Inertness of the $[Re_6Se_5Cl_3]^{5+}$ cluster core to substitution by OH^- in organic solutions: synthesis, structural and liquid secondary ion mass spectroscopy characterization of $K(H_2O)_2[Re_6Se_5Cl_9]$ and $(n\text{-}Bu_4N)[Re_6Se_5Cl_9]$ and the crystal structure of $(n\text{-}Bu_4N)_2[Re_6Se_6Cl_8]$

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When ethanol solutions of $K[Re_6Se_5Cl_9]$ are allowed to crystallize, the compound formulated $K(H_2O)_2[Re_6Se_5Cl_9]$ (**1**) is obtained. Extensive characterization, which includes chemical analysis, X-ray structure determination and liquid secondary ion mass spectrometry (LSIMS), supports this formulation, which differs from that proposed earlier, $K[Re_6Se_5(OH)_2Cl_7] \cdot H_2O$. This conclusively demonstrates that no substitution of an inner μ-core halogen by OH^- occurs within the cluster core. This is discussed and shown to be fully consistent with the present well-documented chemistry, which requires that substitutions of halogen by divalent elements only are allowed. The paper is complemented by the crystal structures of $(n\text{-}Bu_4N)[Re_6Se_5Cl_9]$ and $(n\text{-}Bu_4N)_2[Re_6Se_6Cl_8]$, which had not yet been properly reported.

Alkali metal salts of chalcohalide hexanuclear rhenium cluster monoanions, $K[Re_6Se^i_5Cl^i_3(Cl^a_6)]$ (where i stands for an inner μ_3-ligand capping a face of the Re_6 octahedron and a for an apical terminal ligand linked to a single rhenium atom), isostructural and isoelectronic with the Chevrel–Sergent cluster cores, $[Mo_6Q_8]^{4-}$, have been shown to be soluble in alcohol where cation exchange with organic cations proceeds readily.[1] There has been a strong research effort[2–6] aimed at developing the organic solution chemistry of molecular forms of such mineral clusters, also isostructural and isoelectronic with the molybdenum halides MoX_2 ($X = Cl, Br, I$).[7,8] One remarkable facet of this chemistry is the propensity of the alkylammonium salts of the cluster *monoanions*, $(n\text{-}Bu_4N)[Re_6Q^i_5Cl^i_3(Cl^a_6)]$, to undergo substitution of one inner μ-Cl^- ligand by divalent elements, a process that proved to be particularly efficient and versatile upon reaction with silylated reagents such as $[(CH_3)_3Si]_2E$ ($E = O, S, Se, Te$)[4] and $[(CH_3)_3Si]_2NR$.[9] A major driving force for this substitution reaction, occurring right within the inner cluster core ligand shell, is the formation of the thermodynamically more stable alkylammonium cluster *dianion* salts, for example $(n\text{-}Bu_4N)_2[Re_6Q^i_5(\mu\text{-}E)Cl^i_2(Cl^a_6)]$, and their subsequent, ready precipitation out of the organic solution.

In this context, the reports by Perrin *et al.*[10] of the structure of a compound formulated to be $K[Re_6Se_5(OH)_2Cl_7] \cdot H_2O$, on the basis of the crystal structure determination (trigonal, space group $R\bar{3}$, $a = 8.9354(9)$ Å, $\alpha = 65.672(8)°$, $U = 566.56$ Å^3), continue to intrigue since this tends to suggest that two inner chloride ligands would have been substituted by OH^- upon crystallization of $K[Re_6Se_5Cl_9]$ in ethanol, which contradicts the presently well-documented substitution chemistry. In addition, it would remain the sole example of an inner μ_3-ligand substitution that would leave the net cluster charge intact, an issue that would provide additional perspective on the reactivity of these chalcohalide clusters in solution. This paper reports our investigations of the reactivity of the cluster monoanion forms and demonstrates the inertness of Re_6 cluster monoanions towards substitution of one inner μ_3-Cl^- by μ_3-$(OH)^-$ or μ_3-SCH_3 in organic solutions. Thus, no substitution of an inner chloride ligand by monovalent elements occurs within the cluster monoanion core. Hence, the proper formulation for the reaction product $K[Re_6Se_5Cl_9] \cdot 2H_2O$ (**1**), is supported by the present reinvestigation of its crystal structure, on the one hand, and both consistent chemical analysis data and liquid secondary ion mass spectrometry characterization of the intact cluster core, on the other hand. In addition, this contribution is complemented by the crystal structures of $(n\text{-}Bu_4N)[Re_6Se_5Cl_9]$ (**2**) and $(n\text{-}Bu_4N)_2[Re_6Se_6Cl_8]$ (**3**), which have yet to be properly reported after recent discussions of their direct or indirect synthesis in organic solution by means of excision, thermal treatment, metathesis or solution reactions.[2–4]

Experimental

$K[Re_6Se_5Cl_9]$[2,11] and $Ca[Re_6Se_6Cl_8]$[12] are prepared from $ReCl_5$, Re, Se and KCl or anhydrous $CaCl_2$ under solid-state high temperature conditions, as described previously. $(n\text{-}Bu_4N)[Re_6Se_5Cl_9]$ was obtained by metathesis in ethanol from $K[Re_6Se_5Cl_9]$ as described previously[13] and $(n\text{-}Bu_4N)_2[Re_6Se_6Cl_8]$ by metathesis from ethanol solutions of $Ca[Re_6Se_6Cl_8]$.

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$K(H_2O)_2[Re_6Se_5Cl_9]$, 1

Pristine $K[Re_6Se_5Cl_9]$ (100 mg) was dissolved in ethanol (100 mL) at room temperature. The solution was filtered off to eliminate a black residue and reduced to *ca.* 15 mL. Good X-ray quality rhombohedral red single crystals were readily obtained by slow evaporation of the solvent. Anal. calc. for $K(H_2O)_2[Re_6Se_5Cl_9]$ (found): K 2.05 (1.93); Re 58.61 (58.55); Se 20.71 (20.80); Cl 16.74 (16.24)%.

Liquid secondary ion mass spectrometry

The compounds were analyzed by using liquid secondary ion mass spectrometry (LSIMS). Negative LSIM spectra were recorded on a VG-Autospec (VG Analytical, Manchester, UK) high resolution trisector EBE mass spectrometer. Ions were produced by a 30 keV primary beam of caesium ions, extracted and accelerated by a 8 kV potential. Samples were dissolved in acetonitrile and mixed with the *m*-nitrobenzyl alcohol matrix on the target. Scans were obtained in the 3000–300 mass range at *ca.* 1500 resolving power (measured as peak width at 5% height) and at a scan rate of 10 s decade^{-1}. Mass calibration was achieved with the use of reference spectra of caesium iodide and a maximum error of 0.3 mass unit was obtained. Data processing was achieved using the VG-OPUS v2.1 software. Spectra reported are the average of at least 10 scans. The calculated isotopic ion distributions are based on the following natural isotopic abundances: ^{185}Re: 37.40, ^{187}Re: 62.60, ^{35}Cl: 75.77, ^{37}Cl: 24.23, ^{74}Se: 0.90, ^{76}Se: 9.00, ^{77}Se: 7.60, ^{78}Se: 23.50, ^{80}Se: 49.60, ^{82}Se: 9.40%.

X-Ray crystallography

Crystallographic data for compounds **1**, **2** and **3** are given in Table 1. In each case a suitable single crystal was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed on a κ-axis Enraf–Nonius CAD4-F diffractometer using graphite monochromated Mo-Kα radiation. Unit cell dimensions and the crystal orientation matrix were derived from least-squares refinement of setting angles of 25 reflections. Intensity data were collected using the $\omega - 2\theta$ scan mode. Data were corrected for background, Lorentz, polarization and absorption effects. The structures were solved by direct methods and refined by full-matrix least-squares calculations, initially with isotropic and finally with anisotropic thermal parameters for non H-atoms. The atomic scattering factors and anomalous dispersion corrections were from the *International Tables for X-ray Crystallography*. All calculations were performed by using the Enraf–Nonius SDP/PLUS[14] and XTAL3.2[15] suites of programs.

CCDC reference number 146272–146274. See http://www.rsc.org/suppdata/nj/b0/b005231k/ for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis and reactions

When ethanol solutions of $K[Re_6Se_5Cl_9]$ are allowed to crystallize, the new compound, formulated as $K(H_2O)_2[Re_6Se_5Cl_9]$, **1**, is obtained instead of $K[Re_6Se_5(OH)_2Cl_7] \cdot H_2O$.[10] This result, ascertained by elemental analysis, demonstrates that the monoanionic cluster core, $[Re_6Se_5Cl_9]^-$, has remained intact in ethanol. This is further demonstrated by LSIMS experiments and by the single crystal X-ray structure determination. Furthermore, when metathesis in an alcoholic solution of **1** is performed in the presence of (n-Bu$_4$N)X (where X = Cl$^-$, SCN$^-$, *etc.*), red–orange crystalline precipitates are obtained and recrystallized from acetonitrile to give (n-Bu$_4$N)[Re$_6$Se$_5$Cl$_9$], **2**, regardless of the nature of X, as unequivocally demonstrated by elemental, LSIMS and single crystal X-ray structure analysis. All these experiments indicate that, in contradiction to the previous reports, no inner μ_3-chloride ligand exchange by monoanionic ligands like OH$^-$ is observed within the cluster core $[Re_6Se_5Cl_9]^-$.

Crystal structures

Six chlorine atoms and the oxygen atoms of the two water molecules contribute to the inner first-coordination sphere of the eight-coordinated potassium cation in $K(H_2O)_2[Re_6Se_5Cl_9]$, **1**. It is now well-established that modifications of both the nature and proportion of the set of eight inner μ_3-ligands within the hexanuclear rhenium cluster core induce significant changes in the geometry of the cluster.[3,4,16] For the μ_3-sulfido-μ_3-chloro monoanions, the substitution of one μ_3-chlorine atom by a group with a μ_3-heteroelement of the second period (μ_3-oxo[4] or μ_3-imido[9]), leads to dianionic species that experience a significant contraction of the single Re$_3$ face capped by the μ_3-heteroelement. Thus, in (n-Bu$_4$N)$_2$[Re$_6$S$_5$OCl$_8$], the Re–Re distances within the Re$_3$ face

Table 1 Crystallographic data for $K[Re_6Se_5Cl_9] \cdot 2H_2O$, **1**, ($n$-Bu$_4$N)[Re$_6Se_5Cl_9$], **2**, and ($n$-Bu$_4$N)$_2$[Re$_6Se_6Cl_8$], **3**

	1	2	3
Formula	$H_4Cl_9O_2Re_6Se_5$	$C_{16}H_{36}Cl_8NRe_6Se_5$	$C_{32}H_{72}Cl_8N_2Re_6Se_6$
Formula weight	1906.18	2073.55	2359.48
T/K	293	293	293
Crystal system	Trigonal	Triclinic	Monoclinic
Space group	$R\bar{3}$	$P\bar{1}$	$P2_1/n$
a/Å	8.892(1)	10.775(2)	12.833(3)
b/Å		17.101(4)	11.588(2)
c/Å		10.602(2)	18.563(4)
α/°	65.63(2)	100.83(2)	
β/°		99.61(2)	90.04(3)
γ/°		87.51(2)	
U/Å^3	557.92(26)	1891.6(7)	2760.3(10)
Z	1	2	2
μ/mm^{-1}	41.828	24.58	17.472
No meas. reflect.	2791	6715	4605
No indep. reflect.	904	3946	2657
R_{int}	0.026	0.017	0.024
R^a	0.038	0.030	0.053
$R_w{}^b$	0.078	0.035	0.061

^{a} $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o^2|]^{1/2}$; $w = [\sigma^2(I) + (pF_o^2)^2]^{-1}$; $p = 0.04$.

Table 2 Room temperature unit cell parameters for **2**, **3** and their sulfido analogs

Compound	a/Å	b/Å	c/Å	α/°	β/°	γ/°	U/Å^3
$(n\text{-Bu}_4\text{N})\text{Re}_6\text{Se}_5\text{Cl}_9$, **2**	10.775(2)	17.101(4)	10.602(2)	100.83(2)	99.61(2)	87.51(2)	1892(1)
$(n\text{-Bu}_4\text{N})\text{Re}_6\text{S}_5\text{Cl}_9$ [3]	17.147(4)	9.792(3)	22.294(5)	—	—	—	3743(3)
$(n\text{-Bu}_4\text{N})_2\text{Re}_6\text{Se}_6\text{Cl}_8$, **3**	12.833(3)	11.588(2)	18.563(4)	—	90.04(3)	—	2760(1)
$(n\text{-Bu}_4\text{N})_2\text{Re}_6\text{S}_6\text{Cl}_8$ [3]	12.444(6)	11.820(7)	18.492(4)	—	90.44(3)	—	2719(2)

capped by the μ_3-oxo ligand [2.516(1)–2.531(1) Å] are shorter than those for the remaining Re_3 faces capped by the μ_3-chloro and μ_3-sulfido ligands [2.573(1)–2.601(1) Å].[4] Shortening of the Re–Re distances of the face capped by the μ_3-imido ligand [2.562(1)–2.568(1) Å] when compared to the other Re_3 faces [2.582(1)–2.592(1) Å] is also observed in $(n\text{-Bu}_4\text{N})_2[\text{Re}_6\text{S}_5(\text{NMe})\text{Cl}_8]$,[9] although the bond length discrepancy is somewhat smaller because the μ_3-NMe ligand is disordered on two opposite cluster faces. The same observation has been made by Holm *et al.* for the μ_3-seleno-μ_3-chloro anions substituted by μ_3-oxo ligands.[2] The Re–Re distances of the μ_3-oxo ligand capped Re_3 faces are shorter [2.532(1)–2.537(1) and 2.516(2)–2.535(3) Å] than the Re–Re distances of the μ_3-chloro and μ_3-seleno ligand capped Re_3 faces [2.592(2)–2.601(2) and 2.608(2)–2.614(2) Å] in α-$(n\text{-Pr}_4\text{N})_2[\text{Re}_6\text{Se}_4\text{O}_2\text{Cl}_8]\cdot 2\text{DMF}$ and β-$(n\text{-Pr}_4\text{N})_2[\text{Re}_6\text{Se}_4\text{O}_2\text{Cl}_8]$, respectively.[2] A similar cluster core distortion was observed recently in $(n\text{-Bu}_4\text{N})_4[\text{Re}_6\text{S}_5\text{OCl}_7]_2\text{O}$, a structure that contains two μ_3-oxo face-capping ligands, the averaged Re–Re distance within these cluster faces being 2.530(6) Å.[17] No such distortion is found in the cluster core structure of **1** and the observed bond distances [2.602(1)–2.607(1) Å] are similar to those determined for the starting and ending compounds, $\text{K}[\text{Re}_6\text{Se}_5\text{Cl}_9]$ [2.608(1) Å][11] and $(n\text{-Bu}_4\text{N})[\text{Re}_6\text{Se}_5\text{Cl}_9]$, **2** [2.605(1)–2.611(1) Å], respectively. Note also that the refinements of the inner positions proceed smoothly, considering statistical occupancies [(5Se + 3Cl)/8] for each independent position. In particular, there was no evidence for additional electron density, which would have required the introduction of a contribution from an additional oxygen atom (for the hydroxy groups) to improve the results of the structure determination. Finally, the Re–Cl^a distances in **1** [2.376(2) to 2.381(2) Å] are identical to those for the series of such rhenium cluster monoanions with a given core chalcogen, equal to 2.373(6) Å for $\text{K}[\text{Re}_6\text{Se}_5\text{Cl}_9]$[11] and ranging from 2.345(5) to 2.355(6) Å for $(n\text{-Bu}_4\text{N})[\text{Re}_6\text{Se}_5\text{Cl}_9]$, **2**. Thus, the structural data are all consistent with the formulation and rule out any core halogen substitution by OH^-.

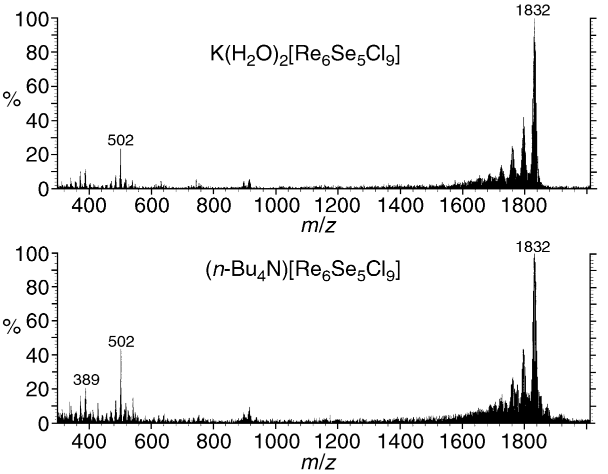

Fig. 1 Negative LSIMS for $\text{K}(\text{H}_2\text{O})_2[\text{Re}_6\text{Se}_5\text{Cl}_9]$, **1** and $(n\text{-Bu}_4\text{N})[\text{Re}_6\text{Se}_5\text{Cl}_9]$, **2**. Peak assignment is given in Table 3.

Table 3 Peaks in the negative ion LSIMS of **2** and **3**

Assignment	m/z^a (rel. int. (%))
$[\text{Re}_6\text{Se}_5\text{Cl}_9]^-$	1832.0(100)
$[\text{Re}_6\text{Se}_5\text{Cl}_8]^-$	1797.1(37)
$[\text{Re}_6\text{Se}_5\text{Cl}_7]^-$	1762.1(19)
$[\text{Re}_6\text{Se}_5\text{Cl}_6]^-$	1725.1(8)
	502, 389

[a] m/z value of the most abundant ion in the isotopic distribution. Peaks above m/z = 300 and greater than 2% are included.

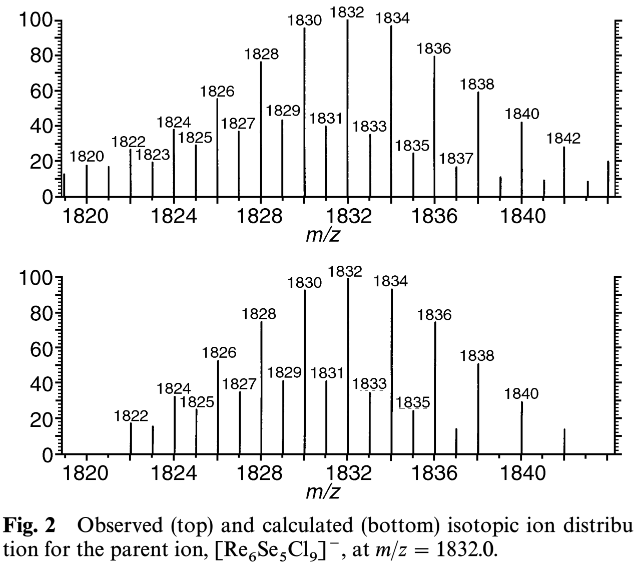

Fig. 2 Observed (top) and calculated (bottom) isotopic ion distribution for the parent ion, $[\text{Re}_6\text{Se}_5\text{Cl}_9]^-$, at m/z = 1832.0.

$(n\text{-Bu}_4\text{N})[\text{Re}_6\text{Se}_5\text{Cl}_9]$ is not isostructural to $(n\text{-Bu}_4\text{N})[\text{Re}_6\text{S}_5\text{Cl}_9]$ (Table 2). This is in stark contrast with the $(n\text{-Bu}_4\text{N})_2[\text{Re}_6\text{Q}_5\text{ECl}_8]$ (Q = S, E = Se and Q = Se, E = S, Te) series in which typically identical space group, unit cell and atomic parameters are consistently observed, with the sole difference being $(n\text{-Bu}_4\text{N})_2[\text{Re}_6\text{S}_5\text{OCl}_8]$, for which the μ_3-oxygen atom is neatly localized onto one single lattice position.[4]

In contrast, $(n\text{-Bu}_4\text{N})_2[\text{Re}_6\text{Se}_6\text{Cl}_8]$, **3**, is indeed isostructural to $(n\text{-Bu}_4\text{N})_2[\text{Re}_6\text{S}_6\text{Cl}_8]$ (Table 2) and to the series of heterosubstituted cluster dianions, $(n\text{-Bu}_4\text{N})_2[\text{Re}_6\text{Q}_5\text{ECl}_8]$ (Q = S, E = Se and Q = Se, E = S, Te) as well.[3,4,16] The present structure of $(n\text{-Bu}_4\text{N})_2[\text{Re}_6\text{Se}_6\text{Cl}_8]$ [monoclinic, $P2_1/n$, U = 2760.3 Å^3] is in turn identical to the structure determined earlier on crystals obtained by thermal reaction in water[18] but differs, however, from that reported by Holm *et al.*[2] [tetragonal, $I4/mmm$, U = 2849.2(8) Å^3]. The larger cell volume observed in the latter phase may reflect the presence of additional solvent molecules.

Mass spectrometry

LSIMS has been successfully used to characterize molybdenum halide cluster anions[19] and proved to be a powerful tool to characterize many, and eventually heterosubstituted, rhenium chalcohalide cluster anions.[4,9,12] As shown in Fig. 1, the negative LSIMS of $\text{K}(\text{H}_2\text{O})_2[\text{Re}_6\text{Se}_5\text{Cl}_9]$, **1** and $(n\text{-Bu}_4\text{N})[\text{Re}_6\text{Se}_5\text{Cl}_9]$, **2** are identical and both exhibit the same characteristics, with the highest mass peak corresponding to the monoanion $[Re_6Se_5Cl_9]^-$ ($m/z = 1832$). Mass peaks of lower intensities are due to loss of chlorine atoms (see Table 3). The experimental and calculated isotopic distributions for $[Re_6Se_5Cl_9]^-$ in **1** are identical (Fig. 2), which conclusively ascertains the cluster composition and compound formulation. The formation of aggregates between the matrix and the solvent (*m*-nitrobenzyl alcohol–acetonitrile) is responsible for the peaks at *m*/*z* 502 (3 : 1) and 389 (2 : 2).

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