

Crystal Chemistry of Octahedral Cluster Rhenium Chalcogenides $\text{Re}_6\text{X}_4\text{Y}_{10}$ ($\text{X} = \text{S}, \text{Se}, \text{Te}$; $\text{Y} = \text{Cl}, \text{Br}$)

SERGEY F. SOLODOVNIKOV, YURI V. MIRONOV, SPARTAK S. YAROVYOV,
ALEXANDER V. VIROVETS and VLADIMIR E. FEDOROV

*Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences,
Pr. Akademika Lavrentyeva 3, Novosibirsk 630090 (Russia)*

Abstract

X-ray structure analysis of hexanuclear rhenium selenium bromide $\text{Re}_6\text{Se}_4\text{Br}_{10}$ ($a = 9.230 \text{ \AA}$, $b = 9.310 \text{ \AA}$, $c = 12.975 \text{ \AA}$, $\alpha = 83.36^\circ$, $\beta = 84.10^\circ$, $\gamma = 82.33^\circ$, $Z = 2$, space group $P \bar{1}$, $R = 0.047$), which is a member of a series of isostructural molecular cluster compounds $\text{Re}_6\text{X}_4\text{Y}_{10}$ ($\text{X} = \text{S}, \text{Se}, \text{Te}$; $\text{Y} = \text{Cl}, \text{Br}$), and their comparative crystallochemical study has been performed. Distances $\text{Re}-\text{Re}$ and $\text{Re}-\text{Y}$ are found to be slightly increasing in the row $\text{S} \rightarrow \text{Se} \rightarrow \text{Te}$ simultaneously with decreasing electronegativity of chalcogen X . Compounds $\text{Re}_6\text{X}_4\text{Y}_{10}$ with distorted cubic close packing of isolated clusters $[\text{Re}_6(\mu_3\text{-X})_4(\mu_3\text{-Y})_4]\text{Y}_6$ may be considered as founders of phases $A_m[\text{Re}_6\text{X}_{4+n}\text{Y}_{4-n}]\text{Y}_6$ ($n = 0-3$, $m \leq n$, $A = \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{Tl}, \text{Ba}, \text{Pb}, \text{Ag}$, etc.) with preferable filling of octahedral holes by A-cations.

INTRODUCTION

For the last years a permanent interest in the chemistry of cluster rhenium(III) chalcogenides, which contain octahedral cluster fragment-core $[\text{Re}_6\text{Q}_8]$ where Q stands for chalcogenide or halide ions, has been shown [1–5]. The majority of known compounds of this group has been structurally characterized; however, the attention of investigators has been practically completely focused on rather stereochemical features of the clusters than their crystal chemistry. From this point of view it is of the greatest interest to reveal the series of structurally related compounds where crystallochemical regularities would be seen in relief. The most appropriate candidates for this role seem to be isostructural molecular cluster chalcogenides $\text{Re}_6\text{X}_4\text{Y}_{10}$ which, in turn, are the end members of the series $\text{Re}_6\text{X}_{4+n}\text{Y}_{10-2n}$ ($n = 0-4$) where n determines the extent of cluster condensation [1, 6–8]. Most of phases $\text{Re}_6\text{X}_4\text{Y}_{10}$, namely $\text{Re}_6\text{Se}_4\text{Cl}_{10}$ [9], $\text{Re}_6\text{Te}_4\text{Cl}_{10}$ [10] and $\text{Re}_6\text{Te}_4\text{Br}_{10}$ [11], have been synthesized and structurally studied for the first time by us. In order to con-

tinue these works we performed synthesis and X-ray structure investigation of $\text{Re}_6\text{Se}_4\text{Br}_{10}$ and also carried out a comparative crystallochemical study of the whole series of compounds $\text{Re}_6\text{X}_4\text{Y}_{10}$ with the purpose to reveal their structural peculiarities and relations with structures of other rhenium chalcogenides.

EXPERIMENTAL

Synthesis of $\text{Re}_6\text{Se}_4\text{Br}_{10}$

Single crystals of $\text{Re}_6\text{Se}_4\text{Br}_{10}$ were obtained from elements by the gas transport method in an evacuated silica tube at a temperature gradient of 800/850 °C. Dark red crystals suitable for X-ray structure analysis were selected from the cold zone of the tube.

X-ray structure analysis of $\text{Re}_6\text{Se}_4\text{Br}_{10}$

X-ray diffraction data for refinement of cell parameters and determination of crystal structure of $\text{Re}_6\text{Se}_4\text{Br}_{10}$ were collected using conventional technique on an automated diffracto-

TABLE 1
Crystallographic and X-ray structure analysis data for $\text{Re}_6\text{Se}_4\text{Br}_{10}$

Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell parameters:	
<i>a</i> , Å	9.230(2)
<i>b</i> , Å	9.310(1)
<i>c</i> , Å	12.975(1)
α, deg	83.36(1)
β, deg	84.10(1)
γ, deg	82.33(1)
Unit cell volume, (Å ³)/ <i>Z</i>	1093.3(3)/2
Calculated density, g/cm ³	6.781
μ(MoKα), cm ⁻¹	580.00
Crystal dimensions, mm	0.16 × 0.20 × 0.22
Range of θ, deg	1.59–27.47
Index ranges	0 ≤ <i>h</i> ≤ 11, -11 ≤ <i>k</i> ≤ 12, -16 ≤ <i>l</i> ≤ 16
Number of reflections used <i>n</i> [<i>I</i> > 2σ(<i>I</i>)]	4129
Number of refinement parameters <i>p</i>	182
$S = [\sum w[F_{\text{exp}}^2 - F_{\text{calc}}^2]^2 / (n - p)]^{1/2}$	0.786
$R(F) = \sum \ F_{\text{exp}} - F_{\text{calc}}\ / \sum F_{\text{exp}} $	0.0472
$wR(F^2) = [\sum w[(F_{\text{exp}}^2 - F_{\text{calc}}^2)^2 / \sum (w[F_{\text{exp}}^2]^2)]^{1/2}$	0.1118
Extinction coefficient	0.00109(6)
Residual extrema Δρ _{max} /Δρ _{min} , e ⁻ /Å ³	6.031/-4.685

meter CAD-4 “Enraf-Nonius” (λMoKα, graphite monochromator, ω/2θ-scan at a variable rate). Measured intensities of reflections were corrected for absorption using 4 curves of azimuthal scan. The structure was solved by direct

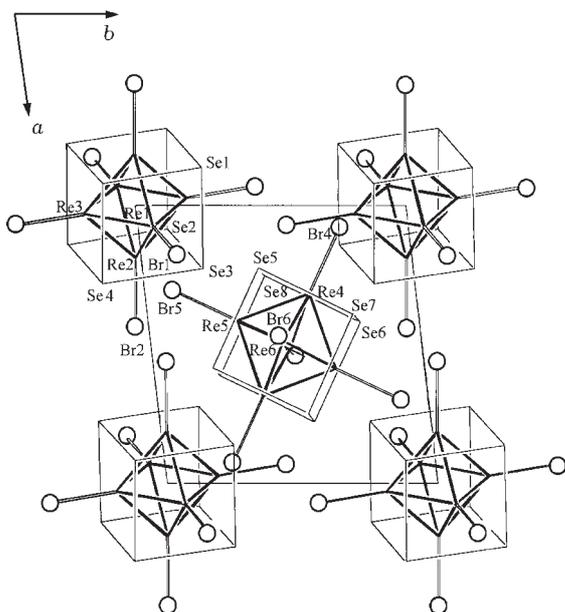


Fig. 1. Projection of the crystal structure of $\text{Re}_6\text{Se}_4\text{Br}_{10}$ along the *c*-axis.

methods with the SHELX-86 program [12] within the framework of space group $P\bar{1}$ and refined by full-matrix least-squares with the SHELX-97 package [13] first in isotropic approximation and then in anisotropic one. Some numerical characteristics of the X-ray structure experiment are given in Table 1, the refined coordinates of basic atoms and their equivalent isotropic thermal parameters are listed in Table 2, and selected interatomic distances are presented in Table 3.

RESULTS AND DISCUSSION

According to the data of X-ray structure analysis, $\text{Re}_6\text{Se}_4\text{Br}_{10}$ contains in its unit cell two independent centrosymmetrical isolated neutral clusters $[\text{Re}_6(\mu_3\text{-Se})_4(\mu_3\text{-Br})_4]\text{Br}_6$ (Fig. 1), for which owing to practical indistinguishability of atom scattering factors for Se and Br we assumed completely disordered distributions of them over $\mu_3\text{-Q}$ positions. As for other members of the series $\text{Re}_6\text{X}_4\text{Y}_{10}$, the data on irregularity of such a distribution were obtained only for $\text{Re}_6\text{Te}_4\text{Br}_{10}$ [11] where the tellurium content in

TABLE 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\times 10^3 \text{ \AA}^2$) in the crystal structure of $\text{Re}_6\text{Se}_4\text{Br}_{10}$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^*
Re(1)	736(1)	582(1)	1138(1)	8(1)
Re(2)	1874(1)	-204(1)	-676(1)	9(1)
Re(3)	286(1)	-1925(1)	575(1)	9(1)
Re(4)	3162(1)	6072(1)	4988(1)	9(1)
Re(5)	4150(1)	3295(1)	5077(1)	8(1)
Re(6)	4847(1)	4884(1)	6446(1)	9(1)
Q(1)**	-1390(4)	2624(4)	1209(3)	14(1)
Q(2)	0827(4)	1084(4)	-2314(3)	15(1)
Q(3)	2264(4)	2253(4)	-107(3)	14(1)
Q(4)	2803(4)	-1509(4)	999(3)	16(1)
Q(5)	2247(4)	4286(4)	6461(3)	16(1)
Q(6)	4182(4)	7818(3)	3532(3)	13(1)
Q(7)	3890(4)	7569(4)	6319(3)	15(1)
Q(8)	2533(4)	4484(4)	3672(3)	16(1)
Br(1)	1728(4)	1342(4)	2661(3)	25(1)
Br(2)	4412(4)	-495(4)	-1553(3)	25(1)
Br(3)	705(4)	-4511(4)	1354(3)	23(1)
Br(4)	703(4)	7512(4)	4935(4)	31(1)
Br(5)	3017(4)	999(4)	5189(3)	18(1)
Br(6)	4656(4)	4743(4)	8394(3)	26(1)

* U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

**Assumed Q = (Se + Br)/2.

TABLE 3

Selected interatomic distances in the crystal structure of $\text{Re}_6\text{Se}_4\text{Br}_{10}$, \AA

Re(1)—Re(2) ¹	2.618(2)	Re(4)—Re(5) ²	2.617(2)
Re(1)—Re(2)	2.619(2)	Re(4)—Re(5)	2.618(2)
Re(1)—Re(3) ¹	2.620(2)	Re(4)—Re(6) ²	2.622(2)
Re(1)—Re(3)	2.621(2)	Re(4)—Re(6)	2.623(2)
Re(2)—Re(3) ¹	2.621(2)	Re(5)—Re(6)	2.618(2)
Re(2)—Re(3)	2.624(2)	Re(5)—Re(6) ²	2.627(2)
Re(1)—Q(2) ¹	2.533(4)	Re(4)—Q(7)	2.534(4)
Re(1)—Q(1)	2.545(4)	Re(4)—Q(6)	2.536(4)
Re(1)—Q(4)	2.546(4)	Re(4)—Q(5)	2.537(4)
Re(1)—Q(3)	2.560(4)	Re(4)—Q(8)	2.541(4)
Re(2)—Q(2)	2.532(4)	Re(5)—Q(6) ²	2.533(4)
Re(2)—Q(4)	2.536(4)	Re(5)—Q(8)	2.536(4)
Re(2)—Q(1) ¹	2.539(4)	Re(5)—Q(5)	2.542(4)
Re(2)—Q(3)	2.564(4)	Re(5)—Q(7) ²	2.545(4)
Re(3)—Q(4)	2.530(4)	Re(6)—Q(7)	2.530(4)
Re(3)—Q(2) ¹	2.545(4)	Re(6)—Q(5)	2.533(4)
Re(3)—Q(1) ¹	2.550(4)	Re(6)—Q(8) ²	2.550(4)
Re(3)—Q(3) ¹	2.556(4)	Re(6)—Q(6) ²	2.553(4)
Re(1)—Br(1)	2.473(3)	Re(4)—Br(4)	2.480(4)
Re(2)—Br(2)	2.492(4)	Re(5)—Br(5)	2.486(3)
Re(3)—Br(3)	2.497(4)	Re(6)—Br(6)	2.506(4)

¹, ²Symmetry operations: $-x, -y, -z$ and $-x+1, -y+1, -z+1$, respectively.

TABLE 4
Some crystal structure data for $\text{Re}_6\text{X}_4\text{Y}_{10}$ (X = S, Se, Te; Y = Cl, Br)

Compound	<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	α , deg	β , deg	γ , deg	Bond length, Å		<i>R</i>	Reference
							Re—Re	Re—Y		
$\text{Re}_6\text{S}_4\text{Cl}_{10}$	8.842	8.910	12.441	83.68	84.21	82.39	2.592–2.599 (2.595)	2.301–2.330 (2.319)	0.034	[15]
$\text{Re}_6\text{Se}_4\text{Cl}_{10}$	8.829	8.928	12.591	83.30	84.59	82.10	2.599–2.613 (2.206)	2.31–2.34 (2.32)	0.084	[9]
$\text{Re}_6\text{Te}_4\text{Cl}_{10}$	9.004	9.000	12.963	85.25	85.55	82.45	2.618–2.638 (2.629)	2.325–2.353 (2.339)	0.048	[10]
$\text{Re}_6\text{S}_4\text{Br}_{10}$ *	9.189	9.265	12.822	82.92	84.20	82.76	–	–	–	[16]
$\text{Re}_6\text{Se}_4\text{Br}_{10}$	9.230	9.310	12.975	83.36	84.10	82.33	2.617–2.627 (2.621)	2.473–2.506 (2.489)	0.047	Our data
$\text{Re}_6\text{Te}_4\text{Br}_{10}$	9.347	9.403	13.348	84.46	84.64	82.11	2.636–2.649 (2.643)	2.496–2.528 (2.512)	0.038	[11]

Note. In parentheses the mean values are given.

*Structure is not known.

μ_3 -positions varies within 32–64 %. The both independent clusters have about the same geometrical characteristics: mean values of bond lengths of Re—Re, Re—Q and Re—Br for them are 2.621 and 2.621; 2.537 and 2.539; 2.487 and 2.491 Å, respectively. The cluster packing in the structure is typical for molecular crystals, the shortest intercluster contacts Q...Q and Q...Br are 3.535–3.669 Å though these magnitudes are 0.4 Å smaller than sums of corresponding van der Waals radii and should be rightfully referred to the number of shortened ones [14].

Comparison of metrical characteristics of clusters $\text{Re}_6\text{X}_4\text{Y}_{10}$ without taking into account “statistical” distances Re—Q (Table 4) shows that on rising the atom number of X a slight increase of the Re—Re and Re—Y bonds length occurs that may be connected with a progressive transfer of electron density to antibonding molecular orbitals of a cluster with decreasing chalcogen electronegativity. It is obvious that to confirm this assumption will be possible only on the basis of appropriate quantum-chemical calculations.

TABLE 5
Crystallographic data for octahedral cluster rhenium chalcogenides with f. c. c. motifs of cluster arrangement

Compound, space group, Z, reference	<i>a</i> , <i>b</i> , <i>c</i> , Å	α , β , γ , deg	Transition matrix to f. c. c. array	<i>a</i> , <i>b</i> , <i>c</i> , Å	α , β , γ , deg	Cation arrangement
$\text{Re}_6\text{Se}_4\text{Br}_{10}$ <i>P</i> $\bar{1}$, 2 (our data)	9.230	83.36	1 1 0	13.957	89.40	No cations
	9.310	84.10	1 -1 0	12.204	98.34	
	12.975	82.33	0 0 -1	12.975	90.50	
$\text{Re}_6\text{Se}_6\text{Cl}_6$ <i>Cmca</i> , 2 [8]	13.892	90	1 0 0	13.892	90	No cations, cluster connection <i>via</i> 4 μ_2 -Cl
	11.286	90	0 1 0	11.286	90	
	11.310	90	0 0 1	11.310	90	
$\text{Re}_6\text{Te}_{15}$ <i>Pbca</i> , 4 [17]	13.003	90	1 0 0	13.003	90	μ_4 -Te in all O-holes
	12.935	90	0 1 0	12.935	90	
	14.212	90	0 0 1	14.212	90	
$\text{KRe}_6\text{Se}_5\text{Cl}_9$ <i>Pn</i> $\bar{3}$, 4 [18]	13.034	90	1 0 0	13.034	90	K atoms in all O-holes
	13.034	90	0 1 0	13.034	90	
	13.034	90	0 0 1	13.034	90	
$\text{KRe}_6\text{S}_5\text{Br}_9$ <i>C2/c</i> , 4 [19]	16.914	90	0 -1 0.5	12.992	94.15	The same
	9.526	127.41	1 0 0.5	13.512	94.21	
	17.671	90	0 1 0.5	12.992	94.15	
$\text{KRe}_6\text{Se}_5\text{Cl}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$ <i>R</i> $\bar{3}$, 1 [7]	8.9534	65.672	-1 1 1	13.208	94.64	K atoms in all O-holes, 1/2H ₂ O in all T-holes
	8.9534	65.672	1 -1 1	13.208	94.64	
	8.9534	65.672	1 1 -1	13.208	94.64	
$\text{Rb}_{2.5}\text{Re}_6\text{S}_{6.5}\text{Cl}_{7.5}$ <i>Pn</i> $\bar{3}$, 4 [15]*	13.342	90	1 0 0	13.342	90	Rb atoms in O- and T-holes?
	13.342	90	0 1 0	13.342	90	
	13.342	90	0 0 1	13.342	90	

*Complete structure data in the paper are absent.

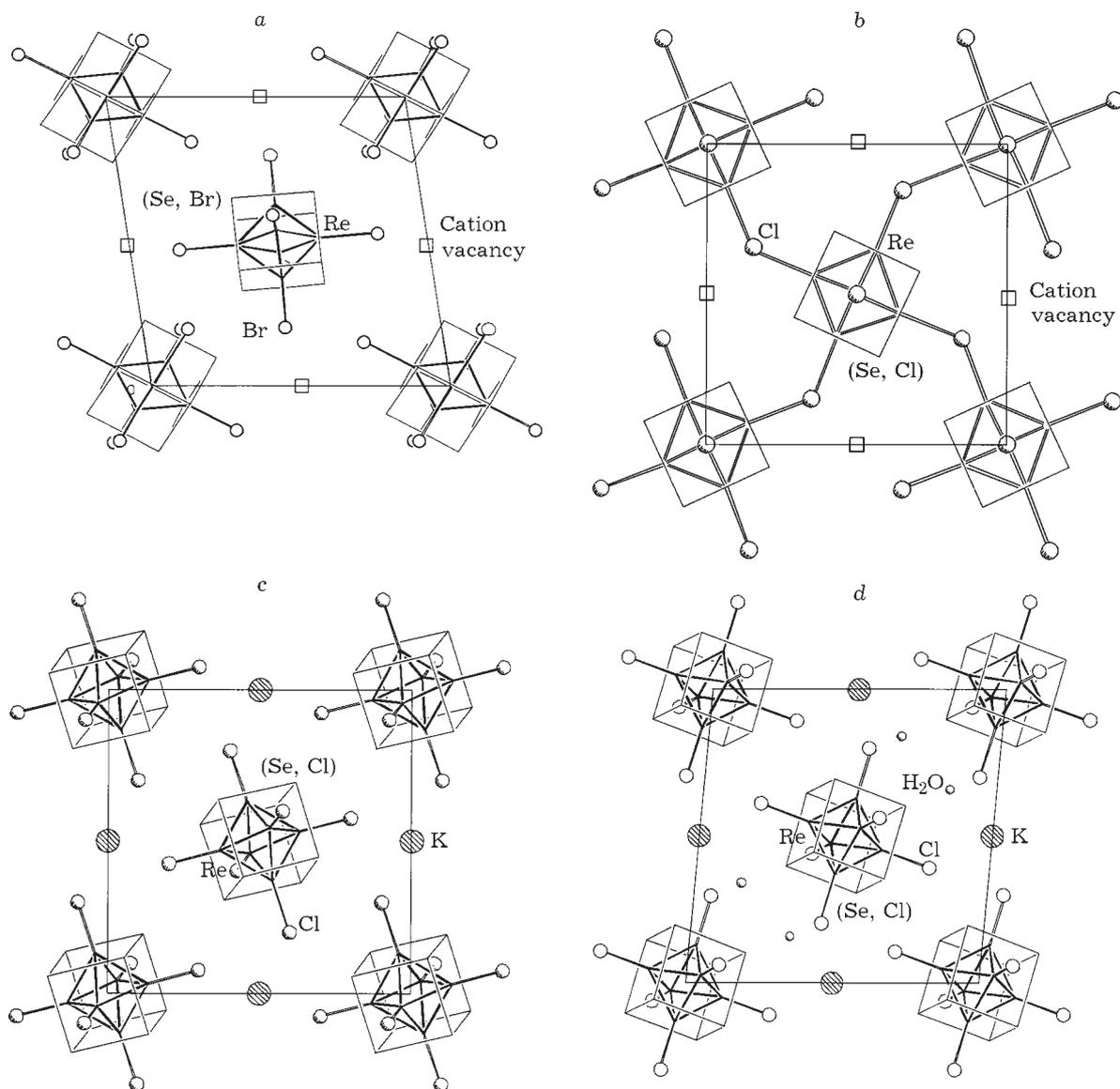


Fig. 2. Projections of the fragments of rhenium(III) chalcocyanide structures with f.c.c. motifs in comparable settings: *a* - $\text{Re}_6\text{Se}_4\text{Br}_{10}$ along the *c*-axis, *b* - $\text{Re}_6\text{Se}_6\text{Cl}_6$ along the *a*-axis, *c* - $\text{KRe}_6\text{Se}_5\text{Cl}_9$ along the *c*-axis, *d* - $\text{KRe}_6\text{Se}_5\text{Cl}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$ along [111]; on the projections the outlines of comparable unit cells are shown (see Table 5), projecting directions are given respecting original settings.

More definite conclusions follow from considerations of mutual arrangement of $\text{Re}_6\text{X}_4\text{Y}_{10}$ clusters, their centres repeating a distorted cubic close packing (face-centered cubic - f. c. c.) motif. Most likely, the distortion seems to be caused by requirements of the closest contacts of adjacent clusters resulting in their mutual turn and a compression of ideal f. c. c. packing approximately in a twofold axis direction. Since a close-packed motif of the structure does not allow simultaneous arrangement of cations and anions over its nodes, an ionic character of compounds $\text{Re}_6\text{X}_4\text{Y}_{10} = \{[\text{Re}_6\text{X}_{4-\delta}\text{Y}_{4+\delta}]Y_6\}^{\delta+}$

$\{[\text{Re}_6\text{X}_{4+\delta}\text{Y}_{4-\delta}]Y_6\}^{\delta-}$ suggested in [11] is hardly probable.

Molecular close-packed rhenium chalcocyanides $\text{Re}_6\text{X}_4\text{Y}_{10}$ may be considered as founders of a series of compounds $A_m[\text{Re}_6\text{X}_{4+n}\text{Y}_{4-n}]Y_6$ ($n = 0-3$, $m \leq n$, $A = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cu}, \text{Ag}, \text{Cd}, \text{Pb}, \text{Eu}, \text{etc.}$) [6-8, 17-19] and related phases with approximately f. c. c. arrangement of cluster fragments $[\text{Re}_6\text{Q}_8]$ (Table 5). As in $\text{Re}_6\text{Se}_4\text{Br}_{10}$ (Fig. 2, *a*), in $\text{Re}_6\text{Se}_6\text{Cl}_6$ [6, 8] additional cations *A* absent, however in the last compound cluster cores $[\text{Re}_6\text{Se}_6\text{Cl}_2]$ are connected with each other through Cl bridges forming layers (see Fig. 2, *b*). In the crystal

structures of $\text{Re}_6\text{Te}_{15} = \{[\text{Re}_6\text{Te}_8]\text{Te}_6\}\text{Te}$ [17], $\text{KRe}_6\text{Se}_5\text{Cl}_9$ [18], $\text{KRe}_6\text{S}_5\text{Br}_9$ [19], where A-cations fill all octahedral holes (O-holes) of f. c. c. packing, a NaCl-like motif is clearly seen (see Fig. 2, c). A more complicated structure is realized in $\text{KRe}_6\text{Se}_5\text{Cl}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$ [7] where K^+ ions fill O-holes and water molecules (s.o.f. = 0.5) occupy all tetrahedral holes (T-holes) (see Fig. 2, d). Perhaps, in the case of $\text{Rb}_{2.5}\text{Re}_6\text{S}_{6.5}\text{Cl}_{7.5}$ [15] we also encountered simultaneous filling of O- and T-holes by Rb atoms.

There is no doubt that a number of examples with the f. c. c. packing motif of the cluster cores $[\text{Re}_6\text{Q}_8]$ arrangement may be expanded if the matter is not restricted to rhenium(III) chalcogenides. In any case, we can call immediately several cluster Mo(II) halides – MoCl_2 [20] and $\text{HgMo}_6\text{Cl}_{14}$ [21] with its analogs [22] isostructural to $\text{Re}_6\text{Se}_6\text{Cl}_6$ and $\text{KRe}_6\text{Se}_5\text{Cl}_9$, respectively. Even from here we can see that a series of related cluster compounds with the f. c. c. packing motif will be rather expansive that in principle gives wide prospects for a chemical design of such phases. In this case, however, we should take into account also crystallochemical restrictions of their possible existence: the total amount of A-cations cannot exceed 3 per cluster core and their maximum sizes are determined by dimensions of O-holes which possibly cannot accept a cation larger than Rb^+ .

REFERENCES

- 1 V. E. Fedorov, A. V. Mishchenko and V. P. Fedin, *Uspekhi khimii*, 54 (1985) 694.
- 2 A. Perrin and M. Sergent, *New J. Chem.*, 12 (1988) 337.
- 3 S. Uriel, K. Boubekeur, P. Batail *et al.*, *Inorg. Chem.*, 34 (1995) 5307.
- 4 J. R. Long, A. S. Williamson and R. H. Holm, *Angew. Chem. (Int. Ed. Engl.)*, 34 (1995) 226.
- 5 J. R. Long, L. S. McCarty and R. H. Holm, *J. Amer. Chem. Soc.*, 118 (1996) 4603.
- 6 L. Leduc, A. Perrin and M. Sergent, *Compt. rend. Acad. Sci. Paris, Ser. II*, 296 (1983) 961.
- 7 A. Perrin, *New J. Chem.*, 14 (1990) 561.
- 8 A. Perrin, L. Leduc and M. Sergent, *Eur. J. Solid State Inorg. Chem.*, 28 (1991) 919.
- 9 V. E. Fedorov, A. V. Mishchenko, B. A. Kolesov *et al.*, *Koordinatsionnaya khimiya*, 11 (1985) 1701.
- 10 Yu. V. Mironov, J. A. Cody and J. A. Ibers, *Acta crystallogr.*, C52 (1996) 281.
- 11 S. S. Yarovoi, Yu. I. Mironov, Yu. V. Mironov *et al.*, *Mater. Res Bull.*, 32 (1997) 1271.
- 12 G. M. Sheldrick, *Acta crystallogr.*, A46, Suppl. (1990) 467.
- 13 G. M. Sheldrick, SHELX-97, Release 97-2, University of Goettingen, 1997.
- 14 Yu. V. Zefirov, *Kristallografiya*, 42 (1997) 936.
- 15 J.-C. Gabriel, K. Boubekeur and P. Batail, *Inorg. Chem.*, 32 (1993) 2894.
- 16 L. Leduc, A. Perrin, M. Sergent *et al.*, *Mater. Lett.*, 3 (1985) 209.
- 17 K. Klaiber, W. Petter and F. Hulliger, *J. Solid State Chem.*, 46 (1983) 112.
- 18 A. Perrin, L. Leduc, M. Potel and M. Sergent, *Mater. Res. Bull.*, 25 (1990) 1227.
- 19 A. Slougui, A. Perrin and M. Sergent, *Acta crystallogr.*, C48 (1992) 1917.
- 20 H. Schaefer, H. G. von Schnering, J. Tillack *et al.*, *Z. anorg. allg. Chem.*, 353 (1967) 281.
- 21 H. G. von Schnering, *Ibid.*, 385 (1967) 75.
- 22 M. Potel, C. Perrin, A. Perrin and M. Sergent, *Mater. Res. Bull.*, 21 (1988) 1239.