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# First molecular octahedral rhenium cluster complexes with terminal As- and Sb-donor ligands

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Six new molecular octahedral cluster complexes with the general formulas *trans*-$[\{Re_6(\mu_3\text{-}Q)_8\}(EPh_3)_4Br_2]$ and *fac*-$[\{Re_6(\mu_3\text{-}Q)_7(\mu_3\text{-}Br)\}(AsPh_3)_3Br_3]$ (Q = S or Se and E = As or Sb) were synthesized by the reactions of the cesium salts of the $[\{Re_6(\mu_3\text{-}S)_8\}Br_6]^{4-}$, $[\{Re_6(\mu_3\text{-}Se)_8\}Br_6]^{3-}$, and $[\{Re_6(\mu_3\text{-}Q)_7(\mu_3\text{-}Br)\}Br_6]^{3-}$ anions with molten triphenylarsine ($AsPh_3$) and triphenylantimony ($SbPh_3$), respectively. The compositions and structures of the resulting complexes were established by single-crystal X-ray diffraction and confirmed by elemental analysis and vibrational spectroscopy. The compositions and structures of the complexes depend on the composition of the cluster core in the starting salts. The luminescence spectra were recorded for powdered samples of all these compounds and the earlier described complexes *trans*-$[\{Re_6Q_8\}(PPh_3)_4Br_2]$ and *fac*-$[\{Re_6Q_7Br\}(PPh_3)_3Br_3]$.

**Key words:** rhenium, octahedral chalcogenide clusters, triphenylarsine, triphenylantimony, crystal structure.

Octahedral rhenium cluster complexes with the general formula $[Re_6Q_8L_6]$ (Q = S, Se, or Te; L are inorganic or organic ligands) have been extensively studied in recent years. This class of compounds has attracted great attention because these compounds exhibit interesting properties, in particular, the redox, luminescence, and magnetic properties. Hybrid metal clusters with organic ligands are of particular interest. Rhenium cluster complexes with organic N- and P-donor ligands are the most typical representatives of this class of compounds.[1,2] For many years, the main approach to the synthesis of such complexes has been based on the replacement of terminal ligands in solutions. In most cases, the oxidized anionic complexes $[Re_6Q_8Y_6]^{3-}$ (Q = S or Se; Y = Cl, Br, or I), which are characterized by higher reactivity compared to the unoxidized complexes, were used as the starting compounds.[1—9] Recently, we have shown that the reactions of molten organic ligands are equally efficient for the replacement of terminal ligands in both oxidized and unoxidized chalcogenide cluster complexes. We have used this method to synthesize complexes with 3,5-dimethylpyrazole (3,5-$Me_2$pzH)[10,11] and triphenylphosphine ($PPh_3$).[12] As a continuation of our investigations, in the present study we performed the reactions of cesium salts of the anionic cluster complexes $[\{Re_6S_8\}Br_6]^{4-}$, $[\{Re_6Se_8\}Br_6]^{3-}$, and $[\{Re_6Q_7Br\}Br_6]^{3-}$ (Q = S or Se) with molten triphenylarsine and triphenylantimony and obtained a representative series of molecular complexes containing the cluster cores $\{Re_6Q_8\}^{2+}$ and $\{Re_6Q_7Br\}^{3+}$.

## Results and Discussion

Six new molecular octahedral rhenium cluster complexes, *trans*-$[\{Re_6S_8\}(AsPh_3)_4Br_2]$ (**1**), *trans*-$[\{Re_6Se_8\}(AsPh_3)_4Br_2]$ (**2**), *trans*-$[\{Re_6S_8\}(SbPh_3)_4Br_2]$ (**3**), *trans*-$[\{Re_6Se_8\}(SbPh_3)_4Br_2]$ (**4**), *fac*-$[\{Re_6S_7Br\}(AsPh_3)_3Br_3]$ (**5**), and *fac*-$[\{Re_6Se_7Br\}(AsPh_3)_3Br_3]$ (**6**), were synthesized. The cesium salts of the anionic chalcobromide complexes $Cs_4[Re_6S_8Br_6] \cdot 2H_2O$,[13] $Cs_3[Re_6Se_8Br_6] \cdot 2H_2O$,[14] and $Cs_3[Re_6Q_7Br_7] \cdot H_2O$ (Q = S or Se)[15] were used as the starting reagents. The reactions were carried out with an excess of the corresponding ligand. The reaction mixtures were kept in sealed tubes at 200 °C for two days. To obtain single crystals, the furnace was slowly cooled to room temperature at a rate of 10 deg $h^{-1}$. Crystals suitable for X-ray diffraction were selected directly from the solidified melts.

In all cases, we prepared octahedral rhenium cluster complexes, in which the $Re_6$ octahedron is located inside the $Q_8$ cube (compounds **1—4**) or the $Q_7$Br cube (compounds **5** and **6**), where Q = S or Se.

The Re—Re and Re—Q distances in isostructural compounds **1—4** are typical of octahedral rhenium chalcogenide cluster complexes. Four Re atoms of the cluster core $\{Re_6Q_8\}$ in the equatorial plane are coordinated by $EPh_3$ molecules. The other two Re atoms are coordinated by bromine atoms to form molecular complexes with the general formula *trans*-$[\{Re_6(\mu_3\text{-}Q)_8\}(EPh_3)_4Br_2]$ (Fig. 1). Selected interatomic distances in the structures of **1—4** are given in Table 1.

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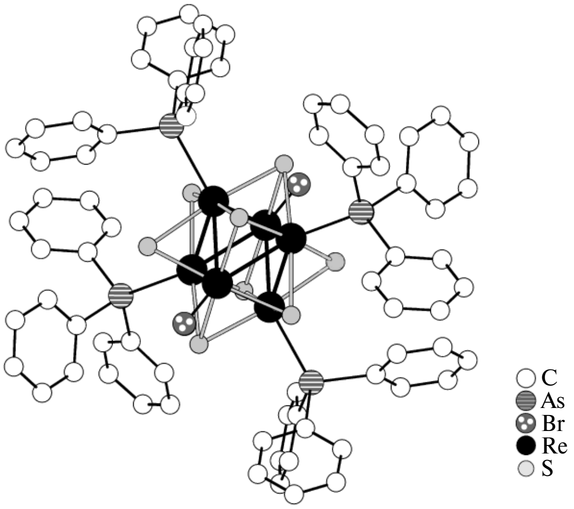

**Fig. 1.** Structures of molecular complexes **1—4** exemplified by *trans*-$[\{Re_6S_8\}(AsPh_3)_4Br_2]$ (**1**) (hydrogen atoms are omitted).

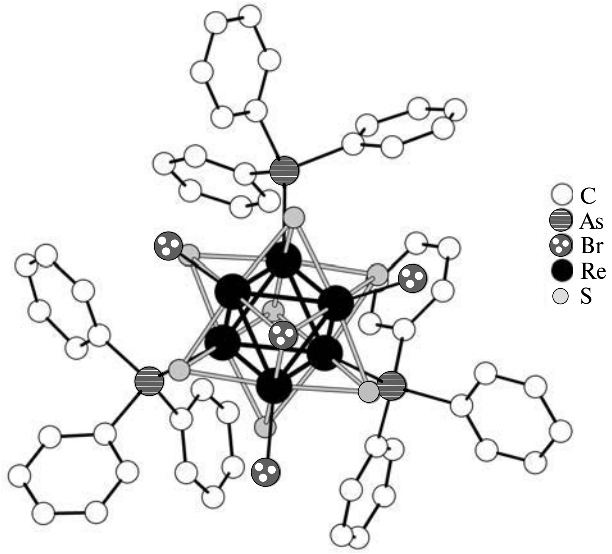

**Fig. 2.** Structures of molecular complexes **5** and **6** exemplified by *fac*-$[\{Re_6S_7Br\}(AsPh_3)_4Br_3]$ (**5**) (hydrogen atoms are omitted).

The crystal structures of isostructural compounds **5** and **6** consist of the molecular cluster complexes *fac*-$[\{Re_6(\mu_3\text{-}Q)_7(\mu_3\text{-}Br)\}(AsPh_3)_3Br_3]$. The cluster core $\{Re_6(\mu_3\text{-}Q)_7(\mu_3\text{-}Br)\}$ is composed of the $Re_6$ octahedron located inside the $Q_7Br$ pseudocube, in which the $\mu_3$-Br ligand is coordinated to three rhenium atoms bound to three terminal Br ligands. The other three rhenium atoms are coordinated by $AsPh_3$ molecules. The structure of the complexes *fac*-$[\{Re_6(\mu_3\text{-}Q)_7(\mu_3\text{-}Br)\}(AsPh_3)_3Br_3]$ in compounds **5** and **6** is presented in Fig. 2.

In compound **5**, the Re—Re distances between the three rhenium atoms coordinated by the $\mu_3$-bromine atom (2.6207(5)—2.6297(5) Å) are longer than the Re—Re distances between the rhenium atoms coordinated by the $\mu_3$-S atoms (2.5808(5)—2.6077(5) Å). This fact is accounted for by the difference in the atomic radii of S and Br (the matrix effect). There are no such differences in the interatomic distances in the cluster core of compound **6**, because the bromine and selenium atoms have similar radii (see Table 1).

**Table 1.** Selected interatomic distances (*d*)

| Complex | *d*/Å | | | | |
|---|---|---|---|---|---|
| | Re—Re | Re—($\mu_3$-Q) | Re—($\mu_3$-Br) | Re—E | Re—$Br_{terminal}$ |
| **1** | 2.5963(2)—2.6065(2) | 2.3964(9)—2.4151(10) | — | 2.5466(4)—2.5876(4) | 2.5466(4) |
| **2** | 2.6257(6)—2.6394(6) | 2.5092(12)—2.5297(11) | — | 2.5906(13)—2.5936(12) | 2.5651(12) |
| **3** | 2.5828(6)—2.5979(6) | 2.382(3)—2.422(3) | — | 2.7319(8)—2.7345(9) | 2.5419(12) |
| **4** | 2.5938(7)—2.6161(6) | 2.4850(16)—2.5203(12) | — | 2.7030(9)—2.7054(9) | 2.5449(13) |
| **5** | 2.5808(5)—2.6297(5) | 2.376(2)—2.433(2) | 2.6095(10)—2.6187(10) | 2.5679(10)—2.5883(10) | 2.5151(10)—2.5391(11) |
| **6** | 2.6117(5)—2.6485(4) | 2.4900(9)—2.5317(8) | 2.6133(9)—2.6195(9) | 2.5748(9)—2.5926(9) | 2.5352(10)—2.5602(10) |
| $[Re_6S_8(PPh_3)_4Br_2]$[12] | 2.5884(3)—2.5972(3) | 2.3807(16)—2.4128(15) | — | 2.517(2)—2.522(2) | 2.5471(7) |
| $[Re_6Se_8(PPh_3)_4Br_2]$[12] | 2.6284(4)—2.6542(4) | 2.5013(7)—2.5267(7) | — | 2.515(2)—2.522(2) | 2.5672(7) |
| $[Re_6S_7Br(PPh_3)_3Br_3]$[12] | 2.5822(5)—2.6268(5) | 2.381(2)—2.469(2) | 2.5874(11)—2.5970(11) | 2.498(2)—2.515(1) | 2.5190(10)—2.5443(10) |
| $[Re_6Se_7Br(PPh_3)_3Br_3]$[12] | 2.6130(6)—2.6578(7) | 2.4864(10)—2.5303(11) | 2.6107(11)—2.6184(11) | 2.504(3)—2.539(2) | 2.5374(13)—2.5643(12) |

Numerous examples of octahedral chalcogenide cluster complexes of rhenium and other transition metals (Cr, Fe, Co, Mo, Ru, and W) with terminal P-donor ligands, in particular, with $PPh_3$ and $PEt_3$, have been described in the literature.[3,4,12,16–27] However, only one structure of an octahedral transition metal cluster complex with terminal As-donor ligands was found in the Cambridge Structural Database. This is the structure of the compound containing a zirconium complex with trimethylarsine with the formula *trans*-$[\{Zr_6(\mu_3\text{-}H)_4(\mu_2\text{-}Cl)_{12}\}(AsMe_3)_4Cl_2] \cdot CH_2Cl_2$.[28] In addition, the structure of the octahedral rhenium cluster complex $[\{Re_6S_6As_2\}(PPr_3)_6] \cdot CH_3CN$ containing an As atom as the $\mu_3$-bridging ligand and the tripropylphosphine ($PPr_3$) molecules as the terminal ligands was documented.[29] No other examples of octahedral transition metal cluster complexes, in which the metal atom of the cluster core is bound to the arsenic atom, were found in the literature. Examples of $M_6$ clusters with Sb-donor ligands are also lacking.

The compounds described in the present study extend the range of the already known complexes with the general formulas *trans*-$[\{Re_6Q_8\}(PPh_3)_4Br_2]$ and *fac*-$[\{Re_6Q_7Br\}(PPh_3)_3Br_3]$ (Q = S or Se).[12] Compounds **1—4** are isostructural with *trans*-$[\{Re_6Q_8\}(PPh_3)_4Br_2]$; compounds **5** and **6**, with *fac*-$[\{Re_6Q_7Br\}(PPh_3)_3Br_3]$. Selected interatomic distances in the clusters under consideration and in related hexarhenium triphenylphosphine cluster complexes are given in Table 1. The Re—E (E = P, As, or Sb) and Re—Q (Q = S or Se) distances in the octahedral clusters increase in the series P < As < Sb and S < Se, respectively, which is attributed to an increase in the atomic radius in the series P < As < Sb and S < Se, respectively.

The distinguishing feature of compounds **5** and **6** is that the bromine atom in the cluster core $\{Re_6Q_7Br\}$ is ordered. Earlier, only a few octahedral rhenium cluster complexes with ordered $\mu_3$-ligands in mixed-ligand chalcogenide cluster cores with the formulas *fac*-$[\{Re_6Q_7Br\}(PPh_3)_3Br_3]$, *cis*-$[\{Re_6S_6Br_2\}(PPh_3)_2Br_4]$, *trans*-$[\{Re_6S_6Br_2(PPh_3)_2\}Br_4]$,[12] and *cis*-$[\{Re_6Te_6Cl_2\}(TeCl_2)_2Cl_4]$ (see Ref. 30) have been described. However, the $\mu_3$-coordinated atoms in the majority of the known $Re_6$ complexes with heteroligand cluster cores are disordered over eight sites. In the structures of **5** and **6**, the Br atom occupies the only site in the vicinity of three rhenium atoms bound to the terminal Br atoms. All known octahedral rhenium cluster complexes with the ordered arrangement of the internal acido ligands are characterized by the following feature: the neutral terminal ligands are coordinated to the rhenium atoms, which are bound exclusively to the $\mu_3$-Q atoms (Q = S, Se, or Te) to form molecular (neutral) complexes. Presumably, the specific electron density distribution at the rhenium atoms in the starting complexes $[Re_6Q_7Br_7]^{3-}$ (Q = S or Se) is one of the factors responsible for the coordination of the neutral terminal ligands to the rhenium atoms, which are bound exclusively to the $\mu_3$-Q atoms, as demonstrated earlier for the isostructural complexes *fac*-$[\{Re_6Q_7Br\}(PPh_3)_3Br_3]$.[12]

The luminescence spectra were recorded for powdered samples of compounds **1—6**, as well as for the

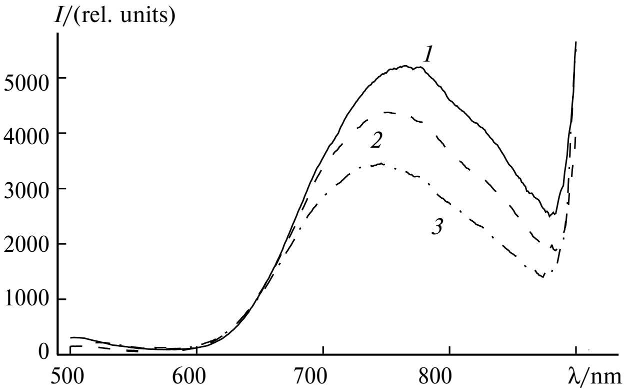

**Fig. 3.** Luminescence spectra of *trans*-$[\{Re_6S_8\}(PPh_3)_4Br_2]$ (*1*) and compounds **1** (*2*) and **3** (*3*).

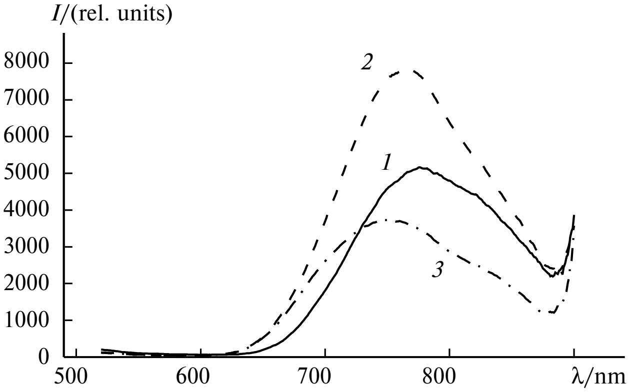

**Fig. 4.** Luminescence spectra of *trans*-$[\{Re_6S_8\}(PPh_3)_4Br_2]$ (*1*) and compounds **2** (*2*) and **4** (*3*).

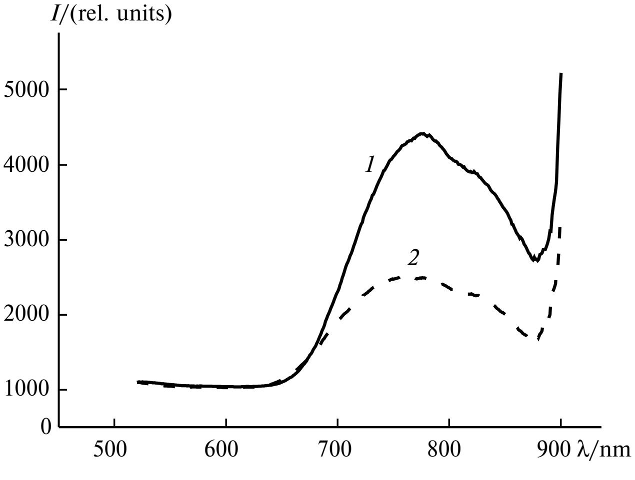

**Fig. 5.** Luminescence spectra of *fac*-$[\{Re_6Se_7Br\}(PPh_3)_3Br_3]$ (*1*) and compound **6** (*2*).

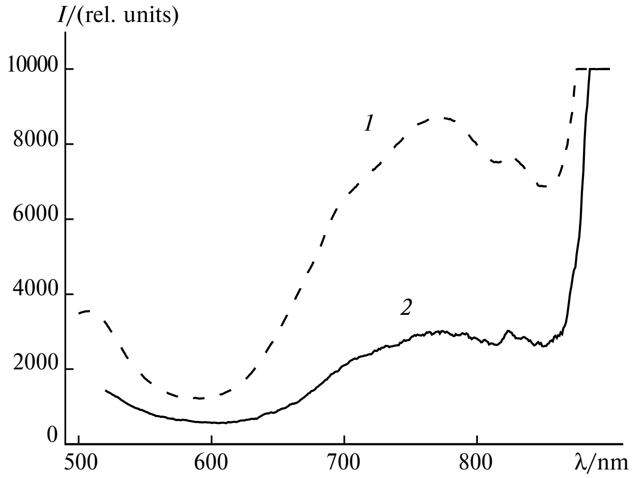

**Fig. 6.** Luminescence spectra of compound **5** (*1*) and *fac*-$[\{Re_6S_7Br\}(PPh_3)_3Br_3]$ (*2*).

earlier described complexes *trans*-$[\{Re_6Q_8\}(PPh_3)_4Br_2]$ and *fac*-$[\{Re_6Q_7Br\}(PPh_3)_3Br_3]$[12] (Figs 3—6). In all spectra, the emission maxima for the selenium-containing clusters slightly shift to longer wavelengths relative to those of their sulfur-containing analogs and depend also on the nature of the donor atoms of the terminal ligands (Table 2). The wavelength corresponding to the luminescence maximum depends on the nature of terminal ligands and increases in the series $SbPh_3 < AsPh_3 < PPh_3$. This dependence is clearly seen in Figs 3 and 5 by exemples of the complexes *trans*-$[\{Re_6S_8\}(EPh_3)_4Br_2]$ (E = P, As, or Sb) and *fac*-$[\{Re_6Se_7Br\}(EPh_3)_3Br_3]$ (E = P or As).

Earlier, it has been noted[12] that the *fac*-$[\{Re_6S_7Br\}(PPh_3)_3Br_3]$ compound does not exhibit luminescence in solution. It appeared that this compound, like the $AsPh_3$-containing analog (**5**), is almost non-emissive in the solid state as well (Fig. 6).

**Table 2.** Luminescence properties of compounds **1—6**, *trans*-$[\{Re_6Q_8\}(PPh_3)_4Br_2]$, and *fac*-$[\{Re_6Q_7Br\}(PPh_3)_3Br_3]$ (Q = S or Se)

| Compound | λ/nm |
|---|---|
| *trans*-$[\{Re_6S_8\}(PPh_3)_4Br_2]$ | 765 |
| *trans*-$[\{Re_6Se_8\}(PPh_3)_4Br_2]$ | 780 |
| *trans*-$[\{Re_6S_8\}(AsPh_3)_4Br_2]$ (**1**) | 750 |
| *trans*-$[\{Re_6Se_8\}(AsPh_3)_4Br_2]$ (**2**) | 765 |
| *trans*-$[\{Re_6S_8\}(SbPh_3)_4Br_2]$ (**3**) | 745 |
| *trans*-$[\{Re_6Se_8\}(SbPh_3)_4Br_2]$ (**4**) | 750 |
| *fac*-$[\{Re_6S_7Br\}(PPh_3)_3Br_3]$ | 770 |
| *fac*-$[\{Re_6Se_7Br\}(PPh_3)_3Br_3]$ | 775 |
| *fac*-$[\{Re_6S_7Br\}(AsPh_3)_3Br_3]$ (**5**) | 770 |
| *fac*-$[\{Re_6Se_7Br\}(AsPh_3)_3Br_3]$ (**6**) | 770 |

## Experimental

The starting salts $Cs_4[Re_6S_8Br_6] \cdot 2H_2O$, $Cs_3[Re_6Se_8Br_6] \cdot 2H_2O$, and $Cs_3[Re_6Q_7Br_7] \cdot H_2O$ (Q = S or Se) were synthesized by the high-temperature ampoule method according to procedures described earlier.[13—15]

The elemental analysis was carried out on a Carlo Erba 1106 instrument. The ratios of the heavy elements were determined by energy dispersive X-ray analysis (EDAX) on a JSM-6700F scanning electron microscope. The IR spectra were recorded on a Scimitar IFS2000 Fourier-transform IR spectrometer. The IR spectra of compounds **1—6** show all peaks assigned to vibrations of the organic ligand. The luminescence spectra of powdered samples were recorded at room temperature on a Hitachi F-4500 spectrofluorimeter.

**Synthesis of complexes 1—6.** Cesium salts of the corresponding octahedral cluster complexes were heated with excess $AsPh_3$ or $SbPh_3$ (the salts of the cluster complexes and the ligands were taken in amounts of 100 mg) in sealed glass tubes to 200 °C and allowed to stand for two days. Then the reaction mixture was cooled to room temperature at a rate of 10 °C $h^{-1}$. The reaction product was washed off from the excess organic ligand with diethyl ether; CsBr, which was formed in the reaction, and the unconsumed cluster complex were washed off with water. Single crystals suitable for X-ray diffraction studies were taken from the solidified melts.

***trans*-Octakis($\mu_3$-sulfido)tetrakis(triphenylarsino)dibromohexarhenate (Re—Re), *trans*-$[\{Re_6S_8\}(AsPh_3)_4Br_2]$ (1).** The yield was 54 mg (47.4%). Found (%): C, 31.04; H, 2.32; S, 9.27. $C_{72}H_{60}Br_2As_4Re_6S_8$. Calculated (%): C, 31.35; H, 2.19; S, 9.30. According to EDAX data, the element ratio in the sample Re : S : Br : As = 6 : 7.7 : 2.1 : 4.2. IR (KBr), ν/cm$^{-1}$: 416 (Re—S).

***trans*-Octakis($\mu_3$-selenido)tetrakis(triphenylarsino)dibromohexarhenate (Re—Re), *trans*-$[\{Re_6Se_8\}(AsPh_3)_4Br_2]$ (2).** The yield was 113 mg (95.5%). Found (%): C, 27.64; H, 1.86. $C_{72}H_{60}Br_2As_4Re_6Se_8$. Calculated (%): C, 27.60; H, 1.93. According to EDAX data, the element ratio in the sample Re : Se : Br : As = 6 : 8.1 : 2 : 3.9.

***trans*-Octakis($\mu_3$-sulfido)tetrakis(triphenylantimony)dibromohexarhenate (Re—Re), *trans*-$[\{Re_6S_8\}(SbPh_3)_4Br_2]$ (3).** The yield was 60 mg (43.3%). Found (%): C, 29.41; H 2.00; S, 8.70. $C_{72}H_{60}Br_2Sb_4Re_6S_8$. Calculated (%): C, 29.36; H, 2.05; S, 8.71. According to EDAX data, the element ratio in the sample Re : S : Br : Sb = 6 : 7.8 : 2.3 : 3.7. IR (KBr), ν/cm$^{-1}$: 415 (Re—S).

***trans*-Octakis($\mu_3$-selenido)tetrakis(triphenylantimony)dibromohexarhenate (Re—Re), *trans*-$[\{Re_6Se_8\}(SbPh_3)_4Br_2]$ (4).** The yield was 93 mg (74.2%). Found (%): C, 25.99; H, 1.91. $C_{72}H_{60}Br_2Sb_4Re_6Se_8$. Calculated (%): C, 26.04; H, 1.82. According to EDAX data, the element ratio in the sample Re : Se : Br : Sb = 6 : 8.2 : 1.8 : 3.8.

***fac*-Heptakis($\mu_3$-sulfido)($\mu_3$-bromido)tris(triphenylarsino)tribromohexarhenate (Re—Re), *fac*-$[\{Re_6S_7Br\}(AsPh_3)_3Br_3]$ (5).** The yield was 30 mg (27.8%). Found (%): C, 25.64; H, 1.72; S, 8.55. $C_{54}H_{45}As_3Br_4Re_6S_7$. Calculated (%) C, 25.14; H, 1.76; S, 8.70. According to EDAX data, the element ratio in the sample Re : S : Br : As = 6 : 6.9 : 4.3 : 2.8. IR (KBr), ν/cm$^{-1}$: 419 (Re—S).

***fac*-Heptakis($\mu_3$-selenido)($\mu_3$-bromido)tris(triphenylarsino)tribromohexarhenate (Re—Re), *fac*-$[\{Re_6Se_7Br\}(AsPh_3)_3Br_3]$ (6).** The yield was 100 mg (93.5%). Found (%): C, 22.22; H, 1.53. $C_{54}H_{45}As_3Br_4Re_6Se_7$. Calculated: C, 22.30; H, 1.56. According to EDAX data, the element ratio in the sample Re : Se : Br : As = 6 : 7.1 : 3.8 : 2.9.

**X-ray diffraction study.** The X-ray diffraction data for the structure determination were collected according to a standard

**Table 3.** Crystallographic data for compounds **1—3**

| Parameter | **1** | **2** | **3** |
|---|---|---|---|
| Molecular formula | $C_{72}H_{60}As_4Br_2Re_6S_8$ | $C_{72}H_{60}As_4Br_2Re_6Se_8$ | $C_{72}H_{60}Sb_4Br_2Re6S8$ |
| Molecular weight | 2758.38 | 3133.58 | 2945.70 |
| Crystal dimensions/mm | 0.10×0.08×0.06 | 0.12×0.10×0.06 | 0.80×0.10×0.10 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1/c$ | $P2_1/c$ |
| $a$/Å | 12.4453(3) | 12.4314(5) | 12.5680(13) |
| $b$/Å | 16.4323(4) | 16.4658(11) | 17.9594(16) |
| $c$/Å | 19.3363(5) | 19.6441(13) | 18.4964(12) |
| $\alpha$/deg | | | |
| $\beta$/deg | 100.716(1) | 100.983(2) | 95.970(4) |
| $\gamma$/deg | | | |
| $V$/Å | 3885.4(2) | 3947.4(4) | 4152.2(6) |
| $Z$ | 2 | 2 | 2 |
| $\rho_{calc}$/g cm$^{-3}$ | 2.358 | 2.636 | 2.356 |
| $\mu$/mm$^{-1}$ | 12.282 | 15.566 | 11.184 |
| $2\theta$/deg | | | |
| Transmission factors | 0.526; 0.373 | 0.455; 0.257 | 0.401; 0.041 |
| Number of measured/independent reflections | 28192/9625 | 32597/9552 | 41481/10018 |
| $R_{int}$ | 0.0250 | 0.0729 | 0.0623 |
| Number of observed reflections | 7965 | 5017 | 5603 |
| Number of refined parameters | 415 | 415 | 343 |
| $R$ ($I > 2\sigma(I)$) | | | |
| $R_1$ | 0.0222 | 0.0510 | 0.0497 |
| $wR_2$ | 0.0513 | 0.1099 | 0.1319 |
| $R$ (based on all reflections) | | | |
| $R_1$ | 0.0322 | 0.1039 | 0.0947 |
| $wR_2$ | 0.0536 | 0.1243 | 0.1414 |

**Table 4.** Crystallographic data for compounds **4—6**

| Parameter | **4** | **5** | **6** |
|---|---|---|---|
| Molecular formula | $C_{72}H_{60}Sb_4Br_2Re_6Se_8$ | $C_{54}H_{45}As_3Br_4Re_6Se_7$ | $C_{54}H_{45}As_3Br_4Re_6Se_7$ |
| Molecular weight | 3320.90 | 2579.92 | 2908.22 |
| Crystal dimensions/mm | 0.15×0.10×0.10 | 0.10×0.10×0.08 | 0.16×0.14×0.08 |
| Crystal system | Monoclinic | Triclinic | Triclinic |
| Space group | $P2_1/c$ | $P\bar{1}$ | $P\bar{1}$ |
| $a$/Å | 12.543(2) | 11.8167(5) | 11.8123(7) |
| $b$/Å | 17.821(3) | 14.8575(7) | 15.0302(8) |
| $c$/Å | 18.772(3) | 20.2311(9) | 20.4986(9) |
| $\alpha$/deg | 77.081(1) | 77.449(2) | |
| $\beta$/deg | 96.749(7) | 76.129(2) | 75.319(2) |
| $\gamma$/deg | 90 | 67.721(1) | 67.930(2) |
| $V$/Å | 4166.8(13) | 3155.9(2) | 3232.2(3) |
| $Z$ | 2 | 2 | 2 |
| $\rho_{calc}$/g cm$^{-3}$ | 2.647 | 2.715 | 2.988 |
| $\mu$/mm$^{-1}$ | 14.439 | 15.820 | 19.162 |
| $2\theta$/deg | | | |
| Transmission factors | 0.326; 0.221 | 0.364; 0.301 | 0.301; 0.150 |
| Number of measured/independent reflections | 26243/10232 | 38064/15092 | 28883/15282 |
| $R_{int}$ | 0.0496 | 0.0552 | 0.0282 |
| Number of observed reflections | 6595 | 9096 | 8446 |
| Number of refined parameters | 343 | 667 | 667 |
| $R$ ($I > 2\sigma(I)$) | | | |
| $R_1$ | 0.0523, | 0.0478, | 0.0378, |
| $wR_2$ | 0.1575 | 0.1125 | 0.0821 |
| $R$ (based on all reflections) | | | |
| $R_1$ | 0.0915, | 0.0910 | 0.0848, |
| $wR_2$ | 0.1710 | 0.1270 | 0.0919 |

procedure on a single-crystal automated Bruker-Nonius X8APEX CCD diffractometer (MoKα radiation, λ = 0.71073 Å, graphite monochromator) at room temperature. Semiempirical absorption corrections were applied using the SADABS program.[31]

The structures were solved by direct methods followed by calculations of difference Fouier maps and the refinement of the positional and anisotropic thermal parameters by the full-matrix least-squares method with the use of the SHELX-97 program package.[32] The hydrogen atoms in the $AsPh_3$ and $SbPh_3$ molecules were positioned geometrically. The X-ray diffraction data collection and refinement statistics are given in Tables 3 and 4. The structural data for complexes **1—6** were deposited with the Cambridge Structural Database (CCDC 646770—646775, respectively) and can be obtained from the authors.

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