Facile Introduction of ^{15}N into Chalcogen–Nitrogen Systems using ^{15}N-Labelled Ammonia

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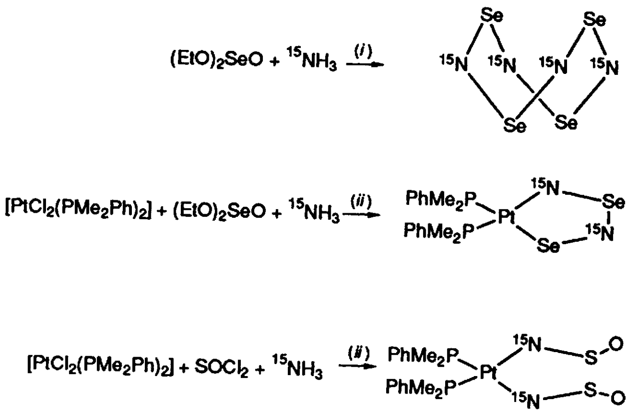
Reaction of ^{15}N-labelled ammonia with a toluene solution of $(EtO)_2SeO$ under reduced pressure gives $Se_4{}^{15}N_4$; in the presence of $[PtCl_2(PMe_2Ph)_2]$ (with CH_2Cl_2 as solvent) the same reagents yield $[Pt(Se_2{}^{15}N_2)(PMe_2Ph)_2]$ whilst $^{15}NH_3$, $[PtCl_2(PMe_2Ph)_2]$ and $SOCl_2$ react to form $[Pt(^{15}NSO)_2(PMe_2Ph)_2]$.

The chemistry of sulfur–nitrogen species and their metal complexes has a long and varied history,[1] with S_4N_4 as the single-most important compound. By way of contrast the chemistry of selenium–nitrogen systems is in its infancy[2] with few characterised species {Se_4N_4, Se_4N_2[3] and $[(Se_3N_2)_n]^{2+}$ (ref. 4)} and little by way of metal selenium–nitrogen chemistry. The most effective preparation of the latter class of complex utilises the reaction of $[PtCl_2(PR_3)_2]$ ($PR_3 = PMe_2Ph$, $PMePh_2$ or PPh_3) with $SeCl_4$[5] (or, more efficiently, $SeOCl_2$[6]) in liquid ammonia to generate $[Pt(Se_2N_2)(PR_3)_2]$, which contains the $Se_2N_2{}^{2-}$ ligand. Complexes of Se_3N^- (ref. 7) and $NSeCl$[8] are also known. Recently it has become clear that Se_4N_4, whilst undoubtedly more chemically inert than its sulfur counterpart, does have significant chemistry in its own right.

Previous work with sulfur–nitrogen species has shown that, by introducing ^{15}N into the system, insights into the mechanism of reaction and the nature of the products may be obtained.[9,10] In many cases this may be achieved by the use of $S_4{}^{15}N_4$, which is readily (and *relatively* cheaply) prepared from commercially available $[^{15}NH_4]Cl$; however, no route has yet been reported to $Se_4{}^{15}N_4$. The two most common preparative routes to Se_4N_4 use either a large amount of liquid ammonia (treated with $SeCl_4$ under pressure) or an excess of the gas [bubbled through a solution of $(EtO)_2SeO$[11]] rendering them prohibitively expensive if undertaken with $^{15}NH_3$. We have now modified the latter reaction to use stoichiometric amounts of the gas, giving $Se_4{}^{15}N_4$ in reasonable yield. The technique may be applied to other systems allowing the preparation of complexes of $Se_2{}^{15}N_2{}^{2-}$ and $^{15}NSO^-$ (Scheme 1), the latter application being particularly important as it is not possible to prepare this ligand from $S_4{}^{15}N_4$.



Scheme 1 Summary of reactions using $^{15}NH_3$ gas. (*i*) Xylene; (*ii*) CH_2Cl_2

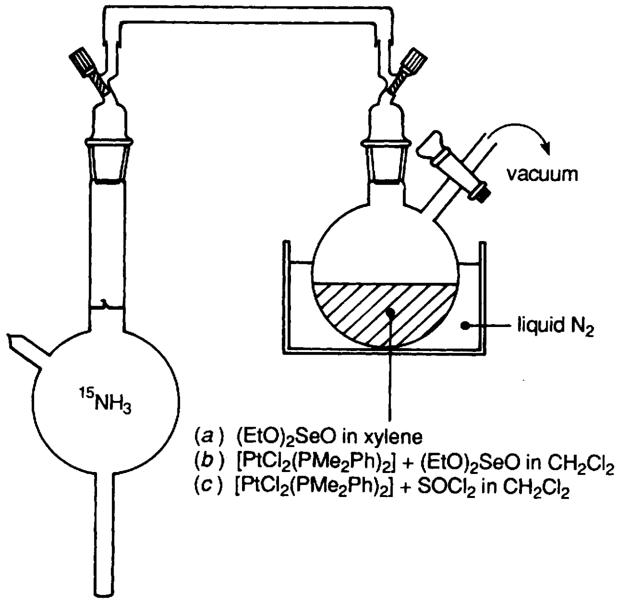


Fig. 1 Apparatus for the synthesis of ^{15}N-labelled compounds from $^{15}NH_3$: (*a*) $Se_4{}^{15}N_4$, (*b*) $[Pt(Se_2{}^{15}N_2)(PMe_2Ph)_2]$ and (*c*) $[Pt(^{15}NSO)_2(PMe_2Ph)_2]$

The apparatus used for the preparation of $Se_4{}^{15}N_4$ is shown in Fig. 1. **CAUTION**: This preparation should only be undertaken with due consideration to the explosive nature of the product. A solution of $(EtO)_2SeO$ (0.87 g, 4.7 mmol) in xylene (50 cm^3) was connected to a vacuum line and a break-seal flask containing $^{15}NH_3$ (250 cm^3, Aldrich) as shown. With the solution frozen in liquid nitrogen the apparatus was evacuated, the tap to the vacuum-line closed and the solution allowed to warm to near room temperature. The break-seal was then punctured and the $^{15}NH_3$ allowed to enter the reaction vessel; a colourless solid precipitated almost immediately. This solid gradually turns green and then orange within a few hours; after stirring overnight it was filtered off (onto paper, *not* sintered glass) then washed with ethanol (2 × 100 cm^3) followed by water (100 cm^3). This results in a reddish sample of

Table 1 Comparison of the IR bands (cm^{-1}) of Se_4N_4 and $Se_4{}^{15}N_4$

Se_4N_4	$Se_4{}^{15}N_4$
799mw	774
782m	762
571s	551
534w	522
424m	417
309w	303
270m	263

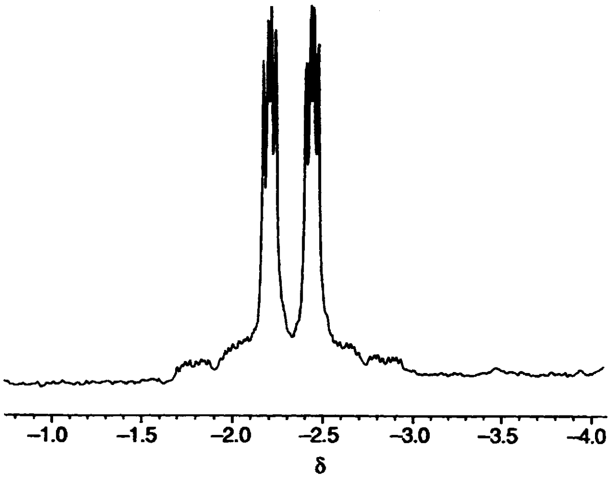


Fig. 2 Part of the $^{31}P-\{^1H\}$ NMR spectrum of $[Pt(Se_2{}^{15}N_2)(PMe_2Ph)_2]$ (in $CDCl_3$) showing the signal due to the phosphorus atom *trans* to selenium ($^{195}Pt-^{31}P$ coupling omitted for clarity). Couplings to the other phosphorus atom, both ^{15}N atoms and both ^{77}Se atoms (*ca.* 7% abundant) can be resolved

impure $Se_4{}^{15}N_4$ which can be purified by washing with dilute KCN solution. Washing with water (5 × 100 cm^3) followed by ethanol (2 × 100 cm^3) gave the pure compound as an orange solid. Typical yield *ca.* 60 mg. The IR spectrum of the product shows the same pattern of lines as seen in the unlabelled case, each shifted to lower frequency by between 6 and 25 cm^{-1} (Table 1). The most notable feature of the reaction is that the yield of $Se_4{}^{15}N_4$ is comparable to that obtained in the standard preparation, in which a massive excess of ammonia is used, indicating a high degree of efficiency.

Clearly, investigations using $Se_4{}^{15}N_4$ will greatly aid the study of many other systems, in particular metal complexes and the selenium–nitrogen cations mentioned earlier; the above preparation allows the labelled compound to be prepared within reasonable financial constraints. Future work will involve optimising the time of reaction to give maximum yields; if the reaction is stopped after only a few hours the yield is low due to the presence of unidentified intermediates, whereas there is clearly some decomposition of the reagents when the reaction is left overnight (*ca.* 16 h), necessitating the purification with cyanide solution.

If the above reaction is performed in the presence of $[PtCl_2(PMe_2Ph)_2]$ it provides a direct route to the first example of a labelled complex of $Se_2{}^{15}N_2{}^{2-}$. A mixture of $[PtCl_2(PMe_2Ph)_2]$ (50 mg, 0.09 mmol) and $(EtO)_2SeO$ (0.1 cm^3, *ca.* 1.5 mmol) in CH_2Cl_2 (50 cm^3) was frozen and treated with $^{15}NH_3$ (250 cm^3) as above. After stirring overnight the resulting dark red solution was filtered from the red precipitate and the solvent removed *in vacuo* to yield crude $[Pt(Se_2{}^{15}N_2)(PMe_2Ph)_2]$. We have found that any preparation of the latter from CH_2Cl_2 invariably results in partial protonation of the product by residual HCl in the solvent, reflecting the high degree of basicity of the metal-bound nitrogen; treatment of the product with 1,8-diazabicyclo[5.4.0]undec-7-ene gives the fully deprotonated species. Both the phosphorus atoms couple to both nitrogens; the phosphorus *trans* to nitrogen shows couplings of 22 and 8 Hz to the metal-bound and diimide nitrogen atoms respectively whilst the phosphorus *trans* to selenium (Fig. 2) exhibits analogous couplings of 3 and 5 Hz.

When $[PtCl_2(PMe_2Ph)_2]$ (0.2 g, 0.36 mmol) in CH_2Cl_2 (50 cm^3) was treated with $SOCl_2$ (0.1 cm^3, 1.4 mmol) and then $^{15}NH_3$ (250 cm^3) introduced as above the product obtained, after stirring overnight, was $[Pt(^{15}NSO)_2(PMe_2Ph)_2]$ which to our knowledge constitutes the first example of a labelled complex of the now well known NSO^- ligand. It may be isolated by filtering the crude pale orange solution then reducing its volume *in vacuo* and precipitating the product with pentane. The ^{31}P NMR spectrum confirms that the product is very pure and reveals a complex AA′BB′ splitting pattern with *cis* and *trans* $^2J(^{15}N-^{31}P)$ couplings of 6 and 21 Hz respectively.

In conclusion, the proven versatility of this technique suggests that it will be applicable to a wide range of systems and that as a result the use of ^{15}N labelling will continue to provide valuable insights into chalcogen–nitrogen chemistry.

Acknowledgements

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References

1 P. F. Kelly and J. D. Woollins, *Polyhedron*, 1986, **5**, 607; T. Chivers and F. Edelmann, *Polyhedron*, 1986, **5**, 1661.
2 P. F. Kelly, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *Chem. Soc. Rev.*, in the press.
3 K. Dehnicke, F. Schmock, K. F. Kohler and G. Frenking, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 577.
4 E. G. Awere, J. Passmore, P. S. White and T. Klapötke, *J. Chem. Soc., Chem. Commun.*, 1989, 1415.
5 I. P. Parkin and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1990, 925.
6 V. C. Ginn and J. D. Woollins, unpublished work.
7 P. F. Kelly, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Chem. Commun.*, 1989, 408.
8 J. Adel, A. El-Kholi, W. Willing, U. Muller and K. Dehnicke, *Chimia*, 1988, **42**, 70; J. Adel and K. Dehnicke, *Chimia*, 1988, **42**, 413.
9 C. W. Allen, P. F. Kelly and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1991, 1343.
10 M. L. Caltayud, J. A. Ramirez and J. Faus, *J. Chem. Soc., Dalton Trans.*, 1991, 2995.
11 J. Adel, C. Ergezinger, R. Figge and K. Dehnicke, *Z. Naturforsch., Teil B*, 1988, **43**, 639.

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