X-Ray Crystal Structure of Tetrameric Platinum(II) Acetate: a Square-cluster Complex with Short Pt–Pt Bonds and Octahedral Co-ordination Geometry

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Summary An *X*-ray crystallographic study shows that tetrameric platinum(II) acetate has a structure, of approximate symmetry D_{2d}, in which each side (length 2·495 Å) of a metal–metal bonded square of platinum atoms is spanned by two acetate groups.

PALLADIUM(II) acetate[1] is a well characterised compound, and it has been shown to have a cyclic trimeric structure.[2] As regards the equivalent platinum complex the situation is less clear. In its original preparation it was stated to be also trimeric, though not isomorphous with $[Pd(acetate)_2]_3$. Determination of the structure of $Pt_4(acetate)_6(NO)_2$[3,4] revealed, however, that the method of preparing platinum(II) acetate by the reduction of Pt^{IV} in nitric acid–acetic acid[1,5] may lead to nitrogen-containing products. Use of silver acetate[6] provides a simpler and more reliable route, and a form of platinum(II) acetate has now been obtained[7] in a crystalline state. An *X*-ray determination has shown it to have a novel tetrameric structure.

Starting from a specimen of almost black platinum(II) acetate made† by the I.C.I. method, brown plate-like crystals were obtained from glacial acetic acid. The crystals are tetragonal, with unit-cell dimensions $a = 10{\cdot}254$, $c = 50{\cdot}494$ Å, $U = 5309{\cdot}2$ Å^3, space group $P4_32_12$ and $Z = 8$ tetrameric molecules. Using Cu-K_α radiation the intensity data were collected (to $\theta = 70°$) on a Siemens four-circle diffractometer. A total of 2904 independent reflexions were measured, of which 221 were judged to be 'unobserved'. The structure was solved by Patterson and Fourier methods, and least-squares refinement has now reached $R = 0{\cdot}033$.

A strongly metal–metal bonded square cluster of four platinum atoms forms the core of the structure, with Pt–Pt–Pt angles ranging from 89·08 to 90·04° (σ 0·03°). The four independent Pt–Pt distances fall within a very narrow range: 2·492–2·498 Å (σ 0·001 Å), with a mean value of 2·495 Å. They are markedly shorter than the Pt–Pt bonds of 2·58—2·65 Å found in binuclear[8] or triangular platinum clusters.[9] Eight bridging acetate groups complete the structure, and are arranged around the square as shown in the Figure, with four groups in the plane of the cluster and four alternately above and below it. The molecule has approximate $\bar{4}2m$ (D_{2d}) point symmetry. The main departure from this idealised model is caused by a slight twisting of the molecule easily visible in the Figure, so that the platinum cluster is not absolutely flat (Pt atoms ± 0·108 Å from the best plane). This could be a crystal-packing effect.

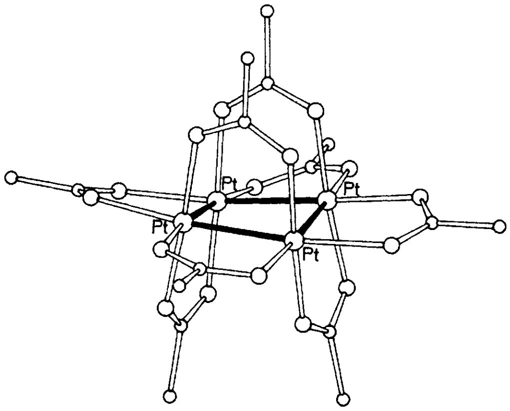

FIGURE. Molecular structure of $[Pt(acetate)_2]_4$.

An unusual co-ordination is found for the platinum atoms. While in trimeric palladium(II) acetate and in $Pt_4(acetate)_6(NO)_2$ the geometry, although distorted, is undoubtedly square planar, in the title complex it is of the SF_4-type if one considers only the oxygen ligands. However, it is clearly better to view it as having octahedral geometry, including the *cis* metal–metal bonds in the co-ordination geometry.

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Two groups of platinum–acetate linkages are distinguishable. The eight Pt–O bonds approximately normal to the Pt plane have lengths which are unexceptional: a range of 1·971—2·022 Å (σ 0·011 Å) with a mean of 2·002 Å. On the other hand the eight Pt–O bonds lying in the plane of the cluster are rather long: a range of 2·133—2·187 Å (σ 0·012 Å), with a mean of 2·162 Å. This lengthening could be due to any *trans* influence of a strong Pt–Pt bond, or steric hindrance in this plane because of the crowding of oxygen lone pairs, or a combination of both factors.

Although the co-ordination geometry in the title complex is quite different from that found in $Pt_4(acetate)_6(NO)_2$, and the latter molecule shows only a weak Pt–Pt interaction, there is nevertheless a strong resemblance between the two structures (compare with Fig. 1a in Ref. 4).

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[1] T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, 1965, 3632.

[2] A. C. Skapski and M. L. Smart, *Chem. Comm.*, 1970, 658.

[3] P. de Meester, A. C. Skapski, and J. P. Heffer, *J.C.S. Chem. Comm.*, 1972, 1039.

[4] P. de Meester and A. C. Skapski, *J.C.S. Dalton*, 1973, 1194.

[5] J. M. Davidson and C. Triggs, *Chem. and Ind.*, 1966, 306.

[6] B.P. 1,214,552, 1970 (to I.C.I. Ltd.).

[7] F. L. Phillips and A. C. Skapski, unpublished work.

[8] A. C. Skapski and P. G. H. Troughton, *J. Chem. Soc.* (*A*), 1969, 2772; J. G. Albano, G. Ciani, M. I. Bruce, G. Shaw, and F. G. A. Stone, *J. Organometallic Chem.*, 1972, **42**, C99.

[9] L. T. Guggenberger, *Chem. Comm.*, 1968, 512; J. C. Calabrese, L. F. Dahl, P. Chini, G. Longoni, and S. Martinengo, *J. Amer. Chem. Soc.*, 1974, **96**, 2614.