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Crystal Structure of Chloropentakis(pyrimidine-2-thionato)diplatinum(III): a Dinuclear Pt(III) Complex Obtained from a Pt(IV) Precursor

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In our previous studies [1] of the dinuclear Pt(III) complexes formed by pyrimidine-2-thione (= pymSH) and some related ligands we obtained not only compounds of type $[Pt(pymS)_2X]_2$, in which halide ions X occupied the terminal positions of the dinuclear unit, but also two in which one of the halide ions was replaced by the $pymS^-$ anion bonded to the platinum via the sulphur atom. In one case, $[Pt_2(pymS)_5Cl]$, the complex was not obtained in a crystalline form suitable for X-ray studies. In the other, $[Pt_2(pymS)_4BrL]$ (**1**), the X-ray analysis showed that L corresponded to both $pymS^-$, coordinated by S, and Br^-, with estimated relative occupancies of 80% and 20% respectively. As these samples were obtained by the reaction of pymSH with the appropriate PtX_4^{2-} ion, we have since sought an alternative route to these compounds by the reduction of a Pt(IV) precursor, *viz.* $PtCl_6^{2-}$. This approach has now provided a crystalline sample of $[Pt_2(pymS)_5Cl]\cdot 0.5H_2O$ (**2**) for which we report the results of an X-ray structural study.

Experimental

Preparation

A concentrated aqueous solution of $Na_2PtCl_6\cdot 6H_2O$ (0.1 g) was slowly added to a warm methanolic solution of pyrimidine-2-thione (0.1 g in 40 cm^3). The mixture was heated and the red powdery solid which precipitated was filtered off, washed with diethyl ether and air-dried. *Anal.* Found: C, 24.08; H, 1.62; N, 14.40; Cl, 3.97. Calc. for $Pt_2(C_4H_3N_2S)_5Cl$; C, 24.48; H, 1.54; N, 14.28; Cl, 3.61. Calc. for $Pt_2(C_4H_3N_2S)_5Cl\cdot 0.5H_2O$: C, 24.25; H, 1.63; N, 14.15; Cl, 3.58%. The mother liquor from the above reaction gave, on standing for several days, some red crystals of the complex suitable for X-ray diffraction analysis.

X-ray Studies

$(C_4H_3N_2S)_5ClPt_2\cdot 0.5H_2O$, $M = 990.40$, monoclinic, $a = 12.476(4)$, $b = 14.439(2)$, $c = 15.095(3)$ Å, $\beta = 90.55(2)°$, $U = 2719$ Å^3, space group $P2_1/n$, $Z = 4$, $D_c = 2.42$ g cm^{-3}, μ(Cu Kα) = 240 cm^{-1}, $F(000) = 1831$. 2784 independent reflections ($\theta \leqslant 50°$) were measured on a Nicolet R3m diffractometer with Cu Kα radiation (graphite monochromator) using ω-scans. Of these 2501 had $|F_o| > 3\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarisation factors; a numerical absorption correction (face indexed crystal) was applied. The structure was solved by the heavy atom method and the non-hydrogen atoms refined anisotropically. A ΔF map revealed there to be rotational disorder in the axial pyrimidine ring attached to S(52). This disorder could not be resolved into alternate partial site occupancies. The pyrimidine geometry was therefore idealised, and the ring refined as a rigid body. A partial occupancy water molecule was also located, which was refined isotropically. The positions of the hydrogen atoms were idealised, C–H = 0.96 Å, assigned isotropic thermal parameters, $U(H) = 1.2\ U_{eq}(C)$, and allowed to ride on their parent carbon atoms. Refinement was by block-cascade full-matrix least-squares and converged to give $R = 0.082$, $R_w = 0.085$ $[w^{-1} = \sigma^2(F) + 0.00100\ F^2]$. Computations were carried out on an Eclipse S140 computer using the SHELXTL program system [2]. Salient bond lengths and angles are listed in Table I (see also 'Supplementary Material').

Results and Discussion

The X-ray analysis shows that $[Pt_2(pymS)_5Cl]$ (**2**) is essentially isostructural with **1**. Figure 1 shows

TABLE I. Bond Lengths and Angles

Bond lengths (Å)			
Cl(1)–Pt(1)	2.494(7)	Pt(1)–Pt(2)	2.547(2)
Pt(1)–S(12)	2.301(8)	Pt(1)–S(22)	2.294(8)
Pt(1)–N(31)	2.046(23)	Pt(1)–N(41)	2.137(22)
Pt(2)–N(11)	2.104(22)	Pt(2)–N(21)	2.096(22)
Pt(2)–S(32)	2.292(8)	Pt(2)–S(42)	2.307(8)
Pt(2)–S(52)	2.438(8)		
Bond angles (°)			
Cl(1)–Pt(1)–Pt(2)	175.8(2)	Cl(1)–Pt(1)–S(12)	86.6(3)
Pt(2)–Pt(1)–S(12)	89.5(2)	Cl(1)–Pt(1)–S(22)	88.8(3)
Pt(2)–Pt(1)–S(22)	89.6(2)	S(12)–Pt(1)–S(22)	90.0(3)
Cl(1)–Pt(1)–N(31)	93.5(6)	Pt(2)–Pt(1)–N(31)	90.3(6)
S(12)–Pt(1)–N(31)	179.1(7)	S(22)–Pt(1)–N(31)	89.1(7)
Cl(1)–Pt(1)–N(41)	91.3(6)	Pt(2)–Pt(1)–N(41)	90.4(6)
S(12)–Pt(1)–N(41)	91.8(6)	S(22)–Pt(1)–N(41)	178.3(7)
N(31)–Pt(1)–N(41)	89.1(9)	Pt(1)–Pt(2)–N(11)	90.1(6)
Pt(1)–Pt(2)–N(21)	90.0(6)	N(11)–Pt(2)–N(21)	88.4(9)
Pt(1)–Pt(2)–S(32)	89.8(2)	N(11)–Pt(2)–S(32)	179.5(5)
N(21)–Pt(2)–S(32)	92.0(6)	Pt(1)–Pt(2)–S(42)	88.6(2)
N(11)–Pt(2)–S(42)	89.7(6)	N(21)–Pt(2)–S(42)	177.7(6)
S(32)–Pt(2)–S(42)	89.9(3)	Pt(1)–Pt(2)–S(52)	172.8(2)
N(11)–Pt(2)–S(52)	95.9(7)	N(21)–Pt(2)–S(52)	94.1(6)
S(32)–Pt(2)–S(52)	84.2(3)	S(42)–Pt(2)–S(52)	87.4(3)

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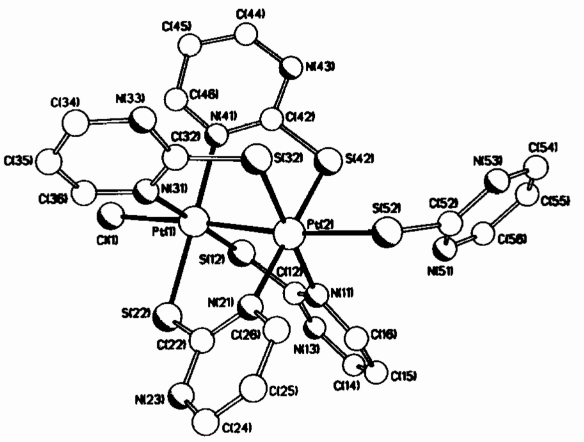

Fig. 1. Molecular structure of $Pt_2(pymS)_5Cl$, giving the crystallographic numbering scheme.

a perspective view of 2 and gives the crystallographic numbering scheme. This result confirms the dinuclear nature of the molecule postulated [1] for the compound originally obtained by the alternative route from $PtCl_4^{2-}$, and demonstrates that an S-bonded pyrimidine-2-thione anion can fully replace at least one of the halide ions in the terminal positions.

One significant feature of the structure of 2 is the difference in the arrangement of the bridging ligands as compared to those in $[Pt_2(pymS)_4Cl_2]$ (3). In 3 the Pt atoms were found [1] to have inequivalent donor atom sites: Pt(1) being bonded to three sulphur atoms and one nitrogen atom, and Pt(2) to three nitrogens and one sulphur. In 2, however, each Pt atom has a *cis*-arrangement of 2N and 2S atoms from the bridging ligands, as was observed for the other $[Pt_2(pymS)_4X_2]$ (X = Br, I) compounds [1, 3] and for 1.

The Pt–Pt distance in 2 (2.547(2) Å) is comparable with that in 1 (2.554(1) Å), though both of these are noticeably longer than that (2.518(1) Å) in the dichloro-compound (3). Replacement of one of the chloride ligands by the sulphur bonded $pymS^-$ anion results in a lengthening of the remaining Pt–Cl bond (2.494(7) Å; compare for 3 Pt–Cl 2.440(3) and 2.464(3) Å). As might be expected, the Pt–S bond to the terminal thione ligand (Pt(2)–S(52) in Fig. 1) is longer (2.438(8) Å) than the Pt–S bonds involving the bridging ligands (2.292–2.307(8) mean 2.299 Å). These latter Pt–S bond distances are, however, similar to the analogous Pt–S bonds in the other pyrimidine-2-thione dimers [1, 3]. The Pt–N bonds in 3 also do not differ significantly from those in that group of compounds.

The bond angles about each Pt atom within the PtN_2S_2 groups formed by the bridging ligands do not differ appreciably from 90°, the biggest deviation being for N(21)–Pt(2)–S(32) (92.0(6)°). However, whereas 3 was found [1] to have a nearly linear Cl–Pt–Pt–Cl chain (Pt–Pt–Cl = 179.7(1) and 178.7(1)°), the Cl–Pt–Pt–S chain in 2 is non-linear, with the sulphur atom of the terminal thione ligand showing greater displacement from the Pt–Pt axis (Pt(1)–Pt(2)–S(52) 172.8(2)°) than the chlorine atom (Cl(1)–Pt(1)–Pt(2) 175.8(2)°). Interestingly, in the less well-defined structure of 1 the degree of non-linearity was similar.

The characterisation of $[Pt_2(pymS)_5Cl]$ confirms that dinuclear Pt(III) complexes with $\overset{\frown}{N\ S}$ bridging ligands of this type can be obtained as readily from Pt(IV) precursors as from Pt(II), and suggests that analogous $[Pt_2L_6]$ compounds with thione ligands in both terminal positions may well be obtainable.

Supplementary Material

A list of fractional atomic coordinates and isotropic thermal parameters is available from the authors on request.

Acknowledgements

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