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SINGLE-CRYSTAL STRUCTURE OF THE $Cs_2Re_6S_6Br_8$ RHENIUM THIO-BROMIDE WITH ACENTRIC Re_6 OCTAHEDRAL CLUSTER UNITS

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$Cs_2Re_6S_6Br_8$ (trigonal, $a = 10.001(5)$ Å, $c = 14.676(5)$ Å) exhibits the same structure as $Cs_2Mo_6Cl_8Br_6$ and $Cs_2Mo_6Br_{14}$ that were described in a non-centro- and centrosymmetric space groups, respectively. The structure has been refined in $P31c$ space group from a single crystal of actual composition $Cs_{1.95(1)}Re_6S_{5.82(3)}Br_{8.19(3)}$ close to the cesium-rich end of the solid solution $Cs_2Re_6S_6Br_8$ — $CsRe_6S_5Br_9$. The centrosymmetry is respected by almost all the atoms of the asymmetric unit, but it is clearly broken by significant differences in the S/Br statistical distribution of the disordered ″inner″ ligands around the Re_6 cluster. Structural refinements from data collected at 100 K revealed that the Cs cation disorder is static. From the structure refinements, the stable isomers of the $[Re_6S_6Br_2]$ and $[Re_6S_5Br_3]$ cluster cores have been unambiguously determined.

K e y w o r d s : rhenium, octahedral cluster, structure, disorder.

INTRODUCTION

Shortly after the early demonstration of the ability of Re(III) to be involved in the building of octahedral clusters, illustrated by the mixed cluster $Mo_2Re_4S_8$ Chevrel phase [1], the first synthesis of a pure Re-based octahedral cluster, namely the compounds $Re_3Y_2X_5$ (X = halogen, Y = chalcogen), has been reported by the V.E. Fedorov group [2]. Their structures were elucidated by the structural description of the analogous $Re_6Se_4X_{10}$ (X = Cl, Br) [3, 4]. Following this pioneering work, a number of Re_6 cluster compounds have been reported [5 and references therein]. They are based on the various connectivities of the $Re_6 L_8^i L_6^a$ building blocks [6], where the eight ″inner″ L^i ligands cap the faces of the rhenium octahedron and the six ″apical″ L^a ligands lie over the apices of this octahedron, a geometry similar to that encountered with molybdenum and tungsten octahedral clusters [7]. Based on electronic properties and bonding considerations, the Re_6 clusters occur mainly in chalcohalides like the ternary Re—Y—X and the quaternary systems such as M—Re—Y—X (M = cation, X = halogen, Y = chalcogen). Owing to the wide combining possibilities of the X—Y couples and countercations of different charge and size, this crystallochemistry is extremely rich, as illustrated by an extensive study of the above quaternary diagrams, where Y = S, X = Br and M = alkaline [8]. In these systems, continuous trigonal solid solutions extending from $MRe_6S_5Br_9$ to $M_2Re_6S_6Br_8$ (M = Rb and Cs) have been evidenced and structurally characterized. These compounds exhibit the same structure as the early re-

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ported mixed halides, $Cs_2W_6Cl_8Br_6$ and $Cs_2Mo_6Cl_8Br_6$ [9] as well as the more recently characterized $Cs_2Mo_6Br_{14}$ and $Cs_2Mo_6I_{14}$ halides [10]. While the two first mixed halides were described in the acentric $P31c$ space group on the basis of the observation of too much close Cs positions in the centro-symmetric model, the two later ones were described in the centrosymmetric $P\text{-}31c$ space group. We have refined the crystal structure of $Cs_2Re_6S_6Br_8$, in order to derive an unambiguous conclusion concerning the actual symmetry of the space group.

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EXPERIMENTAL SECTION

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Synthesis and single crystal preparation. The compound $Cs_2Re_6S_6Br_8$ has been prepared by solid state reaction from a stoechiometric mixture of CsBr (Prolabo, I.R. grade), Re (Goodfellow, 99.99 %) and S (Prolabo) powders and from liquid bromine (Merck, analysis grade). The starting powders (about 300 mg) were mixed together, grinded and pressed as a pellet and then introduced into a silica tube (7 mm internal diameter) under argon atmosphere. The liquid Br_2 (in excess of about 10 %) was then measured with a micro-pipette, introduced under argon atmosphere into the silica tube and subsequently frozen with liquid nitrogen. Finally, the tube was quickly sealed under an argon residual pressure of 10^{-2} Torr and heated at 800 °C in a vertical oven for 90 hours.

X-ray powder pattern of the final sample did not reveal the presence of any impurity. However, the crystals are strongly imbricated in a compact mass, from which it is difficult to extract specimens suitable for structure determination. The single-crystal used in this work was obtained during a synthesis targeted to a slightly different composition (close to $Cs_{1.5}Re_6S_8Br_{3.5}$) at 850 °C. Individual well-shaped, red transparent crystals easy to select without damaging them were condensed on the walls of the tube, instead of being embedded in the pellet. The crystals, stable under ambient atmosphere, have been analyzed by EDS microanalysis after calibration with $Cs_2Re_6S_6Br_8$ crystals previously obtained by the normal route.

Structural determination by X-ray diffraction. The selected single crystal has been mounted as usually on the top of a glass fiber. The data collections have been carried out on a Nonius KappaCCD X-ray area-detector diffractometer operated with $MoK\alpha_1$ radiation ($\lambda = 0.71073$ Å). Details are reported in Table 1. The compound crystallizes in the trigonal system with a P lattice. Once the data have been processed through the KappaCCD analysis software [11], the unitcell constants have been refined to the values: $a = 10.001(5)$ Å, $c = 14.676(5)$ Å. An effective absorption correction has been carried out through SORTAV. Among the possible space groups deduced from the extinction conditions, the refinement procedure has allowed to retain the $P31c$ and $P\text{-}31c$ space groups. In a first step, the structure was successfully solved in the $P31c$ space group, by the direct method using SIR97 [12]. The least-squares refinement and Fourier syntheses have been performed with CRYSTALS [13], and the model was transferred to the $P\text{-}31c$ space group. The standard Hamilton test was in agreement with the centrosymmetric model but, in contrast, the program DIFABS [14] within PLATON [15] indicated that some atom positions of the cluster did not respect the $P\text{-}31c$ symmetry.

After the first cycle of refinement, a random distribution of S and Br on several L^i positions was detected, as currently observed in Re_6 chalcohalide crystallochemistry [16]. Bromine and sulphur were then introduced on these positions with the same positional and thermal parameters, the sum of their occupancies being restricted to the value corresponding to a fully occupied position. These constraints were progressively relaxed during the convergence, leading to final positions in agreement with reliable Re-(S, Br) interatomic distances. Once the structure skeleton was refined, the Cs cations were located by Fourier difference syntheses. A first Cs1 atom was located on a $2b$ Wyckoff position and all of its anisotropic displacement parameters (U_{11}, U_{22} and U_{33}) converged normally. At this stage, Fourier difference electron density maps showed diffuse maxima along the $[00z]$ axis, each of them, when refined as Cs, leading to large and strongly anisotropic displacement parameter. Two additional Cs positions (Cs2 and Cs3) were then located on this axis and refined with incomplete occupancy.

Details on the crystal data and structure refinement parameters are summarized in Table 1. The final atomic parameters are reported in Table 2 and selected interatomic distances are given in Table 3. Additional materials, anisotropic thermal parameters, observed and calculated structure factors can be obtained upon request from the authors.

Crystallographic data for the structure determination of $Cs_2Re_6S_6Br_8$

Crystal data	
Formula	$Cs_2Re_6S_6Br_8$
Formula weight	2214.7
a (Å)	10.001(5)
c (Å)	14.676(5)
V (Å^3)	1271.2(10)
Z	2
D_{calc}, g.cm^{-3}	5.79
μ (mm^{-1})	44.54
T (K)	293
Structure refinement data	
Space group	$P31c$
Refined formula	$Cs_{1.95(1)}Re_6S_{5.82(3)}Br_{8.19(3)}$
Calculated VEC	24.1(1)
Total reflections collected	40731
R_{int} (all reflections)	0.117
Observed reflections [$I > 3\sigma$ (I)]	1313
Refined parameters	89
R [$I > 3\sigma$ (I)]	0.0275
wR	0.0328
Goodness of fit	1.107
Flack parameter	0.06(6)
$\Delta\rho_{min}/\Delta\rho_{max}$ (e·Å^{-3})	–2.74/1.86

Positional atomic and displacement parameters for $Cs_2Re_6S_6Br_8$

Atom	Wyckoff position	x	y	z	occupancy	Ueq (Å^2)
Re1	6c	0.5158(3)	0.1821(3)	0.1815(6)	1	0.0213
Re2	6c	0.6654(3)	0.1821(3)	0.3250(6)	1	0.0225
Br1	6c	0.3098(5)	0.9653(6)	0.0858(6)	1	0.0422
Br2	6c	0.6532(6)	0.9664(6)	0.4210(6)	1	0.0427
S1	2b	2/3	1/3	0.4538(9)	0.736(8)	0.0277
Br11	2b	2/3	1/3	0.4669(12)	0.264(8)	0.0131
Br21	2b	2/3	1/3	0.0392(6)	1	0.0350
S3	6c	0.3854(11)	0.0533(8)	0.3191(7)	1	0.0281
S4	6c	0.3908(13)	0.3345(15)	0.1803(8)	0.693(2)	0.0261
Br41	6c	0.6743(14)	0.0445(15)	0.1865(9)	0.307(2)	0.0456
Cs1	2b	2/3	1/3	0.7500	0.955(3)	0.0705
Cs2	2a	0	0	0.9988(13)	0.881(3)	0.1009
Cs3	2a	0	0	0.735(5)	0.113(3)	0.1287

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Selected interatomic distances (Å) *in* $Cs_2Re_6S_6Br_8$

Re6 cluster						
Re1—Re1	2.616(4)	Re1—Re2	2.583(1)			
Re2—Re2	2.609(4)	Re1—Re2	2.598(1)			
Re—L^i distances *level z = 0.460*						
Re2—S1	2.418(8)	Re2—Br11	2.570(14)			
level z = 0.039						
Re1—Br21	2.577(5)					
level z = 0.319						
Re2—S3	2.439(7)	Re2—S3	2.430(9)	Re1—S3	2.400(7)	
level z = 0.518 and 0.526						
Re1—S4	2.389(12)	Re1—S4	2.407(11)	Re2—S4	2.469(10)	
Re1—Br41	2.507(13)	Re1—Br41	2.568(8)	Re2—Br41	2.481(12)	
Re—Br^a distances						
Re1—Br1	2.539(5)	Re2—Br2	2.528(6)			
Cs$^+$ environment						
Cs1—Br1	3.942(12)	Cs1—Br2	3.984(12)	Cs1—Br41	3.73(3)	
Cs1—S3	3.770(11)	Cs1—S4	3.79(2)			
Cs2—Br1	3.525(12)	Cs2—Br2	3.504(11)			
Cs3—Br1	3.95(10)	Cs3—S4	3.74(5)			
Cs3—S3	3.83(6)	Cs3—Br41	3.57(4)			

RESULTS

The crystal structure of this compound is based on the usual ($Re_6 L_8^i L_6^a$) unit (with L = S, Br). As shown in Figure 1 which displays the general features of the structure, the Re_6L_{14} units (shown in Figure 2) are centered on the 1/3 2/3 3/4 and 2/3 1/3 1/4 special positions of the trigonal unit cell, while a Cs$^+$
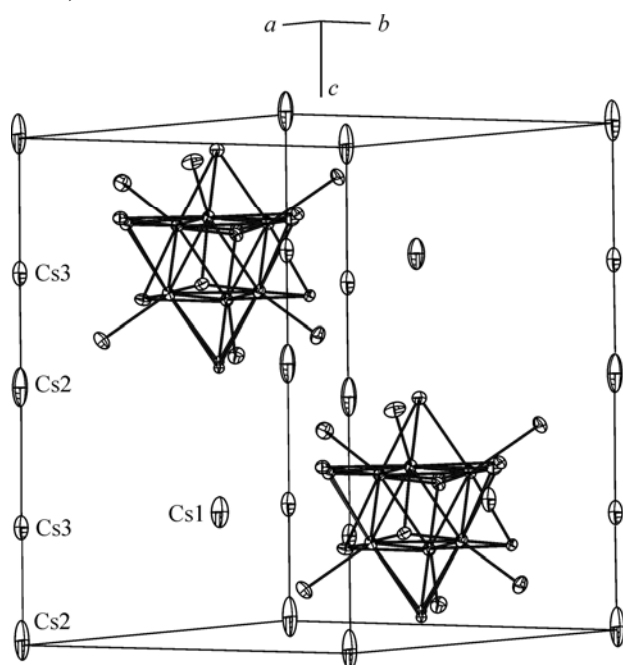

Fig. 1. Unitcell contents of the $Cs_2Re_6S_6Br_8$ structure

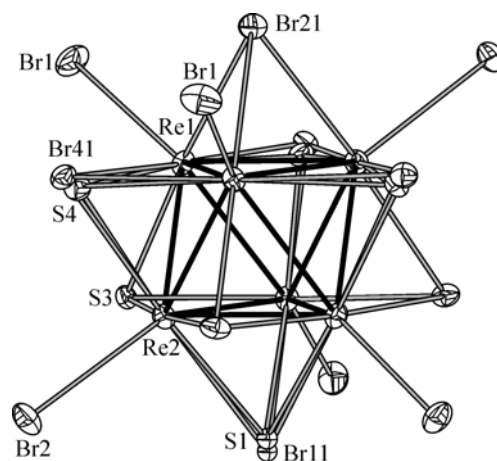*Fig. 2.* The $Re_6L_8^i L_6^a$ cluster unit in the $Cs_2Re_6S_6Br_8$ structure. A S/Br statistical occupancy occurs on L^i positions excepted for the inner positions occupied by Br21 and S3
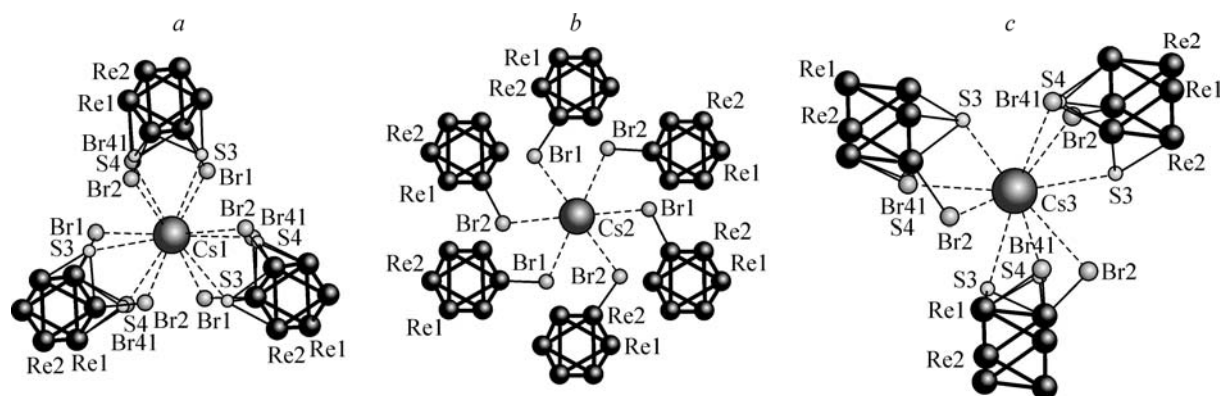
Fig. 3. Cs1 (**a**), Cs2 (**b**) and Cs3 (**c**) environments in the $Cs_2Re_6S_6Br_8$ structure

ion occupies the second set of 1/3 2/3 1/4 positions. This location derives from space group symmetry in $P\text{-}31c$ hypothesis while, in the $P31c$ model, the z coordinate has to be fixed and was choosen as 0.25 and 0.75 for convenience of comparison. At this stage, the two models are very close to each other. The additional Cs^+ ion is located on the c axis and distributed on several positions with statistical occupancy. After comparing their electron density maps along the c axis, the two models are similar. This result does not provide any argument for the choice of the actual symmetry.

A much more convincing argument about the actual symmetry merged when examining the details of the cluster environment, as displayed in Figure 2, relative to the acentric model. It appears clearly that the two *para*- L^i ligands located on the ternary axis in $2b$ positions are respectively only Br at $z = 0.039$ and, in majority, sulphur at the pseudo-symmetric position ($z \approx 0.45$). This situation strongly contrasts with a centrosymmetric model, where both of them would be close to 50 % bromine and 50 % sulphur. A similar situation occurs for the $6c$ L^i positions, corresponding to sulphur only in the triangle at $z = 0.319$ and 0.31 Br + 0.69 S for $z \approx 0.18$. It is then clear that the acentric model has to be retained because the observed distribution of ligands in the cluster unit cannot be derived from a centrosymmetric model.

The Re—Re distances range between 2.583(1) and 2.616(4) Å in close agreement with the data previously reported for Re_6 clusters [5, 6, 8] with 24 valence electrons in the metal-metal bonding states of the Re_6L_{14} molecular orbital diagram.

As mentioned above, the different positions corresponding to inner ligand affected by statistical distribution have been refined using the CRYSTALS program [13], allowing the independent refinement of the two types of atoms on very close positions. The corresponding average distances Re—S^i (2.42 Å) and Re—Br^i (2.53 Å) correspond well to previous values reported in compounds where they could have been determined separately as pure S^i ligands [17—19], or in some examples of mixed L^i ligands where S^i and Br^i could be refined independently [20]. Indeed, $Cs_2Re_6S_6Br_8$ appears to be the first example of Re_6 cluster with a pure Br^i ligand in its environment.

The environment of the cluster is completed by six apical bromine ligands. The actual Re—Br^a distance is strongly sensitive to the coulombic charge of the unit. For instance, it was in the range 2.53—2.55 Å for various two negatively charged units [17], values close to those obtained for the title compound (2.528(6) and 2.539(5) Å). The structural cohesion is done by coulombic interactions between the discrete $[Re_6L_{14}]^{2-}$ anionic units and the Cs^+ counter-cations. Figure 3 shows that Cs2 is pseudo-octahedrally environed by six Br^a belonging to six different Re_6L_{14} units, with Cs—Br distances (3.504(11) and 3.525(12) Å) lower than the sum of ionic radii (3.64 Å [21]) owing to the partial occupancy of the Cs2 site (88.1 %). The environments of Cs1 and Cs3 are much more complex as displayed in Figure 3: Cs1 is in a XII-coordination site formed by six Br^a and six L^i belonging to three $[Re_6L_{14}]$ units, while Cs3 is bonded to three Br^a and six L^i belonging to three adjacent units that form a IX-coordinance environment.

Finally, Figure 4 shows a projection of the structure viewed along the c-axis direction, evidencing the presence of channels, where are located Cs2 and Cs3. The later exhibit important anisotropic
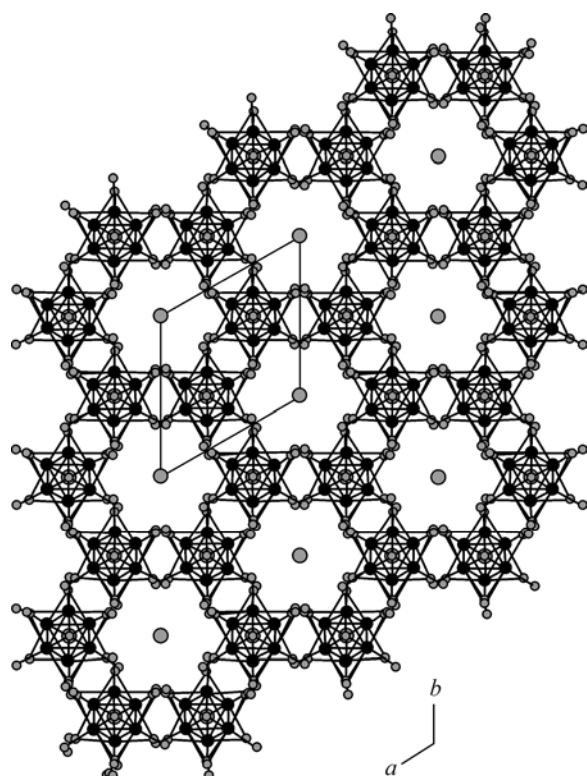
Fig. 4. Projection of the $Cs_2Re_6S_6Br_8$ structure along *c*-axis

atomic displacement parameters U_{33}, characteristic of an electronic delocalization. It appears clearly that these channels do not present any bottle neck, but their smallest equivalent diameter is ≈ 2.7 Å, significantly smaller than the diameter of a Cs^+ ion (≈ 3.9 Å, depending on the environment).

In order to determine whether the cationic distribution observed along the c axis of the unit cell was essentially static or dynamic, a data collection was performed at 100 K using the same single crystal. The resolution of the $Cs_2Re_6S_6Br_8$ structure at 100 K does not present any significant change compared to the structure at 293 K. The unit-cell volume is significantly reduced ($a = = 9.954(5)$ Å and $c = 14.568(5)$ Å). These data imply a large and anisotropic thermal expansion factor ($\alpha = 24.2 \cdot 10^{-6}$ / °C along $\langle 100 \rangle$ and $38.4 \cdot 10^{-6}$ / °C along [001] axis). The large anisotropy of 58 % is clearly related to the atomic displacements of Cs ions in their sites (including Cs1) as shown in Table 4. The atomic displacement parameters of the Re_6L_{14} units and of the Cs cations are concomitantly slightly reduced at low temperature, as expected (see Table 4), while the occupancy factors of the cesium sites are not changed. It means that the cesium distribution on the sites along *c*-direction is static and that no long range motion of Cs along this axis could be expected.

DISCUSSION

From the above data it appears clearly that $Cs_2Re_6S_6Br_8$ adopts the *P*31*c* space group early assigned to $Cs_2W_6Cl_8Br_6$ and $Cs_2Mo_6Cl_8Br_6$ [9]. Let us recall that the two later mixed halides were assumed acentric only on the basis of the merging of two too much close Cs 00*z* peaks in the difference Fourier density within the *P*-31*c* model. However, the possibility of splitting this position into two half-occupied ones was not examined at that time. Finally the accuracy of the model (R = 0.11 and R = 0.12 for $Cs_2W_6Cl_8Br_6$ and $Cs_2Mo_6Cl_8Br_6$, respectively) appears too poor to draw unambiguous conclusions. The *P*-31*c* space group in which were refined the $Cs_2Mo_6Br_{14}$ and $Cs_2Mo_6I_{14}$ structures strongly suggests that $Cs_2W_6Cl_8Br_6$ and $Cs_2Mo_6Cl_8Br_6$ could be actually centric. Concerning the title compound, the Cs atoms are distributed on several 00*z* positions, some of them associated to small occupancy, and very large and anisotropic displacement factors, and it is difficult to conclude on their centro-symmetry. More convincing argument in favor of the *P*31*c* space group is the acentric arrangement of the inner ligands around the Re_6 cluster as described above. However, the deviations to centro-symmetry are very subtle if one considers the Hamilton test [22], that is understandable when considering that the symmetry breaking is due to only the lightest atoms of the structure. In the recent

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Anisotropic atomic displacement parameters of Cs *atoms in* $Cs_2Re_6S_6Br_8$

Cation	Wyckoff position	293 K		100 K	
		$U_{11} = U_{22}$	U_{33}	$U_{11} = U_{22}$	U_{33}
Cs1	2*b*	0.0448(8)	0.122(3)	0.0215(6)	0.082(2)
Cs2	2*a*	0.0373(9)	0.228(5)	0.0159(7)	0.135(4)
Cs3	2*a*	0.035(7)	0.32(9)	0.013(4)	0.05(2)

Positional parameters and occupancy for Cs *atoms in* $Cs_2Re_6S_6Br_8$, $Cs_2Mo_6Br_{14}$ *and* $Cs_2Mo_6I_{14}$ *for comparison*

$Cs_2Re_6S_6Br_8$	(*P31c*)				
Atom	*position*	*x*	*y*	*z*	*occupancy*
Cs1	2*b*	2/3	1/3	0.7500	0.955(3)
Cs2	2*a*	0	0	0.999(2)	0.881(3)
Cs3	2*a*	0	0	0.737(8)	0.113(3)
$Cs_2Mo_6I_{14}$	(*P-31c*)				
Atom	*position*	*x*	*y*	*z*	*occupancy*
Cs1	2*c*	2/3	1/3	3/4	1
Cs2	2*b*	0	0	0	1
$Cs_2Mo_6Br_{14}$	(*P-31c*)				
Atom	*position*	*x*	*y*	*z*	*occupancy*
Cs1	2*c*	2/3	1/3	3/4	0.919(5)
Cs2	4*e*	0	0	0.0171(5)	0.5
Cs3	2*a*	0	0	3/4	0.117(8)

structural determination of $Cs_2Mo_6Br_{14}$ and $Cs_2Mo_6I_{14}$ the Mo_6X_{14} units (X = Br, I) have been obviously found centro-symmetric. In the iodide, the Cs atoms fully occupy the 0,0,0 site (Cs2) and the 2/3, 1/3, 3/4 site (Cs1) (see Table 5). In the bromide, Cs2 is slightly shifted from the origin on the *c*-axis (4*e* position) with an occupancy of 50 % while Cs1 partly occupies its site (92 %). An additional Cs3 is located on 0,0,3/4 (2*a* position) with an occupancy of 12 %. The two latter Cs positions and occupancies (Cs1 and Cs3) are very similar in $Cs_2Re_6S_6Br_8$ and in $Cs_2Mo_6Br_{14}$. If one considers reasonable distances between Cs atoms on the *c*-axis, the simultaneous presence of Cs2 and Cs3 is not possible. Consequently, the full occupancy of Cs2 position implies an empty Cs3 site and a full Cs1 site like in $Cs_2Mo_6I_{14}$. Oppositely, in $Cs_2Mo_6Br_{14}$ the shift of Cs atom towards a 4*e* position with half occupancy leads to a short and to a long Cs2—Cs3 interatomic distances, the latter only being realistic. In this case, the Cs3 site and one of the two equivalent 4*e* positions can be simultaneously occupied. The noticeable difference between $Cs_2Mo_6X_{14}$ and $Cs_2Re_6S_6Br_8$ is that in the two molybdenum structures the site at (or close to) the origin is fully occupied by Cs2, while in the rhenium compound this site is only partly occupied (88 %). This is obviously explained by the existence of a continuous solid solution between $CsRe_6S_5Br_9$ and $Cs_2Re_6S_6Br_8$ [8]. Indeed, in the structure of the title compound we have evidenced a slight defect of sulphur (5.82 instead of 6) and correlatively an excess of bromine (8.19 instead of 8) compensating the slight caesium deficiency to maintain 24 valence electron per Re_6 cluster.

Finally, if one considers the cluster units in the solid solution between $Cs_2Re_6S_6Br_8$ and $CsRe_6S_5Br_9$, a 6/2 Br/Se ligand distribution on the inner positions of the cluster unit implies the possibility of 3 isomers while a 5/3 one implies also 3 possible isomers (Figure 5). In most examples of mixed ligands cluster compounds, solid state structures exhibit a rotational disorder, so that it is impossible to determine the local stoechiometry and the isomery of the cluster units actually present in the structure from the X-ray data, that give only access to averaged units. Solution chemistry separation can help to solve this problem, as shown for $Cs_4[Nb_6F_{8,5}^{\,i}I_{3,5}^{\,i}F_6^{\,a}]$ [23]. In the case of $Cs_2Re_6S_6Br_8$, it is undoubtedly that almost only ≈75 % of one $Re_6S_6Br_8$ isomer (isomer **b**) and ≈25 % of one $Re_6S_5Br_9$ isomer (isomer **e**) are present (see details in Figure 5), while they are rotated around the unitcell ternary axis. It must be pointed out from theoretical calculations performed for $[(Mo_6I_6^{\,i}Se_2^{\,i})I_6]^{n-}$ cluster unit, exhibiting a similar geometry as for $Cs_2Re_6S_6Br_8$, that the isomer (**a**) is the most stable, while (**b**) is slightly less stable and isomer (**c**) is the least stable. Experimental results were in agreement with these theoretical calculations because it has been found that $Cs_3Mo_6I_6^{\,i}I_{2-x}^{\,i}Se_x^{\,i}I_6^{\,a}$ solid solution is built up from such (**a**) isomers [24]. For the title compound, the
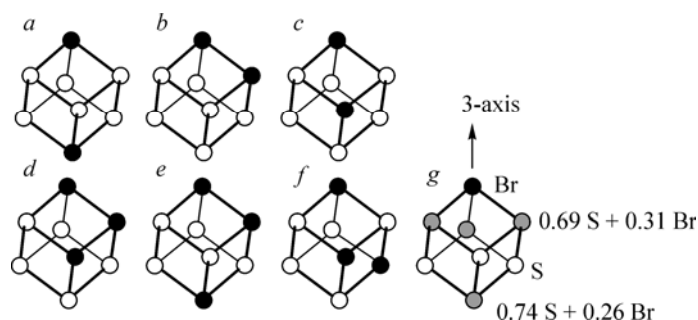
Fig. 5. (top) possible isomers of the $Re_6Se_6Br_2$ sub-unit (Re omitted for clarity; open circles are S and filled circles are Br atoms): (**a**) D_{3d}, (**b**) and (**c**) C_{2v}; (middle): possible isomers of the $Re_6Se_5Br_3$ sub-unit: (**d**) to (**f**) C_s ; (bottom): (**g**) the actual model derived from the title structure with rotational disorder included, grey atoms are 0.69 S + + 0.31 Br and light grey are 0.74 S + 0.26 Br which corresponds to $\approx$ 75 % isomer (**b**) + + $\approx$25 % isomer (**e**)

different characteristics of the metal and the ligands should influence significantly the energy and consequently the relative stability of the three isomers when compared to $[(Mo_6I_6^iSe_2^i)I_6]^{n-}$ units.

The last feature to point out is the presence, in this structure, of channels developing along the *c*-axis of the unit cell, where are distributed half of the Cs ions present in the compound. Taking into account the number of 00*z* sites and the shape of the ellipsoids, the possibility of some motion of these ions in the channels evidenced by the projection of Figure 4 cannot be ruled out. However, the smallest free diameter of the channels is about 2.7 Å, clearly smaller than the ionic diameter of Cs^+ (3.9 Å) [21]. Meanwhile, the ionic conductivity has been checked for, using both a pellet (6 mm diameter, 1 mm thick) of pressed powder and a hexagonal prism-shaped (about 0.5·0.5·0.5 mm) single crystal. The latter was mounted with conductive Pt paint electrodes on the (0001) faces in order to have the electrical field aligned with the channels. No signature of any appreciable electronic nor ionic conductivity has been observed up to 300 °C. Above this temperature, a signal has been obtained, but only due to some decomposition, as it did not disappear when the temperature was lowered again. In fact, the absence of ionic conductivity closely agrees with the results of the refinement of the low temperature data, as the 00*z* Cs positions are not significantly affected, when compared to the distribution determined at room temperature. This result implies a static distribution of these cesium ions.

CONCLUSION

In summary, the structure of $Cs_2Re_6S_6Br_8$ could be refined with similar *R* factors and electronic residual peaks either in the *P*-31*c* or *P*31*c* space groups. Our structural analysis shows that the structure is quasi-centrosymmetric, the symmetry being broken only by small variations in the Cs distribution along the *z*-axis and, more convincingly, by an uneven distribution of the S and Br ligands lying on the inner positions around the rhenium cluster. The latter argument was obviously inexistent in the case of the parent structures $Cs_2W_6Cl_8Br_6$ and $Cs_2Mo_6Cl_8Br_6$, where no ligand distribution could arise on the inner positions. From the presence of Cs ions distributed along the *z*-axis oriented channels in the structure, some ionic conductivity could be expected. However, the absence of the latter agrees with the shape of the channels and with the results of low temperature structural determination which are in accordance with a static distribution of these ions.

Finally, such rhenium cluster compounds built from discrete $[Re_6L_{14}]^{n-}$ cluster units are relevant precursors for solution chemistry [25]. Such synthetic soft chemistry route can give access to apical ligand substitutions, for instance cyano-groups substitution that provides cyano-cluster units useful for further elaborations of solid frameworks with various dimensionalities by complexation with transition metal cations [26—30].

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