$[NBu^n_4]_4[(Re_6S_5OCl_7)_2O]$, an oxo-bridged siamese twin cluster of two hexanuclear oxochalcohalide rhenium clusters

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A report of the solid state synthesis and X-ray crystal structure analysis of $[NBu^n_4]_4[(Re_6S_5OCl_7)_2O]$, the first oxo-bridged, tetravalent hexanuclear oxochalcohalide rhenium cluster.

The potassium and rubidium salts of hexanuclear chalcohalide rhenium clusters, $M[Re_6(Q_5Cl_3)Cl_6]$ (M = Rb, Q = S; M = K, Q = Se), obtained from high temperature solid state reactions, are soluble in a variety of organic solvents,[1] and have been shown to be splendid starting materials for a variety of heterosubstituted or functionalized rhenium clusters.[2–5] These reactions, performed at room temperature and in organic solvents, always lead to the cluster dianions, $[NBu^n_4]_2[Re_6(Q^i_5E^iCl^i_2)Cl^a_6]^{2-}$ (E = O, S, Se, Te, NH, NMe, NBz), and involve the substitution of one of the μ_3-face-capping chloride ligand of the Re_6L_8 cluster core in $[NBu^n_4][Re_6(Q_5Cl_3)Cl_6]$ (Q = S, Se), with a divalent anion or its synthetic equivalent, for example the silylated main group reagents $E(SiMe_3)_2$.[4,5] We now report a novel high temperature solid state reaction, in the presence of minute amounts of water which (*i*) achieves the concomitant solid state synthesis and former transformation of the cluster monoanion form into the corresponding dianion upon a single core ligand substitution, and (*ii*) involves a single apical-chloride displacement and a subsequent linkage of two clusters across an oxo-bridge, both unprecedented in this chemistry.

The compound $[NBu^n_4]_4[(Re_6S_5OCl_7)_2O]$ was synthesized by mixing Re (206 mg, 1.11 mmol), $ReCl_5$ (200 mg, 0.55 mmol), KCl (30 mg, 0.40 mmol) and S (35 mg, 1.09 mmol) in an inert gas atmosphere. The powder was then pressed into a pellet and placed in a silica tube (inner diameter 10 mm, external diameter 12 mm; *ca.* 105 mm long), into which H_2O (0.014 ml, 0.78 mmol) was carefully condensed (the hydrolysis of $ReCl_5$ leads to the formation of $HReO_4$, ReO_2 and HCl).[6] After 10 min the system was evacuated to 10^{-2} Torr, sealed and heated for 4 days at 850 °C in a furnace, using a 30 °C h^{-1} rate for heating and cooling ramps. The crude material was washed with water and dissolved in ethanol. An ethanolic solution of NBu^n_4Cl was then added, forming rapidly an orange precipitate, which was recrystallized from acetone to give 470 mg of dark red crystals [Yield = 42% (based on Re). Anal. for $C_{64}H_{144}Cl_{14}N_4O_3S_{10}Re_{12}$. Calc. C, 18.89; H, 3.57; N, 1.38; Cl, 12.20; S, 7.88. Found: C, 16.95; H, 3.10; N, 1.33; Cl, 12.21; S, 8.13%].

The structure was solved by single crystal X-ray diffraction.‡ The asymmetric unit contains one cluster tetra-anion and four tetrabutylammonium cations. The cluster anion (Fig. 1) consists of two identical $[Re_6(S_5OCl_2)]^{4+}$ cores linked by an apical oxygen ligand [O(2)], the ten other apical positions being occupied by chlorine atoms. Thus, the charge of each cluster moiety is 2−. The average rhenium to apical chloride bond length (Re–Cl^a, where Cl^a denotes such a chlorine atom in Schäfer's notation)[7] is 2.380(4) Å [range 2.367(4)–2.389(3) Å], as expected for a cluster dianion.[3,4] The Re–Q distances observed for the μ_3-bridging, disordered Cl and S inner atoms (Q = S^i, Cl^i) are in the range of 2.385(3)–2.450(3) Å, whereas the μ_3-bridging oxo ligands are much closer to the Re atoms [2.090(7)–2.105(8) Å]. This distance is similar to that found in the oxygen substituted cluster, $[NBu^n_4]_2[Re_6S_5OCl_8]$ [average Re–(S^i, Cl^i) 2.415(11) Å, Re–O 2.087(6) Å].[4] It is important to note that there is no evidence for disorder in the position of the oxo ligands, a rare event in this type of chemistry.[4,5] Finally, the rhenium octahedra are slightly distorted, a manifestation of the closer approach of the face capping oxo ligand, consistent with the shortening of the Re–Re bond lengths observed for rhenium octahedra when one goes from the Re–Se–Cl to Re–S–Cl system.[3,8,9] In the structure of $[NBu^n_4]_4[(Re_6S_5OCl_7)_2O]$, the three rhenium atoms capped by the μ_3-oxo ligands have regular Re–Re distances [$< d_{Re-Re} >$ = 2.530(6) Å], whereas the opposing triangular Re_3 face is also regular, $< d_{Re-Re} >$ = 2.595(8) Å, but with Re–Re distances similar to those observed in all hexanuclear clusters in the Re–S–Cl system.[3,9] The remaining Re–Re bond lengths, that connect these two Re_3 triangles, are intermediate to the two former, $< d[Re_3(O)–Re_3(S)] >$ = 2.585(8) Å, very close to the barycentre calculated as $[(2.530 \times 1 + 2.595 \times 7)/8]$ = 2.587 Å.

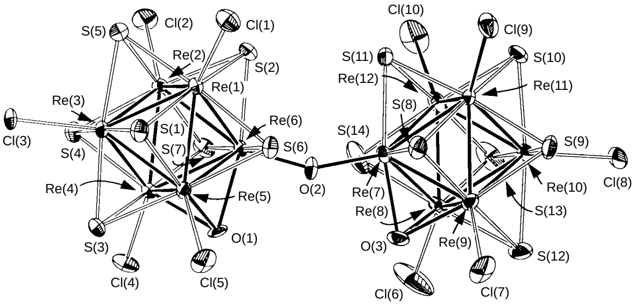

Fig. 1 ORTEP drawing and numbering scheme for the cluster $[(Re_6S_5OCl_7)_2O]^{4-}$ in $[NBu^n_4]_4[(Re_6S_5OCl_7)_2O]$. The thermal ellipsoids are drawn at the 50% probability level. Face-capping ligands S are composite S/Cl atoms (ratio: 5/2), the two face-capping O ligands are located. The cluster molecule is totally asymmetric. The relevant bond lengths are described in the text.

The present oxo-bridged siamese twin cluster compound differs from $[Re_{12}Se_{16}(PEt_3)_{10}][SbF_6]_4$, which was recently reported by Zheng *et al.*,[10] since, in the latter case, the two rhenium clusters are connected *via* two bonds, one Re–Se^{a-i} and the other Re–Se^{i-a}, in a similar fashion to the Chevrel phases.[11] The novel class of solid state reaction disclosed in this work opens the way for an infinite oxo-bridged cluster polymer.

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Notes and References

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‡ *Crystal structure analysis* for $[NBu^n_4]_4[(Re_6S_5OCl_7)_2O]$: A dark red crystal (0.25 × 0.15 × 0.20 mm) of the title compound was selected for X-ray diffraction analysis and mounted on a Stoe IPDS single ϕ-axis diffractometer with a 2D area detector based on imaging plate technology. 289 images (frames) were recorded at 150 K using the rotation method ($0 \leqslant \phi \leqslant 260.1°$) with $\Delta\phi$ = 0.9° increments, an exposure time of 3 min and a crystal-to-plate distance of 60 mm (program EXPOSE).[12] The images were processed with the suite of programs provided by Stoe (DISPLAY, INDEX, PROFILE, INTEGRATE).[12] *Crystal data* for $C_{64}H_{144}Cl_{14}N_4O_3Re_{12}S_{10}$, *M* = 4069.13, *F*(000) = 7512, monoclinic, space group $P2_1/c$ (no. 14),

a = 24.378(3), b = 18.025(2), c = 24.044(3) Å, β = 93.69(1)°, U = 10544(2) Å^3, Z = 4, graphite monochromated Mo-Kα radiation (λ = 0.710 73 Å), T = 150 K, D_c = 2.563 Mg m^{-3}; 132 608 reflections measured ($3.8 \leqslant 2\theta \leqslant 56.3°$; $-32 \leqslant h \leqslant 31$, $-23 \leqslant k \leqslant 23$, $-31 \leqslant l \leqslant 31$), 25 138 were unique ($R_{\text{int}}$ = 0.093) and 13 071 have $I > 2\sigma(I)$, no decay was observed. Corrections were made for absorption [μ(Mo-Kα) = 14.3 mm^{-1}] by empirical methods (max. and min. transmission 0.2033 and 0.0690). The structure was solved by direct methods (SHELXS-86)[13] and subsequent Fourier difference techniques and refined by full-matrix least squares, on F^2 (program SHELXL-93).[14] All non-hydrogen atoms were refined anisotropically except for a few carbon atoms for which thermal motion precluded such refinement. The positions of the H atoms were calculated for idealized positions. The final $wR(F^2)$ was 0.0777, with conventional $R(F)$ = 0.0373 (R factors defined in ref. 14), for 909 parameters, GOF = 0.629, $w^{-1} = \sigma^2(F_o^2) + (0.0001\,p)$,^{2} where p = [max (F_o^2, 0) + 2 F_c^2)/3], $(\Delta/\sigma)_{\max}$ = 0.000. Minimum and maximum $\Delta\rho$ were −4.047 and 3.285 e Å^{-3}, respectively, in the vicinity of Re atoms. The cluster core face-capping chlorine and sulfur atoms were disordered and were refined as sulfur atoms. CCDC 182/790.

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