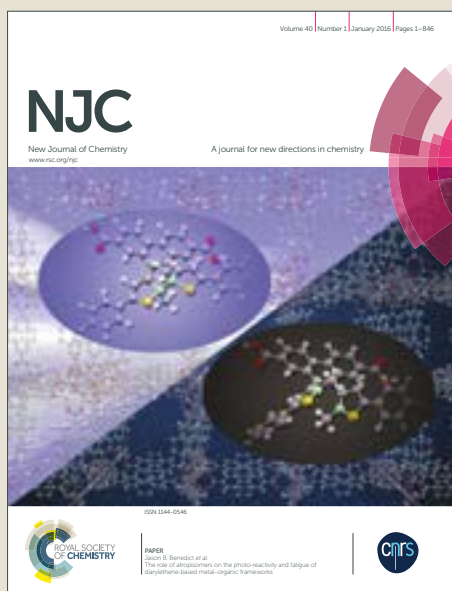


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Synthesis, molecular structures and EPR spectra of the paramagnetic cuboidal clusters with Mo₃S₄Ga core†

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Electron precise [Mo₃(μ₃-S)(μ-S)₃(diphos)₃Br₃]Br (diphos = dppe, dmpe) incomplete cuboidal clusters with six cluster skeletal electrons (CSE) were converted into paramagnetic cuboidal [Mo₃(GaBr)(μ₃-S)₄(diphos)₃Br₃] clusters by treatment with elemental Ga. The new heterobimetallic complexes with nine CSE possess a doublet ground state with the unpaired electron density delocalized over the three molybdenum atoms.

The cubane-type M₄S₄ unit is known for many metals including molybdenum and gallium.¹ Heterobimetallic Mo₃M'S₄ cores are also known for both transition and post-transition metals and they are synthesized by incorporating the M' metal into a preformed Mo₃(μ₃-S)(μ-S)₃ fragment, represented in Scheme 1. The most common sources of this Mo₃S₄ fragment are the [Mo₃S₄(H₂O)₉]⁴⁺ aqua ion, the Mo₃S₄(η⁵-Cp[#])₃⁺ (Cp[#] = C₅H₅, C₅H₄Me, or C₅Me₅) cations and the [Mo₃S₄(diphosphane)₃X₃]⁺ (X = halogen) complexes.² However, up to date post-transition groups 13–15 metals have only been incorporated into the [Mo₃S₄(H₂O)₉]⁴⁺ ion to afford single cubanes as well as corner-shared double cubane structures (see Scheme 1, metal–metal bonds are omitted for clarity).³ Interconversion between single and double cubane structures is initiated by a redox change. In the case of gallium, only single cubane structures have been characterized to date. The [Mo₃GaS₄(H₂O)₁₂]⁵⁺ and [Mo₃GaS₄(H₂O)₁₂]⁶⁺ complexes have been prepared by reacting the [Mo₃S₄(H₂O)₉]⁴⁺ aqua ion with gallium metal in 0.5 and 2 M HCl(aq), respectively.^{4a} Reaction of the Mo₃S₄⁴⁺ aqua ion with Ga³⁺ in the presence of NaBH₄ as reducing agent exclusively affords the [Mo₃GaS₄(H₂O)₁₂]⁵⁺ cluster cation.^{4b}

Our groups have extensively investigated the chemistry of diphosphane-substituted Mo₃S₄ complexes and we have isolated a series of heterobimetallic single cubane Mo₃M'S₄ derivatives for M' = Fe⁵, Co⁶, Ni⁷ and Cu⁸. In an attempt to extend this chemistry to post-transition metals, we reacted the cationic [Mo₃S₄(dppe)₃Br₃]⁺ cluster (dppe = 1,2-bis(diphenylphosphinoethane) with an excess of gallium metal resulting in the one-electron reduction of the cluster core, to afford unusual paramagnetic [Mo₃S₄(dppe)₃Br₃] complex.⁹ In a similar way, its tungsten congener [W₃S₄(dppe)₃Br₃] has also been isolated.¹⁰ These [M₃S₄(dppe)₃Br₃] paramagnetic clusters with seven cluster skeletal electrons (CSE) constitute rare examples of Mo₃Q₄ complexes, which are, in general, electron precise with 6 CSE for the formation of three metal–metal bonds. It is noteworthy that the reaction of the analogous [Mo₃Se₄(dppe)₃Br₃]⁺ cluster selenide with gallium results in a core transformation to afford a bicapped Mo₃Se₅ cluster complex.¹¹ These results evidence the unique reactivity of gallium and prompted us to further study its incorporation into the Mo₃S₄ core in order to obtain diphosphane Mo₃GaS₄ derivatives.

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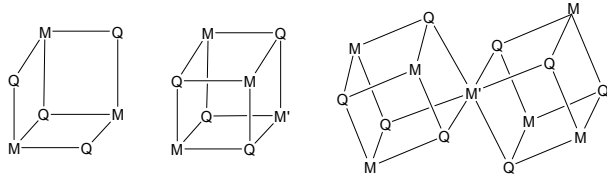
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† Electronic Supplementary Information (ESI) available: Experimental details, structural data, magnetic susceptibility data and EPR spectra. See DOI: 10.1039/x0xx00000x

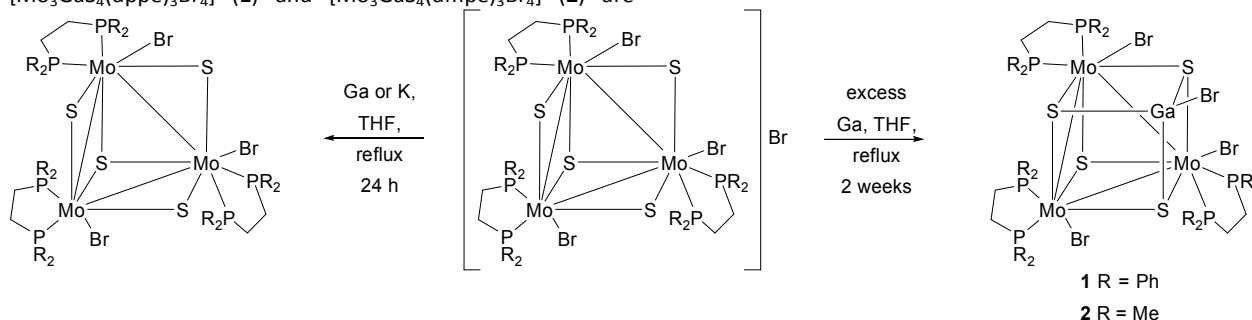
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Scheme 1

As highlighted in the introduction, metallic gallium can serve as one-electron reductant transforming the 6 CSE electron precise Mo_3S_4 diphosphane cluster cation to its neutral 7 CSE congener. When the reaction between $[\text{Mo}_3\text{S}_4(\text{diphosphane})_3\text{Br}_3]\text{Br}$ and gallium is carried out under rigorous air-free conditions for two weeks reaction time, as represented in Scheme 2, cubane type clusters $[\text{Mo}_3\text{GaS}_4(\text{dppe})_3\text{Br}_4]$ (**1**) and $[\text{Mo}_3\text{GaS}_4(\text{dmpe})_3\text{Br}_4]$ (**2**) are



Scheme 2

Table 1 Selected average bond distances (Å) for cluster complexes with a Mo_3GaS_4 core.^a

Distance	1	2	$[\text{Mo}_3\text{GaS}_4(\text{H}_2\text{O})_{12}]^{5+}$	$[\text{Mo}_3\text{GaS}_4(\text{H}_2\text{O})_{12}]^{6+}$
Mo–Mo	2.795[18]	2.7784(6)	2.713[3]	2.679[6]
Mo–Ga	3.33[4]	3.2704(8)	3.52[2]	3.60[2]
Mo–(μ_3 -S) ^b	2.354[2]	2.3624(13)	2.32[2]	2.332[3]
Mo–(μ_3 -S) ^c	2.399[5] ^d	2.4296(11) ^d	2.303[5]	2.335[4]
	2.391[14] ^e	2.3904(11) ^e		
Ga–S	2.34[2]	2.3099(12)	2.534[7]	2.50[1]
Ga–Br	2.3488(10)	2.3632(14)	–	–
Reference	this work	this work	4a	4a

^aStandard deviations are given in parentheses; standard deviations for averaged values are given in square brackets. ^b μ_3 -S capping Mo_3 face. ^c μ_3 -S capping Mo_2Ga face. ^dDistance *trans* to the Mo–P bond. ^eDistance *trans* to the Mo–Br bond.

The crystal structures of **1**·4.5THF and **2**·THF were determined by single crystal X-ray diffraction, and both complexes share identical structural features.† An ORTEP drawing of the

formed, and can be isolated in moderate yields (see Scheme 2). It is reasonable to assume that the reduced $\text{Mo}_3\text{S}_4(\text{diphosphane})_3\text{Br}_3$ species with 7 CSE are formed first along with low valent gallium halides, resulting from the oxidation of gallium metal. Then, formal addition of a GaBr vertex to the trimetallic 7 CSE cluster produces **1** and **2**, both containing 9 CSE. The two other Mo_3Ga clusters reported to date $[\text{Mo}_3\text{GaS}_4(\text{H}_2\text{O})_{12}]^{5+}$ and $[\text{Mo}_3\text{GaS}_4(\text{H}_2\text{O})_{12}]^{6+}$ contain 8 and 7 CSE, respectively. Incidentally, reaction of $[\text{Mo}_3\text{S}_4(\text{dppe})_3\text{Cl}_3]\text{Cl}$ or $[\text{W}_3\text{S}_4(\text{dppe})_3\text{Br}_3]\text{Br}$ with an excess of gallium metal always stops at the reduction stage and without evidence for Mo_3GaS_4 or W_3GaS_4 species. Moreover, we were unable to isolate the reduced 7 CSE $\text{Mo}_3\text{S}_4(\text{dmpe})_3\text{Br}_3$ derivative with a less bulkier and more basic diphosphane than dppe, and reaction of $[\text{Mo}_3\text{S}_4(\text{dmpe})_3\text{Br}_3]\text{Br}$ with gallium always yielded invariably to **2** as the only isolable product.

molecular structure of **2** is represented in Figure 1. Both structures consist of discrete molecules of **1** and **2** with a central Mo_3Ga core. Compound **2** crystallizes in trigonal $R\bar{3}c$

space group with the S4, Br4 and Ga1 atoms lying on a C_3 axis with a unique Mo–Mo bond distance of 2.7784(6) Å and a S4–Ga1–Br4 angle of 180°. The Mo₃ triangle in **1** shows small deviations from a three-fold symmetry (ESI, Fig. S1). The Mo–Mo bond lengths in **1** fall within the range 2.7756(7)–2.8132(7) Å and the Br atom coordinated to Ga is deviated from the central S4–Ga1 axis (\angle S4–Ga1–Br4 equals 175.52(5)°). Table 1 lists the most relevant bond distances of compounds **1** and **2** together with those reported for the closely related Mo₃GaS₄ aqua clusters.

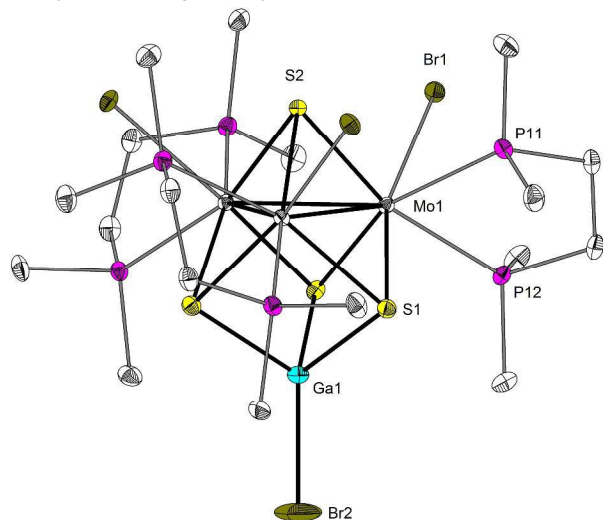


Fig. 1 ORTEP drawing of **2** with 50 % thermal ellipsoids and atom-numbering scheme. Hydrogen atoms are omitted for clarity.

The average Mo–Mo bond distance in **1** of 2.795[18] Å is slightly shorter, by 0.03 Å, than that observed for its parent cluster [Mo₃S₄(dppe)₃Br₃] with 7 CSE (2.82[3] Å).⁹ The shortening of the Mo–Mo or W–W bond is typical when a post-transition element is added to the M₃S₄ unit to form a heterocubane M₃M'S₄ core. The opposite tendency is found for the Mo–Mo bond distances in [Mo₃GaS₄(H₂O)₁₂]⁵⁺ (2.735[8] Å) and [Mo₃S₄(H₂O)₉]⁴⁺ (2.713[3] Å). There is an increase in the Mo–Mo bond lengths on going from [Mo₃GaS₄(H₂O)₁₂]⁶⁺ with 7 CSE to [Mo₃GaS₄(H₂O)₁₂]⁵⁺ with 8 CSE and to **1** and **2** with 9 CSE. This increase in Mo–Mo bond lengths is accompanied by a significant decrease of ca. 0.2–0.3 Å in the Mo–Ga bond distances. The coordination environment of molybdenum in **1** and **2** is similar to that of their trimetallic [Mo₃S₄(diphosphane)₃X₃] precursors. The gallium atom in **1** and **2** has tetrahedral coordination in contrast with the octahedral environment found for the Mo₃GaS₄ aqua clusters. Compounds **1** and **2** with an odd number of electrons are expected to be paramagnetic. At 300 K the product of the molar magnetic susceptibility times the temperature, $\chi_m T$, for **1** (see Figure S2) and **2** equals ca. 0.34 emu K mol⁻¹ in both compounds (near the expected value of 0.375 for one unpaired electron) and remains almost constant when the temperature is decreased, as expected for a paramagnetic system. The isothermal magnetization at 2 K (Figure S3) shows a saturation values close to 1 μ_B , confirming the presence of

single unpaired electron in both compounds. The Q-band solid state EPR spectra of solid samples of **1** and **2** are very similar (Figures 2 and S4, respectively) with only one signal whose intensity increases upon decreasing the temperature. The signal presents axial anisotropy in both compounds although in compound **2** it shows a rhombic anisotropy at very low temperatures. This fact may be due to the larger distortions in the Mo coordination environment in **2**. Thus, **2** has a more rhombic coordination environment with three different Mo–S bond distances (2.3624(13), 2.3904(11) and 2.4296(11) Å, Table 1) whereas in **1** we observe a more axial distortion since two of these distances are almost identical (ca. 2.354, 2.391 and 2.399 Å). Both compounds show no hyperfine splitting at low temperature indicating that the unpaired electron is delocalized over the three metal centres. In contrast, the unpaired electron density in the trinuclear cluster [Mo₃S₄(dppe)₃Br₃] is localized on one metal centre.⁹ The electronic structures calculated for [Mo₃GaS₄(H₂O)₁₂]^{5+/6+} using the spin polarized discrete variational DV-X α method shows that the orbitals in the HOMO-LUMO region consist mainly of Mo 4d atomic orbitals. These results are in agreement with the absence of hyperfine splitting at low temperatures in the registered EPR spectra.⁴

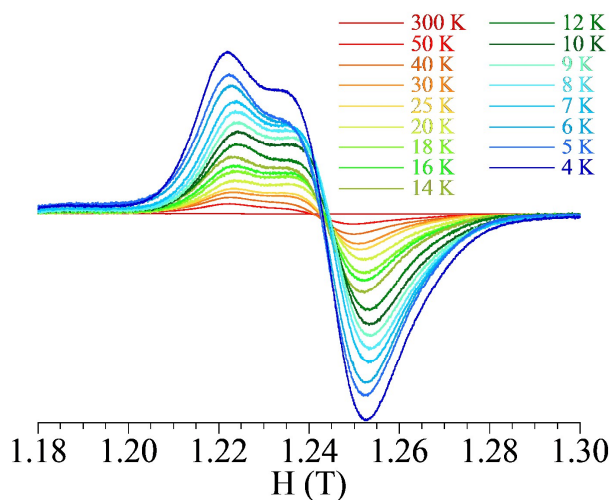


Fig. 2 Q-band solid state EPR spectrum of **1** at different temperatures.

In conclusion, interaction of the trimetallic Mo₃S₄ clusters with gallium causes transformation of the cluster core to afford the first examples of a Mo₃Ga(μ_3 -S)₄ cluster core coordinated by diphosphane ligands. The cubane-like core formation likely goes through the step of one electron reduction of the Mo₃S₄ unit. The two isolated heterobimetallic cluster complexes possess an odd number of electrons resulting in a $S = 1/2$ ground state. The latter was evidenced by means of magnetic susceptibility measurements and confirmed by EPR spectroscopy.

Conflict of interest

There are no conflicts to declare.

Acknowledgements

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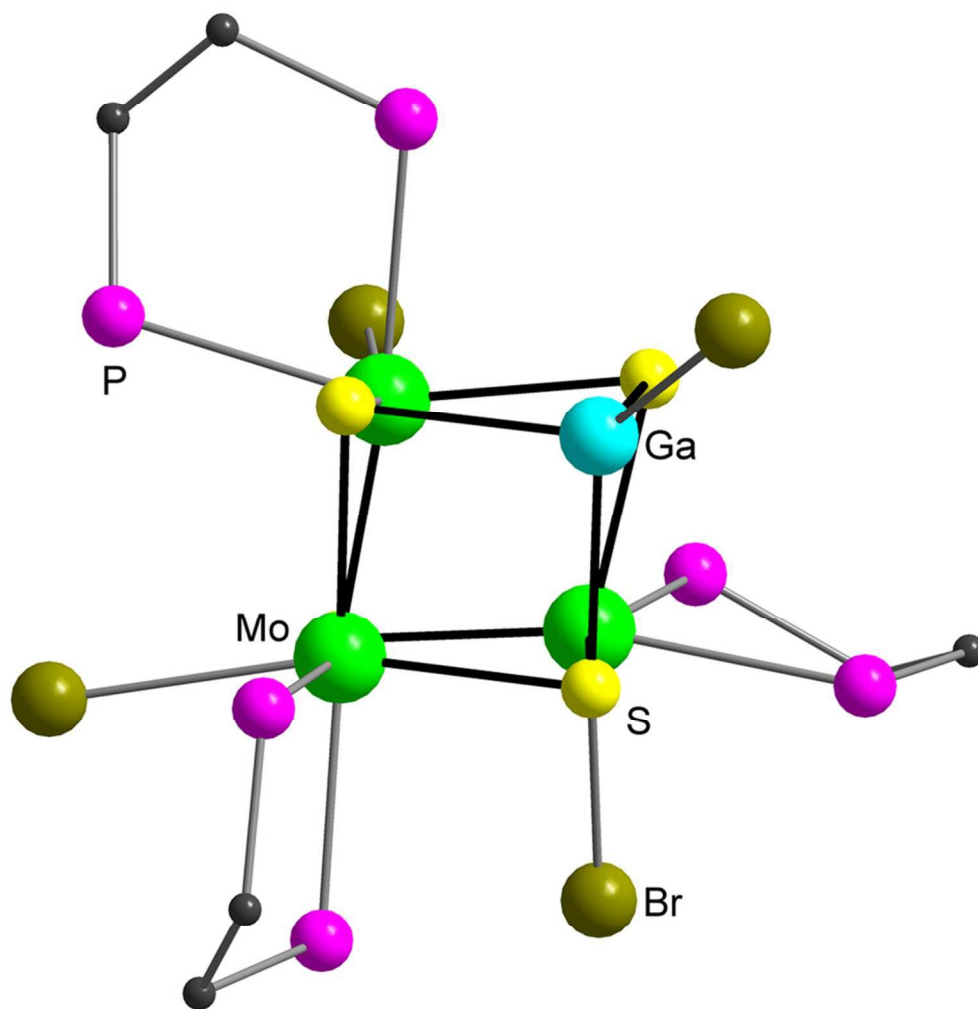
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Notes and references

‡ Crystal data for **1**·4.5C₄H₈O: C₉₆H₁₀₈Br₄GaMo₃O_{4.5}P₆S₄, *M_r* = 2325.15, monoclinic, space group *C2/c*, *a* = 41.507(3) Å, *b* = 18.0564(11) Å, *c* = 28.275(2) Å, α = 90°, β = 110.780(1)°, γ = 90°, *V* = 19813(2) Å³, *Z* = 8, 58589 reflections measured, 20131 independent reflections (*R_{int}* = 0.0430). Final *R* indices: *R*₁ = 0.0654 and *wR*₂ = 0.1833 [*I* > 2σ(*I*)]; *R*₁ = 0.0942 and *wR*₂ = 0.2083 (all data). Largest diff. peak and hole: 3.245 and −1.006 e Å^{−3}. CCDC 1542006. Crystal data for **2**·C₄H₈O: C₂₂H₅₆Br₄GaMo₃OP₆S₄, *M_r* = 1327.91, trigonal, space group *R3c*, *a* = *b* = 15.4061(2) Å, *c* = 31.5053(9) Å, α = β = 90°, γ = 120°, *V* = 6475.9(2) Å³, *Z* = 6, 13227 reflections measured, 2862 independent reflections (*R_{int}* = 0.0280). Final *R* indices: *R*₁ = 0.0175 and *wR*₂ = 0.0455 [*I* > 2σ(*I*)]; *R*₁ = 0.0182 and *wR*₂ = 0.0458 (all data). Largest diff. peak and hole: 1.089 and −1.284 e Å^{−3}. CCDC 1542007.

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The paramagnetic cuboidal clusters $[\text{Mo}_3(\text{GaBr})(\mu_3\text{-S})_4(\text{diphos})_3\text{Br}_3]$ (diphos = dppe, dmpe) were synthesized by reduction of triangular clusters $[\text{Mo}_3\text{S}_4(\text{diphos})_3\text{Br}_3]\text{Br}$ with elemental Ga.



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