

## COMMUNICATION

### THE PREPARATION AND X-RAY STRUCTURES OF $\text{Pt}(\text{SeSN}_2)(\text{PMe}_2\text{Ph})_2$ AND $[\text{Pt}(\text{SeSN}_2\text{H})(\text{PMe}_2\text{Ph})_2]\text{BF}_4$

CAROLINE A. O'MAHONEY, IVAN P. PARKIN, DAVID J. WILLIAMS and  
J. DEREK WOOLLINS\*

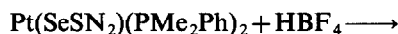
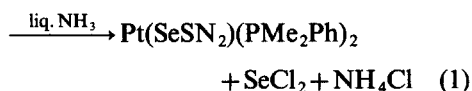
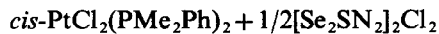
Department of Chemistry, Imperial College of Science, Technology and Medicine,  
South Kensington, London SW7 2AY, U.K.

(Received 4 April 1989; accepted 17 May 1989)

**Abstract**—Reaction of  $[\text{Se}_2\text{SN}_2]_2\text{Cl}_2$  with  $\text{PtCl}_2(\text{PMe}_2\text{Ph})_2$  in liquid ammonia gives  $\text{Pt}(\text{SeSN}_2)(\text{PMe}_2\text{Ph})_2$  (**4**), which may be protonated with  $\text{HBF}_4$  to form  $[\text{Pt}(\text{SeSN}_2\text{H})(\text{PMe}_2\text{Ph})_2]\text{BF}_4$  (**5**); the new compounds being characterized by IR, NMR and X-ray crystallography.

Recently, we have described the synthesis of metalla-sulphur-nitrogen complexes containing  $\text{S}_2\text{N}_2^{2-}$ ,  $\text{S}_2\text{N}_2\text{H}^-$  or  $\text{S}_3\text{N}^-$  ligands.<sup>1–4</sup> Complexes of the type  $[\text{Pt}(\text{S}_2\text{N}_2\text{H})(\text{PR}_3)_2]\text{X}$  (**1**) are of particular interest since they form one dimensional stacked structures with channels of cations and anions. Clearly, it would be advantageous to replace the sulphur atoms by seleniums in the  $\text{PtSN}$  rings to enhance the electronic interactions between the layered cations, a strategy that has been found to be useful for organic metals. However, the synthesis of selenium substituted analogues of **1** is non-trivial since there is a paucity of suitable starting materials, although we have been able to prepare  $\text{Pt}(\text{Se}_3\text{N})\text{Cl}(\text{PMe}_2\text{Ph})$  in low yield from a high temperature reaction involving  $\text{Se}_4\text{N}_4$ .<sup>5</sup> One very successful

strategy for the preparation of  $\text{M—S—N}$  complexes has been to perform the reaction in liquid ammonia using cations such as  $[\text{S}_3\text{N}_2\text{Cl}]^+$  or  $[\text{S}_4\text{N}_3]^+$ .<sup>6</sup> Here, we report on the reaction of  $[\text{Se}_2\text{SN}_2]_2\text{Cl}_2$  (**2**) with *cis*- $\text{PtCl}_2(\text{PMe}_2\text{Ph})_2$  (**3**) in liquid ammonia to give  $\text{Pt}(\text{SeSN}_2)(\text{PMe}_2\text{Ph})_2$  (**4**) [eq. (1)], which can be protonated using  $\text{HBF}_4$  to give  $[\text{Pt}(\text{SeSN}_2\text{H})(\text{PMe}_2\text{Ph})_2]\text{BF}_4$  (**5**) [eq. (2)]. Compounds **4** and **5** are the first examples of complexes containing  $\text{S—Se—N}$  anions as ligands.



In a typical reaction, **2** (1 mmol) was dissolved in liquid ammonia (5 cm<sup>3</sup>) at  $-78^\circ\text{C}$  and **3** (1 mmol) was added. After stirring for 1 h the reaction was allowed to warm to room temperature and the ammonia allowed to evaporate off. The product, **4**, was obtained by extraction into  $\text{CH}_2\text{Cl}_2$  and crystallized from  $\text{CH}_2\text{Cl}_2$ –petrol ether (yield *ca* 0.7 mmol, 70%). Protonation of **4** to form **5** was carried out in THF–benzene, the isolated yield being 70%.†

The spectroscopic properties of **4** and **5** are as expected.‡ The <sup>31</sup>P NMR spectra are of the AX type with <sup>195</sup>Pt and <sup>77</sup>Se satellites; the chemical

\* Author to whom correspondence should be addressed.

† Microanalyses (calculated values in parentheses):  $\text{Pt}(\text{SeSN}_2)(\text{PMe}_2\text{Ph})_2$  (**4**) C, 31.0(31.4); H, 3.5(3.5); N, 4.8(4.6).  $[\text{Pt}(\text{SeSN}_2\text{H})(\text{PMe}_2\text{Ph})_2]\text{BF}_4$  (**5**) C, 27.2(27.5); H, 3.1(3.3); N, 3.9(4.0).

‡ For **4**: <sup>31</sup>P  $\delta_A - 6.7$ ,  $\delta_B - 27.1$  ppm <sup>1</sup>J<sub>A</sub> 2837, <sup>1</sup>J<sub>B</sub> 2799 Hz; for (**5**):  $\delta_A - 12.4$ ,  $\delta_B - 30.1$ , <sup>1</sup>J<sub>A</sub> 2687, <sup>1</sup>J<sub>B</sub> 3227, <sup>2</sup>J{<sup>31</sup>P–<sup>31</sup>P} 24 Hz. Poorly resolved shoulders suggesting <sup>2</sup>J–{<sup>31</sup>P–<sup>77</sup>Se} couplings of *ca* 30 Hz are also observed. IR (**4**): 1071(vs) [ν(SN)], 642(s) [ν(SN)], 546(m) [ν(SeN)], 401(m), 356(m) [δ(SN)]; **5**: 3299(s) [ν(NH)], band at *ca* 1070 obscured by  $\text{BF}_4^-$  vibrations, 645(m) [ν(SN)], 519(m), [ν(SeN)], 447(m), 331(m) cm<sup>–1</sup>, 323(sh) [δ(SN)].

shifts and coupling constants being similar to the M—S—N analogues. The mass spectra show the parent ion with the appropriate isotopic substitution pattern for compounds containing one selenium and one platinum atom.

Despite the significantly larger covalent radius of selenium relative to sulphur, the X-ray structures\* of **4** and **5** are isostructural with their  $\text{PtS}_2\text{N}_2$  analogues.<sup>2</sup> In the neutral compounds both the  $\text{PtS}_2\text{N}_2/\text{PtSeSN}_2$  rings display similar rotational disorder. Figure 1 shows a schematic representation of the disorder in **4**. Despite the disorder, the analysis shows unequivocally that the selenium atom is bound to platinum. Because of the inevitably poor accuracy of the bond lengths and angles in the  $\text{PtSeSN}_2$  ring in the structure of **4** we determined the structure of the protonated compound **5**. In **5**, as a consequence of the synthetic route employed, the selenium atom is again bound to platinum and furthermore, the structure still displays the characteristic stacking seen previously

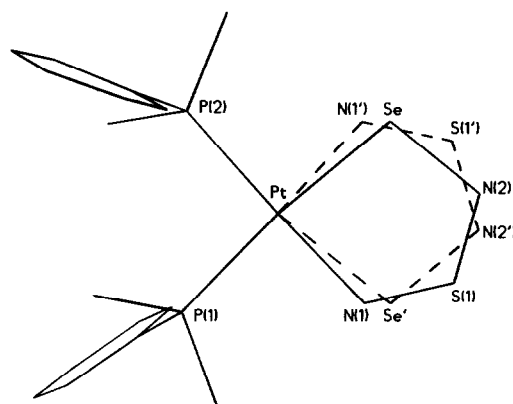


Fig. 1. A schematic representation of the disordered structure of  $\text{Pt}(\text{SeSN}_2)(\text{PMe}_2\text{Ph})_2$  (**4**).

\* Crystal data **4**,  $\text{C}_{16}\text{H}_{22}\text{N}_2\text{P}_2\text{PtSSe}$ , monoclinic,  $a = 17.170(3)$ ,  $b = 13.879(3)$ ,  $c = 17.921(4)$  Å,  $\beta = 109.46(2)^\circ$ ,  $U = 4027$  Å<sup>3</sup>, space group  $C2/c$ ,  $Z = 8$ ,  $M = 610.4$ ,  $D_c = 2.01$  g cm<sup>-3</sup>,  $\mu(\text{Cu-K}\alpha) = 178$  cm<sup>-1</sup>. Data were measured on a Nicolet R3m diffractometer with graphite monochromated Cu-K $\alpha$  radiation using  $\omega$ -scans. The structure was solved by the heavy-atom method. The structure displays partial two-fold disorder in the  $\text{PtSeSN}_2$  ring about an axis bisecting the P—Pt—P angle. The occupancies of the two orientations refined to 0.85 and 0.15, respectively. The non-hydrogen atoms were refined anisotropically with the exception of the 0.15 occupancy atoms which were refined isotropically using absorption corrected data (empirical absorption correction, maximum and minimum transmission factors: 0.59 and 0.23, respectively) to give  $R = 0.052$ ,  $R_w = 0.054$  for 2439 independent observed reflections [ $|F_o| > 3\sigma(|F_o|)$ ,  $\theta \leq 58^\circ$ ].

**5**,  $\text{C}_{16}\text{H}_{23}\text{BF}_4\text{N}_2\text{P}_2\text{PtSSe}$ , monoclinic,  $a = 8.514(2)$ ,  $b = 17.179(7)$ ,  $c = 16.119(1)$  Å,  $\beta = 104.41(4)^\circ$ ,  $U = 2283$  Å<sup>3</sup>, space group  $P2_1/n$ ,  $Z = 4$ ,  $M = 698.2$ ,  $D_c = 2.03$  g cm<sup>-3</sup>,  $\mu(\text{Cu-K}\alpha) = 161$  cm<sup>-1</sup>. Data were measured on a Nicolet R3m diffractometer with graphite monochromated Cu-K $\alpha$  radiation using  $\omega$ -scans. The structure was solved by the heavy-atom method and refined anisotropically using absorption corrected data (numerical absorption correction based on faced indexed crystal, maximum and minimum transmission factors: 0.246 and 0.054, respectively) to give  $R = 0.043$ ,  $R_w = 0.047$  for 2921 independent observed reflections [ $|F_o| > 3\sigma(|F_o|)$ ,  $\theta \leq 58^\circ$ ]. The atomic coordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K. Any request should be accompanied by a full literature citation for this communication.

for  $[\text{Pt}(\text{S}_2\text{N}_2\text{H})(\text{PR}_3)_2]\text{X}$  compounds.<sup>3</sup> The bond lengths for atoms not connected to selenium in **5** are the same as in  $[\text{Pt}(\text{S}_2\text{N}_2\text{H})(\text{PMe}_2\text{Ph})_2]\text{BF}_4$  (**6**), there being a characteristic shortening of the Pt—P(2) bond length (*trans* to nitrogen) relative to Pt—P(1). With the exception of the angle at platinum ( $85.5(2)$  in **5**, cf.  $84.6(2)^\circ$  in **6**), the angles within the metallacycle are contracted in **5** compared to **6** as a result of the longer bonds around the selenium atom. There is a hydrogen bond ( $3.19$  Å) between N(1)—H in the cation and F(1) in the anion. (The X-ray structure of **5** is shown in Fig. 2.) As mentioned above, the

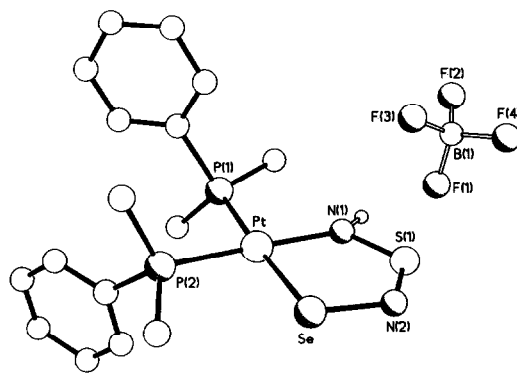


Fig. 2. The X-ray structure of  $[\text{Pt}(\text{SeSN}_2\text{H})(\text{PMe}_2\text{Ph})_2]\text{BF}_4$  (**5**), showing the cation-anion hydrogen bonding. Selected bond lengths (Å) and angles ( $^\circ$ ):

Pt—P(1)	2.301(2)	N(1)—S(1)	1.602(7)
Pt—P(2)	2.262(2)	S(1)—N(2)	1.514(9)
Pt—Se	2.401(1)	N(2)—Se	1.833(9)
Pt—N(1)	2.030(7)		
P(1)—Pt—P(2)	94.3(1)		
N(1)—Pt—Se	85.5(2)		
Pt—N(1)—S(1)	122.8(4)		
N(1)—S(1)—N(2)	111.4(4)		
S(1)—N(2)—Se	120.1(4)		
N(2)—Se—Pt	100.2(2)		

monoselenated cations and anions in **5** form infinite stacks of dimer pairs, without any significant increase in the interlayer separations relative to **6** (intra-dimer separation: 3.54 Å; inter-dimer separation: 4.55 Å in **5**). The interaction between adjacent metallacycles has not been influenced by the introduction of a selenium atom as the synthesis resulted in the selenium being bound to the platinum in a site which does not overlap with adjacent rings.<sup>3</sup> Work on the preparation of the fully substituted PtSe<sub>2</sub>N<sub>2</sub> analogues and on the use of **4** and **5** in the synthesis of new heterocycles is in progress.

*Acknowledgement*—We are grateful to Johnson Matthey plc for loans of K<sub>2</sub>PtCl<sub>4</sub>.

## REFERENCES

1. R. Jones, P. F. Kelly, C. P. Warrens, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Chem. Commun.* 1986, 711.
2. R. Jones, C. P. Warrens, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Dalton Trans.* 1987, 907.
3. R. Jones, P. F. Kelly, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Dalton Trans.* 1988, 803.
4. R. Jones, T. G. Purcell, D. J. Williams and J. D. Woollins, *Polyhedron* 1987, 6, 2165.
5. P. F. Kelly, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Chem. Commun.*, accepted for publication.
6. P. S. Belton, I. P. Parkin, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Chem. Commun.* 1988, 1479.