Re_6S_{12}, a New Binary Rhenium Cluster Chalcogenide

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Topotactic oxidation of $Na_4Re_6S_{12}$ at ambient temperature results in the formation of the new binary cluster chalcogenide Re_6S_{12} that is able to react as a (4 + 2) electron-transfer host lattice.

Rhenium disulfide ReS_2, characterized by a distorted CdI_2 type layer structure, is the only crystalline binary sulfide reported for the Group 7 element rhenium.[1] The preparation of an amorphous phase Re_2S_7 has been described,[2] but the structure of this compound has not yet been established. Among the ternary rhenium chalcogenides a series of monoclinic phases $A_4Re_6X_{12}$ (X = S, Se) with monovalent metal ions (A = Na, K, Rb, Cs, Tl, Cu) is known, which can be described by Re_6X_8 cluster units connected by X atoms to form planes which are joined by X_2 groups in the direction of the *a* axis in the *a*/*c* plane (Fig. 1).[3,4,5] Greaney and Greenblatt reported the partial deintercalation of Tl^+ ions from the selenide $Tl_4Re_6Se_8$ up to a composition of $Tl_{1.8}Re_6Se_{12}$; attempts at further deintercalation resulted in irreversible decomposition of the material.[4] We observed that Na^+ ions in the sulfide $Na_4Re_6S_{12}$ are mobile at room temperature and report the formation, characterization and reactivity of the new binary rhenium cluster chalcogenide Re_6S_{12} *via* topotactic oxidation at ambient temperature from the ternary sodium compound.

Single crystals of monoclinic $Na_4Re_6S_{12}$ were prepared as described earlier[3] and characterized by chemical composition and lattice parameters. Oxidation of the sodium compound was performed by chemical and electrochemical procedures, yielding identical reaction products. Upon oxidation of single crystals in MeCN–I_2, MeCN–Br_2 or 30% aqueous H_2O_2, the colour changes from transparent red to opaque black; series of cracks appear parallel to the (100) face. After a reaction time of 14 days the analytical data yielded a ratio Re : S of 1 : 2, no sodium could be detected by EDX measurements. X-Ray reflections were found to have broadened; it was possible, however, to determine symmetry type and monoclinic unit-cell parameters by single-crystal techniques (Laue, rotation). These data were used for least-squares refinement of powder patterns (Table 1). It could be shown by single-crystal X-ray techniques that there is a close orientational relationship between the matrix $Na_4Re_6S_{12}$ and the product R_6S_{12}: $b_m \parallel b_p$; $c_m \parallel c_p$. As is well known, the solid-state transformation 'single-crystal–single-crystal' and the existence of orientational relationship between a matrix and a product are specific features of topotactic reactions.[6] Laue patterns of Re_6S_{12} contain specific streaks which result from a one-dimensional disorder of the crystal structure as a consequence of the deintercalation process. We assume that this structural disorder is due to the reorientation of the flexible S_2 groups located in the *b*/*c* plane. X-Ray powder patterns show a decrease in line intensity and a broadening of the Bragg reflections.

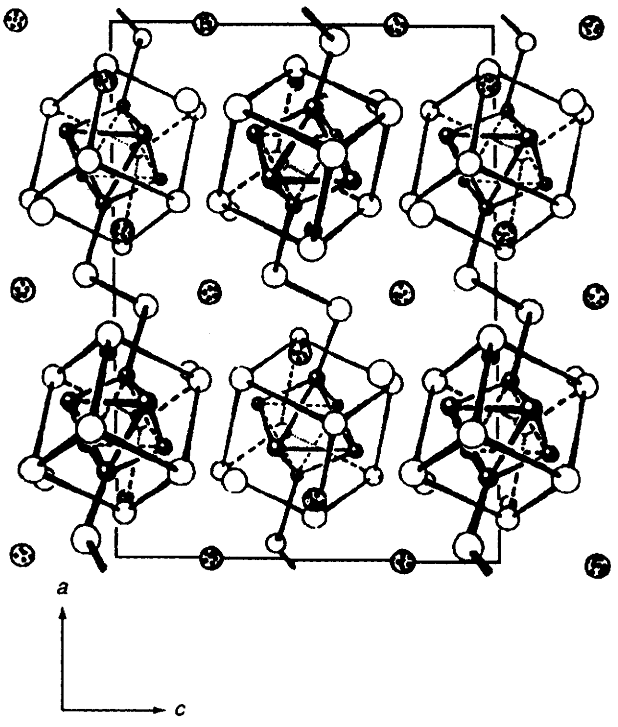

Fig. 1 Structure scheme for $A_4Re_6S_{12}$ phases; black small circles = Re; open white circles = S; dotted circles A atoms. Note covalent connections of Re_6S_{10} cluster planes (*b*/*c*) *via* S–S bridges in direction of the *a*-axis (in-plane connection of cluster units *via* sulfur atoms omitted).

TG and DTA curves obtained in Ar atmosphere with a heating rate of 4 °C min^{-1} from room temperature to 800 °C indicate a weight loss of 4.2–4.5% in the temperature range 400–700 °C accompanied by a broad endothermal effect. The mass change corresponds to the removal of two sulfur atoms from the Re_6S_{12} structure and is in agreement with analytical data (sulfur/rhenium ratio) of the reaction product. X-Ray patterns of samples with a composition Re_6S_{10} display a few broad reflections which are difficult to index.

Table 1 Monoclinic lattice parameters of binary and ternary Re_6 cluster compounds

Compound	Unit cell parameters			
	a_0/Å	b_0/Å	c_0/Å	β/°
$Na_4Re_6S_{12}$	15.858(1)	9.6082(6)	11.494(8)	92.570(1)
Re_6S_{12}	14.428(3)	8.732(2)	11.650(3)	96.73(1)
$Cu_4Re_6S_{12}$	15.761(3)	9.413(3)	11.597(3)	91.31(3)
$Cu_6Re_6S_{12}$	16.738(4)	10.132(2)	12.600(2)	93.08(2)

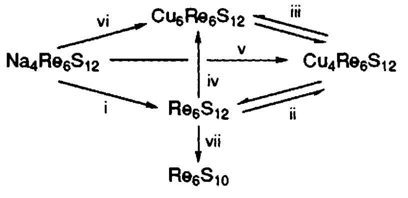

Fig. 2 Scheme of topotactic reactions of $Na_4Re_6S_{12}$; i, electrochemical or chemical oxidation of $Na_4Re_6S_{12}$ to the new binary Re-cluster compound; ii, reversible electrochemical intercalation of Cu; four-electron transfer *via* metal cluster redox centre; iii, reversible electrochemical intercalation of two additional Cu ions by two-electron transfer *via* nonmetal redox centre; vi, direct reduction of Re_6S_{12} in short circuit cell $Cu^0|Cu^+$, MeCN$|Re_6S_{12}$; combined ion exchange and redox reaction; v, ion-exchange reaction of $Na_4Re_6S_{12}$ in CuCl–MeCN electrolyte; vi, reaction in short-circuit cell $Cu^0|Cu^+$, MeCN$|Na_4Re_6S_{12}$; vii, thermal decomposition of Re_6S_{12} at 600 °C

Electrochemical oxidation of $Na_4Re_6S_{12}$ was carried out in galvanostatic mode (three-electrode cell, electrolyte 0.5 mol dm^{-3} Na_2SO_4–H_2O) with polycrystalline material pressed into Pt grids along with 1% mass of Teflon powder as working electrodes. According to the galvanostatic potential/charge transfer curves and *in situ* X-ray measurements there are two separate regions. Up to a charge transfer of *ca.* 2 e mol^{-1} a single phase range is observed [eqn. (1)] with a minor X-ray line shift [change of (200) reflection from $2\theta = 11.16°$ to $2\theta = 10.95°$] and a simultaneous decrease in monoclinic splitting of the (11 − 1) and (111) reflections which corresponds to an expansion of the a_0 parameter of the starting phase for 0.3 Å and a decrease in the monoclinic angle.

$$Na_4Re_6S_{12} \rightarrow Na_{4-x}Re_6S_{12} + xNa^+ + xe^- \quad (0 < x < 2) \qquad (1)$$

Beyond $x \approx 2$ a two-phase region is found characterized by a decrease in intensity of the $Na_2Re_6S_{12}$ lines and appearance of the reflections of the binary product Re_6S_{12} [eqn. (2)].

$$Na_2Re_6S_{12} \rightarrow Re_6S_{12} + 2Na^+ + 2e^- \qquad (2)$$

The ternary starting material $Na_4Re_6S_{12}$ can be described in terms of formal oxidation states as $(Na^+)_4\{[(Re^{3+})_6(S^{2-})_8](S^{2-})_{4/2}(S_2^{2-})_{2/2}\}$; the Re_6 cluster has thus 24 electrons with two-electron Re–Re bonding. Upon oxidation to Re_6S_{12}, the four-electron transfer leads to a 20 e$^-$ Re_6-cluster system with an average oxidation state for Re of +3.66. Similar to the related Mo_6 cluster phases[7,8] reductive four-electron intercalation processes with guest cations of an appropriate size should be possible with the new host lattice Re_6S_{12}. We decided to test the reactivity by electrochemical intercalation of Cu ions which are known to have high ionic mobility in chalcogenide lattices at ambient temperature.

The reduction was performed in galvanostatic mode with pressed working electrodes of the binary rhenium sulfide in aqueous 0.1 mol dm^{-3} $CuSO_4$–0.1 mol dm^{-3} H_2SO_4 electrolyte and in 0.5 mol dm^{-3} CuCl–MeCN aprotic electrolyte. The results were rather surprising since two copper phases could be identified by X-ray diffraction and elemental analysis: $Cu_4Re_6S_{12}$ and $Cu_6Re_6S_{12}$. The lattice parameters of the copper compounds are given in Table 1. The formation of $Cu_4Re_6S_{12}$ [eqn. (3)] corresponding to a four-electron transfer and resulting in a 24-electron Re_6 cluster system was expected similar to the formation of $Cu_4Mo_6S_8$ from Mo_6S_8.[8] Further electrochemical reduction of $Cu_4Re_6S_{12}$ or direct reaction of Re_6S_{12} in a short-circuit cell $Cu^0|Cu^+$, MeCN$|Re_6S_{12}$ yielded the copper compound $Cu_6Re_6S_{12}$ as the product [eqn. (4)]. The reactions described are reversible; upon chemical or electrochemical oxidation of $Cu_6Re_6S_{12}$ or $Cu_4Re_6S_{12}$ the binary phase Re_6S_{12} is obtained (Fig. 2).

$$Re_6S_{12} + 4Cu^+ + 4e^- \leftrightarrows (Cu^+)_4[Re_6S_{12}]^{4-} \qquad (3)$$

$$Cu_4Re_6S_{12} + 2Cu^+ + 2e^- \leftrightarrows (Cu^+)_6[Re_6S_{12}]^{6-} \qquad (4)$$

Since the Re_6-cluster redox system is saturated after a transfer of four electrons it is to be concluded that a second intrinsic redox system with a lower electrochemical potential must exist in the host matrix. It is in fact well known from molecular chemistry and from biochemical processes that disulfide groups can act as reversible two-electron transfer systems [eqn. (5)].

$$X\text{–}S\text{–}S\text{–}X + 2e^- \leftrightarrows X\text{–}S^- + {}^-S\text{–}X \qquad (5)$$

Re_6S_{12} is actually provided with S_2 groups in the *a*/*b* plane (Fig. 1) and their number accounts precisely to a corresponding uptake of two electrons per formula unit; the maximum electron transfer amounts then to 6 e$^-$ per Re_6S_{12} unit. We observe here thus the case of a host lattice with two different intrinsic redox centres of different potential based on both a *metal* redox system (Re_6) and a *nonmetal* redox system (S_2) as indicated in eqns (6) and (7). The reductions of the sulfide bridges between the Re_6-cluster planes results formally in a reduced dimensionality in terms of covalent bonding between the matrix elements.

$$\underset{(20\ e^-\ \text{cluster})}{Re_6S_{12}} + 4e^- \leftrightarrows \underset{(24\ e^-\ \text{cluster})}{[Re_6S_{12}]^{4-}} \qquad (6)$$

$$S_2{}^{2-} + 2e^- \leftrightarrows 2S^{2-} \qquad (7)$$

We assume that a binary selenide Re_6Se_{12} may be prepared in a similar way as the sulfide by low-temperature topotactic oxidation from the corresponding ternary selenide phase $Na_4Re_6Se_{12}$. Re_6S_{12} is of interest as a novel six-electron transfer host lattice for intercalation reactions as well as in terms of potential catalytic properties.

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