Inorg. Chem. **1997,** *36,* 6045−6049 **6045**

Cs_8Ga_{11}, a New Isolated Cluster in a Binary Gallium Compound. A Family of Valence Analogues $A_8Tr_{11}X$: A = Cs, Rb; Tr = Ga, In, Tl; X = Cl, Br, I

Robert W. Henning and John D. Corbett*

Department of Chemistry and Ames Laboratory—DOE,[1] Iowa State University, Ames, Iowa 50011

Received July 18, 1997[⊗]

Fusion of the elements, and alkali-metal halide when appropriate, in stoichiometric amounts in Ta containers followed by slow cooling results in high yields of the title compounds. X-ray structures refined for rhombohedral Cs_8Ga_{11} ($R\bar{3}c$, $Z = 6$, $a = 9.9962(5)$ Å, $c = 50.839(6)$ Å) and $Cs_8Ga_{11}Cl$ ($R\bar{3}\bar{3}c$, $Z = 6$, $a = 10.0111(7)$ Å, $c = 50.504(6)$ Å) reveal isolated clusters of pentacapped, trigonal prismatic gallium anions, Ga_{11}^{7-}, the former compound being isostructural with K_8In_{11} and A_8Tl_{11} (A = K, Rb, Cs). The clusters are arranged in pseudo-ccp layers separated by double layers of cesium atoms. The halide in $Cs_8Ga_{11}Cl$ is bound in a preformed cavity within the cesium double layers where it is surrounded by eight cations. Of the nine examples reported for $A_8Tr_{11}X$, three chlorides occur in systems in which the binary A_8Tr_{11} do not form, Rb−Ga, Rb−In, and Cs−In. These halides are the first examples of Tr_{11}^{7-} compounds that are valence phases and do not contain an extra alkali-metal cation and electron. Magnetic susceptibility data indicate an apparently localized electron in paramagnetic Cs_8Ga_{11} and diamagnetism for $Cs_8Ga_{11}Cl$.

Introduction

The alkali-metal-gallium systems are rich in novel cluster chemistry, predominantly in interbonded network structures.[2] Many of the units are analogues of deltahedral clusters commonly found in borane chemistry, *closo*-Ga_8, -Ga_{11}, and -Ga_{12} as well as their nido derivatives, for instance, and these can also be related via Wade's rules.[3,4] Larger species are also encountered, Ga_{15} and Ga_{17} for example. In the absence of exo bonded ligands (H, R, etc.), the higher charges ideally associated with these cluster anions have in practice always been reduced through extensive intercluster σ bonding, sometimes via one, two, or three metal atom spacers. Even so, some of the resulting 2-D or, more often, 3-D gallium networks in fact appear to be closed-shell in electron count, or nearly so.[2] A discrete gallium cluster has been reported in a binary phase only as the tetrahedral units seen in $Ca_{11}Ga_7$.[5] In considerable contrast, the heavier congener indium forms several isolated, sometimes centered, clusters in alkali-metal systems, formally In_4^{8-},[6] In_{11}^{7-},[7] $In_{10}Zn^{8-}$,[8] and $In_{10}Ni^{10-}$,[9] for instance. A number of network structures also appear, most of which are different from those of gallium. The trend to discrete cluster species continues with thallium, which forms many other isolated clusters (Tl_5^{7-}, Tl_9^{9-}, Tl_{13}^{11-}, etc.)[4,10,11] and very few networks. We have now reexamined the alkali-metal-gallium systems for isolated clusters and herein report the first example in Cs_8Ga_{11}. This compound is isostructural with indium and thallium examples, which have been formulated as $(A^+)_8Tr_{11}^{7-}\ e^-$ (Tr = In,[7] Tl[12]) on the basis of calculations and properties. Although these phases are electron-rich, the anions are significantly electron-poor (hypoelectronic) in cluster bonding electrons relative to Wade's rules. In addition, the halide derivatives of many A_8Tr_{11} phases have also been synthesized, affording the first examples of the valence-precise compounds $A_8Tr_{11}X$.

The Cs−Ga phase diagram reported in 1970 by Thümmel and Klemm[13] indicated the existence of three phases. The phases $CsGa_7$ and $CsGa_3$ were structurally characterized in 1985 by X-ray powder diffraction studies,[14] but "Cs_5Ga_8" (analogous to "K_5In_8"[7]) has not been studied further. van Vucht reported a powder pattern for a new cesium-rich phase, but he was unable to determine the structure.[14] Both pertain to the Cs_8Ga_{11} compound reported here.

Experimental Section

Stoichiometric amounts of the elements and, where appropriate, cesium or rubidium halide were welded in Ta tubing using techniques described previously.[15] Cesium (99.9%, Johnson-Matthey), rubidium (99.9%, Alpha), gallium (99.99%, Johnson-Matthey), indium (99.999%, Cerac), and the alkali-metal halides (99.9%, Fisher) were used as received, while the surface of thallium (99.998%, Johnson-Matthey) was cleaned with a scalpel. All materials were handled in a N_2-filled glovebox. All known A_8Tr_{11} ("A_5Tr_8") compounds appear to melt congruently, and "Cs_5Ga_8" has the highest melting point in its system, ~625 °C, so the mixtures were allowed to react at 700 °C for 24 h to ensure homogeneity and then cooled to room temperature at a rate of 3 °C/h. Single crystal refinements were obtained for Cs_8Ga_{11} and $Cs_8Ga_{11}Cl$, while the remaining $A_8Tr_{11}X$ were identified by Guinier powder patterns. Analogous binary phases were not obtained with K or Rb.

Cs_8Ga_{11}. This very brittle product had a metallic luster and contained many crystals with smooth faces. The yield was substantially quantitative. Small crystals were selected, sealed in thin-walled capillaries, and checked for singularity by Laue and oscillation film techniques. Most of the crystallites turned out to be multiple, but a suitable crystal was obtained from an otherwise unsuccessful reaction loaded as $Cs_8Ga_{10}Cu_2$. Lattice parameters for Cs_8Ga_{11} that were determined from

---

[⊗] Abstract published in *Advance ACS Abstracts*, December 1, 1997.

(1) This research was supported by the Office of the Basic Energy Sciences, Materials Sciences Division, U. S. Department of Energy. The Ames Laboratory is operated by Iowa State University under Contract No. W-7405-Eng.82.

(2) Belin, C.; Tillard-Charbonnel, M. *Prog. Solid State Chem.* **1993**, *22*, 59.

(3) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

(4) Corbett, J. D. *Struct. Bonding* **1997**, *87*, 157.

(5) Fornasini, M. L.; Merlo, F. *Z. Kristallogr.* **1989**, *187*, 111.

(6) Sevov, S. C.; Corbett, J. D. *J. Solid State Chem.* **1993**, *103*, 114.

(7) Sevov, S. C.; Corbett, J. D. *Inorg. Chem.* **1991**, *30*, 4875.

(8) Sevov, S. C.; Corbett, J. D. *Inorg. Chem.* **1993**, *32*, 1059.

(9) Sevov, S. C.; Corbett, J. D. *J. Am. Chem. Soc.* **1993**, *115*, 9089.

(10) Dong, Z.; Corbett, J. D. *J. Am. Chem. Soc.* **1994**, *116*, 3429.

(11) Dong, Z.; Corbett, J. D. *J. Am. Chem. Soc.* **1995**, *117*, 6447.

(12) Dong, Z. C.; Corbett, J. D. *J. Cluster Sci.* **1995**, *6*, 187.

(13) Thümmel, R.; Klemm, W. *Z. Anorg. Allg. Chem.* **1970**, *376*, 44.

(14) van Vucht, J. H. N. *J. Less-Common Met.* **1985**, *108*, 163.

(15) Dong, Z. C.; Corbett, J. D. *J. Am. Chem. Soc.* **1994**, *116*, 3429.

S0020-1669(97)00904-X CCC: $14.00

Table 1. Selected Data Collection and Refinement Parameters

formula	Cs_8Ga_{11}	$Cs_8Ga_{11}Cl$
fw	1830.2	1865.6
space group	$R\bar{3}c$ (No. 167)	$R\bar{3}c$ (No. 167)
Z	6	6
temp, °C	23	23
lattice params[a]		
a, Å	9.9962(5)	10.0111(7)
c, Å	50.839(6)	50.504(6)
V, Å^3	4399.4(9)	4383.5(8)
d_{calc}, g/cm^3	4.144	4.240
residuals R, R_w,[b] %	2.2, 3.3	2.6, 2.2

[a] Guinier data with Si as an internal standard, $\lambda = 1.540\ 562$ Å, 23 °C. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$, $w = 1/\sigma_F{}^2$.

Guinier powder data and least squares analyses for samples loaded both as Cs_8Ga_{11} and as $Cs_8Ga_{10}Cu_2$ were within 3σ (0.003 Å) of each other, so copper is not necessary for compound formation. A bar like single crystal (0.25 × 0.28 × 0.40 mm) was selected for data collection on a Rigaku AFC6R single crystal diffractometer. Twenty-five reflections obtained from a random search were indexed with a rhombohedral unit cell. Four octants of data ($\pm h$, $+k$, $\pm l$, hexagonal setting) were collected at room temperature with Mo Kα radiation up to 50° in 2θ and corrected for Lorentz and polarization effects. No violations of the R-centering condition were observed. The average of six ψ-scans collected at different 2θ angles were utilized for absorption correction. Systematic absences and Wilson plot statistics suggested space group $R\bar{3}c$ (No. 167). Application of direct methods[16] revealed two positions with separations appropriate for Cs−Cs contacts and three positions suitable for gallium. The routine refinement of the positional and anisotropic thermal parameters with the TEXSAN[17] package on a VAX station converged at an $R(F)$ factor of 2.2%. The largest positive and negative peaks in the difference map were +0.77 e$^-$/Å^{-3} (3.6 Å from Ga3) and −0.96 e$^-$/Å^{-3}.

$Cs_8Ga_{11}Cl$. As for the binary phase, this product was obtained phase pure, had metallic luster, and was brittle. Select crystals were sealed in thin-walled capillaries and checked for singularity as before. An irregular shaped crystal (0.14 × 0.20 × 0.25 mm) was selected for data collection on the same diffractometer. Twenty-five reflections obtained from a random search were indexed with a rhombohedral unit cell (hexagonal setting). Two octants of reflection data ($\pm h$, $+k$, $+l$) were collected at room temperature with Mo Kα radiation up to 50° in 2θ and corrected for Lorentz and polarization effects. No violations of the R-centering were observed. The average of three ψ-scans collected at different 2θ angles were used for absorption correction. Systematic absences and Wilson plot statistics suggested the same space group as that for the binary compound, $R\bar{3}c$ (No. 167), and direct methods provided substantially the same cesium and gallium positions. Refinement of the positional and isotropic thermal parameters was followed by a difference Fourier analysis that revealed one peak appropriate for chlorine. Anisotropic refinement of all atoms reduced $R(F)$ to 2.6%. The largest positive and negative peaks in the difference map were +0.72 e$^-$/Å^3 (2.9 Å from Ga2) and −1.56 e$^-$/Å^3.

Some crystal data for both studies are listed in Table 1, and atomic positions and isotropic-equivalent parameters are in Table 2. Additional data collection and refinement parameters and the anisotropic thermal parameters are given in the Supporting Information. These and the F_o/F_c data are also available from J.D.C.

Property Measurements. Samples loaded as Cs_8Ga_{11} and $Cs_8Ga_{11}Cl$ were pure according to Guinier powder patterns, but to ensure that cesium metal was not present, these were enclosed in two evacuated, sealed Pyrex tubes and heated at 100 °C for 24 h. The opposite end of the tubing that protruded outside of the furnace allowed a trace of excess cesium to accumulate, but none was found.

Table 2. Positional and Thermal Parameters for Cs_8Ga_{11} and $Cs_8Ga_{11}Cl$[a]

atom	Wyckoff	x	y	z	B_{eq}[b] (Å^2)
Ga1	18e	0.813 7(1)	0	$^1/_4$	1.79(5)
		0.812 8(2)			1.54(8)
Ga2	12c	0	0	0.705 94(2)	1.90(3)
				0.705 65(3)	1.72(5)
Ca3	36f	0.410 93(8)	0.329 69(8)	0.056 23(1)	2.17(3)
		0.414 2(1)	0.332 3(2)	0.0562 3(2)	1.97(4)
Cs1	36f	0.074 60(5)	0.364 85(6)	0.022 718(9)	3.02(2)
		0.076 1(1)	0.361 76(9)	0.022 51(1)	2.45(3)
Cs2	12c	0	0	0.077 80(2)	3.34(3)
				0.074 53(2)	2.95(3)
Cl	6b	0	0	0	2.7(2)

[a] Data for $Cs_8Ga_{11}Cl$ are listed second. [b] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\vec{a}_i\vec{a}_j$.

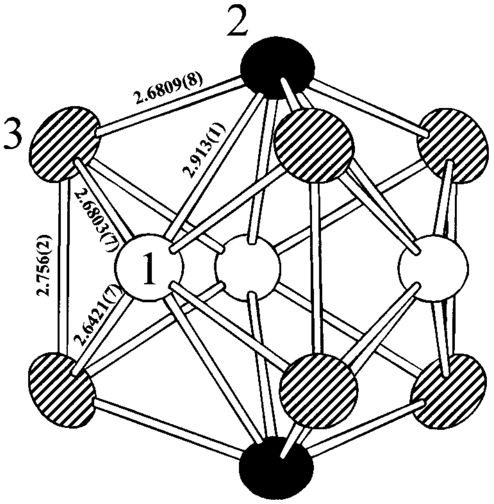

Figure 1. Isolated $Ga_{11}{}^{7-}$ cluster in Cs_8Ga_{11} with the 3-fold (c) axis vertical. Thermal ellipsoids are drawn at the 90% probability level.

Magnetic susceptibility data were collected on a Quantum Design MPMS SQUID magnetometer. Powdered Cs_8Ga_{11} (40.9 mg) and $Cs_8Ga_{11}Cl$ (42.3 mg) in separate containers were held under helium between two silica rods, one which had already been sealed into a fused silica tube. The susceptibilities of each sample were measured in a field of 3 T over the temperature range of 6−300 K. Corrections were applied to the raw data to account for the sample holder, core diamagnetism, and Larmor precession of the cluster-based electrons.[18] The core correction factors for Cs_8Ga_{11} and $Cs_8Ga_{11}Cl$ were -3.36×10^{-4} and -3.62×10^{-4} emu/mol, respectively, while the Larmor precession correction was -2.35×10^{-4} emu/mol for each. Field dependent measurements were also performed at 60 and 110 K on the Cs_8Ga_{11} sample. The resistivity of Cs_8Ga_{11} was determined by the electrodeless "Q" method[19] over 100−293 K and 34 MHz. The 126.1 mg sample with an average grain size of ∼200 μm was diluted with dry chromatographic Al_2O_3. ESR measurements were carried out on a Bruker ER-200D spectrometer (X-band, 95 GHz) at room temperature and under liquid-nitrogen-cooled conditions.

Results and Discussion

Structure Descriptions. Cs_8Ga_{11} is isostructural with K_8In_{11},[7] Rb_8In_{11},[20] and A_8Tl_{11} (A = K, Rb, and Cs).[12] The predominant structural feature in Cs_8Ga_{11} is likewise the isolated, pentacapped trigonal-prismatic gallium cluster, Figure 1, where Ga3 atoms define the trigonal prism. The cluster has pseudo-D_{3h} symmetry, but a slight twist (2.7°) of the opposite ends of the trigonal prism reduces the symmetry to D_3. The cluster is coordinated by 24 cesium atoms (18 Cs1 and 6 Cs2) in characteristically regular roles, as shown in Figure 2. The Cs1 atoms in double layers each cap Ga1−Ga2−Ga3 faces, bridge Ga2−Ga3 edges, and bond exo to Ga3 atoms on three different

---

(16) Sheldrick, G. M. *SHELXS-86*; Universität Göttingen, Göttingen: Germany, 1986.

(17) *TEXSAN*, version 6.0; Molecular Structure Corp.: The Woodlands, TX, 1990.

(18) Sevov, S. C.; Corbett, J. D. *Inorg. Chem.* **1992**, *31*, 1895.

(19) Shinar, J.; Dehner, B.; Beaudry, B. J.; Peterson, D. T. *Phys. Rev. B* **1988**, *37*, 2066.

(20) Blase, W.; Cordier, G.; Müller, V.; Häussermann. U.; Nesper, R.; Some, M. *Z. Naturforsch. B* **1994**, *48*, 754.

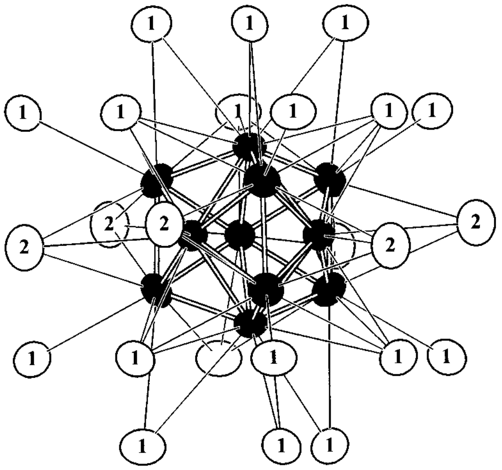

Figure 2. Cesium coordination environment around the Ga$_{11}{}^{7-}$ cluster.

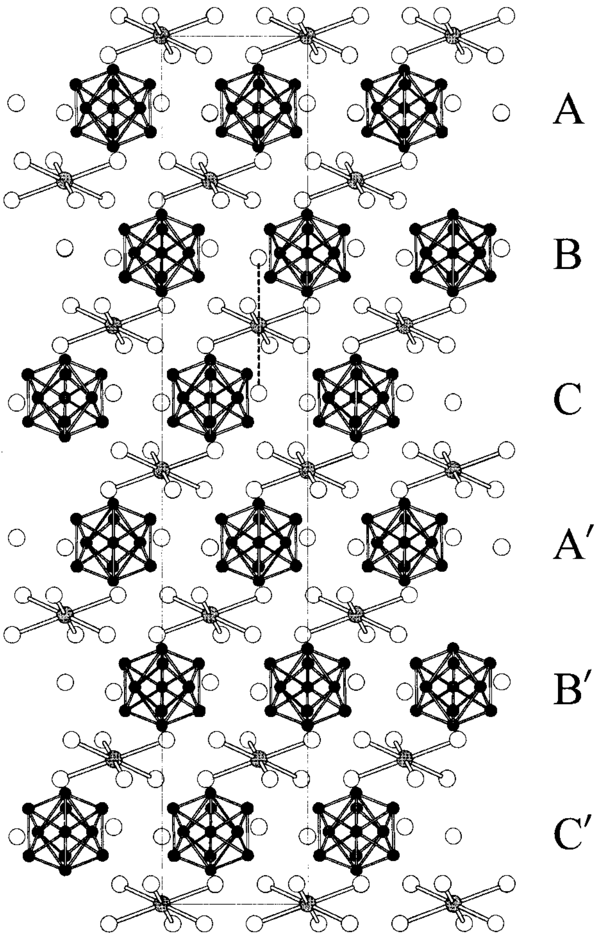

Figure 3. [100] view of Cs$_8$Ga$_{11}$Cl. The clusters are arranged in pseudo-ccp layers of clusters plus Cs2. These are interleaved with double layers of Cs1 atoms (open) with Cl in compressed, augmented trigonal antiprismatic cavities. Cs2 neighbors to one chlorine are dashed in.

clusters. Likewise, six Cs2 atoms around the waist of each cluster cap Ga1−Ga3−Ga2−Ga3 faces, and each does so on three clusters. The closest contact between clusters is 5.763(1) Å (Ga1−Ga3). The clusters exhibit pseudo-cubic-close-packing normal to the *c*-axis with double layers of the Cs1 atoms between the cluster layers, i.e., Figure 3 without the chlorine. The Cs1 atoms in the pair of cation layers have the same orientation as the nearest cluster layer. Since the closed shell anions in K$_8$In$_{11}$ and A$_8$Tl$_{11}$ are Tr$_{11}{}^{7-}$, an extra cation appears necessary for packing, and the compounds have accordingly always[7] been formulated as the metallic (A)$^+{}_8$Tr$_{11}{}^{7-}$ e$^-$.

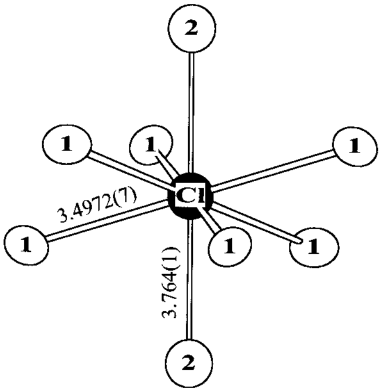

Figure 4. Environment around the Cl atom in Cs$_8$Ga$_{11}$Cl.

The cesium and gallium positions in Cs$_8$Ga$_{11}$Cl are essentially the same as in the binary except for some minor distortions following the addition of the chlorine, which occupies a $\bar{3}$ void at the origin. The first coordination sphere around chlorine is a very compressed trigonal antiprism of Cs1 atoms at a distance of 3.4972(7) Å plus two Cs2 atoms at 3.764(1) Å along $\vec{c}$ that cap the trigonal faces, Figure 4. The dimensions of this cavity in Cs$_8$Ga$_{11}$ are 3.513 Å to Cs1 and 3.950 Å to Cs2 (Table 3), so the contraction in the former on chlorine accommodation is quite small. The height of the trigonal antiprism increases by 0.04 Å in the process. The symmetry-equivalent Cs1−Cl contacts of 3.4972(7) Å are consistent with the sum of the six-coordinate crystal radii, 3.48 Å.[21] The most significant shift in atomic positions between the two structures occurs with Cs2. In Cs$_8$Ga$_{11}$, Cs2 sits in a relatively large cavity coordinated by three different clusters in the *a*−*b* plane with all Cs−Ga contacts greater than 3.9 Å (vs ~3.72 Å about Cs1), consistent with its slightly larger thermal ellipsoid. Coulombic forces presumably are responsible for the 0.19 Å shift of Cs2 along the *c*-axis toward the intercalated chlorine, while all the other distances in the structure change by less than 0.07 Å. The Cs2 change also appears to affect the three closest Ga3 atoms and to reduce the amount of twist of the basal ends of the cluster to ~0°. The cluster in Cs$_8$Ga$_{11}$Cl thus has an effective point symmetry of D_{3h}, but the structure does not contain the horizontal mirror plane. Bonding of chlorine in the structure also compresses the Cs1−Ga$_{11}$−Cs1 slab by 0.095 Å and reduces the overall *c* dimension by 0.33 Å.

Other Halide Examples. The discovery of Cs$_8$Ga$_{11}$Cl prompted us to search for other pseudo-8:11 phases that are stabilized by halide. In these cases, we inferred ternary compound formation from the changes in lattice dimensions and volumes. These are generally rather telling since reproducibility of cell volumes is around ±2/4000 or less. Table 4 lists the lattice parameters for nine new A$_8$Tr$_{11}$X phases together with those of their corresponding binaries where formed. All reactions were run under the same conditions as those for Cs−Ga−Cl. The binary Cs$_8$Ga$_{11}$ and the corresponding ternary halides (Cl, Br, and I) all form in 95−97% yields according to their Guinier powder patterns. The larger bromine and iodine mainly increase the *c* dimensions relative to the values with chlorine. The Rb−Ga system is interesting in that although we have been unable to synthesize Rb$_8$Ga$_{11}$, the corresponding Rb$_8$Ga$_{11}$Cl is stable. This suggests that, in general, halide derivatives are more stable than the corresponding binaries; a volume contraction is often associated with the formation of derivatives with smaller interstitials. Reactions with the larger halides have not been attempted in the Rb−Ga system. Nothing new was found in the K−Ga−Cl system.

---

(21) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32,* 751.

Table 3. Selected Bond Distances in Cs_8Ga_{11} and $Cs_8Ga_{11}Cl$ (Å)

		Cs_8Ga_{11}	$Cs_8Ga_{11}Cl$			Cs_8Ga_{11}	$Cs_8Ga_{11}Cl$
Ga1−Ga3	2×	2.6421(7)	2.644(1)	Cs1−Cl			3.4972(7)
Ga1−Ga3	2×	2.6803(3)	2.655(1)	Cs1−Ga1		3.7159(7)	3.719(1)
Ga1−Ga2	2×	2.913(1)	2.920(2)	Cs1−Ga3		3.7210(8)	3.739(1)
Ga1−Cs1	2×	3.7159(7)	3.719(1)	Cs1−Ga3		3.9384(8)	3.930(1)
Ga1−Cs2	2×	4.2711(7)	4.285(1)	Cs1−Ga3		3.9770(9)	4.001(1)
				Cs1−Ga3		4.037(1)	4.008(1)
Ga2−Ga3	3×	2.6809(8)	2.669(1)	Cs1−Ga2	2×	4.0189(5)	4.0503(9)
Ga2−Ga1	3×	2.913(1)	2.920(2)	Cs1−Ga2		4.233(1)	4.211(1)
Ga2−Cs1	3×	4.0189(5)	4.0503(9)	Cs1−Cs1[a]	2×	4.0587(7)	4.0135(9)
Ga2−Cs1	3×	4.233(1)	4.211(1)	Cs1−Cs1		4.3566(8)	4.401(2)
				Cs1−Cs2		4.3928(9)	4.224(1)
Ga3−Ga1		2.6421(7)	2.644(1)	Cs1−Cs2		4.3928(9)	4.523(1)
Ga3−Ga1		2.6803(7)	2.655(1)				
Ga3−Ga2		2.6809(8)	2.669(1)				
Ga3−Ga3		2.756(2)	2.737(2)	Cs2−Cl			3.764(1)
Ga3−Cs1		3.7210(8)	3.739(1)	Cs2−Ga3	3×	3.9242(7)	3.914(1)
Ga3−Cs2		3.9242(7)	3.914(1)	Cs2−Ga3	3×	4.1609(8)	4.226(1)
Ga3−Cs1		3.9384(8)	3.930(1)	Cs2−Ga1	3×	4.2711(7)	4.285(1)
Ga3−Cs1		3.9770(9)	4.001(1)				
Ga3−Cs1		4.037(1)	4.008(1)	Cl−Cs1	6×		3.4972(7)
Ga3−Cs2		4.1609(8)	4.226(1)	Cl−Cs2	2×		3.764(1)

[a] d(Cs−Cs) < 4.8 Å.

Table 4. Lattice Parameters[a] of the $A_8Tr_{11}X$ Compounds

	a (Å)	c (Å)	V (Å^3)	lines indexed
$Rb_8Ga_{11}Cl$	9.7036(5)	49.079(4)	4002.2(5)	80
Cs_8Ga_{11}	9.9962(5)	50.839(6)	4399.4(9)	37
$Cs_8Ga_{11}Cl$	10.0111(7)	50.504(6)	4383.5(8)	84
$Cs_8Ga_{11}Br$	10.0587(5)	50.620(4)	4435.4(6)	73
$Cs_8Ga_{11}I$	10.1067(9)	50.820(8)	4495(1)	49
Rb_8In_{11}[b]	10.301(3)	52.367(7)	4812(2)	
$Rb_8In_{11}Cl$	10.250(2)	52.33(2)	4762(2)	21
$Cs_8In_{11}Cl$	10.5612(4)	53.820(4)	5198.8(6)	42
Cs_8Tl_{11}[c]	10.553(1)	53.771(9)	5186(2)	38
$Cs_8Tl_{11}Cl$	10.543(4)	53.23(5)	5124(6)	16
$Cs_8Tl_{11}Br$	10.595(4)	53.60(4)	5211(5)	25
$Cs_8Tl_{11}I$	10.603(1)	53.75(1)	5233(2)	47

[a] Guinier data with Si as an internal standard, $\lambda = 1.540\,562$ Å, 23 °C. [b] Reference 20. [c] Reference 12.

The Cs−In system is likewise interesting in that only the Cs_2In_3[22] binary is stable near this stoichiometry while $Cs_8In_{11}Cl$ forms in the presence of the chloride in similarly high yield. Reactions with the other halides have not been attempted in this system, but the heavier $Cs_8In_{11}X$ compounds should form. The Rb−In system is also unusual in that both Rb_2In_3[22] and Rb_8In_{11}[20] have been reported in the literature, although they are very close in composition, 60.0 and 57.9 at. % In, respectively. However, we have been unable to reproduce the Rb_8In_{11} synthesis in either this or earlier work.[23] Slow cooling, annealing, or quenching from the melt have all produced only Rb_2In_3 and rubidium metal. However, when the reaction is loaded as $Rb_8In_{11}Cl$ and slowly cooled, the characteristic pattern of an 8:11 phase, appreciable Rb_2In_3, and, in contrast to other reactions, 5−10% RbCl are evident in the powder pattern. (The last two are in about the right proportion for the incomplete formation of $Rb_8In_{11}Cl$, although an equilibrium chlorine content <1 can probably not be ruled out.) Since Rb_8In_{11} does not form without RbCl, we presume the product must be $Rb_8In_{11}Cl$. The apparent lattice constant changes between those of the reported Rb_8In_{11} and $Rb_8In_{11}Cl$, Table 4, are irregular relative to those in the Cs−Ga−Cl and Cs−Tl−Cl systems. Reactions incorporating bromine or iodine in $Rb_8In_{11}X$ should probably work.

The $Cs_8Tl_{11}X$ results obtained after slow cooling follow the same trend as the Cs−Ga reactions, but the halides could not be obtained in 100% yield. A known binary, $Cs_{15}Tl_{27}$,[24] is present in about 30% yield as well as the corresponding amount of cesium halide. Attempts to form pure $Cs_8Tl_{11}X$ phases by annealing quenched samples at 380 °C, above the peritectic melting point of $Cs_{15}Tl_{27}$ (~350 °C), produced the same results. However, the lattice constant trends make it clear that the halides have formed. In the case of $Rb_8Tl_{11}Cl$, patterns of both the Rb_8Tl_{11} and $Rb_{15}Tl_{27}$ types were observed as well as RbCl, as above, but the lattice constants of the possible chloride fell within 3σ of those of Rb_8Tl_{11}. Although it is thus doubtful that $Rb_8Tl_{11}Cl$ forms, reactions with the heavier halides may provide better information. A few reactions in the gallium and indium systems were loaded with RbF or KF, but only the known binaries formed. Apparently, fluorine is too small for proper coordination.

Binary Phase Formation. The stability of any particular phase is naturally also dependent on the stability of alternate phases. In the present A−Tr systems (Tr = Ga, In, Tl), the existence of either one or the other of the close-lying A_2Tr_3 and A_8Tr_{11} (60.0 and 57.9 at. % Tr, respectively), but not both, provides a good correlation in seven systems. In the present Cs−Ga, modeling of the unknown Cs_2Ga_3 with the anion parameters of K_2Ga_3 results in Cs−Cs distances that are probably too short, about 3.6 Å. The one contradiction is reports of both Rb_2In_3 and Rb_8In_{11}, but we have described the basis for our serious doubts about the existence of the latter. The only other contrary result, in a negative sense, is the existence of neither Rb_2Ga_3 or Rb_8Ga_{11}, $RbGa_3$ being the alkali-metal-richest phase that evidently forms.

Properties of Cs_8Ga_{11}(X). The molar susceptibilities as a function of temperature for pure Cs_8Ga_{11} shown in Figure 5 exhibit some unusual features. An apparent transition below 90 K (confirmed in a second sample of Cs_8Ga_{11}) is believed to reflect a structural change, which is accompanied, or followed, by a magnetic transition near 75 K. Such effects have not been observed with the other A_8Tr_{11} compounds or for $Cs_8Ga_{11}Cl$. It has not been possible to obtain any structural information on the low-temperature phase. Field-dependence measurements of the susceptibilities at 60 and 110 K over a range of 0−6 T show a linear M−T relationship with a positive slope, indicating paramagnetism at both temperatures. A slight positive curvature of the 60 K data suggests that the low-temperature phase is antiferromagnetic, but this is unconfirmed. Equally unusual,

---

(22) Sevov, S. C.; Corbett, J. D. *Z. Anorg. Allg. Chem.* **1993**, *619*, 128.
(23) Sevov, S. C. Ph.D. Dissertation, Iowa State University, 1993.
(24) Dong, Z. C.; Corbett, J. D. *Inorg. Chem.* **1996**, *35*, 1444.

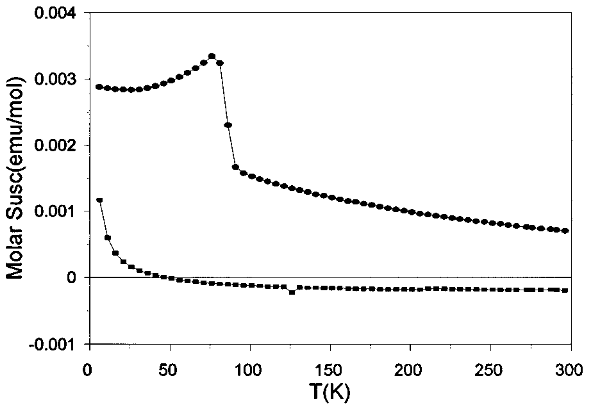

Figure 5. Temperature dependence of the magnetic susceptibilities of Cs_8Ga_{11} and $Cs_8Ga_{11}Cl$ at 3 T.

Cs_8Ga_{11} is paramagnetic and follows the linear Curie–Weiss law very well above 100 K to yield a magnetic moment of 1.43(1)μ_B and a Weiss Θ of -61.1 K. This too is in apparent contrast to the other A_8Tr_{11} phases which appear to be Pauli-paramagnetic and are customarily formulated as metallic, $(A^+)_8Tr_{11}{}^{7-}$ e^-. The extra electron in Cs_8Ga_{11} is evidently localized within the solid. The resistivity in the 100–300 K range is high, >920 $\mu\Omega{\cdot}$cm, the limitations of the *Q* method precluding a more precise measurement. *Q* measurements on the other 8:11 phases have shown metallic conductivity. No ESR signal could be detected for Cs_8Ga_{11} at room and liquid-nitrogen temperatures, the electron relaxation evidently being fast at the ESR time scale. Fortunately, the situation with the diamagnetic $Cs_8Ga_{11}Cl$ is clearer (Figure 5) and consistent with the Zintl formulation $(Cs^+)_8Ga_{11}{}^{7-}Cl^-$.

The question naturally arises as to how and where the odd electron might be bound. Localization on the cluster is unlikely considering its closed-shell electronic structure. An extra cluster electron should also cause the cluster to distort, which is not evident. Localization on a single cesium does not seem physically reasonable, in contrast to the situation with Cs^+(18-crown-6)$_2e^-$,[25] but trapping of spin-free electrons within cesium polyhedral cavities or a narrow LUMO band seems plausible. The behavior of semiconducting Pr_2Br_5 and its relatives seems pertinent; the individual cations there all appear to be Pr^{3+} with the electrons in some sort of Mott insulating state.[26] The site that becomes occupied by chloride is one attractive possibility here. ^{133}Cs NMR could be helpful in defining the interactions.

The occurrence of $Ga_{11}{}^{7-}$ only with Cs^+ cations is an interesting result. For $In_{11}{}^{7-}$, the best cation seems to be K^+, and for $Tl_{11}{}^{7-}$, K^+, Rb^+, and Cs^+, so the disparate ion sizes in the isostructural Cs_8Ga_{11} are unusual. One explanation may be that larger cavities are necessary to trap the odd electron, even though the cation field therein is less, while the metallic version is unstable. As a matter of fact, the properties of the indium and thallium A_8Tr_{11} analogues are a little “odd”. The resistivities are moderately high, 230–630 $\mu\Omega{\cdot}$cm, with positive temperature coefficients of 0.18–0.32% K^{-1}, while all show a modestly temperature-independent “Pauli-like” paramagnetism in the range of $(2-4.6) \times 10^{-4}$ emu·mol^{-1}. Many cluster compounds of the heavier main-group elements that otherwise appear to be Zintl phases exhibit metal-like conductivities, while the negative signs of their magnetic susceptibilities seem to be much more consistent with their apparent valence properties.[27]

Summary. The alkali-metal-gallium systems contain a wide variety of unusual clusters which, when combined with different methods of intercluster bonding, provide an interesting array of network structures. Cs_8Ga_{11} and the corresponding halides are unique in this system because they contain isolated clusters. The only other known isolated gallium clusters are $Ga_{10}Ni^{10-}$, $Ga_6{}^{8-}$, and $Ga_4{}^{8-}$ in $Na_{10}Ga_{10}Ni$,[28] $Ba_5Ga_6H_2$,[29] and $Ca_{11}Ga_7$,[5] respectively. In the first, the high cluster charge is evidently stabilized by the central nickel atom and a small cation, while hydride is needed in the second to balance the electron count. The first two examples illustrate the significance of Zintl phase concepts in these types of systems, while the third is an unstudied exception (but not a hydride, we have established). The clearly stabilizing effect of halide in $A_8Tr_{11}X$ compounds is especially evident in the Rb–Ga, Rb–In, and Cs–In systems, where we have not been able to prepare the binary A_8Tr_{11} phases but do achieve the chlorides (Table 4). The preference of closed-shell electronic states is evidently a strong driving force in the formation of these structures. This fact makes Cs_8Ga_{11} more interesting in that it does not completely conform to the traditional Zintl concept. Although, the extra electron would be expected to behave like those in the isostructural K_8In_{11} and A_8Tl_{11} (A = K, Rb, and Cs) compounds, the property measurements suggest otherwise. Further work is anticipated.

The overall existence not only of 14 phases containing isolated $Tr_{11}{}^{7-}$ ions but also of other homoatomic species such as $Tr_6{}^{8-}$, $Tl_5{}^{7-}$, and $Tl_{13}{}^{11-}$ bring to question the suitability of the descriptor “Zintl boundary” that was defined by Zintl and later so-named by Laves in a memorial article.[30] Zintl differentiated the triel from the tetrel and later elements (groups 13 vs group 14) in several ways. The latter in their formally most negative oxidation states yielded salt-like compounds with active metals, often with familiar structural types. These were likewise named Zintl phases by Laves, and the breadth of this classification was later greatly extended by Klemm and Busmann.[31] These are now taken to be valence compounds that in classical cases follow octet rules. On the other hand, Zintl noted that analogous compounds of the triels and earlier elements were alloy-like in properties and structures, often with notable nonstoichiometries. Likewise, this distinction was supported by earlier studies of “Zintl ions”[32] that he identified in solution in liquid ammonia as alkali-metal salts of polyanionic species such as $Tr_9{}^{4-}$ for Sn, Pb, and so forth. Naturally, modern chemistry has greatly extended our knowledge of Zintl phases and ions. In the present cases, we see that considerable Coulombic stabilization of many polyanionic compounds of the triel elements is achieved in their neat alkali-metal salts, in Cs_8Tr_{11} for example, preceding the Zintl boundary.[27] “Modern” definitions of valence rules for Zintl phases now must also include the so-called electron-deficient, delocalized bonding found in many clusters, a feature which also applies to the Zintl anions of the tetrel elements.[33]

Acknowledgment. We are grateful to J. Ostenson for the magnetic measurements and D. Scott for the ESR data.

Supporting Information Available: Tables listing more crystallographic data and the anisotropic displacement parameters (2 pages). Ordering information is given on any current masthead page.

IC970904U

---

(25) Dye, J. L. *Science* **1990**, *247*, 663.

(26) Meyer, H.-J.; Hoffmann, R. *J. Solid State Chem.* **1991**, *95*, 14. Tian, Y.; Hughbanks, T. *Inorg. Chem.* **1993**, *32*, 400.

(27) Corbett, J. D. In *Chemistry, Structure and Bonding of Zintl Phases and Ions*; Kauzlarich, S., Ed.; VCH Publishers: New York, 1996; Chapter 3.

(28) Henning, R. W.; Corbett, J. D. To be submitted for publication.

(29) Henning, R. W.; Leon-Escamilla, E. A.; Zhao, J.-T.; Corbett, J. D. *Inorg. Chem.* **1997**, *36*, 1282.

(30) Laves, F. *Naturwissenschaften* **1941**, *17*, 244.

(31) Klemm, W.; Busmann, E. *Z. Anorg. Allg. Chem.* **1963**, *319*, 297.

(32) Adolphson, D. G; Corbett, J. D.; Merryman, D. J. *J. Am. Chem. Soc.* **1976**, *98*, 7234.

(33) *Chemistry, Structure and Bonding of Zintl Phases and Ions*; Kauzlarich, S., Ed.; VCH Publishers: New York, 1996.