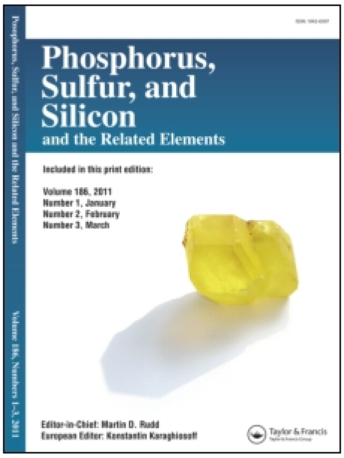

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METAL ADDUCTS OF DISELENIUM DINITRIDE

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Adducts of diselenium dinitride, a species as yet unknown in the free state, may be prepared with either palladium or aluminium as the metal centre. Thus salts of $[Pd_2X_6]^{2-}$ (X = Cl or Br) react with Se_4N_4 at 100°C in CH_2Cl_2 to give $[Pd_2X_6(Se_2N_2)]^{2-}$ while AlX_3 reacts with the same reagent, at ambient temperatures in CH_2X_2, to give $[(AlX_3)_2(Se_2N_2)]$. When X = Cl in the latter case the product cannot be obtained in pure crystalline form; here we present IR data which confirms the presence of the neutral Se_2N_2 unit.

<u>Keywords</u>: Selenium, nitride, adducts, palladium, aluminium.

INTRODUCTION

Recent years have seen a wide range of developments within the area of chalcogen-nitrogen chemistry, leading to the growing conclusion that many heavy-chalcogen analogues of known sulfur-nitrides will ultimately prove isolable. We have developed routes to adducts in which diselenium dinitride, Se_2N_2, is coordinated to a metal centre. As the free nitride is as yet unknown, it follows that the isolation of such complexes constitutes an important advance in our understanding of Se-N chemistry.

RESULTS AND DISCUSSION

Reactions of Se_4N_4 with palladium halide complexes

No reaction is apparent upon stirring a suspension of Se_4N_4 in a dichloromethane solution of $[A]_2[Pd_2X_6]$ ($A = [PPh_4]^+$ or $[^nBu_4N]^+$, X = Cl or Br) at ambient temperatures. If, however, the mixture is transferred to a sealed (Young's joint) tube and heated to100°C for a few hours (**safety note: Se_4N_4 is an extremely explosive material whose pernicious properties are exacerbated by the use of high temperatures**) salts of the type $[A]_2[Pd_2X_6(Se_2N_2)]$ may be isolated.[1],[2] In the case of the $[PPh_4]^+$ salts pure material is best generated by slow diffusion of ether into CH_2Cl_2 solutions of the crude products while the $[^nBu_4N]^+$ salts can be isolated in highly crystalline form by concentrating and cooling the crude solutions. Yields for the four species prepared in this way vary from ca.20 % (based upon Pd) for $[PPh_4]_2[Pd_2Cl_6(Se_2N_2)]$ to 67% in the case of $[^nBu_4N]_2[Pd_2Br_6(Se_2N_2)]$.[2]

All the aforementioned products contain a neutral, four-membered Se_2N_2 ring bridging the PdX_3 units *via* Pd-N bonds (Fig.1). Once formed, these products appear to be surprisingly air stable (for example, slow evaporation of a CH_2Cl_2 solution of $[^nBu_4N]_2[Pd_2Br_6(Se_2N_2)]$ in air regenerates crystalline product with no appreciable decomposition) and, in marked contrast to Se_4N_4, are not explosive. This stability is confirmed by the fact that

$[PPh_4]_2[Pd_2Br_6(Se_2N_2)]$ results unexpectedly from the reaction of $Se(NSO)_2$ with $[PPh_4]_2[Pd_2Br_6]$.[2]

Reactions of Se_4N_4 with aluminium trihalides.

Unlike the palladium halide dimers, aluminium tribromide reacts with Se_4N_4 at ambient temperatures. Thus stirring the two in CH_2Br_2 results in a dark solution from which air sensitive yellow crystals of $[(AlBr_3)_2(Se_2N_2)]$ precipitate overnight.[3] Again X-ray crystallography reveals the presence of the Se_2N_2 ring bound through the nitrogens (Fig. 1). Unlike its sulfur analogue it does not undergo halogen exchange in CH_2Cl_2, precluding preparation of $[(AlCl_3)_2(Se_2N_2)]$ in this manner.

Attempts to prepare the latter by direct reaction of $AlCl_3$ with Se_4N_4 appear to be only partially successful. The result is an off-white product whose infra-red spectrum suggests the presence of impure $[(AlCl_3)_2(Se_2N_2)]$. As Fig.2 shows, comparison of the spectrum of $[(AlBr_3)_2(S_2N_2)]$ with that of $[(AlBr_3)_2(Se_2N_2)]$ reveals the three bands associated with the Se_2N_2 unit (ie those that show a significant move to lower frequency on going fron S to Se): at 787, 658 and 422 cm^{-1}. Analogous bands may be seen at 794, 666 and 407 cm^{-1} in the impure $[(AlCl_3)_2(Se_2N_2)]$.

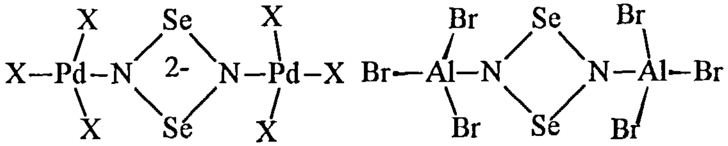

Figure 1 The structure of the first adducts of Se_2N_2

The presence of impurities in the latter can be confirmed by the broad band at ca 1100cm^{-1}, but the spectrum is sufficiently informative (note in particular the distinctive pair of peaks in the 600-1000 cm^{-1} region that are common to all three) to confirm the presence of the Se_2N_2 adduct. Work on producing pure samples of the compound is underway.

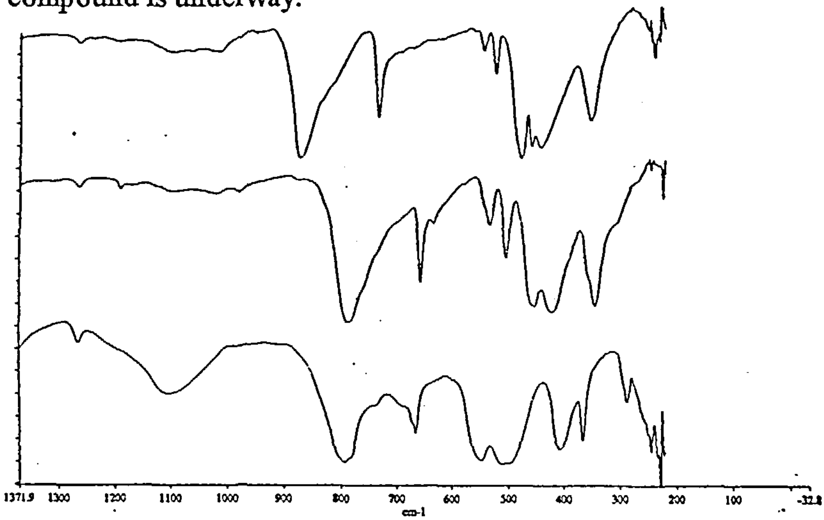

FIGURE 2 Comparison of the IR spectra of (from top) $[(AlBr_3)_2(S_2N_2)]$, $[(AlBr_3)_2(Se_2N_2)]$ and $[(AlCl_3)_2(Se_2N_2)]$.

Acknowledgements

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