

Electronic Supplementary Information (ESI) available:

Experimental

Materials and syntheses

ReS₂ and MoS₂ were prepared from Re and Mo annealed in H₂ atmosphere and commercially available sulfur powder, 99+%. Other reagents were purchased from commercial sources and used without further purification.

UV/Vis spectra in the wavelength range 200-1100 nm were recorded on Ultrospec 3300 pro spectrometer. IR spectra in KBr pellets were recorded on a Bruker Scimitar FTS 2000 spectrometer in the range 4000-375 cm⁻¹. Elemental analysis was made on a Euro EA3000 analyzer. Inductively coupled plasma emission spectroscopy (ICP-ES) was made on iCAP 6500 spectrometer. Cyclic voltammetry was made on Elins P-30S potentiostat.

EPR spectra of powdered samples were recorded on Varian E-109 EPR spectrometer in X-band at 300 K. Diphenyl-picrylhydrazil (DPPH) was used as etalon of g-value with g = 2.0036. For the estimation of cluster concentration was used CuSO₄·5H₂O sample. Simulation of EPR spectra was made by Bruker Simfoniya program.

Preparation of K₆[Mo₃Re₃S₈(CN)₅] (1): MoS₂ (160 mg, 1.00 mmol), ReS₂ (250 mg, 1.00 mmol) and KCN (1 g, 15.36 mmol) were placed into a quartz ampoule. Ampoule was evacuated and sealed, and then heated to 750°C for 8 days. Melt containing black crystals was washed with EtOH/H₂O on porous glass filter. Crystals were separated from ReS₂ and MoS₂ by density distribution in EtOH*. Yield: 380 mg (78%). EDS: K:Re:Mo:S = 5.9:3.1:2.9:8.2. Elemental analysis for C₅K₆Mo₃N₅Re₃S₈: calcd (% mas.) C 4.09, N 4.77, S 17.48, found C 4.12, N 4.90, S 17.34. ICP-ES**: K:Re:Mo:S = 6.0:3.1:2.9:7.8. IR (cm⁻¹): ν(CN) 2071.

*Sample containing compound **1** and unreacted disulphides placed on the concaved glass. Some EtOH was added to the sample, and then made the glass of circular movements. Less dense disulphides were dropped to the edges of the glass, while compound **1** remains closer to the center.

** Samples for ICP-ES were prepared by decomposition of **1** in 1:2 mixture of concentrated H₂O₂/H₂O and NH₃/H₂O.

Preparation of CaK₄[Re₃Mo₃S₈(CN)₆]·8H₂O (2): Compound **1** (200 mg, 0.14 mmol) was dissolved in hot H₂O with KCN (50 mg, 0.77 mmol). Resulting brown solution was filtered and CaCl₂ (20 mg, 0.18 mmol) was added. Solution was evaporated to a volume about 20 ml and cooled to the room temperature. The formed black

crystals were filtered off, washed with 10 ml EtOH/H₂O (3:1) and dried on air. Yield: 180 mg (85%). EDS: Ca:K:Re:Mo:S = 0.9:4.2:3.1:2.9:8.3. Elemental analysis for C₆CaH₁₆K₄Mo₃N₆O₈Re₃S₈: calcd (% mas.): calcd. C 4.50, H 1.01, N 5.25, S 16.04, found C 4.40, H 0.98, N 5.14, S 15.86. ICP-ES: K:Re:Mo:S = 4.1:3.0:3.0:7.8. IR/cm⁻¹: ν(OH) 3487, δ(OH) 1597, ν(CN) 2089. UV/Vis (M⁻¹·cm⁻¹): 453 (1340), 482 (1614), 755 (388).

Crystallography. Single-crystal X-ray diffraction data were collected with the use of graphite monochromatized Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 298(2) K on a Bruker Nonius X8 Apex diffractometer equipped with a 4K CCD area detector. The standard ϕ - and ω -scan techniques were employed to measure intensities. Absorption corrections were applied using the SADABS program¹. The crystal structures were solved by direct methods and refined by full-matrix least squares techniques with the use of the SHELXTL software package². All non-hydrogen atoms were refined anisotropically. Hydrogens of water molecules were not located. Crystallographic data as well as details of data collection and structure refinement for compounds **1** and **2** are given in Table S4. Selected bond lengths are tabulated in Table S2. Complete crystallographic data have been deposited at the Inorganic Crystal Structure Database (CSD no. 426317 and 426316 for compounds **1** and **2**, respectively) and may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany.

(fax: (+49)7247-808-666; e-mail: crysdta@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html).

Computational details. The geometry optimization with VWN+BP86³⁻⁶ functional and all electron TZ2P⁷ basis set were done for *mer*- and *fac*-isomers of [Re₃Mo₃S₈(CN)₆]⁶⁻ cluster in ADF2012 code⁸ in order to achieve the formation energies. The scalar relativistic effects were taken into account by ZORA method⁹. The all optimized geometries show no imaginary frequencies. Restricted Open-Shell calculation was done for paramagnetic clusters.

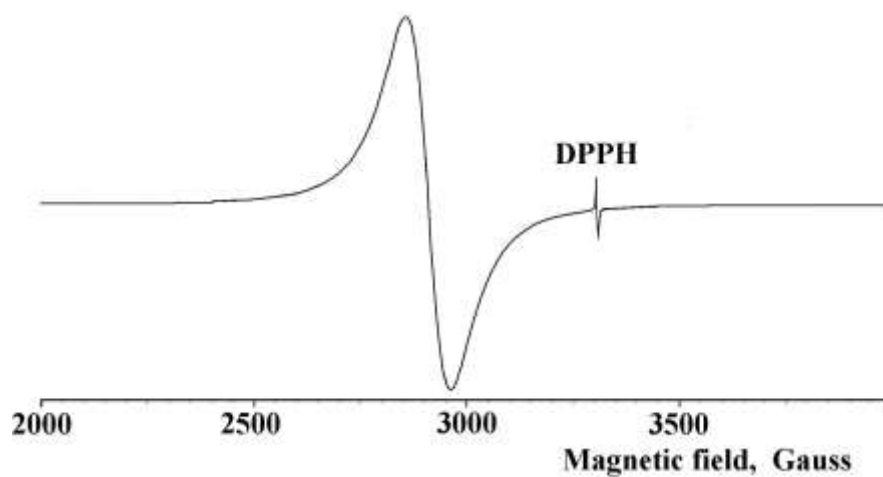


Figure S1. EPR spectra of powdered sample of 2.

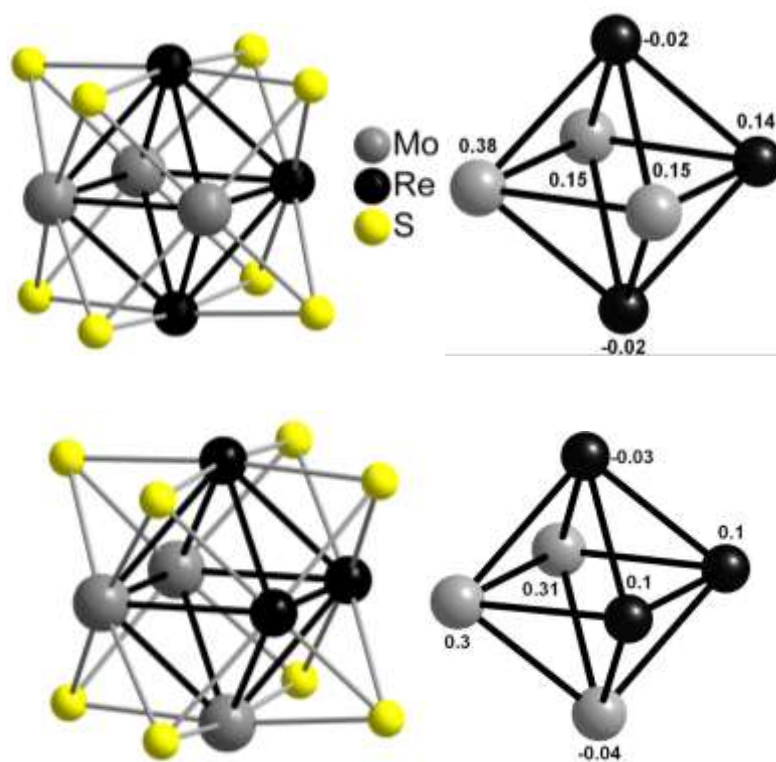


Figure S2. View of *mer*- (top) and *fac*- (bottom) isomers of $\{Re_3Mo_3S_8\}^0$ 23e cluster core and maps of spin density on the metal atoms.

	M – M range	M – M average	M – S range	M – S average
$[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_5]^{6-}$ (24 CVE, in 1)	2.6323(3) – 2.6400(4)	2.636(4)	2.4343(9) – 2.4541(9)	2.443(8)
$[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]^{6-}$ (23 CVE, in 2)		2.6273(8)		2.439(2)
$[\text{Re}_6\text{S}_8(\text{CN})_6]^{3-}$ (23 CVE) ¹⁰	2.591 – 2.609	2.599(6)	2.383 – 2.431	2.407(13)
$[\text{Re}_6\text{S}_8(\text{CN})_6]^{4-}$ (24 CVE) ¹¹		2.602(4)		2.413(9)
$[\text{Mo}_6\text{S}_8]^{4+}$ (24 CVE) ¹²	2.650(1) – 2.713(2)	2.68(2)	2.407(3) – 2.591(4)	2.47(5)
$[\text{Mo}_6\text{S}_8(\text{CN})_6]^{7-}$ (21 CVE) ¹³		2.6656(9)		2.4565(12)

Table S1. Selected measured bond length for cluster anions $[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_5]^{6-}$ and $[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]^{6-}$ in comparison with $[\text{M}_6\text{S}_8(\text{CN})_6]^{n-}$ clusters (M = Re, Mo).

	E	HOMO	LUMO	HOMO-LUMO
<i>fac</i> - $[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]^{7-}$	-170.49	15.299	16.957	1.658
<i>mer</i> - $[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]^{7-}$	-170.61	15.281	16.651	1.370
<i>fac</i> - $[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]^{6-}$	-184.18	12.250	13.957	1.707
<i>mer</i> - $[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]^{6-}$	-184.24	12.199	13.925	1.726

Table S2. Binding energy and HOMO-LUMO gap.

	Re – Re		Re – Mo		Mo – Mo		Re – S		Mo – S	
	Range	Average	Range	Average	Range	Average	Range	Average	Range	Average
<i>fac</i> - $[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]^{7-}$ (DFT)	2.6863 – 2.6871	2.6866(4)	2.7079 – 2.7090	2.7085(4)	2.7058 – 2.7066	2.7063(4)	2.4584 – 2.4681	2.463(3)	2.4958 – 2.5156	2.506(7)
<i>mer</i> - $[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]^{7-}$ (DFT)	2.6950 – 2.6965	2.696(1)	2.6974 – 2.7131	2.703(6)	2.7001 – 2.7009	2.7005(6)	2.4586 – 2.4648	2.462(2)	2.4971 – 2.5102	2.504(5)
<i>fac</i> - $[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]^{6-}$ (DFT)	2.6587 – 2.6794	2.67(1)	2.6723 – 2.7128	2.69(2)	2.6843 – 2.7776	2.72(5)	2.4398 – 2.4706	2.45(1)	2.4711 – 2.5191	2.49(2)
<i>mer</i> - $[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]^{6-}$ (DFT)	2.6689		2.6645 – 2.7027	2.68(2)	2.7410		2.4420 – 2.4722	2.46(1)	2.4773 – 2.4913	2.485(6)

Table S3. Calculated bond lengths in *fac*- and *mer*-isomers of $[\text{Re}_3\text{Mo}_3\text{S}_8(\text{CN})_6]^{7-/6-}$ cluster cores

	1	2
Empirical formula	C ₅ K ₆ Mo ₃ N ₅ Re ₃ S ₈	C ₆ H ₁₆ CaK ₄ Mo ₃ N ₆ O ₈ Re ₃ S ₈
<i>M</i>	1467.60	1599.63
Space group, <i>Z</i>	<i>I4/m, 2</i>	<i>Fm-3m, 4</i>
<i>a</i> (Å)	11.4231(8)	15.2562(4)
<i>c</i> (Å)	9.2449(6)	
<i>V</i> (Å ³)	1206.3(1)	3550.9(2)
<i>T</i> (K)	296(2)	150(2)
μ _{Mo Kα} (mm ⁻¹)	18.239	12.335
<i>D</i> _{calc} (g cm ⁻³)	4.040	2.992
Crystal size (mm)	0.15x0.15x0.15	0.12x0.10x0.06
θ scan range (deg)	2.83 – 27.47	2.31 – 29.97
Ranges of <i>h</i> , <i>k</i> and <i>l</i>	-11 ≤ <i>h</i> ≤ 14 -12 ≤ <i>k</i> ≤ 14 -8 ≤ <i>l</i> ≤ 12	-21 ≤ <i>h</i> ≤ 17 -21 ≤ <i>k</i> ≤ 21 -16 ≤ <i>l</i> ≤ 21
Measured reflns	2674	9384
Independent reflns	719	314
Observed reflns [<i>I</i> > 2σ(<i>I</i>)]	709	306
Parameters refined	42	23
Restraints	0	0
Goof	1.162	1.377
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²)	0.0164, 0.0376	0.0265, 0.1039
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.860, -0.706	2.218, -3.721

Table S4. Selected Crystal, Collection and Refinement Data for **1** and **2**.

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