

assistance in using the XRAY system, and Mr R. Minner for preparing the single crystals.

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A Square-Cluster Platinum Complex with Short Metal–Metal Bonds: X-ray Crystal Structure of the Tetragonal Form of *cyclo*-Tetrakis[di- μ -acetato-platinum(II)]

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The structure of $[\text{Pt}(\text{CH}_3\text{COO})_2]_4$ has been refined with 2894 counter reflexions to $R = 0.032$. Eight tetrameric molecules occupy a tetragonal cell with $a = 10.254$ (1), $c = 50.494$ (5) Å; the space group is $P4_32_12$. The molecular structure is based on a strongly metal–metal bonded square cluster of four Pt atoms, with Pt–Pt lengths in the range 2.492–2.498 Å. Eight bridging acetate groups are arranged around the square such that four groups are in the plane of the cluster and four are alternately above and below it, giving Pt an octahedral coordination. The eight Pt–O bonds in the plane of the cluster are rather long, with a mean distance of 2.162 Å, while those approximately normal to the plane have a mean length of 2.002 Å. A second crystal form of platinum(II) acetate has been found which is monoclinic, with $a = 12.031$ (1), $b = 10.583$ (1), $c = 20.090$ (2) Å, $\beta = 91.10$ (1)°, space group $P2_1/c$.

Introduction

Pd acetate, a useful catalyst for a number of oxidation reactions of olefins, was shown to have a cyclic trimeric structure in which three Pd atoms are connected by double acetate bridges, with no metal–metal bonding (Skapski & Smart, 1970). It was originally suggested that Pt acetate was also trimeric, though not isomorphous with $[\text{Pd}(\text{acetate})_2]_3$ (Stephenson, Morehouse, Powell, Heffer & Wilkinson, 1965). Attempts to obtain a crystalline specimen of Pt acetate revealed that the method of preparing this compound by the reduction of Pt^{IV} in nitric acid–acetic acid (Stephenson *et al.*, 1965; Davidson & Triggs, 1966) may lead to N-containing products, such as $\text{Pt}_4(\text{acetate})_6(\text{NO})_2$. An X-ray structure determination of this compound showed it to be tetranuclear with bridging nitrosyl as well as bridging acetate groups (de

Meester, Skapski & Heffer, 1972; de Meester & Skapski, 1973).

A more recent method of preparing Pt acetate (ICI Ltd, 1970) from Ag acetate is simpler and more reliable. Starting from a specimen obtained by this route we have been able to obtain (Phillips & Skapski, 1975) crystals suitable for X-ray analysis. This has shown that the crystal form studied has a cyclic tetrameric molecular structure in which double acetate bridges span a strongly metal–metal bonded square of Pt atoms.

A preliminary report has been published (Carrondo & Skapski, 1976).

Experimental

Crystals of $[\text{Pt}(\text{CH}_3\text{COO})_2]_4$ were obtained as thin plates by recrystallizing from glacial acetic acid the

black platinum(II) acetate made by the ICI method. The plates were yellow to brown depending on thickness.

Photographs showed the crystals to be tetragonal* with *c* normal to the plate, and systematic absences $h00: h = 2n + 1, 00l: l = 4n + 1$. These absences are consistent with the enantiomorphous space groups $P4_2,2$ and $P4_3,2,2$. Subsequent refinement of the structure showed the latter to be correct for the particular crystal used for data collection. Measurement of high-angle α_1 axial reflexions on a diffractometer gave $a = 10.254(1)$, $c = 50.494(5)$ Å, $U = 5309.2$ Å³ (at 10°C). Other crystal data are: $D_c = 3.13$ g cm⁻³ for $Z = 8$ tetrameric molecules of formula $C_{16}H_{24}O_{16}Pt_4$, $M_r = 1252.35$, $F(000) = 4480$, and $\mu(Cu K\alpha) = 410.5$ cm⁻¹.

A crystal $0.16 \times 0.12 \times 0.03$ mm was mounted with a parallel to the ϕ axis of a Siemens off-line automatic four-circle diffractometer. Intensities were measured with Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) at a take-off angle of 3.0°, a Ni β -filter, and a Na(Tl)I scintillation counter. The θ - 2θ scan technique was employed with a five-value measuring procedure: one side of peak, background, full peak, background on other side of peak, other side of peak (Allen, Rogers & Troughton, 1971). 2904 independent reflexions were measured to $\theta = 70^\circ$ and, of these, 221 were judged to be unobserved with $I < 2.58\sigma(I)$. The 0,1,21 reflexion was measured as a reference every 50 reflexions and its net count did not alter noticeably over the period of data collection (ca 7 d). Data were scaled by use of the reference reflexion, and Lorentz and polarization corrections were applied.

At a later stage the data were corrected for absorption by the Gaussian integration method (Busing & Levy, 1957), with a $12 \times 12 \times 12$ grid, and with crystal path lengths determined by the procedure of Coppens, Leiserowitz & Rabinovich (1965).

Solution and refinement of the structure

The structure was solved by Patterson and Fourier synthesis methods. First, two correct Pt positions were found, to give $R = 0.49$, then three ($R = 0.39$), and finally R was 0.197 for all four Pt atoms. The acetate groups were located without difficulty and isotropic refinement gave $R = 0.154$.

Application of an absorption correction and refinement as previously reduced R to 0.063. Refinement with anisotropic thermal parameters, introduction of the anomalous dispersion correction for Pt, and the

* Further examination of the crystallization mixture from which the tetragonal crystals were found showed also the presence of dark-brown prismatic monoclinic crystals with $a = 12.031(1)$, $b = 10.583(1)$, $c = 20.090(2)$ Å, $\beta = 91.10(1)^\circ$, $U = 2557.4$ Å³, and space group $P2_1/c$. There also exists a blue-black, apparently amorphous form as a major component of this mixture.

Table 1. Atomic coordinates with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
Pt(1)	0.04395 (7)	0.59140 (6)	0.18444 (1)
Pt(2)	-0.05224 (7)	0.37941 (6)	0.16989 (1)
Pt(3)	-0.26901 (7)	0.45525 (7)	0.18614 (1)
Pt(4)	-0.17910 (7)	0.67916 (7)	0.19261 (1)
O(11)	0.2285 (11)	0.5074 (11)	0.1737 (3)
O(12)	0.1370 (11)	0.3298 (12)	0.1555 (2)
C(11)	0.2332 (18)	0.4011 (18)	0.1620 (4)
C(12)	0.3705 (16)	0.3514 (18)	0.1552 (4)
O(13)	0.0638 (11)	0.5056 (11)	0.2202 (2)
O(14)	0.0060 (11)	0.3120 (11)	0.2045 (2)
C(13)	0.0490 (17)	0.3841 (17)	0.2222 (4)
C(14)	0.0811 (22)	0.3278 (21)	0.2488 (4)
O(21)	-0.1460 (12)	0.1948 (11)	0.1619 (2)
O(22)	-0.3316 (13)	0.2542 (11)	0.1815 (2)
C(21)	-0.2608 (17)	0.1736 (17)	0.1699 (3)
C(22)	-0.3187 (22)	0.0389 (17)	0.1641 (4)
O(23)	-0.1123 (11)	0.4376 (11)	0.1339 (2)
O(24)	-0.3182 (12)	0.4778 (12)	0.1481 (2)
C(23)	-0.2312 (17)	0.4689 (15)	0.1299 (3)
C(24)	-0.2713 (22)	0.4915 (20)	0.1021 (3)
O(31)	-0.4516 (12)	0.5354 (13)	0.1989 (2)
O(32)	-0.3791 (13)	0.7419 (13)	0.1971 (2)
C(31)	-0.4688 (17)	0.6540 (19)	0.2025 (3)
C(32)	-0.5969 (19)	0.7035 (28)	0.2114 (5)
O(33)	-0.2360 (13)	0.4263 (12)	0.2248 (2)
O(34)	-0.1871 (12)	0.6365 (12)	0.2313 (2)
C(33)	-0.2124 (19)	0.5264 (18)	0.2398 (3)
C(34)	-0.2224 (24)	0.5097 (21)	0.2688 (3)
O(41)	-0.0847 (11)	0.8641 (11)	0.2025 (2)
O(42)	0.1131 (11)	0.7773 (11)	0.2003 (2)
C(41)	0.0335 (18)	0.8683 (18)	0.2047 (3)
C(42)	0.0919 (24)	0.9960 (21)	0.2149 (4)
O(43)	-0.1765 (13)	0.7335 (12)	0.1541 (2)
O(44)	0.0342 (13)	0.6780 (12)	0.1492 (2)
C(43)	-0.0684 (19)	0.7292 (18)	0.1413 (4)
C(44)	-0.0654 (26)	0.7877 (26)	0.1140 (4)

removal of the two strongest reflections thought to be suffering from extinction, reduced R to 0.035. At this stage there were already strong indications that the correct space group was $P4_3,2,2$. Positions of the methyl H atoms were obtained from a difference synthesis, and they were included as a fixed-atom contribution with the isotropic temperature factors of their parent C atoms to give $R = 0.033$. Introduction of a weighting scheme and removal of eight more strong low-angle extinction reflections reduced R to its final value of 0.032. (The same refinement in space group $P4_1,2,2$ gave $R = 0.038$, which is a significant difference in favour of $P4_3,2,2$.) The final difference synthesis was featureless except for some peaks of up to 1.4 e Å⁻³ in the immediate vicinity of the Pt atoms, and concentrated round the metal–metal bonded square.

In the later stages of refinement the weighting scheme was that suggested by Hughes (1941), where $w = 1$ for $F < F^*$, $\sqrt{w} = F^*/F$ for $F \geq F^*$, with $F^* = 200$ as the optimum value. The scattering factors of Cromer & Waber (1965) and, for H, of Stewart, Davidson & Simpson (1965) were used, while the anomalous

Table 2. Fractional coordinates of the H atoms

The atoms are numbered so that the first two digits correspond to those of the parent C atom.

	<i>x</i>	<i>y</i>	<i>z</i>
H(121)	0.439	0.417	0.161
H(122)	0.387	0.268	0.165
H(123)	0.379	0.338	0.136
H(141)	0.115	0.395	0.261
H(142)	0.001	0.285	0.256
H(143)	0.149	0.256	0.246
H(221)	-0.250	-0.015	0.154
H(222)	-0.341	-0.005	0.180
H(223)	-0.396	0.049	0.152
H(241)	-0.369	0.517	0.101
H(242)	-0.222	0.567	0.094
H(243)	-0.259	0.413	0.091
H(321)	-0.593	0.802	0.214
H(322)	-0.667	0.681	0.199
H(323)	-0.620	0.666	0.230
H(341)	-0.246	0.417	0.274
H(342)	-0.140	0.534	0.278
H(343)	-0.295	0.568	0.277
H(421)	0.191	0.989	0.216
H(422)	0.071	1.070	0.202
H(423)	0.060	1.019	0.233
*H(441)	0.022	0.779	0.105
H(442)	-0.132	0.740	0.102
H(443)	-0.092	0.883	0.114
H(441')	-0.155	0.827	0.109
H(442')	0.001	0.858	0.112
H(443')	-0.048	0.717	0.100

* For the C(44) methyl group the H atoms appear to occupy two alternative positions.

dispersion correction for Pt was that given by Cromer & Liberman (1970). The XRAY 72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used for the solution and refinement of the structure. Calculations were performed on the University of London CDC 7600 computer, while structural illustrations were drawn with the Imperial College CDC 6400.

The coordinates of the non-hydrogen atoms are given in Table 1 and the unrefined coordinates of the H atoms are listed in Table 2.*

Description of the structure and discussion

This study has shown that the title complex has a tetrameric structure (Fig. 1). Fig. 1 also shows the thermal vibration ellipsoids of the non-hydrogen atoms (Johnson, 1965). In the molecule eight bridging acetate groups are arranged about a metal-metal bonded

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33359 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

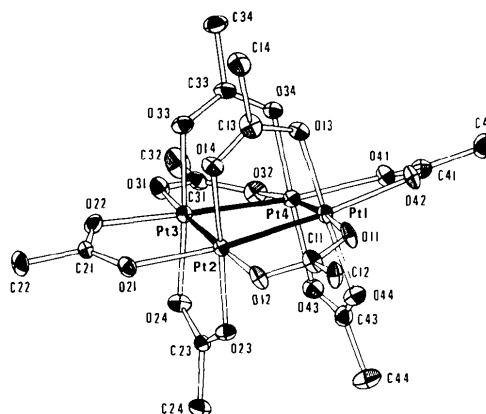


Fig. 1. Molecular structure of $[\text{Pt}(\text{acetate})_2]_4$. Thermal vibration ellipsoids are scaled to enclose 20% probability.

Table 3. Interatomic distances (Å) with e.s.d.'s in parentheses

Pt(1)—Pt(2)	2.498 (1)	Pt(2)—Pt(3)	2.494 (1)
Pt(1)—Pt(4)	2.492 (1)	Pt(3)—Pt(4)	2.496 (1)
Mean Pt—Pt		2.495	
Pt(1)—O(11)	2.149 (12)	Pt(1)—O(13)	2.019 (11)
Pt(1)—O(42)	2.186 (11)	Pt(1)—O(44)	1.990 (11)
Pt(2)—O(12)	2.134 (12)	Pt(2)—O(14)	1.970 (11)
Pt(2)—O(21)	2.161 (11)	Pt(2)—O(23)	2.012 (10)
Pt(3)—O(22)	2.172 (12)	Pt(3)—O(24)	1.999 (11)
Pt(3)—O(31)	2.144 (12)	Pt(3)—O(33)	2.001 (11)
Pt(4)—O(32)	2.161 (14)	Pt(4)—O(34)	2.004 (10)
Pt(4)—O(41)	2.187 (11)	Pt(4)—O(43)	2.024 (11)
Mean Pt—O (in plane)	2.162	Mean Pt—O (⊥ to plane)	2.002
O(11)—C(11)	1.241 (22)	O(13)—C(13)	1.259 (21)
O(12)—C(11)	1.270 (22)	O(14)—C(13)	1.242 (22)
C(11)—C(12)	1.537 (25)	C(13)—C(14)	1.500 (29)
O(21)—C(21)	1.263 (21)	O(23)—C(23)	1.276 (21)
O(22)—C(21)	1.248 (21)	O(24)—C(23)	1.284 (20)
C(21)—C(22)	1.531 (25)	C(23)—C(24)	1.481 (23)
O(31)—C(31)	1.241 (23)	O(33)—C(33)	1.301 (21)
O(32)—C(31)	1.316 (23)	O(34)—C(33)	1.236 (22)
C(31)—C(32)	1.478 (27)	C(33)—C(34)	1.475 (23)
O(41)—C(41)	1.218 (22)	O(43)—C(43)	1.284 (23)
O(42)—C(41)	1.260 (22)	O(44)—C(43)	1.243 (23)
C(41)—C(42)	1.529 (29)	C(43)—C(44)	1.503 (28)
Mean C—O (in plane)	1.257	Mean C—O (⊥ to plane)	1.266
Mean C—C (in plane)	1.519	Mean C—C (⊥ to plane)	1.490

square of Pt atoms. Four of the bridging groups lie approximately in the plane of the cluster, while the other four are alternately above and below the plane. Thus the Pt atoms have an octahedral coordination. If one considers only the O ligands then the geometry is of the SF_4 type; however, it is better to take account of the *cis* metal-metal bonds as well and to view it as octahedral. Table 3 lists the more important bond lengths, while the bond angles are given in Table 4.

Table 4. Bond angles ($^{\circ}$) with e.s.d.'s in parentheses

Pt(2)–Pt(1)–Pt(4)	90.03 (3)	Pt(1)–Pt(2)–Pt(3)	89.08 (3)	Pt(2)–Pt(3)–Pt(4)	90.04 (3)	Pt(1)–Pt(4)–Pt(3)	89.15 (3)
Pt(2)–Pt(1)–O(11)	85.7 (3)	Pt(3)–Pt(2)–O(21)	86.5 (3)	Pt(4)–Pt(3)–O(31)	86.0 (4)	Pt(1)–Pt(4)–O(41)	86.8 (3)
Pt(4)–Pt(1)–O(42)	85.5 (3)	Pt(1)–Pt(2)–O(12)	87.1 (3)	Pt(2)–Pt(3)–O(22)	86.1 (4)	Pt(3)–Pt(4)–O(32)	86.4 (4)
O(11)–Pt(1)–O(42)	99.0 (4)	O(12)–Pt(2)–O(21)	97.6 (5)	O(22)–Pt(3)–O(31)	97.9 (5)	O(32)–Pt(4)–O(41)	97.9 (5)
Pt(2)–Pt(1)–O(13)	85.6 (3)	Pt(1)–Pt(2)–O(14)	85.7 (3)	Pt(4)–Pt(3)–O(33)	86.9 (4)	Pt(3)–Pt(4)–O(34)	85.0 (4)
Pt(4)–Pt(1)–O(13)	95.8 (3)	Pt(3)–Pt(2)–O(14)	95.1 (3)	Pt(2)–Pt(3)–O(33)	97.1 (4)	Pt(1)–Pt(4)–O(34)	96.9 (4)
O(42)–Pt(1)–O(13)	91.1 (5)	O(21)–Pt(2)–O(14)	89.6 (5)	O(22)–Pt(3)–O(33)	90.8 (5)	O(41)–Pt(4)–O(34)	89.1 (5)
O(11)–Pt(1)–O(13)	87.9 (5)	O(12)–Pt(2)–O(14)	86.7 (5)	O(31)–Pt(3)–O(33)	84.9 (5)	O(32)–Pt(4)–O(34)	85.6 (5)
Pt(4)–Pt(1)–O(44)	86.6 (4)	Pt(3)–Pt(2)–O(23)	86.1 (3)	Pt(2)–Pt(3)–O(24)	86.8 (4)	Pt(1)–Pt(4)–O(43)	85.9 (4)
Pt(2)–Pt(1)–O(44)	96.1 (4)	Pt(1)–Pt(2)–O(23)	97.4 (3)	Pt(4)–Pt(3)–O(24)	96.5 (4)	Pt(3)–Pt(4)–O(43)	97.6 (3)
O(11)–Pt(1)–O(44)	89.8 (5)	O(12)–Pt(2)–O(23)	92.3 (5)	O(31)–Pt(3)–O(24)	91.4 (5)	O(32)–Pt(4)–O(43)	91.8 (5)
O(42)–Pt(1)–O(44)	87.4 (5)	O(21)–Pt(2)–O(23)	87.4 (4)	O(22)–Pt(3)–O(24)	86.1 (5)	O(41)–Pt(4)–O(43)	88.6 (5)
Pt(2)–Pt(1)–O(42)	174.2 (3)	Pt(3)–Pt(2)–O(12)	175.6 (3)	Pt(4)–Pt(3)–O(22)	175.3 (4)	Pt(1)–Pt(4)–O(32)	174.7 (4)
Pt(4)–Pt(1)–O(11)	174.1 (3)	Pt(1)–Pt(2)–O(21)	173.2 (3)	Pt(2)–Pt(3)–O(31)	175.5 (4)	Pt(3)–Pt(4)–O(41)	172.4 (3)
O(13)–Pt(1)–O(44)	177.0 (5)	O(14)–Pt(2)–O(23)	176.7 (5)	O(24)–Pt(3)–O(33)	174.8 (5)	O(34)–Pt(4)–O(43)	176.3 (5)
Pt(1)–O(11)–C(11)	120.4 (1.1)	Pt(2)–O(21)–C(21)	120.4 (1.0)	Pt(3)–O(31)–C(31)	122.9 (1.1)	Pt(4)–O(41)–C(41)	119.5 (1.1)
Pt(2)–O(12)–C(11)	118.8 (1.1)	Pt(3)–O(22)–C(21)	120.5 (1.1)	Pt(4)–O(32)–C(31)	118.7 (1.1)	Pt(1)–O(42)–C(41)	120.0 (1.1)
O(11)–C(11)–O(12)	126.7 (1.7)	O(21)–C(21)–O(22)	125.3 (1.6)	O(31)–C(31)–O(32)	122.8 (1.6)	O(41)–C(41)–O(42)	127.1 (1.7)
O(11)–C(11)–C(12)	115.7 (1.5)	O(21)–C(21)–C(22)	117.1 (1.5)	O(31)–C(31)–C(32)	120.4 (1.8)	O(41)–C(41)–C(42)	116.8 (1.7)
O(12)–C(11)–C(12)	117.6 (1.6)	O(22)–C(21)–C(22)	117.6 (1.6)	O(32)–C(31)–C(32)	116.6 (1.8)	O(42)–C(41)–C(42)	116.1 (1.7)
Pt(1)–O(13)–C(13)	119.4 (1.1)	Pt(2)–O(23)–C(23)	120.5 (9)	Pt(3)–O(33)–C(33)	119.0 (1.0)	Pt(4)–O(43)–C(43)	119.2 (1.1)
Pt(2)–O(14)–C(13)	122.5 (1.1)	Pt(3)–O(24)–C(23)	120.3 (1.1)	Pt(4)–O(34)–C(33)	123.2 (1.0)	Pt(1)–O(44)–C(43)	121.4 (1.2)
O(13)–C(13)–O(14)	125.1 (1.7)	O(23)–C(23)–O(24)	124.8 (1.3)	O(33)–C(33)–O(34)	123.8 (1.4)	O(43)–C(43)–O(44)	125.6 (1.6)
O(13)–C(13)–C(14)	115.2 (1.6)	O(23)–C(23)–C(24)	116.9 (1.5)	O(33)–C(33)–C(34)	118.3 (1.6)	O(43)–C(43)–C(44)	117.8 (1.8)
O(14)–C(13)–C(14)	119.6 (1.6)	O(24)–C(23)–C(24)	118.3 (1.6)	O(34)–C(33)–C(34)	117.7 (1.6)	O(44)–C(43)–C(44)	116.6 (1.8)

The square cluster of four Pt atoms has Pt–Pt angles in the range 89.08 to 90.04 $^{\circ}$, while the four sides are almost identical, ranging from 2.492 to 2.498 Å. This square is best seen in Fig. 2. The mean Pt–Pt distance of 2.495 Å is markedly shorter than the distances found in other complexes containing definite Pt–Pt bonds. Thus in binuclear species such as Pt₂(μ-C₁₀H₁₀)(Cp)₂ (Cheung, Cross, Forrest, Wardle & Mercer, 1975) Pt–Pt is 2.581 Å, in Pt₂(1,5-C₈H₁₂)₂{(CF₃)₂CO} (Green, Howard, Laguna, Murray, Spencer & Stone, 1975) it is 2.585 Å, and in Pt₂S(CO)(PPh₃)₃ (Skapski & Troughton, 1969) it is 2.647 Å. In a trinuclear complex, though related to the latter [Pt₂Fe(CO)₅{P(OPh)₃}₃] (Albano, Ciani, Bruce, Shaw & Stone, 1972), Pt–Pt is 2.633 Å. In a series of triangular complexes of formula [Pt₃(CO)₃(μ-CO)₃]_n²⁻ (Calabrese & Dahl, 1974) the mean Pt–Pt distance is 2.66 Å, and in [Pt₃(BuⁿNC)₆] (Green, Howard, Spencer & Stone, 1975) it is 2.65 Å. In a pentanuclear complex containing a Pt triangle (C₈H₁₂)₃Pt₃(SnCl₃)₂ the mean Pt–Pt length is 2.58 Å (Guggenberger, 1968).

The reason why these Pt–Pt bonds are longer than those found in the title compound may well be that they are bent bonds (Corey & Dahl, 1962) where the orbital overlap is not as complete as that which is possible in the octahedral geometry of [Pt(acetate)₂]₄.

Approximate 42m (*D*_{2d}) point symmetry is found for the Pt acetate molecule. A slight twisting (Fig. 1), however, causes a small departure from this idealized symmetry. The extent of the twisting can be approximately judged from the angle between the lines formed by the O atoms of acetate groups on opposite sides of

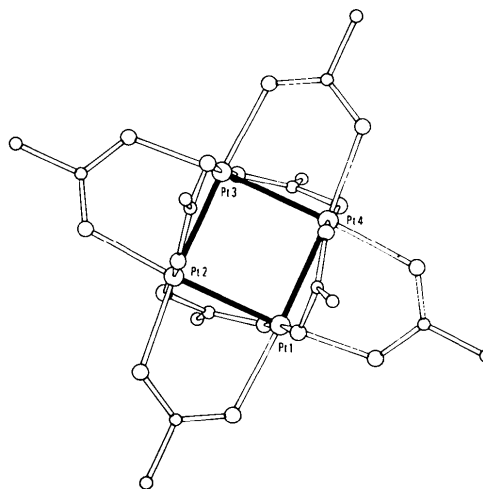
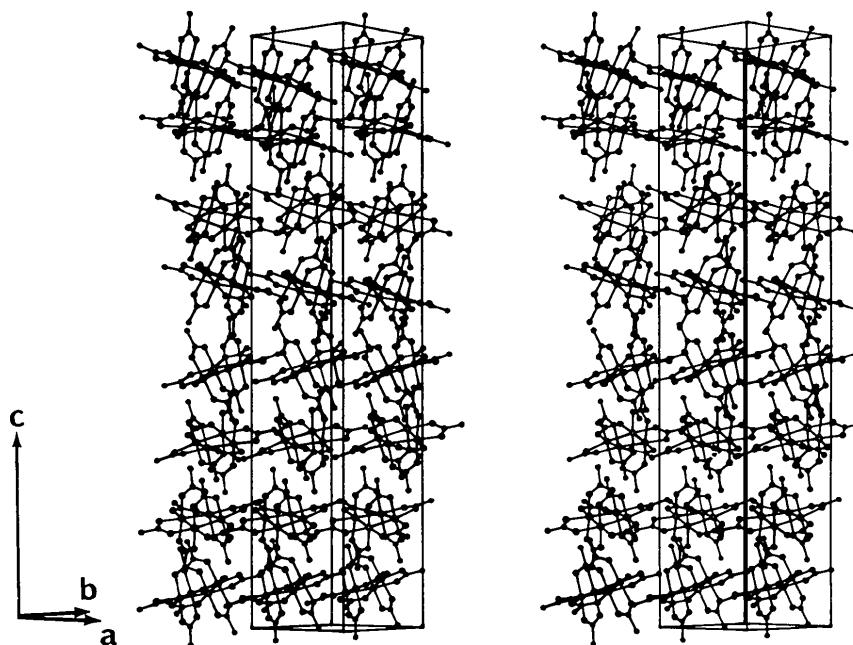


Fig. 2. A view of the molecule normal to the least-squares plane through the Pt atoms.

the Pt square. Thus the angle between O(11)–O(12) and O(31)–O(32) is 27.5 $^{\circ}$, and that between O(21)–O(22) and O(41)–O(42) is 24.2 $^{\circ}$. This twisting means that the Pt cluster is not absolutely flat, and a least-squares calculation shows the Pt atoms to be ± 0.108 Å from the best plane. Details of this and other planes are given in Table 5.

The molecular geometry of [Pt(acetate)₂]₄ bears a resemblance to that of Pt₄(acetate)₆(NO)₂. Although the latter is in no way a precursor of Pt acetate, certainly not in the preparation involving Ag acetate (ICI Ltd, 1970), a comparison of Fig. 1 with Fig. 1(a)

Fig. 3. A stereoscopic view showing the packing of $[\text{Pt}(\text{acetate})_2]_4$ molecules.Table 5. Planarity of groups of atoms in the structure and distances (\AA) from the least-squares planes

Equations of the planes are expressed as $Px + Qy + Rz = S$ in direct space.

Plane 1 $1.55x - 2.96y + 47.74z = 7.01$
 Pt(1) 0.108, Pt(2) -0.108, Pt(3) 0.108, Pt(4) -0.108
 Not defining plane: O(11) 0.128, O(12) -0.354, C(11) -0.109,
 C(12) -0.074, O(21) -0.087, O(22) 0.387, C(21) 0.178,
 C(22) 0.210, O(31) 0.197, O(32) -0.388, C(31) -0.011,
 C(32) 0.069, O(41) -0.036, O(42) 0.422, C(41) 0.238,
 C(42) 0.436.

Plane 2 $0.51x - 4.81y + 44.52z = 5.40$
 O(11) 0.002, O(12) 0.002, C(11) -0.005, C(12) 0.001
 Not defining plane: Pt(1) -0.017, Pt(2) 0.307

Plane 3 $3.60x - 3.38y + 44.26z = 5.98$
 O(21) -0.003, O(22) -0.003, C(21) 0.008, C(22) -0.002
 Not defining plane: Pt(2) 0.063, Pt(3) -0.254

Plane 4 $3.25x - 0.72y + 47.76z = 7.65$
 O(31) -0.008, O(32) -0.007, C(31) 0.021, C(32) -0.006
 Not defining plane: Pt(3) 0.034, Pt(4) 0.473

Plane 5 $-0.90x - 3.27y + 47.66z = 6.90$
 O(41) 0.005, O(42) 0.005, C(41) -0.013, C(42) 0.003
 Not defining plane: Pt(4) 0.222, Pt(1) -0.083

Plane 6 $-9.62x + 1.60y + 15.68z = 3.64$
 O(13) 0.005, O(14) 0.006, C(13) -0.015, C(14) 0.004
 Not defining plane: Pt(1) -0.227, Pt(2) 0.131

Plane 7 $2.31x + 9.93y + 5.30z = 4.80$
 O(23) -0.004, O(24) -0.004, C(23) 0.012, C(24) -0.003
 Not defining plane: Pt(2) -0.252, Pt(3) 0.087

Table 5 (cont.)

Plane 8 $9.97x - 2.37y + 1.43z = -3.04$
 O(33) -0.005, O(34) -0.005, C(33) 0.015, C(34) -0.004
 Not defining plane: Pt(3) 0.458, Pt(4) -0.083

Plane 9 $2.83x + 8.98y + 19.96z = 9.17$
 O(43) -0.003, O(44) -0.003, C(43) 0.008, C(44) -0.002
 Not defining plane: Pt(4) 0.270, Pt(1) -0.050

in de Meester & Skapski (1973) shows that if one removes the NO groups which hold the Pt atoms apart, and replaces them by two further bridging acetate groups, strong Pt-Pt bonds become possible as in the structure of the title compound.

The Pt-acetate linkages form two distinct groups. The eight Pt-O bonds which are approximately normal to the Pt cluster have lengths in the range 1.970-2.024 \AA , mean 2.002 \AA . These distances are unexceptional, and may be compared with 2.015 \AA in $\text{K}_4[\text{Pt}(\text{oxalate})_2(\text{SCN})_2] \cdot 4\text{H}_2\text{O}$ (Chiesi Villa, Gaetani Manfredotti, Giacomelli, Guastini & Indelli, 1975), and 1.994 and 2.044 \AA in $\text{PtCl}(\text{acac})(\text{CH}_2\text{CHOH})$ (Cotton, Francis, Frenz & Tsutsui, 1973). On the other hand the eight Pt-O bonds approximately in the plane of the cluster are all rather long. They lie in the range 2.134-2.187 \AA , mean 2.162 \AA . Such distances are found where there is a marked *trans* influence, for instance in a group of octahedral Pt^{IV} 1,3-diketone complexes where Pt-O bonds *trans* to a methyl group

are in the range 2.16–2.19 Å (Hazell & Truter, 1960; Robson & Truter, 1965). Thus one explanation for this difference in the title complex might be a *trans* influence due to the strong Pt–Pt bonds. An alternative explanation is that the Pt–O bonds are long because crowding of the acetate groups in the cluster plane causes repulsion between the O atom lone pairs.

The C–O and C–C bonds in the acetate groups are consistent with the long and the short Pt–O bonds. Thus in the in-plane acetate groups the mean C–O is 1.257 Å and the mean C–C is 1.519 Å, while the shorter Pt–O bonds are matched by a longer mean C–O of 1.266 Å and a shorter mean C–O of 1.490 Å.

Fig. 3 shows the packing of the molecules in the unit cell with its spiral arrangement. There are no groups in the molecule capable of forming a network of hydrogen bonds.

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