Electronic Supplementary Information

An Unprecedented Pentanary Chalcohalide with the Mn Atoms in Two Chemical Environments: Unique Bonding Characteristics and Magnetic Properties

Yu-Jun Zheng,[a] Yong-Fang Shi,[a] Chong-Bin Tian,[a] Hua Lin,[*,a] Li-Ming Wu,[*,b] Xin-Tao Wu,[a] and Qi-Long Zhu[*,a]

[a]*State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China.*
[e]*Key Laboratory of Theoretical and Computational Photochemistry, Ministry of Education, College of Chemistry, Beijing Normal University, Beijing 100875, P. R. China.*
*E-mail: linhua@fjirsm.ac.cn, liming_wu@fjirsm.ac.cn and qlzhu@fjirsm.ac.cn.

Experimental Section

Materials and Instruments

Energy dispersive X-ray (EDX, Oxford INCA) spectra were performed on a field emission scanning electron microscope (FESEM, JSM6700F) equipped with an X-ray spectroscope. Powder X-ray diffraction (PXRD) patterns of polycrystalline material were collected on a Rigaku Mini-Flex II powder diffractometer by using Cu-K_α radiation (λ = 1.5416 Å) in the range of 10–60° (2ϴ) with a step size of 0.02°. The PXRD data were analyzed using a profile fitting by a least-squares method employing the computer program GSAS implemented with EXPGUI.[1] The UV–Vis–NIR diffuse reflectance spectra were measured on a Perkin-Elmer Lambda 950 UV–Vis spectrophotometer at room temperature in the wavelength range of 190−2500 nm and

$BaSO_4$ was used as a standard (100% reflectance). The absorption spectrum was calculated from the reflection spectra using the Kubelka–Munk function: $\alpha/S = (1-R)^2/2R$, where α was the absorption coefficient, S was the scattering coefficient, and R was the reflectance.[2] Magnetic measurements were performed using a commercial Quantum Design Physical Property Measurement System (PPMS). The ground single-crystal power sample was placed in a gel capsule sample holder suspended in a plastic drinking straw. Magnetic susceptibility was measured at 1000Oe from 300 to 2K, and magnetization was measured at 2K in an applied field from –8 to 8 T (field scan of 0.1 T per step). Moreover, low-temperature magnetic susceptibility was also measured with field cooling (FC) and zero-field-cooling (ZFC) regimes from 2 to 50K under 50 Oe.

Synthesis of $Cs_2[Mn_2Ga_3S_7Cl]$ (1). The title compound resulted unexpectedly, since the initial objective was to prepare single crystals of quaternary "$CsMn_4Ga_5S_{12}$". Compound **1** was obtained from a mixture of 4.0 mmol Mn (5N, Alfa Aesar China (Tianjin) Co., Ltd.), 5.0 mmol Ga (5N, Sinopharm Chemical Reagent Co., Ltd.) and 12.0 mmol S (5N, Sinopharm Chemical Reagent Co., Ltd.) together with 5.0 mmol CsCl (4N, Sinopharm Chemical Reagent Co., Ltd.) in a fused-silica tube under 10^{-3} Pa atmosphere, and finally placed in a temperature-controlled tube furnace. The reactants were gradually heated to 1223 K and held there for 3 days, then slowly cooled to 623 K at a rate of 3K/h before cutting off the furnace. The products were washed with distilled water and dried by an ethanol, after such a treatment, light-orange plates of **1** (70% yield) and red blocks of $CsMn_3Ga_5S_{11}$[3] were obtained. Many attempts to increase the yield were failed, including starting reaction, loading radio, and annealing temperature. Therefore, handpicked crystals of **1** were used to measure all the properties reported herein. The purity of target product was confirmed by PXRD study, in which the experimental PXRD pattern is in good agreement with the simulated data based on the single-crystal XRD model. The crystals of **1** were stable in the air for several months.

Single crystal X-ray Crystallography. The single-crystal diffraction data collections was taken on a Mercury CCD equipped with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at room-temperature. The absorption correction was done[4] and the structure was solved by the direct methods and refined by the full-matrix least-square fitting on F^2 using the *SHELX–2014* software.[5] All of the non-hydrogen atoms were refined with anisotropic thermal parameters and the coordinates were standardized using *STRUCTURE TIDY*.[6] It is difficult to distinguish S and Cl atoms by diffraction data because their X-ray scattering factors are similar, but the identity can be assigned according to the valence bond sum (VBS) method, $V_i = \Sigma S_{ij}$, where the bond valence (S_{ij}) is calculated by $Sij = \exp[(R_{ij}–d_{ij})/0.37]$, dij is bond length between nearest neighboring atoms i–j, and R_{ij} is the tabulated parameter. Moreover, such VBS results about the S/Cl ratio were in good agreement with the EDX data and charge balance requirement.[7] The refinement details are summarized in Table S1. The positional coordinates and isotropic equivalent thermal parameters are given in Table S2, and the slected bond distances are listed in Table S3.

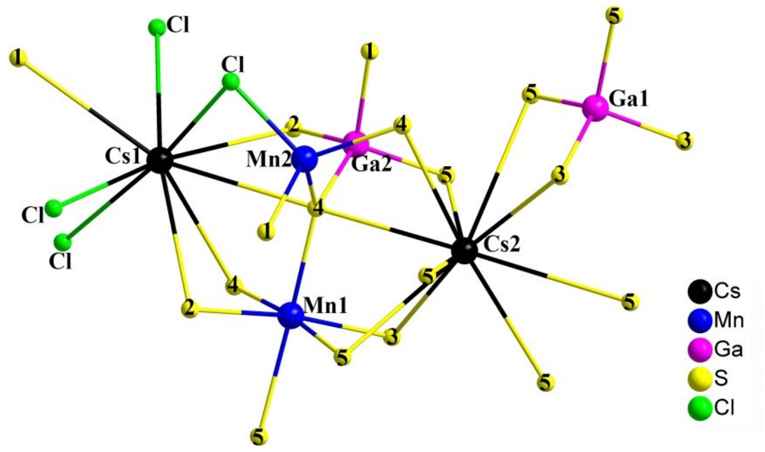


Figure S1. Coordination geometry of $Cs_2[Mn_2Ga_3S_7Cl]$.

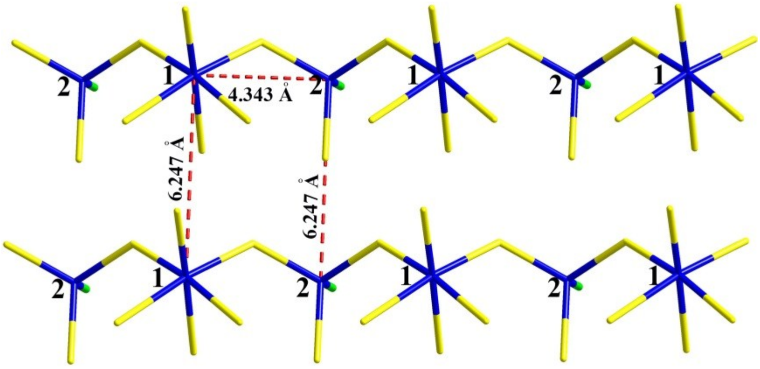
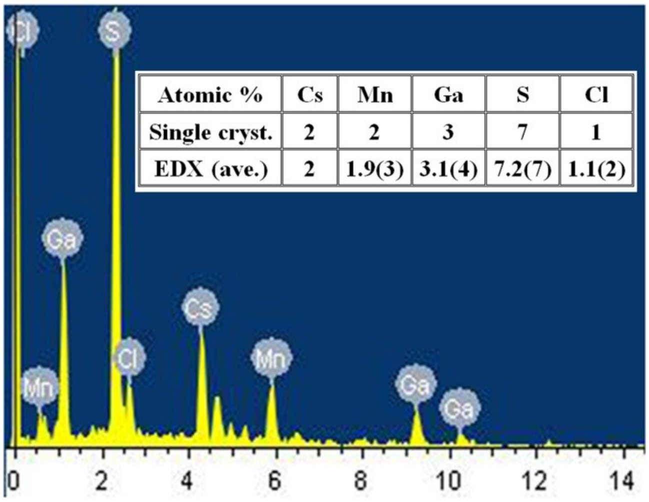


Figure S2. Schematic of 1D $[Mn_2S_7Cl]^{11-}$ chain, chains of [Mn1S$_6$]and [Mn2S$_3$Cl] connected by sharing S atoms. Blue: Mn; yellow: S; green: Cl.



Atomic %	Cs	Mn	Ga	S	Cl
Single cryst.	2	2	3	7	1
EDX (ave.)	2	1.9(3)	3.1(4)	7.2(7)	1.1(2)

Figure S3. The EDX results of $Cs_2[Mn_2Ga_3S_7Cl]$.

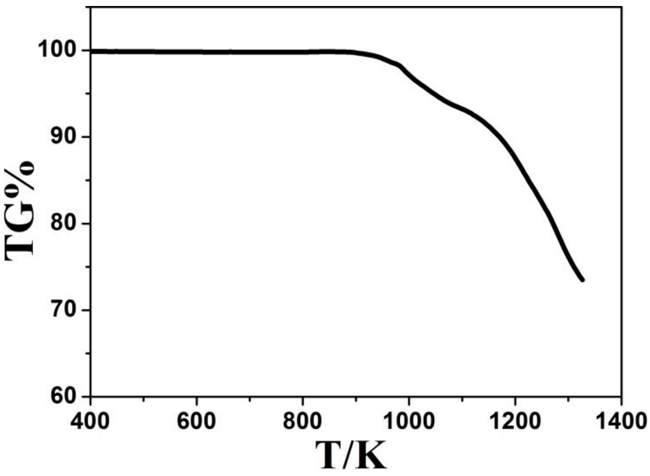


Figure S4. The TG curve of $Cs_2[Mn_2Ga_3S_7Cl]$.

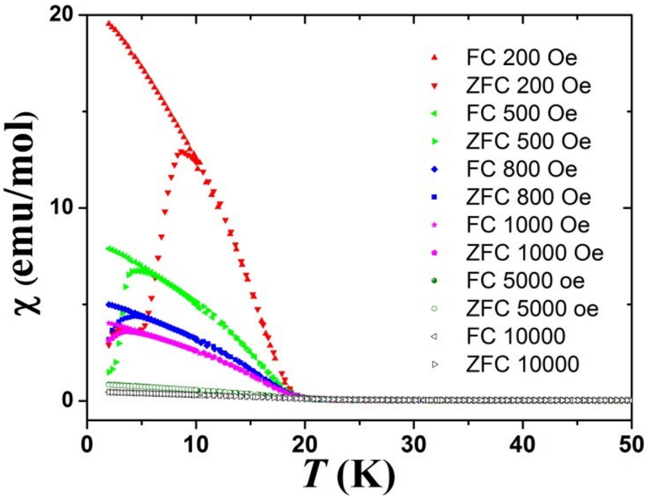


Figure S5. FC and ZFC curves at different fields.

Table S1. Crystallographic data and refinement details for $Cs_2[Mn_2Ga_3S_7Cl]$.

Empirical formula	$Cs_2[Mn_2Ga_3S_7Cl]$
Formula weight	844.73
Temperature(K)	293(2)
Crystal system	Orthorhombic
Space group	*Pnma* (No.62)
a (Å)	6.2467(6)
b (Å)	7.3879(8)
c (Å)	33.600(3)
V (Å^3)	1550.6(3)
Z	4
D_c (g·cm^{-3})	3.62
μ (mm^{-1})	12.43
GOOF on F^2	1.092
R_1, wR_2 ($I > 2\sigma(I)$) [a]	0.0381, 0.0944
R_1, wR_2 (all data)	0.0492, 0.1000
Largest diff. peak and hole (e·Å^{-3})	1.592, –1.415

[a]: $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2. Atomic coordinates and equivalent isotropic displacement parameters of $Cs_2[Mn_2Ga_3S_7Cl]$.

Atom	*Wyckff*	*x*	*y*	*z*	U_{eq}(Å)^a
Cs1	4*c*	0.2727(2)	0.25	0.02641(2)	0.0292(2)
Cs2	4*c*	0.2320(2)	0.25	0.71113(2)	0.0290(3)
Mn1	4*c*	0.0630(3)	0.25	0.15392(5)	0.0149(4)
Mn2	4*c*	0.3530(3)	0.25	0.58777(5)	0.0132(4)
Ga1	4*c*	0.1450(2)	0.25	0.28237(3)	0.0107(3)
Ga2	8*d*	0.1378(2)	0.0039()	0.37622(2)	0.0116(2)
S1	4*c*	0.2463(4)	0.25	0.91021(7)	0.0114(6)
S2	4*c*	0.2894(4)	0.25	0.40663(7)	0.0125(6)
S3	4*c*	0.2799(5)	0.25	0.21961(7)	0.0151(6)
S4	8*d*	0.2798(3)	0.0064(2)	0.12214(6)	0.0165(5)
S5	8*d*	0.2818(3)	0.0013(2)	0.31330(5)	0.0136(4)
Cl	4*c*	0.2731(5)	0.25	0.51931(9)	0.0340(8)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S3. Selected bond lengths (Å) of $Cs_2[Mn_2Ga_3S_7Cl]$.

Mn1–S4 ×2	2.493(2)	Cs1–S4 ×2	3.686(2)
Mn1–S3	2.590(3)	Cs1–S2	3.765(3)
Mn1–S2	2.657(3)	Cs1–S1	3.908(3)
Mn1–S5 ×2	2.771(2)	Cs1–S2	3.935(3)
Mn2–S4 ×2	2.368(2)	Cs1–Cl	3.478(3)
Mn2–S1	2.458(3)	Cs1–Cl	3.483(3)
Mn2–Cl	2.354(3)	Cs1–Cl ×2	3.7126(5)
Ga1–S3	2.271(3)	Cs2–S4 ×2	3.540(2)
Ga1–S5 ×2	2.278(2)	Cs2–S5 ×2	3.653(2)
Ga1–S3	2.281(3)	Cs2–S3 ×2	3.7057(5)
Ga2–S4	2.237(2)	Cs2–S5 ×2	3.797(2)
Ga2–S2	2.291(2)	Cs2–S5 ×2	3.904(2)
Ga2–S5	2.297(2)		
Ga2–S1	2.312(2)		

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[2] $CsMn_3Ga_5S_{11}$: monoclinic, Pc, a = 8.986(1) Å, b = 15.1621(1) Å, c = 13.957 Å, β = 105.35(1)°, V = 1833.7(9) Å^3, to be published work in our group.

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