Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: CAD-4 *Software*. Data reduction: *SDP* (Frenz, 1982). Program(s) used to solve structure: *SDP*. Program(s) used to refine structure: *SDP*. Molecular graphics: *ORTEP* (Johnson, 1965).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1167). Services for accessing these data are described at the back of the journal.

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# Re₆Se₇Br₄

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## Abstract

The crystal structure of the semiconductor hexarhenium heptaselenium tetrabromide has been studied by single-crystal X-ray diffraction. The results show that it may be included in the group of Chevrel phases which are very common in molybdenum cluster compounds. Re₆Se₇Br₄ crystallizes with well defined Re₆|Se₇Br| clusters linked in three dimensions by bromide bridges. Accurate single-crystal X-ray investigations showed that a rhombohedral space group describes the structure best.

## Comment

A number of compounds containing octahedral rhenium clusters have been investigated and related to Chevrel phases (Perrin & Sergent, 1988). The ternary compounds Re₆$X_iY_j$ ($X$ = Se, S; $Y$ = Cl, Br) crystallize with well defined clusters of Re₆$L_8$ ($L$ = $X$ and/or $Y$). In each cluster, the Re atoms define an octahedron which is located in the centre of a cube defined by the 8 $L$ atoms; the $L$ atoms are called inner ligands. In general, the links between the clusters are made *via* the $Y$ atoms.

The crystal structures of several compounds in the Re₆Se$_i$Br$_j$ family have been investigated for different types and different numbers of inter-cluster atoms. The 12 single covalent Re—Re bonds in the octahedron involve 24 of the 42 valence electrons (six Re atoms in the $4f^{14}5d^56s^2$ state). The 18 remaining electrons are used in a subtle charge transfer through ionic bonds between the halogen and chalcogen atoms. By controlling the chalcogen number $i$ and the halogen number $j$ and preserving $i + 2j = 18$, structures with Re₆$L_8$ clusters linked by halogen bridges in one, two or three dimensions can be obtained, as reported by Perrin & Sergent (1988).

In related studies, the crystal structures of Re₆Se₅Cl₃Cl₄Cl$_{2/2}$ (Perrin, Leduc & Sergent, 1991) and Re₆Se₈Br$_{4/2}$ (Speziali *et al.*, 1988) have been reported. In the first compound, successive Re₆Se₅Cl₃Cl₄ units are linked by one-dimensional *trans*-chlorine bridges, while in the second compound, the Re₆Se₈ clusters are linked in two dimensions *via* Br atoms.

In the title compound, Re₆|Se₇Br|Br₃, the Re₆|Se₇Br| clusters are linked *via* halogen bridges in three dimensions. From the X-ray diffraction point of view, Se ($Z$ = 34) and Br ($Z$ = 35) atoms are very similar, and, as a
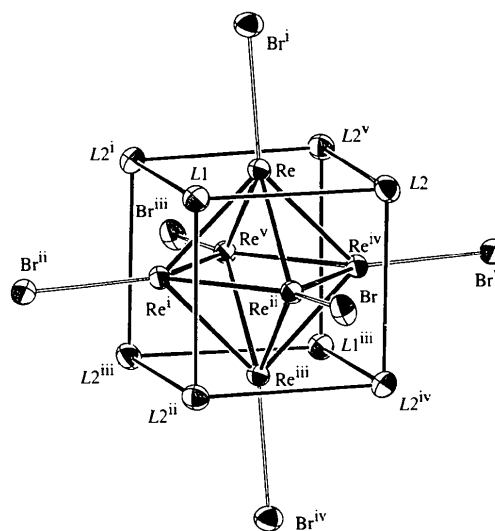


Fig. 1. The Re₆$L_8$Br₃ molecule. Displacement ellipsoids are shown at the 60% probability level. The ternary rotation axis passes through the $L$1 and $L$1$^{iii}$ atoms.

consequence, it is difficult to distinguish between the Se and the Br atoms in the inner ligand positions of the $Re_6|Se_7Br|$ cluster. In order to avoid ambiguity concerning Br and Se, the cluster will also be represented from now on as $Re_6L_8$.

The greatest experimental difficulty when dealing with crystals of $Re_6|Se_7Br|Br_3$ is their high X-ray absorption $[\mu(Ag\ K_\alpha) = 37$ and $\mu(Mo\ K_\alpha) = 67\ mm^{-1}]$. In order to minimize this absorption problem, data were collected on different samples. The best results were obtained using a cylindrical sample and Ag $K\alpha$ radiation. The value of $\mu r$ (3.0) used in the cylindrical absorption correction was empirically optimized.

There is no ambiguity in the number of Se and Br atoms in the chemical formula $Re_6|Se_7Br|Br_3$ of the samples studied. Rough experiments showed that the electrical conductivity of these samples is compatible with that observed in semiconductors. Changing the ratio 7Se:4Br would give some free electrons in the structure and the sample would be a metallic conductor.

## Experimental

Crystals were obtained by chemical transport reactions.

### Crystal data

$Re_6Se_7Br_4$
$M_r = 1989.56$
Rhombohedral
$R\bar{3}c$ (hexagonal axes)
$a = 9.827\ (4)\ \text{Å}$
$c = 31.658\ (6)\ \text{Å}$
$V = 2648\ (3)\ \text{Å}^3$
$Z = 6$
$D_x = 7.49\ Mg\ m^{-3}$
$D_m$ not measured

Ag $K\alpha$ radiation
$\lambda = 0.56083\ \text{Å}$
Cell parameters from 33 reflections
$\theta = 8.00–14.97°$
$\mu = 36.65\ (4)\ mm^{-1}$
Room temperature
Cylinder
0.06 (radius) × 0.15 mm (length)
Black

### Data collection

Siemens P4 diffractometer
$\theta/2\theta$ scans
Absorption correction: cylindrical
$T_{min} = 0.015,\ T_{max} = 0.029$
5152 measured reflections
883 independent reflections
681 reflections with $F \geq 3\sigma(F)$

$R_{int} = 0.051$
$\theta_{max} = 22.5°$
$h = -9 \rightarrow 10$
$k = -12 \rightarrow 11$
$l = -43 \rightarrow 42$
3 standard reflections every 197 reflections intensity decay: none

### Refinement

Refinement on $F$
$R = 0.026$
$wR = 0.037$
$S = 3.304$
689 reflections
28 parameters
Weighting scheme based on measured s.u.'s
$w = 1/[\sigma(F)]$

$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 1.26\ e\ \text{Å}^{-3}$
$\Delta\rho_{min} = -2.06\ e\ \text{Å}^{-3}$
Extinction correction: Larson (1967)
Extinction coefficient: 0.188 (8)
Scattering factors from Cromer & Mann (1968)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters $(\text{Å}^2)$*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

| | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| Re | 0.15980 (4) | 0.01426 (4) | 0.03397 (1) | 0.0140 (2) |
| L1 | 0 | 0 | 0.09781 (5) | 0.0185 (3) |
| L2 | 0.0274 (1) | −0.2816 (1) | 0.03120 (3) | 0.0187 (4) |
| Br | −1/3 | −0.3899 (1) | 1/12 | 0.0209 (4) |

Table 2. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Re—Re$^i$ | 2.607 (1) | Re—L2$^v$ | 2.497 (2) |
| Re—Re$^{ii}$ | 2.607 (1) | Re—Br$^j$ | 2.604 (1) |
| Re—Re$^{iii}$ | 3.701 (1) | L1—L1$^{iii}$ | 6.192 (3) |
| Re—Re$^{ix}$ | 2.6267 (6) | L2—L2$^{iii}$ | 6.149 (3) |
| Re—Re$^v$ | 2.6267 (7) | L1—L2 | 3.595 (2) |
| Re—L1 | 2.519 (1) | L1—L2$^{iii}$ | 5.015 (2) |
| Re—L2 | 2.524 (1) | L2—L2$^{ix}$ | 3.519 (2) |
| Re—L2$^i$ | 2.521 (2) | L2—L2$^i$ | 5.042 (3) |
| Re$^i$—Re—Re$^{ii}$ | 60.00 (4) | L1—L2$^{ii}$—L1$^{iii}$ | 90.45 (5) |
| Re$^{ix}$—Re—Re$^v$ | 59.50 (3) | L1—L2—L2$^v$ | 89.66 (4) |
| L2—L1—L2$^i$ | 89.07 (5) | L2$^i$—L2—L2$^{ix}$ | 89.99 (4) |
| L2$^{ii}$—L1—L2$^v$ | 89.55 (5) | L1—L2—L2$^{ix}$ | 89.66 (4) |
| L2—L1—L2$^{ii}$ | 89.07 (4) | L2$^{ix}$—L2—L2$^v$ | 91.53 (5) |
| L2$^i$—L1—L2$^{ii}$ | 89.08 (5) | Re$^{ii}$—Br—Re$^{vi}$ | 118.16 (6) |

Symmetry codes: (i) $-y, x - y, z$; (ii) $-x + y, -x, z$; (iii) $-x, -y, -z$; (iv) $y, -x + y, -z$; (v) $x - y, x, -z$; (vi) $x - y - \frac{2}{3}, -\frac{1}{3} - y, \frac{1}{6} - z$.

It was found that different sets of parameters could be used to describe the unit cell. In order to avoid biased results, the lowest symmetry (triclinic) was used for the data collection. A total of 5152 reflections were collected in the triclinic system in such a way that each one of the 883 non-equivalent reflections in the rhombohedral system was measured on average approximately six times.

The refinement was performed in very careful steps using small damping-factor values. The strategy of alternately fixing some parameters was applied; only at the very end were the complete set of parameters refined together. After a $\Delta F$ calculation, the largest difference peak was found in the neighbourhood of the Re atom. The structure refinement based on a disorder model which considers the inner-ligand population parameter $L = 7/8Se + 1/8Br$ did not affect the results.

Data collection: *XSCANS* (Siemens, 1991). Cell refinement: *SHELXTL/PC* (Sheldrick, 1990). Data reduction: *XRAY72* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Program(s) used to solve structure: *FOURR* in *XRAY72*. Program(s) used to refine structure: *CRYLSQ* in *XRAY72*. Molecular graphics: *ORTEPIII* (Bunnett & Johnson, 1996).

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# Ba₂ErCl₇

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## Abstract

Dibarium erbium heptachloride has a network structure composed of $ErCl_7$ and $BaCl_9$ polyhedra. Since the array of the Ba and Er atoms is isostructural with the alloy $Co_2Si$, the structure can be considered as a stuffed $Co_2Si$-type structure. The mean bond distances are 2.704 Å for $ErCl_7$, 3.221 Å for $Ba1Cl_9$, and 3.212 Å for $Ba2Cl_9$. Some of the Cl atoms form tunnels running parallel to the $c$ axis.

## Comment

An efficient infrared-to-green up-conversion luminescence has been reported for $ErCl_3$–$BaCl_2$ compounds by Wang & Ohwaki (1993). In the systems $RECl_3$–$BaCl_2$ ($RE$ = La, Sm, Gd and Yb), the presence of a 1:2 compound such as $REBa_2Cl_7$ is reported by Blachnik, Alberts & Enninga (1985). No detailed crystallographic information on the Ba–Er–Cl system has been reported so far. The present study has thus been undertaken in the course of a survey to find potent materials showing superior up-conversion properties.

The structure of $Ba_2ErCl_7$ is shown in Figs. 1 and 2. The Er and Ba atoms are coordinated by seven and nine Cl atoms, respectively. The $ErCl_7$ polyhedron is surrounded by the $Ba1Cl_9$ and $Ba2Cl_9$ polyhedra to form a network. The mean Er—Cl distance in the $ErCl_7$ polyhedra is 2.704 Å, which is about 3.3% longer than reported for the $ErCl_6$ octahedra in $Na_3ErCl_6$ (2.616 Å;
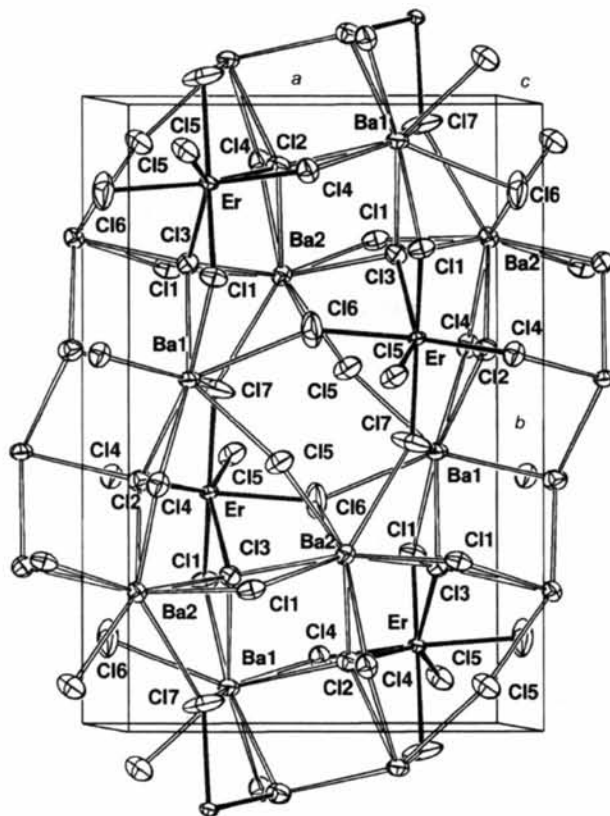


Fig. 1. The crystal structure of $Ba_2ErCl_7$ viewed approximately along the $c$ axis. Displacement ellipsoids are shown at the 90% probability level.
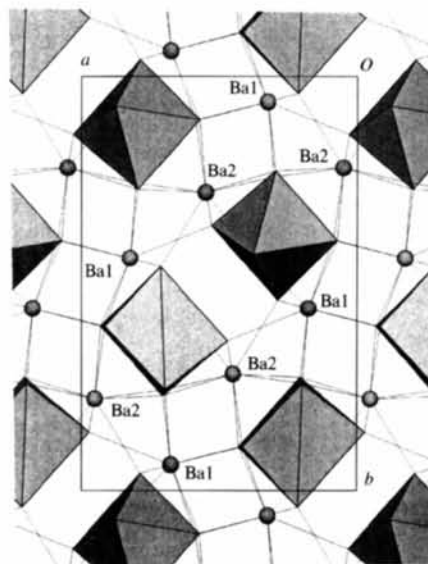


Fig. 2. The $ErCl_7$ polyhedra in $Ba_2ErCl_7$ viewed along the $c$ axis.