The Preparation and *X*-Ray Structure of Pt(Se_3N)Cl(PMe_2Ph)

Paul F. Kelly, Alexandra M. Z. Slawin, David J. Williams, and J. Derek Woollins*

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

Reaction of Se_4N_4 with [$PtCl_2(PMe_2Ph)]_2$, in refluxing $CHCl_3$, results in Pt(Se_3N)Cl(PMe_2Ph), (**1**), the first example of a metal selenium–nitrogen complex, which contains the bidentate, selenium-bound Se_3N^- ligand; from *X*-ray crystallography (**1**) is square planar with a bidentate Se_3N^- ligand co-ordinated through two selenium atoms.

Tetrasulphur tetranitride, S_4N_4, has long been recognised as an extremely versatile reagent for the preparation of sulphur–nitrogen species, *via* reaction with both organic and inorganic compounds.[1] Reactions with transition metal species result in the formation of a number of different metalla sulphur–nitrogen complexes, including complexes of $S_2N_2^{2-}$, $S_2N_2H^-$, S_3N^-, and $S_2N_3^{3-}$.[2] In contrast, however, reports of reactions involving Se_4N_4 are rare, and there is only one example (recently reported) of a successful reaction with a transition metal complex;[3] that between Se_4N_4 and WCl_6 which resulted in [$WCl_4(NSeCl)]_2$, the first example of a complex of NSeCl, analogous to the NSCl ligand which has been characterised in numerous systems.

In an attempt to expand the chemistry of Se_4N_4 we have utilised the reactive dimeric platinum species [$PtCl_2(PMe_2Ph)]_2$, which we have recently shown to react with S_4N_4 to give a complex of $S_4N_4^{2-}$.[4] Reaction of this dimer with Se_4N_4 in $CHCl_3$ at 90 °C results in a number of species and can be monitored by t.l.c. Two species, which can be detected as purple and green bands, gradually appear with time. After twelve hours at 90 °C t.l.c. reveals these two species are present in reasonable amounts and they can then be separated from the mixture by elution on a Bio-beads gel-permeation column. Both species elute together as a slow moving pale blue/purple band, and can then be separated from each other by p.t.l.c. on silica, the green species having a substantially higher R_F value (eluent CH_2Cl_2) than the purple.

Slow diffusion of hexane into a concentrated CH_2Cl_2

solution of the green species results in poorly formed, very dark crystals. *X*-Ray crystallography reveals† the compound to be Pt(Se_3N)Cl(PMe_2Ph), (**1**), the first example of a metalla selenium-nitrogen complex. It is directly analogous to the sulphur-nitrogen species Pt(S_3N)Cl(PMe_2Ph) which we have recently shown to be formed in the reaction of $PtCl_2(PMe_2Ph)_2$ with S_4N_4 at 160 °C.[5] In contrast Se_4N_4 is inert to the bis-phosphine complex, even at this high temperature.‡ We have yet to characterise the purple species which is formed along with (**1**), although it would appear likely that it is also a selenium–nitrogen complex.

The crystal structure of (**1**) reveals that the platinum has slightly distorted square planar geometry with Pt, P, Cl, and Se(3) lying in the co-ordination plane with Se(1), N(1), and Se(2) all being *ca.* 0.1 Å out of this plane [N–Se(3)–Pt–P torsion angle 177(1)°]. There is a noticeable difference in the two Pt–Se distances with Pt–Se(1) (*trans* to PMe_2Ph) being longer [2.385(2) Å] than Pt–Se(3) [*trans* to Cl 2.302(3) Å]. Within the $PtSe_3N$ ring the two Se–N and the Se–Se bond lengths are in the expected ranges. The P–Ph bond lies almost co-planar with the $PtSe_3N$ ring [Se(3)–Pt–P–C(1) torsion angle 6.0(0.9)°] with the planes of the rings almost perpendicular [Pt–P–C(1)–C(6) torsion angle 88.7(1.7)°]. The molecules pack with the $PtSe_3N$ rings approximately co-planar with partial overlap of adjacent pairs (minimum non-bonded contact N–N′ 3.35 Å), though there is no formation of continuous stacks. There is, however, a short in plane intermolecular Cl(1)–Se(1)′ interaction of 3.49 Å which is significantly shorter than the sum of the Van de Waals radii (3.8 Å).

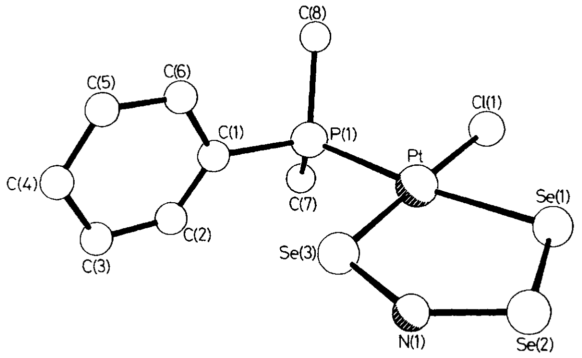

Figure 1. The *X*-ray structure of Pt(Se_3N)Cl(PMe_2Ph), (**1**). Selected bond lengths and angles: Pt–Se(1) 2.385(2), Pt–Se(3) 2.302(3), Pt–Cl 2.349(6), Pt–P 2.262(5), Se(1)–Se(2) 2.281(4), Se(2)–N(1) 1.710(21), N(1)–Se(3) 1.806(21) Å; Se(1)–Pt–Se(3) 95.9(1), Se(1)–Pt–Cl 84.0(2), Se(3)–Pt–P 92.3(2), P–Pt–Cl 87.8(2), Pt–Se(1)–Se(2) 102.4(1), Se(1)–Se(2)–N 107.4(7), Se(2)–N–Se(3) 124.5(13), N–Se(3)–Pt 109.8(7)°.

It has long been established that unco-ordinated sulphur–nitrogen anions such as S_3N^-, S_4N^-, SN_2^{2-}, and, as we have recently proposed,[6] $S_2N_2^{2-}$ exist, and this work suggests that there is potential for the discovery, and utilisation, of analogous selenium species.

We are grateful to Johnson Matthey for loans of K_2PtCl_4.

Received, 29th November 1988; Com. 8/04717K

References

1 'The Inorganic Heterocyclic Chemistry of Sulphur, Nitrogen, and Phosphorus,' H. G. Heal, Academic Press, 1980.

2 P. F. Kelly and J. D. Woollins, *Polyhedron*, 1986, **5**, 607; P. F. Kelly and J. D. Woollins, *Transition Met. Chem.*, 1988, **13**, 77.

3 J. Adel, A. El-Kholi, W. Willing, U. Muller, and K. Dehnicke, *Chimia*, 1988, **42**, 70.

4 M. B. Hursthouse, P. F. Kelly, M. Motavelli, and J. D. Woollins, *Polyhedron*, in press.

5 J. M. Jolliffe, P. F. Kelly, and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, submitted.

6 P. S. Belton, I. P. Parkin, D. J. Williams, and J. D. Woollins, *J. Chem. Soc., Chem. Commun.*, 1988, 1479.

---

† *Crystal Data* (**1**): $C_8H_{11}ClNPPtSe_3$, M = 619.6, monoclinic, a = 16.871(6), b = 8.996(5), c = 19.771(5) Å, β = 106.83(3)°, U = 2872 Å^3, space group *C*2/*c*, Z = 8, D_c = 2.87 g cm^{-3}, μ(Cu-K_α) = 301 cm^{-1}. Crystal dimensions 0.4 × 0.05 × 0.22 mm. Data were measured on a Nicolet R3m diffractometer with graphite monochromated Cu-K_α radiation using ω-scans. The structure was solved by direct methods and refined anisotropically using absorption corrected data to give R = 0.066, R_w = 0.066 for 1552 independent observed reflections [$|F_o| > 3\sigma(|F_o|)$, $\theta \leqslant 58°$]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors Issue No. 1.

‡ *Safety Note:* Se_4N_4 is an even more powerful explosive than S_4N_4; in consequence extra care should be taken during handling, and during any reaction performed at high temperatures. Similar precautions should also be taken with the initial product of $SeCl_4$ and ammonia, obtained during the preparation of Se_4N_4, which we have found to explode with friction or on contact with water.