

Synthesis, structure, and ^{77}Se NMR study of the $(\text{PPh}_4)_2[\text{Re}_6\text{Se}_6\text{Br}_8]$ complex

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The octahedral cluster anion $[\text{Re}_6\text{Se}_6\text{Br}_8]^{2-}$ was prepared by high-temperature synthesis from elementary substances in the presence of KBr. This cluster anion was isolated and structurally characterized by single-crystal X-ray diffraction analysis as the $(\text{PPh}_4)_2[\text{Re}_6\text{Se}_6\text{Br}_8]$ complex (**1**). Refluxing of polymeric rhenium selenide bromide $\text{Re}_6\text{Se}_6\text{Br}_6$ in DMF in the presence of Bu_4NBr led to the cleavage of the $\text{Re}-\text{Br}-\text{Re}$ bridges to form the complex $(\text{Bu}_4\text{N})_2[\text{Re}_6\text{Se}_6\text{Br}_8]$. Comparative analysis of the interatomic distances in the octahedral rhenium(III) selenide bromide clusters was carried out.

Key words: rhenium, octahedral clusters, selenium, chalcogenide bromide complexes, ^{77}Se NMR spectroscopy, crystal structure.

A broad spectrum of compounds containing octahedral chalcogenide cluster fragments with composition $[\{\text{Re}_6\text{Q}_{4+z}\text{Y}_{4-z}\}\text{X}_6]^{-z}$ ($\text{Q} = \text{S}, \text{Se}, \text{or Te}$; Y and $\text{X} = \text{Cl}, \text{Br}, \text{or I}$; $z = 0-4$) have been synthesized.¹ Of these compounds, only three rhenium selenide bromide complexes, viz., neutral $\text{Re}_6\text{Se}_4\text{Br}_{10}$ ² and two salts with the single- and triple-charged cluster anions ($\text{AgRe}_6\text{Se}_5\text{Br}_9$ ³ and $\text{Cs}_3\text{Re}_6\text{Se}_7\text{Br}_7 \cdot \text{H}_2\text{O}$, respectively⁴), have been structurally characterized.

The aim of the present study was to synthesize and study the $[\text{Re}_6\text{Se}_6\text{Br}_8]^{2-}$ anionic complex, which is one of the lacking members of the selenide bromide series.

Results and Discussion

In the present study, we used two approaches to the synthesis of the cluster anionic complex $[\text{Re}_6\text{Se}_6\text{Br}_8]^{2-}$ with organic cations. The $(\text{PPh}_4)_2[\text{Re}_6\text{Se}_6\text{Br}_8]$ salt was prepared from the potassium salt by the ion-exchange reaction with PPh_4Br in water. The starting potassium salt, in turn, was prepared by high-temperature synthesis from elementary substances in the presence of KBr.

Another approach involves refluxing of polymeric rhenium selenide bromide $\text{Re}_6\text{Se}_6\text{Br}_6$, which was previously synthesized from elementary substances, in DMF in the presence of Bu_4NBr . In our opinion, the $(\text{Bu}_4\text{N})_2[\text{Re}_6\text{Se}_6\text{Br}_8]$ salt containing the $[\text{Re}_6\text{Se}_6\text{Br}_8]^{2-}$ cluster anion was generated through the cleavage of the $\text{Re}-\text{Br}-\text{Re}$ μ_2 -bridges in the structure of polymeric rhenium selenide bromide $\text{Re}_6\text{Se}_6\text{Br}_6$. Both salts were studied by ^{77}Se NMR spectroscopy. Single crystals of the $(\text{PPh}_4)_2[\text{Re}_6\text{Se}_6\text{Br}_8]$ complex were grown and the struc-

ture of this complex was established by X-ray diffraction analysis.

The unit cell of $(\text{PPh}_4)_2[\text{Re}_6\text{Se}_6\text{Br}_8]$ (Fig. 1, *a*) contains one isolated centrosymmetrical $\{[\text{Re}_6(\mu_3\text{-Se})_6(\mu_3\text{-Br})_2]\text{Br}_6\}^{2-}$ cluster anion (Fig. 1, *b*). The charge of this anion is compensated by two crystallographically equivalent tetraphenylphosphonium cations. The rhenium atoms form a virtually regular octahedron. The $\text{Re}-\text{Re}$ edge lengths are in the range of 2.611(1)–2.631(1) Å. The $\text{Re}-(\mu_3\text{-E})$, where $\text{E} = (6/8 \text{ Se} + 2/8 \text{ Br})$, and $\text{Re}-\text{Br}$ bond lengths are in the ranges of 2.497(2)–2.577(2) and 2.534(2)–2.546(2) Å, respectively. The $\text{P}-\text{C}$ and $\text{C}-\text{C}$ distances in the PPh_4^+ cation have standard values (1.78(1)–1.80(1) and 1.31(2)–1.42(2) Å, respectively). Direct van der Waals contacts between the cluster anions are absent due to the presence of the bulky tetraphenylphosphonium cations.⁵

The available data on the crystal structures of a broad spectrum of octahedral rhenium(III) chalcogenide clusters provide grounds for analysis of the dependence of the $\text{Re}-\text{Re}$, $\text{Re}-\text{Q}$, and $\text{Re}-\text{Y}(\text{X})$ interatomic distances on the composition and charge of the cluster core (Table 1 and 2). The geometric parameters of the cluster anion are virtually independent of the nature of the cation. Let us compare the $[\text{Re}_6\text{Q}_{4+z}\text{Y}_{4-z}]$ cluster cores ($z = 0-4$) containing mixed ligands in which the halide and chalcogenide ligands have similar ionic radii ($\text{S}^{2-}-\text{Cl}^-$ and $\text{Se}^{2-}-\text{Br}^-$ pairs). As can be seen from Table 1, the heterovalent replacement with the crystallochemically similar (indistinguishable by X-ray diffraction analysis) ligands (S^{2-} with Cl^- or Se^{2-} with Br^-) has virtually no effect on the average rhenium–rhenium distance.

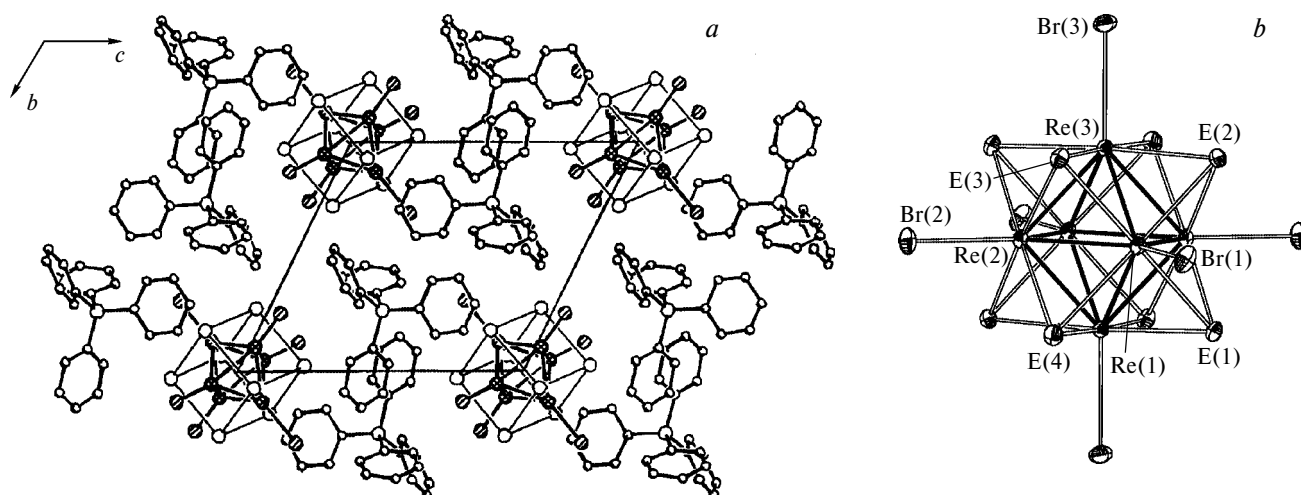


Fig. 1. Structure of $(\text{PPh}_4)_2[\text{Re}_6\text{Se}_6\text{Br}_8]$ projected along the axis a (a) and the overall view of the $[\text{Re}_6\text{Se}_6\text{Br}_8]^{2-}$ cluster anion (b).

Table 1. Average Re—Re distances in the octahedral clusters containing the mixed-composition core $[\text{Re}_6\text{Q}_{8-n}\text{Y}_n]$ ($\text{Q} = \text{S}, \text{Y} = \text{Cl}; \text{Q} = \text{Se}, \text{Y} = \text{Br}$)

Compound	Re—Re /Å	Reference
$\text{Re}_6\text{S}_4\text{Cl}_{10}$	2.595	6
$\text{Re}_6\text{S}_5\text{Cl}_8$	2.596	6
$(\text{Bu}_4\text{N})_2[\text{Re}_6\text{S}_6\text{Cl}_8]$	2.573	6
$(\text{Bu}_4\text{N})_3[\text{Re}_6\text{S}_7\text{Cl}_7]$	2.599	6
$\text{Cs}_3[\text{Re}_6\text{S}_8\text{Cl}_7]$	2.597	7
$\text{Ti}_2[\text{Re}_6\text{S}_8\text{Cl}_4]$	2.603	7
$\text{Re}_6\text{Se}_4\text{Br}_{10}$	2.621	2
$\text{Re}_6\text{Se}_5\text{Br}_8$	2.614	8
$\text{Re}_6\text{Se}_7\text{Br}_4$	2.617	9
$(\text{PPh}_4)_2[\text{Re}_6\text{Se}_6\text{Br}_8]$	2.619	*
$\text{Cs}_3[\text{Re}_6\text{Se}_7\text{Br}_7] \cdot \text{H}_2\text{O}$	2.615	4
$[\text{Pr}(\text{DMF})_8][\text{Re}_6\text{Se}_7\text{Br}_7]$	2.621	8
$[\text{Gd}(\text{DMF})_8][\text{Re}_6\text{Se}_7\text{Br}_7]$	2.625	8
$\text{Cs}_2[\text{Re}_6\text{Se}_8\text{Br}_4]$	2.62	10

* The present study.

The heterovalent replacement of the halide ligands Y^- in the $\{\text{Re}_6\text{Q}_{4+z}\text{Y}_{4-z}\}^{(6-z)+}$ cluster core with the chalcogenide ligands Q^{2-} giving rise to the $\{\text{Re}_6\text{Q}_8\}^{2+}$ composi-

tion leads to a decrease in the total positive charge of the cluster core and, consequently, to an increase in the negative charge of the $[\{\text{Re}_6\text{Q}_{4+z}\text{Y}_{4-z}\}\text{X}_6]^{-z}$ complex anions. An increase in the total negative charge of the cluster complex is accompanied by an increase in the Re—X distances (Table 2). If the cluster core is taken as the central atom in classical coordination chemistry, the interactions of the apical ligands with the positively charged core are analogous to interactions in mononuclear octahedral complexes.

Eight internal μ_3 -ligands of the $[\{\text{Re}_6\text{Se}_7\text{Br}\}\text{Br}_6]^{3-}$ anion form the Se_7Br cube. One vertex of the cube is occupied by the bromine atom. From the viewpoint of symmetry (point symmetry group of the cluster is C_{3v}), seven selenium atoms located in other vertices of the coordination cube can be divided into three groups according to their arrangement with respect to the bromine substituent. Three selenium atoms share edges with the bromine atom (E), three other selenium atoms share faces with the bromine atom (F), and the seventh selenium atom shares the body diagonal of the cube with the bromine substituent (C) (Fig. 2, a). Theoretically, the ^{77}Se NMR spectrum of this complex should have three lines with an intensity ratio of 3 : 3 : 1. In fact, the spectrum of

Table 2. Relation between the Re—Br distances and the charge of the cluster core

Compound	Cluster complex	Re—Br/Å	Reference
$\text{K}[\text{Re}_6\text{S}_5\text{Br}_9]$	$[\{\text{Re}_6\text{S}_5\text{Br}_3\}\text{Br}_6]^-$	2.52	11
$(\text{PPh}_4)_2[\text{Re}_6\text{S}_6\text{Br}_8] \cdot \text{CH}_3\text{C}_6\text{H}_5$	$[\{\text{Re}_6\text{S}_6\text{Br}_2\}\text{Br}_6]^{2-}$	2.54	12
$\text{Rb}_3[\text{Re}_6\text{S}_7\text{Br}_7]$	$[\{\text{Re}_6\text{S}_7\text{Br}\}\text{Br}_6]^{3-}$	2.555	13
$\text{Cs}_4[\text{Re}_6\text{S}_8\text{Br}_6] \cdot \text{H}_2\text{O}$	$[\{\text{Re}_6\text{S}_8\}\text{Br}_6]^{4-}$	2.569	14
$\text{Re}_6\text{Se}_4\text{Br}_{10}$	$[\{\text{Re}_6\text{Se}_4\text{Br}_4\}\text{Br}_6]$	2.52	2
$(\text{PPh}_4)_2[\text{Re}_6\text{Se}_6\text{Br}_8]$	$[\{\text{Re}_6\text{Se}_6\text{Br}_2\}\text{Br}_6]^{2-}$	2.541	*
$\text{Cs}_3[\text{Re}_6\text{Se}_7\text{Br}_7] \cdot \text{H}_2\text{O}$	$[\{\text{Re}_6\text{Se}_7\text{Br}\}\text{Br}_6]^{3-}$	2.573	4

* The present study.

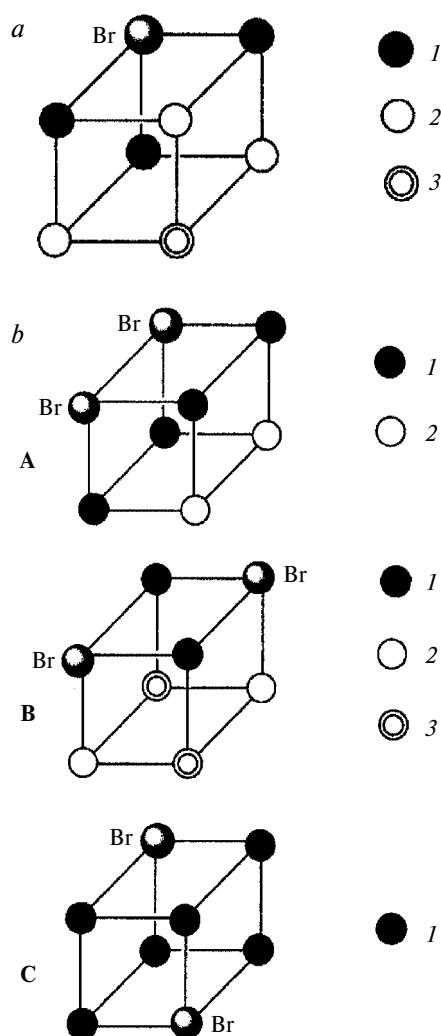


Fig. 2. Mutual arrangement of the μ_3 -ligands in the $[\text{Re}_6\text{Se}_7\text{Br}_7]^{3+}$ cluster cores (a) and three geometric isomers of $[\text{Re}_6\text{Se}_6\text{Br}_2]^{4+}$ (b). a, $[\text{Re}_6\text{Se}_7\text{Br}_7]^{3+}$, point symmetry group C_{3v} ; 1, edge (E); 2, face (F); 3, body diagonal (C); b, $[\text{Re}_6\text{Se}_6\text{Br}_2]^{4+}$, point symmetry groups C_{2v} (A), C_{2v} (B), and D_{3d} (C). The expected number of signals in the ^{77}Se NMR spectrum taking into account the difference in influence of the substituents (Br): A: (1) $\delta_1 = \Delta E + \Delta F$, $\delta_1 = \Delta E + \Delta C$; (2) $\delta_2 = \Delta F + \Delta C$, $\delta_2 = 2\Delta C$; B: (1) $\delta_3 = 2\Delta E$, $\delta_3 = 2\Delta E$; (2) $\delta_4 = \Delta E + \Delta C$, $\delta_1 = \Delta E + \Delta C$; (3) $\delta_5 = 2\Delta F$, $\delta_2 = 2\Delta C$; C: (1) $\delta_1 = \Delta E + \Delta F$, $\delta_1 = \Delta E + \Delta C$.

$(\text{Bu}_4\text{N})_3[\text{Re}_6\text{Se}_7\text{Br}_7]$ has only two signals at $\delta -223$ and -282 with an intensity ratio of 4 : 3 (Table 3).⁸

Earlier,^{15,16} the chemical shifts of the ^{77}Se and ^{125}Te signals in the spectra of the analogous octahedral cluster cores $[\text{Re}_6\text{Te}_{8-x}\text{Q}_x]^{2+}$, where Q = S or Se, were interpreted advantageously with the use of the concept of additivity of the contributions to the chemical shifts from the substituents, which share an edge (ΔE), face (ΔF), and body diagonal of the cube (ΔC) with the atom under consideration. However, this approach appeared to be inapplicable to the $[\{\text{Re}_6\text{Se}_{8-x}\text{Br}_x\}\text{Br}_6]^{(x-4)-}$ system. The

Table 3. Ratios of the line intensities (I) in the ^{77}Se NMR spectrum of the $[\text{Re}_6\text{Se}_7\text{Br}_7]^{3-}$ cluster anion determined from a series of independent experiments

Sample	I_{-223}	I_{-282}	Ratio* I_{-223}/I_{-282}
1	65	48	1.35
2	8	6	1.33
3	63	45	1.40
4	37	27	1.37
5	49	33	1.38
6	74	58	1.28
7	60	45	1.33
8	25	19	1.32

* The average value is 1.35.

replacement of the double-charged selenide ion by the single-charged bromide ion leads to a change in the total charge of the cluster core, and the effect of the substituents becomes more complex than that described by a simple additive scheme. It is conceivable that the chemical shift of the ^{77}Se atom, which shares the body diagonal of the cube with the bromine atom, in the $[\text{Re}_6\text{Se}_7\text{Br}_7]^{3-}$ anion is equal to the chemical shift of one of two other symmetrically equivalent groups of the selenium nuclei, *viz.*, $\Delta C = \Delta E$ or $\Delta F = \Delta C$. The latter assumption seems to be more probable, *i.e.*, the effect of the substituent (Br) on the Se atoms located on the same face is approximately equal to the effect of this substituent on the Se atoms located on the same body diagonal, *viz.*, $\Delta F = \Delta C$. This assumption provides a reasonable explanation for the experimental spectrum of the $[\text{Re}_6\text{Se}_7\text{Br}_7]^{3-}$ anion.

The $[\text{Re}_6\text{Se}_6\text{Br}_2]^{4+}$ cluster core can exist as three isomers with the symmetry C_{2v} , C_{2v} , or D_{3d} (Fig. 2, b), which can give five signals in the ^{77}Se NMR spectrum. However, taking into account the above-mentioned assumption ($\Delta F = \Delta C$), three groups of signals with the chemical shifts ($\Delta E + \Delta C$), ($2\Delta C$), and ($2\Delta E$) would be expected to be present in the spectrum, and the intensity distribution over these groups would be equal to 6 : 2 : 1 if all three isomers are formed in equal amounts. It can be seen

Table 4. Ratios of the line intensities in the ^{77}Se NMR spectrum of the $[\text{Re}_6\text{Se}_6\text{Br}_8]^{2-}$ cluster anion determined from a series of independent experiments

Sample	Lines recorded in the spectrum of $[\text{Re}_6\text{Se}_6\text{Br}_8]^{2-}$		
	-167	-192	-200
1	6.28	1	2.54
2	7.00	1	2.58
3	5.76	1	2.64
4	6.30	1	2.40
Average value	6.34	1	2.54

(Table 4) that the intensity ratio in the experimental spectrum is somewhat different from the calculated pattern. This difference can also be attributed to the fact that particular isomers of the cluster core are formed preferentially, whereas a complete agreement can be achieved only when all three isomers are formed in equal amounts.

In the case of the $[\text{Re}_6\text{Se}_7\text{Br}_7]^{3-}$ cluster core, only one isomer with the symmetry C_{3v} can exist. Within the framework of the assumption $\Delta F = \Delta C$, the intensity ratio of the signals should be equal to $4 : 3 = 1.33$, which is actually observed (see Table 3).

Experimental

Synthesis of tetraphenylphosphonium bis(μ_3 -bromo)hexakis(μ_3 -selenido)hexabromohexarhenate(III), $(\text{PPh}_4)_2[\text{Re}_6\text{Se}_6\text{Br}_8]$. Stoichiometric amounts (with respect to the composition $\text{K}_2\text{Re}_6\text{Se}_6\text{Br}_8$) of rhenium, selenium, and KBr (Re, 1.5 g, 8.0 mmol; Se, 0.64 g, 8.0 mmol; KBr, 0.32 g, 2.7 mmol) were thoroughly mixed. The reaction mixture was placed in a quartz tube, which was evacuated and filled with argon. Then Br_2 (0.64 g, 4.0 mmol) was added. The tube with the reagents was frozen in a Dewar flask with liquid nitrogen, sealed, heated to 850°C with a rate of $0.5^\circ\text{C min}^{-1}$, kept at this temperature for 72 h, and then cooled to -20°C (6°C min^{-1}). The reaction product was dissolved with heating in water with the addition of several drops of HBr. The resulting solution was filtered and PPh_4Br (0.8 g) was added. The precipitate that formed was filtered off and recrystallized from CH_3CN . The resulting dark-red crystals were filtered off and dried in air. The compound was obtained in a yield of 3.5 g (90%). Found (%): C, 19.33; H, 1.41. $(\text{PPh}_4)_2[\text{Re}_6\text{Se}_6\text{Br}_8]$. Calculated (%): C, 19.82; H, 1.39. ^{77}Se NMR (solution in acetonitrile), δ : -167 , -192 , and -200 .

Synthesis of tetrabutylammonium bis(μ_3 -bromo)hexakis(μ_3 -selenido)hexabromohexarhenate(III), $(\text{Bu}_4\text{N})_2[\text{Re}_6\text{Se}_6\text{Br}_8]$. Stoichiometric amounts (with respect to the composition $\text{Re}_6\text{Se}_6\text{Br}_6$) of rhenium and selenium (Re, 1.5 g, 8.0 mmol; Se, 0.64 g, 8.0 mmol) were placed in a quartz tube, which was evacuated and filled with argon. Then Br_2 (0.7 g, 4.4 mmol) was added. The tube with the reagents was frozen in a Dewar flask with liquid nitrogen, sealed, heated to 850°C with a rate of $0.5^\circ\text{C min}^{-1}$, kept at this temperature for 72 h, and then cooled to -20°C (6°C min^{-1}). The resulting compound was washed with acetone and dried. Then the product of high-temperature syn-

thesis (1 g) was refluxed in DMF in the presence of Bu_4NBr . The resulting solution was filtered off and an excess of diethyl ether was added. The precipitate that formed was recrystallized from CH_3CN . Found (%): C, 14.51; H, 2.67; N, 1.10. $(\text{Bu}_4\text{N})_2[\text{Re}_6\text{Se}_6\text{Br}_8]$. Calculated (%): C, 14.16; H, 2.64; N, 1.03. ^{77}Se NMR (solution in acetonitrile), δ : -167 , -192 , and -200 ($[\text{Re}_6\text{Se}_6\text{Br}_8]^{2-}$ anion).

X-ray diffraction study of $(\text{PPh}_4)_2[\text{Re}_6\text{Se}_6\text{Br}_8]$. The X-ray diffraction data required for the solution of the structure of $(\text{PPh}_4)_2[\text{Re}_6\text{Se}_6\text{Br}_8]$ were collected to $2\theta = 55^\circ$ on an automated Enraf-Nonius CAD-4 diffractometer ($\lambda\text{MoK}\alpha$ radiation, graphite monochromator, $\omega/2\theta$ scan technique with a variable rate) from a platelet-like crystal of dimensions $0.17 \times 0.26 \times 0.32 \text{ mm}^3$ according to a standard procedure. The refined triclinic unit cell parameters were as follows: $a = 10.973(2)$, $b = 11.721(2)$, $c = 13.106(2) \text{ \AA}$, $\alpha = 116.06(2)$, $\beta = 94.25(2)$, $\gamma = 92.80(2)^\circ$, $V = 1503.8(4) \text{ \AA}^3$, $Z = 1$, $\rho_{\text{calc}} = 2.872 \text{ g cm}^{-3}$. The intensities of 5727 measured reflections (of which 5456 reflections were independent, $R_{\text{int}} = 0.0355$) were corrected for absorption ($\mu = 21.037 \text{ mm}^{-1}$) with the use of three azimuth scan curves. The structure was solved by direct methods (space group $P\bar{1}$) and refined anisotropically by the full-matrix least-squared method with the use of the SHELX-97 program package¹⁷ to $R(F) = 0.0321$, $wR(F^2) = 0.0697$, $S = 0.714$ for 3073 reflections with $F(hkl) > 4\sigma(F)$; 317 parameters were refined. Since the atomic scattering curves of Se and Br are virtually indistinguishable, we assumed the completely disordered distribution of these atoms over the $\mu_3\text{-E}$ positions in the $\{\text{Re}_6(\mu_3\text{-E})_8\}$ cluster core. The positions of the hydrogen atoms of the phenyl groups were calculated geometrically and refined in the rigid-body approximation with isotropic thermal parameters equal to 120% of the equivalent thermal parameters of the corresponding carbon atoms. The principal interatomic distances are given in Table 5.

The compound under consideration was characterized by powder X-ray diffraction analysis performed at -20°C on a Philips APD 1700 diffractometer ($\text{CuK}\alpha$ radiation, graphite monochromator, $5^\circ \leq 2\theta \leq 60^\circ$, scan step was 0.02° , count time per step was 1 s). The positions and intensities of the lines in the powder X-ray diffraction pattern are in good agreement with the data calculated from the results of the single-crystal X-ray diffraction study.

NMR spectroscopic study. The ^{77}Se NMR spectra of solutions of the samples in organic solvents (acetonitrile, dimethylformamide) with the effective total concentration of $\sim 0.03\text{--}0.04 \text{ mol L}^{-1}$ were recorded at -20°C on a Bruker CXP-300 spectrometer (57.2 MHz) using HP detectors (tubes

Table 5. Principal interatomic distances (d) in the $(\text{PPh}_4)_2[\text{Re}_6\text{Se}_6\text{Br}_8]$ structure

Bond	$d/\text{\AA}$	Bond	$d/\text{\AA}$	Bond	$d/\text{\AA}$
Re(1)—Re(2')	2.611(1)	Re(1)—E(2)	2.500(2)	Re(2)—E(3)	2.530(2)
Re(1)—Re(3')	2.616(1)	Re(1)—E(1)	2.524(2)	Re(2)—E(4)	2.566(2)
Re(1)—Re(3)	2.617(1)	Re(1)—E(3)	2.529(2)	Re(3)—Br(3)	2.544(2)
Re(1)—Re(2)	2.627(1)	Re(1)—E(4)	2.577(2)	Re(3)—E(3)	2.501(2)
Re(2)—Re(3)	2.613(1)	Re(2)—Br(2)	2.546(2)	Re(3)—E(1')	2.518(2)
Re(2)—Re(3')	2.631(1)	Re(2)—E(1')	2.497(2)	Re(3)—E(2)	2.534(2)
Re(1)—Br(1)	2.534(2)	Re(2)—E(2')	2.525(2)	Re(3)—E(4')	2.575(2)

Note. Atoms with primed labels are related to unprimed atoms by the symmetry operation $-x + 1, -y, -z$.

with diameter $\phi = 10$ mm, the axis of the tube with the sample was perpendicular to the axis of the solenoid). The chemical shifts were measured relative to the external standard (saturated aqueous solution of H_2SeO_3 , δ 1282¹⁸) and recalculated with respect to the signal of SeMe_2 taken as zero. The positive shift corresponds to the downfield shift of the signal.

The chemical shifts in the ^{77}Se NMR spectra of the compounds under study depend only slightly on the nature of both the cation ($\text{M} = \text{K}^+$, Bu_4N^+ , or PPh_4^+) and solvent (DMF or acetonitrile).

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