Preparation and Characterisation of $[PPh_4][\textit{fac}\text{-}PtX_3(S_4N_4)]$ (X = Cl, Br or I)

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Reaction of $[PPh_4]X$ (X = Cl or Br) with $K_2[PtX_4]$ in water leads to either $[PPh_4]_2[PtCl_4]$ or a mixture of $[PPh_4]_2[PtBr_4]$ and $[PPh_4]_2[Pt_2Br_6]$, depending upon the halogen present; reaction of PtI_2 with KI and $[PPh_4]I$ leads to $[PPh_4]_2[Pt_2I_6]$ as the sole product. All of these compounds react with S_4N_4 in CH_2Cl_2 to give the platinum(IV) species $[PPh_4][PtX_3(S_4N_4)]$ which contain the $S_4N_4^{2-}$ ligand. The chloro species may also be obtained by metathesis from $K[PtCl_3(S_4N_4)]$ which is itself prepared by reaction of S_4N_4 with Zeise's salt, $K[PtCl_3(C_2H_4)]$, in tetrahydrofuran. Comparison of the ^{15}N NMR spectra of labelled complexes with that of $[Ir(CO)Cl(S_4{}^{15}N_4)(PPh_3)]$ indicates that in all cases this ligand adopts a facial co-ordination mode, bound by two sulfurs and one nitrogen. Two $^2J(^{15}N-^{15}N)$ interactions of magnitude 3 and 5.5 Hz are observed within the ligand.

Until recently conventional wisdom suggested that reactions of S_4N_4 with transition-metal complexes would invariably result in gross disruption of the S_4N_4 structure and the production of ligands such as $S_2N_2^{2-}$, S_3N^-, $S_2N_3^{3-}$, *etc.*[1] This assumption was eventually proved incorrect by Roesky and co-workers[2a] who reinvestigated the reaction of $[Ir(CO)Cl(PPh_3)_2]$ with S_4N_4[2b] and showed that the product, $[Ir(CO)Cl(S_4N_4)(PPh_3)]$ **1**, contained the novel $S_4N_4^{2-}$ ligand, co-ordinated facially *via* two sulfurs and one nitrogen. Subsequently we reported on the reaction of S_4N_4 with $[PtCl_2(PMe_2Ph)]_2$[3] which yields $[PtCl_2(S_4N_4)(PMe_2Ph)]$; the latter contains a meridionally bound $S_4N_4^{2-}$ ligand. Upon heating, this compound isomerises to a complex of the same ligand bound by two nitrogens and one sulfur[4] (and not a facially co-ordinated analogue of the starting material, as we had originally proposed[5]).

Here we report on the reaction of Zeise's salt, $K[PtCl_3(C_2H_4)]$, with S_4N_4 in tetrahydrofuran (thf) which leads to $K[PtCl_3(S_4N_4)]$ **2**. Furthermore, we have also prepared $[PPh_4][PtX_3(S_4N_4)]$ by an alternative strategy. Comparison of the ^{15}N NMR spectra of the labelled complexes with that of labelled **1** shows that they all have the same (*i.e.* facial) co-ordination mode.

Experimental

General.—Microanalyses were performed by University College, London, Microanalytical service; IR spectra were recorded as KBr disks using a PE 1720X FT IR spectrometer. The starting materials $K_2[PtX_4]$ (X = Cl or Br) and PtI_2 were used as received (Johnson Matthey). All the reactions involving S_4N_4 (**CAUTION:** explosive!) were performed under an inert atmosphere (N_2) using standard Schlenk techniques. Solvents were dried and distilled before use: thf and Et_2O from sodium–benzophenone, CH_2Cl_2 from calcium hydride. The compound $S_4{}^{15}N_4$ was prepared by the literature method[6] from 98% ^{15}N-enriched NH_4Cl (Aldrich). The ^{15}N and ^{195}Pt NMR spectra were recorded on a JEOL JNM EX270 spectrometer using CD_2Cl_2 as solvent and operating at either 27.38 MHz (^{15}N referred to liquid ammonia) or 58 MHz {^{195}Pt, referred to $Na_2[PtCl_6]$ (aq)}; the ^{14}N spectrum was recorded on a Bruker CXP 300 spectrometer operating at 21.682 MHz.

Preparation of Starting Materials.—The salt $[PPh_4]_2[PtCl_4]$ was prepared by the reaction of $K_2[PtCl_4]$ (0.5 g, 1.2 mmol) in water (100 cm^3) with a solution of $[PPh_4]Cl$ (0.45 g, 1.2 mmol) in water–EtOH (6:1, 350 cm^3). The resulting pink precipitate was filtered off, washed with water and Et_2O and recrystallised from CH_2Cl_2–toluene (Found: C, 56.0; H, 4.1. Calc.: C, 56.8; H, 3.9%). The ^{195}Pt NMR spectrum revealed a singlet at δ −1438.

Reaction of $K_2[PtBr_4]$ (0.5 g, 0.8 mmol) in water (100 cm^3) with $[PPh_4]Br$ (0.35 g, 0.8 mmol) in water (200 cm^3) resulted in a yellow precipitate which was filtered off, washed with water then Et_2O and recrystallised from CH_2Cl_2–toluene to give golden-green crystals. The ^{195}Pt NMR spectrum of this product revealed it to be a mixture of $[PPh_4]_2[PtBr_4]$ (δ −2407) and $[PPh_4]_2[Pt_2Br_6]$ (δ −2233) in the approximate ratio 2:1. Microanalysis confirms the presence of a mixture, in the ratio 3:1 monomer to dimer (Found: C, 45.3; H, 3.0. Calc. for 3:1 mixture: C, 45.3; H, 3.2%).

Potassium iodide (5.0 g, 0.3 mmol) was dissolved in boiling water (250 cm^3) and treated with PtI_2 (0.5 g, 1.1 mmol); the resulting solution was filtered hot and added to a boiling solution of $[PPh_4]I$ (0.52 g, 1.1 mmol) in water (150 cm^3). The resulting buff coloured precipitate was filtered off, washed with water, EtOH and Et_2O and recrystallised from CH_2Cl_2–toluene (Found: C, 31.5; H, 2.1. Calc. for $[PPh_4]_2[Pt_2I_6]$: C, 31.5; H, 2.2%). The ^{195}Pt NMR spectrum consisted of a singlet at δ −5070.

Preparation of Complexes **2**–**5**.—*Crude* $K[PtCl_3(S_4N_4)]$ **2**. A vigorously stirred solution of S_4N_4 (0.105 g, 0.57 mmol) in thf (20 cm^3) was treated with a solution of $K[PtCl_3(C_2H_4)]$[7] (0.2 g, 0.54 mmol) in the same solvent (20 cm^3), added dropwise over a period of *ca.* 5 min. The colour of the solution slowly darkened to orange-red and after 2 h was reduced to 5 cm^3 *in vacuo*. Addition of Et_2O (100 cm^3) yielded an orange solid which was filtered off and washed with CH_2Cl_2 (2 × 50 cm^3) and dried *in vacuo*. Yield 0.22 g, 77%. Nitrogen content 9.8% (calc. 10.7%).

$[PPh_4][PtCl_3(S_4N_4)]$ **3**. (*i*) The salts $K[PtCl_3(S_4N_4)]$ (0.2 g, 0.38 mmol) and $[PPh_4]Cl$ (0.135 g, 0.36 mmol) were dissolved in thf–CH_2Cl_2 (1:1, 30 and 20 cm^3 respectively) and the resulting solutions combined with vigorous stirring. After 15 min the solvent was removed *in vacuo* and the resulting solid extracted into CH_2Cl_2 (50 cm^3), filtered through Celite then concentrated and compound **3** precipitated as a pale red-orange solid by addition of Et_2O (100 cm^3). Yield 0.215 g, 69% based upon the potassium salt. Crystalline samples were prepared by

Table 1 Nitrogen-15 chemical shift values and coupling constants (Hz) for complexes **1** and **3**–**5**

Compound	Nitrogen atom	δ	$^2J(^{15}N-^{15}N)$	$J(^{195}Pt-^{15}N)$
$[Ir(CO)Cl(S_4N_4)(PPh_3)]$	N^1	406	3.0	—
	N^2	270	3.0	—
	N^3	179	5.5	—
	N^4	355	5.5	—
$[PPh_4][PtCl_3(S_4N_4)]$	N^1	434	3.2	173
	N^2	287	3.1	*
	N^3	170	5.9	12
	N^4	351	5.8	*
$[PPh_4][PtBr_3(S_4N_4)]$	N^1	433	3.0	150
	N^2	283	3.0	6
	N^3	164	5.6	16
	N^4	343	5.6	*
$[PPh_4][PtI_3(S_4N_4)]$	N^1	441	3.0	173
	N^2	283	3.0	*
	N^3	165	5.6	*
	N^4	336	5.6	*

* Coupling not resolved.

slow diffusion of Et_2O into CH_2Cl_2 solutions (Found: C, 34.4; H, 2.2; N, 6.6. Calc.: C, 34.9; H, 2.4; N, 6.8%).

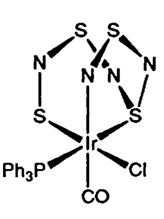
(*ii*) The salt $[PPh_4]_2[PtCl_4]$ (0.117 g, 0.09 mmol) and S_4N_4 (0.035 g, 0.19 mmol) were dissolved in CH_2Cl_2 (30 cm^3) and the resulting orange solution stirred for 6 d. Slow diffusion of Et_2O into the concentrated solution resulted in very dark crystals of compound **3** (Found: C, 36.2; H, 2.7; N, 6.6%).

$[PPh_4][PtBr_3(S_4N_4)]$ **4**. The salt $[PPh_4]_2[PtBr_4]$–$[PPh_4]_2[Pt_2Br_6]$ (0.153 g) and S_4N_4 (0.037 g, 0.2 mmol) were dissolved in CH_2Cl_2 (30 cm^3) and the resulting red solution stirred for 24 h. Addition of Et_2O (60 cm^3) yielded an orange-red solid which was filtered off, washed with Et_2O (20 cm^3) and then dried *in vacuo* (crude yield 0.15 g). Slow diffusion of Et_2O into a concentrated CH_2Cl_2 solution of this solid resulted in very dark crystals of compound **4** (Found: C, 30.4; H, 2.0; N, 5.5. Calc.: C, 30.1; H, 2.1; N, 5.8%).

Crude $[PPh_4][PtI_3(S_4N_4)]$ **5**. The salt $[PPh_4]_2[Pt_2I_6]$ (0.183 g, 0.1 mmol) and S_4N_4 (0.038 g, 0.2 mmol) were dissolved in CH_2Cl_2 (100 cm^3) and the resulting dark red solution stirred overnight. After filtration through Celite, Et_2O (60 cm^3) was added yielding a dark brown solid which was filtered off, washed with Et_2O (20 cm^3) and dried *in vacuo* (crude yield 90 mg) (Found: C, 30.5; H, 2.1; N, 3.2. Calc.: C, 26.2; H, 1.8; N, 5.1%). IR (non-PPh_4 bands): 1059m, 949s, 882s, 642s, 599m, 450m, 407s and 357m cm^{-1}.

Results and Discussion

The discovery by Roesky and co-workers[2a] that $[Ir(CO)Cl(S_4N_4)(PPh_3)]$ **1**, the product of the reaction between S_4N_4 and $[Ir(CO)Cl(PPh_3)_2]$, is actually a complex of $S_4N_4^{2-}$ as opposed to a simple adduct as had previously been assumed raised the possibility that this novel ligand could be accommodated in a number of other systems. During investigations along these lines we were able to isolate $[PtCl_2(S_4N_4)(PMe_2Ph)]$ from the reaction of S_4N_4 with $[PtCl_2(PMe_2Ph)]_2$. As shown these two complexes both have the ligand co-ordinated *via* two sulfurs and one nitrogen but the ligand geometry is quite different in the two cases. While the ligand in the iridium complex is facially co-ordinated, retaining most of the geometry of free S_4N_4, the platinum species contains a meridionally bound ligand which is planar apart from one nitrogen and one sulfur. Clearly this difference suggests that there is great potential for chemistry involving $S_4N_4^{2-}$ in a variety of co-ordination modes, a conclusion backed up by our recent observations that the platinum species can isomerise to a complex wherein co-ordination is achieved through one sulfur and two nitrogens[4] (and not two sulfurs and one nitrogen bound facially, as we had previously suggested[5]). In an attempt to expand the chemistry of this ligand we have investigated the reaction of S_4N_4 with a variety of platinum species including $K[PtCl_3(C_2H_4)]$, $[PtCl_4]^{2-}$ and $[Pt_2I_6]^{2-}$.



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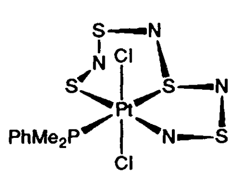


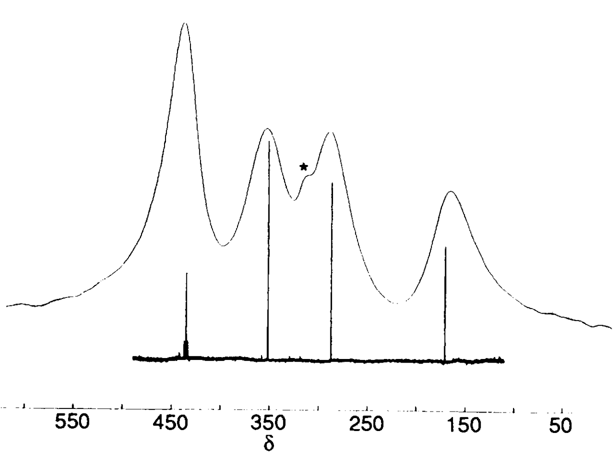


Fig. 1 Comparison of the ^{14}N (upper) and ^{15}N NMR spectra of $[PtCl_3(S_4N_4)]^-$. The ^{14}N spectrum contains peaks at δ 437, 352, 288 and 165; the peak marked * is due to dissolved nitrogen. The ^{15}N spectrum contains ^{15}N–^{15}N couplings which cannot be seen here because of the scale used

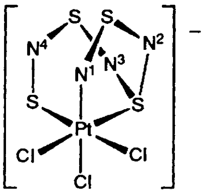
When a solution of S_4N_4 in thf is treated with $K[PtCl_3(C_2H_4)]$ in the same solvent the product is an orange compound which readily undergoes metathesis with $[PPh_4]Cl$ [equation (1)] to give a compound analysing as $[PPh_4][PtCl_3(S_4N_4)]$ **3**.

$$K[PtCl_3(S_4N_4)] + [PPh_4]Cl \longrightarrow [PPh_4][PtCl_3(S_4N_4)] + KCl \quad (1)$$

Compound **3** can readily be crystallised by slow diffusion of diethyl ether into a CH_2Cl_2 solution, though unfortunately we have been unable to solve the structure by X-ray techniques due to disorder problems. We can, however, unequivocably assign a structure to **3** by the use of ^{15}N labelling, which allows us to probe the nature of the ligand by ^{15}N NMR spectroscopy. Although an expensive technique, this is offset by the many advantages it offers when compared to ^{14}N NMR. This is well illustrated by Fig. 1 which compares the ^{14}N and ^{15}N NMR spectra of **3** in unlabelled and labelled forms respectively. The first point of note is that although the linewidths in the ^{14}N case are very large one can easily resolve four different resonances and conclude that the four nitrogens are inequivalent. However, this is the limit to the information that can be gleaned from the spectrum. In contrast, the ^{15}N spectrum has very much smaller linewidths and as a result two important types of coupling can be resolved. First, there is a ^{195}Pt–^{15}N coupling of 173 Hz associated with the peak at δ 434; clearly, therefore, this resonance is associated with a metal-bound nitrogen. In addition pairs of peaks show the presence of ^{15}N–^{15}N interactions. Thus the two signals at δ 434 and 287 couple to each other with a splitting of 3.1 Hz while those at

Table 2 Platinum-195 chemical shift values for starting materials and complexes **3**–**5**

Complex	δ X = Cl	Br	I
$[PPh_4]_2[PtX_4]$	−1438	−2407	—
$[PPh_4]_2[Pt_2X_6]$	—	−2233	−5070
$[PPh_4][PtX_3(S_4N_4)]$	−1502	−2222	−3662



δ 351 and 170 show a 5.8 Hz coupling. These results confirm the presence of four inequivalent nitrogens, with one bound to the metal, but cannot in themselves distinguish between the meridional geometry seen in $[PtCl_2(S_4N_4)(PMe_2Ph)]$ and the facial structure of **1**. This problem is resolved, however, when we consider the ^{15}N NMR spectrum of labelled **1** (Table 1). The chemical shift values for the nitrogens in **1** are very similar in value to those of **3** and related complexes **4** and **5** (see below), indicating similar environments. This correlation is further enhanced by the similarity in the $^{2}J(^{15}N-^{15}N)$ coupling constants; in the meridional complexes coupling between N(2) and N(3) is also observed.[4] Thus we can conclude that the anions in **2** and **3** have the structure shown above.

In order to expand the chemistry of these systems we have investigated the reaction of S_4N_4 with a number of other species. Compounds of the type $[Pt_2X_6]^{2-}$ (X = Cl, Br or I) have obvious potential to react with S_4N_4 *via* cleavage of the bridging halide bonds. Reaction of PtI_2 with KI and $[PPh_4]I$ gives $[PPh_4]_2[Pt_2I_6]$ in good yield; however, attempts to prepare analogous chloro and bromo species by reaction of $[PPh_4]X$ with $K_2[PtX_4]$ in the ratio 1 : 1 actually result in the formation of $[PPh_4]_2[PtCl_4]$ and a mixture of $[PPh_4]_2[PtBr_4]$ and $[PPh_4]_2[Pt_2Br_6]$ respectively. Both these products, together with the iodo species, react with S_4N_4 to give $[PPh_4][PtX_3(S_4N_4)]$; if $S_4{}^{15}N_4$ is used then the ^{15}N NMR spectra of the products may be measured. In the chloro case the spectrum is identical to that of **3** indicating that a *fac* isomer has again been formed; the spectra of the other species are also similar to **3** and indicate that they have analogous structures.

The contrast between the reaction of $[PPh_4]Cl$ with $K_2[PtCl_4]$ and that of the bromo analogues cannot readily be explained. In both cases mixing a 1 : 1 ratio of starting materials would be expected to result in precipitation of the dimeric species $[PPh_4]_2[Pt_2X_6]$; in fact in the bromo case this is actually obtained as a mixture with the monomer $[PPh_4]_2[PtBr_4]$ while in the chloro case only the monomer is formed. These products have been characterised by ^{195}Pt NMR spectroscopy: $[PPh_4]_2[PtCl_4]$ is seen as a singlet at δ −1438 which compares well to a literature value[8] of δ −1437. The spectrum of the bromo products consists of two singlets at δ −2407 and −2233. We could find no literature value for the chemical shift of either $[PPh_4]_2[PtBr_4]$ or $[PPh_4]_2[Pt_2Br_6]$ although the $[NBu_4]^+$ salt of the former appears[8] at δ −2446 and, given that for $[PtCl_4]^{2-}$ the chemical shift change[8] on going from $[NBu_4]^+$ to $[PPh_4]^+$ is +24 ppm, one can calculate that $[PPh_4]_2[PtBr_4]$ should appear at *ca.* δ −2422; this compares well with the observed value of δ −2407. We have prepared $[NBu_4]_2[Pt_2Br_6]$ by reaction of $[NBu_4]Br$ with $K_2[PtBr_4]$ and measured its chemical shift as δ −2293. Thus the effect of changing from monomer to dimer is to increase the chemical shift by 153 ppm, suggesting a figure of δ −2254 for $[PPh_4]_2[Pt_2Br_6]$ which is very close to our observed value of δ −2233. Hence, we can be confident that these are indeed the two products.

Table 3 Vibrational bands (cm^{-1}) for complexes **2**–**4**

2	**3**	**4**	Assignment
1056ms	1066 (1027)m	1048 (1027)m	ν(N–S)
962ms	963 (930)s	955 (928)s	ν(N–S)
893s	897 (869)vs	890 (867)s	ν(N–S)
661s	651 (639)vs	652 (633)s	δ(N–S)
623ms	623 (605)m	609 (600)m	δ(N–S)
586ms	582 (582)s	586 (578)s	δ(N–S)
465m	466 (459)m	460 (454)m	δ(N–S)
420ms	421 (414)s	416 (409)s	δ(N–S)
367m	368 (360)m	363 (356)m	δ(N–S)
313ms	316 (314)ms		ν(Pt–Cl)
		257 (254)ms	ν(Pt–Br)

Non-$[PPh_4]^+$ bands only; ^{15}N-labelled values given in parentheses.

The reason for the variation between the two reactions is unclear but it can be related to the solubilities of the initial $[PPh_4]^+$ salts since dimer formation is favoured in the case where this salt is more soluble in water (*i.e.* the bromide). The instability of $[PtI_4]^{2-}$ precludes its formation during the preparation of $[PPh_4]_2[Pt_2I_6]$; the ^{195}Pt NMR spectrum of the latter consists of a singlet at δ −5070, which is comparable with the literature value[9] of δ −5121 observed for the $[NBu_4]^+$ salt.

The observation that S_4N_4 can react with $[PtCl_4]^{2-}$ *via* oxidative addition is somewhat surprising since previous work suggested that the presence of either a labile leaving group (such as the ethylene in Zeise's salt) or a readily cleaved bridging bond was a pre-requisite for such a reaction. We have monitored the reaction by ^{195}Pt NMR spectroscopy (see below) and have found no evidence for the formation of any long-lived intermediates prior to **3**. The reaction with $[PPh_4]_2[Pt_2I_6]$ can be shown by ^{15}N NMR spectroscopy to give $[PPh_4][PtI_3(S_4N_4)]$ **5** but unfortunately the product cannot be isolated in pure form due to the presence of impurities which crystallise out with **5**.

The ^{195}Pt chemical shifts of complexes **3**–**5** decrease in the order Cl > Br > I (Table 2), a trend which has been noted in other systems, such as $[PtX_3(PMe_3)]^-$ (X = Cl, Br or I).[10] Each spectrum consists of a doublet brought about by the presence of the large $^{1}J(^{15}N-^{195}Pt)$ coupling associated with the metal-bound nitrogen. As this coupling can also be resolved in the ^{15}N NMR spectra of the complexes it provides a useful correlation between the two techniques; this is particularly important in the case of **5**, which cannot be isolated in pure form.

The IR spectra of complexes **2**–**4** show distinctive bands due to the $S_4N_4{}^{2-}$ ligand (Table 3). On ^{15}N labelling the bands of **3** and **4** show a drop in frequency of around 10–20 cm^{-1} reflecting the presence of the heavy atoms. One disadvantage of the presence of $[PPh_4]^+$ in these systems is that it shows a number of very strong bands in the IR spectrum and thus has the potential to obscure important features of the spectrum of the anion. This problem is alleviated, however, in the spectrum of **2** which contains K^+ as cation and yet does not show any band not seen for the other species. It is difficult to rationalise the spectra except to point out that they contain bands that are very similar in frequency to those seen for other complexes of smaller ligands, such as $S_2N_2{}^{2-}$ or S_3N^-, but the overall spectrum is much more complicated than in either of these cases, reflecting the structural complexity of the $S_4N_4{}^{2-}$ ligand.

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