Group 13−Group 16 Heterocubanes [RM(μ_3-E)]$_4$ (R = H, CH$_3$; M = Al, Ga, In; E = O, S, Se, Te) and Group 13 Cubanes [RM(μ_3-M)]$_4$ (R = F, Cl, CH$_3$, NO$_2$; M = Al, Ga, In): A Structural Study

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Twenty-four group 13−group 16 chalcogen heterocubanes [RM(μ_3-E)]$_4$ (R = H, CH$_3$; M = Al, Ga, In; E = O, S, Se, Te) and 12 group 13−group 13 pure cubanes [RM(μ_3-M)]$_4$ (R = F, Cl, CH$_3$, NO$_2$; M = Al, Ga, In) have been studied using density functional theory. Geometries and thermodynamic properties were computed at the B3LYP/SRLC level. All structures were found to be true minima with at most 0.08 Å and 2.5° deviation from the limited experimental geometries. These chalcogen heterocubanes appear thermodynamically resistant to fragmentation. The M$_4$E$_4$ core for each structure proved to be insensitive to ligand choice for the group 13−group 16 heterocubanes. By contrast, the electron-deficient M$_8$ cores of the pure cubanes were variously affected by the electronegativity of various R groups. The entropically disfavored nature of the synthesis may hold the key to the as-yet-unsynthesized [RAl(μ_3-O)]$_4$.

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Introduction

Geometrically uniform molecules have often channeled the imagination of chemists into the development of new species and synthetic methods. It seems that chemical synthesis, descended from the fervent symbolism of alchemy, occasionally meets with its mystical past. Consider cubane, C$_8$H$_8$: a perfect cube of carbon atoms, each holding exactly 90° angles to its brethren, with eight hydrogens on the vertexes. Remarkably, this beautiful molecule can be synthesized and substituents included in myriad ways,[1] one of which is the high-energy-density material (HEDM) octanitrocubane.[2] With the synthesis of cubane came the realization that other cubic structures previously thought impossible might be possible after all. Especially tantalizing were heterocubanes, single molecules arrayed in a simple unit cell pattern (see Figure 1). Such chemical species have lattice energies on the order of ionic salts but with superior mobility, especially in the gas phase. This ability to store energy has made heterocubanes prime targets for both HEDMs3 and metal-oxide chemical vapor deposition (MOCVD).[4] Heterocubanes isoelectronic to cubane (group 13−group 15) exist, as well as electron-rich group 14−group 16, but electron-poor compounds such as group 13−group 14 typically form tetrahedrane-like structures instead.[5−8] The group 13−group 16 heterocubanes are the most recent entrants to this category.

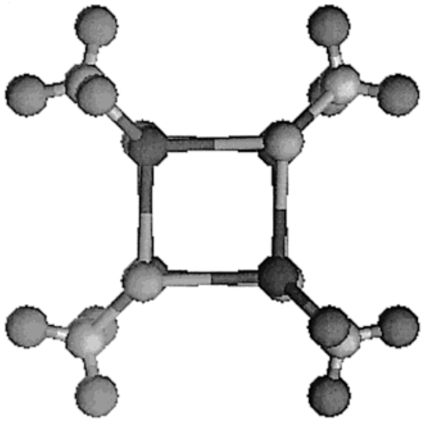

Figure 1. Structure of a group 13−group 16 heterocubane (shown as an idealized perfect cube).

Cowley and co-workers reported on this new class of heterocubanes in 1991. The first synthesis of a gallium heterocubane resulted from the addition of elemental sulfur to tBu$_3$Ga in toluene:

$$4t\mathrm{Bu}_3\mathrm{Ga} + 4\mathrm{S} \rightarrow [t\mathrm{BuGa}(\mu_3\text{-S})]_4 + t\mathrm{Bu}_2\mathrm{S} + \text{other products} \quad (1)$$

The resulting heterocubane was characterized by NMR and found to exist in the T_d point group (i.e., the tBu groups were symmetry equivalent). A further refinement allowed the pathway to proceed in high yield for the sulfur heterocubane:

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$$4t\mathrm{Bu}_3\mathrm{Ga} + 4\mathrm{H}_2\mathrm{S} \rightarrow [t\mathrm{BuGa}(\mu_3\text{-S})]_4 + 4t\mathrm{BuH} \quad (2)$$

Notably, using $t\mathrm{Bu}_3\mathrm{Al}$ in place of the gallium reagent produced both the desired heterocubane and a bridged $[t\mathrm{BuAl}\{\mu_2\text{-E}(t\mathrm{Bu})\}]_2$ compound with a planar $\mathrm{M}_2\mathrm{E}_2$ moiety that converts to the heterocubane upon heating.[9] Power and Barron independently confirmed the $[t\mathrm{BuGaS}]_4$ synthesis[10] and remarked that the structure, while not perfectly cubic, bore a striking resemblance to the well-known biological iron−sulfur clusters.[11] Harlan, Gillan, Bott, and Barron later revealed the versatility and efficacy of reaction 2 for all but the oxygen heterocubanes,[12] making that reaction the generally preferred method of synthesis.[13−16] Barron and co-workers have since demonstrated that these compounds (especially gallium heterocubanes) make excellent single-source MOCVD precursors. GaS, GaSe, and various indium heterocubanes have been used industrially to cleanly produce both cubic and hexagonal surfaces for metal−insulator-semiconductor field-effect transistor (MISFET) applications.[4,17−30]

The oxygen heterocubanes remain synthetically elusive. Reaction 2 works for S, Se, and Te, but apparently no one has yet attempted the experiment with ultrareactive atomic oxygen. Efforts to produce heterocubanes by exposure to molecular oxygen have proved difficult,[31] and while there exists a stepwise exchange reaction between tellurium heterocubanes and the corresponding selenium and sulfur species, this pathway is not available for oxygen.[32] Even dimerization of the bridged $[t\mathrm{BuAlO}]_2$, a generally effective synthetic pathway, ultimately failed.[33,34] Why has $[\mathrm{RAl}(\mu_3\text{-O})]_4$ proven so inaccessible? This work aims to answer that question as we survey the properties of the group 13−group 16 heterocubanes. As an addendum to the main thrust of the paper—and in deference to symmetry's historical role as the harbinger of discovery—we also consider the only heterocubane combination with no experimental data, the group 13−group 13 "pure" cubanes.

Computational Methods

All computations were carried out using density functional theory from the Q-Chem package.[35] All structures R = H were initially optimized in the C_1 (no symmetry) point group and found to collapse to T_d symmetry; thus geometries of R = CH_3 and larger substituents were optimized solely in tetrahedral symmetry. Vibrational frequencies were computed, and no structure exhibited imaginary frequencies; these molecules are therefore true minima on their respective energy surfaces. In the isolated cases of R = Cp and *t*Bu, symmetry was relaxed to allow motion of the large rings on Cp and the hydrogens in *t*Bu (*T* symmetry). Thermodynamic partition functions and the associated enthalpies and entropies were computed using the most stringent criteria. The ubiquitous B3LYP[36,37] was chosen as the sole functional, since test calculations demonstrated changes of at most 0.5° in angles and 0.01 Å in bond distance for the pure functionals BLYP and BP86. It has been reported that B3LYP is problematic for predicting strain energies and heats of formation, while BLYP approaches G2 accuracy for group 14 cubanes and tetrahedranes.[38] However, our own investigation suggests this distinction does not apply to group 13, perhaps because of the lesser role strain plays for heavier analogues.[39] Large-core effective core potentials (ECPs) of the Stuttgart−Bonn variety were used for their relative accuracy and availability across the *p*-block (denoted SRLC).[40] Original investigations with all-electron basis sets generated similar results with a significant performance penalty relative to ECPs, so the former basis sets were not included in the full study. The default pruned Lebedev grid (SG1) of Q-Chem was applied, as it has overall good performance with excellent speed.[35]

Results and Discussion

Tables 1 and 2 report predicted geometries for the hydrogen- and methyl-substituted group 13−group 16 heterocubanes. Tables 3 and 4 provide theoretical thermodynamic information for the heterocubanes.

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Table 1. Geometric Properties of the Group 13−Group 16 Heterocubanes with Formula $[HM(\mu_3\text{-}E)]_4$ as Computed by the B3LYP/SRLC Method[a]

E =	O			S			Se			Te		
M =	Al	Ga	In	Al	Ga	In	Al	Ga	In	Al	Ga	In
M−E (Å)	1.89	1.98	2.11	2.43	2.45	2.57	2.56	2.58	2.70	2.76	2.77	2.90
Expt I		1.97	2.14	2.38	2.38	2.55	2.46	2.51	2.67	2.73	2.72	2.86
Expt II					2.35	2.56	2.48	2.47	2.66	2.72	2.67	2.87
M−E−M (deg)	94.5	93.9	95.7	85.4	85.4	87.3	82.8	83.0	84.4	80.7	81.1	82.0
Expt I		93.9	95.2	86.4	86.4	87.0	80.3	85.5	85.3		85.1	95.7
Expt II					82.6	85.7	85.1	98.9	82.8	84.5	79.1	80.0
E−M−E (deg)	85.3	86.0	84.0	94.4	94.4	92.6	96.8	96.6	95.3	98.6	98.3	97.5
Expt I		86.0	84.6	93.5	93.4	92.9	99.0	94.3	94.5		94.7	83.8
Expt II					96.8	94.9	94.7	80.0	96.6	95.3	99.6	98.6
M···M (Å)	2.77	2.90	3.13	3.30	3.32	3.55	3.38	3.41	3.63	3.57	3.60	3.80
E···E (Å)	2.56	2.70	2.82	3.56	3.60	3.72	3.82	3.84	3.99	4.18	4.19	4.36

[a] Experimental bond distances and bond angles are an average of the X-ray structures reported for most bulky substituent heterocubanes (denoted I: refs 12, 13, 27, 28, 31) and Cp* (denoted II: refs 14, 15, 18, 25).

Table 2. Geometric Properties of the Group 13−Group 16 Heterocubanes with Formula $[H_3CM(\mu_3\text{-}E)]_4$ as Computed by the B3LYP/SRLC Method[a]

E =	O			S			Se			Te		
M =	Al	Ga	In	Al	Ga	In	Al	Ga	In	Al	Ga	In
M−E (Å)	1.89	1.99	2.12	2.43	2.46	2.58	2.56	2.58	2.71	2.77	2.78	2.90
M−E−M (deg)	94.3	93.6	95.5	85.4	85.6	87.3	83.0	83.4	84.6	81.1	81.6	82.2
E−M−E (deg)	85.6	86.2	84.2	94.4	94.2	92.6	96.6	96.2	95.1	98.3	97.8	97.3
M···M (Å)	2.77	2.90	3.13	3.29	3.34	3.56	3.39	3.44	3.64	3.60	3.63	3.81
E···E (Å)	2.57	2.72	2.84	3.56	3.60	3.73	3.82	3.85	3.99	4.19	4.19	4.36

[a] See previous table for experimental structures.

Table 3. Computed Stability of the Group 13−Group 16 Heterocubanes with Respect to Dissociation into Four RME Fragments (kcal/mol)

M	E	E_{stab}(HME)	E_{stab}(H_3CME)
Al	O	280	351
Al	S	229	300
Al	Se	223	291
Al	Te	206	271
Ga	O	165	269
Ga	S	203	305
Ga	Se	204	304
Ga	Te	196	293
In	O	203	300
In	S	251	353
In	Se	252	351
In	Te	243	341

Table 4. Reaction Energetics for $[HAl(\mu_3\text{-}O)]_4$ and $[HGa(\mu_3\text{-}O)]_4$[a] **'**

core	ΔH (kcal/mol)	ΔS (cal/mol K)	ΔG_{298} (kcal/mol)	T_{cr} (K)
AlO	−11.1	−0.0476	+3.01	245
GaO	−12.7	−0.0454	+0.808	293

[a] T_{cr} is the crossover temperature (at which $\Delta G = 0$).

Table 5 lists the geometries for various group 13−group 13 pure cubane structures. No thermodynamic data are included for the experimentally unknown pure cubanes.

Structures of Group 13−Group 16 Heterocubanes. Table 1 compares the computed geometries of the hydrogen-substituted heterocubanes to experiment whenever available. In most experiments, synthesis becomes possible through the exploitation of steric considerations. Bulky ligands such as *t*Bu, $C(SiMe_3)_3$, and $C(Et_2Me)$ operate on this principle.[12,13,16,27,28,31] For the larger heterocubanes, the more successful syntheses incorporate electron-rich ligands such as Cp* (Cp* = η^5-$C_5(CH_3)_5$),[14,15,18] $[Cp(CO)_2Fe]_2$,[25] and 2,2,6,6-tetramethylpiperidine.[41] Because this distinction is generally considered critical, the results appear separately (denoted Expt II) from other experiments (denoted Expt I) in Table 1.

The computed geometries match experimental structures to an unusually good degree for these kinds of systems. Indeed, the GaO heterocubane shows a fortuitous consonance with the experiment. The B3LYP functional provides results that are at most 0.08 Å off in bond distances and 2.5° off in bond angles. In general, B3LYP overshoots the M−E bond distance. Predictions about the bond angles are more difficult to generalize, as in some cases the experiments are evenly split; it appears that M−E−M is underpredicted for Al and overpredicted for In. The data indicate that the size of the chalcogen dramatically affects the overall distortion of cubicity for these systems. All oxygen heterocubanes have M−E−M angles larger than 90°, while the others have angles less than 90°. The most distorted of the heterocubanes is the AlTe system, which also has the greatest disparity in atomic radii of the set, while InS is the most cubelike.

Bonding analyses of the heterocubanes suggest a geometrically interesting arrangement. All chalcogens display a Mulliken charge of around +1, and all group 13 elements show a corresponding increase in negative charge. At no point do the ligands contribute more than 0.1 electron to each group 13 element. Core molecular orbitals, formed from the group 13 and chalcogen core s orbitals, have a quasi-spherical shape. The highest occupied molecular orbitals (triply degenerate) are bonding in nature, creating π-bonds across each face between the chalcogen atoms. It would appear that most bonding is ionic in nature, but that weak π-bonds between chalcogens provide some covalent character.

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Table 5. Geometric Properties of Various Group 13 Cubanes with Formula $[RM(\mu_3\text{-}M')]_4$ as Computed by the B3LYP/SRLC Method[a]

R =	F			Cl			CH_3			NO_2		
M,M′ =	Al	Ga	In	Al	Ga	In	Al	Ga	In	Al	Ga	In
M−M′ (Å)	2.67	2.81	3.10	2.67	2.80	3.09	2.67	2.68	3.01	2.75	2.81	3.09
M−R (Å)	1.73	1.83	1.96	2.21	2.27	2.41	1.98	2.02	2.17	1.77	1.90	2.03
M···M (Å)	4.38	3.90	4.29	4.38	3.91	4.29	4.34	4.13	4.58	4.44	3.94	4.34
M′···M′ (Å)	2.91	4.05	4.46	2.91	4.02	4.45	2.95	3.38	3.88	2.98	3.99	4.41
M−M′−M (deg)	109.6	87.8	87.6	109.7	88.5	87.9	108.8	100.7	99.0	107.8	89.3	89.0
M′−M−M′ (deg)	65.7	92.2	92.3	65.7	91.6	92.1	67.1	78.2	80.2	65.8	90.6	90.9

[a] M′ represents an atom not connected to R.

On the basis of these data, a few concrete statements may be made. The original study by Cowley and co-workers reported a crystal structure for the GaS heterocubane that differs from the current consensus geometry,[10,17] so it has not been included.[9] Included for comparison out of sheer paucity of available results are the pioneering studies on GaSe[25] and InTe[27] heterocubanes. However, the resolution on those X-ray structures appears poor in comparison to the resolution for similar compounds included here; given the general agreement between our theoretical results and the newer, more accurate X-ray structures of heterocubanes, we are inclined to disbelieve the older GaSe and InTe experiments. Regarding ligand effects on geometry, Table 2, containing methyl-substituted results, mirrors Table 1 in every way, and there is no reason to assume this trend would change. To verify this hypothesis, separate geometry optimizations of $[CpAlO]_4$ and $[t\text{BuAlO}]_4$ were performed, and the resulting predicted geometries (not given here) were not qualitatively different from those in the tables. Clearly, the cores of these heterocubanes are largely inert, and we can confirm Harlan and co-workers' assertion that the distortion from cubicity is linearly proportional to the ratio of covalent nuclei in the core.[12]

Thermodynamics of Group 13−Group 16 Heterocubanes. Stabilization energies of the tetrameric heterocubane species $[RME]_4$ relative to the monomeric RME fragments are given in Table 3. For the methyl-substituted systems (the smallest systems for which experiment would be practicable), the stabilization energy averages 75 kcal/mol per fragment, which is a significant (but not unprecedented) amount. It can be seen that the addition of methyl groups merely raises the energies uniformly for all species. Oxygen heterocubanes vary more than other chalcogens for a given M. Compared to the lattice energies of ionic unit cells, these energies are perfectly believable and certainly bolster the case for using these kinds of structures for energy storage. Unfortunately, they hold no clues to the enigma of $[RAl(\mu_3\text{-O})]_4$ synthesis.

So why is it that GaO heterocubanes can be made but not AlO heterocubanes? Table 4 suggests an answer. A full consideration, encompassing zero-point correction energies and thermodynamic partition functions, of all reaction species reveals that both reactions are favored by enthalpy but disfavored by entropy. The entropic change between the two is not large, but even for GaO it has the effect of halting the reaction above 293 K (ambient thermal energy is enough to combat this deficiency). The less favored AlO apparently stops forming the heterocubane around 245 K. Even at standard thermodynamic conditions, there is not enough ambient energy to overcome the entropic effect. Thus it appears that the reaction may proceed *if attempted at low temperature*. Whether this computed difference is real or merely artifactual depends principally on two propositions: (1) whether B3LYP's relative energetics are accurate enough to discern two main-group systems separated by less than 2 kcal/mol; and (2) whether reaction 2 can be realistically applied to oxygen heterocubanes. Proposition 1 is questionable at best. While experiment is presently silent on proposition 2, our theoretical work for GaS deems it valid. Furthermore, recent low-temperature studies by Schnöckel appear to have produced AlO heterocubanes in low yield;[42] validation of these experiments is forthcoming.[43]

Group 13−Group 13 Cubanes. Following the group 13−group 16 cubanes, which are capable of achieving some parity electronically, we considered the electron-deficient pure group 13 cubanes. Directly analogous to cubane, such structures make more sense as HEDMs, especially when octasubstituted.[2,3] Sadly, no neutral M_8R_8 structures were found to be minima, though related dianions and a neutral Ga_8R_6 compound are experimentally known.[44] Thus the investigation was limited to M_8R_4 structures of topology similar to the above chalcogen heterocubanes. Table 5 includes the relevant geometric information, for which no experimental comparison is possible. All of these structures were found to be true minima on their respective potential energy surfaces. Bond distances in the cubes are in line with expected trends in atomic radius and are not appreciably different for the electronegative ligands. For the methyl ligand, however, we see that the Ga and In cubes are severely distorted and the metal−metal bond distances shortened in order to maximize the electronic density available in this woefully deficient species. Regardless of the ligand, Al proves much more easily distortable than the larger metals. Most of the electronegative ligands produce relatively cubic species, strangely enough. Nitro groups, prized for their power in high-energy-density materials, do not line up as NO_2 but retain their bent structure in ONO connectivity.

The absence, at first glance, of the octasubstituted group 13 cubanes implies a delicate interplay between steric and electronic effects for electron-deficient cubes. Aluminum cubanes are highly distorted. On the other hand, the larger cubanes are relatively unperturbed by electronegative differences among the various substituents. It seems that steric factors and the geometric principle of minimum repulsion trump electronic effects for these cubes where substitution is concerned. We submit that the general principles of cubane chemistry, where 1,3,5,7-tetrasubstitution is favored above all, may hold here as well, provided the substituents are sufficiently electron-rich.[1]

Concluding Remarks

Geometries and thermodynamic information for the group 13–group 16 chalcogen heterocubanes have largely confirmed the suspicions of experimentalists. Density functional theory (in particular, B3LYP) has shown itself to be reliable in this study, predicting bond lengths and angles to within the resolution of the X-ray structures being compared. Geometric differences among the heterocubanes are chiefly a packing effect of the inert core, changing almost imperceptibly with the choice of substituent. The AlO heterocubane variant may be (and perhaps has been)[42] synthesized if the reaction is undertaken at low temperature.

For the group 13–group 13 pure cubanes, geometries are generally affected by the size of the metal and only secondarily controlled by electronic effects due to the substituents. Substitution patterns for group 13 cubanes should be similar to those of cubane, but octasubstitution might not be possible, so none of these species are likely to be effective as a high-energy-density material. This finding does not diminish the aesthetic aspects, however, of the astonishing breadth of unusual cubic structures, especially in light of the presupposed strain energy therein. When geometry fashions a compromise for atoms in unpleasant electronic circumstances, a cube is undoubtedly the first choice.

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