Synthesis and Structure of [Pt($C_5H_5NOS)_2(C_5H_4NOS)$]Cl, where C_5H_5NOS = 3-hydroxy-2-mercaptopyridine; Formation of a $Pt^{II}S_3O$ Coordination Arrangement

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We recently reported [1] the facile preparation of a dinuclear Pt(III) complex, $[Pt(PymS)_2I]_2$, by the reaction of pyrimidine-2-thione (PymSH) with K_2PtI_4 in aqueous methanol. Because of current interest in Pt(III) compounds [2] we have been studying the extent to which heterocyclic amine thiones favour the stabilization of Pt(III) in this way. Wishing to incorporate a second ionizable proton in the thione ligand, whilst retaining the potentially bridging N–C–S unit, we explored the coordination behaviour of 3-hydroxy-2-mercaptopyridine (HMPy) with Pt(II). Reaction of a methanolic solution of HMPy with an aqueous solution of K_2PtCl_4 and KI did not produce a Pt(III) dimer but gave orange crystals with elemental analyses close to the stoichiometry $Pt(C_5H_5NOS)_2(C_5H_4NOS)Cl\cdot 2H_2O$. This unexpected result and the potential versatility of HMPy as a ligand prompted us to determine the structure of the complex by X-ray diffraction methods.

Experimental

3-Hydroxy-2-mercaptopyridine (0.092 g) in hot methanol (60 cm^3) was added dropwise to an aqueous solution of K_2PtCl_4 (0.1 g) and KI (0.2 g). The resulting solution formed orange needles on storage in a refrigerator. *Anal*: Calc. for $Pt(C_5H_5NOS)_2(C_5H_4NOS)Cl\cdot 2H_2O$, C, 27.84; H, 2.80; N, 6.50; S, 14.86. Found: C, 27.22; H, 2.30; N, 6.19; S, 14.63%. (The subsequent X-ray studies suggested partial loss of the lattice water to give a Pt:H_2O ratio of 1:1.25 in the crystal used).

X-ray Study

$\{[Pt(C_5H_5NOS)_2(C_5H_4NOS)]Cl\}_2\cdot 2.5H_2O$ crystallizes as orange needles. The crystal data are: monoclinic, $a = 15.909(3)$, $b = 16.103(6)$, $c = 16.945(6)$ Å, $\beta = 96.65(2)°$, $V = 4312$ Å^3, space group $P2_1/c$, $Z = 8$ (2 independent molecules), $M_r = 633.5$, $D_c = 1.96$ g cm^{-3}, μ(Cu Kα) = 164 cm^{-1} – Refined unit cell parameters for a crystal of approximate dimensions 0.08 × 0.08 × 0.20 mm were obtained by centering 12 reflections on a Nicolet R3m diffractometer. 4431 independent reflections ($\theta \leqslant 50°$) were measured with graphite monochromated Cu Kα radiation using the omega-scan measuring routine. Of these, 3207 had $|F_o| > 3\sigma(|F_o|)$ and were considered observed. Seven reflections for which $|F_o| \ll |F_c|$ were suspected of being affected by extinction and were removed. Lorentz, polarisation and a numerical absorption correction were applied.

The structure was solved by the heavy-atom method, which revealed the two independent platinum atoms. The remaining non-hydrogen atoms were located in the ensuing ΔF map, which also confirmed the presence of 2.5 H_2O molecules. It was not possible to locate any hydrogen atoms, probably due to the fairly high degree of thermal anisotropy in the structure. The C–H hydrogen atoms were placed in idealised positions (C–H = 0.96 Å) and assigned isotropic thermal parameters $U(H) = 1.2\ U_{eq}(C)$, and allowed to ride on their parent carbon atoms. The non-hydrogen atoms were refined anisotropically. Refinement was by block-cascade full-matrix least-squares to $R = 0.070$, $R_w = 0.075$ ($w^{-1} = \sigma^2(F) + 0.001F^2$).

Computations were carried out on an Eclipse S140 computer using the SHELXTL program system [3]. Scattering factors were from ref. 4. Important bond lengths and angles are listed in Table I*.

TABLE I. Bond lengths and angles

Bond lengths (Å)			
Pt–S(2)	2.281(6)	Pt'–S(2')	2.286(6)
Pt–S(12)	2.296(6)	Pt'–S(12')	2.335(6)
Pt–S(22)	2.280(6)	Pt'–S(22')	2.272(6)
Pt–O(3)	2.049(14)	Pt'–O(3')	2.049(15)
Bond angles (deg)			
S(2)–Pt–O(3)	86.4(5)	S(2')–Pt'–O(3')	85.1(5)
O(3)–Pt–S(12)	98.2(5)	O(3')–Pt'–S(12')	99.3(4)
O(3)–Pt–S(22)	175.9(5)	O(3')–Pt'–S(22')	176.4(4)
S(2)–Pt–S(12)	174.8(2)	S(2')–Pt'–S(12')	175.6(2)
S(2)–Pt–S(22)	90.4(2)	S(2')–Pt'–S(22')	91.3(2)
S(12)–Pt–S(22)	85.1(2)	S(12')–Pt'–S(22')	84.3(2)

Results and Discussion

The compound consists of $[Pt(C_5H_5NOS)_2(C_5H_4NOS)]^+$ cations, in which C_5H_4NOS represents depro-

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*See also 'Supplementary Material'.

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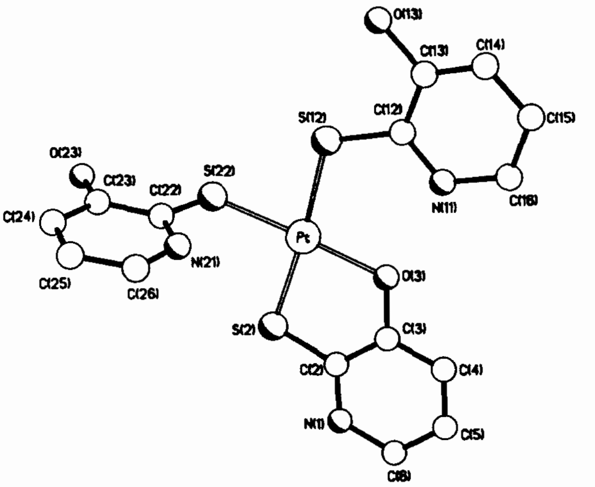

Fig. 1. Molecular structure of the $[Pt(C_5H_5NOS)_2(C_5H_4NOS)]^+$ cation, where C_5H_5NOS = 3-hydroxy-2-mercaptopyridine, showing the crystallographic numbering scheme; the numbering for the other independent molecule is the same but with primes.

tonated 3-hydroxy-2-mercaptopyridine and C_5H_5NOS the neutral ligand and chloride anions. The molecular geometry of the cation is shown in Fig. 1. (There are, in fact, two crystallographically independent molecules in the asymmetric unit but differences in the cation geometry are very small – see Table I).

The two neutral ligands coordinate to platinum via the sulphur atoms, whilst the third, formally deprotonated, ligand chelates via sulphur and oxygen. This ambidentate behaviour on the part of HMPy produces a slightly distorted square-planar PtS_3O coordination arrangement. To our knowledge, this is the first example demonstrated by X-ray diffraction methods of a set of organic ligands producing a $Pt^{II}S_3O$ mixed donor atom arrangement.

Two of the ligands are essentially co-planar with the platinum coordination sphere whilst the third ligand is rotated by 82 and 83° (for molecules **1** and **2** respectively) from this plane.

The Pt–S (2.27–2.34 Å) and Pt–O (2.05 Å) bond lengths are unexceptional, *cf.* Pt–S 2.158 Å in [5], 2.479 Å in [6], Pt–O 1.935 Å in [7], 2.308 Å in [7]. In the only structural example (to our knowledge) of an S, O bidentate ligand coordinated to platinum the Pt–S and Pt–O distances are 2.267 and 2.043 Å respectively [8].

One significant feature of the structure in the context of the observed stoichiometry and coordination modes is the short potential hydrogen bond (N(11)–O(3) = 2.56 Å; N(11′)–O(3′) = 2.63 Å) formed between the proton formally located on the nitrogen atom, N(11) of one of the neutral HMPy ligands and the O(3) atom coordinated to Pt from the formally deprotonated HMPy. The greatest deviations from planarity for the Pt–O(3)–N(11)–C(12)–S(12) system are 0.01 [for S(12)] and 0.04 Å [for C(12′)] for molecules **1** and **2** respectively. This presumably has a structure stabilising influence on the formation of the PtS(2)O(3) chelate ring giving rise to the rather unexpected donor atom set. Such an intramolecular hydrogen bond would also lessen the chances of the formation of N–C–S bridges between pairs of platinum atoms after initial coordination of HMPy through the sulphur atoms.

Although both chloride and iodide ions were present in the reaction medium both are excluded from coordination to platinum by the formation of the Pt–O(3) bond of the chelated ligand. The inclusion of chloride as the counter anion in the lattice is presumably due to more favourable lattice energy and/or packing factors for the smaller ion.

Elemental analysis suggested the presence of lattice water. There are three water sites within the unit

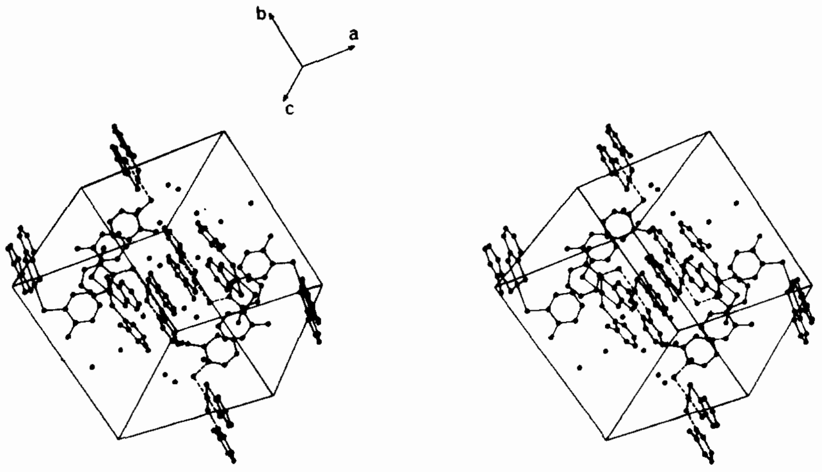

Fig. 2. Stereoscopic view of the packing.

cell with partial occupancy corresponding to a Pt: H_2O ratio of 2:2.5. These lattice water molecules have no significant influence on the cation geometry.

The two full weight waters had high thermal parameters W(1) is 2.6 Å from O(23), 3.2 Å from Cl(1) and 3.0 Å from Cl(2); W(2) is 2.9 Å from N(1), 3.3 Å from Cl(1) and 3.0 Å from O(23).

Inspection of the packing of the molecules in the unit cell (Fig. 2) reveals a continuous parallel stacking of the ligands in space. This applies to both the in-plane and out-of-plane ligands. The minimum interatomic separation between the out-of-plane ligands is 3.61 Å between C(24) and O(23′) in one direction and 3.65 Å between C(26′) and C(25) in the adjacent symmetry related molecule in the other direction. The minimum interatomic separation between the in-plane ligands is 3.27 Å in one direction between C(16) and C(16′) and 3.51 Å in the other between C(12) and S(2) in the adjacent symmetry related molecule. There is also a short intermolecular interlayer Pt–Pt contact of 3.61 Å.

Supplementary Material

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

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