$[Re_9Se_{11}Br_6]^{2-}$: the first example of an Re_9 condensed cluster†

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A new type of rhenium condensed cluster $[Re_9Se_{11}Br_6]^{2-}$ has been synthesized by the reaction of Re_3Br_9 and PbSe at 550 °C and structurally characterised; the structure of $[Re_9Se_{11}Br_6]^{2-}$ contains the bioctahedral rhenium cluster Re_9 which can be considered as the result of progressive uniaxial condensation of three Re_3 clusters.

Condensation of fragments with the formation of polyhedral clusters is one of the most promising methods in synthetic cluster chemistry.[1] The most remarkable examples of the applicability of this method are seen in the syntheses of some octahedral clusters, for example, the zirconium halide cluster $[Zr_6Cl_{12}(PMe_2Ph)_6]$ which is formed from three binuclear complexes $[Zr_2Cl_6(PMe_2Ph)_4]$,[2] or of sulfide and selenide cluster complexes of molybdenum and tungsten $[M_6Y_8(PEt_3)_6]$ by reductive dimerization of two triangular cluster complexes $[M_3S_4Cl_4(PEt_3)_x]$.[3] Recently[4] we have developed a condensation method for the high yield synthesis of the octahedral rhenium cluster chalcobromides $Re_6E_4Br_{10}$ and $Re_6E_8Br_2$ (E = S, Se, Te) using the triangular cluster rhenium bromide Re_3Br_9 and lead or cadmium chalcogenides (PbE or CdE where E = S, Se and Te) as starting compounds. We have found that given condensation reactions can yield not only octahedral clusters but also other cluster complexes.

Here we present the preparation‡ and structural characterisation§ of a new cluster complex $[PPh_4]_2[Re_9Se_{11}Br_6]$ containing the bioctahedral rhenium cluster anion $[Re_9Se_{11}Br_6]^{2-}$. This type of cluster was not known for rhenium previously. It can be considered as the result of progressive uniaxial condensation of three Re_3 clusters.

$[PPh_4]_2[Re_9Se_{11}Br_6]$ crystallises with triclinic symmetry to form dark red prisms. The $[Re_9Se_{11}Br_6]^{2-}$ unit (Fig. 1) is structurally identical to that of $Co_9Se_{11}(PPh_3)_6$[7] and Mo_9E_{11} (E = S, Se) which was found in some ternary molybdenum chalcogenides.[8–14] In the crystal structures of the latter, the metal ion is bonded to six X atoms belonging to the adjacent Mo_9E_{11} cluster units, so $[Mo_9E_{11}X_{6/2}]$ units similar to $[Re_9Se_{11}Br_6]^{2-}$ are formed.

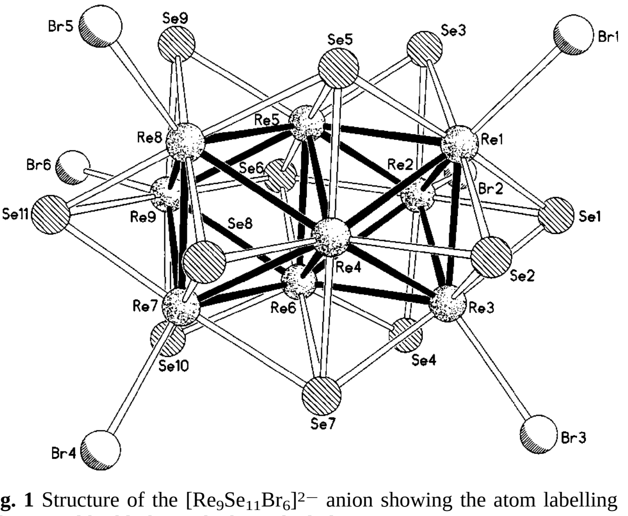

Fig. 1 Structure of the $[Re_9Se_{11}Br_6]^{2-}$ anion showing the atom labelling scheme and highlighting the bioctahedral Re_9 core

The environments of the external Re atoms (Re1–3 and Re7–9) in $[Re_9Se_{11}Br_6]^{2-}$ are similar and consist of four Re atoms, four Se atoms forming a quasi-planar square, and one Br atom. The internal Re atoms Re4–6 are connected to six Re and four Se atoms.

The Re–Re distances within the Re_9 cluster can be classified into three groups. The first corresponds to the distances within the two external Re_3 triangles formed by the Re1–3 and Re7–9 atoms, here the mean distances are 2.596(1) and 2.594(1) Å respectively; these are the shortest Re–Re distances in the Re_9 cluster. The second group is formed by Re4–6 atoms of the internal Re_3 triangle, these Re–Re distances are the longest in the cluster with a mean of 2.687(1) Å. And finally, the third group comprises the Re–Re bonds between these Re_3 triangles (inter-triangle distances) which range from 2.645(1) to 2.663(1) Å. So, in the $[Re_9Se_{11}Br_6]^{2-}$ cluster the two external Re_3Se_3 triangles are compressed whereas the middle Re_3Se_3 triangle is expanded by comparison.

It is well known that the metal–metal distances in octahedral condensed clusters depend on the number of the valence electrons on the metal atom [the so-called valence electron concentration (VEC)], which are available for the metal–metal intracluster bonding.[15] Comparing the Re_9 obtained here and the Mo_9 cluster which is found in some ternary molybdenum selenides,[8–14] we can see that an increased charge on this cluster leads mainly to an increase in the size of the median triangle. For example, going from $In_2Mo_{15}Se_{19}$ to $In_{3.33}Mo_{15}Se_{19}$, the corresponding Mo–Mo distances increase from 2.681 to 2.768 Å[8] showing that the same tendency is found here.

To provide a further strategy for the synthesis of other condensed rhenium clusters, it is interesting to consider the VEC and the stability of related compounds. For example, in the series of condensed clusters $[Mo_9E_{11}]^0$, $[Mo_{12}E_{14}]^{2-}$, $[Mo_{18}E_{20}]^{4-}$, $[Mo_{24}E_{26}]^{6-}$, $[Mo_{30}E_{32}]^{8-}$, $[Mo_{6/2}E_{6/2}]^{2-}$ the number of valence electrons per metal atom (VEC) available for M–M bonding is increased from 3.56, 3.83, 4, 4.08, 4.13 to 4.33, respectively,[16] to allow an increase in the order of the metallic bonding. In other words, the formal oxidation state of metal atoms is lowered. In rhenium cluster chemistry, the situation is the same, namely, the VEC for $[Re_6E_8]^{2+}$ and $[Re_9Se_{11}Br_6]^{2-}$

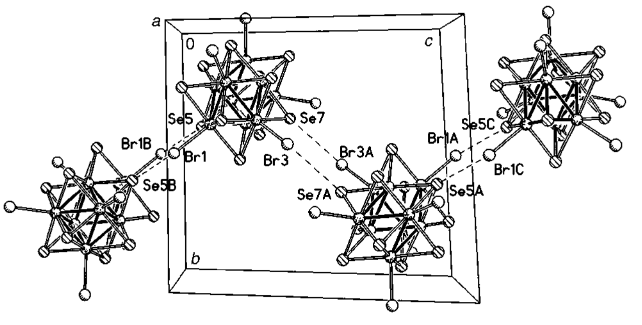

Fig. 2 Intercluster interactions *via* Se···Br short contacts

cluster units is 4 and 4.11, respectively. Here it is interesting to remark that for the hypothetical $[Re_{12}E_{14}Br_6]^{2-}$ dianion (the unknown member from the next step of progressive condensation of Mo_3X_3 units) the VEC would be 4.33, that is the same as in $[Mo_{6/2}E_{6/2}]^{2-}$ clusters.

An interesting feature of the structure is the infinite chains of clusters along the crystallographic *c* axis: each cluster unit $[Re_9Se_{11}Br_6]^{2-}$ exhibits interactions to two neighbours *via* Se···Br short contacts across inversion centres (Fig. 2): Br1–Se5A 3.547 Å, Br3–Se7B 3.840 Å.

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Notes and References

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‡ *Experimental procedure*: Re_3Br_9, PbSe and KBr in molar ratio 1 : 4 : 6 were heated in an evacuated fused-silica tube at 550 °C for 2 d. The reaction mixture was washed with water and a small amount of boiled HBr. The resulting solid was washed with MeOH to give a dark red solution. An excess of $[PPh_4]Br$ was added to this solution causing precipitation of a brown powder. Recrystallisation from MeCN leads to the formation of two types of crystals, dark red prisms and pyramids. The prism crystals were used for X-ray analysis.

§ *X-Ray structure analysis*: $(PPh_4)_2Re_9Se_{11}Br_6$, dark red prism, crystal dimensions, 0.33 × 0.19 × 0.18 mm, triclinic, space group $P\bar{1}$, a = 13.3335(9), b = 15.3791(11), c = 17.1175(12) Å, α = 84.687(2), β = 73.086(2), γ = 77.672(2)°, Z = 2, V = 3279.1(4) Å^3 [T = 160(2) K]. D_c = 3.750 g cm^{-3}, Bruker SMART CCD diffractometer, $2\theta_{max}$ = 50.00; Mo-Kα radiation, $\lambda(K\alpha_1)$ = 0.710 73 Å; ω rotation with narrow frames, 20 611 reflections measured, 11 412 independent reflections (R_{int} = 0.0399) all of which were included in the refinement; data corrected for Lorentz and polarisation effects[5] and for absorption by a semi-empirical method based on high data redundance, μ = 263.8 cm^{-1}, min, max. transmission = 0.0257, 0.0659, solution by direct methods,[6] anisotropic refinement on F^2 by full-matrix least squares[6] to give: $R_w = \{\Sigma[w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]\}^{1/2}$ = 0.0901, conventional R = 0.0371 for 8028 reflections having $F_o^2 > 2\sigma(F_o^2)$, goodness of fit on F^2 values = 0.956 for 686 refined parameters. The largest features in the final difference electron density map were within ±2.87 e Å^{-3} close to the Re atoms. CCDC 182/956.

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