

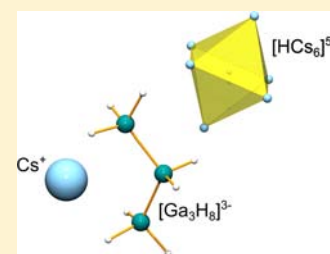
Cs₁₀H[Ga₃H₈]₃: A Hydrogenous Zintl phase Containing Propane-Like Polyanions [Ga₃H₈]³⁻ and Interstitial Hydrogen

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Supporting Information

ABSTRACT: The hydrogenous Zintl-phase Cs₁₀H[Ga₃H₈]₃ containing propane-like polyanions [Ga₃H(D)₈]³⁻ was successfully synthesized by direct hydrogenation of a 1:1 Cs/Ga metal mixture and characterized by powder X-ray and neutron diffraction. The charge of the polyanions is balanced by two different species of cations, hydrogen-centered octahedra [H(D)Cs₆]⁵⁺ and isolated Cs⁺. The structure crystallizes in the hexagonal space group *P6₃/mcm* (193) with the cell parameters *a* = 11.1108(3) Å, *c* = 18.2149(5) Å, *Z* = 2.



1. INTRODUCTION

Mixed metal environments provide rich opportunities for functionalizing structures and properties of hydrides. This has been shown extensively with combinations of transition metals *T* and electropositive active metals *M* (i.e., alkali, alkaline earth, or rare earth), leading to a wide range of hydrido complexes TH_{*n*}^{*m*-}.^{1–6} Less known and investigated are combinations between *M* and *p*-block metals/semimetals from groups 13–15 leading to hydrogenous Zintl phases.

The peculiar feature of hydrogenous Zintl phases is the coexistence of hydrogen and polymeric anions composed of *p*-block atoms. Hydrogen may be incorporated in Zintl phases in two different ways: either hydridic where H is exclusively coordinated by electropositive metals (interstitial hydrides), or as part of the polyanion where it acts as a covalently bonded ligand (polyanionic hydride).⁷ Both scenarios provide novel coordination environments and bonding scenarios for the atoms involved. This makes hydrogenous Zintl phases important model systems for fundamental studies of hydrogen–metal interactions.

For a long time polyanionic hydrides appeared restricted to compositional variations of the SrAl₂H₂⁸ and SrAlSiH⁹ crystal structures, which are based on two-dimensional, hydrogen terminated polyanions. The recent discovery of RbGaH₂ and Rb₈Ga₅H₁₅ featuring the hydrocarbon-like polyanions [GaH₂]_{*n*}^{*n*-} and [Ga₅H₁₂]⁵⁻ respectively, uncovered a new dimension of structural chemistry for polyanionic hydrides.¹⁰ [GaH₂]_{*n*}^{*n*-} conforms to the structure of polyethylene and [Ga₅H₁₂]⁵⁻ to that of neopentane. Interestingly, in Rb₈Ga₅H₁₅ hydrogen occurs partially interstitially (i.e., exclusively coordinated by rubidium) and partially covalently bonded to gallium. This ambivalent phenomenon has not been observed earlier with hydrogenous Zintl phases. But it is known from complex transition metal hydrides.¹¹

The realization of polyanionic hydrocarbon analogues with group 13 element backbones represents a truly new feature of metal hydrides and opens the door to a rich, yet to be explored

part in the world of Zintl phases. Olson et al. recently speculated on the basis of theoretical calculations that hydrocarbon analogues may also exist for borohydrides.¹² One of the predicted analogues was [B₃H₈]³⁻ in Li₃B₃H₈. Here we report on the synthesis and structure characterization of Cs₁₀Ga₉H₂₅ (Cs₁₀H[Ga₃H₈]₃), a hydrogenous Zintl phase with a propane-like polyanion with low valent Ga(I) and Ga(II). Similarly to Rb₈Ga₅H₁₅, the hydrogen occurs in both hydridic and covalently bonded forms. [Ga₃H₈]³⁻ is structurally related to earlier reported compounds with low-valent Ga stabilized by soft donor-ligands e.g. Ga₃I₅·3PEt₃.^{13,14}

2. EXPERIMENTAL METHODS

Synthesis. All sample handling was carried out in an argon filled glovebox with continuously purified atmosphere. Mixtures of cesium (ABCR 99.98%) and gallium (ABCR 99.9999%) were placed in a corundum crucible which was subsequently positioned in a stainless steel autoclave with a K-type thermocouple attached. The autoclave was pressurized to 50 bar with hydrogen(deuterium), placed inside a tube furnace and heated to 588 K for 12 h. The product from this step was ground, pressed to a pellet and the hydrogenation repeated at the same pressure, temperature and dwelling conditions to obtain a homogeneous sample. The final product, which kept the shape of the pellet, was ground and prepared for powder diffraction analyses.

Structure Characterization. Powder X-ray diffraction data were collected on samples protected with Kapton tape employing a Panalytical X'pert Pro diffractometer with monochromatic CuK_{α1} radiation ($\lambda = 1.540598$ Å). Reaction mixtures with a Cs:Ga ratio around 1 yielded the title phase, Cs₁₀Ga₉H₂₅, as the major product, together with varying amounts (5–25% weight fraction) of a second phase, Cs₈Ga₅H₁₅. The latter phase is isostructural to recently reported Rb₈Ga₅H₁₅¹⁰ and could be easily identified in the diffraction patterns. The diffraction lines from Cs₁₀Ga₉H₂₅ could be indexed with a hexagonal cell using TREOR,¹⁵ and the lattice constants were subsequently refined by least-squares methods to be *a* = 11.1108(3) Å and *c* = 18.2149(5) Å (*V* = 1947.4(1) Å³). From the reflection

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conditions $hh-2kl=2n$, $000l=2n$ the space group $P6_3/mcm$ (193) was assigned which is the one with the highest symmetry fulfilling these conditions. The structure of the metal positions was solved using direct methods as implemented in the suites EXPO2006¹⁶ and JANA2006.¹⁷ Rietveld refinement of the two-phase powder diffraction patterns was performed with JANA2006.¹⁷

To elucidate the positions of the hydrogen atoms about 4 g of a deuterated sample was prepared and sealed in a vanadium container. Powder neutron diffraction data were collected at the JEEP-II reactor in Kjeller with constant wavelength neutrons ($\lambda = 1.5556 \text{ \AA}$) using the PUS diffractometer. Initial deuterium positions were obtained using the parallel tempering algorithm as implemented in the program FOX¹⁸ and inputting the metal atom positions from the powder X-ray refinement. The full structure of $\text{Cs}_{10}\text{Ga}_9\text{H}_{25}$ was refined by least-squares refinement (FULLPROF2000¹⁹) together with the impurity phase $\text{Cs}_8\text{Ga}_5\text{H}_{15}$. The result of the refinement is presented in Figure 1 and Tables 1–3.

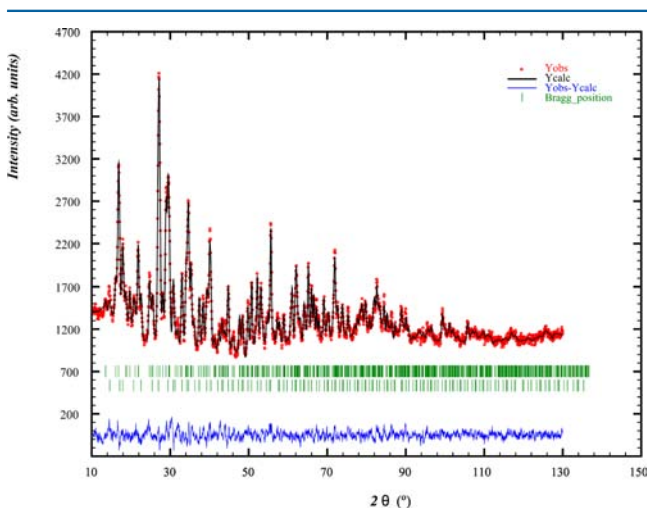


Figure 1. Rietveld fit to the powder neutron diffraction data of a two-phase mixture $\text{Cs}_{10}\text{H}[\text{Ga}_3\text{D}_8]_3$ and $\text{Cs}_8\text{Ga}_5\text{H}_{15}$ ($\lambda=1.5556 \text{ \AA}$).

Table 1. Cell Parameters and Refinement Parameters of $\text{Cs}_{10}\text{H}[\text{Ga}_3\text{D}_8]_3$ ^a

space group, Z	$P6_3/mcm$, 2
a , Å	11.1108(3)
c , Å	18.2149(5)
V , Å ³	1947.4(1)
R_F , %	4.56
R_{wp} , %	3.85

^aCell parameters were obtained from X-ray diffraction from the hydride, SUs in parentheses.

IR spectroscopy. The IR-spectra were obtained at room temperature (298K) on a Varian 670-IR FT-IR spectrometer equipped with a Golden Gate ATR.

3. RESULTS AND DISCUSSION

The ternary metal hydride $\text{Cs}_{10}\text{Ga}_9\text{H}_{25}$ is obtained as a gray microcrystalline powder from reacting mixtures of cesium and gallium with proportions close to 1:1 in a hydrogen atmosphere at elevated temperatures. Initially it was expected that these reactions would yield either CsGaH_4 with separated $[\text{GaH}_4]^-$ entities,²⁰ or possibly CsGaH_2 containing polyanionic linear chains $[\text{GaH}_2]_n^-$, analogous to RbGaH_2 . The IR spectrum of $\text{Cs}_{10}\text{Ga}_9\text{H}_{25}$ is shown in Figure 2 together with those of RbGaH_2 and $\text{Rb}_8\text{Ga}_5\text{H}_{15}$. The stretching bands are centered at about 1500 cm^{-1} , which is at higher energies and lower energies

Table 2. Atomic and Temperature Parameters of $\text{Cs}_{10}\text{H}[\text{Ga}_3\text{H}_8]_3$ ^a

atom	Wyckoff position	x	y	z	U (Å ²)
Cs1	4c	2/3	1/3	1/4	0.057(6)
Cs2	4d	2/3	1/3	0	0.054(7)
Cs3	12k	0.2324(8)	0	0.1101(5)	0.035(3)
Ga1	6g	0.701(1)	0	1/4	0.064(4)
Ga2	12k	0.5898(7)	0	0.1321(4)	0.028(2)
D1	2b	0	0	0	0.11(1)
D2	12j	0.841(1)	0.123(2)	1/4	0.23(2)
D2 ₁ ^b	12j	0.836(2)	0.180(2)	1/4	0.053(5)
D2 ₂ ^b	12j	0.857(1)	0.062(2)	1/4	0.058(6)
D3	12k	0.6725(8)	0	0.0564(6)	0.12(1)
D4	24l	0.4354(8)	0.8735(5)	0.8779(5)	0.113(7)

^aSUs in parentheses. ^bD2 split in 2 positions.

Table 3. Selected Distances and Angles in $\text{Cs}_{10}\text{H}[\text{Ga}_3\text{H}_8]_3$ ^a

atoms	distance, Å
Ga1-D2 ×2	1.49(1)
Ga1-D2* ×2	1.52(1)
Ga1-D2* ×2	1.80(1)
Ga1-Ga2	2.48(1)
Ga2-D4 ×2	1.572(8)
Ga2-D3	1.65(1)
D1-Cs3 ×6	3.262(7)
D2-Ga1	1.49(1)
D2-Cs3 ×2	2.97(1)
D2-Cs1	3.72(2)
D3-Ga2	1.65(1)
D3-Cs3 ×2	3.20(1)
D3-Cs3	3.380(5)
D3-Cs2 ×2	3.863(5)
D4-Ga2	1.574(7)
D4-Cs2	2.977(8)
D4-Cs3	3.22(1)
D4-Cs1	3.046(8)
	Angle, deg
Ga2-Ga1-Ga2	120.1(2)
D2-Ga1-D2	105.1(9)
D3-Ga2-D4	104.5(3)
D4-Ga2-D4	101.2(3)

^aSUs in parentheses.

when compared to RbGaH_2 (around 1400 cm^{-1}) and CsGaH_4 (1800 cm^{-1}),²¹ respectively. We note that the location of the Ga–H stretching mode for $\text{Cs}_{10}\text{Ga}_9\text{H}_{25}$ is very similar to $\text{Rb}_8\text{Ga}_5\text{H}_{15}$ containing neopentane-like $[\text{Ga}_5\text{H}_{15}]^{5-}$ polyanions. This suggests that the polyanionic substructure of both compounds is similar. Interestingly, although the ratio of metal atoms is very similar to CsGaH_4 and RbGaH_2 the crystal chemistry of $\text{Cs}_{10}\text{Ga}_9\text{H}_{25}$ is different, and yet another hydrocarbon analogue $[\text{Ga–H}]$ polyanion is realized. This emphasizes the phase and structural variability of the heavier alkali metal–Ga–H systems. The Ga–H deformation/bending

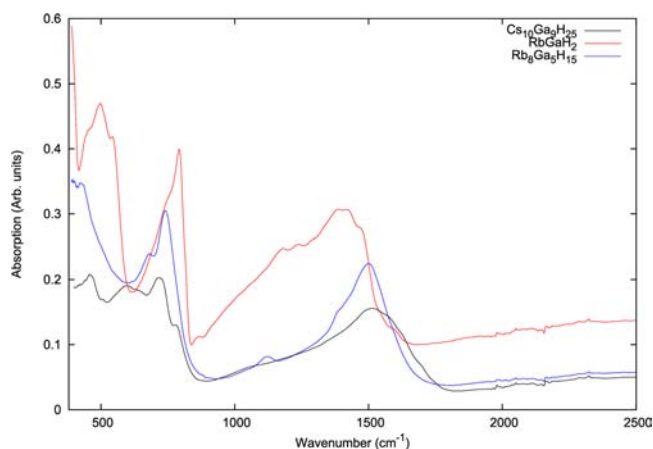


Figure 2. IR-spectrum of $\text{Cs}_{10}\text{H}[\text{Ga}_3\text{H}_8]_3$ (compared with RbGaH_2 and $\text{Rb}_8\text{Ga}_5\text{H}_{15}$).

modes in the IR-spectra can also be observed as rather sharp bands around 700 cm^{-1} .

$\text{Cs}_{10}\text{Ga}_9\text{H}_{25}$ crystallizes with the hexagonal space group $P6_3/mcm$ (193) and contains two formula units in the unit cell, which are distributed over 9 atomic positions (Cs1–3, Ga1, Ga2, H1–4). Most conspicuous is the presence of propane-like $[\text{Ga}_3\text{H}_8]^{3-}$ entities built from all Ga and three of the H sites (Figure. 3). To make Ga_3H_8 isoelectronic to propane, a charge

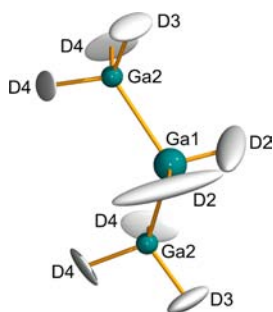


Figure 3. $[\text{Ga}_3\text{H}_8]^{3-}$ refined with thermal ellipsoids showing a larger ellipsoid for Ga1 and D2. Color representations: Ga, green; D, white ellipsoids. The thermal ellipsoids at drawn at a 50% probability.

of -3 is assigned, $[\text{Ga}_3\text{H}_8]^{3-}$, which is in accord with the Zintl–Klemm concept. The Ga–Ga distance is 2.48 \AA and compares very well with the Ga–Ga distances in the neo-pentane unit $[\text{Ga}_5\text{H}_{15}]^{5-}$ of recently discovered $\text{Rb}_8\text{Ga}_5\text{H}_{15}$ (2.46 \AA). Thus Ga–Ga distances in molecular-like (“zero-dimensional”) polyanionic moieties appear shorter than in one-dimensional (2.52 \AA in $[\text{GaH}_2]_n^{n-}$ (RbGaH_2)) and two-dimensional ones (2.56 \AA in $[\text{GaH}]_n^{2n-}$ (SrGa_2H_2)), all formally corresponding to Ga–Ga single bonds. Similar Ga–Ga distances can also be observed in gallium Zintl-phases, for example, typically Ga–H distances in gallium hydride compounds range from 1.55 to 1.65 \AA ^{22,23} and this is also the case for the terminal $-\text{GaH}_3$ groups in $[\text{Ga}_3\text{H}_8]^{3-}$. However, the bond length between hydrogen (or rather deuterium) atoms attached to the central Ga1 atom is unreasonable short (1.49 \AA). At the same time these hydrogen atoms (D1) have a largely anisotropic displacement parameter, suggesting disorder probably of both static and dynamical origin. Attempts to describe the elongated displacement parameter by an (isotropic) split position, thus emulating (static) torsional disorder within the Ga_3 backbone,

were not successful. This procedure resulted in two different Ga2–H distances, of which one was still too short (1.52 \AA) and the other unreasonably large (1.82 \AA) (cf. * in Table 3). At this point the origin of short Ga2–D2 distances and large displacement parameters for D2 thus remains unclear. Hydrogen disorder may resolve when describing the structure in an orthorhombic super cell and/or a space group with lower symmetry. However, the quality of our diffraction data did not permit more detailed analysis in this direction. We also note that it was not possible to refine Ga positional parameters anisotropically. However, the isotropic thermal parameter for Ga1 is substantially larger compared to Ga2 (cf. Figure 3 and Table 2), which may indicate involvement in torsional disorder.

With the presence of polyanions $[\text{Ga}_3\text{H}_8]^{3-}$ the compound formula $\text{Cs}_{10}\text{Ga}_9\text{H}_{25}$ may be reformulated as $\text{Cs}_{10}\text{H}[\text{Ga}_3\text{H}_8]_3$. The cationic part can be further divided into $\text{Cs}_4[\text{HCs}_6]^{9+}$, which emphasizes the presence of H-centered Cs octahedra for which the (first) hydrogen site D1 is utilized. A propane-analogue polyanion $[\text{Ga}_3\text{H}_8]^{3-}$ is surrounded by four octahedra $[\text{HCs}_6]^{5+}$ and six Cs^+ ions (Figure 4). The arrangement gives

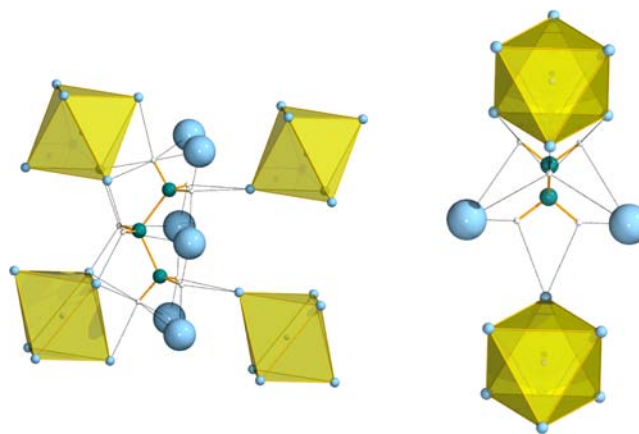


Figure 4. Local environment around $[\text{Ga}_3\text{H}_8]^{3-}$ polyanions, along the $[110]$ (left) and the $[001]$ (right) direction respectively. Color representations: Cs, blue; Ga, green; D, white; and $[\text{HCs}_6]^{5+}$, yellow octahedra.

the hydrogen site D3 a quasi-octahedral environment by five Cs and one Ga, and the sites D2 and D4 a quasi-tetrahedral environment by three Cs and one Ga (cf. Table 3).

The occurrence of octahedra $[\text{HCs}_6]^{5+}$ is peculiar because it implies the simultaneous presence of hydridic hydrogen (centering Cs octahedra) and covalently bonded hydrogen being part of the polyanion in a single compound. This is a new feature for hydrogenous Zintl phases and has been previously observed only for $\text{Rb}_8\text{Ga}_5\text{H}_{12}$ featuring neo-pentane like polyanions. The Cs–D distance in $[\text{HCs}_6]^{5+}$ is 3.262 \AA and thus somewhat longer than in NaCl-type CsH. The octahedron $[\text{HCs}_6]^{5+}$ may be considered as a drastically enlarged, soft and polarizable cation whose presence appears necessary for stabilizing packings with bulky propane- and neo-pentane-like polyanions in a crystal structure.

Per unit cell there are six propane units, two octahedra $[\text{HCs}_6]$, and four isolated Cs ions. The complete structure can be described as being built up from slabs which represent stacks of the structure fragment shown in Figure 4 along the c direction (Figure 5). In the complete structure the slabs are related by the operations of the 6_3 axis. Layers of $[\text{HCs}_6]$ octahedra and Cs2 at $z = 0$ and 0.5 alternate with layers of Cs1

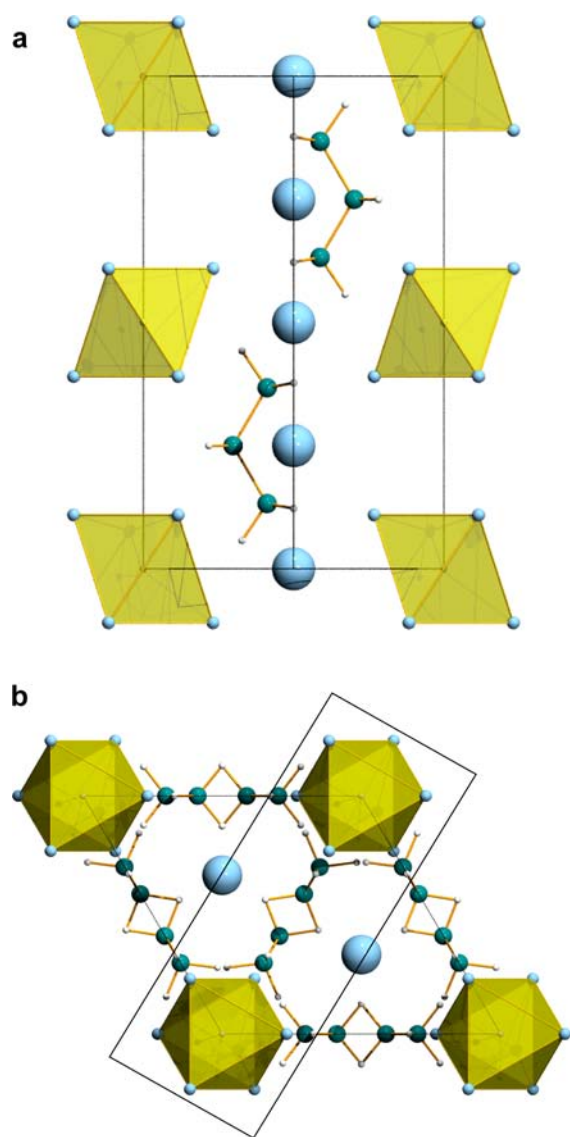


Figure 5. (a) Slab of $[\text{Ga}_3\text{D}_8]^{3-}$ -polyanions together with the counterions seen from the $[110]$ direction. (b) Arrangement of slabs in the complete structure, the unit cell seen from the $[001]$ direction. The rectangle represents the slab presented in panel a. Color representations same as Figure 4.

at $z = 0.25$ and 0.75 . The latter layers host also the centers of the polyanions.

Finally, the discovery of the hydrocarbon-like species $[\text{Ga}_5\text{H}_{12}]^{5-}$, $[\text{Ga}_3\text{H}_8]^{3-}$ provide an interesting link to Ga subhalides containing Ga–Ga bonds, which can be obtained as neutral aggregates when stabilized with donor-ligands.^{13,24} One particular example is $\text{Ga}_3\text{I}_5 \cdot 3\text{PEt}_3$ which is (valence-) isoelectronic with the propane-like $[\text{Ga}_3\text{H}_8]^{3-}$.¹⁴ The geometry of the Ga backbone of the neutral molecule is remarkably similar to $[\text{Ga}_3\text{H}_8]^{3-}$ (Ga–Ga distance 2.45–2.46 Å, angle 122 deg. Ga–Ga ($[\text{Ga}_3\text{H}_8]^{3-}$: 2.48 Å and 120 deg.)). The oxidation state assignment (Ga(I) terminal and Ga(II) center) can in principle also be applied to $[\text{Ga}_3\text{H}_8]^{3-}$ when considering hydrogen as a (two-electron) donor hydride ligand. Molecular species with Ga–Ga bonds have hitherto only been obtained with halogens as ligands; the hydrogen ligand may be exclusive to solid state chemistry.

4. CONCLUSIONS

The new ternary metal hydride $\text{Cs}_8\text{Ga}_3\text{H}_{25}$ represents yet another example of a hydrogenous Zintl phase exhibiting a hydrocarbon-like polyanion. Its crystal structure consist of three building units, $[\text{HCs}_6]^{5+}$, Cs^+ , and $[\text{Ga}_3\text{H}_8]^{3-}$. Accordingly, the compound formula can be reformulated as $(\text{Cs}^+)_4[\text{HCs}_6]^{5+}([\text{Ga}_3\text{H}_8]^{3-})_3$, which emphasizes that $\text{Cs}_8\text{Ga}_3\text{H}_{25}$ is electron precise. This is in agreement with its light color, indicating a sizable band gap (above 3 eV). The novel polyanion $[\text{Ga}_3\text{H}_8]^{3-}$ is isostructural and valence isoelectronic to propane. Drastically elongated thermal displacement parameters for the H atoms bonded to the central Ga atom (i.e., the “methylene” group) indicate strongly the presence of torsional disorder in the crystal structure. It is noteworthy that hitherto hydrocarbon-analogue polyanions are observed only with gallium backbones, and it will be interesting to see if they can be realized as well based on aluminum and boron.

■ ASSOCIATED CONTENT

📄 Supporting Information

Cif-file and anisotropic thermal parameters for D2, D3 and D4. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Černý, R.; Joubert, J.-M.; Kohlmann, H.; Yvon, K. *J. Alloys Compd.* **2002**, *340*, 180–188.
- (2) Olofsson-Mårtensson, M.; Häussermann, U.; Tomkinson, J.; Noréus, D. *J. Am. Chem. Soc.* **2000**, *122*, 6960–6970.
- (3) Yvon, K. *Z. Kristallogr.* **2003**, *218*, 108–116.
- (4) Bronger, W. *Angew. Chem., Int. Ed.* **1991**, *30*, 759–768.
- (5) Olofsson, M.; Kritikos, M.; Noréus, D. *Inorg. Chem.* **1998**, *37*, 2900–2902.
- (6) Kadir, K.; Moser, D.; Münzel, M.; Noréus, D. *Inorg. Chem.* **2011**, *50*, 11890–11895.
- (7) Häussermann, U. *Z. Kristallogr.* **2008**, *223*, 628–635.
- (8) Gingl, F.; Vogt, T.; Akiba, E. *J. Alloys Compd.* **2000**, *306*, 127–132.
- (9) Björling, T.; Noréus, D.; Jansson, K.; Andersson, M.; Leonova, E.; Edén, M.; Hålenius, U.; Häussermann, U. *Angew. Chem., Int. Ed.* **2005**, *44*, 7269–7273.
- (10) Fahlquist, H.; Noréus, D.; Callear, S.; David, W. I. F.; Hauback, B. C. *J. Am. Chem. Soc.* **2011**, *133*, 14574–14577.
- (11) Chotard, J.-N.; Filinchuk, Y.; Revaz, B.; Yvon, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 7770–7773.
- (12) Olson, J. K.; Boldyrev, A. I. *Chem. Phys. Lett.* **2012**, *523*, 83–86.

- (13) Linti, G.; Schnöckel, H. *Coord. Chem. Rev.* **2000**, 206–207, 285–319.
- (14) Schnepf, A.; Doriat, C.; Möllhausen, E.; Schnöckel, H. *Chem. Commun.* **1997**, 2111–2112.
- (15) Werner, P. E.; Eriksson, L.; Westdahl, M. *J. Appl. Crystallogr.* **1985**, 18, 367–370.
- (16) Altomare, A.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G.; Rizzi, R.; Werner, P. E. *J. Appl. Crystallogr.* **2000**, 33, 1180–1186.
- (17) Petricek, V.; Dusek, M.; Palatinus, L. *Jana 2006, The crystallographic computing system*; Institute of Physics: Praha, Czech Republic, 2006.
- (18) Favre-Nicolin, V.; Černý, R. *J. Appl. Crystallogr.* **2002**, 35, 734–743.
- (19) Rodríguez-Carvajal, J. *Phys. B: Condens. Matter* **1993**, 192, 55–69.
- (20) Dymova, T. N.; Dergachev, Y. M. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1981**, 30, 935–940.
- (21) Kurbakova, A. P.; Leites, L. A.; Gavrilenko, V. V.; Karaksin, Y. N.; Zakharkin, L. I. *Spectrochim. Acta, Part A* **1975**, 31, 281–286.
- (22) Aldridge, S.; Downs, A. J. *Chem. Rev.* **2001**, 101, 3305–3366.
- (23) Wang, X.; Andrews, L. *J. Phys. Chem. A* **2003**, 107, 11371–11379.
- (24) *The Group 13 Metals Aluminium, Gallium, Indium and Thallium: Chemical Patterns and Peculiarities*; Aldridge, S., Downs, A. J., Eds.; John Wiley & Sons, Ltd: Chichester, U.K., 2011; pp 246–341.