Synthesis and Crystal Structures of New Palladium–Sulfur–Nitrogen Complexes†

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The compound S_4N_4 reacts with $[PPh_4]_2[Pd_2X_6]$ (X = Cl or Br) in CH_2Cl_2 to give a mixture of $[PPh_4]_2[Pd_2(\mu\text{-}S_2N_2)X_6]$, $[PPh_4]_2[Pd_2(\mu\text{-}S_3N_2)X_4]$ and $[PPh_4][Pd(S_2N_2H)X_2]$. Reaction of $[PPh_4]_2[Pd_2I_6]$ with S_4N_4 in the same solvent yields an insoluble solid of empirical formula $[PPh_4][Pd_2S_6N_6I_3]$. All these reactions were investigated by ^{15}N NMR spectroscopy using samples prepared from $S_4{}^{15}N_4$. Thermolysis of $[PPh_4]_2[Pd_2(\mu\text{-}S_2N_2)Cl_6]$ in $CHCl_3$ gives an alternative polymorph (β form) of this, whereas photolysis causes the species to decompose. The crystal structures of $[PPh_4][Pd(S_2N_2H)Cl_2]$, β-$[PPh_4]_2[Pd_2(\mu\text{-}S_2N_2)Cl_6]$ and $[PPh_4]_2[Pd_2(\mu\text{-}S_2N_2)Br_6]$ have been determined.

The chemistry of complexes containing sulfur–nitrogen ligands has been extensively studied[1] and includes a wide range of ligands, such as $S_2N_2H^-$, $S_2N_2{}^{2-}$, S_3N^- and $S_2N_3{}^{3-}$. The majority of these complexes are mononuclear although notable exceptions include $[\{Pt(S_2N_2)(PPh_3)\}_2]\cdot CH_2Cl_2$[2] and $K_2[\{Ni(S_2N_2)(CN)\}_2]$,[3] which are binuclear and contain bridging $S_2N_2{}^{2-}$ groups. We have recently reported on the reaction of $[PPh_4]_2[Pd_2Cl_6]$ **1** with S_4N_4[4] which proceeds *via* cleavage of the bridging metal–halide bonds to give two dimeric products $[PPh_4]_2[Pd_2(\mu\text{-}S_2N_2)Cl_6]$ **2** and $[PPh_4]_2[Pd_2(\mu\text{-}S_3N_2)Cl_4]$ **3**. Compound **2** has a neutral bridging S_2N_2 ligand bound to the metal by the nitrogen atoms; in **3** the bridging $S_3N_2{}^{2-}$ ligand is bound to the metal through sulfurs. Here we report on further investigations into this reaction which have revealed that a third product is also formed, shown by X-ray crystallography to be $[PPh_4][Pd(S_2N_2H)Cl_2]$ **4**. This contains the $S_2N_2H^-$ ligand which we have characterised in a number of other systems and has obvious potential as a synthon utilising the reactive chloride groups.

Furthermore we have investigated reactions involving bromo and iodo analogues of **1**. In the case of the bromo compound products analogous to **2**–**4** are formed, and the crystal structure of $[PPh_4]_2[Pd_2(\mu\text{-}S_2N_2)Br_6]$ **5** is reported. In contrast the iodo species, $[PPh_4]_2[Pd_2I_6]$, reacts with S_4N_4 to give an insoluble product of empirical formula $[PPh_4][Pd_2S_6N_6I_3]$. As part of the characterisation of the new complexes the $^{15}N\text{-}\{^1H\}$ NMR spectra of ^{15}N-labelled **2**–**4**, prepared from $S_4{}^{15}N_4$, have been measured, along with those for the analogous bromo products.

Experimental

General.—Microanalyses were performed by University College, London analytical service; IR spectra were recorded as KBr discs using a PE 1720X spectrometer.

Palladium starting materials were used as received (Johnson Matthey), and converted into the desired binuclear compounds by an adaptation of the literature methods.[5] The salt $[PPh_4]_2[Pd_2Cl_6]$ **1** was prepared by the reaction of $[PPh_4]Cl$ (1.02 g, 2.7 mmol) with $Na_2[PdCl_4]$ (1.0 g, 2.7 mmol) in water (350 cm^3). The resulting precipitate was recrystallised from CH_2Cl_2–toluene; $[PPh_4]_2[Pd_2Br_6]$ was prepared by the reaction of $[PPh_4]Br$ (0.42 g, 1.0 mmol) with $K_2[PdBr_4]$ (0.5 g, 1.0 mmol) in a similar manner. The salt $[PPh_4]_2[Pd_2I_6]$ was prepared by addition of a hot, filtered solution of NaI (3.0 g, 20 mmol) and PdI_2 (0.80 g, 2.2 mmol) in EtOH (100 cm^3) to a hot solution of $[PPh_4]I$ (1.04 g, 2.2 mmol) in the same solvent (100 cm^3).

The compound S_4N_4 was prepared by the literature method[6] and handled according to accepted safety procedures.[7]

Preparation of Complexes **2**–**7**.—Reactions with S_4N_4 (**CAUTION**: explosive! see ref. 7) were performed in an inert atmosphere (N_2) using standard Schlenk techniques. Solvents were dried and distilled before use: CH_2Cl_2 from calcium hydride, pentane from sodium–benzophenone. In a typical reaction $[PPh_4]_2[Pd_2X_6]$ (X = Cl, Br or I) (0.1 mmol) and S_4N_4 (37 mg, 0.2 mmol) were mixed as solids and then CH_2Cl_2 (30 cm^3) added with stirring.

(*i*) X = Cl. A deep red solution was produced on mixing which gradually lightened over the next 24 h. After stirring for 5 d the volume of the solution was reduced to a few cm^3 *in vacuo* and the solution was transferred to a 10 mm diameter tube where it was layered with pentane. Slow diffusion of the pentane for 48 h resulted in the growth of three types of well formed crystals: dark brown and red plates and orange needles. These were separated from each other manually; IR spectroscopy[4] showed the brown and orange crystals to be $[PPh_4]_2[Pd_2(\mu\text{-}S_2N_2)Cl_6]$ **2** and $[PPh_4]_2[Pd_2(\mu\text{-}S_3N_2)Cl_4]$ **3** respectively. X-Ray crystallography revealed the red compound to be $[PPh_4][Pd(S_2N_2H)Cl_2]$ **4** (yield 5 mg, 4%, based on palladium) (Found: C, 46.8; H, 3.3; N, 4.1. Calc.: C, 47.3; H, 3.5; N, 4.6%).

(*ii*) X = Br. On mixing a dark red solution was produced. This was stirred for 5 d and then filtered through Celite. Slow diffusion of pentane into the concentrated solution resulted in well formed crystals which were separated manually into brown and red-brown plates and orange flakes. Microanalysis and IR spectroscopy showed the brown plates to be $[PPh_4]_2[Pd_2(\mu\text{-}S_2N_2)Br_6]$ **5** (yield 27 mg, 18%) (Found: C, 39.4; H, 2.8; N, 1.9. Calc.: C, 39.4; H, 2.7; N, 1.9%) and the orange flakes to be $[PPh_4]_2[Pd_2(\mu\text{-}S_3N_2)Br_4]$ **6** (yield 21 mg, 15%) (Found: C, 42.9; H, 2.9; N, 2.0. Calc.: C, 43.1; H, 3.0; N, 2.1%). The structure of **5** was also confirmed by X-ray crystallography (see below). The red-brown plates (yield 17 mg) were shown by $^{15}N\text{-}\{^1H\}$ NMR and microanalysis to be a mixture of **6** and $[PPh_4][Pd(S_2N_2H)Br_2]$ **7**; unfortunately this similarity in colour precludes the isolation of pure **7**.

(*iii*) X = I. A red-brown solution formed on mixing; after 24 h

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 X-Ray data collection, solution and refinement details

Compound	**4**	β-**2**	**5**
Empirical formula	$C_{24}H_{21}Cl_2N_2PPdS_2$	$C_{48}H_{40}Cl_6N_2P_2Pd_2S_2$	$C_{48}H_{40}Br_6N_2P_2Pd_2S_2$
Colour, habit	Red prisms	Red plates	Brown plates
Crystal size (mm)	0.18 × 0.20 × 1.0	0.04 × 0.08 × 0.55	0.036 × 0.090 × 0.666
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$C2/c$	*Pbca*
Diffractometer, radiation	Nicolet *R3m*, Cu-Kα	Siemens *P*4, Mo-Kα	Siemens *P*4, Mo-Kα
a/Å	13.667(8)	28.041(5)	13.500(2)
b/Å	13.812(6)	9.496(2)	18.225(4)
c/Å	14.166(7)	20.238(3)	20.631(4)
β/°	109.99(4)	109.65(1)	
U/Å^3	2513	5075	5076
Z	4	4	4
M	609.8	1196.4	1463.1
D_c/Mg m^{-3}	1.612	1.566	1.915
μ/mm^{-1}	10.19	1.194	5.612
F(000)	1224	2392	2824
2θ Range/°	0–116	0–45	3–50
Independent reflections (R_{int})	3378 (0.044)	4477 (0.0285)	4464 (0.00)
Observed reflections [$F > 3.0\sigma(F)$]	3313	2250	2170
Absorption correction	Face-indexed, numerical	None	Face-indexed, numerical
Minimum, maximum transmission	0.0476, 0.266	—	0.6029, 0.8132
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0005F^2$	$w^{-1} = \sigma^2(F) + 0.0013F^2$	$w^{-1} = \sigma^2(F) + 0.0007F^2$
No. of parameters refined	294	233	281
Final R (R')	0.0772 (0.0945)	0.0794 (0.0737)	0.0649 (0.0543)
Largest and mean Δ/σ	0.257, 0.047	1.467, 0.158	0.040, 0.009
Data/parameter ratio	11.3	9.7	7.7
Largest difference peak, hole/e Å^{-3}	1.65, −0.81	1.14, −0.48	0.74, −0.70

a brown precipitate **8** had appeared and on further stirring more solid was produced which was allowed to settle, the red solution was decanted and the solid washed with CH_2Cl_2 (3 × 30 cm^3) before being dried *in vacuo* (Found: C, 21.1; H, 1.6; I, 28.4; N, 6.1; S, 13.6%).

^{15}N-*Labelled Experiments.*—^{15}N NMR measurements were carried out under an inert atmosphere (N_2) using a JEOL JNM EX270 spectrometer operating at 27.38 MHz and are referred to NH_3 (l); CD_2Cl_2 was used as received. 98% Nitrogen-15-enriched $S_4{}^{15}N_4$ was made by literature methods[8] from enriched NH_4Cl (Aldrich). In a typical reaction $[PPh_4]_2[Pd_2X_6]$ (X = Cl, Br or I) (0.1 mmol) and $S_4{}^{15}N_4$ (38 mg, 0.2 mmol) were mixed as solids and then CH_2Cl_2 (30 cm^3) added with stirring. For X = Cl or Br the resulting solutions were stirred for 3 d before they were reduced to 2–3 cm^3 in volume and the ^{15}N-{^{1}H} NMR spectrum (CD_2Cl_2) of the solution recorded. Slow diffusion of pentane into the concentrated solutions yielded brown, orange and red crystals as before; these were separated manually and the ^{15}N-{^{1}H} NMR spectrum of each was measured. In the case of the iodo complex reaction for 3 d resulted in an insoluble product for which an NMR spectrum could not be obtained; details of its IR spectrum are given later.

Crystal Structure Determinations.—Details of the data collections and refinements are given in Table 1. All three structures were solved by direct methods and refined by full-matrix least-squares methods using the SHELXTL PC system.[9]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Recently we have shown that S_4N_4 reacts with $[PPh_4]_2[Pd_2Cl_6]$ **1** in CH_2Cl_2 to give a mixture of $[PPh_4]_2[Pd_2(\mu\text{-}S_2N_2)Cl_6]$ **2** and $[PPh_4]_2[Pd_2(\mu\text{-}S_3N_2)Cl_4]$ **3**, which may be crystallised in the form of brown plates and orange needles respectively (yields 38 and 13%). Further investigation shows that in addition to these two products a small yield of a red crystalline solid is also obtained. This was separated manually from **2** and **3** and shown by X-ray crystallography to be $[PPh_4][Pd(S_2N_2H)Cl_2]$ **4** which contains the $S_2N_2H^-$ ligand, protonated on the metal-bound nitrogen as was observed in the related complexes $[Pd(S_2N_2H)(PMe_2Ph)_2]BF_4$[10] and $[Pd(S_2N_2H)Cl(PMe_2Ph)]$.[11]

Compound **4** (IR spectrum in Table 2) is the first example of an $S_2N_2H^-$ species to contain two metal-bound chlorine atoms. Clearly, there is potential for substitution reactions to take place, for example where both of these reactive chlorines are replaced by a bidentate ligand to form a chelated compound. However in order to utilise this potential a satisfactory method must be found which gives **4** in a reasonable yield; efforts to do this have so far been unsuccessful. Assuming that the $S_2N_2H^-$ species could be formed by rearrangement and elimination of a chlorine from **2**, attempts were made to prepare **4** from the bridging S_2N_2 species by thermolysis and photolysis. Photolysis gave an intractable oil. Thermolysis of a pale yellow solution of **2** in $CHCl_3$ for 1 h at 95 °C gave an orange solution from which, on cooling, an orange-brown crystalline solid was obtained. The IR spectrum of this solid is similar to that of **2** (Table 3) and X-ray crystallography showed it to have the same molecular structure, though in a different polymorphic form (see later).

We have also carried out investigations into the reactions of S_4N_4 with the bromo and iodo analogues of **1**, $[PPh_4]_2[Pd_2Br_6]$ and $[PPh_4]_2[Pd_2I_6]$. The bromo species reacts in a similar manner to **1** to give $[PPh_4]_2[Pd_2(\mu\text{-}S_2N_2)Br_6]$ **5** and $[PPh_4]_2[Pd_2(\mu\text{-}S_3N_2)Br_4]$ **6** which crystallise as brown plates and orange flakes respectively. By ^{15}N-{^{1}H} NMR spectroscopy we have been able to show that $[PPh_4][Pd(S_2N_2H)Br_2]$ **7** is also formed, but so far all attempts to isolate this pure have been unsuccessful. Manual separation of the crystalline sample, which can be successfully applied to the chloro species, appears to be the only viable method of purification available for these complexes. Separation on either silica thin-layer chromatography plates or by gel permeation on, for example, a Bio-Beads column, cannot be achieved due to their ionic nature and similarity in size respectively. The structure of **5** has been confirmed by X-ray crystallography (see later).

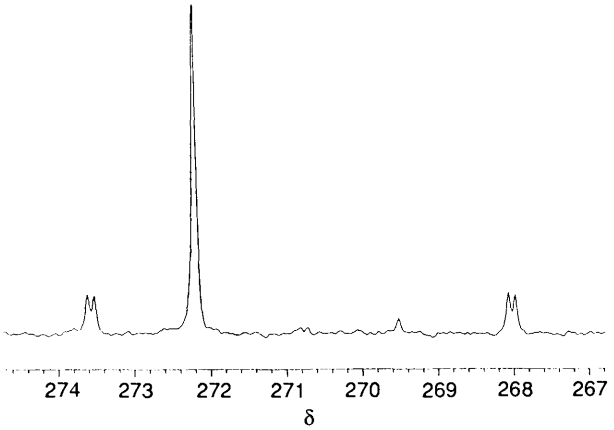

Fig. 1 The $^{15}N-\{^1H\}$ NMR spectrum of compound **2**

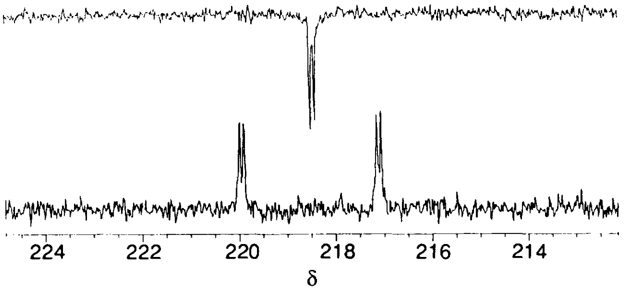

Fig. 2 Part of the $^{15}N-\{^1H\}$ (upper trace) and ^{15}N (lower trace) NMR spectra showing the $^1H-^{15}N$ and $^{15}N-^{15}N$ couplings of N(1) in compound **4**

Table 2 Vibrational bands (cm^{-1}) for $[PPh_4][Pd(S_2N_2H)Cl_2]$ and its ^{15}N-labelled analogue

	Assignment
3060(3060)s*	ν(N–H)
1044(1021)m	δ(N–H)
877mw	ν(N–S)
863(839)m	ν(N–S)
855m	ν(N–S)
848m	ν(N–S)
454(453)mw	ν(M–S)
368(368)mw	ν(M–S)
330(330)mw	ν(M–Cl)
319(311)m	ν(M–Cl)
280(278)m	ν(M–Cl)

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

Table 3 Vibrational bands (cm^{-1})

$[PPh_4]_2[Pd_2(\mu-S_2N_2)X_6]$		$[PPh_4]_2[Pd_2(\mu-S_3N_2)X_4]$		
2 (X = Cl)	**5** (X = Br)	**3** (X = Cl)	**6** (X = Br)	Assignment
877(853)m	868(844)m	643(626)m	642(626)m	ν(N–S)
436(426)mw	434(424)m	387(378)mw	383(375)m	δ(N–S)
340(341)m	265(265)m	309(308)mw	260(257)m	ν(M–X)
282(280)mw	251(250)m	291(291)mw	251(252)m	ν(M–X)

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

Table 4 Nitrogen-15 chemical shift values for palladium complexes

	δ			
Compound		X = Cl		X = Br
$[PPh_4]_2[Pd_2(\mu-S_2{}^{15}N_2)X_6]$		272		274
$[PPh_4]_2[Pd_2(\mu-S_3{}^{15}N_2)X_4]$		339		338
$[PPh_4][Pd(S_2{}^{15}N_2H)X_2]$*	$N^1(H)$	218	N^1	225
	N^2	341	N^2	346

* Observed $^2J(^{15}N-^{15}N)$ couplings for $[PPh_4][Pd(S_2{}^{15}N_2H)X_2]$ are 2.6 Hz.

In the case of the iodo species a different reaction occurs with an insoluble black solid **8** as the final product. Microanalysis (C, H, N, S and I) gives an empirical formula of $[PPh_4][Pd_2S_6N_6I_3]$ for this product. The IR spectrum consists of a number of strong peaks other than those associated with $[PPh_4]^+$ (^{15}N-labelled values in parentheses): 1045(1021)s, 912(886)mw, 820(800)m, 655(641)m, 462(457)m and 366(360) mw cm^{-1}. These data do not allow structural elucidation of **8** although there are similar features in the S–N vibrations to those observed[2] for $[\{Pt(S_2N_2)(PPh_3)\}_2]\cdot CH_2Cl_2$ suggesting that it contains the $[Pd(S_2N_2)]_2$ fragment at least. Compound **8** has only been obtained as microcrystals and has so far not been amenable to X-ray analysis.

The relatively facile preparation of $S_4{}^{15}N_4$ is a very important factor when attempting to study the NMR properties of these compounds; all of the highly abundant isotopes naturally present in the anions are quadrupolar, thus by introducing ^{15}N ($I = \frac{1}{2}$) into the compounds a useful NMR probe is established.

The $^{15}N-\{^1H\}$ NMR spectrum of labelled **2** (Fig. 1) consists of the expected singlet at δ 272, together with an AX set of doublets at δ_A 274 and δ_X 268 (J_{AX} 2.6 Hz), while that of labelled **3** consists of a singlet at δ 339. The spectrum of $[PPh_4][Pd(S_2{}^{15}N_2H)Cl_2]$ (Fig. 2) shows two doublets at δ 218.5 and 340.7 [$^2J(^{15}N-^{15}N)$ 2.6 Hz]. The assignment of the resonance at δ 218.5 as the protonated nitrogen follows the observation of a negative intensity in the $^{15}N-\{^1H\}$ NMR spectrum due to a negative nuclear Overhauser factor [magnetogyric ratio γ (^{15}N) = -2.71×10^7 rad T^{-1} s^{-1}]. Furthermore, when this spectrum is recorded without proton decoupling the doublet at δ 218.5 is split into a doublet of doublets [$^1J(^{15}N-^1H)$ 77.8 Hz]. The observation of $^{15}N-^{15}N$ couplings in the spectrum of **4** is in contrast to that noted for $[Pt(S_2{}^{15}N_2H)Cl(PMe_2Ph)]$ where no significant $^{15}N-^{15}N$ couplings are seen.[12]

The presence of an AX set of doublets in the $^{15}N-\{^1H\}$ NMR spectrum of compound **2** (Fig. 1) cannot be readily explained since the spectrum expected from its crystal structure would consist simply of one singlet, as both nitrogens are equivalent. Even after purification by crystallisation the AX doublet is still observed. The magnitude of the coupling within the AX spectrum is 2.6 Hz which is characteristic of a $^2J(^{15}N-^{15}N)$ coupling (see above); the spectrum is unchanged if measured without ^1H decoupling, implying that no protonated nitrogens are present. The fact that there is just a 6 ppm difference between the two resonances suggests that there is only a slight inequivalence in the environments of the two nitrogens. Two explanations are possible. First **2** undergoes some rearrangement in solution. The ratio of the integrated areas of the singlet to the AX system is approximately 2:1 implying that about $\frac{1}{3}$ of the sample of **2** is involved in this rearrangement. A second explanation is to consider the different chlorine isotopomers (^{35}Cl, abundance = 75.5%, $\gamma = 2.62 \times 10^7$ rad T^{-1} s^{-1}; ^{37}Cl, abundance = 24%, $\gamma = 2.18 \times 10^7$ rad T^{-1} s^{-1}). If we assume that only the chlorines *trans* to each nitrogen are important there are three isotopomers $^{35}Cl^{35}Cl$, $^{35}Cl^{37}Cl$ and $^{37}Cl^{37}Cl$ which should be present in the ratio 9:6:1. The mixed $^{35}Cl^{37}Cl$ isotopomer is expected to give rise to the AX spectrum. Careful examination of the spectrum also reveals a peak which could be due to the $^{37}Cl^{37}Cl$ isotopomer at δ = 269.5.

The $^{15}N-\{^1H\}$ NMR spectra of the bromo complexes are very similar to that of the chloro species, the spectrum of the crude reaction mixture showing **5**–**7** to be the only nitrogen-containing species present (other than residual S_4N_4); no AX set

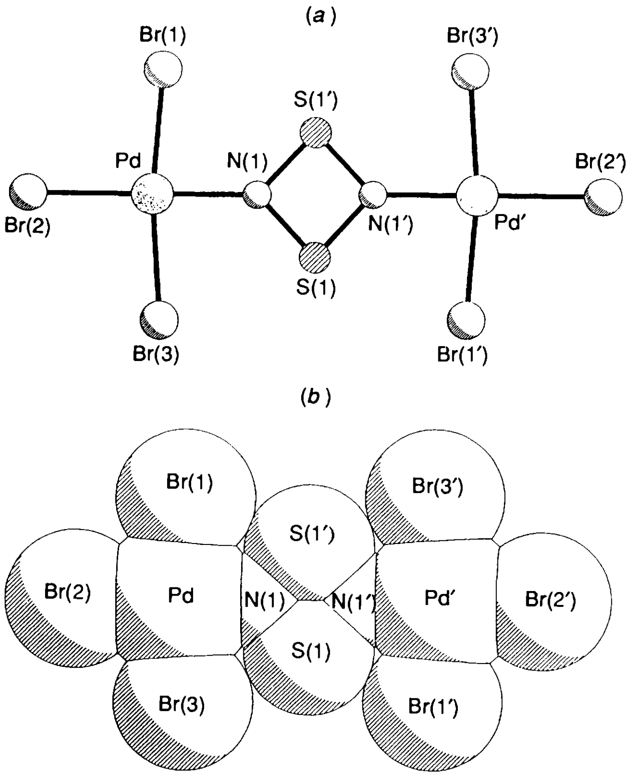

Fig. 3 The X-ray crystal structure of the anion in compound **5**; (*a*) ball-and-stick representation showing the numbering scheme (β-**2** has a similar molecular structure in the anion) and (*b*) space-filling representation showing the close approach of the bromine atoms to the coplanar sulfur atoms

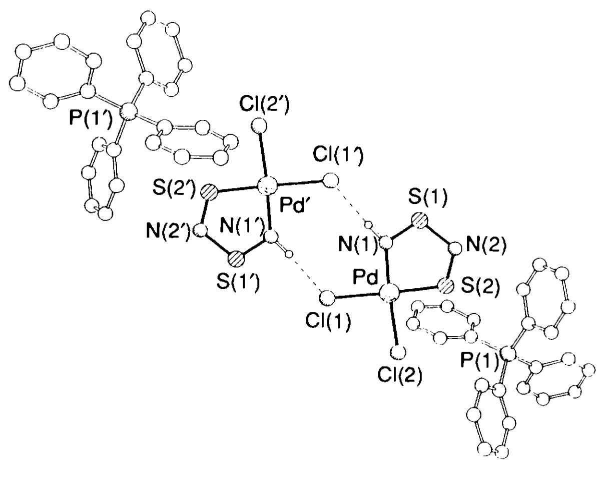

Fig. 4 The X-ray structure of compound **4** showing a pair of hydrogen-bonded anions and their respective $[PPh_4]^+$ cations

Table 5 Selected bond lengths (Å) and angles (°) for $[PPh_4]_2[Pd_2(\mu\text{-}S_2N_2)X_6]$ complexes

	X = Cl		X = Br
	α-**2**[4]	β-**2**	**5**
Pd–X(1)	2.342(2)	2.314(4)	2.422(2)
Pd–X(2)	2.282(2)	2.271(4)	2.388(2)
Pd–X(3)	2.303(2)	2.304(4)	2.431(2)
Pd–N(1)	1.959(6)	1.941(11)	1.992(11)
N(1)–S(1)	1.657(7)	1.663(15)	1.640(11)
N(1)–S(1')	1.642(6)	1.659(10)	1.645(11)
X(1)–Pd–X(2)	96.2(1)	94.6(1)	94.1(1)
X(1)–Pd–X(3)	169.4(1)	171.0(1)	171.4(1)
X(2)–Pd–X(3)	94.3(1)	94.4(1)	94.1(1)
X(1)–Pd–N(1)	85.1(2)	84.4(4)	85.6(3)
X(3)–Pd–N(1)	84.3(2)	86.6(4)	86.3(3)
Pd–N(1)–S(1)	130.3(3)	133.6(6)	132.3(6)
Pd–N(1)–S(1')	134.1(4)	132.3(8)	131.9(6)
S(1)–N(1)–S(1')	95.6(3)	94.1(6)	95.6(6)
N(1)–S(1)–N(1')	84.4(3)	85.9(6)	84.4(6)
Non-bonded distances			
S(1')···X(1)	3.13	3.02	3.14
S(1)···X(3)	2.99	3.15	3.18
S(1)···S(1')	2.44	2.43	2.43
N(1)···N(1')	2.22	2.26	2.21

Table 6 Atomic coordinates (× 10^4) for β-$[PPh_4]_2[Pd_2(\mu\text{-}S_2N_2)Cl_6]$

Atom	*x*	*y*	*z*
Pd	6 573(1)	3 909(2)	8 932(1)
Cl(1)	6 385(1)	4 584(5)	9 915(2)
Cl(2)	5 888(2)	4 987(5)	8 161(2)
Cl(3)	6 870(1)	3 064(7)	8 075(2)
N(1)	7 158(4)	3 013(19)	9 604(5)
S(1)	7 631(1)	2 043(7)	9 527(2)
P(1)	6 212(1)	11 095(5)	5 648(2)
C(1)	5 739(4)	12 532(13)	6 437(4)
C(2)	5 358	13 372	6 531
C(3)	4 958	13 832	5 950
C(4)	4 937	13 452	5 276
C(5)	5 318	12 613	5 181
C(6)	5 718	12 153	5 762
C(7)	5 939(3)	9 239(12)	4 518(5)
C(8)	5 796	8 927	3 804
C(9)	5 779	9 993	3 322
C(10)	5 906	11 371	3 555
C(11)	6 048	11 683	4 268
C(12)	6 065	10 617	4 750
C(13)	7 201(4)	11 492(10)	5 698(5)
C(14)	7 666	12 191	5 913
C(15)	7 737	13 375	6 343
C(16)	7 343	13 861	6 558
C(17)	6 878	13 163	6 344
C(18)	6 807	11 978	5 914
C(19)	5 810(3)	8 941(14)	6 200(5)
C(20)	5 830	7 696	6 574
C(21)	6 295	7 042	6 907
C(22)	6 740	7 635	6 866
C(23)	6 719	8 881	6 493
C(24)	6 255	9 534	6 160

of doublets associated with **5** is seen. The assignment of these resonances is confirmed when spectra of the separated brown and orange crystals are recorded; however, a spectrum of crystals assumed to be only the $S_2N_2H^-$ species consisted of a mixture of **5** and **7**, the similarity in colour of the crystals making isolation of **7** very difficult.

The only other examples of nitrogen chemical shifts reported for $S_2N_2H^-$ complexes of palladium are ^{14}N values for species of the type $[Pd(S_2N_2H)(L\text{–}L)]$ (L–L = bidentate chelating ligand).[13] Typically the $S_2N_2H^-$ ligand gives signals at *ca.* δ 360 and 230 the lower-frequency signal being assigned to the metal-bound nitrogen; these values agree well with those reported here for **4** and **7**. The environments of the S_2N nitrogens in compounds **3**, **4**, **6** and **7** (Table 4) are clearly very similar since their chemical shifts vary little. The nitrogens in the S_2N_2-bridged compounds which are σ-bonded to the metal have a chemical shift which is intermediate between the values observed for the two nitrogens in the $S_2N_2H^-$ cases. Changing the halogen *trans* to the nitrogen atom in **2**–**7** has little effect on its chemical shift value.

The X-ray analyses show that in α-**2**,[4] β-**2** and **5** the $[X_3PdS_2N_2PdX_3]^{2-}$ anions all have the same core structure each with crystallographic C_i symmetry. Comparative selected bond

Table 7 Atomic coordinates (× 10^4) for $[PPh_4]_2[Pd_2(\mu\text{-}S_2N_2)Br_6]$

Atom	*x*	*y*	*z*
Pd	465(1)	9 395(1)	3 633(1)
Br(1)	941(2)	8 278(1)	4 188(1)
Br(2)	736(1)	8 897(1)	2 577(1)
Br(3)	24(1)	10 605(1)	3 231(1)
N(1)	197(8)	9 794(6)	4 514(5)
S(1)	−243(3)	10 584(2)	4 763(2)
P(1)	−896(3)	6 080(2)	4 051(2)
C(1)	−931(13)	7 124(8)	3 082(7)
C(2)	−1 363(14)	7 577(8)	2 636(8)
C(3)	−2 389(15)	7 570(8)	2 564(8)
C(4)	−2 936(12)	7 106(9)	2 941(8)
C(5)	−2 492(12)	6 658(8)	3 392(7)
C(6)	−1 490(10)	6 660(7)	3 460(6)
C(7)	−1 455(13)	7 097(9)	4 962(8)
C(8)	−1 329(14)	7 489(9)	5 543(8)
C(9)	−476(16)	7 413(9)	5 896(8)
C(10)	250(12)	6 923(8)	5 727(8)
C(11)	116(13)	6 514(8)	5 185(7)
C(12)	−713(12)	6 592(6)	4 784(6)
C(13)	1 076(12)	6 244(8)	3 678(7)
C(14)	1 975(12)	5 991(9)	3 450(7)
C(15)	2 088(12)	5 263(10)	3 303(7)
C(16)	1 346(13)	4 785(9)	3 386(7)
C(17)	432(12)	5 016(8)	3 620(7)
C(18)	285(9)	5 745(7)	3 770(6)
C(19)	−1 994(11)	5 113(8)	4 816(7)
C(20)	−2 586(14)	4 507(10)	4 898(9)
C(21)	−2 935(11)	4 114(9)	4 366(11)
C(22)	−2 642(11)	4 326(9)	3 749(9)
C(23)	−2 051(11)	4 926(8)	3 656(7)
C(24)	−1 698(10)	5 315(7)	4 191(7)

Table 8 Atomic coordinates (× 10^4) for $[PPh_4][Pd(S_2N_2H)Cl_2]$

Atom	*x*	*y*	*z*
Pd	1 684(1)	−151(1)	3 977(1)
N(1)	261(7)	394(7)	3 613(7)
N(2)	688(14)	941(10)	1 994(8)
S(2)	1 676(3)	375(3)	2 513(3)
Cl(1)	1 585(2)	−778(2)	5 502(2)
Cl(2)	3 360(2)	−713(2)	4 306(2)
S(1)	−244(3)	952(3)	2 591(3)
P(1)	3 232(2)	−1 207(2)	553(2)
C(1)	3 410(8)	−1 203(8)	−1 342(7)
C(2)	3 636(9)	−1 617(9)	−2 146(8)
C(3)	3 991(7)	−2 571(9)	−2 048(8)
C(4)	4 021(8)	−3 110(9)	−1 234(8)
C(5)	3 783(8)	−2 695(7)	−466(7)
C(6)	3 469(5)	−1 726(6)	−512(6)
C(7)	5 357(7)	−1 544(8)	1 512(7)
C(8)	6 284(7)	−1 438(9)	2 312(9)
C(9)	6 333(9)	−934(9)	3 135(10)
C(10)	5 426(9)	−486(9)	3 210(8)
C(11)	4 488(7)	−574(8)	2 404(7)
C(12)	4 446(6)	−1 104(7)	1 565(7)
C(13)	2 354(9)	−2 004(9)	1 868(8)
C(14)	1 617(9)	−2 555(9)	2 099(9)
C(15)	829(9)	−2 995(8)	1 342(10)
C(16)	822(9)	−2 958(8)	374(10)
C(17)	1 544(8)	−2 423(8)	131(8)
C(18)	2 329(7)	−1 952(7)	890(7)
C(19)	1 659(7)	147(8)	−60(9)
C(20)	1 238(10)	1 067(9)	−293(9)
C(21)	1 903(11)	1 820(9)	−193(9)
C(22)	2 937(9)	1 671(8)	106(8)
C(23)	3 361(8)	767(8)	348(8)
C(24)	2 724(8)	−22(7)	268(7)

lengths and angles are given in Table 5 with fractional atomic coordinates for β-**2** and **5** in Tables 6 and 7. All three compounds crystallise in different crystal systems. The geometries of the anion in the two polymorphs of **2** do not differ significantly, both having the same short S • • • Cl distances of *ca.* 3.0 Å. The most noticeable difference between the two structures is in the packing of the ions in the crystal. Whereas in the α form[4] there is a close approach of the anions (Cl • • • Cl′ 3.50 Å) in β-**2** the closest interanion contact is 4.8 Å.

Table 9 Selected bond lengths (Å) and angles (°) for compound **4**

Pd–N(1)	1.983(10)	Pd–S(2)	2.194(4)
Pd–Cl(1)	2.373(3)	Pd–Cl(2)	2.310(3)
S(1)–N(1)	1.577(10)	S(1)–N(2)	1.753(20)
S(2)–N(2)	1.516(16)		
N(1)–Pd–Cl(1)	91.1(3)	N(1)–Pd–S(2)	86.7(3)
S(2)–Pd–Cl(1)	176.1(1)	N(1)–Pd–Cl(2)	175.6(3)
S(2)–Pd–Cl(2)	89.2(1)	Cl(1)–Pd–Cl(2)	93.1(1)
Pd–N(1)–S(1)	120.4(7)	S(2)–N(2)–S(1)	116.4(8)
Pd–S(2)–N(2)	110.2(7)	N(1)–S(1)–N(2)	106.1(6)

In compound **5** there is a characteristic shortening of the Pd–X bond *trans* to nitrogen as there was in α- and β-**2**. Despite the increased van der Waals radius of bromine *versus* chlorine the Pd-Br(1) and Pd-Br(3) bonds are both in-plane with and folded towards the central S_2N_2 ring [Fig. 3(*a*)]. The Br • • • S distances in **5** are only slightly longer (0.1 Å) than the equivalent Cl • • • S distances in **2**. The close approach of the bromine and sulfur atoms is illustrated in the space-filling representation of **5** [Fig. 3(*b*)]. There is a small increase in the deviations from planarity of the anion in **5** compared to α- and β-**2** [0.1 Å for Br(1) *versus* 0.06 and 0.04 Å for Cl(1) respectively]. As with β-**2** there are no short interanion contacts in **5**.

Fractional atomic coordinates and selected bond lengths and angles for compound **4** are given in Tables 8 and 9. The anion has the expected almost planar geometry [maximum deviation from planarity 0.08 Å for S(2)]. Both the Pd-N and Pd-S bond lengths [1.983(10) and 2.194(4) Å respectively] are shorter than those observed[10] in the related phosphine-substituted complex $[Pd(S_2N_2H)(PMe_2Ph)_2][BF_4]$ [Pd–N 2.031(6), Pd–S 2.290(2) Å] reflecting the difference in the *trans* atoms (Cl *vs.* P). The two Pd–Cl distances in **4** differ from each other [Pd–Cl *trans* to N, 2.310(3); Pd–Cl *trans* to S, 2.373(3) Å]. The Pd–N distance in **4** is very similar to those observed for α-**2**, β-**2** and **5** (Table 5). High thermal anisotropy in the PdS_2N_2 ring precludes detailed discussion of the S–N bond lengths. However, the Pd–N(1)–S(1) angle within the ring is as predicted[10] for protonation on N(1). Also, the hydrogen atom is observed to lie significantly out of the PdS_2N_2 plane (0.15 Å), a feature we have remarked upon previously.[14]

In the crystal of compound **4** the anions form centrosymmetric hydrogen-bonded dimer pairs (Fig. 4) (N • • • Cl 3.22 Å, N–H • • • Cl 174°). This N–H • • • Cl distance is identical to that we observed[15] in $[Pt(S_2N_2H)(PEt_3)_2]_2[(SnMe_2Cl_3)_2]$. There is no stacking of the dimer pairs.

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