X-Ray Crystallographic Determination of the Structure of Tris-[μ-acetato-μ-acetoximato-palladium(ii)]–0.5-Benzene: a Trimeric Compound of Palladium containing a Novel Bridging Ligand

By ANNE MAWBY and G. E. PRINGLE*

(*Department of Inorganic and Structural Chemistry, University of Leeds, Leeds LS2 9JT*)

Summary The trimeric molecule, [Pd(OAc)(ONCMe₂)]₃, contains a non-crystallographic threefold axis: each pair of palladium atoms is bridged by an acetate group and by an acetoximate group, the latter through both nitrogen and oxygen.

By refluxing equimolar quantities of palladium(ii) acetate and acetoxime in acetic acid and recrystallising the reddish product from benzene–light petroleum a compound of

stretching vibrations in the i.r. spectrum showed the absence of free acetoxime and the compound was tentatively formulated as [Pd(OAc)(ONCMe₂)]₃, ½C₆H₆.†

The trimeric formulation of the compound suggested the presence of bridging ligands and the crystal structure was undertaken in order to determine the mode of bonding between acetoximate and palladium.

Crystals of [Pd(OAc)(ONCMe₂)]₃,½C₆H₆ are triclinic, space group $P\bar{1}$ with $a = 15\cdot27$, $b = 9\cdot68$, $c = 9\cdot50$ Å,

Molecular parameters

Pd(1)′–N(1)′	1·97(2)	Pd(1)′–O(3)′	2·00(2)
Pd(1)′–O(4)′	2·04(2)	Pd(1)′–O(9)′	2·05(2)
	Pd····Pd	3·009(3)	
C(1)′–C(3)′	1·43(4)	C(1)′–N(1)′	1·31(4)
C(1)′–C(2)′	1·46(4)	N(1)′–O(1)′	1·37(2)
C(3)′–C(1)′–C(2)′	125(3)	C(3)′–C(1)′–N(1)′	114(3)
C(2)′–C(1)′–N(1)′	115(3)	C(1)′–N(1)′–O(1)′	116(2)
	C(1)′–N(1)′–Pd(2)′	128(2)	
N(1)′–O(1)′–Pd(2)′	112·3(1·3)	Pd(1)′–N(1)′–O(1)′	116·1(1·4)
C(10)′–C(11)′	1·51(4)	C(11)′–O(5)′ ⎫ C(11)′–O(4)′ ⎬	1·22(2) (Mean of 6 values)
C(10)′–C(11)′–O(4)′ ⎫ C(10)′–C(11)′–O(5)′ ⎬	115·2(1·5) (Mean of 6 values)	C(11)′–O(5)′–Pd(2)′ ⎫ C(11)′–O(4)′–Pd(1)′ ⎬	126·5(1·0) (Mean of 6 values)
	O(4)′–C(11)′–O(5)′	129·0 (2·2)	

Average dihedral angles

3Pd–SqPd	80	3Pd–Ac	45
3Pd–Ox	50	Ac–Ox	86

empirical formula C₆H₁₀NO₃Pd separates. [M.p. 220° (correct analysis)]. Osmometry in benzene showed it to be trimeric and integration of the n.m.r. spectrum shows the presence of one molecule of benzene per six acetate groups and per six acetoxime groups. The absence of ν(OH)
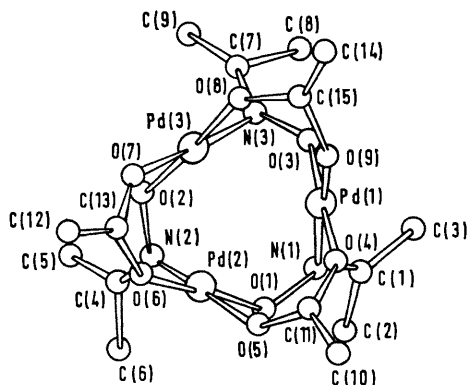
FIGURE

$\alpha = 105\cdot4$, $\beta = 99\cdot8$, $\gamma = 101\cdot9°$, $Z = 2$. Data were collected by the equi-inclination Weissenberg technique with Cu-K_α radiation. 1838 independent reflections, from $hk0$ to $hk6$, were recorded from a square plate-shaped crystal (thickness 0·03 mm) mounted about one of the sides. The structure was solved, from the visually estimated intensities, by Patterson and Fourier techniques. The conventional R factor from the block-diagonal least-squares refinement with anisotropic thermal parameters for the palladium atoms is 13·1%.

The trimeric molecule [Pd(OAc)(ONCMe₂)]₃ contains a non-crystallographic threefold axis. The three palladium-(ii) atoms have square planar co-ordination (none of the angles at the metal atoms is significantly different from 90°), and each pair of palladium atoms is bridged by a planar acetate ligand and also through the nitrogen and oxygen atoms of a planar acetoximate group. The square planes of co-ordination make an average angle of 10° with the normal to the plane containing the three palladium atoms: this tilting reduces the span which the acetoximate ligands would otherwise be required to bridge and has the effect of opening out the acetate O–C–O angle to 129°

which is larger than usual.[1] The geometry of the acetoximate ligand is very similar to that found in crystalline acetoxime, the C–N and N–O bonds in the bridge being approximately double and single respectively. The co-ordination of the acetoximate group to a metal through both nitrogen and oxygen is unusual: the only example is in $[MeZn(ONCMe_2)]_4$ where however, each oxygen is bonded to two zinc atoms and each nitrogen to one zinc atom.[2]

Average values of some important bond lengths (Å) and angles (degrees) with the e.s.d.'s of these mean values in parentheses are given in the Table together with some relevant dihedral angles, where, for example, C(1)′– C(2′)

represents the mean of the three bond lengths C(1)– C(2), C(4)–C(5), and C(7)–C(8) and the abbreviations (a) 3Pd, (b) SqPd, (c) Ac, and (d) Ox refer to the planes containing (a) the three palladium atoms, (b) a palladium atom and the four atoms bonded to it, (c) an acetate group and the two palladium atoms bridged by it, and (d) an acetoximate group and the two palladium atoms bridged by it, respectively. The benzene of crystallization is not involved in co-ordination: the dihedral angle between the plane of the benzene molecule and the plane containing the three palladium atoms is 38°.

[1] M. R. Churchill and R. Mason, *Nature*, 1964, **204**, 777; M. J. Bennett, K. G. Caulton, and F. A. Cotton, *Inorg. Chem.*, 1969, **8**, 1; D. Lawton and R. Mason, *J. Amer. Chem. Soc.*, 1965, **87**, 921; M. J. Bennett, W. K. Bratton, F. A. Cotton, and W. R. Robinson, *Inorg. Chem.*, 1968, **7**, 1570; C. Pannatoni, R. Graziani, G. Bandoli, B. Tarli, and G. Bombieri, *Inorg. Chem.*, 1969, **8**, 320; J. N. van Niekerk and F. R. L. Shoening, *Acta. Cryst.*, 1953, **6**, 227.
[2] G. E. Coates and K. Wade, "Organometallic Compounds," vol. I, "The Main Group Elements," Methuen, London, 1967, p. 139.