Multispin superatoms: seven-nuclear rhenium clusters with unusual magnetic properties

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Experimental Section.

Materials and methods. ReI_3 was prepared as described previously.[1] $RhCl_3 \cdot nH_2O$ was dried in a dynamic vacuum at 200°C for 20 minutes. Other reagents and solvents were used as received from commercial sources.

Electrospray ionization mass spectrometry (ESI-MS) was carried out at the Center of Collective Use «Mass spectrometric investigations» SB RAS with a high-resolution quadrupole time-of-flight mass spectrometer Bruker maXis 4G (negative ion mode, direct injection with automatic syringe at 180 µl/hour, voltage +2200 V, nebulizer pressure 1 bar, dry gas flow 4 L/min, dry gas temperature 180°C). UV/Vis spectra in the wavelength range 200–800 nm were recorded with an Agilent Cary 60 spectrometer. FT-IR spectra in KBr pellets were recorded with a Bruker Scimitar FTS 2000 spectrometer in the range 4000–400 cm^{-1}. Elemental analysis was performed on a Euro-Vector EA3000 Elemental Analyzer. Energy dispersion spectroscopy (EDS) was performed by the use of the Hitachi TM-3000 scanning electron microscope equipped with the Bruker Nano EDS analyzer. X-ray powder diffraction data were collected on a Philips APD 1700 instrument. Cyclic voltammetry was carried out with Elins P-20X8 voltammetry analyzer using three-electrode scheme with GC working, Pt auxiliary and Ag/AgCl/3.5M KCl reference electrodes. Investigations were carried out for $2.5 \cdot 10^{-3}$ M solutions of cluster compounds **1** and **2** in 0.1 M KCl in H_2O under Ar atmosphere. The rest potentials for the aqueous solutions of freshly prepared compounds **1** and **1′** ($E_{1/2}$ = 0.375 V) were found to be –0.005 V and 0.470 V, while the compounds **2** and **2′** ($E_{1/2}$ = 0.196 V) showed the corresponding values of –0.030 and 0.280 V, respectively, vs Ag/AgCl.

Preparation of $Cs_7[\{Re_3S_4(CN)_9\}\{Re_4S_4\}(CN)_9]\cdot 10H_2O$ (1): ReI_3 (0.300 g, 0.53 mmol), $RhCl_3$ (0.019 g, 0.09 mmol), S (0.017 g, 0.53 mmol) and KCN (0.207 g, 3.18 mmol) were mixed in a fused silica tube that was evacuated to 10^{-4} Torr and sealed. The tube was heated to 400°C, held at this temperature for 48 h and then cooled at a rate of 50°C/h. The products of the reaction were dissolved in boiled water and filtered. The brown solution was evaporated to about 3 mL and cooled to the room temperature. Crystallization with the addition of 200 mg CsCl resulted in the formation of brown prism crystal. The yield was 0.120 g (53%). EDS: Cs:Re:S = 7.3:7.0:8.2. Elemental analysis of $C_{18}H_{20}Cs_7N_{18}O_{10}Re_7S_8$: calcd (% mas.) C 6.9, H 0.6, N 8.0, S 8.1, found: C 7.1, H 0.4, N 8.1, S 8.3. IR (cm^{-1}) δ(OH) 1625, ν(CN) 2119, ν(OH) 3450. UV-Vis (H_2O): λ, nm (ε, $M^{-1}cm^{-1}$) 273 (25650), 303 (16950), 446 (8860).

Preparation of $K_7[\{Re_3Se_4(CN)_9\}\{Re_4Se_4\}(CN)_9]\cdot 15H_2O$ (2): Compound **2** was obtained similarly to **1** (excluding CsCl addition step) from ReI_3 (0.300 g, 0.53 mmol), $RhCl_3$ (0.019 g, 0.09 mmol), Se (0.042 g, 0.53 mmol) and KCN (0.207 g, 3.18 mmol). The yield of brown plate crystals was 0.142 g (64%).

EDS: K:Re:Se = 6.8:7.0:8.1. Elemental analysis of $C_{18}H_{30}K_7N_{18}O_{15}Re_7Se_8$: calcd (% mas.) C 7.3, H 1.0, N 8.5, found: C 7,5, H 0,6, N 8,7. IR (cm^{-1}) δ(OH) 1625, ν(CN) 2125, ν(OH) 3444. UV-Vis (H_2O): λ, nm (ε, $M^{-1}cm^{-1}$) 258 (24700), 328 (13600), 459 (7800).

Oxidation of seven-nuclear complexes. In order to obtain oxidized forms of the seven-nuclear complexes, an aqueous solution of H_2O_2 was added dropwise to aqueous solutions **1** and **2** with stirring. The resulted dark-brown solutions were evaporated upon gentle heating until starting of precipitation of the brown powder, and then an excess of methanol was added leading to quantitative precipitation of **1′** and **2′**. Precipitates were washed with methanol and dried in air.

It is assumed based on magnetochemical data that the powder **1′** is composed of the mixture of $Cs_7[\{Re_3S_4(CN)_9\}\{Re_4S_4\}(CN)_9]$ (22 CVE) and $Cs_6[\{Re_3S_4(CN)_9\}\{Re_4S_4\}(CN)_9]$ (21 CVE), while the powder **2′** is almost completely consist of $K_6[\{Re_3Se_4(CN)_9\}\{Re_4Se_4\}(CN)_9]$ (21 CVE) with minor impurity of the non-oxidized anion (see "Magnetic properties" in Results and Discussion). Unfortunately, we were not able to obtain single crystals suitable for single-crystal X-ray diffraction analysis. From UV-Vis spectra (Fig. S1, S2) and powder diffraction patterns (Fig. S6, S6) we can see the changes that occur when the complexes are oxidized. In the UV-Vis spectra, oxidation causes a shift of the absorption band at ~ 450 cm^{-1} to the long wavelength region. All efforts in crystallization of the oxidized compounds from H_2O led to formation of polycrystalline powders, while attempts to carry out metathesis reactions with organic cations led to partial or complete reduction of the compounds.

Single-Crystal Diffraction Studies. Single-crystal XRD data (Table S1) were collected at 150K with a Bruker D8 Venture diffractometer with a CMOS PHOTON III detector and IμS 3.0 microfocus source (MoK_α radiation (λ = 0.71073 Å), collimating Montel mirrors). The crystal structures were solved using the SHELXT[2] and were refined using SHELXL[3] programs with OLEX2 GUI.[4] Atomic displacement parameters were refined anisotropically with the exception for O atoms of water molecules that show strong disorder. The hydrogen atoms were not located. The structures of the compounds were deposited to the Cambridge Crystallographic Data Centre (CCDC numbers 2374493 and 2374494).

DFT Calculations. Geometry optimization, single-point calculations and frequency calculations on optimized geometries of low-spin (LS, S = 0) and high-spin (HS, S = 1) $[\{Re_3S_4(CN)_9\}\{Re_4S_4(CN)_9\}]^{7-}$ and $[\{Re_3Se_4(CN)_9\}\{Re_4Se_4(CN)_9\}]^{7-}$ cluster anions were performed in ADF2022 program suite [5-6] with generalized gradient approximation (GGA) revPBE density functional,[7] all-electron STO's TZ2P basis set,[8] and zero-order regular approximation (ZORA)[9] to take into account scalar relativistic effects. The conductor-like screening model (COSMO)[10] was used to take into account the DMSO environment. The geometry optimization was performed first for each cluster in C_1 symmetry. The spin-restricted and spin-

unrestricted approximations were used for LS and HS clusters, respectively. Then, it was found that geometry of LS clusters is close to C_s symmetry and geometry of HS clusters is close to C_{3v} symmetry, so further optimization was performed using C_s symmetry for clusters with S = 0 (spin-restricted approximation) and C_{3v} symmetry for clusters with S = 1 (spin-unrestricted approximation). All optimized structures showed no imaginary frequencies. The optimized coordinates of the clusters are presented in Tables S1–S4. The calculated bond lengths for the clusters are listed in Table S11. Zero field splitting (ZFS) calculations were made for HS (S = 1) $[\{Re_3S_4(CN)_9\}\{Re_4S_4(CN)_9\}]^{7-}$ and $[\{Re_3Se_4(CN)_9\}\{Re_4Se_4(CN)_9\}]^{7-}$ cluster anions optimized in C_{3v} symmetry with revPBE density functional, TZ2P basis set and zero-order regular approximation. Spin-unrestricted approximation was applied. The exchange coupling constant J values were calculated as J = [E(HS)–E(LS)] / [–$S_{max}(S_{max}+1)$][11].

Magnetochemical analysis. Magnetic properties of polycrystalline samples were studied in the temperature range T = 1.77-300 K at magnetic fields H up to 10 kOe using a Quantum Design MPMS-XL SQUID magnetometer. The paramagnetic component of the molar magnetic susceptibility, $\chi_p(T)$, was determined by subtracting the contributions of temperature-independent core diamagnetism χ_d and ferromagnetism of trace impurities χ_F from the measured values of the total molar susceptibility $\chi=M/H$ (where M is the magnetization). The contribution χ_d was calculated according to the additive Pascal scheme, whereas field dependences $M(H)$ and temperature dependences $M(T)$ at different magnetic fields were measured to evaluate the ferromagnetic contribution χ_F, if any.

UV-Vis spectra

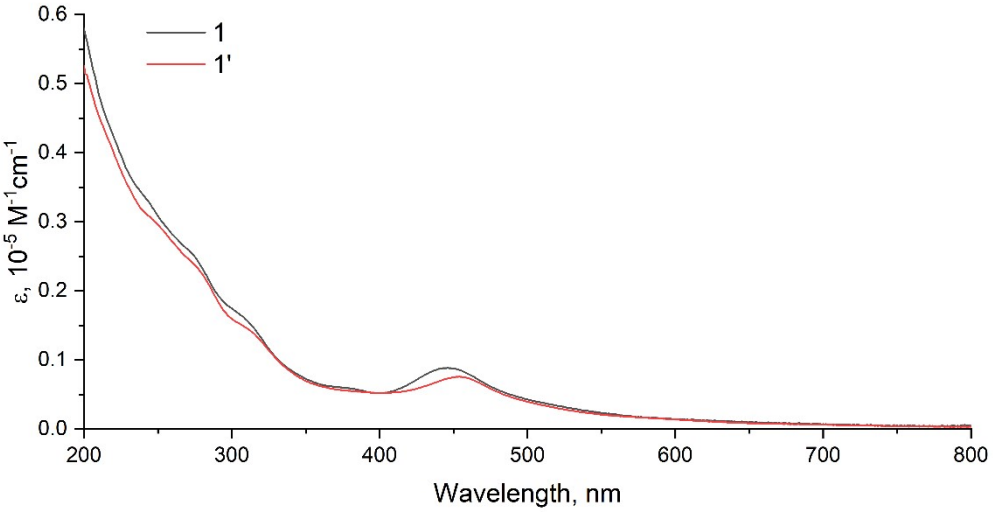


Fig S1. UV-Vis spectra of **1** and **1'** cluster complexes in aqueous solutions.

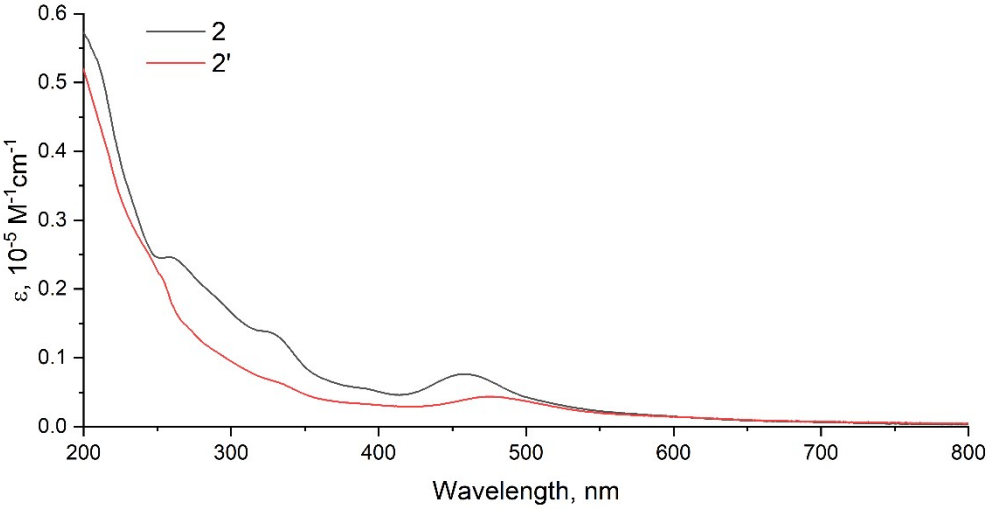


Fig S2. UV-Vis spectra of **2** and **2'** cluster complexes in aqueous solutions.

Crystal data and structure refinement

Table S1. Crystal data and structure refinement for the compounds **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{18}Cs_7N_{18}O_{10.1}Re_7S_8$	$C_{18}K_7N_{18}O_{15}Re_7Se_8$
Formula weight	3140.58	2947.38
Temperature/K	150(2)	150(2)
Space group	$R\bar{3}m$	$P\bar{1}$
a/Å	18.9117(5)	11.8882(3)
b/Å	18.9117(5)	12.4428(3)
c/Å	31.6241(8)	12.6100(3)
α/°	90	104.1560(10)
β/°	90	112.5240(10)
γ/°	120	104.9790(10)
Volume/Å^3	9795.1(6)	1536.14(7)
Z	6.00012	1
ρ_{calc}g/cm^3	3.174	3.186
μ/mm^{-1}	17.072	19.008
F(000)	8117.0	1314.0
Crystal size/mm^3	0.05 × 0.05 × 0.02	0.10 × 0.04 × 0.02
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.138 to 54.188	5.37 to 61.012
Index ranges	$-24 \le h \le 16$, $-23 \le k \le 23$, $-38 \le l \le 40$	$-18 \le h \le 18$, $-19 \le k \le 19$, $-19 \le l \le 19$
Reflections collected	14361	32723
Independent reflections	2574 [R_{int} = 0.0857, R_{sigma} = 0.0453]	11696 [R_{int} = 0.0449, R_{sigma} = 0.0521]
Data/restraints/parameters	2574/3/151	11696/12/393
Goodness-of-fit on F^2	1.103	1.115
Final R indexes [I>=2σ (I)]	R_1 = 0.0459, wR_2 = 0.1061	R_1 = 0.0450, wR_2 = 0.0844
Final R indexes [all data]	R_1 = 0.0547, wR_2 = 0.1123	R_1 = 0.0655, wR_2 = 0.0898
Largest diff. peak/hole / e Å^{-3}	2.01/-2.19	2.321/-2.406

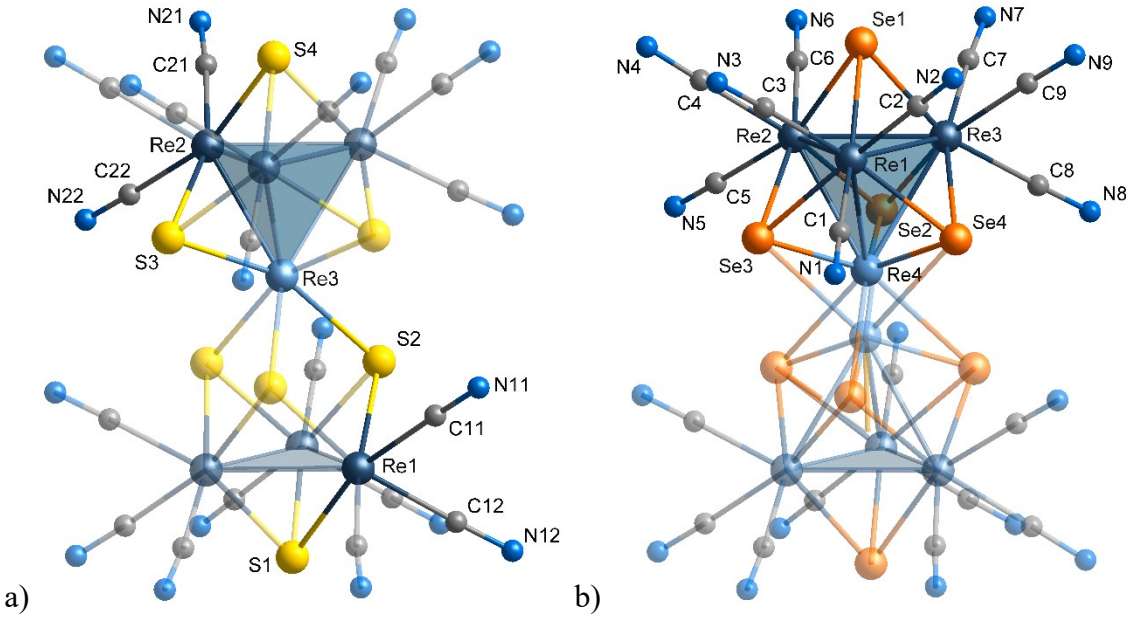


Fig. S3. Structure of clusters 1 and 2 in examples 1 (a; Se disorder not shown) and 3 (b; Re disorder not shown). The crystallographically dependent part is shown as translucent

Table S2. Crystallographically observed bond lengths (Å) within the $[\{Re_3Q_4(CN)_9\}\{Re_4Q_4(CN)_9\}]^{7-}$ (Q = S or Se) cluster anions

Bond	$[\{Re_3S_4(CN)_9\}\{Re_4S_4(CN)_9\}]^{7-}$	$[\{Re_3Se_4(CN)_9\}\{Re_4Se_4(CN)_9\}]^{7-}$
Re–Re $\{Re_3Se_4\}$	2.750(1)	2.785(2)
Re–Q (cap) $\{Re_3Se_4\}$	2.355(5)	2.463(4)
Re–Q (bridge) $\{Re_3Se_4\}$	2.371(3)	2.464(8)
Re–Re $\{Re_4Se_4\}$	2.750(7)	2.799(16)
Re–(μ_3-Q) $\{Re_4Se_4\}$	2.343(13)	2.472(11)
Re–Q (bridge) $\{Re_4Se_4\}$	2.500(4)	2.634(13)

Powder diffraction patterns

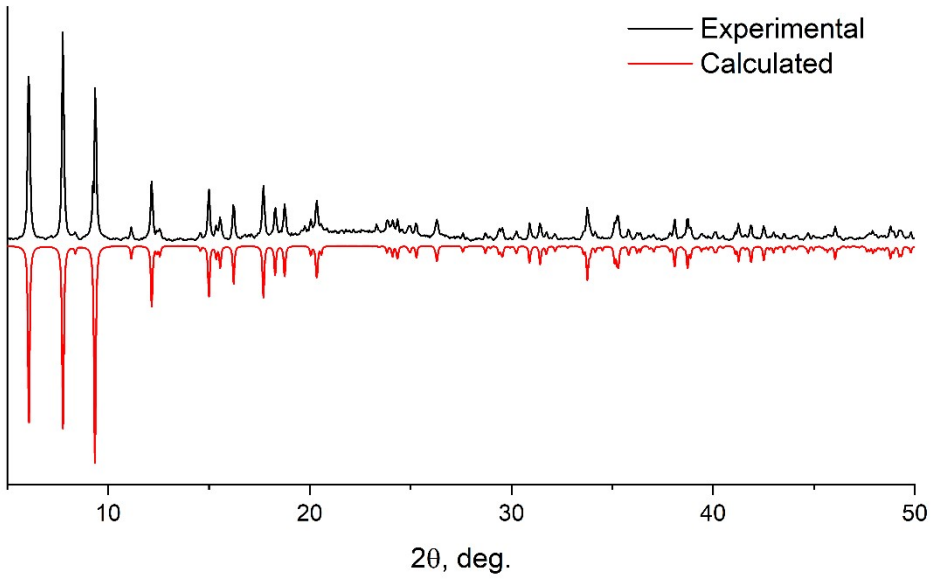


Fig S4. Experimental (top) *vs* calculated (bottom) powder diffraction pattern for compound **1**.

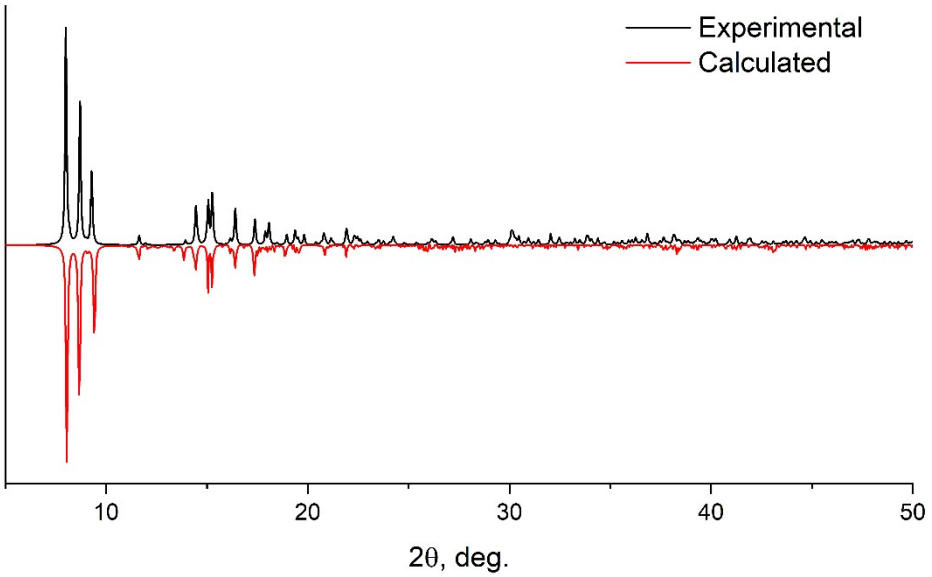


Fig. S5. Experimental (top) *vs* calculated (bottom) powder diffraction pattern for compound **2**.

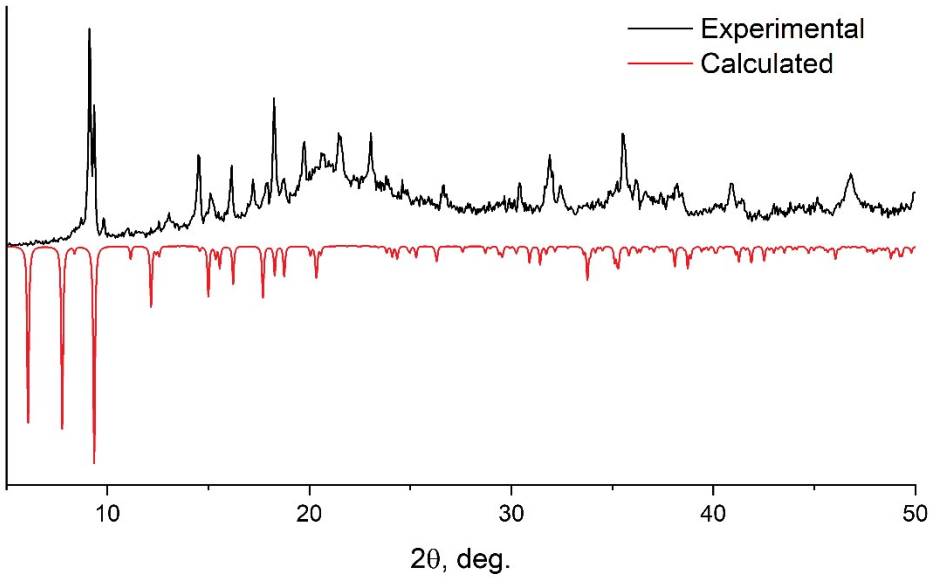


Fig S6. Experimental (top) powder diffraction pattern for compound **1'** *vs* calculated for **1** (bottom.

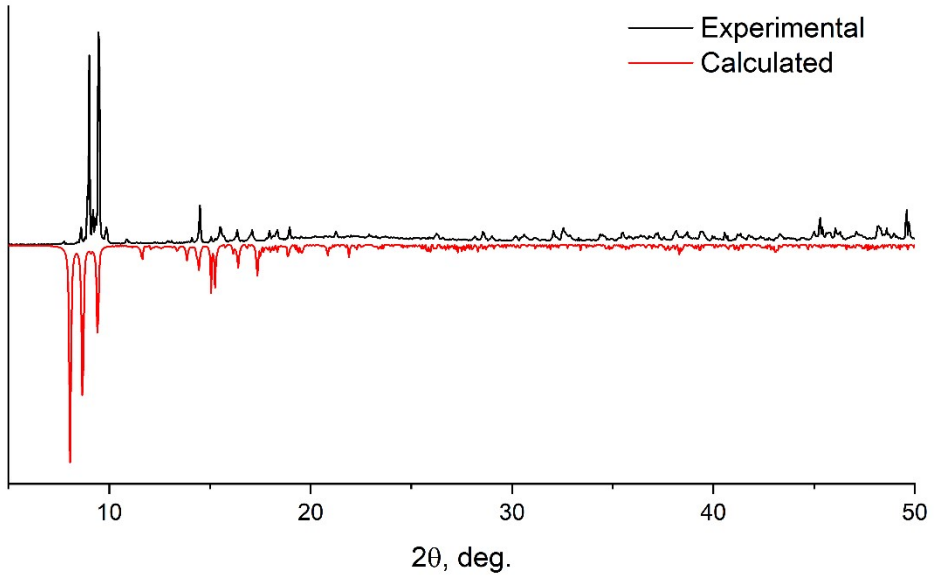
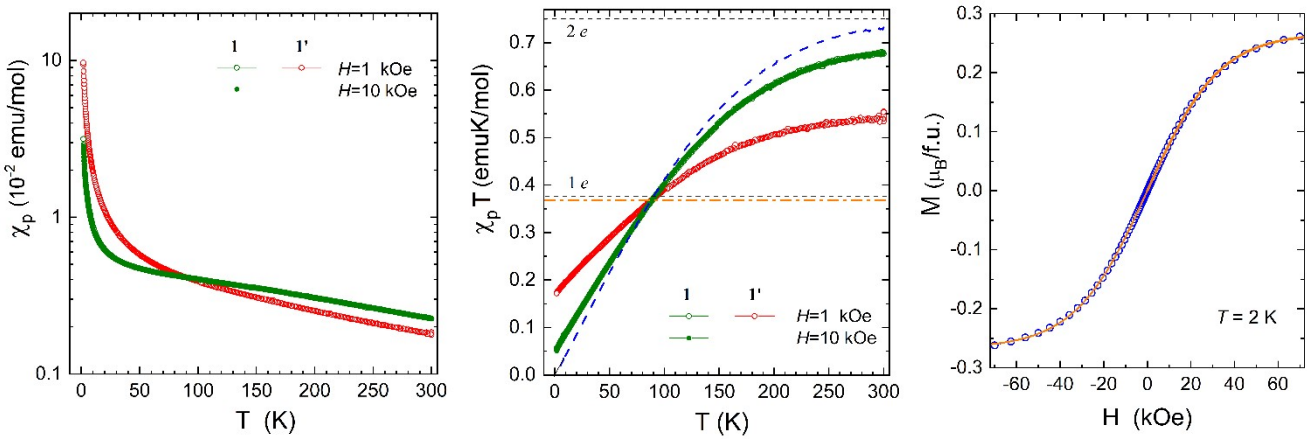


Fig S7. Experimental (top) powder diffraction pattern for compound **2'** *vs* calculated for **2** (bottom).

Magnetic properties



(a) (b) (c)

Fig. S8. (a) Temperature dependences of χ_p measured for two "Re_7S_8" samples (**1**, **1'**) at magnetic fields H = 1, 10 kOe. (b) Temperature dependences of χ_pT for two "Re_7S_8" samples (**1**, **1'**), that can be roughly decomposed into contributions from clusters with odd (orange dash-dotted line) and even (blue dashed line) number of electrons. The black dashed lines mark the levels expected for one and two unpaired electrons per molecule. (c) A representative magnetic-field dependence of the magnetization M measured for a "Re_7S_8" sample at T = 2 K (blue symbols). The orange solid line shows a fit to the data of the conventional theoretical expression based on the Brillouin function with the following parameters: S = 1/2; g-factor g = 1.8, normalized number of paramagnetic S = 1/2 clusters $n/n_0 \approx 26$ mol.%.

According to the magnetic measurements performed, in the case of "Re_7S_8" complex, only essentially heterophase samples were obtained, which contained molecules with both odd (**1'**) and even (**1**) number of electrons in different proportions; representative $\chi_p(T)$ curves are shown in Fig. S8a. Nevertheless, for all the studied samples, the $\chi_p(T)$ and $\chi_pT(T)$ dependences could be decomposed into two basic components being similar to those in the "Re_7Se_8" case. Namely, the first basic component is $\chi_pT(T) \approx 0.36$ emuK/mol (orange dash-dotted line in Fig. S8b), which means the Curie-like behavior of the magnetic susceptibility and is related to the fraction of clusters **1'** with an odd number of electrons. The second one shown by the blue dashed line in Fig. S8b is related to clusters **1** with an even number of electrons; it demonstrates a crossover from the non-magnetic low-temperature state ($\chi_pT = 0$) to the high-temperature S = 1 state. The said deconvolution into the contributions from clusters with different electron counts is justified by the analysis of low-temperature $M(H)$ dependences (Fig. S8c). All the $M(H)$ data obtained could be very well fitted by the conventional theoretical expression based on the

Brillouin function, with the fraction of paramagnetic $S = 1/2$ clusters being the only adjustable parameter (Fig. S8c). For instance, for the sample presented in Fig. S8c, the fit allowed us to evaluate the fraction of clusters with an odd number of electrons at a level of ≈ 26 mol.%. For samples indicated by green and red symbols in Figs. S8a,b fractions of such clusters were 13 and 50 mol.%, respectively. Apparently, the only noticeable difference between the "Re_7S_8" and "Re_7Se_8" complexes is the much narrower range of accessible cluster charges for the former; properties of clusters with integer numbers of electrons in both complexes are virtually the same.

DFT calculations

Table S3. Calculated atomic coordinates (Å) for $[\{Re_3S_4(CN)_9\}\{Re_4S_4(CN)_9\}]^{7-}$ cluster anion with S = 0 optimized in C_1 symmetry

$[\{Re_3S_4(CN)_9\}\{Re_4S_4(CN)_9\}]^{7-}$, **S = 0, C_1**			
Atom	*x*	*y*	*z*
Re	-0.79018699554472	2.85323247522167	-1.40902109687451
Re	1.63984977877605	2.78861723549520	0.00000000000000
Re	-0.79018699554472	2.85323247522167	1.40902109687451
S	0.06108532477912	4.56910948183227	0.00000000000000
S	-2.16078615799069	1.50075208525501	0.00000000000000
S	1.06238944811817	1.43463059412854	1.87488611798257
S	1.06238944811817	1.43463059412854	-1.87488611798257
Re	-0.03485906810090	0.54741737890041	0.00000000000000
C	2.74976761666338	3.95799248455453	-1.36077136370948
C	-0.13696937878665	4.04811945108330	-3.01563650700126
C	-1.73999835510124	1.87629649959186	3.02190151468296
C	-1.73999835510124	1.87629649959186	-3.02190151468296
C	-2.48686989048133	4.08046659084791	1.65506384285857
N	0.16997607264420	4.71248585018072	3.93129946398262
C	-2.48686989048133	4.08046659084791	-1.65506384285857
N	3.41527770889080	4.60121568420313	-2.07993080886486
C	2.74976761666338	3.95799248455453	1.36077136370948
C	-0.13696937878665	4.04811945108330	3.01563650700126
N	0.16997607264420	4.71248585018072	-3.93129946398262
C	3.46841730993726	1.73384470650957	0.00000000000000
N	-3.41935995587321	4.76106801156250	1.85806809801511
N	-2.27821842360963	1.38439507632967	3.93930690378942
N	-3.41935995587321	4.76106801156250	-1.85806809801511
N	-2.27821842360963	1.38439507632967	-3.93930690378942
N	4.50792555972020	1.19280520289869	0.00000000000000
N	3.41527770889080	4.60121568420313	2.07993080886486
S	1.70455764446849	-1.33308507400224	0.00000000000000
S	-0.92341811328967	-1.23033667090279	-1.58645226187778
S	-0.92341811328967	-1.23033667090279	1.58645226187778
Re	0.76680048923242	-2.96189534087833	1.44783940268729
Re	-1.54727451349079	-2.91300909390782	0.00000000000000
Re	0.76680048923242	-2.96189534087833	-1.44783940268729
S	0.02320161561975	-4.69943826027333	0.00000000000000
C	0.05055617121479	-4.03796053197762	3.08650883144797
C	1.67651928162880	-1.92910640115555	3.05214864030636
C	2.51300977995514	-4.09278954905180	1.65432531733438

C	-2.63654269026021	-4.07544751574543	1.38283807689896
C	-2.63654269026021	-4.07544751574543	-1.38283807689896
C	-3.39797660325849	-1.87891093969368	0.00000000000000
C	1.67651928162880	-1.92910640115555	-3.05214864030636
C	2.51300977995514	-4.09278954905180	-1.65432531733438
C	0.05055617121479	-4.03796053197762	-3.08650883144797
N	-0.28560756658040	-4.63794045599497	4.04242708648861
N	2.20370314479620	-1.40216686301325	3.95882827074885
N	3.49323353819522	-4.71275075223690	1.85363296700264
N	-3.31136744521805	-4.70403106457322	2.11054335156707
N	-3.31136744521805	-4.70403106457322	-2.11054335156707
N	-4.44952977364804	-1.35905791736205	0.00000000000000
N	2.20370314479620	-1.40216686301325	-3.95882827074885
N	3.49323353819522	-4.71275075223690	-1.85363296700264
N	-0.28560756658040	-4.63794045599497	-4.04242708648861

Table S4. Calculated atomic coordinates (Å) for $[\{Re_3S_4(CN)_9\}\{Re_4S_4(CN)_9\}]^{7-}$ cluster anion with S = 1 optimized in C_1 symmetry

$[\{Re_3S_4(CN)_9\}\{Re_4S_4(CN)_9\}]^{7-}$, **S = 1, C_1**			
Atom	*x*	*y*	*z*
Re	-0.78324131436317	2.83757896353535	-1.40638134415209
Re	1.65203384896105	2.81339634924678	0.00000000000000
Re	-0.78324131436317	2.83757896353535	1.40638134415209
S	0.04623688020299	4.56681761086823	0.00000000000000
S	-2.14434863867010	1.47724938096795	0.00000000000000
S	1.09349038656317	1.44268969916785	1.86773209897573
S	1.09349038656317	1.44268969916785	-1.86773209897573
Re	0.00372966792665	0.54357470705174	0.00000000000000
C	2.74153625254515	4.00002066509393	-1.36004015553078
C	-0.13351291581131	4.02965001735193	-3.01895676037012
C	-1.72126955389688	1.84696498395053	3.01732154265986
C	-1.72126955389688	1.84696498395053	-3.01732154265986
C	-2.48604274974215	4.05364235028308	1.66126376366133
N	0.16854394121218	4.69074685696364	3.93854441166243
C	-2.48604274974215	4.05364235028308	-1.66126376366133
N	3.39608250080712	4.65537320974094	-2.07838353710641
C	2.74153625254515	4.00002066509393	1.36004015553078
C	-0.13351291581131	4.02965001735193	3.01895676037012
N	0.16854394121218	4.69074685696364	-3.93854441166243
C	3.50053923623131	1.79329274668753	0.00000000000000
N	-3.42269330625972	4.72808772357621	1.86575456454868

N	-2.25365416680718	1.34848361093659	3.93459301757610
N	-3.42269330625972	4.72808772357621	-1.86575456454868
N	-2.25365416680718	1.34848361093659	-3.93459301757610
N	4.55182119754857	1.27544045977978	0.00000000000000
N	3.39608250080712	4.65537320974094	2.07838353710641
S	1.78448767063997	-1.27628063518212	0.00000000000000
S	-0.91143607770535	-1.25041661204676	-1.55778970863066
S	-0.91143607770535	-1.25041661204676	1.55778970863066
Re	0.77552978672384	-2.95240101267858	1.39410679033643
Re	-1.63857865475279	-2.92795778711368	0.00000000000000
Re	0.77552978672384	-2.95240101267858	-1.39410679033643
S	-0.04773902110653	-4.69747322394091	0.00000000000000
C	0.07242533952901	-4.06958439498019	3.02211600773565
C	1.70683677801506	-1.92909139037020	2.99266048560876
C	2.51874163690025	-4.09667306199899	1.60956489787142
C	-2.71410357097089	-4.04039989148920	1.41457870362484
C	-2.71410357097089	-4.04039989148920	-1.41457870362484
C	-3.47346421192438	-1.87668868389452	0.00000000000000
C	1.70683677801506	-1.92909139037020	-2.99266048560876
C	2.51874163690025	-4.09667306199899	-1.60956489787142
C	0.07242533952901	-4.06958439498019	-3.02211600773565
N	-0.24856704495962	-4.68248534265906	3.97318353479641
N	2.23549783561556	-1.41127822450491	3.90344375225991
N	3.49230999580034	-4.72475525109304	1.81228205600727
N	-3.38495970919003	-4.65109473848559	2.16317926561319
N	-3.38495970919003	-4.65109473848559	-2.16317926561319
N	-4.51774607306750	-1.34148729505787	0.00000000000000
N	2.23549783561556	-1.41127822450491	-3.90344375225991
N	3.49230999580034	-4.72475525109304	-1.81228205600727
N	-0.24856704495962	-4.68248534265906	-3.97318353479641

Table S5. Calculated atomic coordinates (Å) for $[\{Re_3Se_4(CN)_9\}\{Re_4Se_4(CN)_9\}]^{7-}$ cluster anion with S = 0 optimized in C_1 symmetry

$[\{Re_3Se_4(CN)_9\}\{Re_4Se_4(CN)_9\}]^{7-}$, **S = 0, C_1**			
Atom	*x*	*y*	*z*
Re	-0.80272027890154	2.96096956543296	-1.43521199279406
Re	1.67446198189700	2.89916550442944	0.00000000000000
Re	-0.80272027890154	2.96096956543296	1.43521199279406
Se	0.06693059620788	4.81197550238586	0.00000000000000
Se	-2.29627399497907	1.54570275652986	0.00000000000000
Se	1.13401776087005	1.47691782307545	1.99444011659758

Se	1.13401776087005	1.47691782307545	-1.99444011659758
Re	-0.02837229655775	0.61880518549942	0.00000000000000
C	2.77076923041153	4.06678257641548	-1.36235904116817
C	-0.14585225515258	4.15064174636277	-3.03612793680175
C	-1.75032855086611	1.98409320960696	3.04180141928571
C	-1.75032855086611	1.98409320960696	-3.04180141928571
C	-2.49531301343249	4.18405414309719	1.67230561861612
N	0.16060671165759	4.81441510848567	3.95366361292437
C	-2.49531301343249	4.18405414309719	-1.67230561861612
N	3.43378499707776	4.71241353581412	-2.08333441671129
C	2.77076923041153	4.06678257641548	1.36235904116817
C	-0.14585225515258	4.15064174636277	3.03612793680175
N	0.16060671165759	4.81441510848567	-3.95366361292437
C	3.50084025555728	1.85226218426212	0.00000000000000
N	-3.42911312722747	4.86497338021584	1.87409492701687
N	-2.28976540465751	1.49006536457410	3.95879685880730
N	-3.42911312722747	4.86497338021584	-1.87409492701687
N	-2.28976540465751	1.49006536457410	-3.95879685880730
N	4.54450080846057	1.31677299749850	0.00000000000000
N	3.43378499707776	4.71241353581412	2.08333441671129
Se	1.81851237700571	-1.35227222140295	0.00000000000000
Se	-0.97288312093786	-1.25161528230501	-1.68312674663621
Se	-0.97288312093786	-1.25161528230501	1.68312674663621
Re	0.77066363833101	-3.08875724748982	1.47755834382999
Re	-1.57384813158083	-3.02838476997700	0.00000000000000
Re	0.77066363833101	-3.08875724748982	-1.47755834382999
Se	0.01883631071192	-4.95969508257441	0.00000000000000
C	0.05928212160677	-4.17150531354456	3.10153830793366
C	1.66932554885430	-2.05785855592006	3.07978939262991
C	2.52820731275527	-4.19519661606632	1.66597897243295
C	-2.66285161480362	-4.17563226389933	1.38474016678642
C	-2.66285161480362	-4.17563226389933	-1.38474016678642
C	-3.40864427371239	-1.98111718866757	0.00000000000000
C	1.66932554885430	-2.05785855592006	-3.07978939262991
C	2.52820731275527	-4.19519661606632	-1.66597897243295
C	0.05928212160677	-4.17150531354456	-3.10153830793366
N	-0.27959329888527	-4.77708946087670	4.05425528438392
N	2.19220445106419	-1.52914635793092	3.98959968490608
N	3.52126801432493	-4.79810798070309	1.85928576379642
N	-3.34055256740916	-4.79394066582369	2.11985773302791
N	-3.34055256740916	-4.79394066582369	-2.11985773302791
N	-4.45925675236989	-1.45616830502535	0.00000000000000

N	2.19220445106419	-1.52914635793092	-3.98959968490608
N	3.52126801432493	-4.79810798070309	-1.85928576379642
N	-0.27959329888527	-4.77708946087670	-4.05425528438392

Table S6. Calculated atomic coordinates (Å) for $[\{Re_3Se_4(CN)_9\}\{Re_4Se_4(CN)_9\}]^{7-}$ cluster anion with S = 1 optimized in C_1 symmetry

$[\{Re_3Se_4(CN)_9\}\{Re_4Se_4(CN)_9\}]^{7-}$, **S = 1, C_1**			
Atom	*x*	*y*	*z*
Re	0.82671837723189	-1.43191824525675	-2.94014045054253
Re	0.82671837723189	1.43191824525675	-2.94014045054253
Re	-1.65343676446377	0.00000000000000	-2.94014045054253
Se	-0.00000000000000	-0.00000000000000	-4.81237822630608
Se	-1.14780137187921	-1.98805030164099	-1.49962831485641
Se	-1.14780137187921	1.98805030164099	-1.49962831485641
Se	2.29560274375842	0.00000000000000	-1.49962831485641
Re	0.00000000000000	-0.00000000000000	-0.61697004987542
C	2.53880949375544	1.67751257688680	-4.13595937687938
C	2.53880949375544	-1.67751257688680	-4.13595937687938
C	-3.50748766851810	0.00000000000000	-1.94006133220911
C	1.75374382925905	-3.03757342447005	-1.94006133220911
C	-2.72217324645158	-1.35991722861260	-4.13595937687938
N	-3.37053163465432	2.07693274973774	-4.80074946359736
C	0.18336376269614	-3.03742980549941	-4.13595937687938
N	3.48394234259885	1.88049964412523	-4.80074946359736
C	0.18336376269614	3.03742980549941	-4.13595937687938
C	-2.72217324645158	1.35991722861260	-4.13595937687938
N	3.48394234259885	-1.88049964412523	-4.80074946359736
C	1.75374382925905	3.03757342447005	-1.94006133220911
N	-3.37053163465432	-2.07693274973774	-4.80074946359736
N	-4.56584532501080	0.00000000000000	-1.43411807716689
N	-0.11341070794453	-3.95743239386296	-4.80074946359736
N	2.28292266250540	-3.95413804186081	-1.43411807716689
N	2.28292266250540	3.95413804186081	-1.43411807716689
N	-0.11341070794453	3.95743239386296	-4.80074946359736
Se	0.95188166602346	1.64870740068040	1.28265448900764
Se	0.95188166602346	-1.64870740068040	1.28265448900764
Se	-1.90376332204692	-0.00000000000000	1.28265448900764
Re	-0.81951551257922	1.41944249990335	3.06935059697304
Re	-0.81951551257922	-1.41944249990335	3.06935059697304
Re	1.63903102515845	-0.00000000000000	3.06935059697304
Se	0.00000000000000	0.00000000000000	4.95877602681530

C	-2.57492578292233	1.62443234374776	4.18371186865855
C	-1.73702601664872	3.00861731237212	2.03267562645531
C	-0.11933678892857	3.04216731227124	4.18371186865855
C	-2.57492578292233	-1.62443234374776	4.18371186865855
C	-0.11933678892857	-3.04216731227124	4.18371186865855
C	-1.73702601664872	-3.00861731237212	2.03267562645531
C	3.47405203329744	-0.00000000000000	2.03267562645531
C	2.69426257185089	1.41773496852348	4.18371186865855
C	2.69426257185089	-1.41773496852348	4.18371186865855
N	-3.56228553307496	1.82276731109220	4.79326825980261
N	-2.26207911214497	3.91803594802547	1.50558230615883
N	0.20257997882484	3.99641342789669	4.79326825980261
N	-3.56228553307496	-1.82276731109220	4.79326825980261
N	0.20257997882484	-3.99641342789669	4.79326825980261
N	-2.26207911214497	-3.91803594802547	1.50558230615883
N	4.52415821428994	-0.00000000000000	1.50558230615883
N	3.35970556425012	2.17364611680449	4.79326825980261
N	3.35970556425012	-2.17364611680449	4.79326825980261

Table S7. Calculated atomic coordinates (Å) for $[\{Re_3S_4(CN)_9\}\{Re_4S_4(CN)_9\}]^{7-}$ cluster anion with S = 0 optimized in C_s symmetry

$[\{Re_3S_4(CN)_9\}\{Re_4S_4(CN)_9\}]^{7-}$, **S = 0, C_s**			
Atom	*x*	*y*	*z*
Re	-0.79019508744678	2.85101577111709	-1.40780182470715
Re	1.63813096735730	2.78561220943406	0.00000000000000
Re	-0.79019508744678	2.85101577111709	1.40780182470715
S	0.06111880460011	4.56808190877136	0.00000000000000
S	-2.16129160896191	1.49702012520598	0.00000000000000
S	1.06198720371938	1.43226216511645	1.87668306626584
S	1.06198720371938	1.43226216511645	-1.87668306626584
Re	-0.03367655404120	0.54637766571893	0.00000000000000
C	2.74671903230159	3.95515606625339	-1.35969139496583
C	-0.13655046118746	4.04502023499225	-3.01320105251298
C	-1.74023314061371	1.87540231089015	3.01953618870080
C	-1.74023314061371	1.87540231089015	-3.01953618870080
C	-2.48613250275036	4.07730581564427	1.65283058942701
N	0.16946942965704	4.70982367802924	3.92885791846555
C	-2.48613250275036	4.07730581564427	-1.65283058942701
N	3.41166569865116	4.59992074231689	-2.07799985831585
C	2.74671903230159	3.95515606625339	1.35969139496583
C	-0.13655046118746	4.04502023499225	3.01320105251298

N	0.16946942965704	4.70982367802924	-3.92885791846555
C	3.46600042799731	1.73269499815612	0.00000000000000
N	-3.41834739168268	4.75837734878235	1.85542624277031
N	-2.27931352366319	1.38414569940809	3.93674025476976
N	-3.41834739168268	4.75837734878235	-1.85542624277031
N	-2.27931352366319	1.38414569940809	-3.93674025476976
N	4.50696863060491	1.19445584296466	0.00000000000000
N	3.41166569865116	4.59992074231689	2.07799985831585
S	1.70780511284806	-1.33335312967795	0.00000000000000
S	-0.92214827900762	-1.22852468422443	-1.58868507143176
S	-0.92214827900762	-1.22852468422443	1.58868507143176
Re	0.76686266728978	-2.96086167935437	1.44695419036419
Re	-1.54492551528750	-2.90916544679357	0.00000000000000
Re	0.76686266728978	-2.96086167935437	-1.44695419036419
S	0.02270519739750	-4.69876135494193	0.00000000000000
C	0.04956165722446	-4.03602815222974	3.08443235140798
C	1.67721838695899	-1.93003495689124	3.05045662441176
C	2.51218549171054	-4.09162079423415	1.65214647472398
C	-2.63463163091083	-4.06980518616681	1.38221600041893
C	-2.63463163091083	-4.06980518616681	-1.38221600041893
C	-3.39355247849654	-1.87416988740610	0.00000000000000
C	1.67721838695899	-1.93003495689124	-3.05045662441176
C	2.51218549171054	-4.09162079423415	-1.65214647472398
C	0.04956165722446	-4.03602815222974	-3.08443235140798
N	-0.28710731765071	-4.63682551533739	4.03967213086089
N	2.20428393959715	-1.40324809782774	3.95727378383635
N	3.49295166849455	-4.71066331216853	1.85155518491993
N	-3.31030336364339	-4.69796769163486	2.10948257107463
N	-3.31030336364339	-4.69796769163486	-2.10948257107463
N	-4.44516794811386	-1.35449250639339	0.00000000000000
N	2.20428393959715	-1.40324809782774	-3.95727378383635
N	3.49295166849455	-4.71066331216853	-1.85155518491993
N	-0.28710731765071	-4.63682551533739	-4.03967213086089

Table S8. Calculated atomic coordinates (Å) for $[\{Re_3S_4(CN)_9\}\{Re_4S_4(CN)_9\}]^{7-}$ cluster anion with S = 1 optimized in C_{3v} symmetry

$[\{Re_3S_4(CN)_9\}\{Re_4S_4(CN)_9\}]^{7-}$, **S = 1, C_{3v}**			
Atom	*x*	*y*	*z*
Re	0.81086074502255	-1.40445201229186	-2.82804538180782
Re	0.81086074502255	1.40445201229186	-2.82804538180782
Re	-1.62172149004511	0.00000000000000	-2.82804538180782

S	0.00000000000000	0.00000000000000	-4.56747652613801
S	-1.07927176502957	-1.86935354278545	-1.45295998521386
S	-1.07927176502957	1.86935354278545	-1.45295998521386
S	2.15854354005913	-0.00000000000000	-1.45295998521386
Re	-0.00000000000000	-0.00000000000000	-0.54279599110018
C	2.52615306387162	1.65746479355520	-4.02498590049121
C	2.52615306387162	-1.65746479355520	-4.02498590049121
C	-3.47986020184343	0.00000000000000	-1.82874662595465
C	1.73993010592171	-3.01364733576240	-1.82874662595465
C	-2.69848314684815	-1.35898033029598	-4.02498590049121
N	-3.34639213959615	2.07724345294622	-4.68704205608853
C	0.17233008297653	-3.01644512385117	-4.02498590049121
N	3.47214166974045	1.85943887697173	-4.68704205608853
C	0.17233008297653	3.01644512385117	-4.02498590049121
C	-2.69848314684815	1.35898033029598	-4.02498590049121
N	3.47214166974045	-1.85943887697173	-4.68704205608853
C	1.73993010592171	3.01364733576240	-1.82874662595465
N	-3.34639213959615	-2.07724345294622	-4.68704205608853
N	-4.53783377321337	0.00000000000000	-1.32470983711493
N	-0.12574953014431	-3.93668232991795	-4.68704205608853
N	2.26891689160669	-3.92987932994839	-1.32470983711493
N	2.26891689160669	3.92987932994839	-1.32470983711493
N	-0.12574953014431	3.93668232991795	-4.68704205608853
S	0.89962710047459	1.55819985377035	1.25638448331788
S	0.89962710047459	-1.55819985377035	1.25638448331788
S	-1.79925420094919	-0.00000000000000	1.25638448331788
Re	-0.80402081335863	1.39260490768316	2.94228051275211
Re	-0.80402081335863	-1.39260490768316	2.94228051275211
Re	1.60804163671727	-0.00000000000000	2.94228051275211
S	-0.00000000000000	-0.00000000000000	4.69709202180160
C	-2.55888478062521	1.60645556635709	4.06616411794234
C	-1.72600120158165	2.98952178308904	1.91049779519143
C	-0.11178893680716	3.01928700597669	4.06616411794234
C	-2.55888478062521	-1.60645556635709	4.06616411794234
C	-0.11178893680716	-3.01928700597669	4.06616411794234
C	-1.72600120158165	-2.98952178308904	1.91049779519143
C	3.45200240316330	0.00000000000000	1.91049779519143
C	2.67067371743237	1.41283143961960	4.06616411794234
C	2.67067371743237	-1.41283143961960	4.06616411794234
N	-3.53899773590287	1.80826354798169	4.68414834511173
N	-2.25098234344893	3.89881578996815	1.38645684436004
N	0.20349669517157	3.96899371785921	4.68414834511173

N	-3.53899773590287	-1.80826354798169	4.68414834511173
N	0.20349669517157	-3.96899371785921	4.68414834511173
N	-2.25098234344893	-3.89881578996815	1.38645684436004
N	4.50196468689786	0.00000000000000	1.38645684436004
N	3.33550104073130	2.16073016987753	4.68414834511173
N	3.33550104073130	-2.16073016987753	4.68414834511173

Table S9. Calculated atomic coordinates (Å) for $[\{Re_3Se_4(CN)_9\}\{Re_4Se_4(CN)_9\}]^{7-}$ cluster anion with S = 0 optimized in C_s symmetry

$[\{Re_3Se_4(CN)_9\}\{Re_4Se_4(CN)_9\}]^{7-}$, **S = 0, C_s**			
Atom	*x*	*y*	*z*
Re	-0.80273547784847	2.96096953709059	-1.43520111933449
Re	1.67442871478901	2.89908911797680	0.00000000000000
Re	-0.80273547784847	2.96096953709059	1.43520111933449
Se	0.06693192888341	4.81196704335157	0.00000000000000
Se	-2.29632364833470	1.54571352170516	0.00000000000000
Se	1.13395152065238	1.47689714393531	1.99447805807483
Se	1.13395152065238	1.47689714393531	-1.99447805807483
Re	-0.02840020759454	0.61887164322631	0.00000000000000
C	2.77079485693101	4.06663772613917	-1.36237670692074
C	-0.14582791746275	4.15067683731832	-3.03607593696808
C	-1.75039605266224	1.98418733253102	3.04181806130305
C	-1.75039605266224	1.98418733253102	-3.04181806130305
C	-2.49532106054647	4.18409469434729	1.67221643259448
N	0.16065937272621	4.81449566495059	3.95356919276948
C	-2.49532106054647	4.18409469434729	-1.67221643259448
N	3.43386644055294	4.71220612172822	-2.08335685507616
C	2.77079485693101	4.06663772613917	1.36237670692074
C	-0.14582791746275	4.15067683731832	3.03607593696808
N	0.16065937272621	4.81449566495059	-3.95356919276948
C	3.50073713532700	1.85206455652254	0.00000000000000
N	-3.42910835848396	4.86503746009911	1.87398727171889
N	-2.28986847640459	1.49021806825506	3.95882425098289
N	-3.42910835848396	4.86503746009911	-1.87398727171889
N	-2.28986847640459	1.49021806825506	-3.95882425098289
N	4.54436013951347	1.31650277123330	0.00000000000000
N	3.43386644055294	4.71220612172822	2.08335685507616
Se	1.81849760957029	-1.35220932088726	0.00000000000000
Se	-0.97287538916271	-1.25161398587253	-1.68308936047290
Se	-0.97287538916271	-1.25161398587253	1.68308936047290
Re	0.77068064955299	-3.08873558326347	1.47753679853909

Re	-1.57382021943858	-3.02842764068456	0.00000000000000
Re	0.77068064955299	-3.08873558326347	-1.47753679853909
Se	0.01891897695465	-4.95973431513699	0.00000000000000
C	0.05933122085496	-4.17158816797859	3.10146666653011
C	1.66922350937427	-2.05784429576159	3.07983770870803
C	2.52831336344196	-4.19504248231058	1.66592900173328
C	-2.66283053267284	-4.17566896166978	1.38474249707688
C	-2.66283053267284	-4.17566896166978	-1.38474249707688
C	-3.40859826076199	-1.98112888726530	0.00000000000000
C	1.66922350937427	-2.05784429576159	-3.07983770870803
C	2.52831336344196	-4.19504248231058	-1.66592900173328
C	0.05933122085496	-4.17158816797859	-3.10146666653011
N	-0.27952829321534	-4.77724117535360	4.05414546103310
N	2.19202841318310	-1.52915940401408	3.98970660251775
N	3.52143089802262	-4.79786469407710	1.85922282102377
N	-3.34056068354326	-4.79394846889743	2.11985732888348
N	-3.34056068354326	-4.79394846889743	-2.11985732888348
N	-4.45918818548765	-1.45613521443346	0.00000000000000
N	2.19202841318310	-1.52915940401408	-3.98970660251775
N	3.52143089802262	-4.79786469407710	-1.85922282102377
N	-0.27952829321534	-4.77724117535360	-4.05414546103310

Table S10. Calculated atomic coordinates (Å) for $[\{Re_3Se_4(CN)_9\}\{Re_4Se_4(CN)_9\}]^{7-}$ cluster anion with S = 1 optimized in C_{3v} symmetry

$[\{Re_3S_4(CN)_9\}\{Re_4S_4(CN)_9\}]^{7-}$, **S = 1, C_{3v}**			
Atom	*x*	*y*	*z*
Re	0.82649569329596	-1.43153254536569	-2.94217786548414
Re	0.82649569329596	1.43153254536569	-2.94217786548414
Re	-1.65299139659192	0.00000000000000	-2.94217786548414
Se	-0.00000000000000	-0.00000000000000	-4.81606026215419
Se	-1.14766332277140	-1.98781119357231	-1.50125407539560
Se	-1.14766332277140	1.98781119357231	-1.50125407539560
Se	2.29532664554279	0.00000000000000	-1.50125407539560
Re	0.00000000000000	0.00000000000000	-0.61840853609075
C	2.53990380763995	1.67635604705433	-4.13620039080307
C	2.53990380763995	-1.67635604705433	-4.13620039080307
C	-3.50708686781600	0.00000000000000	-1.94188635745048
C	1.75354342890800	-3.03722632088018	-1.94188635745048
C	-2.72171881917867	-1.36144319715254	-4.13620039080307
N	-3.37004431308993	2.08100787350889	-4.79823096451152
C	0.18181502153872	-3.03779924420687	-4.13620039080307

N	3.48722784252604	1.87804004938508	-4.79823096451152
C	0.18181502153872	3.03779924420687	-4.13620039080307
C	-2.72171881917867	1.36144319715254	-4.13620039080307
N	3.48722784252604	-1.87804004938508	-4.79823096451152
C	1.75354342890800	3.03722632088018	-1.94188635745048
N	-3.37004431308993	-2.08100787350889	-4.79823096451152
N	-4.56570906854732	0.00000000000000	-1.43648929887857
N	-0.11718352943610	-3.95904792289397	-4.79823096451152
N	2.28285453427366	-3.95402004030200	-1.43648929887857
N	2.28285453427366	3.95402004030200	-1.43648929887857
N	-0.11718352943610	3.95904792289397	-4.79823096451152
Se	0.95122310977519	1.64756674779875	1.28266978429033
Se	0.95122310977519	-1.64756674779875	1.28266978429033
Se	-1.90244620955037	-0.00000000000000	1.28266978429033
Re	-0.81930990546419	1.41908637793372	3.07012091947195
Re	-0.81930990546419	-1.41908637793372	3.07012091947195
Re	1.63861981092839	-0.00000000000000	3.07012091947195
Se	0.00000000000000	0.00000000000000	4.96093958392323
C	-2.57479388290530	1.62387059652962	4.18455773693489
C	-1.73662903906785	3.00792972703258	2.03283907167135
C	-0.11891625157566	3.04177220989666	4.18455773693489
C	-2.57479388290530	-1.62387059652962	4.18455773693489
C	-0.11891625157566	-3.04177220989666	4.18455773693489
C	-1.73662903906785	-3.00792972703258	2.03283907167135
C	3.47325807813569	-0.00000000000000	2.03283907167135
C	2.69371013448096	1.41790161336704	4.18455773693489
C	2.69371013448096	-1.41790161336704	4.18455773693489
N	-3.56189996772666	1.82157621880098	4.79474954719611
N	-2.26130561930894	3.91669621913417	1.50426903891622
N	0.20341871233313	3.99548397236464	4.79474954719611
N	-3.56189996772666	-1.82157621880098	4.79474954719611
N	0.20341871233313	-3.99548397236464	4.79474954719611
N	-2.26130561930894	-3.91669621913417	1.50426903891622
N	4.52261122861788	-0.00000000000000	1.50426903891622
N	3.35848126539353	2.17390775356365	4.79474954719611
N	3.35848126539353	-2.17390775356365	4.79474954719611

Table S11. Calculated bond lengths (Å) within the $[\{Re_3Q_4(CN)_9\}\{Re_4Q_4(CN)_9\}]^{7-}$ (Q = S or Se; 22 CSE) cluster anions optimized in C_s and C_{3v} symmetry for clusters with S = 0 and S = 1, respectively

Bond	$[\{Re_3S_4(CN)_9\}\{Re_4S_4(CN)_9\}]^{7-}$		$[\{Re_3Se_4(CN)_9\}\{Re_4Se_4(CN)_9\}]^{7-}$	
	S = 0 (C_s)	S = 1 (C_{3v})	S = 0 (C_s)	S = 1 (C_{3v})
Re–Re $\{Re_3Q_4\}$	2.7278 (x2) 2.8939	2.7852 (x3)	2.7719 (x2) 2.9551	2.8382 (x3)
Re–Q (cap) $\{Re_3Q_4\}$	2.3791 (x2) 2.3807	2.3802 (x3)	2.4998 (x2) 2.5034	2.5021 (x3)
Re–Q (bridge) $\{Re_3Q_4\}$	2.3723 (x2) 2.3951 (x2) 2.4236 (x2)	2.4025 (x6)	2.5093 (x2) 2.5201 (x2) 2.5411 (x2)	2.5263 (x6)
Re–Re $\{Re_4Q_4\}$	2.7945 2.8046 (x2) 2.8077 (x2) 2.8156	2.8022 (x3) 2.8089 (x3)	2.8459 2.8539 (x2) 2.8636 (x2) 2.8704	2.8517 (x3) 2.8631 (x3)
Re–(μ_3-Q) $\{Re_4Q_4\}$	2.3303 2.3467 (x2) 2.3780 (x2) 2.3798 (x2) 2.3800 2.3844 (x2) 2.3864 (x2)	2.3426 (x3) 2.3782 (x3) 2.3832 (x6)	2.4500 2.4628 (x2) 2.4985 (x2) 2.4986 2.5032 (x2) 2.5085 (x2) 2.5087 (x2)	2.4593 (x3) 2.4988 (x3) 2.5066 (x6)
Re–Q (bridge) $\{Re_4Q_4\}$	2.5424 (x2) 2.5624	2.5445 (x3)	2.6877 (x2) 2.7011	2.6895 (x3)

Table S12. Total bond energies (eV) for $[\{Re_3Q_4(CN)_9\}\{Re_4Q_4(CN)_9\}]^{7-}$ clusters in low-spin and high-spin states

Anion	S = 0		S = 1		ΔE(HS–LS), C_1
	C_1	C_s	C_1	C_{3v}	
$[\{Re_3S_4(CN)_9\}\{Re_4S_4(CN)_9\}]^{7-}$	–435.2253	–435.2257	–435.4206	–435.4158	–0.1953
$[\{Re_3Se_4(CN)_9\}\{Re_4Se_4(CN)_9\}]^{7-}$	–429.7813	-429.7813	–429.9889	–429.9819	–0.2006

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