

Electronic Supplementary Information

The first heterocubane cluster with [W₃GaS₄] core

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Experimental Section

General remarks. All reactions were performed using standard Schlenk and vacuum-line techniques under argon atmosphere. Solvents were distilled over appropriate drying agents under argon prior to use. The $[\text{Mo}_3\text{S}_4(\text{dppe})_3\text{Cl}_3]\text{Cl}$ and $[\text{W}_3\text{S}_4(\text{dppe})_3\text{Br}_3]\text{Br}$ cluster salts [1] and $[\text{GaCp}^*]_6$ [2] were prepared using the described procedures. Elemental analyses were performed with a Euro EA 3000 analyzer. The EPR spectra were recorded with Varian E-109 spectrometer in X-frequency band. Magnetic susceptibility measurements were performed on polycrystalline samples with Quantum Design MPMSXL SQUID magnetometer in the temperature range 2–300 K with magnetic fields up to 5 kOe. The susceptibilities of the samples were corrected for the sample holder contribution, previously measured under the same conditions, and for the diamagnetic contribution of the constituent atoms by using Pascal constant tables. The effective magnetic moment was calculated as $\mu_{\text{eff}}(\text{T}) = [(3k/N_A\mu_B^2)\chi T]^{1/2} \approx (8\chi T)^{1/2}$. Infrared spectra (in KBr pellets) were recorded using an Agilent Cary 660 FTIR spectrometer in 4000 to 400 cm^{-1} range.

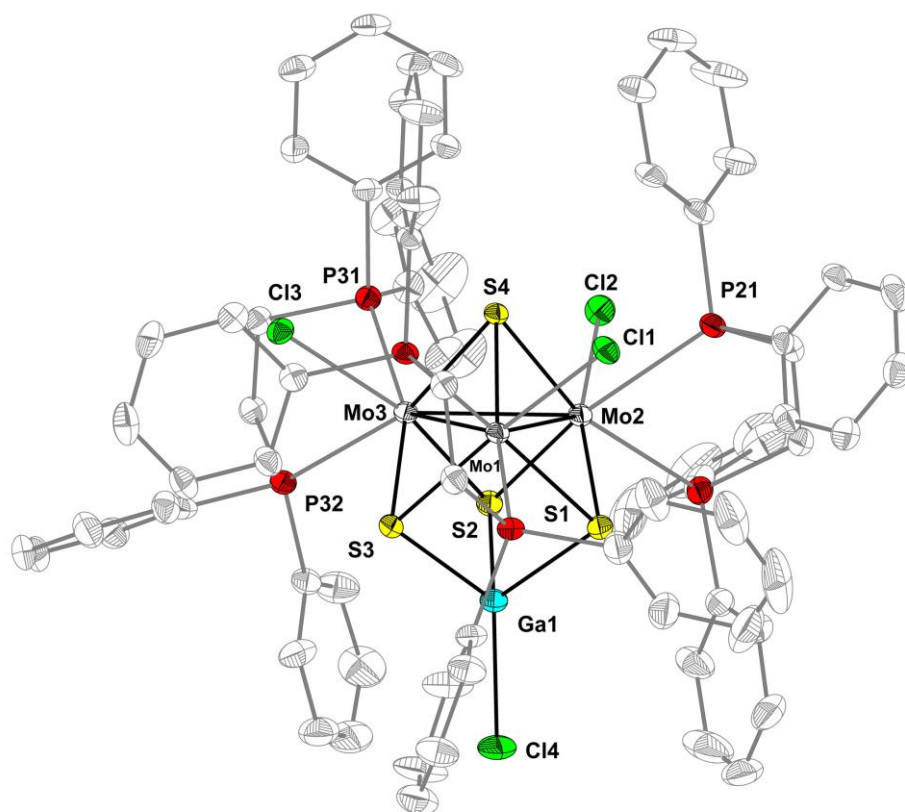
Synthesis of $[\text{Mo}_3\text{S}_4(\text{GaCl})(\text{dppe})_3\text{Cl}_3]$ (3c**).** In a glove-box, solid $[\text{Mo}_3\text{S}_4(\text{dppe})_3\text{Cl}_3]\text{Cl}$ (119 mg, 0.068 mmol) and GaCp^* (90 mg, 0.073 mmol) was placed into the Schlenk tube equipped with a J. Young high-vacuum PTFE valve. The vessel was cooled down to 77 K and THF (*ca.* 20 mL) was condensed into the Schlenk tube under reduced pressure. The mixture was allowed to warm up to room temperature (the precipitate of the initial cluster disappeared) and then heated in an oil bath at 55°C for 24 hours under vigorous stirring. The solvent volume was carefully reduced to approximately half of volume, then *ca.* 15 mL Et_2O was slowly condensed onto the THF solution through vacuum transfer. The slow diffusion of Et_2O afforded almost black crystals suitable for X-ray experiment. Yield 30 %. IR (KBr, ν , cm^{-1}): 3050 (m), 2921 (m), 1571 (m), 1482 (m), 1432 (s), 1309 (w), 1272 (w), 1189 (m), 1159 (w), 1096 (m), 1026 (m), 998 (m), 871 (m), 822 (m), 740 (s), 692 (s), 674 (m), 648 (m), 616 (m), 517 (s), 488 (m), 413 (w). $\text{C}_{78}\text{H}_{72}\text{Cl}_4\text{GaMo}_3\text{P}_6\text{S}_4$ (1822.87): calcd. C 51.39, H 3.98, S 7.05; found: C 51.40, H 4.15, S 6.90.

Synthesis of $[\text{W}_3\text{S}_4(\text{GaBr})(\text{dppe})_3\text{Br}_3]$ (3d**)** was performed similarly starting from $[\text{W}_3\text{S}_4(\text{dppe})_3\text{Br}_3]\text{Br}$ (130 mg, 0.059 mmol) instead of $[\text{Mo}_3\text{S}_4(\text{dppe})_3\text{Cl}_3]\text{Cl}$ and heating the reaction mixture for 14 days. Yield 25 %. IR (KBr, ν , cm^{-1}): 3050 (m), 2915 (m), 2863 (m), 1623 (m), 1585 (m), 1571 (m), 1484 (m), 1433 (s), 1413 (m), 1332 (w), 1310 (w), 1272 (w), 1191 (m), 1159 (m), 1097 (m), 1071 (m), 1027 (m), 999 (m), 872 (m), 821 (w), 740 (s), 693 (s), 673 (m), 649 (m), 616 (w), 518 (m), 494 (m), 421 (w). $\text{C}_{78}\text{H}_{72}\text{Br}_{3.81}\text{Ga}_{0.81}\text{W}_3\text{P}_6\text{S}_4$ (2235.94): calcd. C 41.90, H 3.24, S 5.74, found C 41.10, H 3.05, S 5.80.

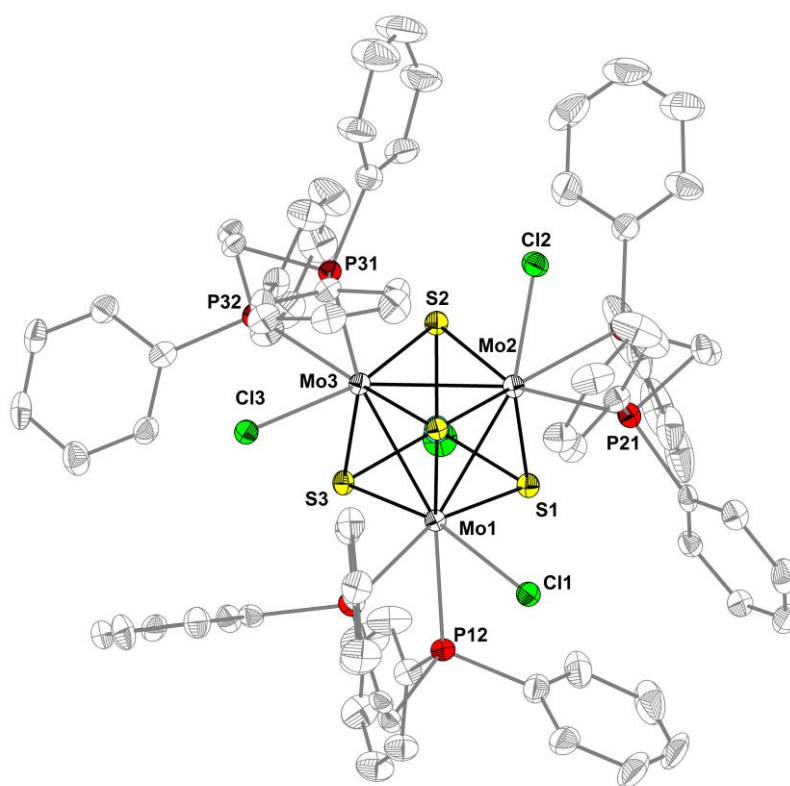
X-ray Studies. Diffraction data were collected at 150 K using a Bruker Nonius X8 Apex CCD diffractometer (graphite monochromated Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å). The ϕ - and ω -scan techniques were employed to measure intensities. Absorption corrections were applied using the SADABS program [3]. The crystal structures were solved by direct methods and refined by the full-matrix least squares techniques with the use of the SHELXTL package [4] and OLEX2 GUI [5]. All non-hydrogen atoms of non-solvent molecules were refined anisotropically. Hydrogen atoms were located geometrically and refined in rigid body approximation. **3c**·3THF contains one non-disordered THF molecule (refined anisotropically) per cluster and two disordered ones with the refined occupancies of 0.55/0.45 and 0.72/0.28 (refined isotropically). For the disordered THFs, DFIX and DANG restraints and EADP constrains were applied. The structure **3d**·5THF also contains solvent molecules; 4 of crystallographically independent ones were located with site occupancies of 1 and one – with occupancy of 0.5 (refined isotropically) due to its proximity to the twofold axis. Due to slight disorder of solvent molecules, DFIX and DANG restraints were applied for some THFs. One solvent THF molecule appeared to be highly disordered and it was difficult to model its position reliably, especially due to its proximity to the special position. Therefore, the structure was treated *via* Solvent Mask procedure [6] to remove the contribution of the electron density in the solvent regions from the intensity data. The total potential solvent accessible void volume was estimated to be *ca.* 650 Å³ and the electron count per unit cell was 280, which were assigned to additional 4 THF molecules per unit cell and 0.5 THF molecule per cluster. The crystallographic parameters and crystal data collection and structure refinement data are summarized in Table S1.

Table S1. Crystal Data and Data Collection and Refinement Details

	3c ·3THF	3d ·5THF
Chemical formula	C ₉₀ H ₉₆ Cl ₄ GaMo ₃ O ₃ P ₆ S ₄	C ₉₈ H ₁₁₂ Br _{3.81} Ga _{0.81} O ₅ P ₆ S ₄ W ₃
Formula weight	2039.06	2596.92
Crystal system, space group	Monoclinic, <i>P2₁/n</i>	Monoclinic, <i>C2/c</i>
Temperature (K)	150	150
<i>a</i> (Å)	19.6347(5)	41.4088(13)
<i>b</i> (Å)	21.1225(5)	18.0186(6)
<i>c</i> (Å)	21.2228(5)	28.4195(9)
β (°)	90.856(1)	110.516(1)
<i>V</i> (Å ³)	8800.8(4)	19859.7(11)
<i>Z</i>	4	8
<i>d</i> _{calcd} (g cm ⁻³)	1.539	1.713
μ (mm ⁻¹)	1.095	5.447
Crystal size (mm)	0.42 × 0.42 × 0.08	0.35 × 0.22 × 0.1
<i>F</i> (000)	4156	10038
Θ range (°)	1.360–26.372	1.522–25.027
<i>h, k, l</i> limits	-24 ≤ <i>h</i> ≤ 24, -26 ≤ <i>k</i> ≤ 26, -26 ≤ <i>l</i> ≤ 26	-49 ≤ <i>h</i> ≤ 46, -13 ≤ <i>k</i> ≤ 21, -31 ≤ <i>l</i> ≤ 33
Measured reflections, collected / independent	73167 / 17994	55752 / 17525
Observed reflections [<i>I</i> > 2σ(<i>I</i>)]	15370 (<i>R</i> _{int} = 0.025)	13983 (<i>R</i> _{int} = 0.043)
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	0.0330, 0.0826	0.0383, 0.0983
<i>R</i> indices (all data)	0.0430, 0.0873	0.0559, 0.1122
Goodness-of-fit on <i>F</i> ²	1.076	1.060
No. of parameters	974	966
No. of restraints	35	30
Δρ _{max} , Δρ _{min} (e Å ⁻³)	1.66, -1.07	2.09, -1.14
CCDC	1813451	1813450



(a)



(b)

Figure S1. Molecular structure of **3c**: (a) side view, (b) view along S4–Ga1 direction. Hydrogen atoms not shown.

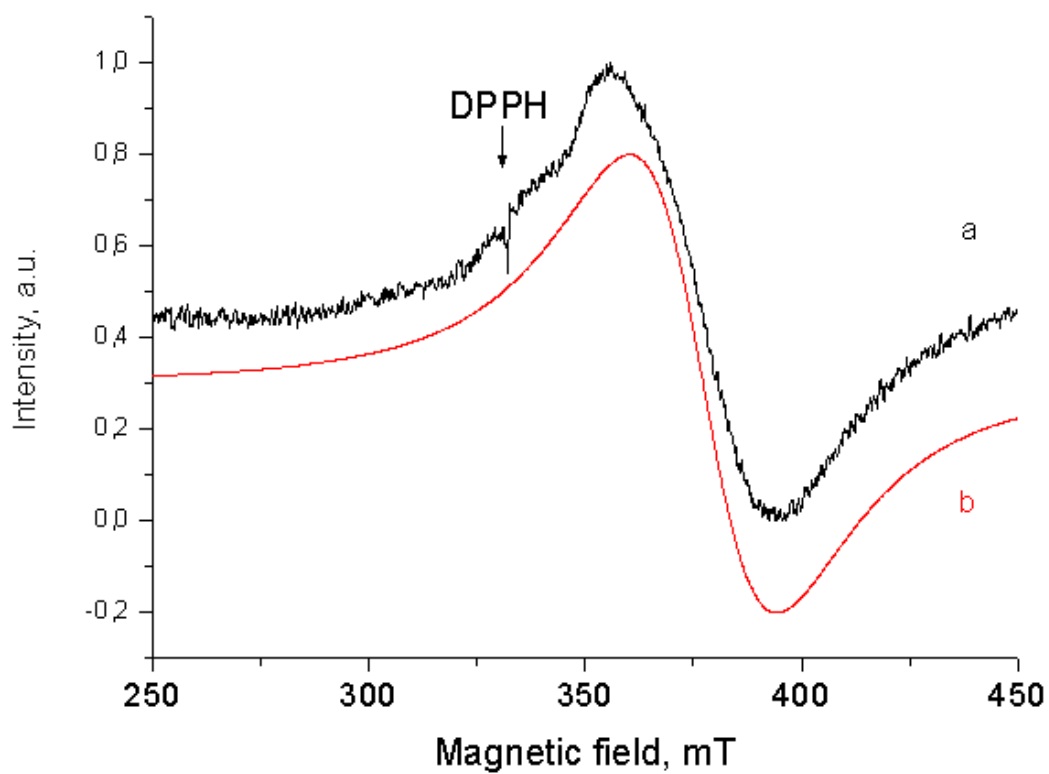


Figure S2. EPR spectra (*a* - experimental, *b* - simulated) of the polycrystalline sample of complex **3d** recorded in X frequency band at 77K. DPPH – 2,2-diphenyl-1-picrylhydrazyl with $g=2.0036$.

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