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X-RAY STRUCTURE OF Pt(dipic)(H_2O) (WHERE H_2dipic = 2,6-PYRIDINEDICARBOXYLIC ACID); THE FIRST STRUCTURALLY CHARACTERIZED MONONUCLEAR COMPLEX WITH A $Pt^{II}(N_1O_3)$ DONOR ATOM SET

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Abstract—Reaction of *trans*-[Pt(Hdipic)$_2$]·2H_2O, where H_2dipic = 2,6-pyridinedicarboxylic acid, with thorium nitrate in water results in the abstraction of one of the dipic ligands and the formation of the compound Pt(dipic)(H_2O). This has been shown by a single-crystal X-ray diffraction study to have the surprisingly rare mononuclear $Pt^{II}(N_1O_3)$ coordination geometry. It appears to be the first structurally characterized example of a mononuclear Pt^{II} complex with that type of donor atom set.

The anti-cancer action of '*cis*-platin' and related complexes has stimulated a major resurgence in the synthesis of new Pt^{II} complexes, and particularly those with combinations of N- and O-donor ligands. Complexes with Pt(N_4), Pt(N_3O_1), Pt(N_2O_2) or Pt(O_4) donor sets are commonplace,[1] but this is not so for the Pt(N_1O_3) system, which seems to be very rare. Indeed, a search of the Cambridge X-ray Crystal Structure database[2] reveals only one structurally characterized example, the tetranuclear, acetate-bridged complex $Pt_4(CH_3CO_2)_6(NO)_2 \cdot 2CH_3CO_2H$.[3] This compares with 248 entries for Pt(N_4), 18 for Pt(N_3O_1), 59 for Pt(N_2O_2) and 12 for Pt(O_4). During work aimed at extending the range of heterometallic complexes formed by the anion of 2,6-pyridinedicarboxylic acid (H_2dipic),[4] we explored[5] the reactions of the known[6] platinum(II) complex *trans*-[Pt(Hdpic)$_2$]·2H_2O (**1**) with a range of metal nitrates. Although some heterometallic Pt/M complexes were formed, crystals of sufficient quality for X-ray characterization were not obtained. However, reaction of **1** with thorium nitrate in water gave yellow crystals of a complex of stoichiometry Pt(dipic)(H_2O) (**2**) a *prima facie* example of a $Pt^{II}(N_1O_3)$ system. Evidence has been advanced for the formation of this compound in solution, by the aquation of the $[Pt(dipic)Cl]^-$ ion,[7] but it does not appear to have been isolated in the solid state. We report here the results of an X-ray structural study on **2**.

EXPERIMENTAL

Synthesis

Thorium(IV) nitrate tetrahydrate (0.06 mmol) in water (10 cm^3) was added to a solution of *trans*-[Pt(Hdipic)$_2$]·2H_2O (0.08 mmol) in hot water (30 cm^3). The mixture was stirred for 10 min, then filtered and cooled slowly over a period of 2 days. Small yellow crystals of X-ray quality were obtained in 40% yield. Found: C, 21.6; H, 1.4; N, 3.6. Calc. for $C_7H_5NO_5Pt$: C, 22.2; H, 1.3; N, 3.7%.

Crystallography

Crystal data for (**2**). $C_7H_5NO_5Pt$, $M = 378.2$, monoclinic, $a = 7.230(2)$, $b = 7.939(2)$, $c =$

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14.000(2) Å, $\beta = 93.42(2)°$, $U = 802.2(3)$ Å^3, space group $P2_1/c$, $Z = 4$, $D_c = 3.132$ g cm^{-3}, μ(Mo-K_α) 17.49 mm^{-1}, $\lambda = 0.71073$ Å, $F(000) = 688$, yellow prisms. The crystals were two-component twins with the twinning perpendicular to 010. A crystal was cut perpendicular to this direction, providing an essentially single crystal of dimensions $0.03 \times 0.05 \times 0.10$ mm.

Data collection and processing

Siemens P4 diffractometer, ω-scan method ($3 < 2\theta < 50°$), using graphite-monochromated Mo-K_α radiation. 1717 reflections were measured; 1419 were unique, $R_{\text{int}} = 0.032$, and of these 1230 had $|F_o| > 3\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarization factors and a numerical absorption correction (face-indexed crystal) was applied. Maximum and minimum transmission factors were 0.412 and 0.222, respectively.

Structure analysis and refinement

The structure was solved by the heavy-atom method. All non-hydrogen atoms were refined anisotropically. The positions of the dipic hydrogen atoms were idealized with C—H = 0.96 Å, assigned a common refined isotropic thermal parameter and allowed to ride on their parent atoms. The aqua-ligand hydrogen atoms were located from a ΔF map and refined isotropically, subject to an O—H distance constraint (O—H = 0.90 Å). The ΔF map revealed a peak equivalent to *ca* 6 e Å^{-3}, which was located at $x, y+0.5, z$ relative to the platinum atom. As this is too far from the platinum atom to be due to residual absorption effects we ascribe it to imperfect separation of the twinned crystal. Introduction of a partial weight platinum atom (4.6% refined occupancy) reduced the R value from $R = 0.0442$ to $R = 0.0338$, $R_w = 0.0332$ [$w^{-1} = \sigma^2(F) + 0.0007F^2$]. The mean and maximum shift/error in the final refinement were 0.000 and 0.001, respectively, and the maximum and minimum residual electron densities in the final ΔF map were 1.53 and -1.12 e Å^{-3}, respectively. The salient interatomic distances are included in the caption to Fig. 1.

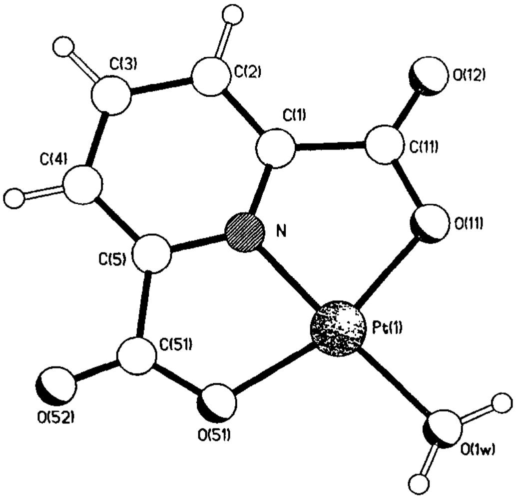

Fig. 1. The structure of **2**. Selected bond lengths (Å) and angles (°): Pt(1)—N 1.898(8); Pt(1)—O(11) 2.011(7); Pt(1)—O(51) 2.045(7); Pt(1)—O(1w) 2.053(7); N—Pt(1)—O(11) 82.2(3); N—Pt(1)—O(51) 81.5(3); O(11)—Pt(1)—O(1w) 95.8(3); O(1w)—Pt(1)—O(51) 100.5(3); N—Pt(1)—O(1w) 177.5(4); O(11)—Pt(1)—O(51) 163.7(3).

RESULTS AND DISCUSSION

The X-ray analysis of **2** shows that the dipic^{2-} anion coordinates to the Pt atom in tridentate fashion, via the ring nitrogen atom and two oxygen atoms, one from each of the two carboxylate groups (Fig. 1). Tridentate binding of this type is well-established for the dipic^{2-} anion and is present in $(n\text{-}Bu_4N)[Pt(dipic)Cl] \cdot 0.5H_2O$[8] (**3**) and in $K[Pt(dipic)I] \cdot 0.5H_2O$[7] (**4**). In **2** the fourth coordination position is occupied by the oxygen atom of the water molecule, producing a $Pt(N_1O_3)$ coordination arrangement.

The molecules in **2** are essentially planar, with a mean deviation from planarity of 0.02 Å. The geometry around Pt is very slightly puckered; the N and O(1w) atoms lie 0.03 and 0.02 Å, respectively, above the mean PtO_3N plane, whilst O(11) and O(51) lie 0.02 and 0.02 Å, respectively, below it. The principal distortion in the PtO_3N coordination geometry is a non-linearity in the dipic O—Pt—O angle [O(11)—Pt(1)—O(51) = 163.7(3)°]; the N—Pt—O(water) bond is essentially linear [177.5(4)°]. The Pt—N bond [1.898(8) Å] is shorter than the Pt—N bonds in the *trans*-$Pt(dipic)_2^{2-}$ anion (2.016 Å),[6,9] but is similar to those observed in **3** and **4** (1.88–1.925 Å). The Pt—O(water) bond length [2.053(7) Å] in **2** is unexceptional.[10–12]

The $Pt(dipic)(H_2O)$ molecules in **2** are arranged in sheets in the crystallographic *ab* plane, with an intersheet separation of *ca* 3.4 Å. Each sheet comprises hydrogen-bonded tapes arranged edge to edge with no cross-linking between them. Adjacent molecules within each tape are linked by hydrogen bonds between the hydrogen atoms of the water ligand to the oxygen atoms of one of the carboxylate groups of neighbouring $Pt(dipic)(H_2O)$

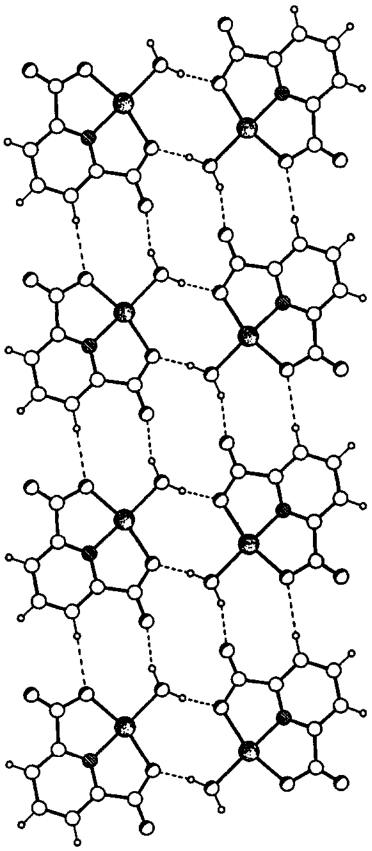

Fig. 2. Part of one of the hydrogen-bonded tapes of molecules in the crystals of **2**.

molecules (Fig. 2) [O(1w)—H ···· O(51) = 2.72 and O(1w)—H ···· O(52) 2.68 Å]. The coordinated oxygen atom O(11) of the other carboxylate group is involved in a strong intermolecular C—H ··· O interaction with the pyridine ring proton on C(4) of an adjacent Pt(dipic)(H_2O) molecule [O(11) ···· C(4) = 3.20, O(11) ···· H(4) = 2.27 Å, O ··· H—C angle = 163°].

Adjacent sheets are oriented such that in one direction the nitrogen atom of one molecule is positioned orthogonally with respect to the platinum atom of another and vice versa. Lying above the platinum atom in the opposite direction is the dipic carbon atom C(3) from a molecule in the next sheet.

The method of formation of the rare $Pt^{II}(N_1O_3)$ coordination arrangement in **2** merits comment. The ability of thorium(IV) nitrate to abstract at least one dipic ligand unit from **1** is readily understood, as the strong tendency for thorium(IV)[13] and the lanthanide[14] ions to bind this ligand in a tridentate fashion is well established. The fact that both dipic ligands were not removed from **1**, with the formation of the $Pt(H_2O)_4^{2+}$ ion, presumably reflects the reluctance of the platinum to form four Pt—O bonds with unidentate O-donors by loss of the remaining $dipic^{2-}$ ligand with its tridentate coordination mode and strong Pt—N bond.

This result suggests that a selective, stepwise chelate-abstraction approach might well provide a useful general method for the preparation of other $Pt(N_1O_3)$ systems, either for obviously analogous tridentate ONO donors or, possibly, by abstraction of a single O,N-chelate from a [Pt(N,O-chelate)$_2$] complex. Additionally, compounds with a $Pt(N_1O_3)$ donor-atom set are potentially attractive precursors for the synthesis of other mixed-ligand Pt^{II} compounds because of the availability of three O-donor sites for replacement by, for example, selected N-donor ligands.

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