Crystal structure of rhenium caesium sulfobromide, $\text{CsRe}_6\text{S}_8\text{Br}_3$, the first cluster compound in the Cs-Re-S-Br system exhibiting two types of inter-unit bridges

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Abstract

$\text{Br}_3\text{CsRe}_6\text{S}_8$, monoclinic, $P12_1/n1$ (No. 14), $a = 6.3481(1)$ Å, $b = 18.5504(3)$ Å, $c = 15.0706(2)$ Å, $\beta = 97.3271(6)^\circ$, $V = 1760.2$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.026$, $wR_{\text{obs}}(F) = 0.030$, $T = 293$ K.

Source of material

The title compound was prepared as a pure sample by solid state synthesis from a stoichiometric mixture of CsBr , Re , S powder and liquid bromine. After being sealed under an argon residual pressure, the silica tube was heated to 1173 K in a vertical furnace during 132 h followed by a cooling to room temperature in 6 h.

Discussion

The octahedral core of the rhenium cluster is slightly distorted: the independent Re-Re bond lengths range from 2.590(1) Å to 2.634(1) Å. The eight inner positions around the cluster are fully occupied by sulfur, while four bromine and two sulfur atoms are fully ordered on the six apical positions. The Re_6 clusters are connected to each other via two different kinds of bridges (Figure). Two of the four bromine apical ligands are shared with two neighbouring clusters via $\text{Re-Br}^{\text{a-a}}\text{-Re}$ bridges. A chain is thereby formed, extending along the [101] direction. In addition, two of the eight sulfur inner ligands participate in trans position in $\text{Re-S}^{\text{a-i,i-a}}\text{-Re}$ bridges towards two neighbouring Re_6 clusters, linking the above mentioned chains to form a layer parallel to the (010) plane. Consequently, the framework is strongly 2-D, as the cohesion along the direction perpendicular to the layers (the [010] one) is obtained only by coulombic interactions involving the caesium ions intercalated between layers. These cations are located inside a complex environment formed by four sulfur atoms (exclusively S^{i}) and five bromine atoms (four Br^{a} and one $\text{Br}^{\text{a-a}}$). The Cs-ligand distances lie between 3.732(2) Å and 3.929(1) Å. The developed formula is: $\{[\text{Re}_6\text{S}_6^{\text{i}}\text{S}_{2/2}^{\text{i-a}}\text{S}_{2/2}^{\text{a-i}}\text{Br}_{2/2}^{\text{a-a}}\text{Br}_2^{\text{a}}]^{-}\}$. $\text{CsRe}_6\text{S}_8\text{Br}_3$ is isostructural with $\text{CsRe}_6\text{Se}_8\text{I}_3$ (although the size of the ligands is significantly different in these two examples), the structure of which has been previously reported [1], but with a limited accuracy ($R = 0.076$). The stacking of the title compound can be compared to that of the neutral, ternary $\text{Re}_6\text{S}_8\text{Br}_2$ one [2] but in the latter the $\text{Br}^{\text{a}}\cdots\text{Cs}\cdots\text{Br}^{\text{a}}$ coulombic interactions are replaced with strong $\text{Re-Br}^{\text{a-a}}\text{-Re}$ bridges, giving rise to a true 3-D structure.

Table 1. Data collection and handling.

Crystal:	black needle, size $0.014 \times 0.018 \times 0.048$ mm
Wavelength:	Mo K_{α} radiation (0.71073 Å)
μ :	508.66 cm^{-1}
Diffractometer, scan mode:	Nonius Kappa-CCD, ϕ
$2\theta_{\text{max}}$:	69.94°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	40418, 7739
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 3 \sigma(I_{\text{obs}})$, 3700
$N(\text{param})_{\text{refined}}$:	164
Programs:	SIRWARE [3], CRYSTALS [4], NUMABS [5], CAMERON [6]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Re(1)	4e	0.29277(6)	0.26187(2)	-0.04120(2)	0.0081(1)	0.0138(1)	0.0080(1)	0.0001(1)	0.0013(1)	-0.0003(1)
Re(2)	4e	-0.06935(6)	0.20471(2)	-0.10254(2)	0.0085(2)	0.0136(2)	0.0080(1)	-0.0001(1)	0.0009(1)	-0.0013(1)
Re(3)	4e	-0.21537(5)	0.24074(2)	0.04452(2)	0.0079(2)	0.0140(1)	0.0081(1)	-0.0002(1)	0.0013(1)	-0.0003(1)
Re(4)	4e	0.14656(6)	0.29770(2)	0.10591(2)	0.0087(2)	0.0134(2)	0.0080(1)	-0.0002(1)	0.0009(1)	-0.0010(1)
Re(5)	4e	-0.04930(6)	0.33942(2)	-0.04705(2)	0.0094(2)	0.0126(1)	0.0089(1)	0.0004(1)	0.0011(1)	-0.0000(1)
Re(6)	4e	0.12653(6)	0.16315(2)	0.05037(2)	0.0093(2)	0.0127(1)	0.0093(1)	0.0005(1)	0.0009(1)	0.0001(1)
Br(1)	4e	-0.2149(2)	0.13191(5)	-0.24721(7)	0.0259(4)	0.0154(4)	0.0119(3)	0.0007(4)	-0.0039(3)	0.0002(4)
Br(2)	4e	0.2452(2)	0.04286(6)	0.11890(9)	0.0321(6)	0.0177(5)	0.0286(6)	0.0052(4)	0.0017(5)	0.0055(4)
Br(3)	4e	-0.1688(2)	0.45963(6)	-0.11596(8)	0.0305(6)	0.0186(5)	0.0258(6)	0.0061(4)	0.0015(4)	0.0056(4)
S(1)	4e	-0.0173(4)	0.2031(1)	0.1822(2)	0.014(1)	0.022(1)	0.0100(9)	-0.0009(8)	0.0016(8)	0.0024(8)
S(2)	4e	0.6249(4)	0.2810(1)	-0.1073(2)	0.010(1)	0.020(1)	0.0110(9)	0.0001(8)	0.0014(7)	-0.0009(8)
S(3)	4e	0.2947(4)	0.3838(1)	0.0118(2)	0.015(1)	0.016(1)	0.016(1)	-0.0028(8)	0.0020(8)	-0.0011(8)
S(4)	4e	0.0936(4)	0.2995(1)	-0.1790(2)	0.015(1)	0.020(1)	0.011(1)	-0.0010(8)	0.0018(8)	0.0018(8)
S(5)	4e	0.4525(4)	0.2217(1)	0.1104(2)	0.0090(9)	0.017(1)	0.0117(9)	0.0005(7)	0.0018(7)	-0.0001(8)
S(6)	4e	-0.1789(4)	0.3642(1)	0.0932(2)	0.013(1)	0.018(1)	0.014(1)	0.0011(8)	0.0030(8)	-0.0028(8)
S(7)	4e	0.2576(4)	0.1385(1)	-0.0895(2)	0.013(1)	0.019(1)	0.016(1)	0.0034(8)	0.0037(8)	-0.0035(8)
S(8)	4e	-0.2178(4)	0.1188(1)	-0.0083(2)	0.013(1)	0.018(1)	0.015(1)	-0.0020(8)	-0.0010(8)	-0.0019(8)
Cs(1)	4e	0.2135(2)	0.97960(6)	0.74809(9)	0.0406(5)	0.0414(5)	0.0661(7)	0.0038(4)	0.0149(4)	-0.0019(5)

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