# Preparation and crystal structure of [(AlBr₃)₂(Se₂N₂)], the first example of a main-group element adduct of diselenium dinitride

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The room temperature reaction of AlBr₃ with Se₄N₄ in CH₂Br₂ generated [(AlBr₃)₂(Se₂N₂)] as an air-sensitive, yellow solid; X-ray crystallography confirmed the presence of the neutral Se₂N₂ ligand, bridging *via* two Al–N bonds.

The recent report of the preparation of the first examples of adducts of diselenium dinitride, Se₂N₂,[1] added weight to the fast developing conclusion that the chemistry of selenium–nitrogen systems may well, ultimately, prove to be as diverse as that of their sulfur counterparts.[2] The adducts in question, salts of [Pd₂Cl₆(Se₂N₂)]²⁻, form in the high-temperature reaction of Se₄N₄ with simple halogen-bridged palladium salts, and appear to be stable both to air and friction (in marked contrast to Se₄N₄ which is a particularly pernicious explosive). Here we report on the preparation of the first example of a main-group metal adduct of diselenium dinitride.

It has long been known that S₄N₄ reacts with AlBr₃ to generate the S₂N₂ adduct [(AlBr₃)₂(S₂N₂)];[3] we have now found that the analogous reaction of Se₄N₄ may be performed. Thus treatment of a suspension of Se₄N₄ (**CAUTION**: severe explosive!) in CH₂Br₂ with solid AlBr₃ (molar ratio 1 : 5), followed by thorough stirring, resulted in the immediate formation of a dark red, clear solution which was allowed to stand overnight. During this time a yellow crystalline solid was deposited; this was separated by decanting the mother liquor, washed with CH₂Br₂ (20 cm³) and dried *in vacuo*.

The crystal structure of this product confirms it to be [(AlBr₃)₂(Se₂N₂)] (see Fig. 1), revealing the presence of a neutral Se₂N₂ unit bridging the two AlBr₃ moieties *via* two Al–N bonds;† *i.e.* isostructural with [(AlBr₃)₂(S₂N₂)].[5] The resulting Al₂Se₂N₂ unit is effectively planar [the largest deviation from planarity being at N(1) 0.06 Å]; this plane also contains one of the bromine atoms on each aluminium. As has been noted many times for adducts of S₂N₂[6] there is a significant interaction between one of the bromines and the chalcogen–nitrogen ring; in this case it can be quantified by

the fact that the N(1)–Al(1)–Br(1) angle is 94.2°, which is some 15° smaller than the average of the corresponding angles to the other bromines. The average Se–N bond length in [(AlBr₃)₂(Se₂N₂)] is effectively identical to that in [Pd₂Cl₆(Se₂N₂)]²⁻.

The IR spectrum of the crystalline product shows an excellent correlation with that of [(AlBr₃)₂(S₂N₂)], in particular the two strong bands which occur in the latter at 870 and 733 cm⁻¹ are seen at 787 and 658 cm⁻¹ in the selenium product (and retain the same intensity ratio). The yield of [(AlBr₃)₂(Se₂N₂)] prepared in this manner, though not particularly high (typically 30 mg from 56 mg Se₄N₄ which equates to 14% based upon selenium) is sufficient to allow investigation into its chemical properties. Such investigations are currently ongoing and two points have emerged so far. The first of these is its severe air sensitivity; while aerial degradation of the S₂N₂ adducts of aluminium halides takes place over a number of seconds, samples of [(AlBr₃)₂(Se₂N₂)] appear to decompose effectively instantaneously, turning a dark brown-black in colour and then lightening over a matter of minutes to orange (a colour consistent with the ultimate formation of Se₄N₄). It is worth noting that while this air sensitivity makes the product a lot harder to handle than the aforementioned palladium adducts (which are perfectly air stable), the fact that the reaction is performed at ambient temperature (rather than the 100 °C required in the latter case) greatly reduces the risk of Se₄N₄ detonation.

The other observation noted is that, unlike [(AlBr₃)₂(S₂N₂)], [(AlBr₃)₂(Se₂N₂)] does not undergo halogen exchange in CH₂Cl₂. Thus we cannot, unfortunately, prepare a pure sample of [(AlCl₃)₂(Se₂N₂)] in this manner. Attempts to prepare the latter by direct reaction of AlCl₃ with Se₄N₄ appear to be only partially successful. The IR spectrum of the off-white product of this reaction suggests that [(AlCl₃)₂(Se₂N₂)] is indeed present but is significantly contaminated with an unidentified by-product.
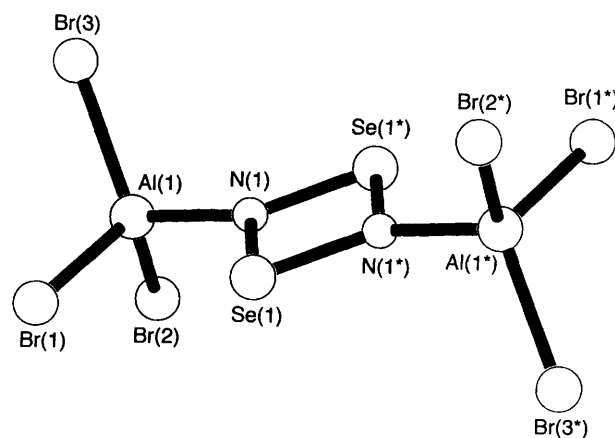
† Crystal data. Al₂Br₆N₂Se₂, M = 719.32, monoclinic, space group P2₁/n (no. 14), a = 7.613(1), b = 9.940(2), c = 9.552(2) Å, β = 110.41(2)°, U = 677.5(2) Å³, Z = 2, Dc 3.53 g cm⁻³, μ(Cu-Kα) = 290.63 cm⁻¹, F(000) = 636.0, dimensions 0.1 × 0.1 × 0.03 mm, T = 298 K. All measurements were made on a Rigaku AFC7S diffractometer with graphite-monochromated Cu-Kα (λ = 1.541 78 Å) radiation and employing the ω–2θ scan technique to a maximum 2θ value of 120.1°. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.387 to 1.00. The structure was solved by direct methods[4] and expanded using Fourier techniques with all atoms refined anisotropically on F (apart from Al and N which were refined isotropically) to give R = 0.074 for 669 observed reflections [I > 3σ(I)]. Maximum shift/error in final cycle 0.10. It should be noted that the air sensitivity of the crystals invariably led to a degree of decomposition upon mounting. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/262.



**Fig. 1** Crystal structure of [(AlBr₃)₂(Se₂N₂)]. Selected bond distances (Å) and angles (°): Al(1)–N(1) 1.92(2), N(1)–Se(1) 1.77(1), N(1)–Se(1*) 1.81(1); N(1)–Al(1)–Br(1) 94.2(5), N(1)–Al(1)–Br(2) 112.7(5), N(1)–Al(1)–Br(3) 108.1(5), Se(1)–N(1)–Se(1*) 97.6(7), N(1)–Se(1)–N(1*) 82.4(7), Se(1)–N(1)–Al(1) 122.4(8), Se(1*)–N(1)–Al(1) 139.9(8)

The isolation of $[(AlBr_3)_2(Se_2N_2)]$ in this manner represents a new class of reaction for $Se_4N_4$. Previous reactions have involved either transition-metal species or selenium cations;[2] this is the first example of reaction with a main-group Lewis acid. As such it only serves to fuel the growing conclusion that a substantial body of chemistry of selenium–nitrogen systems awaits elucidation and suggests that, in view of the extensive range of $S_2N_2$ adducts that have been prepared, many more examples of adducts of $Se_2N_2$ should be possible.

## References

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