The reaction of $[Bu_4N]_2[Pd_2Br_6(Se_2N_2)]$ with [14]aneS_4; an effective source of the diselenium dinitride unit

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Reaction of $[Bu_4N]_2[Pd_2Br_6(Se_2N_2)]$ with [14]aneS_4 results in eventual formation of Se_4N_4; intermediates in this reaction include an air-sensitive insoluble material which reacts with $[PtCl_2(PMe_2Ph)]_2$ to give the first example of a platinum adduct of Se_2N_2 and with $[Pd_2Br_6]^{2-}$ to regenerate the starting material.

The thermolytic splitting of S_4N_4 to the four-membered ring system S_2N_2 is a well known reaction that took on greater significance when the ability of the dinitride to act as precursor to conducting $(SN)_x$ was first demonstrated.[1] While the free material itself has been shown to act as a source of coordination complexes of S_2N_2,[2] the latter are more commonly (and more easily) generated through reactions of S_4N_4.[3] While two examples of selenium analogues of such adducts (containing aluminium[4] and palladium[5]) have been prepared from Se_4N_4, such chemistry has not been extended to anything like the range of the sulfur case. This is due to a combination of the relative inertness (and insolubility) of Se_4N_4 compared to its sulfur counterpart and also its extreme friction sensitivity (which is even greater than that of S_4N_4 and S_2N_2, compounds which are pernicious explosives in their own right). And as thermolytic cracking of Se_4N_4 to Se_2N_2 does not occur, it follows that extension of our understanding of the chemistry of the Se_2N_2 unit requires an amenable source. This is made all the more desirable by the fact that preparation of the putative conducting polymer $(SeN)_x$ has proved elusive. By analogy with the sulfur chemistry, Se_2N_2 has clear potential to act as a source of the latter.

In the light of access to the aforementioned adducts of Se_2N_2, the question of their ability to act as sources of the free nitride becomes germane. While the aluminium adducts are exceedingly air sensitive, the palladium complexes are easily handled in air and thus have clear potential to act as easily utilised sources of free Se_2N_2. In this study we have used $[Bu_4N]_2[Pd_2Br_6(Se_2N_2)]$ **1** (Fig. 1) as the reagent of choice as it forms in highest yield and we have recently confirmed its structure by X-ray crystallography.[5c] While addition of incoming ligands to **1** in order liberate free Se_2N_2 is conceptually straightforward, any such ligands would have to be inert to free Se_2N_2, and by analogy with the reactivity of S_4N_4/S_2N_2 it was concluded that ligands such as cyanide, phosphines, amines *etc.*—which would all have a strong affinity for palladium—were all likely to react with the outgoing nitride. In contrast, to the best of our knowledge, no reactivity of thioether units towards S–N or Se–N systems has been reported. While monodentate thioethers are relatively weak ligands, potentially polydentate species such as macrocyclic [14]aneS_4, are more powerful binding agents and this was the ligand of choice for the study herein. Its suitability was enhanced by the fact that preliminary test reactions of the crown with $[Bu_4N]_2[Pd_2Br_6(S_2N_2)]$ revealed that S_2N_2 was almost immediately released upon addition of the crown and could either be reacted with $[Bu_4N]_2[Pd_2Br_6]$ to regenerate the adduct or allowed to slowly dimerise to S_4N_4 in solution. This observation prompted investigation into the analogous reaction with **1** in the hope of releasing free Se_2N_2.

Addition†‡ of two molar equivalents of [14]aneS_4 to a solution of **1** in CH_2Cl_2 results in the immediate formation of an orange precipitate, which lightens to yellow upon further stirring for 1 h. Spectroscopic measurements performed on the latter solid (which we hereby designate **A**) reveal, *vide infra*, the presence of Pd–crown and selenium–nitrogen units and chemical probing of this material reveals a number of important points (Scheme 1). Solid samples of this product do not appear to decompose when stored for many weeks under a nitrogen atmosphere. In such cases there appears no evidence for the formation of $(SeN)_x$ or for the dimerisation to Se_4N_4 in the purely solid state. The latter reaction is seen, however, if this material is suspended in a solvent. Thus if the original reaction of **1** with the crown is not stopped after 1 h but stirring

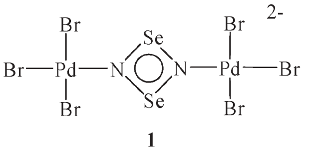

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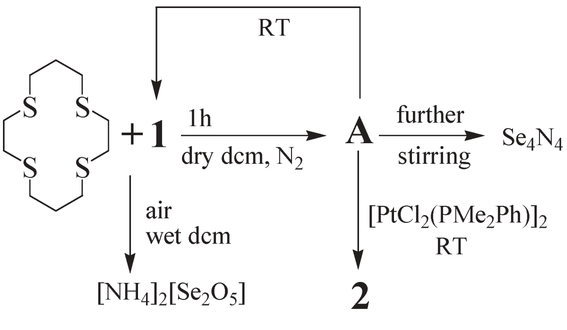
Fig. 1 The structures of **1** and [14]aneS_4.



Scheme 1 Formation and reactions of the novel Se_2N_2 synthon **A**.

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continued, the presence of Se_4N_4 in the resulting mixtures starts to become apparent (by IR spectroscopy) after a further hour stirring. Depending upon the rate of stirring, the presence of significant amounts of Se_4N_4 after 2–3 h is often revealed by the formation of red–orange deposits of the material smeared on the side of the reaction vessel. After 24 h IR spectroscopy reveals the bulk of the Se_2N_2 to have dimerised.

Addition of a solution of $[Bu_4N]_2[Pd_2Br_6]$ in CH_2Cl_2 to a suspension of **A** results in rapid re-formation of $[Bu_4N]_2[Pd_2Br_6(Se_2N_2)]$; a key feature of this reaction is that it proceeds at ambient temperature, which is in stark contrast to the original reaction of Se_4N_4 with $[Bu_4N]_2[Pd_2Br_6]$. The latter only proceeds to the dinitride adduct at 100 °C in superheated CH_2Cl_2 in a sealed-tube system. Addition of solid $[PtCl_2(PMe_2Ph)]_2$ to a suspension of **A** in CH_2Cl_2 results in immediate darkening of the solution followed by some precipitation. Filtration followed by crystallisation by ether diffusion results in well-formed orange/brown crystals of **2**. Microanalysis, IR and X-ray crystallography§ reveal **2** to be $Pt_2X_4(PMe_2Ph)(Se_2N_2)$ wherein X is a 50 : 50 random mix of Cl and Br (Fig. 2). The bromide present in **2** must originate from **1**; identical results are obtained even if KBr is added to the reaction mixture in order to try to take it through to the fully brominated material. Three peaks appear in the ^{31}P NMR spectrum of **2**, consistent with the presence of $P–PtCl_2$, P–PtClBr and $P–PtBr_2$ units (with chemical shifts and $^{31}P–^{195}Pt$ coupling constants very similar to those in $PtX(S_2N_2H)PMe_2Ph$, where X = Cl or Br). The key feature of **2** though is the Se_2N_2 ring within which distances and angles differ little from those in **1**; this is backed up by IR spectroscopy of **2** which shows Se–N bands effectively identical to those in **1** (754 and 322 cm^{-1} *cf.* 753 and 323 cm^{-1} in **1**).

Compound **2** is the first example of a Se_2N_2 adduct of platinum; indeed no S_2N_2 adducts of this metal are known, as reactions of SN species with platinum compounds tend to generate complexes of reduced, chelating anions such as $(S_2N_2)^{2-}$. In addition, reaction of $[PtCl_2(PMe_2Ph)]_2$ with Se_4N_4 has been shown to generate a mixture of $PtCl(PMe_2Ph)(Se_2N_2H)$ and $PtCl(PMe_2Ph)(Se_3N)$ (containing the chelating $(Se_2N_2H)^-$ and $(Se_3N)^-$ ligands), and only at elevated temperatures. Thus again it is clear that **A** is an extremely efficient and amenable source of Se_2N_2.

Such chemical observations on the reactivity of **A** obviously raise the question of its exact chemical nature.

If the initial orange product formed in the reaction of **1** with 14]aneS_4 is recovered by filtration, IR spectroscopy reveals two key points. In the spectrum of **1** (Fig. 3 upper) two strong peaks are observed close to each other at 753 and 740 cm^{-1}; these can be attributed to an Se–N stretch and to a characteristic $[Bu_4N]^+$ vibration respectively. In the orange product the latter band is missing but the former (now shifted very slightly to 760 cm^{-1}) is still present. Thus this first product would appear to be one in which the crown has displaced bromide ligand(s) (with concomitant loss of $[Bu_4N]^+$) but not the nitride, hence the minimal change in frequency of the Se–N vibration. This conclusion is backed up by microanalysis on this insoluble material which confirms the ratio of one crown unit to one Se_2N_2 and we believe the most likely structure for this initial product is polymeric with bridging crowns. It is only upon *further* stirring of the reaction mixture for 1 h to generate "**A**" that spectroscopic evidence for significant reactivity at the Se_2N_2 moiety may be obtained.

The IR spectrum of product **A** (Fig. 3, lower) reveals a complete absence of bands in the area of the spectrum associated with coordinated, bidentate Se_2N_2. A new, strong, band is, however, apparent over 100 cm^{-1} lower in frequency at 647 cm^{-1}, together with a weaker band at 339 cm^{-1}. That these are due to Se–N vibrations is evidenced by the fact that if the reaction is performed using $Se_4{}^{15}N_4$ they both move to lower frequency (627 and 329 cm^{-1}) by amounts commensurate with the inclusion of the heavier isotope (*cf.* changes in the vibrational frequencies of Se_4N_4 upon ^{15}N labelling).[6] Recent calculations by Laitinen and co-workers suggested two main stretches at 660 and 355 cm^{-1} for putative Se_2N_2 and thus the values in this experimental study are supportive of this.[7] Additionally, it is worth noting that the 106 cm^{-1} shift of the higher frequency peak upon liberation of the dinitride is significantly larger than the corresponding difference between peaks in $[Bu_4N]_2[Pd_2Br_6(S_2N_2)]$ and free S_2N_2 (855[5b] *vs.* 785[3] cm^{-1} *i.e.* a 70 cm^{-1} shift upon liberation). The Raman

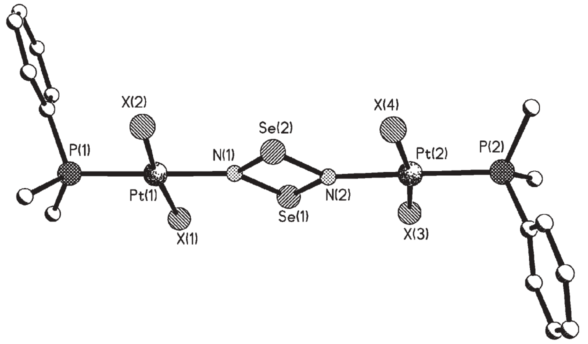

Fig. 2 The X-ray crystal structure of one of the two independent molecules of **2** (note atoms "X" are 50 : 50 Br/Cl occupancy). Selected bond distances (Å) and angles (°): Pt(1)–N(1) 2.034(7), N(1)–Se(2) 1.798(6), Se(2)–N(2) 1.806(6), N(2)–Se(1) 1.797(6), Se(1)–N(1) 1.808(7), N(2)–Pt(2) 2.037(6); Se(1)–N(1)–Se(2) 97.4(3), N(1)–Se(2)–N(2) 82.6(3), Se(2)–N(2)–Se(1) 97.5(3), N(2)–Se(1)–N(1) 82.5(3). Parameters are not significantly different in the other independent molecule.

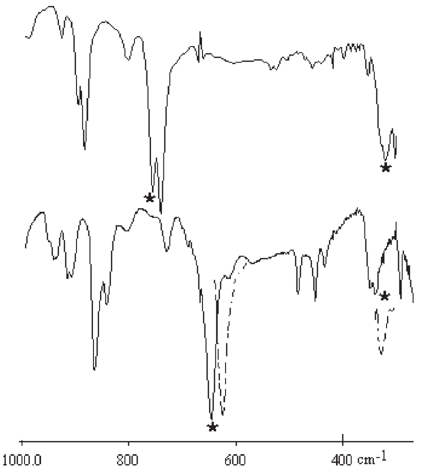

Fig. 3 Comparison of the IR spectrum of **1** (containing coordinated Se_2N_2, upper) with that of the product **A**. Peaks marked with* are due to Se–N vibrations; dashed lines show the peaks in the ^{15}N labelled case.

spectrum of this product proves to be less conclusive than the IR, though a weak, poorly-resolved, broad peak is observed at 892 cm^{-1} which appears to shift to 861 cm^{-1} upon ^{15}N labelling.

In the light of all the above observations—spectroscopic and chemical—we believe the most likely composition of **A** is a mixture of free Se_2N_2 and an unidentified, insoluble Pd–crown by-product. We have yet to find a suitable solvent for any component of this mixture nor is there evidence by mass spectrometry for any volatile material (sublimation of the material leads only to formation of red selenium). The latter observation—and, indeed, the insolubility of the material—is commensurate with the presence of free Se_2N_2 as it mirrors the properties of Se_4N_4, whose volatility and solubility is severely compromised by the presence of intermolecular interactions.

The only other plausible scenario would be a material bearing monodentate Se_2N_2 *i.e.* with one Pd–N bond and one free nitrogen. One example of a sulfur analogue of this bonding mode is known;[8] however, while we cannot rule this out, the shifts in the IR spectra noted above upon formation from **1** appear to make this unlikely. In addition, the selenium-bearing component of this material exhibits a reasonable degree of air sensitivity—thus when samples of the reaction product are exposed to air they darken within minutes and the IR bands due to the dinitride disappear. The nature of the decomposition products in such situations is not clear, though if the entire reaction of **1** with the crown is performed in undried, non-degassed solvent in air then a crop of colourless crystalline material is obtained which proves (by X-ray crystallography) to be $[NH_4]_2[Se_2O_5]$. Details of this structure will be given in due course; suffice to say this clearly indicates that extensive decomposition occurs when the dinitride is liberated in air (note that the palladium adduct **1** is perfectly air-stable indicating that it is the *free* material which is decomposing).

In conclusion, the reaction of **1** with [14]aneS_4 generates a product which acts as a very amenable source of Se_2N_2. Although we cannot prove it absolutely conclusively, we believe that this reflects the presence of free Se_2N_2 in this reaction product and that this is significantly more reactive than Se_4N_4. Of course the fact this reaction procedure does not generate pure material (as the insoluble nitride is mixed with the equally insoluble palladium-crown by-product) is unfortunate, though in the light of the likely explosive nature of the pure dinitride it may be that the presence of the mixture makes the material safer to handle. The ready formation of **2** indicates that the use of this reagent should open up many new areas of research in Se–N species. The results also vindicate the concept of using the thio-crown as a strongly coordinating though unreactive (towards leaving groups) ligand system—a concept which may well be applicable to other pertinent systems.

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Notes and references

† **Important safety note**! Given that Se_4N_4 is extremely friction sensitive it follows that pure Se_2N_2 is likely to be an equally pernicious explosive; due care must also be taken when preparing the starting material **1** from Se_4N_4 as this reaction is performed at elevated temperatures, thereby exacerbating the explosive potential.

‡ All reactions were performed under a nitrogen atmosphere using CH_2Cl_2 freshly distilled from calcium hydride.

Reaction of $[Bu_4N]_2[Pd_2Br_6(Se_2N_2)]$ **1** with [14]aneS_4 **2** to give product **A**.

A solution of **1** (50 mg, 0.037 mmol) in CH_2Cl_2 (10 cm^3) was treated with solid **2** (20 mg, 0.074 mmol), added with vigorous stirring. An immediate orange suspension was obtained (for analysis at this point see below), with the colour of the solution being completely discharged. During 1 h of further stirring the colour of the solid noticeably lightened to yellow at which stage stirring was stopped, the solid allowed to settle, and the solvent removed *via* Pasteur pipette. Fresh CH_2Cl_2 (10 cm^3) was added, the mixture stirred and then allowed to settle again. After decanting of the solvent the yellow solid (mixture of Se_2N_2 and undefined palladium crown species) was dried *in vacuo* (for spectroscopic analysis at this point see text).

Reactions of $Se_4{}^{15}N_4$ were performed in an identical manner.

CHN on initial orange suspension. Found: C 11.3, H 1.8, N 2.7%. Calc. for $C_{10}H_{20}N_2S_4Pd_2Se_2Br_4$: C 12.2, H 2.0, N 2.8%. IR: see text.

In cases where the original reaction of **1** with **2** was allowed to carry on for longer than 1 h a gradual appearance of Se_4N_4 was confirmed by IR, particularly the strongest peaks at 577 and 426 cm^{-1} which appear away from interfering bands from the thio-crown unit.

Reaction of **A** with metal complexes.

A stirred suspension of **A** (prepared *in situ* on the scale noted above) in CH_2Cl_2 (10 cm^3) was treated with solid $[Bu_4N]_2[Pd_2Br_6]$ (43 mg, 0.037 mmol) immediately generating a dark red solution; this was filtered from the yellow precipitate present and reduced in volume. Slow diffusion of ether vapour yielded well formed red crystals of **1**. Yield 33 mg, 66% based on the overall cycle. Found: C 28.4, H 5.0, N 3.9%. Calc. for $C_{32}H_{72}N_4Br_6Pd_2Se_2$ C 28.2, H 5.3, N 4.1%.

IR spectrum of this product was identical to that of **1** (see text).

A stirred suspension of **A** (prepared *in situ* on the scale noted above) in CH_2Cl_2 (20 cm^3) was treated with solid $[PtCl_2(PMe_2Ph)]_2$ (30 mg, 0.037 mmol) immediately generating a dark orange suspension from which more precipitate appeared after 30 min stirring. After overnight stirring the solution was filtered through Celite and concentrated to 2 cm^3 whereupon slow ether diffusion yielded a crop of well-formed dark orange–brown crystals of **2**.

Yield 19 mg, 48% based on Pt. Found: C 17.8, H 2.0, N 2.6%. Calc. for $C_{16}H_{22}Br_2Cl_2N_2P_2Pt_2Se_2$ C 17.7, H 2.1, N 2.6%.

IR (Se–N bands): 754, 322 cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −26.3 ppm ($^1J(^{31}P–^{195}Pt)$ 3400 Hz), −25.3 ppm (3450 Hz), −24.8 ppm (3507 Hz).

§ *Crystal data* for **2**: $C_{16}H_{22}Br_2Cl_2N_2P_2Pt_2Se_2$, M 1083.12; triclinic, $P\bar{1}$; a = 11.2846(14), b = 14.2595(17), c = 17.271(2) Å, α = 74.752(3), β = 89.924(5), γ = 78.084(5)°, Z = 4, V = 2619.4(6) $Å^3$; D_c 2.747 g cm^{-3}; μ(Mo-Kα) = 16.83 mm^{-1}; λ = 0.71073 Å, T = 93(2) K; 23716 reflections, 9231 independent (R_{int} = 0.0777); Solved by direct methods and refined on F^2 values to give R = 0.0554 for 8517 observed data; wR_2 = 0.1443 for all data. All halogen sites were refined as 50% occupancy Cl and Br with appropriate Pt–Cl and Pt–Br distance constraints. CCDC 647930. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b707450f

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