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Synthesis and structure of the first platinum(II) pivalato complexes

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The first crystalline platinum(II) complexes with trimethylacetato ligands, $K_2[Pt(OOCBu^t)_4]\cdot 3THF$ and $Pt_4(OOCBu^t)_4(OOCMe)_4\cdot 2C_6H_6$, were synthesised and structurally characterised by X-ray diffraction analysis.

Branched alkylcarboxylate ligands such as trimethylacetate and 2-methylbutyrate are known to endow transition metal complexes with high solubility in low-polarity organic media.[1–4] This property is important when using noble metal complexes as starting materials in the syntheses of metal clusters and colloids for homogeneous catalysis in aprotic organic solvents. Phosphine and carbonyl ligands are in common use for these purposes.[5,6] Meanwhile, readily removable carboxylato complexes are preferable in many cases.

Among VIII Group metals, the chemistry of platinum(II) homoligand carboxylates is restricted to the poorly soluble acetato[7,8] and haloacetato complexes.[9,10] Although ligand exchange in Pt^{II} acido complexes readily occurs, previous attempts produced alkylcarboxylato compounds as an oil or non-crystalline solid. To our knowledge, none of structurally characterised Pt^{II} pivalate has been documented so far (see the Cambridge Structure Database, Release 2001). In this work, we synthesised and structurally characterised crystalline platinum(II) pivalato complexes $K_2[Pt(OOCBu^t)_4]\cdot 3THF$ **1** and $Pt_4(OOCBu^t)_4(OOCMe)_4\cdot 2C_6H_6$ **2**.

We used two exchange reactions for the synthesis of Pt^{II} pivalates. Mononuclear crystalline complex **1** was prepared by the metathesis of $PtCl_2$ with potassium pivalate in a THF solution.[†] However, the main body of the reaction products is a non-crystalline solid. According to IR and ^1H NMR spectra,[‡] this reaction product contains both bridging and terminal pivalato ligands.

Another synthetic approach was based on the reaction of platinum acetate blue $[Pt(OOCMe)_{\sim 2.5}]_n$ (see ref. 8) with pivalic acid in benzene. Both ligand substitution and redox transformations of the platinum blue occurred in this system to produce several highly soluble Pt^{II} pivalato complexes, from which tetranuclear complex **2** was isolated in a crystalline form.[§] Complex **2** is well soluble in THF, benzene and, to a lesser extent, hexane.

Although crystalline complexes **1** and **2** were prepared in low yields, the non-crystalline solids obtained as the main reaction product in both syntheses was found to be very close in composition to complex **2** (based on the IR spectra and elemental analysis data), the main difference being various number of solvate molecules, C_6H_6 and THF, included. The latter is believed to be the main origin of the non-crystallinity of these reaction products. Meanwhile, preliminary experiments showed that both crystalline complex **2** and the non-crystalline solids behaved identically in reactions with reductants (boron hydrides, alkyllithium, alkylaluminium, *etc*.), producing virtually the same nanoclusters (based on EXAFS, IR, HREM, SAXS and elemental analysis data) when the same reducing agents were used.[11]

According to X-ray diffraction data,[¶] the crystal of complex **1** is built from the $[Pt(OOCBu^t)_4]^{2-}$ anion, K^+ cations and solvate THF molecules, which are held by the ionic and van der Waals interactions and C–H···O bonds. The central Pt atom in the $[Pt(OOCBu^t)_4]^{2-}$ anion is coordinated with four O atoms of monodentate *tert*-BuCOO ligands (Figure 1).

The monodentate coordination of carboxylato ligands is rare in platinum(II) chemistry. Earlier, such a coordination mode was found in the acetato complexes $(PPh_3)_2Pt_2(\mu\text{-}OOCMe)_2(OOCMe)_2$ and $\eta^3\text{-}C_3H_5Pd(\mu\text{-}OOCMe)_2Pt(OOCMe)$.[12,13] In complex **1**, the square plane of the Pt polyhedron containing the oxygen atoms O(1), O(3), O(5) and O(7) is somewhat tetrahedrally distorted. The displacement of the Pt atom from this plane (~0.1 Å) is 0.038 Å. The Pt–O bond length (average 2.011 Å) is comparable with analogous bond lengths in platinum(II) carboxylato complexes.[7–10] The dihedral angles between the planes of pivalate ligands and square-planar four O atoms are 77.3, 65.8, 65.7 and

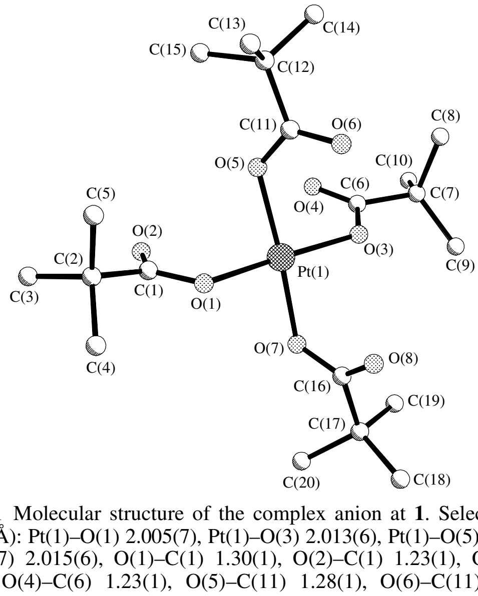

Figure 1 Molecular structure of the complex anion at **1**. Selected bond lengths (Å): Pt(1)–O(1) 2.005(7), Pt(1)–O(3) 2.013(6), Pt(1)–O(5) 2.022(6), Pt(1)–O(7) 2.015(6), O(1)–C(1) 1.30(1), O(2)–C(1) 1.23(1), O(3)–C(6) 1.29(1), O(4)–C(6) 1.23(1), O(5)–C(11) 1.28(1), O(6)–C(11) 1.23(1), O(7)–C(16) 1.29(1), O(8)–C(16) 1.24(1); selected bond angles (°): O(1)–Pt(1)–O(3) 174.4(3), O(1)–Pt(1)–O(5) 87.3(3), O(1)–Pt(1)–O(7) 91.8(2), O(3)–Pt(1)–O(5) 93.5(2), O(3)–Pt(1)–O(7) 88.0(2), O(5)–Pt(1)–O(7) 173.9(2), Pt(1)–O(1)–C(1) 120.9(6), Pt(1)–O(3)–C(6) 122.1(6), Pt(1)–O(5)–C(11) 122.5(6), Pt(1)–O(7)–C(16) 119.5(5), O(1)–C(1)–O(2) 123.5(8), O(3)–C(6)–O(4) 124.2(9), O(5)–C(11)–O(6) 125(1), O(7)–C(16)–O(8) 126.0(8).

[†] A typical experimental procedure was as follows: a slurry of $PtCl_2$ (400 mg, 1.50 mmol) and potassium pivalate (420 mg, 3.00 mmol) in 5 cm^3 of THF was stirred for 2 h and then stored without stirring for 3 days at room temperature. The crystals formed were separated from the mother liquor by decanting, washed with benzene and dried in air to afford 27 mg (20%) of **1** as light-brown needles, one of which (0.01×0.02×0.5 mm) was used for X-ray diffraction analysis.

[‡] ^1H NMR ($CDCl_3$) δ: 1.05 (br. s, ~9H, Me), 1.8 (br. m, ~9H, Me). IR (KBr, ν/cm^{-1}): 443 (w), 651 (w), 786 (w), 807 (w), 890 (w), 1023 (w), 1213 (m), 1340 (s), 1397 (s), 1459 (w), 1482 (m), 1568 (m), 1612 (s), 2871 (w), 2928 (m), 2958 (s).

[§] In a typical experiment, platinum acetate blue (0.5 g, 1.46 mmol) and pivalic acid (0.7 g, 68.6 mmol) were refluxed in benzene (20 ml) for 1 h. The solvent was evaporated on a rotary evaporator. The excess of pivalic acid was washed off with hexane (4×10 ml) and then evaporated in a vacuum (Fisher's pistol, 78 °C, 1 Torr, 5 h). The black residue was dissolved in benzene (10 ml), precipitated with hexane and dried in a vacuum to afford finely crystalline complex **2** in 10% yield. IR (KBr), $\nu(COO)/cm^{-1}$: 1407 (s), 1567 (s); $\nu(COO)_{as} - \nu(COO)_s = 160\ cm^{-1}$, which is typical of the bridging RCOO group. Found (%): C, 25.71; H, 3.73; Pt, 54.44. Calc. for $C_{28}H_{48}O_{16}Pt_4$ (%): C, 23.66; H, 3.40; Pt, 54.91 (remainder was an amorphous solid with nearly the same elemental composition). Bigger crystals for an X-ray diffraction study (0.2×0.3×0.6 mm) were prepared by the slow diffusion of hexane to a benzene solution of **2** in a 5 mm glass tube.

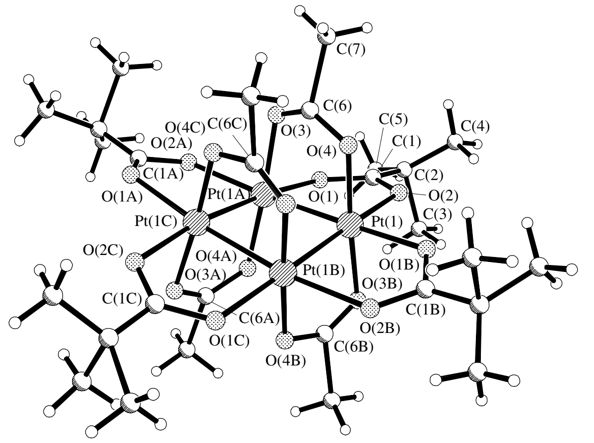

Figure 2 Molecular structure of complex **2** (positions of the atoms: #1 *–y*, *x*, *–z*; #2 *y*, *–x*, *–z*; #3 *–x* + 1, *–y* + 1, *z*). Selected bond lengths (Å): Pt(1)–O(3)#1 1.992(13), Pt(1)–O(4) 1.998(14), Pt(1)–O(2) 2.159(13), Pt(1)–O(1)#1 2.160(12), Pt(1)–Pt(1)#2 2.4869(16), Pt(1)–Pt(1)#1 2.4869(16), O(1)–C(1) 1.292(18), O(1)–Pt(1)#2 2.160(12), O(2)–C(1) 1.235(18), O(3)–C(6) 1.240(16), O(3)–Pt(1)#2 1.992(13), O(4)–C(6) 1.265(17), C(1)–C(2) 1.52(3), C(2)–C(5) 1.55(3), C(2)–C(3) 1.56(3), C(2)–C(4) 1.57(4), C(6)-C(7) 1.512(16); selected bond angles (°): O(3)#1–Pt(1)–O(4) 175.8(6), O(3)#1–Pt(1)–O(2) 88.2(5), O(4)–Pt(1)–O(2) 89.1(6), O(3)#1–Pt(1)–O(1)#1 85.3(5), O(4)–Pt(1)–O(1)#1 91.8(5), O(2)–Pt(1)–O(1)#1 96.5(4), O(3)#1–Pt(1)–Pt(1)#2 97.4(4), O(4)–Pt(1)–Pt(1)#2 85.7(4), O(2)–Pt(1)–Pt(1)#2 86.8(3), O(1)#1–Pt(1)–Pt(1)#2 175.7(3), O(3)#1–Pt(1)–Pt(1)#1 86.1(4), O(4)–Pt(1)–Pt(1)#1 96.8(4), O(2)–Pt(1)–Pt(1)#1 172.8(4), O(1)#1–Pt(1)–Pt(1)#1 87.4(3), Pt(1)#2–Pt(1)–Pt(1)#1 89.526(5), C(1)–O(1)–Pt(1)#2 116.8(11), C(1)–O(2)–Pt(1) 118.5(11), C(6)–O(3)–Pt(1)#2 120.3(11), C(6)–O(4)–Pt(1) 119.0(11), O(2)–C(1)–O(1) 129.5(18), O(2)–C(1)–C(2) 114.8(15), O(1)–C(1)–C(2) 115.8(16), C(1)–C(2)–C(5) 110(2), C(1)–C(2)–C(3) 106(2), C(5)–C(2)–C(3) 111(3), C(1)–C(2)–C(4) 107(2), C(5)–C(2)–C(4) 112(3), C(3)–C(2)–C(4) 111(3), O(3)–C(6)–O(4) 126.1(15), O(3)–C(6)–C(7) 116.6(14), O(4)–C(6)–C(7) 116.9(13).

80.5°, while the dihedral angles between the *trans*-pivalate ligands are 17.2 and 18.6°. The *trans*-carboxylato groups are mutually oriented in such a way that the non-coordinated O atoms are located above and below the square plane. The atoms O(2) and O(4) are shifted by –2.03 and –1.91 Å from the mean square plane O(1)–O(3)–O(5)–O(7), and these values are 1.90 and 2.09 Å for the atoms O(6) and O(8), respectively. These atoms form short contacts with the Pt atom: Pt···O(2),O(4),O(6),O(8) are 3.097, 3.127, 3.147 and 3.113(7) Å, respectively. Two crystallographically independent K^+ cations are present in the structure. The nearest environment of the potassium atoms includes six oxygen atoms, and K^+···O distances are 2.658(7)–2.820(9) Å.

The X-ray diffraction study[††] of a crystal of complex **2** showed that it contains the tetranuclear complex $Pt_4(OOCBu^t)_4(OOCMe)_4$ and C_6H_6 solvate molecules associated in the crystal by the C–H···O bonds and van der Waals interactions. The molecule $Pt_4(OOCBu^t)_4(OOCMe)_4$ (Figure 2) has a –4 crystallographic symmetry, and the inversion four-fold axis passes through the centre of the tetragon formed by four closely spaced platinum atoms. The short Pt–Pt distance [2.487(2) Å] is typical of tetranuclear platinum carboxylates.[7–10] The platinum tetragon is a tetrahedrally distorted rhomb (the Pt–Pt–Pt angles are 89.53°) bearing four pivalato and four acetato bridging ligands on its sides. The planes of the pivalato ligands (without regard for *tert*-butyl groups) are almost coplanar with the mean plane of the platinum tetragon, while the planes of the acetato ligands are nearly perpendicular to the Pt_4 plane [the dihedral angle between the Pt_4 plane and the Pt(1)–Pt(1a)–O(3)–O(4)–C(6) plane is 86.6°]. According to the –4 symmetry of the molecule, the acetate groups located at the opposite sides of the platinum tetragon are oriented in pairs above and below the Pt_4 plane. The opposite Pt_2O_2CMe planes are approximately parallel to each other (the dihedral angle between these planes is 164.7°).

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[¶] *Crystal data for* **1**: $C_{32}H_{60}K_2O_{11}Pt$, M = 894.09, $F(000)$ = 1824, monoclinic, a = 13.029(3), b = 15.948(4), c = 20.253(5) Å, V = 4160(2) Å^3 at 180 K, space group $P2_1/n$, Z = 4, d_{calc} = 1.428 g cm^{-3}, μ = 3.621 mm^{-1}. The intensities of 12386 reflections [6889 with $I \geq 2\sigma$, of which 5670 (R_{int} = 0.0395) are independent] were measured using a Bruker AXS SMART 1000 CCD three-circle diffractometer at 180 K (graphite-monochromated MoKα radiation, λ = 0.7107 Å, ω-scan, $2 \leq 2\theta \leq 60°$). The following software was used: SMART (control) and SAINT (integration) (version 5.0, Bruker AXS Inc., Madison, WI., 1997) for collecting frames of data, indexing, integration of intensity of reflections and scaling and SADABS (G. M. Sheldrick, University of Göttingen, 1997, based on the method of R. H. Blessing, *Acta Crystallogr., A*, 1995, **51**, 33) for empirical absorption correction. The structure was solved by the direct method using the SHELXS97 (G. M. Sheldrick, University of Göttingen, 1997) program and refined against F^2 in an anisotropic approximation for non-hydrogen atoms using SHELXL97 package (G. M. Sheldrick, University of Göttingen, 1997). The H atoms were located on the difference electron density map and refined in a 'ride' approximation. The final R_1 value was 0.0549 [$wR_2(F^2)$ = 0.1307] for 5670 reflections, GOOF = 1.019.

[††] *Crystal data for* **2**: $C_{40}H_{60}O_{16}Pt$, tetragonal at 120 K, a = 13.766(8) and c = 24.157(16) Å, V = 4578(5) Å^3, space group $I\bar{4}2d$, Z = 4, d_{calc} = = 2.306 g cm–3, μ=12.253 cm^{-1}. The intensities of 10942 reflections [3180 with $I \geq 2\sigma$, of which 2484 (R_{int} = 0.1633) are independent] were measured using Bruker AXS SMART 1000 CCD three-circle diffractometer at 120 K (graphite-monochromated MoKα radiation, λ = 0.7107 Å, ω-scan, $2 \leq 2\theta \leq 60°$). The software used was the same as for complex **1**. The structure was solved by direct methods using the SHELXS97 program and refined against F^2 in an anisotropic approximation for non-hydrogen atoms using the SHELXL97 package. The final R_1 value was 0.0727 [$wR_2(F^2)$ = 0.193] for 3180 reflections, GOOF = 1.000. Atomic coordinates, bond lengths, bond angles and thermal parameters for **1** and **2** have been deposited at the Cambridge Crystal-lographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2002. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/104.