First example of the cluster ammine complex $[Re_6Se_7Br(NH_3)_6]^{3+}$: synthesis and structure of the $[Re_6Se_7Br(NH_3)_6][Re_6Se_7BrBr_6] \cdot 12H_2O$ salt

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The reaction of $Cs_3[Re_6Se_7BrBr_6]$ with aqueous ammonia afforded the octahedral rhenium ammine cluster complex cation $[Re_6Se_7Br(NH_3)_6]^{3+}$. This cation crystallized as the $[Re_6Se_7Br(NH_3)_6][Re_6Se_7BrBr_6] \cdot 12H_2O$ compound. The crystal structure of this compound was established. The presence of the NH_3 ligands in the coordination environment about the Re atom was confirmed by thermogravimetry, vibrational spectroscopy, and high-resolution mass spectrometry. The resulting compound is the first example of salts composed of the cluster cation and cluster anion possessing the same $\{Re_6Se_7Br\}$ cluster core.

Key words: rhenium, octahedral clusters, ammine complex, crystal structure.

The anionic complexes of composition $[\{Re_6Q_8\}L_6]^{4-}$ ($Q = S^{2-}$, Se^{2-}, Te^{2-}, Cl^-, Br^-, or I^-; $L = Cl^-$, Br^-, I^-, CN^-, or PR_3; *N* donor ligands) with the $[Re_6Q_8]^{2+}$ cluster core are the most typical hexanuclear rhenium(III) chalcogenide clusters.[1—3] Recent studies demonstrated that the external terminal halide ligands L in these complexes are rather labile and can be replaced by other ligands, including organic ligands. Octahedral rhenium complexes with other apical ligands are generally synthesized by the replacement of the terminal halogen atoms with good leaving groups, *viz.*, $CF_3SO_2^-$, CH_3CN, DMF, or DMSO,[4—6] followed by their replacement with other ligands. An alternative approach involves the direct replacement of the terminal halide ion by a more strongly bound ligand, *viz.*, the pyridine,[7] phosphine,[8,9] cyanide, or rhodanide anions.[10—14] Although a large number of hexanuclear rhenium cluster complexes with various external ligands have been synthesized, aqua and ammine complexes remain virtually unknown. Only one aqua complex, *viz.*, $[Re_6S_8(H_2O)_6]^{2+}$, was prepared in solution, but it was not isolated in the solid state.[15] Data on cluster rhenium ammine complexes or approaches to their synthesis are lacking in the literature.

In the present study, we report the synthesis and crystal structure of the new rhenium cluster complex $[Re_6Se_7Br(NH_3)_6][Re_6Se_7BrBr_6] \cdot 12H_2O$ (**1** $\cdot 12H_2O$) containing the ammine cation $[Re_6Se_7Br(NH_3)_6]^{3+}$.

Results and Discussion

X-ray diffraction study demonstrated that compound **1** $\cdot 12H_2O$ is composed of the $[Re_6Se_7Br(NH_3)_6]^{3+}$ cations and $[Re_6Se_7BrBr_6]^{3-}$ anions (Figs. 1 and 2, Tables 1 and 2). The $[Re_6Se_7Br(NH_3)_6]^{3+}$ cluster cation contains the virtually regular Re_6 octahedron. The Re—Re distances are in the range of 2.6110(12)—2.6123(11) Å (2.6117 Å).* Each face of the octahedron is coordinated by the internal μ_3-Q ligand (Q = 7/8Se + 1/8Br). The Re—Q distances are in the range of 2.526(2)—2.5362(16) Å (2.5308 Å). Each rhenium atom is additionally coordinated by the neutral ammonia ligand with the Re—N distance of 2.135(10) Å. In the crystal structure, the $[Re_6Se_7BrBr_6]^{3-}$ cluster anion remains virtually unchanged. The Re—Re and Re—Q distances are in the ranges of 2.6157(10)—2.6179(10) Å (2.6168 Å) and 2.525(2)—2.5337(16) Å (2.5303 Å), respectively, and the Re—Br distance is 2.5760(16) Å. In the $Cs_3Re_6Se_7BrBr_6$ starting salt, the corresponding distances in the $[Re_6Se_7BrBr_6]^{3-}$ anion are as follows: Re—Re, 2.606(1)—2.625(1) Å (2.615 Å); Re—Q, 2.508(3)—2.542(3) Å (2.524 Å); Re—Br, 2.553(3)—2.587(3) Å (2.573 Å).

To confirm the nature of the terminal ligand in the $\{[Re_6Se_7Br](NH_3)_6\}^{3+}$ cationic complex, the products of thermal decomposition of compound **1** were studied by mass spectrometry. It appeared that only H_2O molecules adsorbed by the sample were present in the gas phase at

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* Hereinafter, the average values are given in parentheses.

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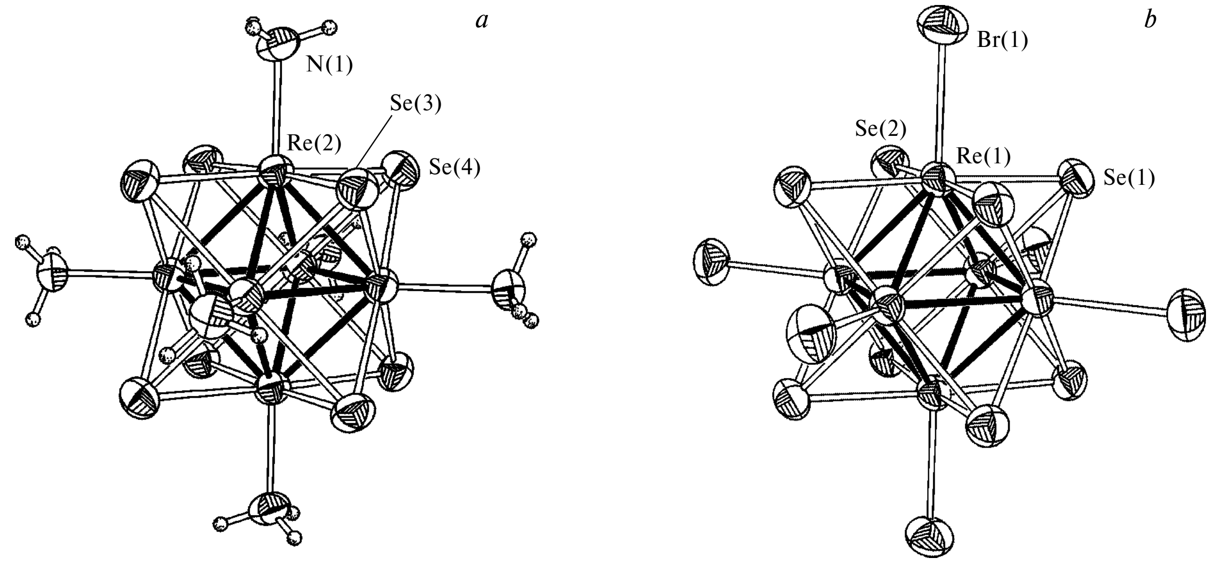

Fig. 1. Structures of the $[Re_6Se_7Br(NH_3)_6]^{3+}$ cation (*a*) and $[Re_6Se_7BrBr_6]^{3-}$ anion (*b*) in compound $\mathbf{1}\cdot 12H_2O$ (thermal ellipsoids with the 50% probability).

temperatures higher than 230 °C. Upon heating above 250 °C, NH_3 was the major gaseous product. This behavior corresponds to the thermal decomposition curve for compound **1** according to which the main weight loss started at >250 °C and the total weight loss was equal to the stoichiometric NH_3 content. The IR spectrum has a set of absorption bands assigned to vibrations of the coordinated NH_3 molecules. The bands at 909 and 1282 cm^{-1} can be attributed to the rocking ($\rho(NH_3)$) and bending ($\delta_s(NH_3)$) vibrations of the coordinated ammonia molecule[16] (note that these vibrations cannot be manifested in the spectrum of the aqua complex).

The formation of ammine complex $\mathbf{1}\cdot 12H_2O$ is attributable to the following processes: the replacement of all six external Br^- ligands in the anionic $[Re_6Se_7BrBr_6]^{3-}$ complex by the NH_3 molecules to form the ammine cations $[Re_6Se_7Br(NH_3)_6]^{3+}$, and the reactions of the triple-charged $[Re_6Se_7Br(NH_3)_6]^{3+}$ cluster cations with the

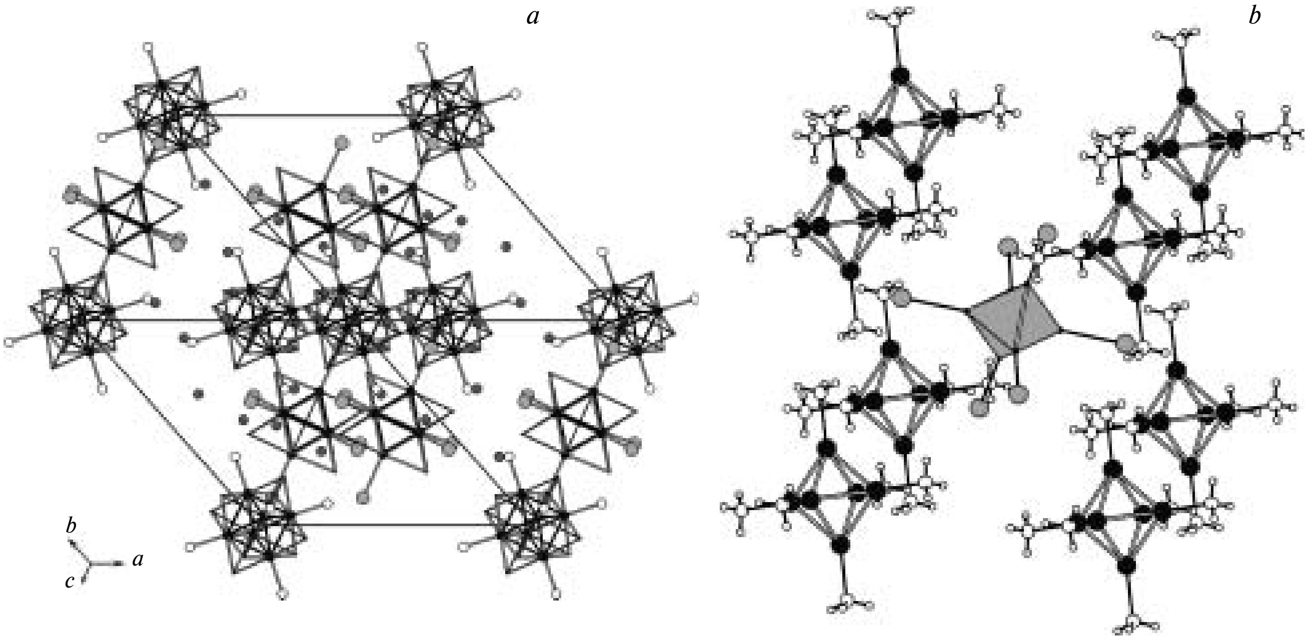

Fig. 2. Crystal structure of compound $\mathbf{1}\cdot 12H_2O$: *a*, projection of the unit cell along the *111* direction; *b*, the fragment of the distorted crystal packing of the CsCl type. The μ_3-Q ligands and H_2O molecules of solvation are omitted. The Re_6 cluster of the $[Re_6Se_7BrBr_6]^{3-}$ anion is represented as a polyhedron.

Table 1. Crystallographic data and parameters of the X-ray diffraction study of compound $\mathbf{1} \cdot 12H_2O$

Parameter	Characteristic
Molecular formula	$H_{21}Br_4N_3O_6Re_6Se_7$
Molecular weight	2148.76
Crystal system	Trigonal
Space group	$R\bar{3}$
a/Å	15.406(5)
c/Å	19.584(5)
γ/deg	120
V/Å^3	4025(2)
Z	6
ρ_{calc}/g cm^{-3}	5.316
μ/mm^{-1}	42.293
$2\theta_{max}$/deg	27.50
Number of measured/independent reflections (R_{int})	14766/2063 (0.1230)
Number of parameters in the refinement	80
Number of reflections with $I > 2\sigma$	2051
R_1 ($I > 2\sigma$)	0.0496
wR_2 (for all reflections)	0.1368

$[Re_6Se_7BrBr_6]^{3-}$ anions present in solution to yield the poorly soluble $[Re_6Se_7Br(NH_3)_6][Re_6Se_7BrBr_6] \cdot 12H_2O$ compound. Experimental observations demonstrated that the duration of the first step is longer than that of the second step, which is associated with the kinetics of the ligand replacement, whereas the second step, *viz.*, the formation of **1**, proceeds apparently rather rapidly. When the concentration of the cluster cations becomes equal to the solubility product, complex **1** precipitates. Since six terminal Br^- ligands in the cluster anion are successively replaced by the NH_3 molecules, the reaction solution can contain also the mixed-ligand complexes $[\{Re_6Se_7Br\}Br_{6-x}(NH_3)_x]^{(-3+x)}$.

The formation of the final solid product of composition $[Re_6Se_7Br(NH_3)_6][Re_6Se_7BrBr_6] \cdot 12H_2O$ indicates that the simple stoichiometric ratio (1 : 1) between the $[Re_6Se_7Br(NH_3)_6]^{3+}$ cations and $[Re_6Se_7BrBr_6]^{3-}$ anions of similar sizes (V_{cat} = 400.5 Å^3 and V_{an} = 461.4 Å^3) is more favorable for the formation of the ionic crystal lattice with the CsCl structure.

Salts composed of the cluster anions and cations have been studied previously in the chemistry of transition metals. A series of salts formed by the tetrahedral cluster cations $[Mo_4(\eta\text{-}C_5H_4R)(\mu_3\text{-}Q)_4]^+$, where R = Pr^i, Me, or H and Q = S or Se, and the $[Fe_4(NO)_4(\mu_3\text{-}S)_4]^-$ and $[Os_6(CO)_{18}]^{2-}$ anions were synthesized.[17] The crystal packings of these salts were analyzed[18] based on the parameters describing the size and shape of the ions. It was found that the packing of the ions in the crystal structure depends substantially on the relative sizes of the cations and anions and is analogous to the packings of simple ionic salts of the CsCl, antifluorite, and *anti*-NiAs types.

The $[Nb_6Cl_{12}(EtOH)_6][Mo_6Cl_8Cl_6] \cdot 3EtOH \cdot 3Et_2O$ cluster salt containing different cores in the $\{Nb_6Cl_{12}\}$ cationic and $\{Mo_6Cl_8\}$ anionic portions was synthesized.[19] The first example of the cluster salt containing identical cluster cores in the cationic and anionic components was reported in Ref. 20. The $[Ta_6Cl_{12}(PrCN)_6][(Ta_6Cl_{12})Cl_6] \cdot 2PrCN$ compound is built from the $[Ta_6Cl_{12}(PrCN)_6]^{2+}$ cation and $[Ta_6Cl_{12}Cl_6]^{2-}$ anion. The cationic and anionic components contain the $\{Ta_6Cl_{12}\}$ cores possessing different number of cluster valence electrons. Therefore, compound $\mathbf{1} \cdot 12H_2O$ is the first representative composed of the cluster anions and cations possessing the same $\{Re_6Se_7Br\}$ cluster core.

The reaction of $Cs_3Re_6Se_7BrBr_6$ with NH_3 afforded the crystals of $\mathbf{1} \cdot 12H_2O$ and powdered compound **1**. The EDAX data for $\mathbf{1} \cdot 12H_2O$ and **1** showed that both compounds have the same ratio of the heavy elements (Re, Se, and Br). The data from elemental analysis and thermogravimetry for **1** demonstrated that this compound, unlike the crystals, does not contain water molecules of crystallization and is described by the formula $[Re_6Se_7Br(NH_3)_6][Re_6Se_7BrBr_6]$. The X-ray diffraction pattern of compound **1** differs from that calculated for $\mathbf{1} \cdot 12H_2O$ and can be indexed in the primitive hexagonal unit cell with the parameters a = 8.95 Å, c = 11.55 Å, V = 925 Å^3 (Z = 2).

Experimental

The $Cs_3Re_6Se_7BrBr_6$ compound was prepared from simple compounds, *viz.*, Re, Se, Br_2, and CsBr, according to a known procedure.[21] The IR spectra were recorded on a Bruker IFS-85 IR Fourier spectrometer. Elemental analysis was carried out on a Carlo Erba 1106 instrument. The mass spectra were recorded on an MX-1310 spectrometer. The thermogravimetric experiments were performed on a TA-7000 instrument (Japan).

Synthesis of (μ_3-bromo)heptakis(μ_3-selenido)hexaamminehexarhenium(III) (μ_3-bromo)heptakis(μ_3-selenido)hexabromohexarhenate(III), $[Re_6Se_7Br(NH_3)_6][Re_6Se_7BrBr_6] \cdot 12H_2O$. The reaction was carried out in aqueous ammonia at ~20 °C. The $Cs_3Re_6Se_7BrBr_6$ compound (0.400 g, 0.151 mmol) was dissolved in a concentrated ammonia solution (30 mL) and kept for 24 h in a closed vessel. The reaction afforded a yellow crystalline precipitate of **1** and red crystals of $\mathbf{1} \cdot 12H_2O$, which were used in the X-ray diffraction study. The precipitate of **1** was obtained in a yield of 0.262 g (0.0642 mmol, 85.0%). IR, cm^{-1}: 481 (ν(Re—N), 909 (ρ(NH_3)), 1282 (δ_s(NH_3)), 1599 (δ_d(NH_3)), 3213, 3284, 3512 (ν(NH_3)). Found (%): H, 0.66; N, 1.80. $Re_{12}Se_{14}Br_8N_6H_{18}$. Calculated (%): H, 0.44; N, 2.06. EDAX: $\mathbf{1} \cdot 12H_2O$ — Re : Se : Br = 6 : 7.1 : 4.2; **1** — Re : Se : Br = 6 : 7.0 : 4.3. Thermogravimetry: the step was 250—320 °C, the weight loss was 2.6% (six NH_3 molecules).

X-ray diffraction study of rhenium cluster complex $[Re_6Se_7Br(NH_3)_6][Re_6Se_7BrBr_6] \cdot 12H_2O$ ($\mathbf{1} \cdot 12H_2O$). Single crystals were taken from the reaction mixture. The X-ray diffraction data were collected on a Nonius Kappa CCD diffrac-

Table 2. Principal bond lengths (*d*) and selected bond angles (ω) in the structure of **1**

$[Re_6Se_7Br(NH_3)_6]^{3+}$ cation		$[Re_6Se_7BrBr_6]^{3-}$ anion	
Bond	*d*/Å	Bond	*d*/Å
Re(2)—Re(2)$^{\#4}$	2.6110(12)	Re(1)—Re(1)$^{\#3}$	2.6157(10)
Re(2)—Re(2)$^{\#2}$	2.6110(12)	Re(1)—Re(1)$^{\#1}$	2.6157(10)
Re(2)—Re(2)$^{\#5}$	2.6123(11)	Re(1)—Re(1)$^{\#4}$	2.6179(12)
Re(2)—Re(2)$^{\#6}$	2.6123(11)	Re(1)—Re(1)$^{\#2}$	2.6179(12)
Re—Re (av)	2.6117	Re—Re (av)	2.6168
Re(2)—Q(3)	2.526(2)	Re(1)—Q*(1)	2.5295(16)
Re(2)—Q(4)$^{\#5}$	2.5297(16)	Re(1)—Q(1)$^{\#1}$	2.5331(16)
Re(2)—Q(4)$^{\#2}$	2.5312(16)	Re(1)—Q(1)$^{\#2}$	2.5337(16)
Re(2)—Q(4)	2.5362(16)	Re(1)—Q(2)	2.525(2)
Re—Q (av)	2.5308	Re—Q (av)	2.5303
Re(2)—N(1)	2.135(10)	Re(1)—Br(1)	2.5760(16)
Angle	ω/deg	Angle	ω/deg
Re(2)$^{\#4}$—Re(2)—Re(2)$^{\#2}$	60.0	Re(1)$^{\#3}$—Re(1)—Re(1)$^{\#1}$	60.05(3)
Re(2)$^{\#4}$—Re(2)—Re(2)$^{\#5}$	90.0	Re(1)$^{\#3}$—Re(1)—Re(1)$^{\#4}$	59.973(16)
Re(2)$^{\#2}$—Re(2)—Re(2)$^{\#5}$	60.017(16)	Re(1)$^{\#1}$—Re(1)—Re(1)$^{\#4}$	90.0
Re(2)$^{\#4}$—Re(2)—Re(2)$^{\#6}$	60.017(16)	Re(1)$^{\#3}$—Re(1)—Re(1)$^{\#2}$	90.0
Re(2)$^{\#2}$—Re(2)—Re(2)$^{\#6}$	90.0	Re(1)$^{\#1}$—Re(1)—Re(1)$^{\#2}$	59.973(16)
Re(2)$^{\#5}$—Re(2)—Re(2)$^{\#6}$	59.97(3)	Re(1)$^{\#4}$—Re(1)—Re(1)$^{\#2}$	60.0
Re(2)—Q(3)—Re(2)$^{\#2}$	62.25(6)	Re(1)—Q(1)—Re(1)$^{\#3}$	62.22(4)
Re(2)—Q(3)—Re(2)$^{\#4}$	62.25(6)	Re(1)—Q(1)—Re(1)$^{\#4}$	62.27(4)
Re(2)$^{\#2}$—Q(3)—Re(2)$^{\#4}$	62.25(6)	Re(1)$^{\#3}$—Q(1)—Re(1)$^{\#4}$	62.16(4)
Re(2)$^{\#6}$—Q(4)—Re(2)$^{\#4}$	62.15(4)	Re(1)$^{\#4}$—Q(2)—Re(1)$^{\#2}$	62.45(6)
Re(2)$^{\#6}$—Q(4)—Re(2)	62.08(4)	Re(1)$^{\#4}$—Q(2)—Re(1)	62.45(6)
Re(2)$^{\#4}$—Q(4)—Re(2)	62.03(3)	Re(1)$^{\#2}$—Q(2)—Re(1)	62.45(6)
Re—Q—Re (av)	62.17	Re—Q—Re (av)	62.33
N(1)—Re(2)—Q(3)	89.8(3)	Br(1)—Re(1)—Q(2)	91.44(6)
N(1)—Re(2)—Q(4)$^{\#5}$	92.8(3)	Br(1)—Re(1)—Q(1)	90.72(5)
N(1)—Re(2)—Q(4)$^{\#2}$	91.0(3)	Br(1)—Re(1)—Q(1)$^{\#1}$	91.48(6)
N(1)—Re(2)—Q(4)	91.7(3)	Br(1)—Re(1)—Q(1)$^{\#2}$	91.95(5)
N—Re—Q(av)	91.32	Br—Re—Q (av)	91.40

* Q = $(Se_7Br)/8$. The atoms are related by the following symmetry operations: $^{\#1}$ $x - y, x - 1, -z + 1$; $^{\#2}$ $-y + 1, x - y - 1, z$; $^{\#3}$ $y + 1, -x + y + 1, -z + 1$; $^{\#4}$ $-x + y + 2, -x + 1, z$; $^{\#5}$ $x - y, x - 1, -z$; $^{\#6}$ $y + 1, -x + y + 1, -z$.

tometer (graphite monochromator, λ(Mo-Kα) = 0.71073 Å) at ~20 °C.

The crystallographic data and the principal parameters of the structure refinement are as follows: the molecular formula is $H_{21}Br_4N_3O_6Re_6Se_8$, the molecular weight is 2148.76, the trigonal system, a = 15.406(5) Å, c = 19.584(5) Å, γ = 120.0°, V = 4025(2) $Å^3$, space group $R\bar{3}$, Z = 6, D_x = 5.316 g cm^{-3}, μ = 42.293 mm^{-1}; the crystal habitus is a truncated octahedron; the crystal dimensions are 0.070×0.065×0.035 mm. The crystal-to-detector distance was 25 mm. The X-ray data were recorded with the use of the COLLECT program.[22] The reflections were measured within the full sphere in reciprocal space up to θ = 27.50°. A total of 14766 reflections were indexed and integrated in the ranges of indices $-20 \le h \le 19$, $-19 \le k \le 20$, $-25 \le l \le 25$ with the use of the DENZO program available for the KappaCCD software. The absorption correction was applied using the GAUSSIAN program (T = 0.1076–0.2605). The intensities were merged within the space group $R\bar{3}$ employing the SCALEPACK program[23] to obtain 2063 independent reflections (R_{int} = 0.1230).

The structure was solved by direct methods[24] and refined by the full-matrix least-squares method using the SHELX-97 program package.[25] The hydrogen atoms were placed in geometrically calculated positions. The final reliability factors were as follows: R_1 = 0.0496, wR_2 = 0.1207 [$I > 2\sigma(I)$], R_1 = 0.0667, wR_2 = 0.1368, $GOOF$ = 1.061 for all independent reflections. The difference electron densities $\Delta\rho_{max}$ and $\Delta\rho_{min}$ of 3.844 eÅ^{-3} and −2.853 eÅ^{-3}, respectively, were localized in the vicinity of the rhenium atoms.

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