



In situ generation of H₂Se and hydrothermal synthesis of new polynuclear rhenium carbonyl polyselenides

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ABSTRACT

Two new polyselenide-bridged rhenium carbonyl complexes, $[\text{Re}_5(\text{CO})_{18}(\text{Se}_2)_3]^-$ and $[\text{Re}_4(\text{CO})_{14}(\text{Se}_2)(\text{Se}_5)]$, were obtained by hydrothermal reaction of $[\text{Re}(\text{CO})_5\text{Cl}]$ with in situ generated H₂Se and have been characterized by X-ray diffraction.

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1. Introduction

Polynuclear complexes usually result from nucleation of metal centers around a certain number of bridging anionic ligands. In this way large soluble aggregates are obtained. The most efficient bridges for such aggregation are oxide/hydroxide, fluoride, sulfide (or other chalcogenides), sometimes in various combination of different types [1–4].

The dichalcogenide bridges can also potentially be useful supporting ligands for multinuclear aggregation, as in $[\text{Cu}_6\text{S}_7(\text{S}_2)_6\text{Mo}_6\text{O}_6]^{2-}$ [5]. Symbiosis of Se_2^{2-} and Se_3^{2-} ligands allows assembly of a unique diamond-crown shaped polynuclear complex, $[\text{Cp}^*\text{Re}(\text{Se}_3)(\mu\text{-Se}_2)]_8$ [6]. Bridging ligands Se_3^{2-} , Se_4^{2-} and Se_5^{2-} , together with oxo- and hydroxobridges, support the core in the octanuclear europium complex $[\text{Eu}_8(\text{O})(\text{OH})_{12}(\text{Se}_3)(\text{Se}_4)_2(\text{Se}_5)_2(\text{DMF})_{13}]$ [7].

Polynuclear Re chalcogenides are of particular interest since rhenium sulfides are even more active than MoS_2 in catalyzing hydrogenations as well as the hydrodesulfurization and hydrodenitrogenation reactions [8–10]. The disulfide complex, $[\text{Cp}^*\text{Re}_2(\text{S}_2)_2]^{2+}$ easily adds acetylene or dihydrogen across the S–S bonds [11]. As both Re–Se and Se–Se bonds are expected to be weaker than the Re–S or S–S bonds, it would be of interest to prepare and study reactivity other Re/Se clusters in such reactions. Such reactions are usually run with polychalcogenide solutions which

are inherently basic. This certainly influences in some ways the course which substitution and condensation reaction would take. To run reactions in acidic media would require use of highly toxic hydrogen selenide. In these paper we report reaction of $[\text{Re}(\text{CO})_5\text{Cl}]$ with in situ generated H₂Se, which gave rise to two new polynuclear rhenium carbonyl selenides.

2. Experimental

2.1. Synthesis

$[\text{Re}(\text{CO})_5\text{Cl}]$ (Aldrich), ZnSe and HCl were used as purchased. CH_2Cl_2 was reagent grade and was distilled over P_4O_{10} before use. IR spectra were recorded ($4000\text{--}400\text{ cm}^{-1}$) on a Scimitar FTS 2000 spectrometer in KBr pellets.

2.1.1. Preparation of $[\text{Re}(\text{CO})_3(\text{H}_2\text{O})_3][\text{Re}_5(\text{CO})_{18}(\text{Se}_2)_3]$ (1) and $[\text{Re}_4(\text{CO})_{14}(\text{Se}_2)(\text{Se}_5)]$ (2)

$[\text{Re}(\text{CO})_5\text{Cl}]$ (0.10 g, 0.28 mmol), ZnSe powder (0.06 g, 0.41 mmol) and 4 ml of 4 M HCl were placed into a glass tube. The tube was evacuated, sealed and heated at 140 °C for 48 h. After cooling and opening up a brown precipitate was collected by filtration and extracted with CH_2Cl_2 . Red solution was adsorbed on a silica gel column. Elution with $\text{CH}_2\text{Cl}_2\text{--C}_6\text{H}_5\text{CH}_3$ (1:1 v/v) gave a yellow-brown solution, after that next, red fraction was eluted with neat CH_2Cl_2 . Slow evaporation of the solutions gave single crystals of a mixture of unsolvated $[\text{Re}_4(\text{CO})_{14}(\text{Se}_2)(\text{Se}_5)]$ (2) and

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Table 1
Crystallographic data for **1**, **2** and **2** · CH₂Cl₂

Compound	1	2	2 · CH ₂ Cl ₂
Formula	C ₂₁ H ₆ O ₂₄ Re ₆ Se ₆	C ₁₄ O ₁₄ Re ₄ Se ₇	C ₁₄ O ₁₄ Re ₄ Se ₇ , CH ₂ Cl ₂
Formula weight	2233.3	1689.7	1774.6
Wavelength (Å)	0.71073 (Mo Kα)	0.71073 (Mo Kα)	0.71073 (Mo Kα)
Temperature (K)	90.0(2)	296(2)	100.0(2)
Space group	P6 ₃ 22	P1	P1
a (Å)	12.70850(10)	9.8896(3)	9.8304(2)
b (Å)	12.70850(10)	12.5609(5)	12.8716(3)
c (Å)	16.4566(3)	12.8091(5)	13.1663(3)
α (°)	90	99.7320(10)	106.7530(10)
β (°)	90	94.4650(10)	97.3490(10)
γ (°)	120	96.2150(10)	93.8380(10)
V (Å ³)	2301.76(5)	1551.53(10)	1572.68(6)
Z	2	2	2
F(000)	1956	1468	1552
D _{calc} (g cm ⁻³)	3.222	3.617	3.747
Crystal form, colour	prism, red	plate, red	block, dark red
Crystal size (mm)	0.13 × 0.13 × 0.11	0.06 × 0.06 × 0.02	0.14 × 0.08 × 0.06
μ (cm ⁻¹)	20.531	23.820	23.674
Diffractometer	Bruker X8Apex CCD	Bruker X8Apex CCD	Bruker X8Apex CCD
Data collection range (°)	1.85–31.38	1.62–27.5	1.95–33.15
Range of h, k, l	–16 → h → 10 –13 → k → 6 –13 → l → 23	–9 → h → 12 –16 → k → 16 –15 → l → 16	–14 → h → 12 –19 → k → 17 –18 → l → 18
Number of measured, independent and observed reflections	9894/2191/2080	12073/6956/5315	21024/9015/7671
Criterion for observed reflections	I > 2σ(I)	I > 2σ(I)	I > 2σ(I)
R _{int}	0.0270	0.0246	0.0202
Number of parameters	87	352	379
R	0.0512	0.0280	0.0275
R _w	0.1167	0.0552	0.0683
Weighting scheme	w = 1/[σ ² F _o ² + 148.1959P], where P = (F _o ² + 2F _c ²)/3	w = 1/[σ ² F _o ² + (0.0179P) ²], where P = (F _o ² + 2F _c ²)/3	w = 1/[σ ² F _o ² + (0.0235P) ² + 19.3023P], where P = (F _o ² + 2F _c ²)/3
Largest peak (e Å ⁻³)	4.231	0.946	2.345
Flack parameter	0.05(5)		

solvated **2** · CH₂Cl₂ (first fraction, 12 mg) and of [Re(CO)₃(H₂O)₃]-[Re₅(CO)₁₈(Se₂)₃] (**1**) (second fraction, 30 mg). IR (ν (CO), CH₂Cl₂): 2108, 2098, 2055, 2035, 2012, 1967 cm⁻¹ (**1**) and 2129, 2089, 2022, 1949, 1922 cm⁻¹ (**2**).

2.2. X-ray crystallography

Slow evaporation of the respective solutions in dichloromethane yielded red-orange crystals of **1**, and a mixture of **2** and **2** · CH₂Cl₂, suitable for X-ray analysis. Crystallographic data and structure refinement details for the compounds are given in Table 1. All diffraction data were collected on a Bruker X8Apex CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å) using φ and ω scans of narrow (0.5°) frames. All structures were solved by direct methods and refined by full-matrix least-squares method against |F|² in anisotropic approximation using SHELXTL programs set [12]. Absorption corrections were applied empirically using SADABS program [13]. All non-hydrogen atoms were refined anisotropically.

3. Results and discussion

Hydrogen selenide H₂Se (pK_{a1} = 3.89; pK_{a2} = 11.0 at 25 °C) is a very reactive compound used for dosage of semiconductors with Se and in the synthesis of organoselenium compounds, which is, however, usually avoided by the synthetic inorganic chemists because of its well-known disadvantages including the nasty smell, a high toxicity (exposure limit 0.3 ppm over an 8 h period) and low stability [14]. The dosage of H₂Se in an open-flow system is difficult. To avoid the use of free H₂Se in an open system, we used in situ generated H₂Se, which is quantitatively generated from ZnSe powder with 4 M HCl. As the reaction of ZnSe with HCl of this concentration takes place only at high temperature, a mixture of a

reagent, ZnSe and 4 M HCl can be safely placed in a glass tube at room temperature. The tube is then evacuated and sealed, and exactly known amount of H₂Se is then released upon heating. In this way the problem of dosage and disposal of unreacted H₂Se is circumvented [15]. The reaction gives two products, a pentanuclear complex [Re(CO)₃(H₂O)₃][Re₅(CO)₁₈(Se₂)₃] (**1**) (Fig. 1) and a tetranuclear complex [Re₄(CO)₁₄(Se₂)(Se₅)] (**2**) (Fig. 2), which are structurally related. Increasing the Re/Se ratio from 2/3 to 1/3 does

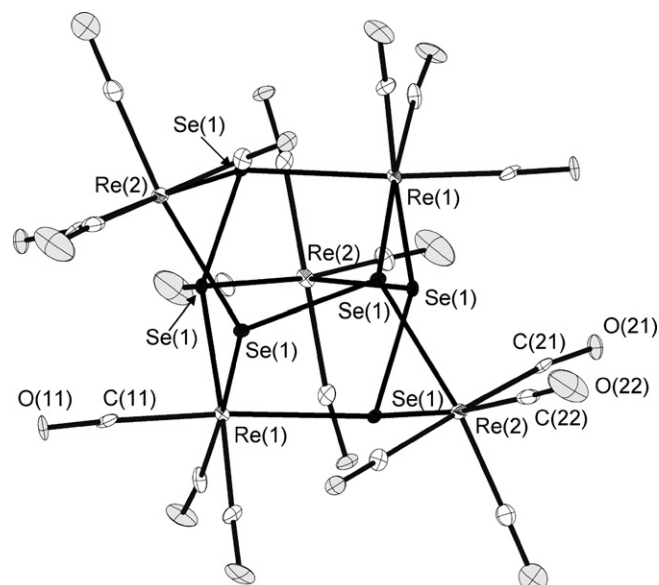


Fig. 1. The anion [Re₅(Se₂)₃(CO)₁₈]⁻ in crystal structure of **1**, a.d.p. ellipsoids (50% probability). The distances (Å) in Re/Se core are (at 90 K): Re(1)–Se(1) 2.5842(14), Re(2)–Se(1) 2.6206(14), Se(1)–Se(1) 2.430(3).

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