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SUPPLEMENTARY INFORMATION

Establishing XANES Signatures of Rhenium Oxidation States: A Combined Theoretical and Experimental Reference Study for Analytical Applications

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1 Synthesis of the materials

Synthesis of HprzReO₄ and (Hprz)₂Re₄O₁₅

Pyrazolium perrhenate was prepared by a modification of the procedure described in [1]. Crystalline Re_2O_7 was dissolved in purified water (TOC > 3 ppm, ℧ > 18 kOm). The prepared rhenium acid with a concentration of 1 M was added to dry pyrazole (99.9% MACKLIN (China)) in a threefold excess of pyrazole. The aqueous solution was left to evaporate at room temperature (20-23 °C) for several days on a watch glass (humidity of about 50%). After two days (48 h), crystals were found on the walls of the watch glass, phase analysis confirmed the formation of pyrazolium perrhenate (Figure S1). The solution remaining in the watch glass was transferred to an evaporating dish of 2 ml and placed in a vacuum desiccator with a lining of calcined calcium chloride. After three hours, the resulting crystals were separated from the mother liquor and dried on filter paper in a vacuum. X-ray phase analysis of the resulting material confirmed the formation of pyrazolium polyrhenate (Figure S2). Elemental analysis for these compounds was not performed.

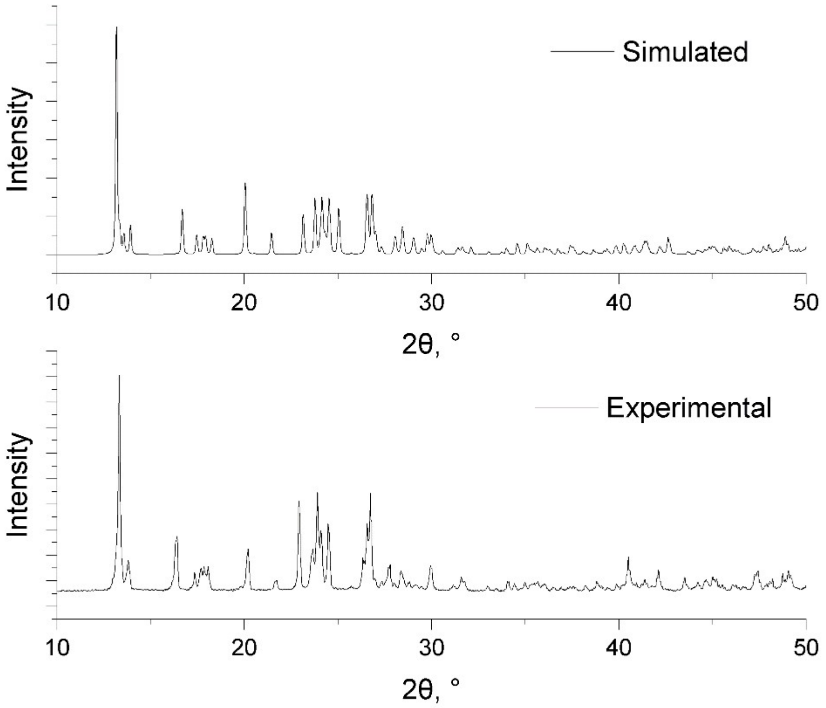

Figure S1. X-ray phase analysis of the obtained pyrazolium perrhenate $HprzReO_4$

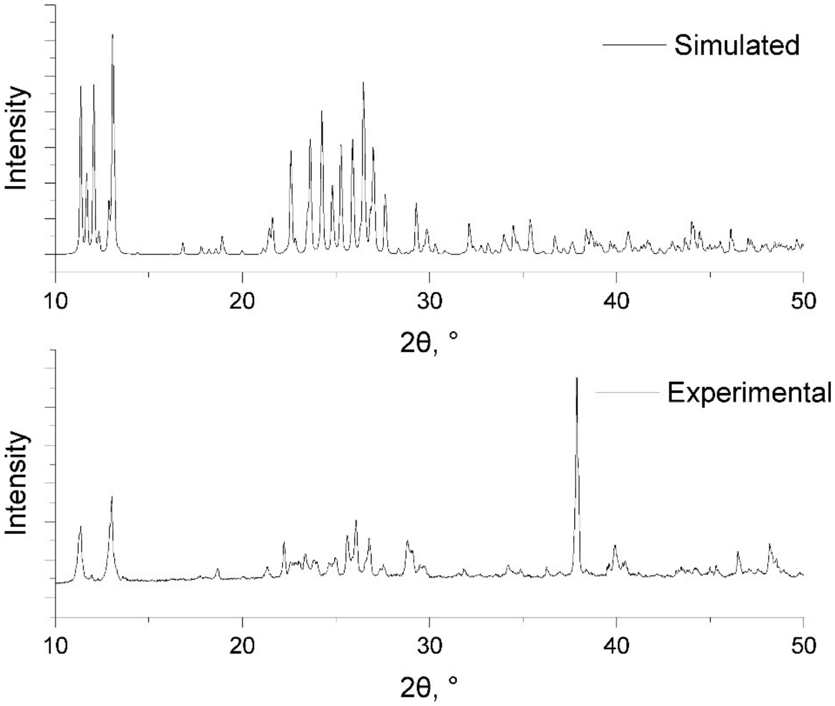

Figure S2. X-ray phase analysis of the obtained pyrazolium polyrrhenate $(Hprz)_2Re_4O_{15}$

Synthesis of ReO_3Br(o-phen)

The compound was prepared exactly according to the method described in the work [2]. 0.5 grams of ammonium perrhenate (https://chemcraft.ru (RU)) was dissolved in 5 ml of 5 M HBr (https://rushim.ru (RU)). 1 g of o-phenanthroline is dissolved in 30 ml of glacial acetic acid separately. When mixing the solutions, a yellow precipitate was formed. The resulting product was washed with ethanol, then with ether and dried on a watch glass. X-ray phase analysis of the obtained material in comparison with the diffraction pattern generated on the basis of the cif-file confirmed the identity of the products (Figure S3). The product yield was lower than in the cited method and amounted to about 50%. Elemental analysis for ReO_3Br(o-phen) calculated/found (%): Re 37.6/37.5; Br 16.2/16.1; C 29.14/30.3; N 5.7/5.6.

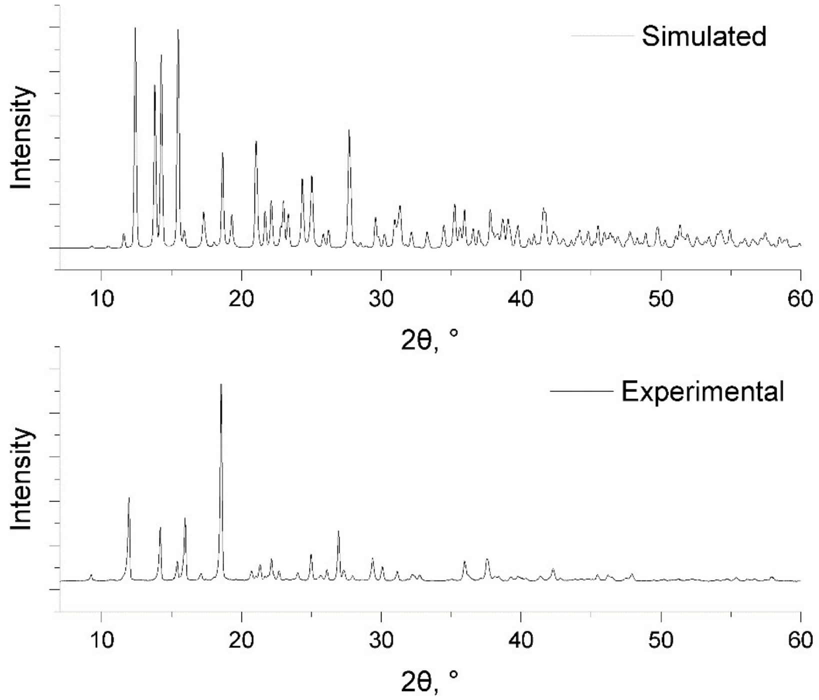

Figure S3. X-ray phase analysis of the complex ReO_3Br(o-phen).

Synthesis of NEt_4ReS_4

The compound was prepared according to the method described in the work [3]. 20 grams of crystalline sulfur (https://rushim.ru (RU)) and 70 ml of methanol (Sigma-Aldrich) were placed in a 200 ml flask. Gaseous ammonia (99.9% «Gasproduct» (RU)) was passed into the suspension with constant stirring for 30 minutes (flow rate of 200 ml/min) until a red solution was formed. Then the supply of ammonia was stopped and wet hydrogen sulfide (the gas was obtained by mixing sodium sulfide and sulfuric acid) was passed to an acidic reaction mixture. The solution was filtered through a paper filter. 4-5 g of Et_4NBr crystals were added to the resulting red solution and stirred until completely dissolved. Then 1 g of dry Re_2O_7 was added to the solution with vigorous stirring. The suspension was heated to 45-50 °C for 5 minutes and quickly filtered from the sediment. The red solution was left until a sediment was formed (24-48 hours). The resulting red crystals were washed with cold methanol and ether and dried in vacuum. The yield of the product was 40%. X-ray phase analysis of the obtained material showed high crystallinity of the material and good agreement with the diffraction pattern generated on the basis of the cif-file (Figure S4). Elemental analysis of the compound Et_4NReS_4 calculated/found (%): Re 41.9/41.9; S 28.8/28.7; C 21.6/22.2; N 3.2/3.0.

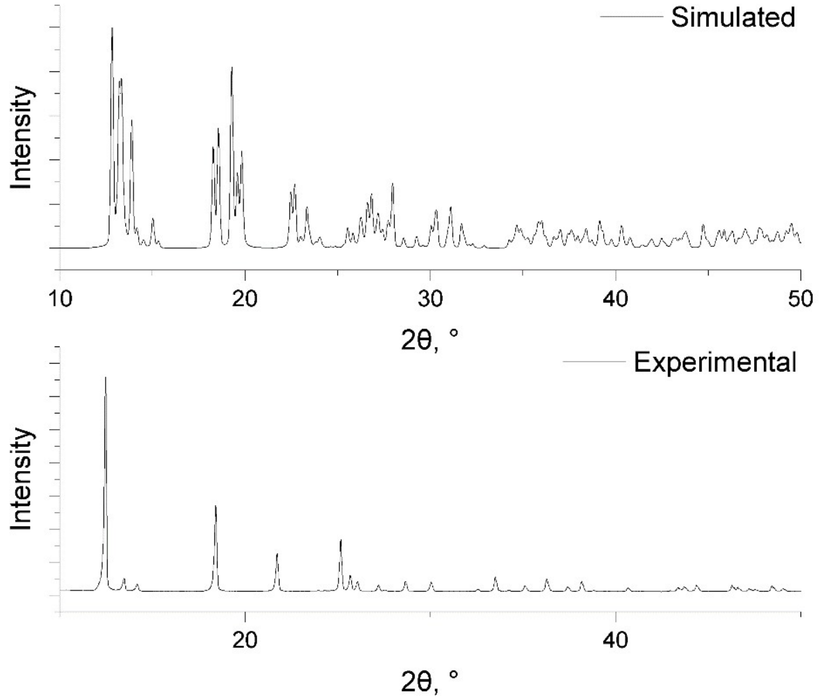

Figure S4. X-ray phase analysis of the NEt_4ReS_4.

Synthesis of $(NH_4)_2ReCl_6$

50 mg of ammonium perrhenate were dissolved in 5 ml of concentrated hydrochloric acid (12.5 M). A solution of $SnCl_2$ (https://rushim.ru (RU) in hydrochloric acid (12.5 M) was added dropwise until the color changed to a stable green. As soon as the emerald color of the solution was obtained, the addition of tin chloride was stopped, the mixture was heated to 60°C and settled overnight at room temperature. After 24 hours, green crystals of the product were obtained, washed in turn with hydrochloric acid, methanol and ether. Dried in air. According to X-ray phase analysis (Figure S5), the product is identical to the previously described $(NH_4)_2ReCl_6$ [4]. Elemental analysis of the material was not carried out. Yield 85%.

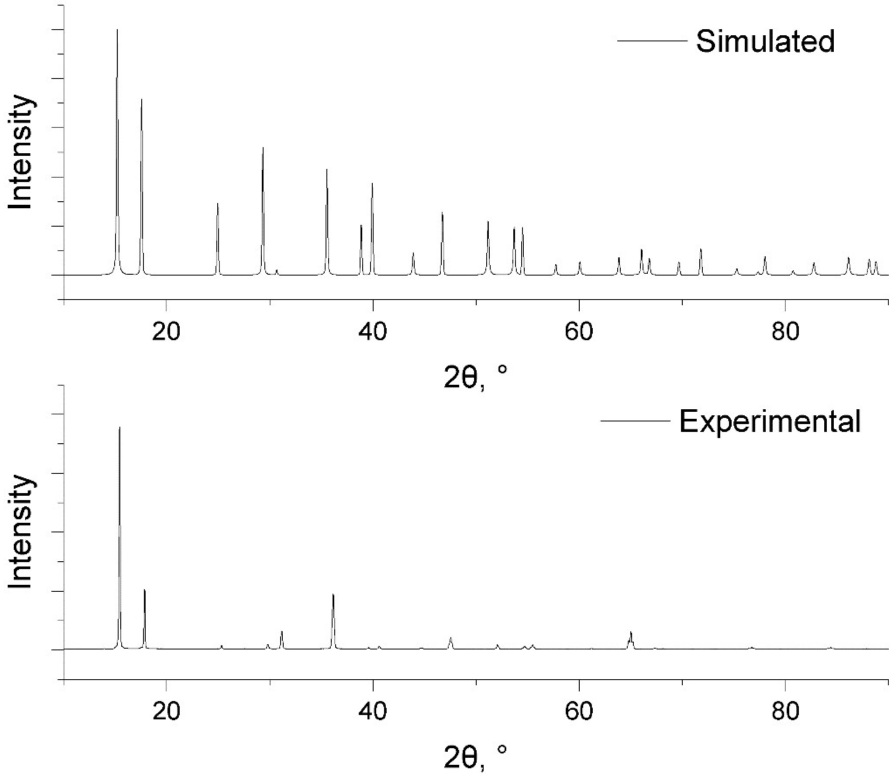

Figure S5. X-ray phase analysis of the $(NH_4)_2ReCl_6$.

Synthesis of $Lu(ReO_4)_3 \cdot nH_2O$

Lutetium nitrate (https://chemcraft.ru (RU)) was dissolved in distilled water and ammonium hydroxide was added until a white precipitate formed. The precipitate was centrifuged and washed with water, centrifuged again, decanted and dissolved in a minimum volume of rhenium acid (1 M). The resulting solution was left to dry on a watch glass for several days. The resulting crystals were separated from the solution after two days and transferred for analysis. The product yield was 50%. X-ray phase analysis showed a match with the product described earlier [5], however, an admixture of another phase was detected in the material (Figure S6). Elemental analysis of $Lu(ReO_4)_3 \cdot nH_2O$ found (%): Lu 18.8; Re 50.5; O 32.1. Elemental analysis corresponds to $Lu(ReO_4)_3 \cdot 10H_2O$, suggesting that the material contains both the previously known perrhenate and a more hydrated form.

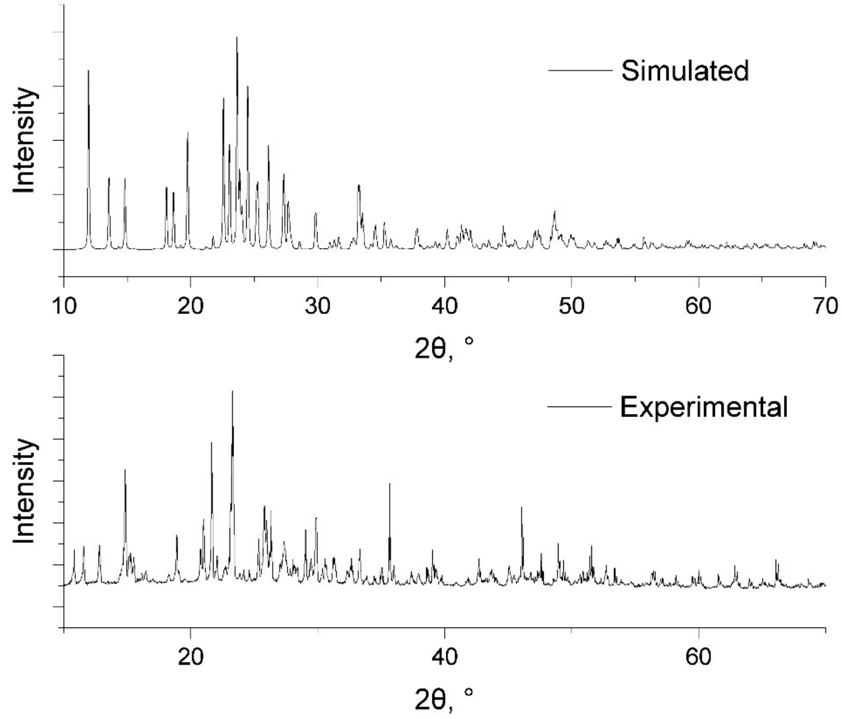

Figure S6. X-ray phase analysis of the $Lu(ReO_4)_3 \cdot nH_2O$.

Synthesis of Re_2O_7

Metallic rhenium was placed in an alundum crucible and heated in a tubular furnace at 600 °C in a flow of pure oxygen (flow 200 ml/minute). Furnace was heated until the material in the crucible was completely burned. The resulting green needles were collected in ampoules without access to air. The yield of the product was not assessed; however, it can be considered close to quantitative. X-ray phase analysis in a sealed holder showed good agreement with theoretical data [6] (Figure S7).

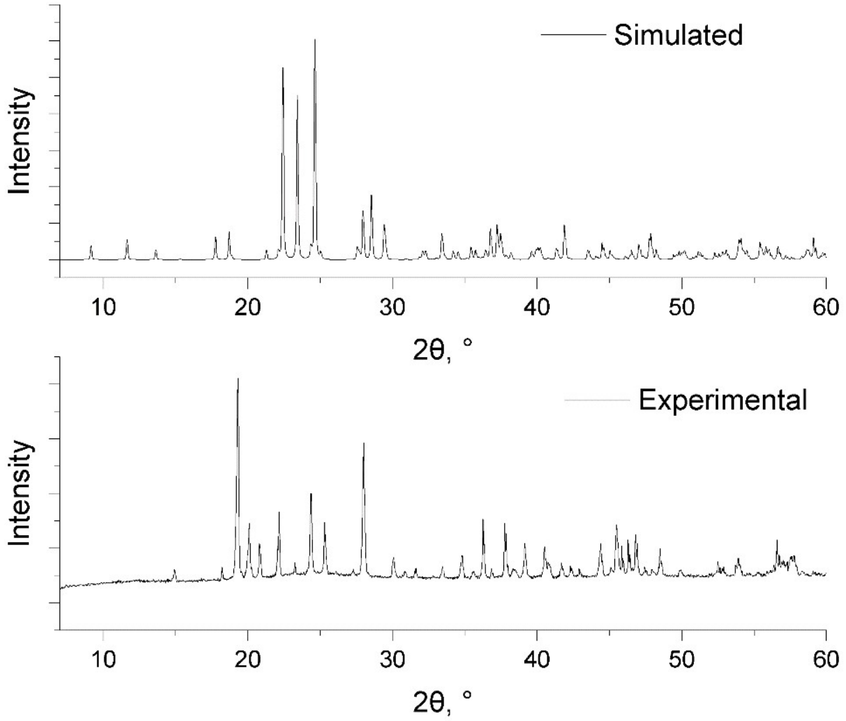

Figure S7. X-ray phase analysis of the Re_2O_7.

Synthesis of $Re_3Cl_9(pyr)_3$

Re_3Cl_9 was dissolved in 10 ml of dry acetonitrile and crystalline pyrazine (MACKLIN) was added to the mixture in a five-fold molar excess of rhenium. The solution was left for a day (24 hours) until a precipitate formed. The resulting crystals were washed with acetonitrile and dried in air. X-ray phase analysis showed excellent agreement with previously known material [7] (Figure S8). Elemental analysis of the compound $Re_3Cl_9(pyr)_3$ calculated/found (%): Re 49.5/50.0; Cl 28.6/28.6; C 12.9/13.0; N 7.5/7.6.

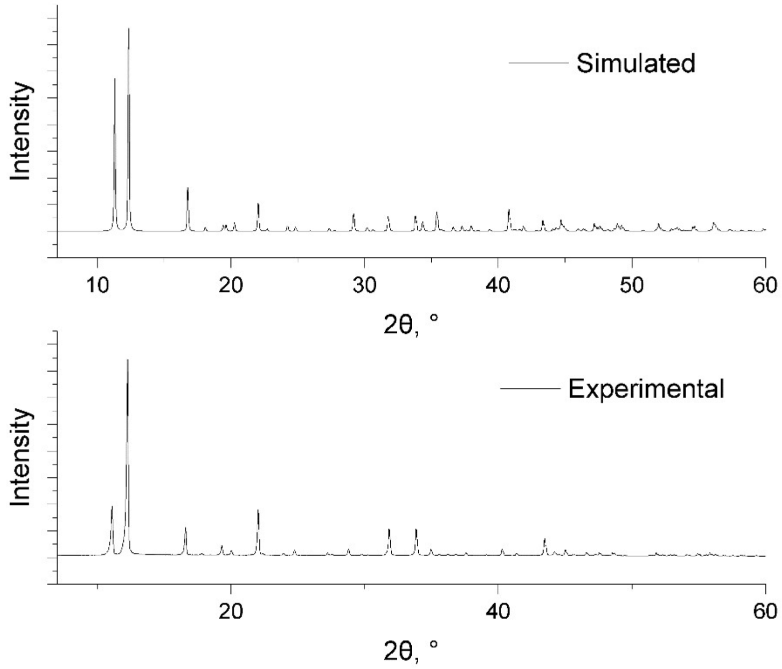

Figure S8. X-ray phase analysis of the $Re_3Cl_9(pyr)_3$.

Synthesis of Re_3I_9

Re_2O_7 1 g was placed in 30 ml of concentrated hydroiodic acid solution (https://chemcraft.ru (RU)). The solution was evaporated with constant stirring to 5 ml. The resulting precipitate was washed with a fresh solution of hydroiodic acid, cold methanol, chloroform and ether. The precipitate was dried in air. X-ray phase analysis showed good agreement with previously known material [8] (Figure S9). Elemental analysis was not performed. The yield is estimated as 60%.

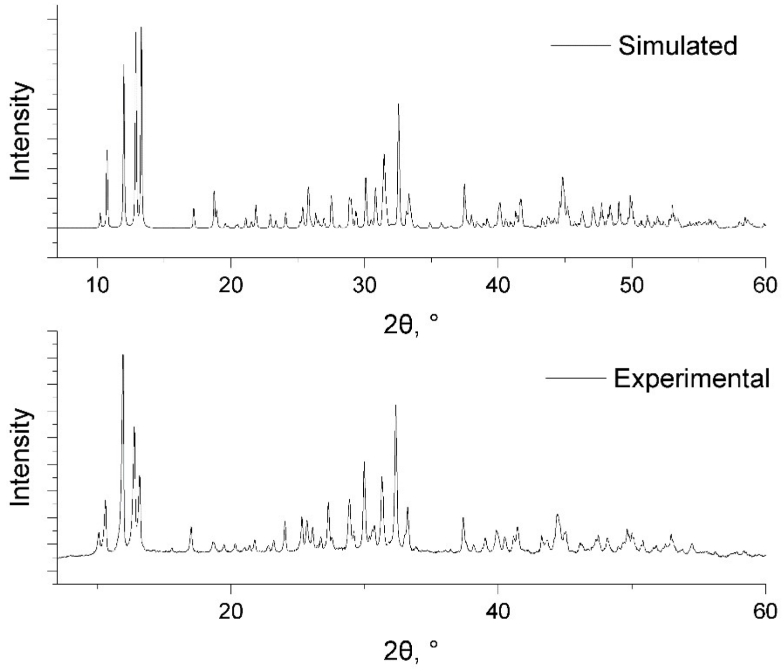

Figure S9. X-ray phase analysis of the Re_3I_9.

Synthesis of ReO_2

Ammonium perrhenate was placed in a quartz crucible and heated in a furnace in a stream of purified argon (200 ml/min) at 700 °C. The resulting black material, according to X-ray phase analysis (Figure S10), is rhenium dioxide [Wyckoff, R.W.G. (1963) Second Edition. Interscience Publishers, New York Note: Cadmium Iodide Structure. Crystal Structure, 1, 239-444]. Elemental analysis of the product has not been performed.

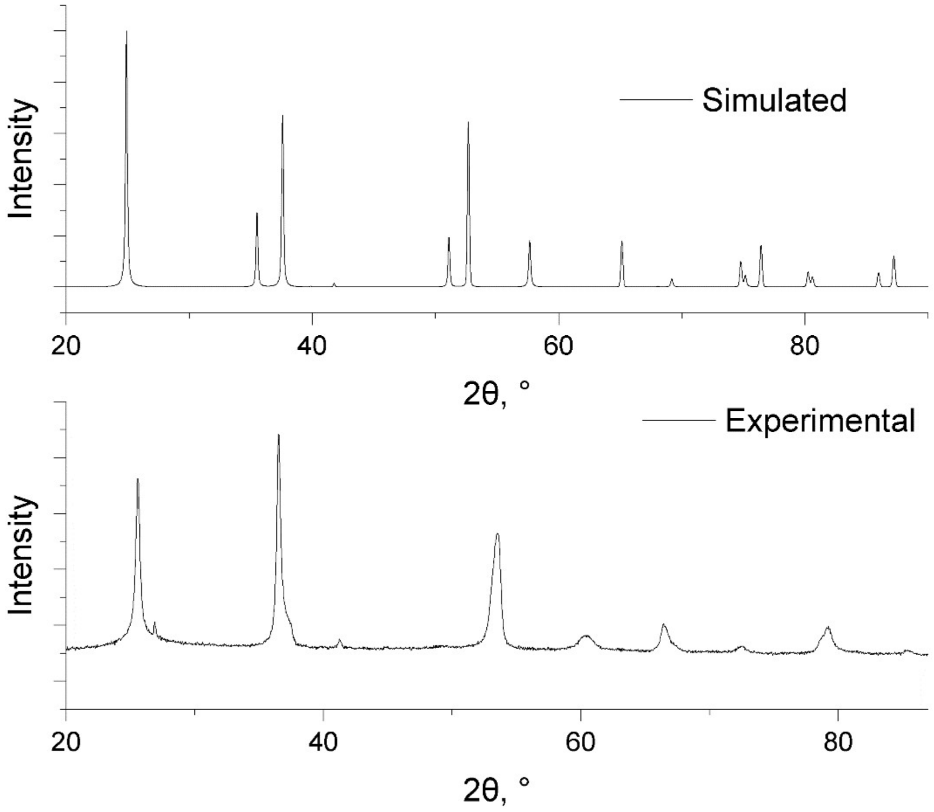

Figure S10. X-ray phase analysis of the ReO_2.

Synthesis of ReO_3

Metallic rhenium was placed in a quartz crucible and heated in a furnace in an oxygen flow (50 ml/min) at 500 °C. When crystals of Re_2O_7 appeared on the cold walls of the quartz tube, the heating was stopped and the oxygen flow was replaced with an argon flow. After the crucible cooled, the red material was transferred to a beaker and washed with water, methanol and ether. X-ray diffraction analysis showed compliance with the previously known product ReO_3 [9] with a slight admixture of ReO_2 (Figure S11). Elemental analysis of the product has not been performed.

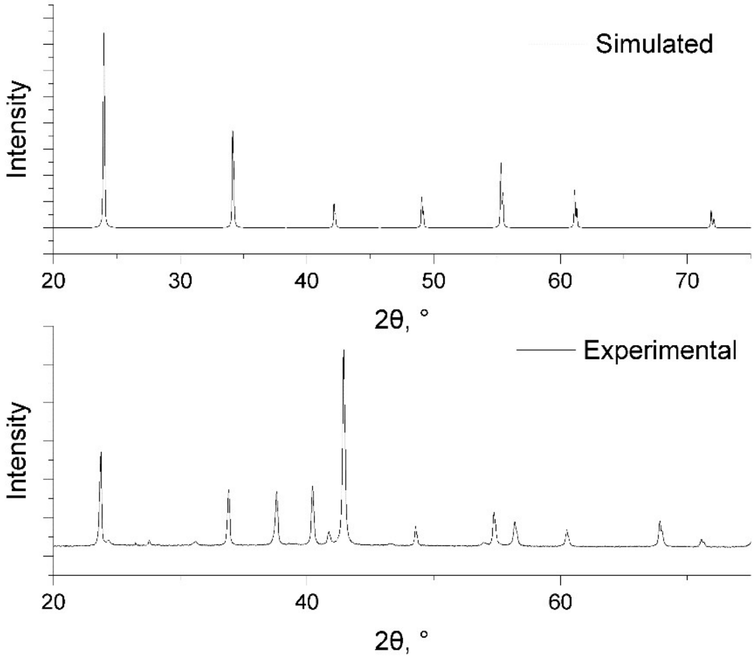

Figure S11. X-ray phase analysis of the ReO_3.

Synthesis of $ReOCl_3(PPh_3)_2$

50 mg of ammonium perrhenate were dissolved in 3 ml of concentrated hydrochloric acid (12.5 M) and diluted to 30 ml with glacial acetic acid. To the solution was added 1 g of triphenylphosphine as a solution in glacial acetic acid (5 ml). The mixture was stirred on a magnetic stirrer for 5 minutes and left overnight to precipitate. According to X-ray phase analysis (Figure S12), the resulting green material was $ReOCl_3(PPh_3)_2$ [10]. Elemental analysis was not performed.

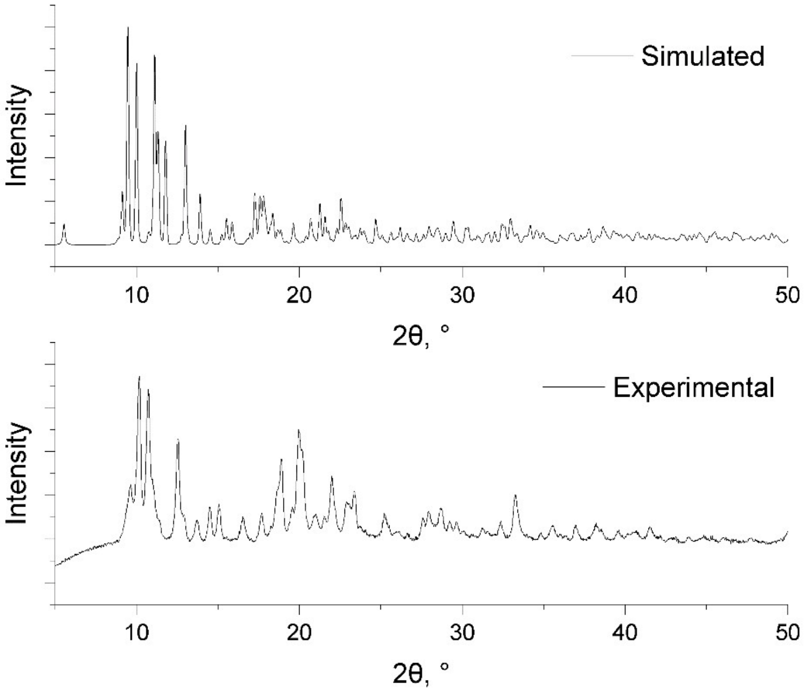

Figure S12. X-ray phase analysis of the $ReOCl_3(PPh_3)_2$.

Synthesis of rhenium metal

Ammonium perrhenate was placed in an alundum crucible and heated in a furnace in a flow of argon-hydrogen mixture (7% hydrogen) (Moscow Gas Processing Plant, Russia) at 1000 °C. Heating was continued for 2 hours, the crucible was cooled in the furnace also in a flow of argon-hydrogen (flow rate 150 ml/min). The resulting gray material, according to X-ray phase analysis (Figure S13), was pure metallic rhenium [11].

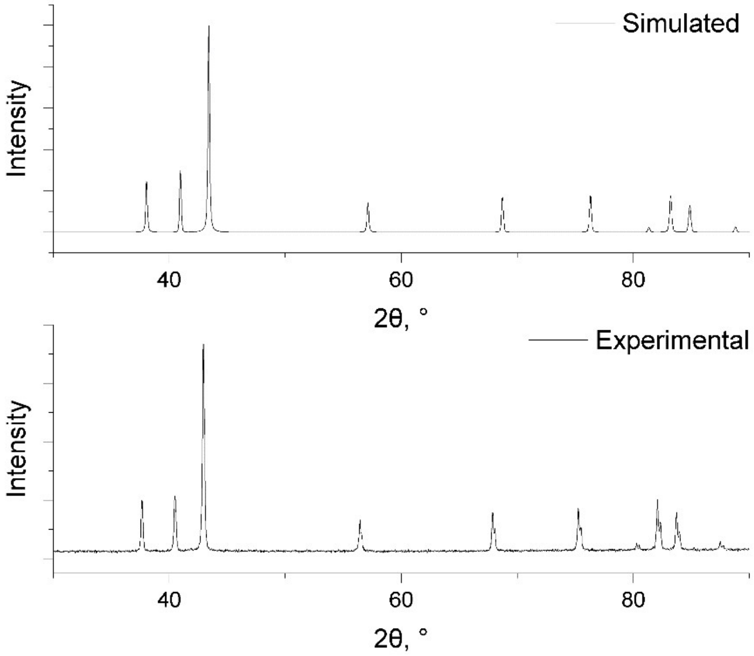

Figure S13. X-ray phase analysis of the Re-metal.

Synthesis of $ReOCl_4(H_2O)$

The product was obtained by the solvothermal method. 5 µl of rhenium acid (5 M) was placed in a thick glass test tube. 500 µl of carbon tetrachloride were added to the acid. The resulting heterogeneous mixture was sealed in an ampoule and heated to 200 °C for 24 hours. The resulting crystals were sensitive to atmospheric moisture. The product was a set of dark red crystals with a metallic luster. The resulting crystals, immediately after opening the ampoule in liquid nitrogen, were placed in a Schlenk apparatus, purged with argon and dried in a vacuum. Identification of the compound was carried out only by X-ray structural analysis of several crystals. Cell parameters: $Pn2_1a$, a = 10.84, b = 11.09, c = 5.53.

2 X-ray phase analysis of purchased compounds

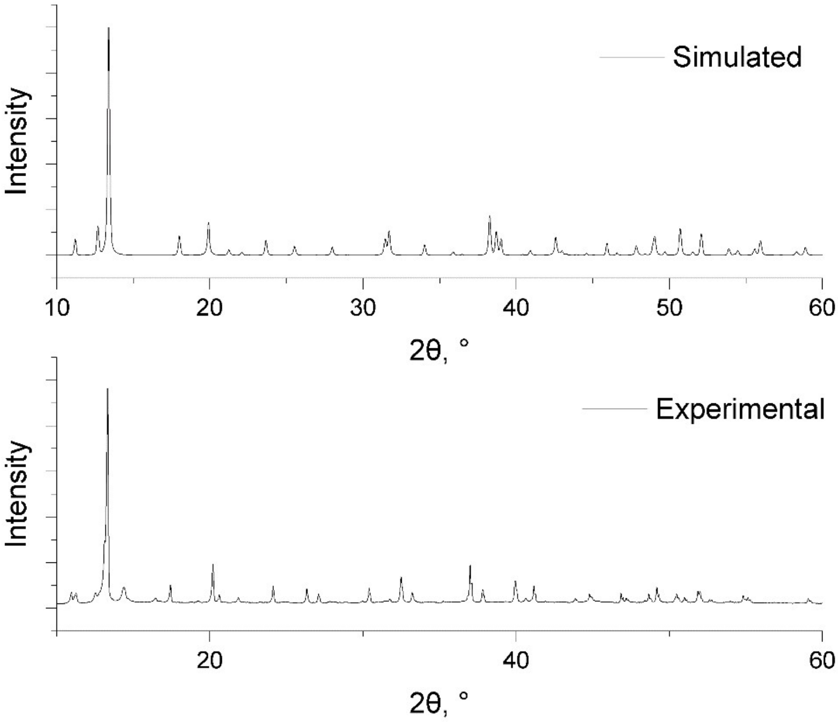

Figure S14. X-ray phase analysis of the Re_3Cl_9 (https://chemcraft.ru) [12].

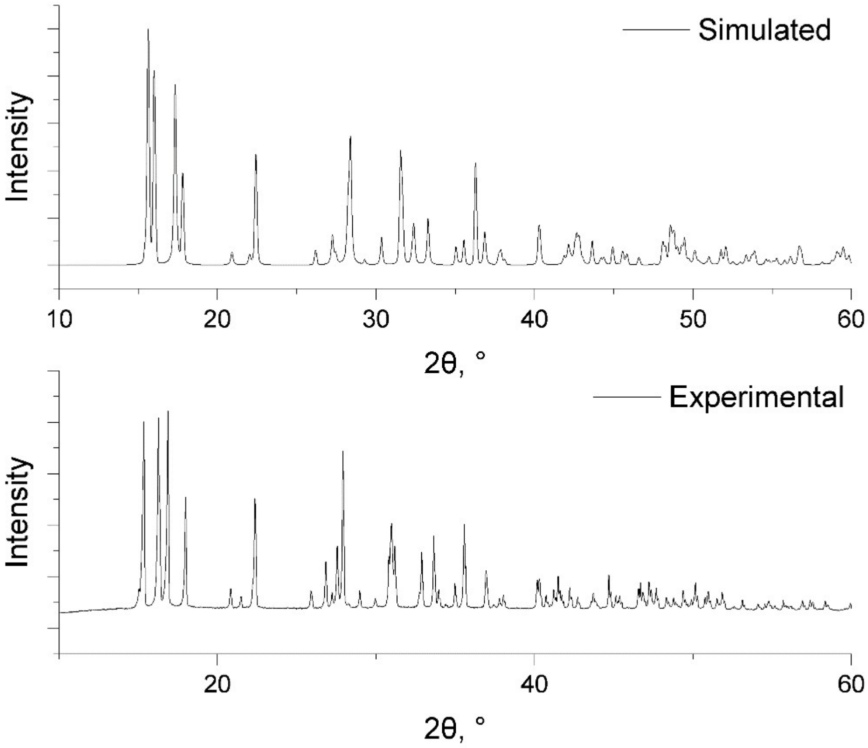

Figure S15. X-ray phase analysis of the $Re(CO)_5Br$ (https://rearus.ru) [13].

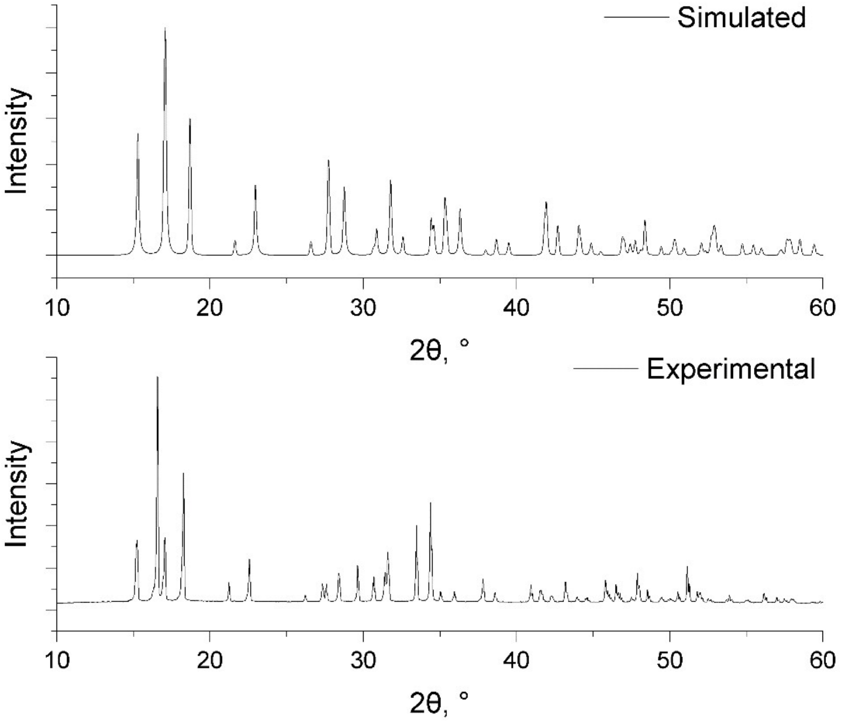

Figure S16. X-ray phase analysis of the $Re(CO)_5Cl$ (https://rearus.ru) [14].

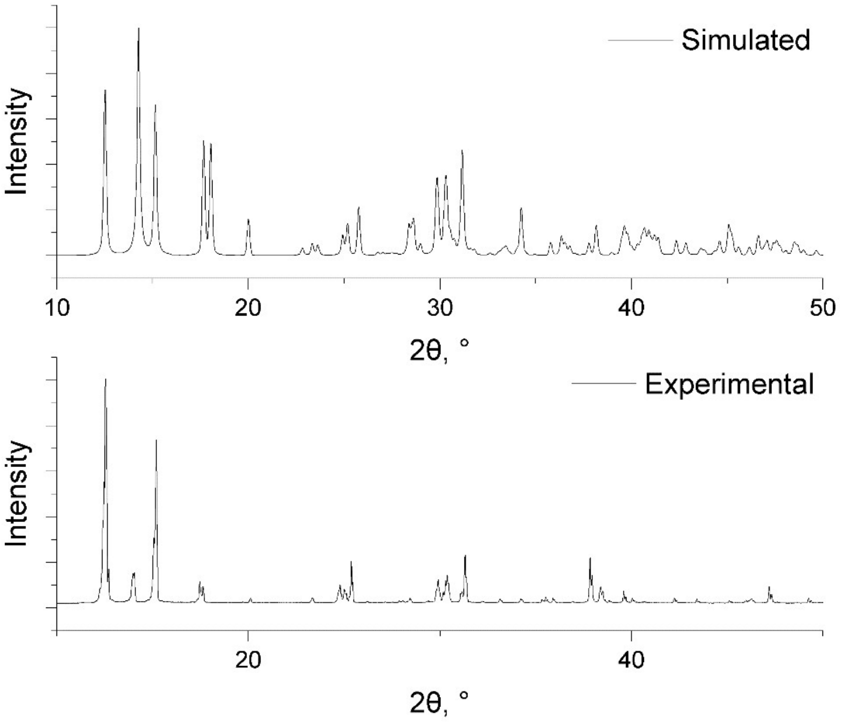

Figure S17. X-ray phase analysis of the $Re_2(CO)_{10}$ (https://rearus.ru) [15].

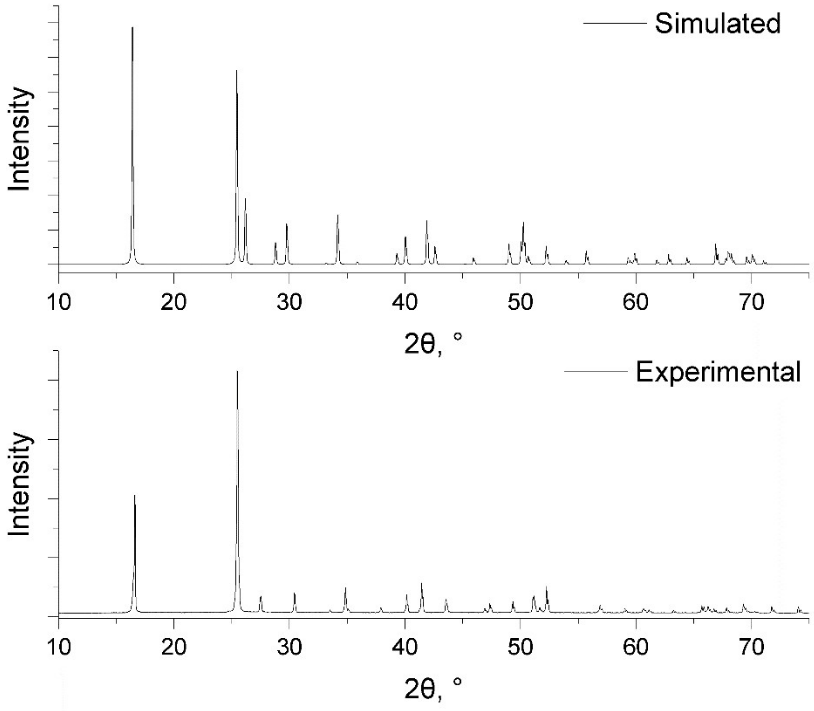

Figure S18. X-ray phase analysis of the NH_4ReO_4 (https://chemcraft.ru) [16].

The cluster $Cs_3Re_6S_7Br_7$ was submitted for X-ray spectroscopy by the compound's authors. The structure and synthesis method are described in [17]. The X-ray phase analysis is shown in **Figure 19.**

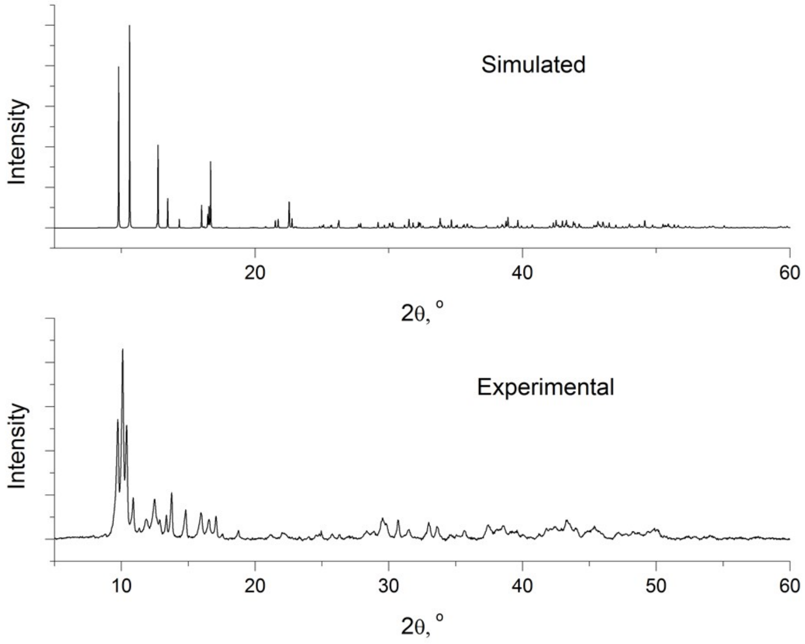

Figure S19. X-ray phase analysis of the $Cs_3Re_6S_7Br_7$ (https://materials.springer.com/isp/crystallographic/docs/sd_1720870) [17].

3 XANES L_3 and L_1 edge absorption spectra

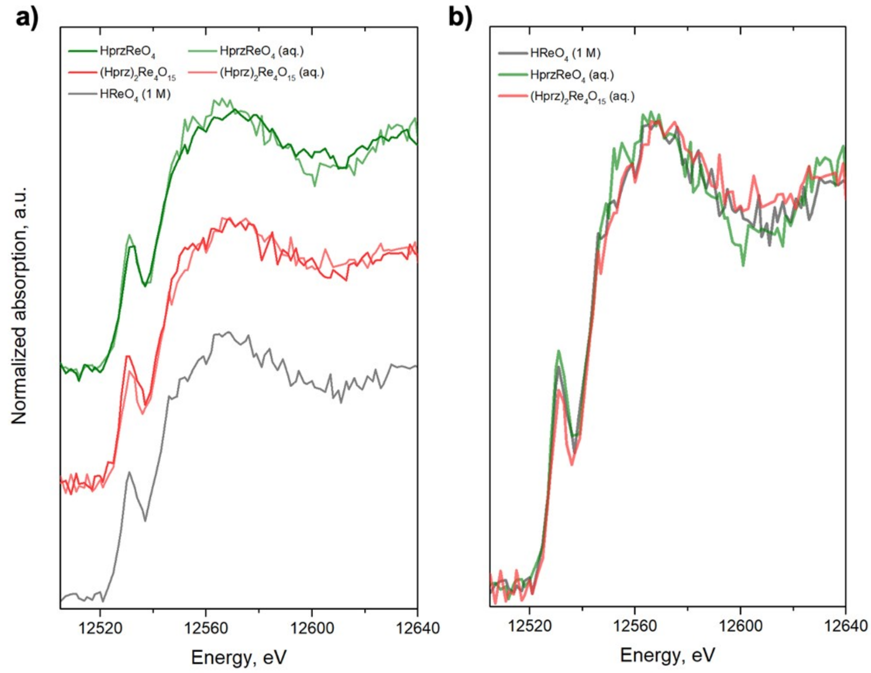

Figure S20. Re L_1 edge XANES spectra of Re_2O_7, ReO_4^- and $Re_4O_{15}^{2-}$ salts and their aqueous solutions (a, b).

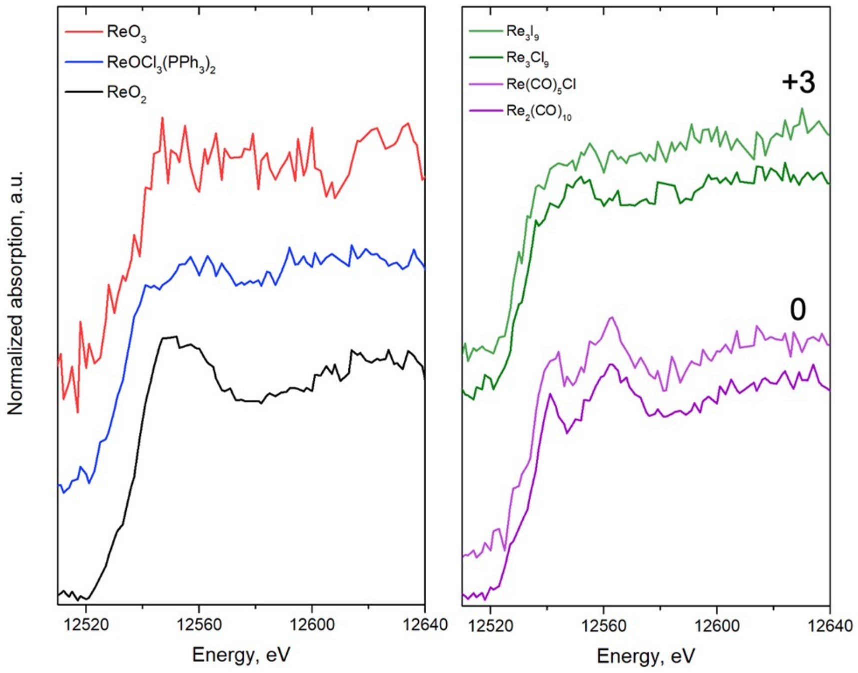

Figure S21. Re L_1 edge XANES spectra of ReO_3, $ReOCl_3(PPh_3)_2$, ReO_2 (a) and Re_3Cl_9, Re_3I_9, $Re(CO)_5Cl$, $Re_2(CO)_{10}$ (b).

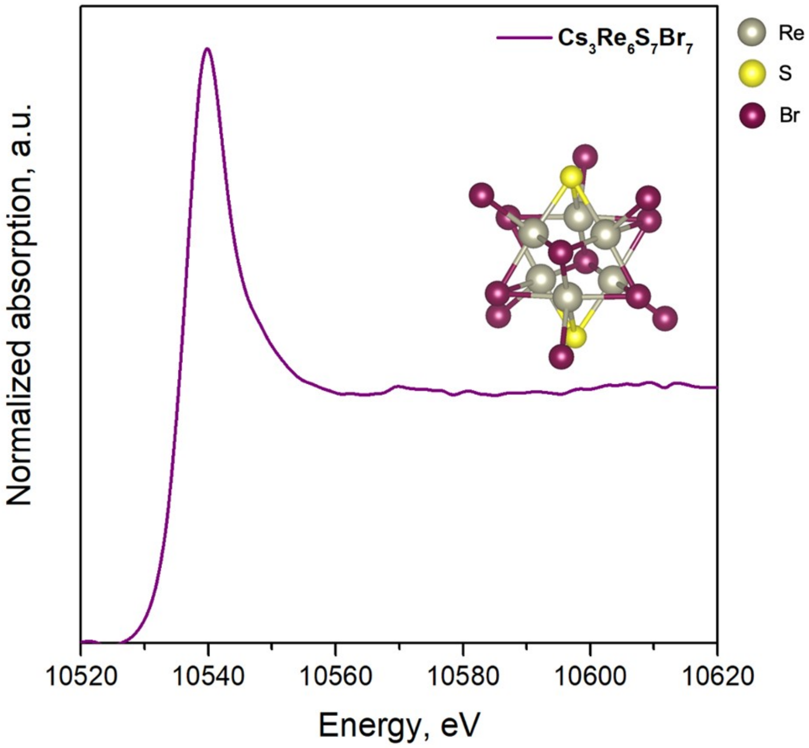

Figure S22. Re L_3 edge XANES spectrum of hexanuclear cluster $Cs_3Re_6S_7Br_7$. Insertion: structural representation of the cluster.

4 White line and inflection points at the Re L_3 edge spectra

Table S1. The positions of the white line and inflection points at the Re L_3 edge for compounds with formal oxidation state (o.s.) of rhenium from +7 to 0.

Sample	Formal o.s.	White line position, eV	Inflection point, eV	Coordination charge	Calc Re charge
Re_2O_7	+7	10542.9	10538.8	4.45	
$HReO_4$	+7	10542.9	10539.0	4.45	
$HprzReO_4$	+7	10542.6	10539.8	4.45	1.97
$(Hprz)_2Re_4O_{15}$	+7	10542.7	10539.8	4.45	2.10
ReO_3Br(o-phen)	+7	10542.6	10539.4	3.49	1.68
NEt_4ReS_4	+7	10540.5	10537.3	1.52	0.69
ReO_3	+6	10541.9	10536.1	3.81	2.17
$ReOCl_4$	+6	10542.0	10539.0	2.60	
$ReOCl_3(PPh_3)_2$	+5	10540.7	10536.1	1.53	
ReO_2	+4	10541.4	10539.1	2.54	
$(NH_4)_2ReCl_6$	+4	10540.0	10537.0	1.33	
Re_3Cl_9	+3	10540.6	10537.8	0.99	0.34
$Re_3Cl_9(pyr)_3$	+3	10540.2	10537.3	0.99	

Re_3I_9	+3	10539.5	10536.0	0.40	0.08
$Re(CO)_5Cl$	+1	10541.8	10538.8		-0.20
$Re(CO)_5Br$	+1	10541.8	10538.8		
$Re_2(CO)_{10}$	0	10541.8	10538.8		-0.47
Re	0	10540.8	10535.0		0

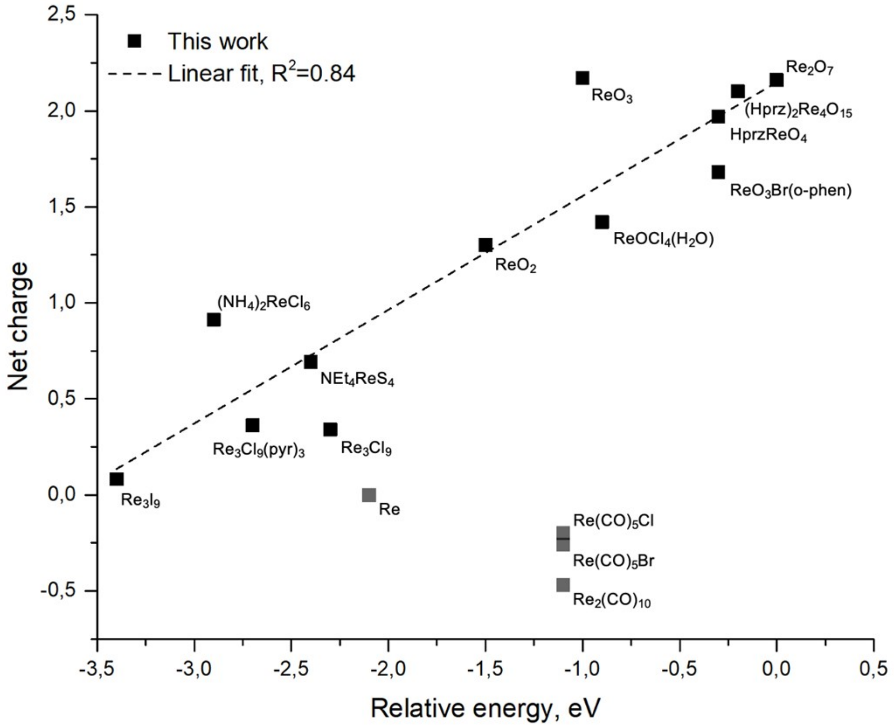

Figure S23. The plot of the relative energy of the white line (0 eV corresponds to Re_2O_7) against the calculated charge calculated using PBE exchange-correlation functional. Grey data points were not included in the linear fit.

5 Calculation of the coordination charge

The ionicity of a bond *k* (i_k) was determined according to the equation

$$i_k = 1 - e^{\left(-\frac{1}{4}\cdot(\chi_{Re}-\chi_k)^2\right)} \qquad (1),$$

where χ_{Re} and χ_k are electronegativities of rhenium and ligand *k*, respectively. We used Allred-Rochow, Pauling and Allen electronegativities. Total ionicity *i* was calculated as a weighted sum of i_k. Finally, the coordination charge η of rhenium in a given compound was obtained according to the equation:

$$\eta = Zi \qquad (2).$$

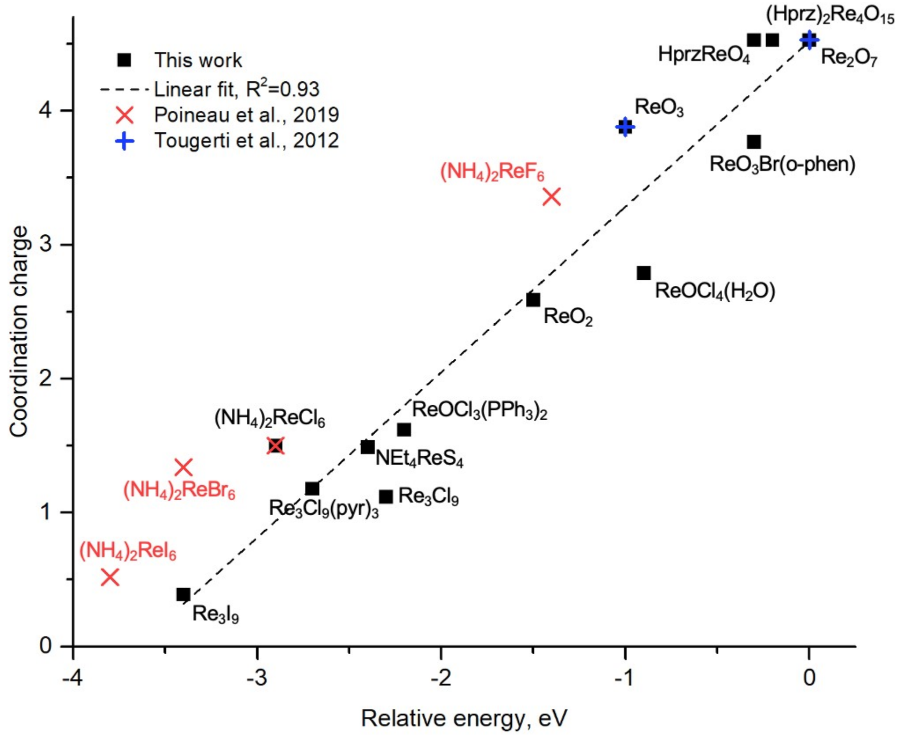

Figure S24. The plot of the relative energy of the white line (0 eV corresponds to Re_2O_7) against the coordination charge calculated using Allred-Rochow electronegativity scale. Literature data adopted from refs [18,19].

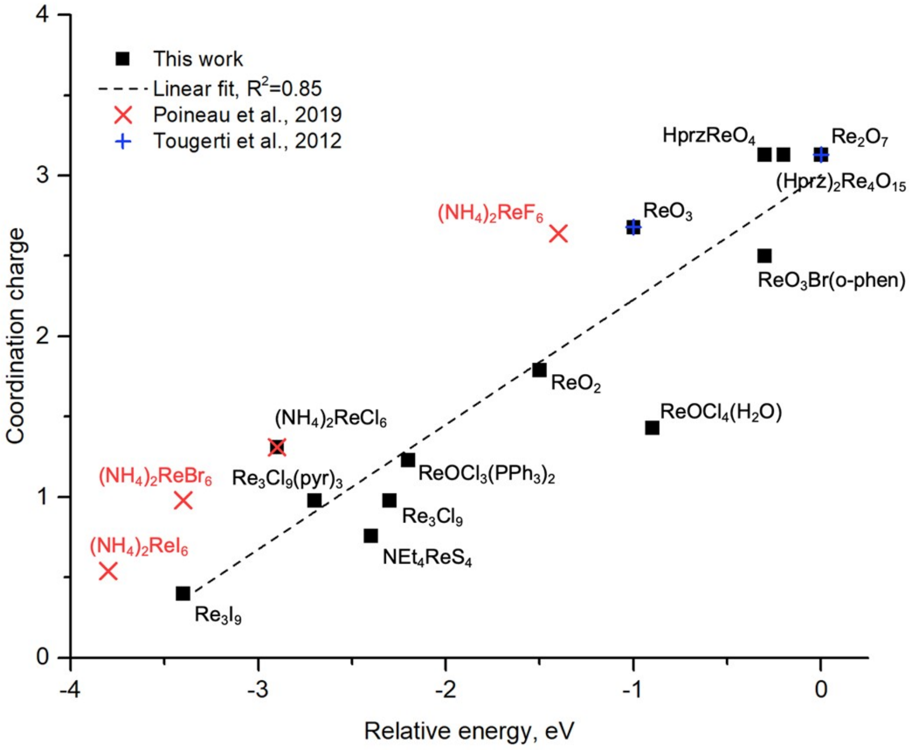

Figure S25. The plot of the relative energy of the white line (0 eV corresponds to Re_2O_7) against the coordination charge calculated using Pauling electronegativity scale. Literature data adopted from refs [18,19].

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