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A ZWITTERIONIC MONOALKYLATED DERIVATIVE OF $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ FROM 1,3-PROPANESULTONE

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Reaction of dinuclear platinum(II) sulfido complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with 1,3-propanesultone gives the novel zwitterionic monoalkylated thiolate complex $[Pt_2(\mu\text{-}S)\{\mu\text{-}S(CH_2)_3SO_3\}\cdot(PPh_3)_4]$, which was characterized by NMR spectroscopy, electrospray ionisation mass spectrometry, and a single crystal X-ray structure determination. Crystals are monoclinic, space group $P2(1)/c$ with unit cell dimensions $a = 16.8957(3)$ Å, $b = 15.5031(3)$ Å, $c = 28.0121(5)$ Å, $\beta = 99.780(1)°$, for $Z = 4$.

K e y w o r d s: platinum complex, alkylation reaction, zwitterions, thiolate ligand, X-ray crystal structure.

The dinuclear platinum(II) sulfido complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** has been known for many years to contain highly nucleophilic sulfide centers [1]. This reactivity can be harnessed in the assembly of multi-metallic sulfide-bridged aggregates [2—5] or alternatively alkyl- or aryl-thiolate ligands can be generated by alkylation [6—11] or arylation [12, 13] reactions using suitable electrophiles. In recent years we have been exploiting this reactivity using electrospray ionisation mass spectrometry [14] which offers advantages in terms of efficiency and simplicity [15]. A wide range of alkylated and arylated derivatives of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ is now known, where one or both sulfide groups are converted into bridging thiolate ligands, namely $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4]^+$ and $[Pt_2(\mu\text{-}SR)(\mu\text{-}SR')(PPh_3)_4]^+$. The vast majority of such alkylated and arylated derivatives are cationic, with counteranions (such as PF_6^- or BPh_4^-) added to effect precipitation and isolation of the complexes.

In this contribution we report investigations into the synthesis and characterization of a novel zwitterionic alkylated derivative of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$, formed by alkylation with 1,3-propanesultone **2** (a well-known alkylating agent [16]) giving a product where the resulting sulfonate ($—SO_3^-$) counterion is retained as part of the alkylthiolate group.

EXPERIMENTAL

Safety note: 1,3-Propanesultone is a potent carcinogen [17] and should be handled using appropriate safety precautions.

The $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ complex was prepared from *cis*-$[PtCl_2(PPh_3)_2]$ and $Na_2S\cdot 9H_2O$ in benzene suspension by the literature procedure [21, 18]. 1,3-Propanesultone was used as supplied from Aldrich. Solvents used were of reagent grade.

Electrospray mass spectra were recorded in positive-ion mode using a Bruker MicrOTOF instrument, typically using a capillary exit voltage of 20 V. Isolated solid products (*ca.* 0.5 mg) were dissolved in a small quantity of CH_2Cl_2 in an Eppendorf tube, diluted with methanol (*ca*. 1.5 ml) and cen-

trifuged. ^{1}H NMR spectra were either recorded in the $CDCl_3$ solution at 400 MHz on a Bruker Avance NMR spectrometer and $^{31}P\{^1H\}$ NMR spectra were recorded at 121.49 MHz in $CDCl_3$. Coupling constants *J* are in Hz. Microelemental analyses were obtained from the Microanalytical Laboratory, University of Otago. IR spectra (as KBr disks) were obtained using a Perkin Elmer Spectrum100 FT-IR.

Synthesis of $[Pt_2(\mu\text{-}S)\{\mu\text{-}S(CH_2)_3SO_3\}(PPh_3)_4]$ (3). 1,3-Propanesultone (81 mg, 0.66 mmol) was added to a stirred suspension of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (100 mg, 0.066 mmol) in methanol (25 ml). Additional 0.66 mmol portions of sultone were added after 5 and 16 hours stirring. After 24 hours, the reaction was shown to be complete, as found by analysis of an aliquot of the reaction mixture by positive-ion ESI MS. Addition of distilled water (5 ml) effected precipitation of the yellow product, which was filtered, washed with water (5 ml) and dried under vacuum to give **3** (80 mg, 74 %). Found: C 52.9; H 4.1; N 0.0. $C_{75}H_{66}O_3P_4Pt_2S_3$ requires C 55.4; H 4.1; N 0.0 %. **3**·$2CH_2Cl_2$·$1.5H_2O$ requires C 50.75; H 4.03 %, suggesting the compound retains some solvent of crystallisation even after drying. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$), δ 24 [br s, $^1J(PtP_a)$ 2617, $^1J(PtP_b)$ 3247]. ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.08—7.42 (m, Ph), 1.65 (2H, m, $CH_2C\underline{\mathbf{H}}_2CH_2$), 2.21 (2H, m, $SC\mathbf{H}_2$), 2.35 (2H, m, $C\mathbf{H}_2SO_3$). IR (KBr disk): ν_{max} 1213, 1183, 1159 cm^{-1} (asym SO_3), 1036 cm^{-1} (sym SO_3). ESI MS: $[M + H]^+$ *m*/*z* 1626.240 (calculated *m*/*z* 1626.251), $[M + Na]^+$ *m*/*z* 1648.223 (calculated *m*/*z* 1648.233).

X-ray crystal structure determination of 3. Pale yellow crystals were obtained by liquid-liquid diffusion of petroleum spirits (boiling point 60—80 °C) into a dichloromethane solution of the complex at room temperature.

Data were collected at 97(2) K on a Bruker Apex II diffractometer equipped with a CCD area detector, using MoK_α radiation (λ = 0.71073 Å). SADABS [19] was used for empirical absorption correction. Structures were solved by the direct methods option of SHELXS-97 [20] and the Pt, S and P atoms were located. The oxygen atoms of the sulfonate group were then located, followed by the car-

T a b l e 1

Crystal data and structure refinement details for the $[Pt_2(\mu\text{-}S)\{\mu\text{-}S(CH_2)_3SO_3\}(PPh_3)_4]$ *complex*

Empirical formula	$C_{77}H_{73}Cl_4O_{4.5}P_4Pt_2S_3$
Formula weight	1822.39
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	*P*2(1)/*c*
Unit cell dimensions *a*, *b*, *c*, Å; β, deg.	16.8957(3), 15.5031(3), 28.0121(5); 99.780(1)
Temperature, K	97(2)
Volume, Å^3	7230.7(2)
Z	4
Density (calculated), g·cm^{-3}	1.674
Absorption coefficient, mm^{-1}	4.240
F(000)	3612
Crystal size, mm	0.31×0.15×0.14
Reflections collected	91156 (99.8 %)
Independent reflections	17403 [R_{int} 0.0475]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.585
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	17403 / 8 / 836
Goodness-of-fit on F^2	1.144
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0544$, $wR_2 = 0.1311$
R indices (all data)	$R_1 = 0.0665$, $wR_2 = 0.1363$
Largest diff. peak and hole, e/Å^{-3}	2.961 and –2.293

bon atoms of the phenyl groups in subsequent refinement. The sulfonate group was disordered over two orientations which refined to a 0.66 [C(1), C(2), C(3)] : 0.34 [C(1a), C(2a), C(3a)] ratio. The consequential disorder of the SO_3 group could not be resolved for S(3), O(1), and O(2) where it appeared as elongated ellipsoids, but O(3) could be split into two components. Two molecules of CH_2Cl_2 were apparent, one ordered and one disordered over three orientations. Two significant residual peaks were assigned as a fully occupied H_2O site, hydrogen bonding between an SO_3 O atom and the non-alkylated S atom, and the other a half-occupied H_2O site associated with disordered CH_2Cl_2. In the final refinement cycles, non-H atoms were assigned anisotropic temperature factors while the C atoms of disordered CH_2Cl_2, the disordered propyl chain C atoms, and the O atoms were treated isotropically. H atoms were included only for ordered C atoms, in calculated positions. All calculations were carried out using the SHELX-97 suite of programs. A summary of crystallographic parameters and refinement details is given in Table 1.

A CIF file containing complete information on the structure has been deposited with CCDC, deposition number 865412, and is freely available from www.ccdc.cam.ac.uk/data_request/cif.

RESULTS AND DISCUSSION

The reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** with excess 1,3-propanesultone **2** was carried out in methanol suspension, resulting in alkylation of one of the sulfide centers, forming the alkanethiolate complex, illustrated formally as **3**. It was found to be beneficial to add the sultone in several portions in order to effect complete conversion of starting complex **1**. The solvent used was not pre-dried and it is possible that reaction with adventitious water might effect hydrolysis of the sultone to unreactive hydroxypropylsulfonic acid. The presence of acid might then effect protonation of starting $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$, generating the known monoprotonated species $[Pt_2(\mu\text{-}S)(\mu\text{-}SH)(PPh_3)_4]^+$ [5, 21] which will be less susceptible towards alkylation by the sultone. The resulting reaction mixture had the characteristic yellow color of a mono-alkylated derivative of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$, and the product was isolated by addition of water, followed by filtration and washing to remove excess alkylating agent and byproducts thereof. Complex **3** is believed to be the first example of an alkylated derivative of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ that is zwitterionic. The attempted synthesis of **3** using $Br(CH_2)_3SO_3Na$ as the alkylating agent (generated by the reaction of 1,3-propanesultone with NaBr [22]) proceeded slowly in methanol, and is not a preferred method for its synthesis.

The IR spectrum of **3** showed bands at 1213 cm^{-1}, 1183 cm^{-1}, and 1159 cm^{-1}, as well as a band at 1036 cm^{-1}, which can be assigned to the asymmetric and symmetric stretches respectively of the SO_3 group, by comparison of literature ranges for these stretches in aliphatic sulfonate salts (1230—1120 cm^{-1} and 1080—1025 cm^{-1} [23]). The $^{31}P\{^1H\}$ NMR spectrum of the complex in the $CDCl_3$ solution showed a single broad central resonance, with two sets of satellites due to coupling to ^{195}Pt [^1J(PtP) 2617 Hz and 3247 Hz] for PPh_3 ligands *trans* to the sulfide and thiolate ligands respectively, with differing *trans* influences [24]. Such spectral features are commonly observed for monoalkylated derivatives of **1**. The ^1H NMR spectrum showed, in addition to the expected complex set of phenyl resonances, three multiplets in the aliphatic region, due to the three CH_2 groups; the spectrum is illustrated in Fig. 1. A distinctive resonance at *ca.* δ 2.2 is assigned as the SCH_2 group, on account of the presence of poorly resolved ^3J(PtH) coupling resulting in a broadened base of the resonance; such coupling is routinely seen in other monoalkylated derivatives $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4]^+$. The central CH_2 group appears as a complex multiplet at δ 1.65, while the $CH_2SO_3^-$ protons are the most deshielded, at δ 2.35. The protons of the propyl

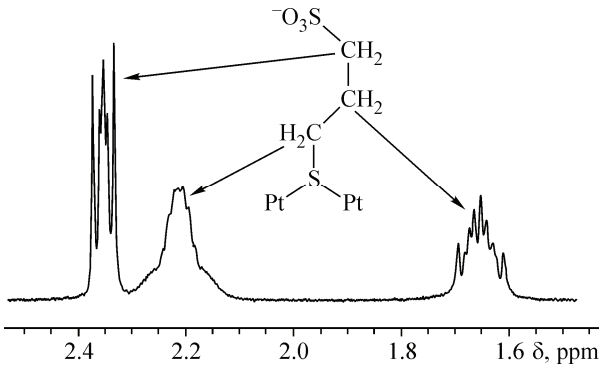

Fig. 1. Part of the ^1H NMR spectrum of **3**, showing the assignment of the CH_2 protons

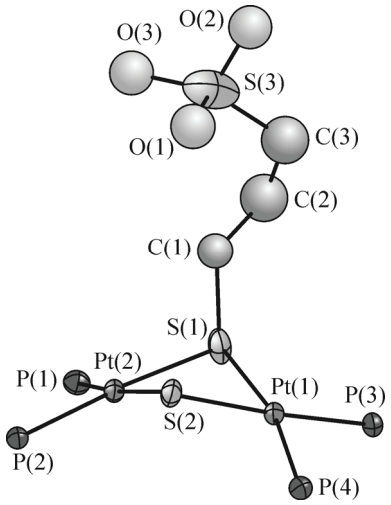

Fig. 2. Molecular structure of **3**, atoms are shown at the 50 % probability level. Only one component of the disordered propyl chain is shown

chain are all shielded relative to their counterparts in the bromopropylsulfonate $Br(CH_2)_3SO_3^-Na^+$ [18].

The positive ion ESI mass spectrum of the isolated product in a dichloromethane-methanol solution showed the ions $[M + H]^+$ (*m*/*z* 1626.240, calculated *m*/*z* 1626.251) and $[M + Na]^+$ (*m*/*z* 1648.223, calculated *m*/*z* 1648.233), with the sulfonate anion being the most likely site for cationization. However, the spectra were low intensity, as might be expected for a neutral coordination complex lacking strongly basic sites for ionisation [14]. Examination of the isotope pattern of the $[M + Na]^+$ ion showed additional weak peaks at 0.5 *m*/*z* separation, assigned to the dimeric species $[2M + 2Na]^{2+}$; the comparable protonated dimer $[2M + 2H]^{2+}$ was not observed, indicating aggregation about the alkali metal cation. Corroboration of the ion assignments was achieved by the addition of a small quantity of NaCl to the analyte solution, which intensified the spectrum, giving a dominant $[M + Na]^+$ ion. Likewise, the addition of a small quantity of KBr to a fresh solution of **3** gave the $[M + K]^+$ ion at *m*/*z* 1663.906.

Despite several attempts, we were unable to obtain satisfactory microelemental analytical data on **3**, with samples repeatedly giving low carbon percentages. Therefore, in order to unambiguously characterize the product, an X-ray structure determination was carried out on crystals of **3** obtained from dichloromethane-diethyl ether. The molecular structure of the complex is shown in Fig. 2, and selected bond lengths and angles are given in Table 2. The structure confirms the formulation of the complex as zwitterionic complex **3**, but suffers considerable disorder in the propyl chain; the sulfonate group S(3), O(1), O(2), and O(3) is also partially disordered. This makes a detailed comparison of bond parameters with those of other monoalkylated derivatives of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ not justified. The complex has the expected butterfly arrangement with a dihedral angle between the two PtS_2 planes of 135.9°, which is typical for monoalkylated derivatives $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4]^+$ [11].

The complex crystallizes with one well-defined dichloromethane of crystallisation which is located near the SO_3^- group, such that the H(4B)—O(2) intermolecular distance is 2.45(1) Å and the C—H···O bond angle is 153.2(6)°. Second dichloromethane is disordered, and adjacent to a water molecule in the lattice [oxygen O(W2)]. Oxygen of the second water molecule [oxygen O(W1), *ca.* 0.5 occupancy] is located in a position between sulfonate oxygen O(1) and sulfide S(2). Although the hydrogen atoms could not be located, the arrangement suggests the possibility of an intramolecularly

Table 2

Selected bond lengths and angles for the $[Pt_2(\mu\text{-}S)\{\mu\text{-}S(CH_2)_3SO_3\}(PPh_3)_4]$ *complex*

Pt(1)—P(4)	2.2857(18)	Pt(1)—P(3)	2.2875(18)	P(3)—Pt(1)—P(4)	99.44(7)
Pt(1)—S(1)	2.3380(19)	Pt(1)—S(2)	2.3480(17)	S(1)—Pt(1)—S(2)	81.97(7)
Pt(2)—P(2)	2.2806(17)	Pt(2)—P(1)	2.298(2)	Pt(1)—S(1)—Pt(2)	88.74(7)
Pt(2)—S(2)	2.3386(19)	Pt(2)—S(1)	2.3567(19)	C(1A)—S(1)—Pt(1)	119.2(11)
S(1)—C(1A)	1.861(17)	S(1)—C(1)	2.076(13)	C(1A)—S(1)—Pt(2)	123.3(11)
S(3)—O(2)	1.436(10)	S(3)—O(3)	1.65(2)	P(1)—Pt(2)—P(2)	98.86(7)
S(3)—O(1)	1.497(10)	S(3)—O(3A)	1.40(2)	S(1)—Pt(2)—S(2)	81.77(7)
S(3)—C(3)	1.910(16)	S(3)—C(3A)	1.876(19)	Pt(1)—S(2)—Pt(2)	88.93(6)
C(1)—C(2)	1.562(17)	C(1A)—C(2A)	1.591(19)	C(1)—S(1)—Pt(1)	100.8(5)
C(2)—C(3)	1.500(18)	C(2A)—C(3A)	1.54(2)	C(1)—S(1)—Pt(2)	98.5(4)

hydrogen-bonded water in the arrangement S···H—O—H···O_3S—CH_2—. The S(2)···O(W1) non-bonded distance is 3.29(1) Å, somewhat shorter than the S···O distance in the crystallographically characterized ethanol solvate $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]\cdot 2EtOH$ [3.42 Å] [25], which contains an ethanol molecule hydrogen bonded to a sulfide center. The O(1)···O(W1) distance is 2.76(2) Å, and the angle S(1)···O(W1)···O(1) angle is 117.7(4)°, consistent with a water molecule hydrogen-bonded in this pocket.

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