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Platinum(II) thiosalicylate and related complexes as ligands towards mercury(II) halides; X-ray crystal structure of the tetrametallic complex $\{[\overline{\mathrm{Pt(SC_6H_4CO_2})}(\mathrm{PPh_3})_2]\cdot\mathrm{HgI_2}\}_2$

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Abstract—The platinum(II) thiosalicylate complex $[\overline{\mathrm{Pt(SC_6H_4CO_2})}(\mathrm{PPh_3})_2]$ **1a** reacts with HgI_2 to form a tetrametallic complex comprising an $\mathrm{IHg}(\mu\text{-I})_2\mathrm{HgI}$ central core with the thiolate sulphur of **1a** coordinated to each mercury centre, completing a distorted tetrahedral coordination environment. Overall, the structural features of the complex, determined by an X-ray diffraction study, are similar to the parent thiosalicylate complex **1a**, but with an increased fold angle (59° compared to 46°) of the thiosalicylate ligand relative to the platinum coordination plane. Reactions of related five-membered ring thiolate complexes $[\overline{\mathrm{Pt(SCHRCO_2})}(\mathrm{PPh_3})_2]$ (R=H or Me) and of **1a** with a range of metal cations were investigated using ^{31}P NMR spectroscopy. Changes in the $^1J(\mathrm{PtP})$ coupling constants are discussed in terms of coordination to the various metal halide moieties. Reactions of the organomercury(II) thiosalicylate complex Thiomersal ($\mathrm{EtHgSC_6H_4CO_2Na}$) with *cis*-$[\mathrm{PtCl_2(PPh_3)_2}]$, or *cis*-$[\mathrm{MCl_2(dppe)}]$ (M=Ni or Pd) leads to complete transfer of the thiosalicylate ligand from the mercury, and isolation of the previously reported thiosalicylate complexes $[\overline{\mathrm{Pt(SC_6H_4CO_2})}(\mathrm{PPh_3})_2]$ and $[\overline{\mathrm{M(SC_6H_4CO_2})}(\mathrm{dppe})]$ (M=Ni, Pd) in high yields. © 1997 Elsevier Science Ltd

Keywords: platinum; mercury; thiolate; thiosalicylate; crystal structure.

Thiosalicylic acid **I** is an interesting heterodifunctional ligand capable of coordinating to both hard and soft metal centres in a variety of bonding modes [1]. In a recent paper [2] we reported the syntheses of a range of platinum(II) **1**, palladium(II) **2** and nickel(II) **3** metallacyclic complexes containing thiosalicylate dianions, together with some related complexes **4** derived from thioglycollic and 2-mercaptopropionic acids. X-ray crystal structure determinations on the platinum and nickel thiosalicylate derivatives $[\overline{\mathrm{Pt(SC_6H_4CO_2})}(\mathrm{PPh_3})_2]$ **1a** and $[\overline{\mathrm{Ni(SC_6H_4CO_2})}(\mathrm{dppp})]$ **3a** [dppp = 1,3-bis(diphenylphosphino)propane] revealed different bonding arrangements of the thiosalicylate ligand towards the two metal ions. These differences were tentatively ascribed to the effects of metals of different sizes coordinated by a relatively inflexible ligand. Metal thiolate complexes are well known to possess ligand properties towards other metal centres [3] and we have previously shown that the five-membered ring thiolate complex **5** coordinates to mercury(II) halides to form tetrametallic complexes consisting of an $\mathrm{XHg}(\mu\text{-X})_2\mathrm{HgX}$ core, with each mercury atom ligated by the sulphur atom of a platinum–thiolate complex, i.e. **6a** [4]. The bis(thiosalicylato) mercury(II) complex $[\mathrm{Hg(tsalH)_2}]$ (containing S-bonded thiosalicylate monoanions) is known to be able to complex other metal ions, such as Zn^{2+}, Cd^{2+} and Pb^{2+} [5]. Metal–thiosalicylate complexes are known to display a range of coordination geometries [1] and thus it was of interest to investigate whether coordination of the sulphur

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atom of **1a** would influence the geometry of the platinum–thiosalicylate moiety.

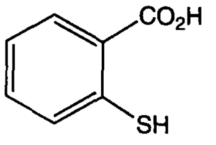
In this contribution we report that the platinum–thiosalicylate complex **1a**, together with the related cyclic thiolate complexes **4**, have analogous ligand properties towards mercury(II) halides. We also report that the thiosalicylate ligand is completely transferred from the organomercury complex $EtHgSC_6H_4CO_2Na$ to platinum(II), palladium(II) and nickel(II) centres.

RESULTS AND DISCUSSION

Synthesis and X-ray crystal structure

Reactions of the platinum(II) cyclic thiolate complexes **1a**, **4a** and **4b** with excess solid $HgBr_2$ or HgI_2 were carried out in dichloromethane solution. Addition of the mercury salt followed by shaking typically resulted in a lightening of the solution (for $HgBr_2$), or little change (for HgI_2), though when smaller quantities of the mercury salt were used, dissolution was observed. In general, crystalline products **6b–6e** were obtained by slow diffusion of diethyl ether into the solution (after removal of excess HgX_2). However, the mercaptopropionate–HgI_2 complex did not crystallise well, though it was analytically pure. The attempted synthesis of a comparable HgI_2 complex of the cyclo-octa-1,5-diene (COD) complex $[Pt(SC_6H_4CO_2)(COD)]$ led only to the crystallisation of the pure platinum starting complex, as shown by elemental microanalytical data.

In order to unambiguously confirm the structure of one derivative (which was considered important given



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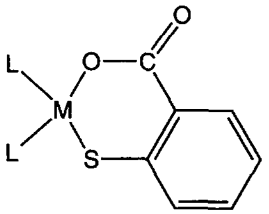
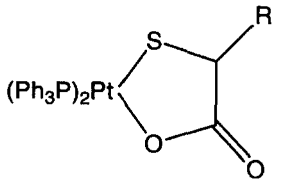


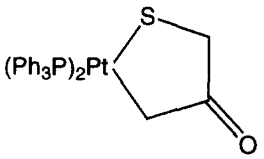
1; M = Pt
1a; L = PPh_3

2; M = Pd
2a; L-L = $Ph_2PCH_2CH_2CH_2PPh_2$

3; M = Ni
3a; L-L = $Ph_2PCH_2CH_2CH_2PPh_2$



4a; R = H
4b; R = Me



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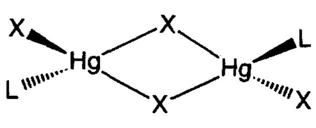
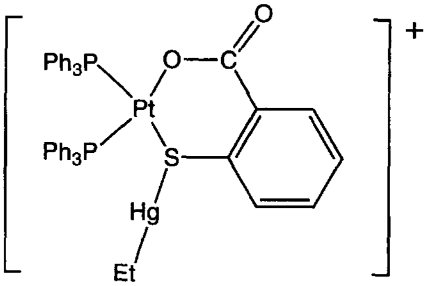


6a; L = **5**; X = Br
6b; L = **1a**; X = I
6c; L = **4a**; X = I
6d; L = **4b**; X = I
6e; L = **4a**; X = Br
6f; L = **1a**; X = Cl



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the known structural complexity of the coordination chemistry of mercury(II) halides with neutral donor ligands [6]) a single-crystal X-ray diffraction study was carried out on the HgI_2 complex **6b**. Since excess mercury halide was used, and complexes of the type $LHgX_2$ are known to commonly have dimeric structures [6] it is likely that the range of related HgX_2 (X=Cl, Br, I) complexes **6** have similar structures.

The structure of **6b** comprises a centrosymmetric dimer with a near-rectangular $Hg_2(\mu\text{-}I)_2$ core. The Hg is further coordinated to a terminal I ligand and to the S atom of a $[\overline{\mathrm{Pt(SC_6H_4CO_2}})(\mathrm{PPh_3})_2]$ molecule. It is related to a range of other $[L(I)Hg(\mu\text{-}I)]_2$ dimers, and three structures have been reported where L is a sulphur donor ligand [7]. Additionally we have previously reported the structure of the related $HgBr_2$ adduct **6a** [4].

The coordination about the Hg atom is distorted tetrahedral, with angles subtended at Hg ranging from 87° to 125°. The iodo-bridge is strongly unsymmetrical with Hg—I distances of 2.7139(5) and 3.2870(5) Å; both of these are longer than the bond to the terminal iodo ligand [2.6667(5) Å]. The large iodo bridge results in an essentially rectangular motif, with I—Hg—I and Hg—I—Hg angles of 87.76(1) and 92.24(1)° respectively. These features are in accord with those in other examples [7].

The attachment of the sulphur atom to the Hg atom has only a small effect on the geometry of the platinum-complex part of the molecule, in comparison with the free species **1a**. The Pt(1)—S(1)—C(7) angle in the mercury adduct is 99.2(2)°, from 103.8(2)° in **1a**, but the Pt—S and S—C distances show negligible change. There is an apparent change in the Pt—O(1)—C(1) angle from 135.8(4) to 126.0(3)°, with a decrease in the Pt—O(1) distance from 2.109(3) to 2.076(3) Å in the adduct, but the significance of this must remain tentative in view of the suspicion that the parameters involving O(1) may be unreliable in the free complex [2]. The S—Pt—O(1) angle and the P(1)—Pt—P(2) angles show no chemically significant differences on attachment to the mercury atom.

The coordination about the platinum atom is essentially planar, with a small twist defined by the dihedral angle of 8.2° between the P(1)—Pt—P(2) and S(1)—Pt—O(1) planes. The CO_2 group of the thios-

Table 1. Selected bond lengths [Å] and angles [°] for complex **6b**

Pt(1)—O(1)	2.076(3)	Pt(1)—P(2)	2.2411(13)
Pt(1)—P(1)	2.2971(14)	Pt(1)—S(1)	2.3159(14)
Hg(1)—S(1)	2.5694(15)	Hg(1)—I(2)	2.6667(5)
Hg(1)—I(1)	2.7139(5)	Hg(1)—I(1)#1	3.2870(5)
I(1)—Hg(1)#1	3.2870(5)	S(1)—C(7)	1.789(6)
P(1)—C(31)	1.809(6)	P(1)—C(11)	1.812(5)
P(2)—C(41)	1.805(6)	P(2)—C(51)	1.815(5)
P(2)—C(61)	1.833(6)	O(1)—C(1)	1.304(7)
O(2)—C(1)	1.229(7)	C(1)—C(2)	1.510(8)
C(2)—C(3)	1.398(8)	C(2)—C(7)	1.406(8)
C(3)—C(4)	1.371(10)	C(4)—C(5)	1.395(12)
C(5)—C(6)	1.368(10)	C(6)—C(7)	1.379(9)
O(1)—Pt(1)—P(2)	176.01(11)	O(1)—Pt(1)—P(1)	81.89(12)
P(2)—Pt(1)—P(1)	98.55(5)	O(1)—Pt(1)—S(1)	85.65(12)
P(2)—Pt(1)—S(1)	94.42(5)	P(1)—Pt(1)—S(1)	165.36(5)
S(1)—Hg(1)—I(2)	106.91(3)	S(1)—Hg(1)—I(1)	124.85(3)
I(2)—Hg(1)—I(1)	125.800(18)	S(1)—Hg(1)—I(1)#1	94.99(3)
I(2)—Hg(1)—I(1)#1	103.898(17)	I(1)—Hg(1)—I(1)#1	87.757(14)
Hg(1)—I(1)—Hg(1)#1	92.244(14)	C(7)—S(1)—Pt(1)	99.2(2)
C(7)—S(1)—Hg(1)	105.78(18)	Pt(1)—S(1)—Hg(1)	96.51(5)
C(31)—P(1)—C(11)	106.0(3)	C(31)—P(1)—C(21)	102.0(3)
C(11)—P(1)—C(21)	105.6(3)	C(31)—P(1)—Pt(1)	115.69(19)
C(11)—P(1)—Pt(1)	102.83(18)	C(21)—P(1)—Pt(1)	123.32(18)
C(41)—P(2)—C(51)	111.4(3)	C(41)—P(2)—C(61)	101.4(3)
C(51)—P(2)—C(61)	102.5(3)	C(41)—P(2)—Pt(1)	111.98(19)
C(51)—P(2)—Pt(1)	112.46(17)	C(61)—P(2)—Pt(1)	116.17(18)
C(1)—O(1)—Pt(1)	126.0(3)	O(2)—C(1)—O(1)	121.1(5)
O(2)—C(1)—C(2)	119.1(5)	O(1)—C(1)—C(2)	119.8(5)
C(3)—C(2)—C(7)	118.4(5)	C(3)—C(2)—C(1)	116.5(5)
C(7)—C(2)—C(1)	125.0(5)	C(4)—C(3)—C(2)	121.6(7)
C(3)—C(4)—C(5)	119.7(7)	C(6)—C(5)—C(4)	119.1(7)
C(5)—C(6)—C(7)	122.3(7)	C(6)—C(7)—C(2)	119.0(6)
C(6)—C(7)—S(1)	115.3(5)	C(2)—C(7)—S(1)	125.7(4)

alicylate ligand is twisted so that O(1) and O(2) are displaced by ca 0.3 Å from the plane of the rest of the ligand. Somewhat unexpectedly, it was found that the thiosalicylate ligand plane of **1a** was inclined at an angle of 46° to the platinum coordination plane. This feature is maintained in the mercury adduct **6b**, with the corresponding angle increased to 59°. This is not an essential requirement to accommodate the Hg atom at the S, since the corresponding $HgBr_2$ adduct **6a** forms by coordination from the S atom in a complex in which the chelating ligand lies essentially within the coordination plane.

NMR spectroscopy and electrospray mass spectrometry

Reactivity of the platinum–thiolate complexes towards mercury(II) halides, and other metal centres, can be conveniently monitored using ^{31}P NMR spectroscopy; chemical shift and coupling constant data are summarised in Table 2. For example, after addition of an excess of solid HgI_2, $HgBr_2$ or $HgCl_2$ to a $CDCl_3$ solution of **1a**, the $^{31}P\text{-}\{^1H\}$ NMR spectra showed overall similar features to the starting complex (*viz* an AB spin system with ^{195}Pt satellites), but with the chemical shifts of all triphenylphosphines shifted to lower δ by about 3–4 ppm; no $^{199}Hg\text{-}^{31}P$ coupling could be ascertained in any of the complexes. The $^1J(PtP)$ coupling constant for the PPh_3 ligand *trans* to the thiolate increases from 2884 Hz in **1a** to 3073, 3112, 3156 Hz on addition of HgI_2, $HgBr_2$ or $HgCl_2$ respectively. These are similar to those observed previously [4] and are consistent with the reduction in the *trans* influence of the thiolate ligand upon coordination to mercury(II). There is a concomitant decrease in the magnitude of $^1J(PtP)$ for the phosphine *trans* to the carboxylate upon coordination of the sulphur atom. The decreasing electron-withdrawing nature in the series $HgCl_2 > HgBr_2 > HgI_2$ influences the strength of interaction; the more electrophilic $HgCl_2$ effects a greater interaction with the Pt—S group, strengthening the *trans* Pt—P bond, increasing its coupling constant. Correspondingly, the $^1J(PtP)$ coupling constant for the phosphine *trans* to oxygen (i.e. *cis* to the thiolate) decreases from the starting complex (3899 Hz) to the $HgBr_2$ complex (3842 Hz), and even further for the $HgCl_2$ complex (3808 Hz).

The trends in $^1J(PtP)$ values are also extended further to the HgI_2 complexes of **1a**, **4a** and **4b**. It is interesting for this series of complexes to compare the magnitude of change in $^1J(PtP)$ values for both triphenylphosphines, upon complex formation with HgI_2. Upon addition of HgI_2 to **1a**, the value of $^1J(PtP)$ for the phosphine *trans* to thiolate increases by 182 Hz, while that for the phosphine *trans* to carboxylate decreases by 88 Hz. For **4a** and **4b** upon addition of HgI_2, the $^1J(PtP)$ values for the phosphines *trans* to thiolate increase by 278 and 304 Hz respectively, while the values of $^1J(PtP)$ for the phosphines *trans* to carboxylate decrease by 151 and 159 Hz respectively. Thus, the changes upon coordination for **4a** and **4b** are almost twice those for **1a**, suggesting a much stronger interaction of the HgI_2 moiety with complexes **4**. This

Table 2. A comparison of ^{31}P NMR spectroscopic data, recorded in $CDCl_3$ solution, for the platinum–thiolate complexes[a] and their HgX_2 adducts, isolated by crystallisation, or generated *in situ*[b]

		PPh_3 *trans* S		PPh_3 *trans* O		
Complex	Added MX_2[c]	δ/ppm	$^1J(PtP)$/Hz	δ/ppm	$^1J(PtP)$/Hz	$^2J(PP)$/Hz
1a	—	24.5	2884	10.2	3899	22
1a	$HgCl_2$	21.0	3156	6.5	3808	21
1a	$HgBr_2$	21.2	3112	7.0	3842	22
1a	HgI_2	21.4	3073	7.6	3807	22
6b	—	23.2	3055	7.8	3811	22
1a	CdI_2	24.3	2893	9.9	3912	22
1a	$CdCl_2$	24.5	2884	10.1	3905	22
1a	$PdCl_2$	24.5	2887	10.1	3903	22
4a	—	22.1	2868	12.1	3766	22
6c	—	19.4	3146	8.4	3615	23
4b	—	22.2	2849	12.5	3790	22
6d	—	19.2	3153	8.3	3631	23

[a] NMR spectroscopic properties for the starting thiolate complexes **1** and **4** are from Ref. [2].

[b] Data are also included for other metal centres where little or no interaction is considered to occur, evidenced by no change in the ^{31}P chemical shifts or coupling constants. Experiments were carried out by dissolving the platinum complex in $CDCl_3$, adding the solid metal salt (where appropriate), briefly shaking, and then recording the ^{31}P NMR spectrum.

[c] Addition of $ZnBr_2$ produced a mixture of products, including *cis*-$[PtBr_2(PPh_3)_2]$.

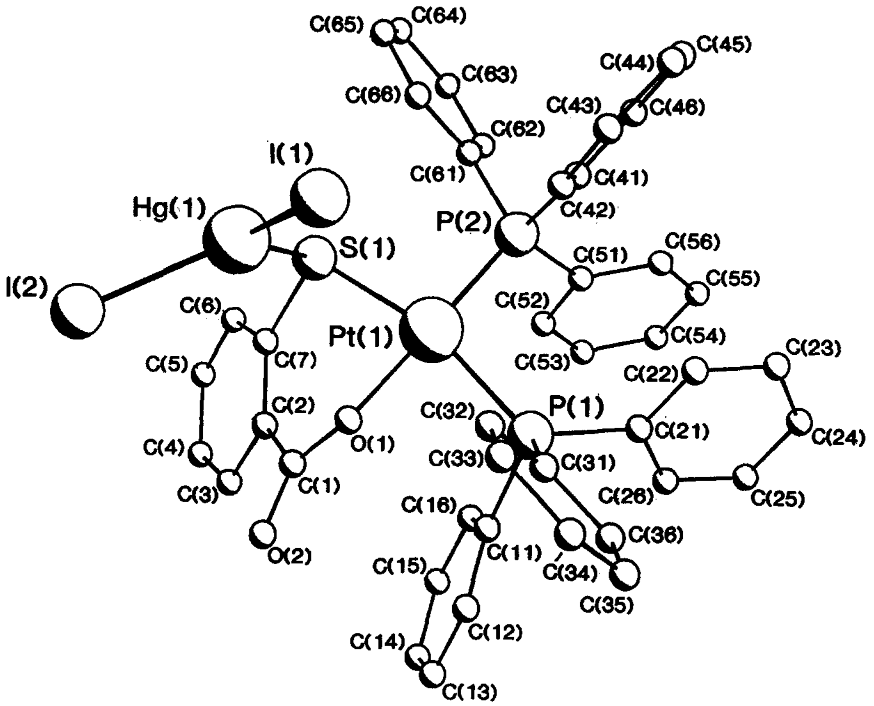

Fig. 1. Molecular structure of the unique half of complex **6b** showing the atom numbering scheme.

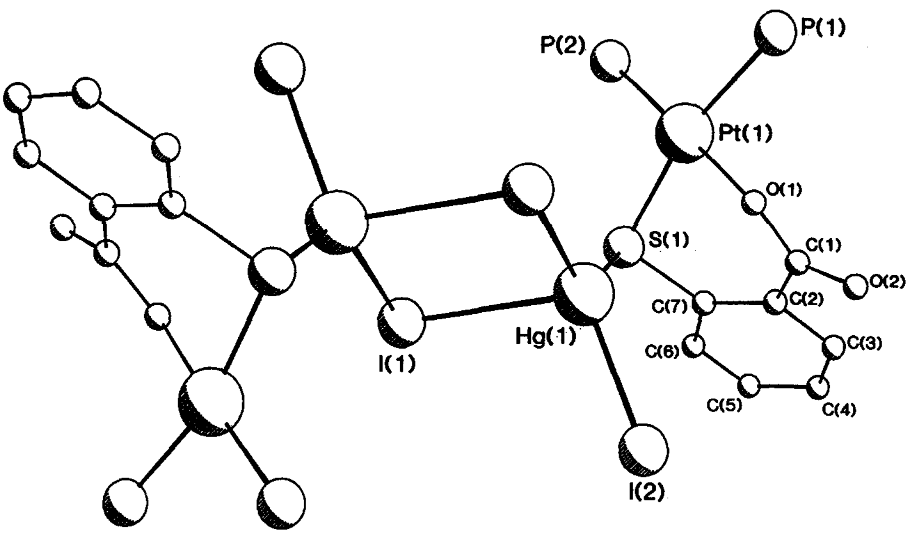

Fig. 2. Diagram showing the central core unit of complex **6b**; all hydrogen and triphenylphosphine carbon atoms have been omitted for clarity.

is not unexpected, since the *ortho*-phenyl hydrogen of the thiosalicylate group is likely to experience a steric interaction with a metal centre coordinated to the sulphur atom.

It is worth noting that a small amount of *cis*-$[PtCl_2(PPh_3)_2]$ is formed as a by-product along with **6f** in the reaction of **1a** with $HgCl_2$, identified by ^{31}P NMR spectroscopy. Upon allowing the solution to stand overnight with excess $HgCl_2$, no additional *cis*-$[PtCl_2(PPh_3)_2]$ was formed. No $[PtBr_2(PPh_3)_2]$ or

$[PtI_2(PPh_3)_2]$ complexes were detected by NMR in the reactions with $HgBr_2$ or HgI_2, presumably due to the less electrophilic nature of these metal centres.

Reaction of **1a** with $Hg(SCN)_2$ produces a rather complex mixture of products, identified by ^{31}P NMR, possibly in part as a result of thiocyanate transfer from mercury to platinum. Similarly, a mixture of products was observed with added $ZnBr_2$, though *cis*-$[PtBr_2(PPh_3)_2]$ could be identified from its $^{31}P\text{-}\{^1H\}$ NMR spectrum. There appeared to be no interaction between **1a** and either $CdCl_2$, CdI_2 or $PdCl_2$, by ^{31}P NMR spectroscopy.

Electrospray mass spectrometry (ESMS) has also been evaluated as a potential technique for characterisation of the complexes formed between the cyclic platinum–thiolate complexes and mercury(II) ions, particularly in light of the NMR results described above. One of the principal attractions of the ESMS technique is that it allows the direct analysis of species in solution [8]. We have previously used ESMS to characterise the neutral thiosalicylate complexes **1**–**3** [2]. However, when crystals of the HgI_2 adduct **6b** were analysed in MeCN—H_2O solution, no Pt—Hg adducts could be observed. Instead, the spectrum indicated that the complex had completely dissociated, with the starting complex $[\mathbf{1a}+H]^+$ being the base peak at *m*/*z* 872, as observed for the pure complex **1a**. Identical results were observed for the complex **6d**. Complexes of mercury(II) halides with thioether ligands would be expected to relatively labile in solution [6], although a thiolate-bridged structure might be expected to be less labile.

Addition of a small quantity of NaCl to the ESMS solution of **6b** in MeCN—H_2O solution yielded the species HgI_3^- (*m*/*z* 583), HgI_2Cl^- (*m*/*z* 491) and $HgICl_2^-$ (*m*/*z* 399) in the negative ion ESMS spectrum; no adducts of the parent thiosalicylate complex **1a** with mercury species were detected.

Thiosalicylate transfer reactions with Thiomersal ($EtHgSC_6H_4CO_2Na$)

Following the successful reactions between the platinum–thiosalicylate complex **1a** and HgX_2, we wished to investigate whether the organomercury complex Thiomersal (Merthiolate, sodium ethylmercurithiosalicylate), which contains a monodentate thiosalicylate ligand, could be used as a ligand towards platinum(II) centres. This was considered as a possible alternative route to other types of platinum–mercury thiosalicylate-bridged complexes. Thiomersal is of interest since it has biological activity and has been used as an antiseptic [9].

The reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with one mole equivalent of Thiomersal in hot methanol yields the platinum–thiosalicylate complex **1a** *via* a thiolate-transfer reaction, eqn (1). In this case, the thiolate ligand is completely transferred from mercury(II) to platinum(II), and thus EtHgCl and NaCl are the presumed byproducts, though no attempt was made to confirm these;

$$cis\text{-}[PtCl_2(PPh_3)_2] + EtHgSC_6H_4CO_2Na \rightarrow [\overline{Pt(SC_6H_4CO_2})(PPh_3)_2] \quad \mathbf{1a}$$

Eq. 1 $(+EtHgCl+NaCl)$

Analogous reactions also proceeded readily when $[PdCl_2(dppe)]$ [dppe = 1,2-bis(diphenylphosphino) ethane] or $[NiCl_2(dppe)]$ were reacted with Thiomersal, also in methanolic solution, giving the previously reported [2] thiosalicyate complexes $[\overline{M(SC_6H_4CO_2})(dppe)]$ (M=Ni, Pd). In methanol solvent, there is a vary rapid colour change to that of the product. However, the reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with Thiomersal can be slowed down by carrying it out in $CDCl_3$, so that the course of the reaction can be followed by ^{31}P NMR spectroscopy. The reaction proceeds smoothly, with consumption of the starting *cis*-$[PtCl_2(PPh_3)_2]$ complex with a concomitant increase in intensity of resonances due to the thiosalicylate product **1a**. Only one very minor additional peak was present, and since $^1J(PtP)$ data could not be discerned, it is not possible to comment upon the identity of this species. Any possible intermediates formed in the reaction, such as **7**, containing Pt—S—Hg thiosalicylate-bridged species clearly do not reach significant concentrations under these conditions.

In a separate experiment, the reaction was monitored by positive-ion ESMS. An equimolar mixture of *cis*-$[PtCl_2(PPh_3)_2]$ and Thiomersal was analysed several minutes after mixing in 1 : 1 MeCN—H_2O. The spectrum showed the platinum–thiosalicylate complex $[\mathbf{1a}+H]^+$ at *m*/*z* 872 as the predominant ion together with a small ion at *m*/*z* 894, assigned as the sodium adduct $[\mathbf{1a}+Na]^+$; this ion is not unexpected, since Thiomersal is a sodium carboxylate salt. Addition of alkali metal salts to pure samples of **1a** also yielded $[M+\text{cation}]^+$ ions in the ESMS spectra [2]. The ion $[(\mathbf{1a})_2+H]^+$ was also observed at *m*/*z* 1744, as observed previously for **1a** [2]. A very weak ion at around *m*/*z* 1100 can be tentatively assigned as the species $[(Ph_3P)_2\overline{Pt(SC_6H_4CO_2})+EtHg]^+$. This complex, for which **7** is a likely structure, is a plausible intermediate in the thiosalicylate transfer reaction. However, an isotope pattern could not be obtained for this ion, and so its assignment remains tentative. The ESMS results therefore parallel the NMR results by showing no significant intermediates. The absence of the ions $[PtCl(PPh_3)_2]^+$ and $[PtCl(MeCN)(PPh_3)_2]^+$ which are observed for *cis*-$[PtCl_2(PPh_3)_2]$ in MeCN—H_2O solutions also confirms the rapid conversion of *cis*-$[PtCl_2(PPh_3)_2]$ into **1a** [10]. No platinum-containing intermediates were observed when the *cis*-$[PtCl_2(PPh_3)_2]$/Thiomersal reaction mixture was analysed in negative-ion mode.

Thiolate transfer reactions have been documented in the literature, generally transferring the thiolate ligand from a harder metal centre to a softer one, which provides a driving force for the reaction [11]. Despite the very strong affinity of mercury for thiolate ("mercaptan") ligands, it is evident that the formation of the chelating thiosalicylate complexes, possibly assisted by precipitation of NaCl, is the major driving force in this exchange reaction. The tendency for mercury(II) thiolate complexes to adopt low coordination numbers, in many cases typified by linear two-coordination, is also likely to bear a major influence [12].

EXPERIMENTAL

General experimental procedures have been described previously [2]. All complexes described in this work are air-stable, and reactions were carried out without regard for the exclusion of air. Diethyl ether and petroleum spirits (bp 40–60°C) were LR grade, while dichloromethane was distilled from CaH_2 prior to use. Standardless EDAX analyses were obtained on a Hitachi S4000 scanning electron microscope.

The following compounds were used as supplied from BDH: red mercury(II) iodide, mercury(II) bromide, mercury(II) chloride, cadmium iodide, cadmium chloride and zinc bromide. The complexes $[\overline{\mathrm{Pt(SC_6H_4CO_2}})\mathrm{(PPh_3)_2}]$ **1a**, $[\overline{\mathrm{Pt(SCH_2CO_2}})\ \mathrm{(PPh_3)_2}]$ **4a** and $[\overline{\mathrm{Pt(SCHMeCO_2}})\mathrm{(PPh_3)_2}]$ **4b** were prepared as described previously [2]. $[\mathrm{PdCl_2(dppe)}]$ was prepared by ligand substitution of the COD ligand of $[\mathrm{PdCl_2(COD)}]$ [13] with 1 mole equivalent of dppe in CH_2Cl_2. $[\mathrm{NiCl_2(dppe)}]$ was prepared by the literature procedure [14].

Synthesis of the thiolate-bridged platinum–mercury complexes **6**. *General method*

To a solution of the platinum complex (ca 100 mg) in dichloromethane (ca 2 cm^3) was added an excess of the solid mercury(II) halide, and the mixture briefly shaken. After allowing the excess mercury salt to settle, the supernatant was removed by a Pasteur pipette and transferred to a glass vial. Vapour diffusion of diethyl ether into the solution yielded a crystalline or microcrystalline product in most cases, which was dried *in vacuo* for 24 h.

$\{[\overline{Pt(SC_6H_4CO_2})(PPh_3)_2]\cdot HgI_2\}_2$

The platinum complex **1a**. 0.33MeOH (82 mg, 0.093 mmol) and HgI_2 (190 mg, 0.418 mmol) gave bright yellow crystals of **6b** (122 mg, 99%), m.p. 198–203°C (decomp.). Despite several attempts, satisfactory elemental analytical data could not be obtained for this compound. Found: C, 35.9; H, 2.1; N, 0.0. $C_{43}H_{34}O_2P_2PtSHgI_2$ requires C, 38.9; H, 2.6; N, 0.0%. The presence of Pt, Hg and I were confirmed using EDAX analysis.

$\{[\overline{Pt(SCH_2CO_2})(PPh)_2]\cdot HgI_2\}_2$

The platinum complex **4a** (75 mg, 0.093 mmol) and HgI_2 (170 mg, 0.374 mmol) gave light yellow microcrystals of **6c** (94 mg, 80%), m.p. 207–209°C (decomp.). Found: C, 36.4; H, 2.4; N, 0.0. $C_{38}H_{32}O_2P_2PtSHgI_2$ requires C, 36.1; H, 2.6; N, 0.0%.

$\{[\overline{Pt(SCHMeCO_2})(PPh_3)_2]\cdot HgI_2\}_2$

The platinum complex **4b** (79 mg, 0.096 mmol) and HgI_2 (224 mg, 0.493 mmol) gave a pale yellow solid of **6d** (59 mg, 48%), m.p. 204–208°C (decomp.). Found: C, 36.8; H, 2.4; N, 0.0. $C_{39}H_{34}O_2P_2PtSHgI_2$ requires C, 36.6; H, 2.7; N, 0.0%.

Attempted synthesis of $\{[\overline{Pt(SC_6H_4CO_2})COD]\cdot HgI_2\}_2$

The platinum complex $[\overline{\mathrm{Pt(SC_6H_4CO_2}})\mathrm{(COD)}]$ and excess HgI_2 gave bright yellow crystals, which were found to be the unreacted platinum complex, by elemental analysis: Found: C, 39.6; H, 3.4. $C_{15}H_{16}O_2PtS$ requires C, 39.6; H, 3.5%.

Thiolate exchange reaction between cis-$[PtCl_2(PPh_3)_2]$ *and* $EtHgSC_6H_4CO_2Na$

A suspension of *cis*-$[\mathrm{PtCl_2(PPh_3)_2}]$ (391 mg, 0.495 mmol) and Thiomersal (200 mg, 0.494 mmol) in methanol (25 cm^3) was refluxed for 2 h; the mixture turned bright yellow over the course of several minutes. Water (50 cm^3) was added, and the resulting yellow precipitate filtered, washed with water and diethyl ether, and dried *in vacuo*. Yield 378 mg (88%). The product was identified as **1a** by ^{31}P-{^{1}H} NMR spectroscopy.

Thiolate exchange reaction between $[PdCl_2(dppe)]$ *and* $EtHgSC_6H_4CO_2Na$

A suspension of $[\mathrm{PdCl_2(dppe)}]$ (109 mg, 0.189 mmol) and Thiomersal (77 mg, 0.189 mmol) was refluxed in methanol (20 cm^3) for 20 min, to give an orange suspension. Water (60 cm^3) was added, the product filtered, washed with water (10 cm^3) and ether (10 cm^3) and dried under vacuum to give 88 mg (71%) of **2a**, identified by ^{31}P-{^{1}H} NMR spectroscopy.

Thiolate exchange reaction between $[NiCl_2(dppe)]$ *and* $EtHgSC_6H_4CO_2Na$

A suspension of $[\mathrm{NiCl_2(dppe)}]$ (77 mg, 0.146 mmol) and Thiomersal (59 mg, 0.146 mmol) was refluxed in methanol (10 cm^3) for 30 min, to give a red-orange solution/suspension. Water (50 cm^3) was added, the product filtered, washed with water (10 cm^3) and ether (10 cm^3) and dried under vacuum to give 60 mg (68%) of $[Ni(SC_6H_4CO_2)(dppe)]$, identified by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy.

Crystal structure determination of $\{[\overline{Pt(SC_6H_4CO_2)}(PPh_3)_2]\cdot HgI_2\}_2$ **6b**.

Bright yellow crystals of **6b** were obtained from the slow diffusion of ether into a CH_2Cl_2 solution. The unit cell dimensions and intensity data were obtained on a Siemens SMART diffractometer. The data collection nominally covered over a hemisphere of reciprocal space, by a combination of three sets of exposures; each set had a different ϕ angle for the crystal and each exposure 0.3° in ω. The crystal to detector distance was 5.0 cm. The data set was corrected empirically for absorption using SADABS [15].

Crystal data and refinement for **6b**

$C_{43}H_{34}HgI_2O_2P_2PtS$. 0.5 $(C_2H_5)_2O$, M_r 1363.24, triclinic, space group $P\bar{1}$, $a = 12.4725(2)$, $b = 12.6573(2)$, $c = 14.9196(1)$ Å, $\alpha = 79.420(1)$, $\beta = 70.357(1)$, $\gamma = 82.106(1)$°, U 2173.27(5) $Å^3$. $D_{calc} = 2.083$ g cm^{-3}, $Z = 2$, $F(000)$ 1278, $\mu(Mo\text{-}K_\alpha) = 8.323\ mm^{-1}$. Crystal size $0.52 \times 0.32 \times 0.24$ mm. A total of 21,943 reflections were collected at 203(2) K in the range $1.5° < \theta < 28.2°$, corresponding to 9691 unique data ($R_{int} = 0.0368$), $T_{max,min}$ 0.2633, 0.1342.

The structure was solved by automatic interpretation of a Patterson map and developed routinely. In a penultimate difference map an Et_2O of crystallisation, disordered across an inversion centre, was revealed. In the final cycles of least-squares refinement based on F^2 against all data, all non-hydrogen atoms were treated anisotropically and hydrogen atoms (other than those of the disordered solvent) were included in their calculated positions. The refinement converged with $R_1 = 0.0387$ [for 6817 data with $I > 2\sigma(I)$], $R_1 = 0.0437$, $wR_2 = 0.1033$, GoF 1.079 (all data). The largest features in a final difference map were $+2.707/-3.634$ e $Å^{-3}$ adjacent to heavy metal atoms. The SHELX-96 package [16] was used for all calculations.

Complete lists of atomic coordinates, bond parameters and tables of thermal parameters and hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre (CCDC), and are available from the authors on request.

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