

Are Cyclogallenes $[M_2(GaH)_3]$ ($M = Li, Na, K$) Aromatic?Yaoming Xie,[†] Peter R. Schreiner,^{†,‡} Henry F. Schaefer III,^{*,†} Xiao-Wang Li,[§] and Gregory H. Robinson[§]

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Abstract: *Ab initio* quantum mechanical methods were applied to examine $M_2(GaH)_3$ ($M = Li, Na, K$) compounds, which are models for the newly synthesized class of Ga_3 three-membered-ring cyclogallene compounds. Basis sets of triple- ζ plus double polarization augmented with diffuse functions (TZ2P+diffuse) quality were employed at the self-consistent field (SCF) and density functional theory (B3LYP) levels of theory. Computed equilibrium geometries, harmonic vibrational frequencies, and chemical shifts are reported. The experimental (X-ray) structures of cyclogallenes are in close agreement with theory. While $Na_2(GaH)_3$ possesses C_3 symmetry (the deviation from C_{3h} symmetry is very small), the remaining two compounds are C_{3h} symmetric. The parent neutral three-membered-ring structure $(GaH)_3$ is not stable as the imaginary vibrational frequencies of $(GaH)_3$ lead to Ga–Ga bond breaking. Upfield changes in the chemical shifts for the alkali metal atoms over and under the ring plane are taken as strong evidence for ring currents in the cyclogallene moiety. This finding and the large negative nucleus independent chemical shifts (NICS) clearly support the proposed aromatic character of the title compounds.

Introduction

In contrast to the rich boron ring and cluster chemistry (boranes and carboranes), there are few relevant examples involving the heavier group 13 congeners. This situation changed very recently when a number of organometallic compounds of aluminum, gallium, and indium containing metal–metal bonds in the form of $[R_2M-MR_2]$,¹ $[RM]_4$,² and $K_2[Al_{12}(iBu)_{12}]^3$ were reported.⁴ Utilization of the 2,6-dimesitylphenyl moiety, 2,6-Mes₂C₆H₃– (Mes = 2,4,6-Me₃C₆H₂–), as an extraordinary bulky ligand for heavier group 13 complexes afforded compounds with unusual and intriguing structural, physical, and chemical properties.⁵ Most notably, stable cyclogallanes of $Na_2[2,6-Mes_2C_6H_3]Ga_3$ ⁶ and $K_2[(2,6-Mes_2C_6H_3)-Ga]_3$ ⁷ have been prepared and characterized. Structural analysis

of $Na_2[(2,6-Mes_2C_6H_3)Ga]_3$ and $K_2[(2,6-Mes_2C_6H_3)Ga]_3$ revealed that metalloaromatic rings, i.e., rings solely composed of heavy main group metals, have been synthesized for the first time.

These organogallium-based substances constitute a new class of compounds known as cyclogallanes. Furthermore, the cyclogallane dianion is isoelectronic to the 2π electron three-membered-ring moiety of the aromatic triphenylcyclopropenium $(PhC)_3^+$ cation. This result strongly challenges borazine's position as the most important aromatic inorganic species. Although significant progress in subvalent group 13 chemistry has been made experimentally, only a few theoretical studies address the metal–metal interactions.⁸ Theoretical papers on boranes and carboranes are plentiful.⁹ While considerable attention has been paid to electron-deficient anion and dianion skeletal structures, studies on simple rings are scarce. Our preliminary theoretical study on $[GaH]_3^{2-}$, the dianion in $K_2-[GaH]_3$, a model for the dianion in $K_2[2,6-Mes_2C_6H_3]Ga_3$, predicted that $K_2[GaH]_3$ has very short Ga–Ga bonds and a well-defined π molecular orbital. This hinted an aromatic character for $[GaH]_3^{2-}$.⁷ For a better understanding of metalloaromaticity, we present here a systematic theoretical study on alkali metal–cyclogallane systems.

Methods

Geometries were fully optimized at the self-consistent field (SCF) and the density functional theory (DFT) levels of theory. For the latter, we employed the hybrid Hartree–Fock B3LYP method, utilizing Becke's three parameter exchange functional¹⁰ and the Lee–Yang–Parr nonlocal correlation functional.¹¹

The basis set was of triple- ζ plus two sets of polarization functions (TZ2P) quality for the alkali metals. The triple- ζ functions for lithium were derived from the (9s5p/4s2p) basis set of Thakkar *et al.*,¹² but

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were recontracted to (9s5p/5s3p). For sodium, TZ functions were taken from McLean and Chandler's basis set (12s9p/6s5p).¹³ For potassium, we used Wachters's (14s9p/10s6p) basis set¹⁴ augmented with two sets of even-tempered *p* functions with exponents 0.085202 and 0.031737,¹⁵ which may be regarded as describing the potassium 4*p* orbital. All TZ functions were augmented by two sets of *d* polarization functions to form the TZ2P basis sets. The orbital exponents for the polarization functions were $\alpha_d(\text{Li}) = 0.400, 0.100$, $\alpha_d(\text{Na}) = 0.350, 0.0875$, $\alpha_d(\text{K}) = 0.200, 0.050$. The technical description of the basis sets is Li(9s5p2d/5s3p2d), Na(12s9p2d/6s5p2d), and K(14s11p2d/10s8p2d).

The basis set for the elements in the (GaH)₃²⁻ dianion fragment, i.e., for Ga and H, was TZ2P augmented with diffuse functions. For Ga, Dunning's 14s11p5d primitive basis set was contracted to 10s8p2d,¹⁶ and then augmented with one *s* and one set of *p* diffuse functions as well as two sets of *d* polarization functions. For H, Huzinaga's 5s primitive set¹⁷ was contracted to 3s, and then augmented with one *s* diffuse function and two sets of *p* polarization functions. The exponents of diffuse and polarization functions were $\alpha_s(\text{Ga}) = 0.01838$, $\alpha_p(\text{Ga}) = 0.01472$, $\alpha_s(\text{H}) = 0.03016$, $\alpha_d(\text{Ga}) = 0.206, 0.068$, and $\alpha_p(\text{H}) = 1.50, 0.375$, respectively. The technical description of this basis set is Ga(15s12p7d/11s9p4d), H(6s2p/4s2p).

Analytic gradient methods were used for geometry optimizations.^{18–20} Harmonic vibrational frequencies (including their infrared intensities) were determined via analytic second-derivative methods.^{21,22} Chemical shifts were computed by the gauge independent atomic orbital (GIAO) method.²³ Our computations were carried out using the programs Gaussian 94²⁴ and PSI 2.0.8.²⁵

In order to assess the aromatic/antiaromatic character of the cyclic π -systems, we computed (at RHF/TZ2P+diff using the GIAO approach)²⁶ the absolute magnetic shieldings, termed the "nucleus independent chemical shifts" (NICS) at selected points in space as a function of the electron density (Table 4), as described by Schleyer *et al.*²⁷ Although NICS are a purely calculational quantity and are not a chemical observable,²⁷ they correlate very well to observable measures of aromaticity such as bond length equalization,²⁸ aromatic stabilization energies (ASE), and magnetic susceptibility exaltations (Λ).²⁹ NICS are taken as negative to conform with chemical convention. The

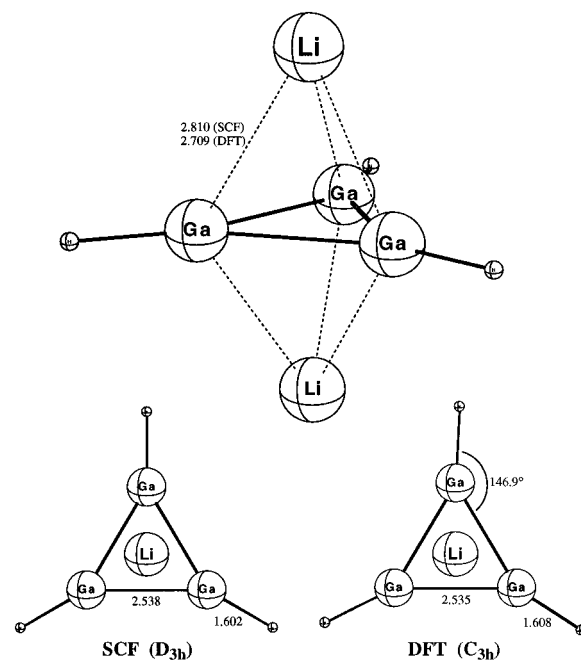


Figure 1. Optimized geometry (bond lengths in Å) for Li₂(GaH)₃ at the SCF TZ2P+diff and DFT TZ2P+diff levels of theory.

geometrical center of the ring's heavy atoms served as the most easily defined reference point. These isotropic chemical shifts yield information about ring currents and the aromatic properties of molecules. Following conventions, aromatic molecules have negative isotropic NICS, while antiaromatic molecules have positive values. The absolute magnitude of a negative NICS is approximately proportional to the aromatic stabilization energy.

Results and Discussion

Geometries. Stationary-point geometries for the title compounds dilithium-, disodium-, and dipotassium-cyclogallene [Li₂(GaH)₃, Na₂(GaH)₃, and K₂(GaH)₃], at the SCF and DFT levels of theory, are presented in Figures 1–3. Initially, we imposed *D*_{3h} symmetry for all structures. Vibrational frequency analysis showed that M₂(GaH)₃ *D*_{3h} structures are minima at the SCF, but transition states at the DFT level. Li₂(GaH)₃ and K₂(GaH)₃ become *C*_{3h} minima, while the minimum for Na₂(GaH)₃ has *C*₃ symmetry. Since sodium lies between lithium and potassium in the periodic table, this result seemed unreasonable at first, but the abnormal behavior of sodium compared to the other alkali metals has been emphasized recently by Lambert and Schleyer.³⁰ However, the *C*₃ symmetry Na₂(GaH)₃ minimum deviates only little from *C*_{3h} geometry. There are almost no changes in geometry (within 0.001 Å for the Ga–Ga and Ga–H and only 0.011 Å for the Na–Ga bond lengths; less than 0.5° for the Ga–Ga–H and only 3.8° for the out-of-plane angle of the H atoms) in going from *C*_{3h} to *C*₃. More importantly, the energy to the *C*₃ structure is only marginally (0.006 kcal/mol) lower than the *C*_{3h} structure (*vide infra*), demonstrating an extremely flat double-well potential with respect to the out-of-plane angle. Since the energy barrier (i.e., the energy of the *C*_{3h} geometry) between the two *C*₃ structures is vastly below the zero-point energy, the experimental measurements must correspond to the averaged *C*_{3h} symmetric structure. The changes of geometries and energies from *D*_{3h} structure to *C*_{3h} are also small. While the Ga–H bonds distort in the molecular plane about 5°, 5°, and 10° from *D*_{3h} symmetry to *C*_{3h} at the DFT level for Li₂(GaH)₃, Na₂(GaH)₃, and K₂(GaH)₃, respec-

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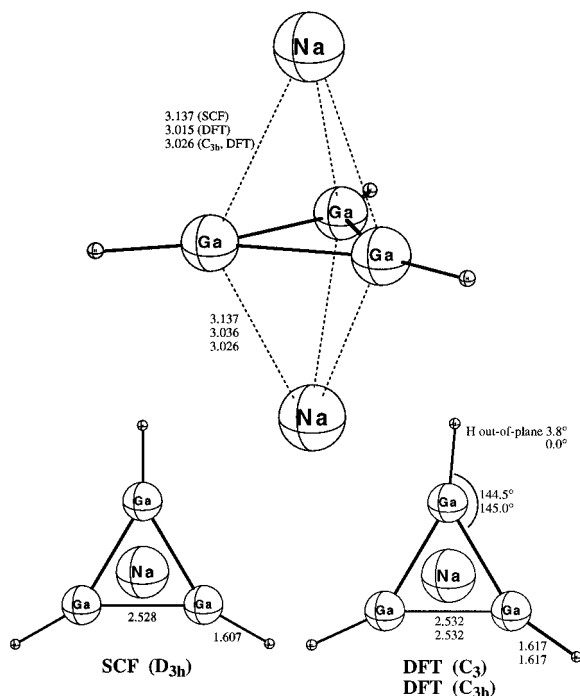


Figure 2. Optimized geometry (bond lengths in Å) for $\text{Na}_2(\text{GaH})_3$ at the SCF TZ2P+diff and DFT TZ2P+diff levels of theory. At the DFT level, the minimum possesses C_3 symmetry (C_{3h} is a transition state).

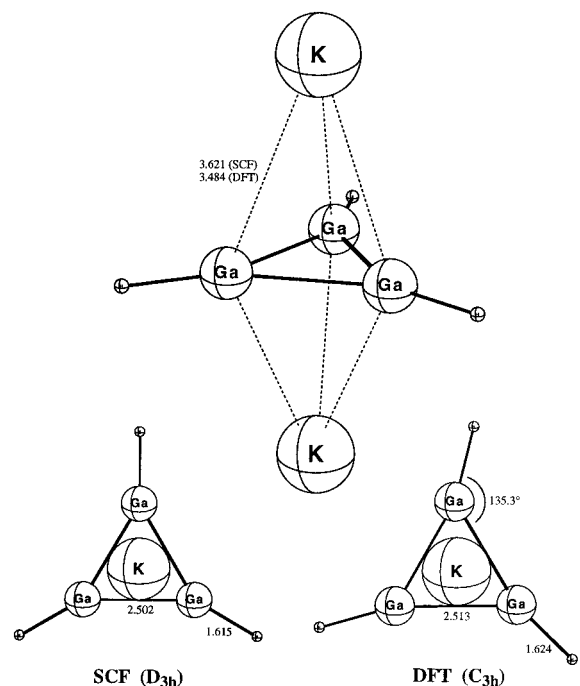


Figure 3. Optimized geometry (bond lengths in Å) for $\text{K}_2(\text{GaH})_3$ at the SCF TZ2P+diff and DFT TZ2P+diff levels of theory.

tively, the corresponding energies decrease by about 0.014, 0.006, and 0.097 kcal/mol.

With the exception of the Ga–Ga bond length of $\text{Li}_2(\text{GaH})_3$, electron correlation increases the Ga–H and Ga–Ga bond lengths by about 0.01 Å, but decreases the Ga–M (M = Li, Na, K) distances by 0.1 Å.

The geometries of the three-membered ring are rather similar in the three alkali metal compounds. The Ga–Ga bond lengths decrease from Li to K (DFT): 2.535 Å for $\text{Li}_2(\text{GaH})_3$, 2.532 Å for $\text{Na}_2(\text{GaH})_3$, and 2.513 Å for $\text{K}_2(\text{GaH})_3$. This is due to the size of M^+ and its electronegativity: a larger metal atom binding at a larger distance should favor ionic bonding, while a smaller

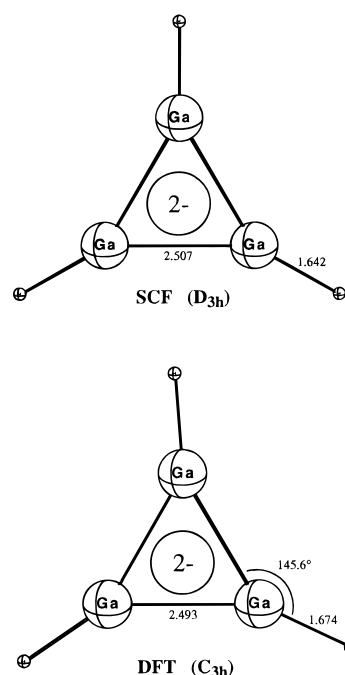
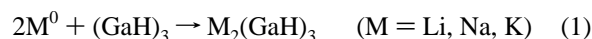


Figure 4. Optimized geometry (bond lengths in Å) for $(\text{GaH})_3^{2-}$ at the SCF TZ2P+diff and DFT TZ2P+diff levels of theory.

electronegativity allows for effective electron transfer (increasing the π bond strength) from the alkali metal to the cyclogallene. Both effects should increase the Ga–Ga bonding interactions. Thus, K^+ (largest cation radius of 1.52 Å³¹ and lowest electronegativity of 0.91³²) is the metal which stabilizes the three-membered ring most, leading to the shortest Ga–Ga distance. While Na^+ (1.16 Å³¹) is larger than Li^+ (0.90 Å),³¹ the reversed electronegativities (0.97 for Li^+ and 1.01 for Na^+)³² compensate for this effect, resulting in almost identical Ga–Ga bond lengths in the two compounds. This argument is further supported by the short Ga–Ga bonds (2.493 Å, Figure 4) in the dianion $(\text{GaH})_3^{2-}$, in which all electron density from the metal is transferred to the π orbital on $(\text{GaH})_3$.

Due to the incomplete inclusion of electron correlation effects in our computation and the large substituents used in the crystal structures, the experimental Ga–Ga bond lengths in $\text{Na}_2[(2,6\text{-Mes}_2\text{C}_6\text{H}_3)\text{Ga}]_3$ (2.441 Å), and in $\text{K}_2[(2,6\text{-Mes}_2\text{C}_6\text{H}_3)\text{Ga}]_3$ (2.419, 2.426, 2.432 Å) are about 0.09 Å shorter than in the model structures at B3LYP (2.532 and 2.513 Å, respectively). The experimental Ga–M (M = K and Na) bond lengths (3.229 for Ga–Na, and 3.529–3.582 Å for Ga–K) are longer than theory (3.026 for Ga–Na, 3.484 Å for Ga–K).^{6,7} However, both experiment and theory show the same trends (Figure 1–3). In agreement with experiment, the cyclogallene substructure in $\text{Na}_2(\text{GaH})_3$ and $\text{K}_2(\text{GaH})_3$ has C_{3h} symmetry (B3LYP). The experimental Ga–Ga–C angles in $\text{Na}_2[(2,6\text{-Mes}_2\text{C}_6\text{H}_3)\text{Ga}]_3$ are 133.7°⁶ and those in $\text{K}_2[(2,6\text{-Mes}_2\text{C}_6\text{H}_3)\text{Ga}]_3$ are 143°⁷ in contrast to the DFT values for the corresponding Ga–Ga–H angles [145° for $\text{Na}_2(\text{GaH})_3$ and 135° for $\text{K}_2(\text{GaH})_3$].

Energies. The hypothetical reaction (eq 1) can be used to assess the relative thermodynamic stabilities of the three little molecules.



For comparison, we also optimized the three-membered neutral $(\text{GaH})_3$. As was found for the $\text{M}_2(\text{GaH})_3$ species, the SCF

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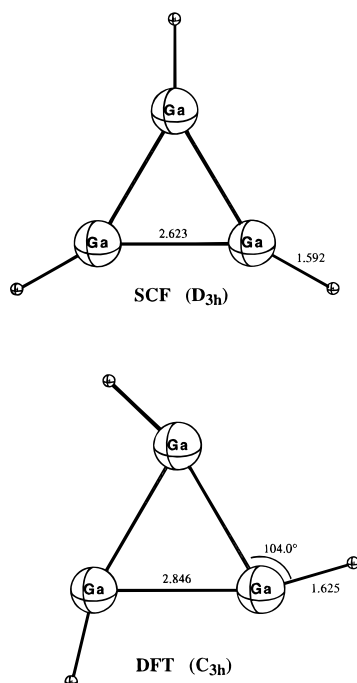


Figure 5. Optimized geometry (bond lengths in Å) for neutral $(\text{GaH})_3$ at the SCF TZ2P+diff and DFT TZ2P+diff levels of theory. This stationary point is not a minimum.

Table 1. ΔH_0 (kcal/mol) refers to the Energy Change of the Hypothetical Reaction (Eq 1) at the SCF and DFT (B3LYP) Levels of Theory^a

	SCF for M =			DFT for M =		
	Li	Na	K	Li	Na	K
ΔH_0	-55.2	-40.5	-41.7	-89.5	-70.3	-68.5

^a C_{3h} symmetry was imposed for the neutral $(\text{GaH})_3$ molecule, and restricted open-shell HF method was employed for alkali metal atom (at 2S_0 state).

stationary point has D_{3h} symmetry, while the DFT structure converges to C_{3h} . However, frequency analysis shows that cyclic neutral $(\text{GaH})_3$ is not a minimum at both levels of theory. Relaxation of the imposed symmetry would lead to an open-chain structure. Note in Figure 5 that the neutral Ga–Ga bond length is significantly larger than that in the dianion (cyclogallene) due to the absence of π -bonding. We use these structures only for the purpose of showing how the alkali metals stabilize $(\text{GaH})_3$.

The reaction enthalpies are quite large (42–90 kcal mol⁻¹; Table 1), due to the low ionization potentials of the alkali metals and the extraordinary stability of the product complexes with respect to ionic dissociation. Furthermore, the absolute value of ΔH_0 increases when electron correlation is included, due to a better description of the ionic product complex. The trends, however, are the same at both SCF and DFT: Na and K show very similar binding energies while the two lithiums bind 15–20 kcal/mol more strongly to the doubly negatively charged cyclogallene fragment. This is due to the relatively short Li–Ga distance which allows stronger electrostatic interaction than in the Na and K cases (the Li–cyclogallene bond distances are about 0.3–0.7 Å shorter). Thus, the yet to be synthesized lithium derivative may ultimately be the most stable complex in the series.

Vibrational Frequencies (Table 2 and 3). With the exception of $\text{Na}_2(\text{GaH})_3$ (C_3), the minimum structure possesses D_{3h} and C_{3h} symmetry at the SCF and DFT levels, respectively. Although the DFT and SCF structures have different symmetry,

Table 2. Harmonic Vibrational Frequencies (cm⁻¹) and Their Infrared Intensities (km/mol, in Parentheses) of $\text{M}_2(\text{GaH})_3$ (M = Li, Na, K) at the SCF Level of Theory

		M =		
		Li (D_{3h})	Na (D_{3h})	K (D_{3h})
e'	Ga–H stretch	1839 (1071)	1813 (1137)	1771 (1228)
a_1'	Ga–H stretch	1835 (0)	1806 (0)	1762 (0)
e'	Ga–H rock	571 (25)	574 (23)	571 (17)
e''	Ga–H wag	340 (0)	324 (0)	299 (0)
a_1'	ring breath	243 (0)	252 (0)	262 (0)
a_2''	Ga–H wag	346 (75)	254 (1)	219 (11)
a_2'	Ga–H rock	225 (0)	199 (0)	198 (0)
e'	ring deformation	192 (3)	186 (1)	192 (1)
a_2''	M–ring stretch	162 (92)	165 (50)	123 (43)
a_1'	M–ring stretch	346 (0)	169 (0)	115 (0)
e''	M–X–M tilt ^a	177 (0)	95 (0)	49 (0)
e'	M–X–M bend ^a	136 (16)	57 (13)	35 (19)

^a The letter X stands for the center of the molecule.

Table 3. Harmonic Vibrational Frequencies (cm⁻¹) and Their Infrared Intensities (km/mol, in Parentheses) of $\text{M}_2(\text{GaH})_3$ (M = Li, Na, K) at the DFT (B3LYP) Level of Theory

		M =			
		Li (C_{3h})	Na (C_{3h})	Na (C_3) ^b	K (C_{3h})
e'	Ga–H stretch	1714 (950)	1671	1666 (1055)	1630 (1134)
a'	Ga–H stretch	1706 (0)	1657	1653 (2)	1613 (0)
e'	Ga–H rock	539 (16)	535	546 (15)	559 (11)
e''	Ga–H wag	343 (0)	261	302 (1)	324 (0)
a'	ring breath	187 (0)	230	230 (<1)	262 (0)
a''	Ga–H wag	105 (65)	194	151 (<1)	199 (<1)
a'	Ga–H rock	218 (0)	173	173 (<1)	193 (0)
e'	ring deformation	191 (5)	172	172 (1)	172 (2)
a''	M–ring stretch	350 (100)	92i	204 (35)	130 (32)
a'	M–ring stretch	358 (0)	106	118 (7)	121 (0)
e''	M–X–M tilt ^a	194 (0)	86	101 (<1)	72 (0)
e'	M–X–M bend ^a	140 (11)	61	60 (10)	37 (14)

^a The letter X stands for the center of the molecule. ^b The irreducible representations of the C_3 point group are a (instead of a' and a'') and e (instead of e' and e'').

the frequencies and infrared intensities are comparable. The DFT frequencies are somewhat smaller for the cyclogallene moiety, but are higher for the modes involving the alkali metals due to shorter cyclogallene–M separations at this level. As expected, the overall differences at the two theoretical levels between the vibrational absorptions related to the Ga–Ga and Ga–H bonds are small for the title compounds.

A direct comparison of the computed with the experimental vibrational frequencies, however, is difficult. There is a very strong (> 1000 km/mol) absorption for the e' Ga–H stretching mode but it can obviously not be compared to the experimental Ga–C counterparts. Several a' and e'' modes are forbidden, and some the ring deformation frequencies are infrared forbidden. The most likely experimental observable is the a'' antisymmetric M–stretching mode which has an appreciable infrared intensity.

Nuclear Magnetic Resonance. Initially, we tried using theory to help interpret the non-conclusive experimental NMR spectra. However, the not very well defined choice of reference (e.g., the salts in aqueous solution) made it impossible to correlate the theoretical with the measured chemical shifts. The problem herein is that the solvation shell strongly interacts with the cation, leading to very different chemical shifts, depending upon the size and the symmetry of the first solvation shell. For instance, while the B3LYP chemical shifts for “naked” Na^+ and K^+ are 624 and 1326 ppm, respectively, they are 570 and 1230 ppm for the hexaqua complexes $[\text{Na}(\text{OH}_2)_6]^+$ and $[\text{K}(\text{OH}_2)_6]^+$, respectively. Even more drastic are the changes in chemical shifts from Ga^{3+} (2614 ppm) to $\text{Ga}(\text{OH}_2)_6^{3+}$ (1845 ppm).

Table 4. Absolute Chemical Shifts (ppm) of $M_2(\text{GaH})_3$ and M^+ ($M = \text{Li, Na, K}$) at the SCF and DFT(B3LYP) Levels of Theory

	SCF for M =			DFT for M =		
	Li	Na	K	Li	Na	K
center	-13 ^a	-15 ^a	-15 ^a			
Ga	1195	1306	1379	857	1102	1101
H	23	24	24	21	21	21
M	90	55	1186	89	567	1218
M^{+b}	95	624	1325	95	624	1326

^a Nucleus independent chemical shifts (NICS), taken negative by convention.²⁶ ^b Isolated cation in the gas phase.

However, the relative changes in chemical shifts (Table 4) for M can be used (apart from the NICS value, see below) to judge the aromatic character of the title compounds.³³ An appreciable ring current³⁴ in the cyclogallene moiety should lead to a reduced magnetic field strength and to an upfield shift for atoms positioned along the center axis of the three-membered ring (as for M). This is indeed the case. The M's are shifted upfield by 6, 57, and 108 ppm for $M = \text{Li, Na, and K}$, respectively. Based on this argument, the cyclogallenes are *aromatic*.

As a second measure, we computed the NICS (see Methods above) for the geometric centers of the cyclogallene moieties in our model compounds. The large negative values (note that NICS of benzene is around -11.5 at comparable levels of theory) indicate *aromatic* ring currents in the cyclogallenes. Note that the neutral $(\text{GaH})_3$ displays $\text{NICS} = +90.6$ which makes it anti-aromatic according to Schleyer's definition.²⁷ A comparison of the NICS values of "free", i.e., without the metal cation associated, $[(\text{GaH})_3]^{2-}$ ($\text{NICS} = -17.6$) with the lighter three-membered-ring D_{3h} homologs $[(\text{BH})_3]^{2-}$ ($\text{NICS} = -23.4$) and $[(\text{AlH})_3]^{2-}$ ($\text{NICS} = -18.5$) indicates that gallium metal

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does not particularly enhance the aromatic effect. The NICS values for both lighter neutrals $[(\text{BH})_3]$ ($\text{NICS} = +20.0$) and $[(\text{AlH})_3]$ ($\text{NICS} = +90.5$) show similar *antiaromatic* behavior as neutral $[(\text{GaH})_3]$ ($\text{NICS} = +90.6$).

Concluding Remarks

The experimental (X-ray) structures of cyclogallenes can be satisfactorily reproduced in models by theory (B3LYP with an augmented TZ basis set). While $\text{Na}_2(\text{GaH})_3$ possesses C_3 symmetry (the deviation from C_{3h} symmetry is very small), the remaining two compounds are C_{3h} symmetric.

The parent neutral three-membered-ring structure $(\text{GaH})_3$ is not stable; the imaginary vibrational frequencies of $(\text{GaH})_3$ lead to Ga-Ga bond breaking.

Upfield changes in the chemical shifts for the alkali metal atoms over and under the ring plane are taken as strong evidence for ring currents in the cyclogallene moiety. This finding and the large negative nucleus independent chemical shifts (NICS) clearly demonstrate that cyclogallenes are *aromatic*.

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Supporting Information Available: Table of absolute energies for neutral $(\text{GaH})_3$, alkali metal atoms M, and the corresponding compounds $M_2(\text{GaH})_3$ (1 page). See any current masthead page for ordering and Internet access instructions.

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