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Crystal Structure of Di-iodotetrakis(μ-pyrimidine-2-thionato-N1,S2)diplatinum(III): a Platinum(III) Dimer Obtained from the Reaction of Pyrimidine-2-thione with the PtI_4^{2-} Ion

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Polynuclear complexes of platinum with the metal in the +3 oxidation state, in combinations of Pt(II) and Pt(III) or Pt(IV), or in less well-defined non-integral formal oxidation states are of current interest. Those forming one-dimensional columns often show unusual electrical or other physical, properties [1] and others, ranging from dimers to short chain-length polynuclear systems, have gained recent prominence in the platinum anti-cancer drug field, [2].

The usual route to dimeric Pt(III) complexes is by oxidative addition to a preformed Pt(II) dimer [2c, 3, 4] or, less commonly, further oxidation of a partially oxidised Pt(II)/Pt(III) polynuclear species [2c]. We report the facile synthesis of a platinum(III) dimer by direct reaction of pyrimidine-2-thione (PymSH) with the PtI_4^{2-} ion, and determination of its molecular structure by X-ray diffraction methods.

Addition of an aqueous solution of K_2PtI_4 (generated *in situ* from K_2PtCl_4 by addition of KI) to a hot methanolic solution of PymSH (Pt:L in 1:2 mole ratio) gave a yellow precipitate of $Pt(Pyms)_2$ (*Anal.* Found: C, 23.45; H, 1.50; N, 13.35; Calcd.: C, 23.02; H, 1.45; N, 13.42%). This complex could be isolated from the reaction mixture if air were excluded, and it is stable in air as a dry solid. However, in the presence of air, the initial yellow precipitate rapidly dissolved to form a crimson solution. Within 10 mins, a diamagnetic, red solid of composition $Pt(PymS)_2I$ separated (*Anal.* Found: C, 18.00; H, 1.19; N, 10.20; I, 23.36; Calcd: C, 17.65; H, 1.11; N, 10.29; I, 23.32%). Refrigeration of the mother liquor gave very dark red crystals of the complex suitable for X-ray studies.

Crystal Data

$C_{16}H_{12}I_2N_8Pt_2S_4$, M = 1088.6, monoclinic, a = 15.874(4), b = 9.729(2), c = 15.983(3) Å, β = 98.02(2)°, U = 2444.2 Å^3 (at 18 °C), space group $P2_1/c$. Z = 4, d_c = 2.96 g cm^{-3}. X-Ray diffraction data were collected on a Nicolet R3m/Eclipse S140 diffractometer system using an ω scan technique with graphite-monochromated Cu-Kα radiation. A total of 2505 independent reflections were measured (to θ = 50°), of which 461 were 'unobserved'. The structure was solved by Patterson and Fourier methods, and least-squares refinement has now reached R = 0.043, [5]. The program system SHELXTL was used throughout the calculations [6].

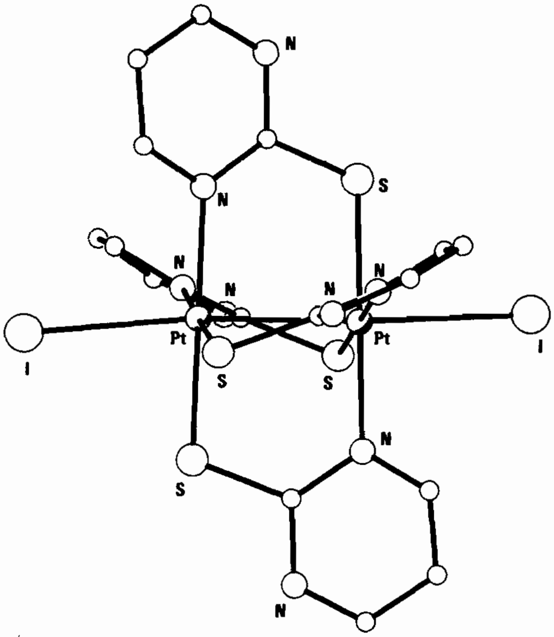

Fig. 1. Molecular structure of $[Pt(PymS)_2I]_2$. Bond lengths: Pt–Pt, 2.554(1); Pt–S, range 2.285(5)–2.301(4), mean 2.294; Pt–N, range 2.087(13)–2.131(12), mean 2.109; Pt–I, 2.768(2) and 2.779(2), mean 2.774 Å. Angles: Pt–Pt–I, 173.8(1) and 172.6(1), mean 173.2°.

The complex is dimeric (Fig. 1) with four bridging pyrimidine-2-thionates. These form a *cis*-planar array of two sulphur and two nitrogen atoms about Pt, with an iodine atom occupying each terminal position of the dimer (Pt–I 2.768 and 2.779 Å). The PtN_2S_2 planes are not fully eclipsed; there is a *ca.* 26° twist about the Pt–Pt axis. Five of the atoms coordinated to each Pt are in a closely octahedral arrangement, but the iodine atoms are displaced by *ca.* 7° from the Pt–Pt axis, due to steric interaction with the pyrimidine rings.

The Pt–Pt distance (2.554 Å) lies between those of quadruply-bridged Pt(III) dimers with O-donors as bridges (2.466–2.494 Å) [7, 8] and that for the $Pt_2(pop)_4Cl_2^{4-}$ ion (2.695 Å) [3] in which the bridges are phosphorus donors.

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