connecting it with the centers of the two metaprisms to which it belongs. In interstitially 'filled-up' β-Mn structures the metaprisms are occupied by C or N, as in Mo_3Al_2C (Jeitschko, Nowotny & Benesovsky, 1964). The distance from the Mn atoms to the center of the hole is 1·98 Å in the elemental structure. The coordination polyhedra for the ternary phase are given in Fig. 1(*a*)–(*c*). The metaprism in the elemental structure is shown in Fig. 2.

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X-ray Crystal Structure of the Monoclinic Form of *cyclo*-Tetrakis[di-μ-acetato-platinum(II)]: A Square-Cluster Platinum Complex

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The structure of the monoclinic form of $[Pt(CH_3COO)_2]_4$ has been determined from X-ray diffractometer data. This polymorph has a unit cell $a = 12{\cdot}031$ (1), $b = 10{\cdot}583$ (1), $c = 20{\cdot}090$ (2) Å, $\beta = 91{\cdot}10$ (1)°, space group $P2_1/c$, $Z = 4$ tetrameric molecules. Refinement of 3908 independent reflexions has reached $R = 0{\cdot}043$. A strongly metal–metal bonded square of Pt atoms, with Pt–Pt distances in the range 2·493–2·501 Å, forms the basis of the molecular structure in which eight bridging acetate groups are distributed round the square. The arrangement is such that four groups are approximately in the cluster plane, while four are alternately above and below it. Pt—O bonds which are perpendicular to the Pt cluster have normal lengths with a mean of 2·014 Å, while the eight which are nearly coplanar with the Pt atoms are all rather long, with a mean distance of 2·157 Å. The molecular structure is very similar to that found in the tetragonal form, but shows a slightly greater twisting distortion away from ideal $\bar{4}2m$ (D_{2d}) point symmetry.

Introduction

We have recently reported details of the crystal structure of the tetragonal form of Pt acetate (Carrondo & Skapski, 1976, 1978), and have shown it to have an unusual tetrameric geometry based on a strongly metal–metal bonded Pt square cluster. The background to this work and the reasons for determining the structure of this compound have been set out in the previous publication.

Starting with a specimen of Pt acetate obtained by the Ag acetate method (ICI Ltd, 1970), crystallization from glacial acetic acid yielded both a tetragonal and a monoclinic form, as well as a blue-black apparently amorphous solid (Phillips & Skapski, 1975).

We report here the determination of the structure of the monoclinic polymorph, in which essentially the same molecular structure is found as in the tetragonal form. The molecule shows a similar twisting distortion, but to a slightly greater degree. This difference can be attributed to the tighter packing observed in the monoclinic form.

Experimental

Preliminary photographs of the dark-brown prismatic crystals of $[Pt(CH_3COO)_2]_4$ showed them to be monoclinic, with systematic absences $h0l$: $l = 2n + 1$, $0k0$: $k = 2n + 1$. These absences uniquely define space group $P2_1/c$. Accurate cell dimensions were obtained by a least-squares calculation based on 22 high-angle α_1 reflexions measured on a diffractometer.

Crystal data

$C_{16}H_{24}O_{16}Pt_4$, $M_r = 1252{\cdot}35$, monoclinic, $a = 12{\cdot}031\,(1)$, $b = 10{\cdot}583\,(1)$, $c = 20{\cdot}090\,(2)$ Å, $\beta = 91{\cdot}10\,(1)°$, $U = 2557{\cdot}5$ Å^3 (at 10°C), $D_c = 3{\cdot}25$ g cm^{-3} for $Z = 4$ tetrameric molecules, $F(000) = 2240$, space group $P2_1/c$, $\mu(\text{Cu } K\alpha) = 426{\cdot}3$ cm^{-1}.

Intensities were measured for a crystal 0·20 × 0·14 × 0·10 mm mounted with **a** parallel to the φ axis of a Siemens off-line automatic four-circle diffractometer. Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å) at a take-off angle of 3°, a Ni filter, and a Na(Tl)I scintillation counter were used. The θ–2θ technique was employed with a five-value measuring procedure (Allen, Rogers & Troughton, 1971).

3921 independent reflexions were measured to $\theta = 60°$, and of these 360 were judged to be unobserved with $I < 2{\cdot}58\sigma(I)$. The 046 reflexion was measured as a reference every 50 reflexions and its net count did not alter noticeably over the period of data collection (*ca* 8 d). Data were scaled by use of the reference reflexion, and Lorentz and polarization corrections were applied.

Solution and refinement of the structure

An origin-removed Patterson synthesis showed a distribution of vector peaks characteristic of a Pt square, and suggested that the molecular structure was similar to that found in the tetragonal form. Isotropic least-squares refinement of the four independent Pt atoms gave $R = 0{\cdot}169$, and the eight acetate groups were located to give $R = 0{\cdot}118$.

At this stage the data were corrected for absorption by the Gaussian integration method (Busing & Levy, 1957), with a 12 × 12 × 12 grid, and with crystal path lengths determined by the vector analysis procedure (Coppens, Leiserowitz & Rabinovich, 1965). This correction could only be approximate because of the irregular shape of the crystal. Refinement as previously, nevertheless, gave an appreciable improvement in R to 0·076. Introduction of the anomalous dispersion correction for Pt and refinement with anisotropic thermal parameters reduced R to 0·059. It was now clear that extinction effects were very marked, and 13 strong low-angle reflexions thought to be most affected were removed to give $R = 0{\cdot}046$.

The methyl H atoms were located from a difference synthesis, and were included as a fixed-atom contribution with isotropic temperature factors of their parent C atoms. Introduction and adjustment of a weighting scheme reduced R to its final value of 0·043.

The June 1974 update of XRAY 72 (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; structural illustrations were drawn with the Imperial College CDC 6400. In the later stages of refinement the weighting scheme used was that suggested by Hughes (1941), where $w = 1$ for $F < F^*$, $\sqrt{w} = F^*/F$ for $F \geq F^*$, with $F^* = 100$ as the optimum value. Scattering factors of Cromer & Waber (1965) and for H of Stewart, Davidson & Simpson (1965) were used; the anomalous dispersion correction for Pt was from Cromer & Liberman (1970).

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

	x	y	z
Pt(1)	0·20615 (4)	0·12427 (5)	0·46009 (2)
Pt(2)	0·24894 (4)	0·02916 (5)	0·34998 (2)
Pt(3)	0·30454 (4)	0·24155 (5)	0·30815 (2)
Pt(4)	0·22510 (5)	0·33823 (5)	0·41038 (3)
O(11)	0·2111 (8)	−0·0647 (10)	0·4985 (4)
O(12)	0·2068 (9)	−0·1500 (9)	0·3962 (5)
C(11)	0·1987 (11)	−0·1525 (12)	0·4562 (8)
C(12)	0·1784 (13)	−0·2831 (11)	0·4870 (7)
O(13)	0·0461 (7)	0·0949 (9)	0·4349 (4)
O(14)	0·0842 (7)	0·0462 (9)	0·3296 (4)
C(13)	0·0175 (11)	0·0630 (14)	0·3781 (6)
C(14)	−0·0990 (12)	0·0427 (16)	0·3617 (8)
O(21)	0·2771 (8)	−0·0404 (9)	0·2507 (5)
O(22)	0·3539 (8)	0·1461 (10)	0·2191 (5)
C(21)	0·3301 (11)	0·0318 (15)	0·2108 (6)
C(22)	0·3630 (16)	−0·0363 (16)	0·1469 (7)
O(23)	0·4101 (7)	−0·0022 (9)	0·3684 (5)
O(24)	0·4567 (7)	0·2009 (9)	0·3471 (4)
C(23)	0·4787 (11)	0·0886 (14)	0·3644 (7)
C(24)	0·5987 (12)	0·0561 (16)	0·3807 (8)
O(31)	0·3560 (9)	0·4321 (8)	0·2812 (5)
O(32)	0·2611 (10)	0·5173 (9)	0·3656 (5)
C(31)	0·3192 (12)	0·5258 (12)	0·3141 (7)
C(32)	0·3466 (17)	0·6543 (15)	0·2899 (9)
O(33)	0·1571 (8)	0·2816 (9)	0·2641 (5)
O(34)	0·0776 (7)	0·3337 (9)	0·3602 (4)
C(33)	0·0760 (11)	0·3113 (13)	0·2988 (7)
C(34)	−0·0360 (14)	0·3194 (20)	0·2649 (8)
O(41)	0·1432 (8)	0·4089 (9)	0·4973 (5)
O(42)	0·1526 (9)	0·2181 (8)	0·5483 (4)
C(41)	0·1287 (11)	0·3364 (14)	0·5443 (6)
C(42)	0·0755 (16)	0·3934 (17)	0·6071 (8)
O(43)	0·3691 (9)	0·3531 (9)	0·4617 (5)
O(44)	0·3648 (8)	0·1500 (10)	0·4918 (4)
C(43)	0·4104 (13)	0·2576 (15)	0·4910 (8)
C(44)	0·5188 (17)	0·2746 (19)	0·5259 (10)

Table 1 lists the coordinates of the non-hydrogen atoms; the unrefined coordinates of the H atoms are given in Table 2.*

Description of the structure and discussion

A structure determination of the monoclinic form of Pt acetate has shown it to have a tetrameric structure like that in the tetragonal form of the same compound. Fig. 1 shows the molecular geometry found in the monoclinic form, and by comparison with Fig. 1 of Carrondo & Skapski (1978) the similarity between them is evident.

Four strongly bonded Pt atoms arranged in a square cluster form the central core of the molecule, with eight bridging acetate groups distributed around the square. Four are approximately coplanar with the Pt cluster while the other four are alternately above and below it. The more important bond lengths and angles are listed in Tables 3 and 4.

Pt–Pt bond distances range from 2·493 to 2·501 Å, and the mean of 2·497 Å is marginally longer than that found in the tetragonal form, 2·495 Å. There are no other tetranuclear Pt cluster compounds with strong metal–metal bonds for comparison. Binuclear and trinuclear complexes reported so far with short Pt–Pt bonds have these distances ranging from 2·58 to 2·66 Å (*e.g.* Cheung, Cross, Forrest, Wardle & Mercer, 1975; Calabrese & Dahl, 1974). In the title complex this value is markedly shorter, probably due to the more complete orbital overlaps which are possible in the octahedral coordination found in the tetramer.

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.

	x	*y*	*z*
H(121)	0·173	−0·276	0·537
H(122)	0·109	−0·320	0·468
H(123)	0·240	−0·342	0·476
H(141)	−0·108	0·018	0·314
H(142)	−0·129	−0·026	0·391
H(143)	−0·141	0·123	0·369
H(221)	0·339	−0·125	0·147
H(222)	0·328	0·010	0·108
H(223)	0·444	−0·031	0·142
H(241)	0·644	0·133	0·375
H(242)	0·605	0·025	0·427
H(243)	0·624	−0·011	0·349
H(321)	0·313	0·719	0·319
H(322)	0·427	0·666	0·290
H(323)	0·318	0·666	0·243
H(341)	−0·091	0·343	0·298
H(342)	−0·035	0·383	0·228
H(343)	−0·055	0·234	0·246
H(421)	0·121	0·363	0·646
H(422)	0·079	0·490	0·601
H(423)	0·000	0·354	0·614
H(441)	0·545	0·364	0·521
H(442)	0·512	0·255	0·575
H(443)	0·574	0·216	0·507

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

Pt(1)–Pt(2)	2·493 (1)	Pt(2)–Pt(3)	2·496 (1)
Pt(1)–Pt(4)	2·497 (1)	Pt(3)–Pt(4)	2·501 (1)
	Mean Pt–Pt	2·497	
Pt(1)–O(11)	2·144 (10)	Pt(1)–O(13)	2·006 (9)
Pt(1)–O(42)	2·141 (9)	Pt(1)–O(44)	2·019 (10)
Pt(2)–O(12)	2·175 (9)	Pt(2)–O(14)	2·025 (8)
Pt(2)–O(21)	2·160 (10)	Pt(2)–O(23)	1·995 (9)
Pt(3)–O(22)	2·149 (10)	Pt(3)–O(24)	2·024 (9)
Pt(3)–O(31)	2·181 (9)	Pt(3)–O(33)	2·012 (9)
Pt(4)–O(32)	2·146 (10)	Pt(4)–O(34)	2·025 (9)
Pt(4)–O(41)	2·156 (10)	Pt(4)–O(43)	2·006 (10)
Mean Pt–O (in plane)	2·157	Mean Pt–O ($\perp$ to plane)	2·014
O(11)–C(11)	1·265 (17)	O(13)–C(13)	1·233 (16)
O(12)–C(11)	1·213 (18)	O(14)–C(13)	1·285 (16)
C(11)–C(12)	1·535 (18)	C(13)–C(14)	1·449 (20)
O(21)–C(21)	1·285 (17)	O(23)–C(23)	1·270 (17)
O(22)–C(21)	1·253 (18)	O(24)–C(23)	1·264 (17)
C(21)–C(22)	1·531 (20)	C(23)–C(24)	1·513 (20)
O(31)–C(31)	1·276 (16)	O(33)–C(33)	1·250 (17)
O(32)–C(31)	1·263 (17)	O(34)–C(33)	1·256 (17)
C(31)–C(32)	1·483 (21)	C(33)–C(34)	1·500 (21)
O(41)–C(41)	1·231 (17)	O(43)–C(43)	1·266 (18)
O(42)–C(41)	1·287 (17)	O(44)–C(43)	1·264 (19)
C(41)–C(42)	1·549 (22)	C(43)–C(44)	1·480 (25)
Mean C–O (in plane)	1·259	Mean C–O ($\perp$ to plane)	1·261
Mean C–C (in plane)	1·525	Mean C–C ($\perp$ to plane)	1·486

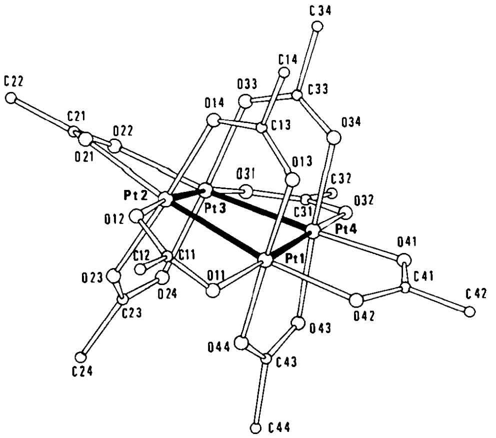

Fig. 1. Molecular structure of [Pt(acetate)$_2$]$_4$.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33815 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Planar arrangements of metal atoms in clusters are infrequent, while those containing a plane square are very rare. Subsequent to our report of the tetragonal form of Pt acetate (Carrondo & Skapski, 1976), a further example has been described involving a square of Cu$^{\rm I}$ atoms in [Cu(CH$_2$SiMe$_3$)]$_4$ (Jarvis, Pearce & Lappert, 1977). There is also a rather distorted square in [Cu(OBu^t)]$_4$ (Greiser & Weiss, 1976).

The four acetate groups which are nearly normal to the Pt cluster plane are held to the Pt atoms by Pt—O bonds of normal length (range 1·995–2·025, mean 2·014 Å). However, those which are almost coplanar with the Pt square have relatively long Pt—O distances (range 2·141–2·181, mean 2·157 Å). A similar lengthening is found in other complexes where there is a marked *trans*-influence acting on the Pt—O bonds (*e.g.* Robson & Truter, 1965). There is another possible reason for this lengthening, which is related to electronic repulsion between the O atom lone pairs of adjacent acetate groups in the crowded equatorial plane of the molecule.* In fact all four equatorial O—Pt—O angles are similar and appreciably greater than 90°, with a mean value of 98·0°. This is, however, an inevitable consequence of the smaller acetate bite (mean 2·26 Å) spanning a larger Pt—Pt distance (mean 2·497 Å).

In its idealized shape the tetrameric molecule has $\bar{4}2m$ (D_{2d}) point symmetry. There is, however, an appreciable twisting distortion in the molecule, clearly visible in Fig. 1, which breaks this symmetry. A measure of this twisting is the value of the angles between lines defined by O atoms of acetate groups on opposite sides of the Pt square. For the title complex these values are 32·0 and 28·1° for the angles between O(11)—O(12) with O(31)—O(32), and O(21)—O(22) with O(41)—O(42) respectively. These angles are *ca* 4° greater than those found in the tetragonal form. A consequence of this twisting is that the Pt square is slightly distorted, with Pt—Pt—Pt angles in the range 89·0–89·8°, and the Pt atoms ±0·116 Å out of the least-squares plane of the cluster (the equivalent value in the tetragonal form is ±0·108 Å).

The difference between the mean equatorial Pt—O and mean axial Pt—O distances is slightly less in the monoclinic form (0·143 as against 0·160 Å in the tetragonal case). This is consistent with the greater twisting distortion observed in this form slightly reducing the distinction between the axial and the

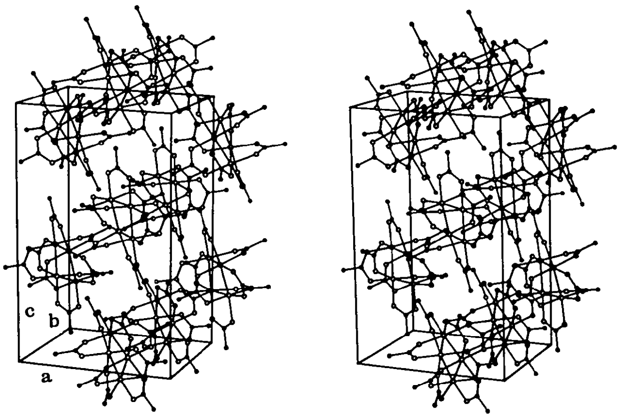

Fig. 2. A stereoscopic view of the packing of [Pt(acetate)$_2$]$_4$ molecules in the monoclinic form.

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

Pt(2)—Pt(1)—Pt(4)	89·38 (2)	Pt(1)—Pt(2)—Pt(3)	89·79 (2)	Pt(2)—Pt(3)—Pt(4)	89·01 (2)	Pt(1)—Pt(4)—Pt(3)	89·81 (2)
Pt(2)—Pt(1)—O(11)	86·4 (3)	Pt(3)—Pt(2)—O(21)	87·0 (3)	Pt(4)—Pt(3)—O(31)	86·6 (3)	Pt(1)—Pt(4)—O(41)	86·8 (3)
Pt(4)—Pt(1)—O(42)	86·6 (2)	Pt(1)—Pt(2)—O(12)	85·4 (3)	Pt(2)—Pt(3)—O(22)	86·4 (3)	Pt(3)—Pt(4)—O(32)	86·2 (3)
O(11)—Pt(1)—O(42)	98·2 (3)	O(12)—Pt(2)—O(21)	98·0 (4)	O(22)—Pt(3)—O(31)	98·3 (4)	O(32)—Pt(4)—O(41)	97·6 (4)
Pt(2)—Pt(1)—O(13)	85·8 (3)	Pt(1)—Pt(2)—O(14)	85·7 (3)	Pt(4)—Pt(3)—O(33)	85·8 (3)	Pt(3)—Pt(4)—O(34)	85·8 (3)
Pt(4)—Pt(1)—O(13)	97·7 (3)	Pt(3)—Pt(2)—O(14)	96·9 (3)	Pt(2)—Pt(3)—O(33)	95·6 (3)	Pt(1)—Pt(4)—O(34)	95·3 (3)
O(42)—Pt(1)—O(13)	88·7 (4)	O(21)—Pt(2)—O(14)	90·8 (4)	O(22)—Pt(3)—O(33)	89·4 (4)	O(41)—Pt(4)—O(34)	90·1 (4)
O(11)—Pt(1)—O(13)	88·0 (4)	O(12)—Pt(2)—O(14)	85·9 (4)	O(31)—Pt(3)—O(33)	87·0 (4)	O(32)—Pt(4)—O(34)	89·7 (4)
Pt(4)—Pt(1)—O(44)	84·9 (3)	Pt(3)—Pt(2)—O(23)	86·9 (3)	Pt(2)—Pt(3)—O(24)	85·7 (3)	Pt(1)—Pt(4)—O(43)	87·1 (3)
Pt(2)—Pt(1)—O(44)	97·1 (3)	Pt(1)—Pt(2)—O(23)	96·8 (3)	Pt(4)—Pt(3)—O(24)	97·3 (3)	Pt(3)—Pt(4)—O(43)	96·6 (3)
O(11)—Pt(1)—O(44)	89·6 (4)	O(12)—Pt(2)—O(23)	90·6 (4)	O(31)—Pt(3)—O(24)	91·9 (4)	O(32)—Pt(4)—O(43)	88·1 (4)
O(42)—Pt(1)—O(44)	88·5 (4)	O(21)—Pt(2)—O(23)	86·9 (4)	O(22)—Pt(3)—O(24)	87·7 (4)	O(41)—Pt(4)—O(43)	87·7 (4)
Pt(2)—Pt(1)—O(42)	172·8 (3)	Pt(3)—Pt(2)—O(12)	174·3 (3)	Pt(4)—Pt(3)—O(22)	173·0 (3)	Pt(1)—Pt(4)—O(32)	173·4 (3)
Pt(4)—Pt(1)—O(11)	172·6 (3)	Pt(1)—Pt(2)—O(21)	175·0 (3)	Pt(2)—Pt(3)—O(31)	174·7 (3)	Pt(3)—Pt(4)—O(41)	174·4 (3)
O(13)—Pt(1)—O(44)	176·1 (4)	O(14)—Pt(2)—O(23)	175·5 (4)	O(24)—Pt(3)—O(33)	176·7 (4)	O(34)—Pt(4)—O(43)	176·6 (4)
Pt(1)—O(11)—C(11)	116·2 (9)	Pt(2)—O(21)—C(21)	117·5 (9)	Pt(3)—O(31)—C(31)	119·1 (9)	Pt(4)—O(41)—C(41)	118·6 (9)
Pt(2)—O(12)—C(11)	117·9 (8)	Pt(3)—O(22)—C(21)	119·9 (8)	Pt(4)—O(32)—C(31)	121·8 (8)	Pt(1)—O(42)—C(41)	118·1 (8)
O(11)—C(11)—O(12)	129·8 (1·3)	O(21)—C(21)—O(22)	127·3 (1·2)	O(31)—C(31)—O(32)	124·9 (1·2)	O(41)—C(41)—O(42)	128·3 (1·2)
O(11)—C(11)—C(12)	114·2 (1·3)	O(21)—C(21)—C(22)	112·5 (1·3)	O(31)—C(31)—C(32)	117·4 (1·3)	O(41)—C(41)—C(42)	116·6 (1·3)
O(12)—C(11)—C(12)	115·9 (1·2)	O(22)—C(21)—C(22)	120·3 (1·2)	O(32)—C(31)—C(32)	117·7 (1·3)	O(42)—C(41)—C(42)	115·1 (1·2)
Pt(1)—O(13)—C(13)	121·7 (9)	Pt(2)—O(23)—C(23)	119·6 (9)	Pt(3)—O(33)—C(33)	120·0 (9)	Pt(4)—O(43)—C(43)	120·2 (9)
Pt(2)—O(14)—C(13)	118·8 (8)	Pt(3)—O(24)—C(23)	119·3 (8)	Pt(4)—O(34)—C(33)	119·4 (8)	Pt(1)—O(44)—C(43)	121·7 (9)
O(13)—C(13)—O(14)	124·9 (1·2)	O(23)—C(23)—O(24)	126·5 (1·2)	O(33)—C(33)—O(34)	126·6 (1·2)	O(43)—C(43)—O(44)	124·0 (1·4)
O(13)—C(13)—C(14)	120·2 (1·2)	O(23)—C(23)—C(24)	115·7 (1·3)	O(33)—C(33)—C(34)	117·8 (1·3)	O(43)—C(43)—C(44)	117·2 (1·4)
O(14)—C(13)—C(14)	115·0 (1·2)	O(24)—C(23)—C(24)	117·8 (1·2)	O(34)—C(33)—C(34)	115·6 (1·2)	O(44)—C(43)—C(44)	118·8 (1·4)

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* In this discussion, by equatorial we mean in the plane of the Pt square, while the approximate $\bar{4}$ axis of the molecule constitutes the axial direction.

equatorial positions. Although statistically not significant, the difference between the mean Pt—Pt distances in the two forms is consistent with a marginally smaller orbital overlap in the more distorted molecule.

Fig. 2 shows the packing in the cell (Johnson, 1965). While the tetragonal and the monoclinic forms contain essentially the same molecules there is an appreciable difference in the economy of packing. Thus in the tetragonal form a single tetrameric molecule occupies 663·7 Å^3, and in the monoclinic case 639·4 Å^3, a difference of *ca* 4%.

It seems to us that the tighter packing in the monoclinic form is responsible for the relatively minor differences in the distortion of the molecules, but that packing forces do not adequately explain the existence of the twisting distortion which is found in both forms to a comparable extent. Thus the twisting of the molecule probably has its origins in the need to relieve some intramolecular pressures, and we will consider what these might be. The twisting observed for the equatorial acetate groups seems an inefficient way of relieving any repulsion between O atom lone pairs on adjacent acetates, since in the actual structure the O atoms concerned are either both above or both below the Pt plane (Table 5). Thus the major cause of distortion may well lie with the axial acetate groups. Given the bite of these groups (observed mean 2·24 Å), the Pt—Pt distance of 2·497 Å, and assuming O—Pt—O angles of 180° (in reality the mean is 176·2°), the calculated separation on the opposite side of the Pt plane between the two parallel acetate groups will be *ca* 2·75–2·8 Å at the level of the O atoms. Therefore in the idealized structure these groups are uncomfortably close together, and are aligned in such a way as to give maximum repulsion between the π-electron clouds on their O—C—O regions. The observed shifting of these groups not only increases the distance between the atoms, but also reduces the alignment of the π-electron clouds. This can be seen in Fig. 3. A consequence of the relative movement of the axial acetate groups would be a twisting of the whole equatorial plane, in line with what is observed.

Table 5. *Planarity of groups of atoms and distances* (Å) *from the least-squares planes*

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

Plane 1 $11{\cdot}21x - 0{\cdot}48y + 6{\cdot}89z = 5{\cdot}30$
Pt(1) 0·117, Pt(2) −0·116, Pt(3) 0·116, Pt(4) −0·116
Not defining plane: O(11) 0·528, O(12) −0·185, C(11) 0·140, C(12) 0·187, O(21) −0·452, O(22) 0·102, C(21) −0·167, C(22) −0·206, O(31) 0·415, O(32) −0·108, C(31) 0·184, C(32) 0·263, O(41) −0·469, O(42) 0·078, C(41) −0·274, C(42) −0·464.

Plane 2 $11{\cdot}82x - 1{\cdot}81y + 1{\cdot}01z = 3{\cdot}11$
O(11) 0·008, O(12) 0·008, C(11) −0·022, C(12) 0·006
Not defining plane: Pt(1) −0·431, Pt(2) 0·136

Plane 3 $10{\cdot}34x - 2{\cdot}83y + 8{\cdot}43z = 5{\cdot}09$
O(21) −0·002, O(22) −0·002, C(21) 0·005, C(22) −0·001
Not defining plane: Pt(2) 0·348, Pt(3) −0·032

Plane 4 $9{\cdot}88x - 0{\cdot}02y + 11{\cdot}13z = 6{\cdot}64$
O(31) 0·000, O(32) 0·000, C(31) 0·000, C(32) 0·000
Not defining plane: Pt(3) −0·205, Pt(4) 0·146

Plane 5 $10{\cdot}85x + 2{\cdot}41y + 7{\cdot}03z = 6{\cdot}04$
O(41) 0·001, O(42) 0·001, C(41) −0·002, C(42) 0·000
Not defining plane: Pt(4) 0·107, Pt(1) −0·264

Plane 6 $-1{\cdot}08x + 10{\cdot}19y - 5{\cdot}11z = -1{\cdot}30$
O(13) 0·001, O(14) 0·001, C(13) −0·003, C(14) 0·001
Not defining plane: Pt(1) −0·002, Pt(2) −0·455

Plane 7 $-2{\cdot}02x + 2{\cdot}49y + 19{\cdot}29z = 6{\cdot}28$
O(23) −0·003, O(24) −0·003, C(23) 0·008, C(24) −0·002
Not defining plane: Pt(2) 0·046, Pt(3) −0·345

Plane 8 $1{\cdot}99x + 10{\cdot}24y - 3{\cdot}91z = 2{\cdot}17$
O(33) −0·002, O(34) −0·002, C(33) 0·005, C(34) −0·001
Not defining plane: Pt(3) −0·291, Pt(4) 0·142

Plane 9 $-5{\cdot}90x + 2{\cdot}64y + 16{\cdot}97z = 6{\cdot}59$
O(43) 0·000, O(44) 0·000, C(43) 0·001, C(44) 0·000
Not defining plane: Pt(4) −0·061, Pt(1) 0·329

Table 5 shows that the planarity of the acetate groups is good with the exception of the acetate centred on C(11). This is an equatorial acetate and the result may well indicate a real flexing of this group, since for the two binding O atoms it has the greatest difference in height relative to the Pt plane, *i.e.* this group shows the greatest twisting. This flexing, however, is probably the result of external packing forces, since one can see no reason why internally generated distortion should affect only one of the four equatorial groups.

By far the most common coordination for Pt^{II} is square planar (Hartley, 1973). The compound structurally most similar to Pt acetate, $Pt_4(acetate)_6(NO)_2$

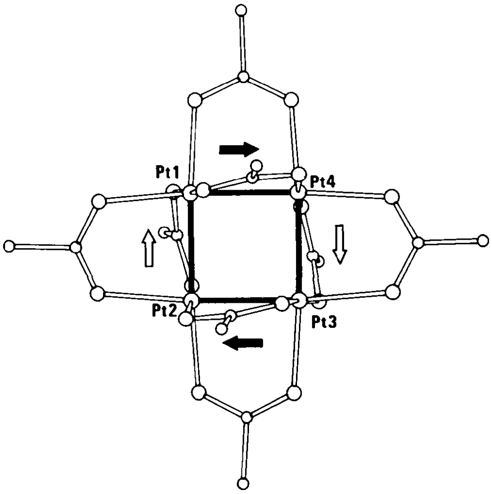

Fig. 3. A view of the molecule normal to the plane through the Pt atoms. Black arrows indicate the shift of acetate groups above the Pt plane, and the white arrows of the groups below this plane.

(de Meester & Skapski, 1973), has a geometry of this type, although somewhat distorted. In a few cases a pseudo-octahedral geometry is observed. It is best described as being a square-planar arrangement with an electrostatic interaction providing the remaining two near neighbours. There are two clear examples of this model, $Pt[C_6H_4(AsMe_2)_2]_2Cl_2$ (Stephenson, 1964) and $Pt[C_6H_4(AsMe_2)_2]_2I_2$ (Stephenson, 1962). In the chloride the Pt···Cl distances are 4·16 Å, while for the iodide Pt···I are shorter at 3·50 Å. The latter distance is intermediate between sums of covalent radii and van der Waals radii, and is probably due to the polarization of the I^- ions.

Some of the few examples of octahedral coordination for Pt^{II} were assumed to be $K_2[Pt(NO)Cl_5]$ and some other nitrosyl derivatives (Griffith, Lewis & Wilkinson, 1961). However, Chernyaev & Nazarova (1963) argue that the nitrosyl group is not coordinated as NO^+. Therefore the above complexes would be six-coordinated Pt^{IV} instead of Pt^{II} derivatives. The X-ray structures of these compounds are not known, and furthermore the latest IUPAC rules count NO as a neutral ligand.

As regards the title complex, a case might be made out to consider it as a Pt^{IV} species. In referring to the complex as Pt^{II} we are taking into account its 1:2 stoichiometry, and following common usage (*e.g.* Cotton & Wilkinson, 1972).

It would be interesting to predict the kind of bonding which is present in this unusual Pt square in terms of the orbitals involved. However, whether one starts from an SF_4-type geometry (Pt—O bonds only), or an octahedral one with the Pt—Pt bonds included, it would be difficult without a detailed calculation to predict with any certainty the relative energy levels of the orbitals, especially since even the Pt—O bonds are not equivalent, the axial being markedly shorter than the equatorial ones. Given that the molecular structure is now known accurately in two crystal forms, the only definitive answer to this question can come from other sources, from a molecular-orbital calculation.

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