An Octahedral Rhenium(III) Cluster: *X*-Ray Crystal Structure of $Na_4Re_6S_{10}(S_2)$

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Summary The reaction of Re, $KReO_4$, or ReS_2 with an excess of Na_2CO_3 or K_2CO_3 and S at 750 °C yields $M^I_4Re_6S_{12}$, Re^{III} compounds containing Re_6 octahedra located in cubes of sulphide ions with sulphide and disulphide bridges between octahedra.

Although rhenium(III) and molybdenum(II) are both d^4 systems and both species form analogous compounds containing metal–metal bonds,[1] until recently octahedral clusters of rhenium(III) had not been reported. Octahedral clusters are well established in molybdenum dihalide and sulphide systems and may be present in the mixed chalconides $Mo_2Re_4X_8$ and $Mo_4Re_2X_8$.[2] Spangenberg and Bronger[3] have reported the preparation and structures of Na, K, and Cs salts of sulphides containing Re_6 clusters with bridging sulphide and disulphide units. We have prepared the Na and K derivatives by another route and have observed a slow phase change in these salts which was not reported by these authors.[3]

The reaction of Re, $KReO_4$, or ReS_2 with a thirty-fold excess by weight of Na_2CO_3 or K_2CO_3 and of S at 750 °C for 1 h[4] produces a mixture of small, optically clear red and metallic black crystals which often contain red inclusions. It has not yet proved possible to separate a sufficient quantity of the individual components for microanalysis, but a single crystal *X*-ray study of the red Na salt has shown it to be $Na_4Re_6S_{12}$. Presumably the black compound has a similar stoicheiometry. The red crystals slowly transform into black crystals upon standing in air, H_2O, Na_2S, or HCl solutions, or in ethanol. The unit cell dimensions of the two compounds are similar. Two-probe resistivity measurements have shown the black Na derivative to be a semiconductor with a gap of 0·18 eV. The red compounds are insulators.

Crystal data: $Na_4Re_6S_{12}$: $M = 1593{\cdot}9$, monoclinic, $a = 15{\cdot}923(2)$, $b = 9{\cdot}605(1)$, $c = 11{\cdot}515(1)$ Å, $\beta = 92{\cdot}29(3)°$, $Z = 4$, space group $C2/c$. Black compound: monoclinic, $a = 16{\cdot}05(2)$, $b = 9{\cdot}42(1)$, $c = 11{\cdot}56(1)$, $\beta = 90{\cdot}8(1)$, space group $C2/c$. Single crystal X-ray diffraction data from an optically clear red crystal were collected with an Enraf-Nonius CAD-4 diffractometer at 23 °C [$\lambda(\text{Mo-}K_\alpha)$, graphite monochromator, ω scan, $2\theta_{\max} = 50°$] giving 1158 reflections with $I_{\text{obs}} > \sigma(I_{\text{obs}})$. The structure was solved using the heavy-atom method and refined by full-matrix least-squares refinement (anisotropic temperature factors, anomalous dispersion corrections, data corrected for absorption) to $R = 0{\cdot}079$. The structure of the cluster is shown in the Figure. The arrangement of the unit cell contents is similar to that reported.[3]

Red crystals of $Na_4Re_6S_{12}$ contain four octahedral Re_6 clusters per unit cell. The clusters are very slightly flattened [Re(3)—Re(3′), 3·662(4); Re(1)–Re(1′) and Re(2)–Re(2′), 3·713(4) Å]. Re(1) to Re(2) or Re(2′) distances average 2·625(3,3,3) Å where the numbers in parentheses are the e.s.d.s and the deviation of the shortest and longest bond distances from the mean, respectively. The distances from Re(3) to Re(1) and Re(2) average 2·608(4,5,5) Å. The six atoms of the cluster are located just outside the faces of an approximate cube of S atoms with a cube edge of 3·38(3,4,4) Å [Re–S, 2·40(1,2,2) Å]. Each Re is bonded to a fifth sulphur lying along the approximate 4-fold axis of the cluster. Four of these S atoms bridge to four adjacent octahedra [Re–S, 2·48(1) Å]; two others are part of an S_2^{2-} bridge between octahedra [Re–S, 2·44(1); S–S, 2·09(2) Å]. The Na atoms, two on 2-fold axes and one in a general position, are located in irregular holes in the S array with co-ordination numbers of 6, 8, and 7, respectively.

The average Re–Re bond lengths, which are consistent[5] with a bond order of one in the cluster, are *ca.* 0·45 Å longer than those found in quadruply bonded $Re_2X_8^{2-}$ systems and *ca.* 0·25 Å longer than those in trimeric clusters.[1] They are equidimensional to the Mo–Mo distances found in the analogous Mo_6Cl_{12} structure.[6]

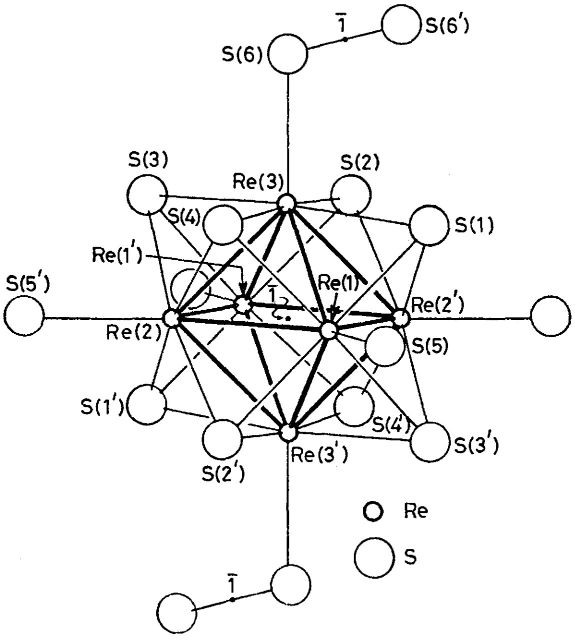

FIGURE. The octahedral Re_6 cluster with bridging sulphide and disulphide units. Primed atoms are related to unprimed atoms by symmetry elements of the unit cell.

Red crystals of $Na_4Re_6S_{12}$ transform to black crystals over a period of several weeks with little loss of crystal integrity, and no change of space group. The cell dimensions of the two crystals are almost identical. The change from a red insulating crystal to a black semi-conducting form may involve oxidation of the Re_6 cluster with concomitant cleavage of the disulphide bond. Structural studies of the black crystals are in progress.

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