z]$ |
| $O(1')\cdots O(2^{ii})$ | 2·92 (2) | $[O(2^{ii})$: $-x,\ 1+y,\ \frac{1}{2}-z]$ |
| $O(2)\cdots O(1^{iii})$ | 2·99 (3) | $[O(1^{iii})$: $x,\ -1+y,\ z]$ |
| $O(2')\cdots O(1^{iv})$ | 2·92 (2) | $[O(1^{iv})$: $-x,\ -1+y,\ \frac{1}{2}-z]$ |

The atoms denoted by a prime are related to the atoms listed in Table 2 by the twofold rotation axis.

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## References

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

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

DAUBEN, C. H. & TEMPLETON, D. H. (1959). *Acta Cryst.* **8**, 841–842.

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

*International Tables for X-ray Crystallography* (1968). Vol. III, 2nd ed., pp. 202–276. Birmingham: Kynoch Press.

*International Tables for X-ray Crystallography* (1969). Vol. I, 3rd ed., p. 101. Birmingham: Kynoch Press.

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

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

ROCHON, F. D. & THEOPHANIDES, T. (1972). *Canad. J. Chem.* **50**, 1325–1330.

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

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# Pentaerythritol Tetranitrate II: Its Crystal Structure and Transformation to PETN I; an Algorithm for Refinement of Crystal Structures with Poor Data*

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The crystal structure of the high-temperature polymorph of pentaerythritol tetranitrate ($C_5H_8N_4O_{12}$) has been determined from the intensity data on one rotation photograph. PETN II crystallizes in space group *Pcnb* ($a=13{\cdot}29$, $b=13{\cdot}49$, and $c=6{\cdot}83$ Å) with four molecules per unit cell and a calculated density of 1·72 g cm$^{-3}$ at 136°C. The intensity data are insufficient for a normal structure determination so that bond distance and angle information from the structure of PETN I and repulsion terms were included as constraints in the least-squares refinement. The geometries of the PETN molecules in PETN I and II are nearly identical. A mechanism is proposed for the observed PETN II to PETN I transformation that accounts for the observed rates of transformation, low activation energy, and correlation between the structures of the polymorphs. The authors believe that this refinement algorithm has great potential for the refinement of crystal structures from powder data when the molecular structure is known.

## Introduction

Two polymorphs of the important explosive pentaerythritol tetranitrate ($C_5H_8N_4O_{12}$) were first reported by Blomquist & Ryan (1944). The common form, PETN I, was thought to be stable to the melting point (142·9°C) even though no transformation of PETN II to PETN I was observed above 130°C. Careful measurement of the melting points of the two polymorphs shows that PETN II actually melts 0·2°C higher than PETN I and hence PETN II must be the stable polymorph at the melting point. The observation of Blomquist & Ryan (1944) that PETN II transforms rapidly to PETN I at temperatures below 130°C is easily confirmed.

The heat of fusion of PETN I is very dependent on the crystallization technique and varies from 38 cal g$^{-1}$ for single, well-formed crystals to 32 cal g$^{-1}$ for rapidly precipitated fine crystals. The melting point of the

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