# Electronic Supplementary Information (ESI) for

# The Selenite-capped Polyoxo-4-aurate(III), [Au<sup>III</sup><sub>4</sub>O<sub>4</sub>(Se<sup>IV</sup>O<sub>3</sub>)<sub>4</sub>]<sup>4-</sup>

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#### 1. Materials and physical measurements

All reagents were purchased from commercial sources and used without further purification. Hydrogen tetrachloroaurate(III) hydrate was purum grade with ~52% Au basis (Sigma-Aldrich).

The <sup>77</sup>Se NMR spectra were recorded on a 400 MHz JEOL ECX instrument at room temperature using 5 mm tubes on non-deaerated solutions of **K-Au<sub>4</sub>Se<sub>4</sub>** in H<sub>2</sub>O / D<sub>2</sub>O (~12 mg/mL; pH 6.1). The resonance frequency was 105.155 MHz, and the chemical shifts are reported with respect to neat (CH<sub>3</sub>)<sub>2</sub>Se. All chemical shifts downfield of the reference are reported as positive values.

Thermogravimetric analysis (TGA) was carried out on a TA Instruments SDT Q600 thermobalance with a 100 mL min<sup>-1</sup> flow of nitrogen; the temperature was ramped from 20 to 1200  $^{\circ}$ C at a rate of 5  $^{\circ}$ C min<sup>-1</sup>.

Elemental analysis was performed by Service Central d'Analyse, Solaize, France. The IR spectrum was recorded on a KBr disk using a Nicolet-Avatar 370 spectrometer between 400 and 4000 cm<sup>-1</sup>.

Mass spectra were taken on two instruments: (I) ESI-Qq time-of-flight mass spectrometer (MicrOTOF-Q II, Bruker Daltonik, Bremen) with a nanospray source and (II) 7T-FT-ICR mass spectrometer (APEX II, Bruker Daltonik, Bremen) using a home-built nanospray source. Positive ion mode spectra were obtained by spraying solution of **K-Au<sub>4</sub>Se<sub>4</sub>** in deionized water with a concentration of ~10<sup>-5</sup> M using home-pulled tipps with opening diameters of several  $\mu$ m.

The electrochemical set-up was an EG & G 273 A driven by a PC with the M270 software. Potentials are quoted against a saturated calomel electrode (SCE). The counter electrode was a platinum gauze of large surface area. All experiments were performed at room temperature. The source, mounting and polishing of the glassy carbon (GC, Tokai, Japan) electrodes have been described.<sup>1</sup> The glassy carbon samples had a diameter of 3 mm. The solutions were deaerated thoroughly for at least 30 min. with pure argon and kept under a positive pressure of this gas during the experiments. The solutions were 8 x 10<sup>-4</sup> M in Au<sub>4</sub>Se<sub>4</sub>. The composition of the aqueous electrolyte was 0.4 M NaNO<sub>3</sub> + NaOH (pH 6.20). The electrochemical experiments were performed in the dark. UV-Vis spectra were recorded with a Lambda 750 Perkin Elmer spectrophotometer. The solutions were placed in quartz cuvettes with an optical path of 1cm or 0.1 cm.

#### 2. Synthesis of K-Au<sub>4</sub>Se<sub>4</sub>.

H[AuCl<sub>4</sub>] (0.210 g, 0.618 mmol) was dissolved in 5 mL of 2 M KOAc solution (pH 7.0). Then the pH of the resulting solution was adjusted to 12 by addition of 6 M KOH solution, accompanied by a color change from bright yellow to orange and then to light yellow. After stirring for 15 min, AgNO<sub>3</sub> (0.425 g, 2.50 mmol) was added under vigorous stirring to precipitate the Cl<sup>-</sup> ions while maintaining the pH at 12 with KOH<sub>aq</sub>. The obtained white precipitate of AgCl containing small amounts of brownish Ag<sub>2</sub>O·nH<sub>2</sub>O was removed by filtration. To this filtrate H<sub>2</sub>SeO<sub>3</sub> (0.08 g, 0.618 mmol) was added, and the pH of the reaction mixture was carefully adjusted to 6.3 with 6 M HNO<sub>3</sub>. The resulting deep yellow solution was stirred at room temperature for 50 min and then filtered to remove a small amount of solid Au(OH)<sub>3</sub>. Slow evaporation of the filtrate at room temperature in an open vial resulted in yellow, block-shaped crystals within two weeks. The obtained crystals were collected by filtration and air dried. Yield: 0.038 g (14% based on Au).

**IR** (2% KBr pellet): v = 3444 (s), 1636 (s), 1384 (s), 869 (s), 721 (s), 674 (s), 638 (w), 590 (w), 508 (m).

**Elemental analysis** (%) calcd for **K-Au<sub>4</sub>Se<sub>4</sub>:** K 11.34, Au 45.7%, Se 18.33, N 0.32, H 0.81; found: K 11.38, Au 44.7, Se:17.83, N 0.33, H 0.74.

#### 3. X-ray crystallography

Data for the structure **K-Au<sub>4</sub>Se<sub>4</sub>** were collected at 100 K on a Bruker Kappa X8 APEX CCD single-crystal diffractometer equipped with a sealed Mo anode tube and graphite monochromator ( $\lambda = 0.71073$  Å). The crystals were mounted in a Hampton cryoloop with light oil. The SHELX software package (Bruker) was used to solve and refine the structures.<sup>2</sup>Absorption corrections were applied empirically using the SADABS program.<sup>3</sup>The structures were solved by direct methods and refined by full-matrix least-squares minimization of ( $\Sigma w(Fo - Fc)^2$ ) with anisotropic thermal parameters for all POM skeleton atoms (Au, Se, O)

and non-disordered K countercations. No H atoms were included in the model. The relative site occupancy factors for the disordered potassiums as well as oxygens of crystal waters were refined with isotropic approximation and then fixed at the obtained values. Additional crystallographic data are summarized in Table S1. Further details of the crystal structure investigation are available free of charge from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD- 424685.

Not unexpectedly, the number of crystal waters found by XRD was slightly lower than that detemined by elemental and thermogravimetric analyses on bulk material of **K-Au<sub>4</sub>Se<sub>4</sub>** (4.5 *vs* 6, respectively), which can be explained by disorder of the crystal waters in the lattice. We decided to use the formula obtained by elemental analysis throughout the paper and in the CIF file for overall consistency.

| Empirical formula  | $C_{1.2}H_{13.8}Au_4K_5N_{0.4}O_{24.4}Se_4$ |  |  |
|--|---|--|--|
| Formula weight, g/mol  | 1723.53                                     |  |  |
| Crystal system   | Triclinic                                   |  |  |
| Space group  | P-1   |  |  |
| A, Å   | 9.5617(11)                                  |  |  |
| <i>B</i> , Å   | 11.3604(12)                                 |  |  |
| <i>c</i> , Å   | 14.4557(17)                                 |  |  |
| <i>α</i> , °   | 89.867(7)                                   |  |  |
| $\beta$ , °  | 73.275(8)                                   |  |  |
| γ, °   | 71.181(7)                                   |  |  |
| Volume, Å <sup>3</sup>   | 1416.3(3)                                   |  |  |
| Ζ  | 2   |  |  |
| $D_{calc}, g/cm^3$   | 4.041                                       |  |  |
| Absorption coefficient   | 26.620                                      |  |  |
| F(000)   | 1532  |  |  |
| Crystal size, mm   | 0.06 x 0.11 x 0.13                          |  |  |
| Theta range for data collection, $^{\circ}$                            | 3.14 - 25.68                                |  |  |
| Completeness to $\Theta_{max}$ , %                                     | 99.5  |  |  |
| Index ranges   | $-11 \le h \le 11,$                         |  |  |
|  | $-13 \le k \le 13$ ,                        |  |  |
|  | -17 ≤ 1 ≤ 17                                |  |  |
| Reflections collected  | 46328                                       |  |  |
| Independent reflections  | 5356  |  |  |
| R(int)   | 0.1061                                      |  |  |
| Observed (I > $2\sigma(I)$ )   | 3909  |  |  |
| Absorption correction  | Semi-empirical from equivalents             |  |  |
| T <sub>min</sub> / T <sub>max</sub>                                    | 0.1446 / 0.3027                             |  |  |
| Data / restraints / parameters   | 5356 / 6 / 308                              |  |  |
| Goodness-of-fit on F2  | 1.029                                       |  |  |
| $R_{1}$ , <sup>[a]</sup> w $R_{2}$ <sup>[b]</sup> (I > 2 $\sigma$ (I)) | $R_1 = 0.0473,$                             |  |  |
|  | $wR_2 = 0.1148$                             |  |  |
| $R_{1}$ , <sup>[a]</sup> w $R_{2}$ <sup>[b]</sup> (all data)           | $R_1 = 0.0731,$                             |  |  |
|  | $wR_2 = 0.1287$                             |  |  |
| Largest diff. peak and hole, e. $Å^{-3}$                               | 4.777 and -2.183                            |  |  |

## Table S1. Crystal data and structural refinement for K-Au<sub>4</sub>Se<sub>4</sub>.

<sup>[a]</sup>  $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$ . <sup>[b]</sup>  $wR_2 = [\sum w (F_0^2 - F_c^2)^2 / \sum w (F_0^2)^2]^{1/2}$ 

## 4. Bond valence sum calculations

Bond valence sum (BVS) calculations were performed on a program copyrighted by Chris Hormillosa & Sean Healy and distributed by I. D. Brown.<sup>4</sup>

The BVS values for different atoms in  $Au_4Se_4$  are presented in Table S2. These values confirm oxidation states of +3 for gold and +4 for selenium and do not suggest protonation for any oxygen of the polyanion.

| Au                          | <b>BVS</b> value | Se                          | <b>BVS</b> value |
|-----------------------------|------------------|-----------------------------|------------------|
| Au1                         | 3.019            | Se1                         | 3.897            |
| Au2                         | 3.010            | Se2                         | 3.877            |
| Au3                         | 3.020            | Se3                         | 3.812            |
| Au4                         | 3.121            | Se4                         | 3.889            |
|                             |                  |                             |                  |
| Terminal oxygens            | <b>BVS</b> value | μ <sub>2</sub> -Ο (Au-O-Au) | <b>BVS</b> value |
| O1S                         | 1.545            | O12                         | 1.633            |
| O2S                         | 1.524            | O23                         | 1.633            |
| O3S                         | 1.537            | O34                         | 1.625            |
| O4S                         | 1.537            | O14                         | 1.616            |
|                             |                  |                             |                  |
| μ <sub>2</sub> -O (Au-O-Se) | <b>BVS</b> value | μ <sub>2</sub> -O (Au–O–Se) | <b>BVS</b> value |
| O1S1                        | 1.881            | O3S3                        | 1.797            |
| O2S1                        | 1.898            | O4S3                        | 1.899            |
| O2S2                        | 1.832            | O4S4                        | 1.930            |
| O3S2                        | 1.969            | O1S4                        | 1.871            |

Table S2. Bond valence sum values for different atoms in K-Au<sub>4</sub>Se<sub>4</sub>.

5.  ${(H_2O)_6K_2[Au^{III}_4O_4(Se^{IV}O_3)_4]_2}^{6-}$  dimers



**Fig. S1.** Combined ball-and-stick / polyhedral (upper) and ball-and-stick (lower) representations of the dimeric assembly  $\{(H_2O)_6K_2[Au^{III}_4O_4(Se^{IV}O_3)_4]_2\}^{6-}$  in the solid state. Color code: Au yellow, Se blue, O purple, K green, and  $\{AuO_4\}$  purple squares. The Au···Au interactions are highlighted by black dotted lines.

## 6. NMR spectroscopy



**Fig. S2**. Room temperature <sup>77</sup>Se NMR spectra of **K-Au<sub>4</sub>Se<sub>4</sub>** redissolved in  $H_2O / D_2O$  at different time intervals. The downfield signal corresponds to **Au<sub>4</sub>Se<sub>4</sub>** and the upfield one to free selenite. The percentage of intact **Au<sub>4</sub>Se<sub>4</sub>** present with respect to total amount of Se in solution is also shown.

#### 7. Thermogravimetric analysis for K-Au<sub>4</sub>Se<sub>4</sub>.

The thermogram of **K-Au<sub>4</sub>Se<sub>4</sub>** from room temperature to 1200 °C under N<sub>2</sub> atmosphere is shown in Fig. S3. The TGA curve of **K-Au<sub>4</sub>Se<sub>4</sub>** exhibits several weight loss steps. The first step begins at 25 °C and is completed at about 175 °C, which corresponds to the loss of 6 water molecules per formula unit K<sub>4</sub>[Au<sub>4</sub>Se<sub>4</sub>O<sub>16</sub>]·0.4KNO<sub>3</sub>·0.6CH<sub>3</sub>COOK·6H<sub>2</sub>O (**K-Au<sub>4</sub>Se<sub>4</sub>**). The observed weight loss of 6.54% is in a good agreement with the calculated value of 6.27%. The weight loss in the temperature range of 200 - 310 °C could be assigned to the release of half an equivalent of SeO<sub>2</sub> per formula unit (3.642 % observed and 3.219% weight loss calculated). The other two consecutive weight loss steps covering the temperature range of 310 - 1190 °C are attributed to the decomposition of the remaining polyanion as well as acetate and nitrate ions. The total observed weight loss at 1190 °C is 49.2 %.



Fig. S3. Thermogram of  $K-Au_4Se_4$  from room temperature to 1200 °C under N<sub>2</sub> atmosphere. The blue curve shows the derivative profile.

## 8. IR spectrum

Figure S4 shows the IR spectrum of **K-Au<sub>4</sub>Se<sub>4</sub>** in the range of 400 - 2100 cm<sup>-1</sup>. The bands at 674, 638, and 507 cm<sup>-1</sup> could be assigned to the vibrations of Au-O-(Au) bonds, while the bands at 590 cm<sup>-1</sup> could be attributed to Au-O-(Se) vibrations. The bands at 868, 722 cm<sup>-1</sup> may arise from vibrations of the terminal and bridging Se-O bonds, respectively. The broad and strong band at 1638 cm<sup>-1</sup> is attributed to asymmetric vibrations of crystal waters as well as COO<sup>-</sup> groups of acetate. The sharp and strong band at 1384 cm<sup>-1</sup> is due to vibrations of NO<sub>3</sub><sup>-</sup> ions and COO<sup>-</sup> groups of acetate.<sup>5</sup>



Fig. S4. IR spectrum of K-Au<sub>4</sub>Se<sub>4</sub>.

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## 9. Mass spectrometry studies

### Positive ion mode K-Au<sub>4</sub>Se<sub>4</sub>



**Fig. S5**. Partial cation mass spectrum of **K-Au<sub>4</sub>Se<sub>4</sub>** comparing experimental (top panel) and calculated isotopomere pattern (bottom panel).



Fig. S6. Partial cation mass spectrum of K-Au<sub>4</sub>Se<sub>4</sub>.

| Species  | m/z, calc |
|--|-----------|
| $[Au_4Se_4O_{16}K_5 \cdot KNO_3]^+$                        | 1657.22   |
| $\left[Au_4Se_4O_{16}K_5 \cdot HNO_3 \cdot KNO_3\right]^+$ | 1720.22   |
| $\left[Au_4Se_4O_{16}K_5 \cdot 2KNO_3\right]^+$            | 1758.17   |
| $[Au_4Se_4O_{16}K_5 \cdot HNO_3 \cdot 2KNO_3]^+$           | 1821.17   |

 Table S3. Peak assignments for positive ion mode.

#### **10. UV-vis absorption spectroscopy**

Figure S7A features the UV-vis absorption spectrum of  $Au_4Se_4$  redissolved in water (pH ~ 6). The spectrum exhibits a small peak at 429 nm ( $\varepsilon$  ca. 697 M<sup>-1</sup>cm<sup>-1</sup>) followed by a shoulder around 300 nm ( $\varepsilon$  ca. 8720 M<sup>-1</sup>cm<sup>-1</sup>) and an intense peak at 228 nm ( $\varepsilon$  ca. 23000 M<sup>-1</sup> cm<sup>-1</sup>). Figure S7B shows, in superimposition, the spectrum in water of  $Au_4Se_4$  and that of a classic Au<sup>III</sup>-containing compound ([AuCl<sub>4</sub>]<sup>-</sup>). Their patterns are unambiguously different, especially the well-defined characteristic absorption peak of [AuCl<sub>4</sub>]<sup>-</sup> (at 291 nm) corresponds to a shoulder (around 300 nm) for  $Au_4Se_4$ . Similar observations are made for  $Au_4Se_4$  in a pH 6.2 nitrate medium. In both media,  $Au_4Se_4$  undergoes slow transformation as a function of time in agreement with NMR and MS results. However, in the nitrate medium, even with  $Au_4Se_4$  concentration as low as 8.2 x 10<sup>-5</sup> M, the decomposition is less than 2.6% after one hour. Thus, the time window during which  $Au_4Se_4$  is stable in this medium is largely sufficient for its cyclic voltammetric characterisation.



**Fig. S7**. UV-vis absorption spectra recorded in water with a 0.1 cm optical path quartz cuvette: A)  $4.3 \times 10^{-4}$  M Au<sub>4</sub>Se<sub>4</sub>; B) superposition of the spectra of Au<sub>4</sub>Se<sub>4</sub> and [AuCl<sub>4</sub>]<sup>-</sup>.

#### **11. Electrochemistry**

We performed solution cyclic voltammetry (CV) of 8 x  $10^{-4}$  M Au<sub>4</sub>Se<sub>4</sub> in a pH 6.2 medium (0.4 M NaNO<sub>3</sub> + NaOH). The CV scan for Au<sub>4</sub>Se<sub>4</sub> reduction at a bare glassy carbon electrode is characterized by a well-defined reduction wave (at +0.250 V vs. SCE) associated, on the reversal potential scan, with a crossover loop (Figure S8). These observations are attributed to the reduction of the Au<sup>III</sup> centers within Au<sub>4</sub>Se<sub>4</sub>. The crossover loop signifies that the current keeps increasing during this backward scan. This CV features the characteristic fingerprint for film formation and growth on electrodes.<sup>6</sup> Such observation is due to the larger overpotential necessary for gold nucleation on the bare glassy carbon compared to that of gold deposition on the gold film. An important positive peak potential shift of 0.350 V is observed for [AuCl<sub>4</sub>]<sup>-</sup> when compared to Au<sub>4</sub>Se<sub>4</sub> in the same medium. In other words, the complexation of Au<sup>III</sup> centers in Au<sub>4</sub>Se<sub>4</sub> is stronger. The CVs reveal that no new species was detected at the time scale of CV characterization. This observation is in agreement with UV-vis spectroscopy results.

![](_page_14_Figure_1.jpeg)

**Fig. S8**. Cyclic voltammograms (CV) of 8 x  $10^{-4}$  M Au<sub>4</sub>Se<sub>4</sub> in a pH 6.2 medium (0.4 M NaNO<sub>3</sub> + NaOH). The scan rate was 10 mV s<sup>-1</sup>. A) First CV pattern on bare glassy carbon electrode (GC); B) CV run after deposition of a thin film of gold on the GC upon repeated cycling.

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