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Electronic Supplementary Information

Synthesis, molecular structures and EPR spectra of the paramagnetic cuboidal clusters with Mo₃S₄Ga 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 $[Mo_3S_4(dppe)_3Br_3]Br$ and $[Mo_3S_4(dmpe)_3Br_3]Br$ cluster salts were prepared using the described procedures [1]. IR spectra were recorded with an Agilent Cary 660 FTIR instrument. Elemental analyses were performed with a Euro EA 3000 analyzer in the Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk. Magnetic measurements were performed on polycrystalline samples with a SQUID magnetometer (Quantum Design MPMS-XL-5) in the temperature range 2–300 K with an applied magnetic field of 0.5 T. Isothermal magnetization measurements were performed on the same samples at 2 K with fields of up to 5 T. 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. EPR measurements were performed with a Q-band Bruker E-580 ELEXSYS spectrometer on polycrystalline powder samples in the 4-300 K temperature range. Synthesis of the {Mo₃Ga} complexes (general procedure). A mixture of solid $[Mo_3S_4(diphos)_3Br_3]Br$ (ca. 100 mg) and Ga (100 mg, 1.43 mmol) was placed into the Schlenk tube equipped with a J. Young high-vacuum PTFE valve and cooled down to 77 K. THF (*ca.* 20 mL) was condensed into the Schlenk tube under reduced pressure. The mixture was allowed to warm up to room temperature and then heated in an oil bath at 55°C for 2 weeks under vigorous stirring. The green precipitate of the initial cluster disappeared and a grey precipitate was formed. The precipitate was filtered off to give a dark brown solution. Slow diffusion of *ca.* 30 mL Et₂O into the solution afforded almost black crystals suitable for X-ray experiment.

1.1.5 C_4H_8O . Yield 35 %. $C_{84}H_{84}Br_4GaMo_3O_{4.5}P_6S_4$ (2108.83): calcd. C 47.84, H 4.01, S 6.08; found: C 47.45, H 3.70, S 6.15. IR (KBr, v, cm⁻¹): 3049 (w), 2915 (w), 1620 (w), 1584 (w), 1571 (w), 1482 (m), 1432 (s), 1413 (w), 1331 (w), 1309 (w), 1272 (w), 1190 (w), 1158 (w), 1096 (m), 1027 (w), 998 (w), 967 (w), 915 (w), 871 (m), 820 (w), 740 (s), 692 (s), 671 (m), 648 (w), 615 (w), 517 (m), 488 (m), 412 (w). **2**· C_4H_8O . Yield 20 %. $C_{22}H_{56}Br_4GaMo_3OP_6S_4$ (1327.95): calcd. C 19.90, H 4.25, S 9.66, found C 19.65, H 4.05, S 9.85. IR (KBr, v, cm⁻¹): 3401 (m), 2967 (m), 2901 (m), 1824 (w), 1626 (m), 1414 (s), 1282 (m), 1246 (w), 1194 (w), 1136 (m), 1100 (m), 1063 (m), 994 (w), 939 (s), 901 (s), 846 (m), 794 (w), 745 (m), 717 (m), 649 (m), 566 (m), 477 (w), 440 (m).

X-ray Studies. Diffraction data were collected at 150 K using a Bruker Nonius X8 Apex CCD diffractometer (graphite monochromated Mo K α radiation, $\lambda = 0.71073$ Å). Data collection and reduction were done using APEX2 program set, absorption correction was performed empirically using SADABS program [2]. The structures were solved by direct methods and refined by full-matrix least-squares techniques using SHELXTL program set [3]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located geometrically and refined in rigid body approximation. The structure 1·4.5C₄H₈O contains solvent molecules; two of them were located with site occupancies of 1 and one – with occupancy 0.5 (refined isotropically). Some of the solvent tetrahydrofuran or diethyl ether molecules appeared to be highly disordered and it was difficult to model their positions reliably. Therefore, the structure was treated via PLATON/SQUEEZE [4] procedure 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*. 2760 Å³ and the electron count per unit cell was 644, which were assigned to 16 THF (or Et₂O) molecules per unit cell and 2 THF (or Et₂O) molecules per formula unit. The crystallographic parameters and crystal data collection and structure refinement data are summarized in Table S1.

1. V.P. Fedin, M.N. Sokolov, Yu.V. Mironov, B.A. Kolesov, S.V. Tkachev, V.Ye. Fedorov, *Inorg. Chim. Acta*, **1990**, *167*, 39.

2. Bruker AXS Inc. (2013). APEX2 (Version 1.08), SAINT (Version 7.03), SADABS (Version 2.11), SHELXTL (Version 6.12). Madison, WI, USA.

3. G.M. Sheldrick, Acta Crystallogr., 2015, A71, 3.

4. A.L. Spek, Acta Crystallogr., 2009, D65, 148.

	$1 \cdot 4.5 C_4 H_8 O$	$2 \cdot C_4 H_8 O$
Chemical formula	$C_{96}H_{108}Br_4GaMo_3O_{4.5}P_6S_4$	$C_{22}H_{56}Br_4GaMo_3OP_6S_4$
$M_{ m r}$	2325.15	1327.91
Crystal system	Monoclinic	Trigonal
Space group	C2/c	R3c
<i>a</i> [Å]	41.507(3)	15.4061(2)
<i>b</i> [Å]	18.0564(11)	15.4061(2)
<i>c</i> [Å]	28.275(2)	31.5053(9)
α [°]	90	90
β [°]	110.780(1)	90
γ [°]	90	120
V[Å ³]	19813(2)	6475.9(2)
Ζ	8	6
T [K]	150	150
Crystal size [mm]	$0.42 \times 0.35 \times 0.24$	$0.32 \times 0.18 \times 0.15$
$\mu(Mo K\alpha) [mm^{-1}]$	2.477	5.606
T_{\min}, T_{\max}	0.423, 0.588	0.267, 0.487
θ range for data collection	2.10-26.37	2.00–26.36
Collected reflections	58684	13227
R _{int}	0.0430	0.0280
GoF on F^2	1.075	0.991
Unique reflections	20117	2862
Parameters	975	158
Restraints	50	41
$R_{l}, wR_{2}[I > 2\sigma(I)]$	0.0654, 0.1833	0.0175, 0.0455
R_1 , wR_2 [all data]	0.0942, 0.2083	0.0182, 0.0458
Residual max/min ρ [e Å ⁻³]	3.245 / -1.006	1.089 / -1.284
CCDC	1542006	1542007

Table S1. Crystallographic Data for $[Mo_3S_4Ga(dppe)_3Br_4]\cdot 4.5THF$ (1·4.5THF) and $[Mo_3S_4Ga(dmpe)_3Br_4]$ (2·THF)



(a)



Figure S1. Molecular structure of **1**: (*a*) side view, (*b*) view along S4–Ga1 direction. Hydrogen atoms not shown.



Figure S2. Thermal variation of the $\chi_m T$ product for compounds 1 and 2



Figure S3. Isothermal magnetization of compounds 1 and 2 at 2 K.



Figure S4. Q-band solid state EPR spectrum of 2 at different temperatures.