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An investigation of the reaction of $[RGa(\mu_3\text{-}Te)]_4$ with O_2, SO_2 and SeO_2 using a combination of experiment and density functional theory †

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Reaction of $[RGa(\mu_3\text{-}Te)]_4$ (R = ^{t}Bu, $CMeEt_2$) and O_2, SO_2 or SeO_2 yields, in addition to tellurium metal, $[RGa(\mu_3\text{-}O)]_n$ (R = ^{t}Bu, $n = 9$; R = $CMeEt_2$, $n = 6$) and the mixed cubanes $[R_4Ga_4(\mu_3\text{-}O)_x(\mu_3\text{-}Te)_{4-x}]$ ($x = 1, 2$); neither $[R_4Ga_4(\mu_3\text{-}O)_3(\mu_3\text{-}Te)]$ or $[RGa(\mu_3\text{-}O)]_4$ are observed; DFT calculations show no global minimum for $[Me_4Ga_4(\mu_3\text{-}Te)_2(\mu_3\text{-}O)_2]$ or $[Me_4Ga_4(\mu_3\text{-}Te)_2(\mu_3\text{-}O)_2]$, suggesting that these structures would rearrange to more favored structures on the pathway to a final geometry lower in energy.

We have reported the occurrence of a facile chalcogenide exchange reaction between $[(^tBu)Ga(\mu_3\text{-}Te)]_4$ and elemental sulfur or selenium, resulting in the stoichiometric formation of the appropriate cubane, $[(^tBu)Ga(\mu_3\text{-}E)]_4$ (E = S, Se), and metallic tellurium.[1] Each of the intermediate cubane compounds, $[(^tBu)_4Ga_4(\mu_3\text{-}E)_x(\mu_3\text{-}Te)_{4-x}]$ ($x = 0$–4; E = S, Se) was spectroscopically characterized, and the rate of the chalcogenide exchange is not only dependent on the chalcogen but also its allotropic form. The exchange reaction was proposed to be heterogeneous in nature and involves the opening of the cubane core;[1] this has been confirmed by DFT calculations.[2] During our studies with the telluride cubane compounds, $[RGa(\mu_3\text{-}Te)]_4$, we observed that upon exposure to air or an oxygen containing compound, such as silicon grease, tellurium metal was formed.[3,4] This observation, in combination with the reports of gallium oxide cubanes,[5,6] prompted our investigation of the tellurium/oxygen exchange reaction for $[RGa(\mu_3\text{-}Te)]_4$.

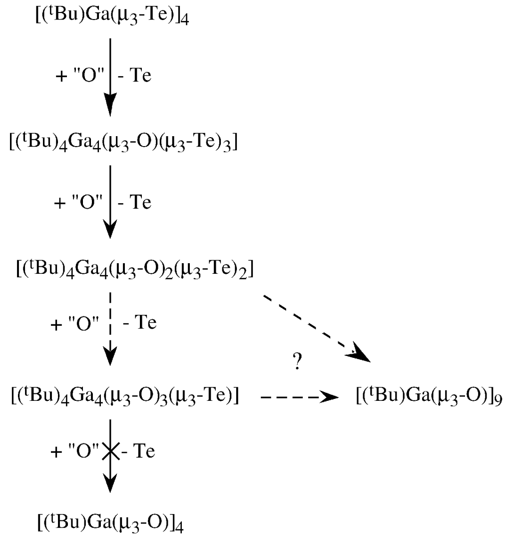
Reaction of $[(^tBu)Ga(\mu_3\text{-}Te)]_4$[7] with O_2, SO_2 or SeO_2 in toluene or hexane results in the immediate formation of a black precipitate, which was determined by EDX analysis to be tellurium metal. Mass spectrometry and NMR spectroscopy analysis on the soluble reaction products indicated a similar product distribution irrespective of the oxide source: $[(^tBu)_4Ga_4(\mu_3\text{-}O)(\mu_3\text{-}Te)_3]$ (**1**, 15%), $[(^tBu)_4Ga_4(\mu_3\text{-}O)_2(\mu_3\text{-}Te)_2]$ (**2**, 65%) and $[(^tBu)Ga(\mu_3\text{-}O)]_9$ (10%).[8]§ The reactions with O_2 and SO_2 occur at room temperature, while the reaction with SeO_2 requires longer reaction times at ambient temperatures or elevated temperatures (60 °C). While the redox reaction observed for O_2 [eqn. (1)] is a direct analogy of the reactions

$$2Te^{2-} + O_2 \longrightarrow 2Te^0 + 2O^{2-} \qquad (1)$$

reported previously,[1] the reactions with SO_2 and SeO_2 occur by oxidation of the sulfur or selenium, eqn. (2). The formation of elemental chalcogen allows for the incorporation of oxide into the gallium cubane.

$$2Te^{2-} + EO_2 \longrightarrow 2Te^0 + E^0 + 2O^{2-}$$
$$E = S, Se \qquad (2)$$

If the reactions are followed by ^1H NMR spectroscopy, it is observed that the yield of $[(^tBu)Ga(\mu_3\text{-}O)]_9$ increases at the expense of compounds **1** and **2**. If the reactions are allowed to proceed to completion only $[(^tBu)Ga(\mu_3\text{-}O)]_9$ is obtained, suggesting that the mixed cubanes are the precursors to the galloxane. Thus, we propose that $[(^tBu)Ga(\mu_3\text{-}O)]_9$ is formed *via* either $[(^tBu)_4Ga_4(\mu_3\text{-}O)_2(\mu_3\text{-}Te)_2]$ or an unstable tri-oxide cubane, $[(^tBu)_4Ga_4(\mu_3\text{-}O)_3(\mu_3\text{-}Te)]$, Scheme 1. It should be noted that $[(^tBu)Ga(\mu_3\text{-}O)]_9$ is the only *tert*-butyl galloxane cage reported to date.[8]



Scheme 1 Proposed stepwise reaction of $[(^tBu)Ga(\mu_3\text{-}Te)]_4$ with the oxygen sources, O_2, SO_2 or SeO_2.

The presence of a bulkier alkyl substituent (CEt_2Me) does not allow for the isolation of tri-oxide and oxo-cubane compounds. The NMR spectra of the reaction products between $[(Et_2MeC)Ga(\mu_3\text{-}Te)]_4$ and O_2 or SeO_2, are difficult to interpret due to having a significantly more complicated spectra than those observed for the analogous *tert*-butyl reaction; mass spectrometry§ clearly confirmed the presence of $[(Et_2MeC)_4Ga_4(\mu_3\text{-}O)(\mu_3\text{-}Te)_3]$ (**3**) and $[(Et_2MeC)_4Ga_4(\mu_3\text{-}O)_2(\mu_3\text{-}Te)_2]$ (**4**). As the reaction continues, the formation of a galloxane cage, $[(Et_2MeC)Ga(\mu_3\text{-}O)]_6$ (**5**), predominates.[4] As with the *tert*-butyl derivative, the mixed cubanes are the precursors to the hexameric galloxane.

The isolation of the larger galloxane cages in place of the cubane may be explained if the latter was thermodynamically inaccessible, however, the recent reports of $[RGa(\mu_3\text{-}O)]_4$ suggest they are indeed isolable.[5,6] It should be noted that

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† Electronic supplementary information (ESI) available: comparison of DFT methods for $[(Me)Ga(\mu_3\text{-}O)]_4$ and comparison of structural parameters for the calculated $[(Me)Ga(\mu_3\text{-}O)]_6$ and empirical $[(^tBu)M(\mu_3\text{-}E)]_6$ structures. See http://www.rsc.org/suppdata/dt/b1/b106998p/

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Table 1 Calculated bond lengths (Å) and angles (°) for mixed chalcogenide cubanes

Compound	Ga–Te	Ga–O	Ga–Te–Ga	Ga–O–Ga	Te–Ga–Te	Te–Ga–O	O–Ga–O
$[MeGa(\mu_3\text{-}Te)]_4$	2.782	—	81.3	—	98.1	—	—
$[Me_4Ga_4(\mu_3\text{-}Te)_3(\mu_3\text{-}O)]$	2.778	1.979	70.6	108.7	99.9	89.8	—
$[Me_4Ga_4(\mu_3\text{-}Te)_2(\mu_3\text{-}O)_2]$	2.779	1.971	69.6	106.6	98.8	91.9	82.9
$[Me_4Ga_4(\mu_3\text{-}Te)(\mu_3\text{-}O)_3]$	2.781	1.992	69.1	104.9	—	92.8	84.8
$[MeGa(\mu_3\text{-}O)]_4$	—	1.931	—	92.99	—	—	87.0

Table 2 Calculated $\Delta G°$, $\Delta H°$, and $\Delta S°$ for gallium chalcogenide exchange reactions at 298 K

Reaction	$\Delta G°$/kJ mol^{-1}	$\Delta H°$/kJ mol^{-1}	$\Delta S°$/J K^{-1} mol^{-1}
$[MeGaTe]_4 + O \longrightarrow [Me_4Ga_4Te_3O] + Te$	−385.7	−383.4	+7.714
$[Me_4Ga_4Te_3O] + O \longrightarrow [Me_4Ga_4Te_2O_2]^\ddagger + Te$	−372.6	−366.2	+21.47
$[Me_4Ga_4Te_2O_2]^\ddagger + O \longrightarrow [Me_4Ga_4TeO_3]^\ddagger + Te$	−366.9	−358.9	+26.83
$[Me_4Ga_4TeO_3]^\ddagger + O \longrightarrow [MeGaO]_4 + Te$	−358.9	−367.9	−30.19
$[MeGaTe]_4 + 4O \longrightarrow [MeGaO]_4 + 4Te$	−1484	−1476	+25.82

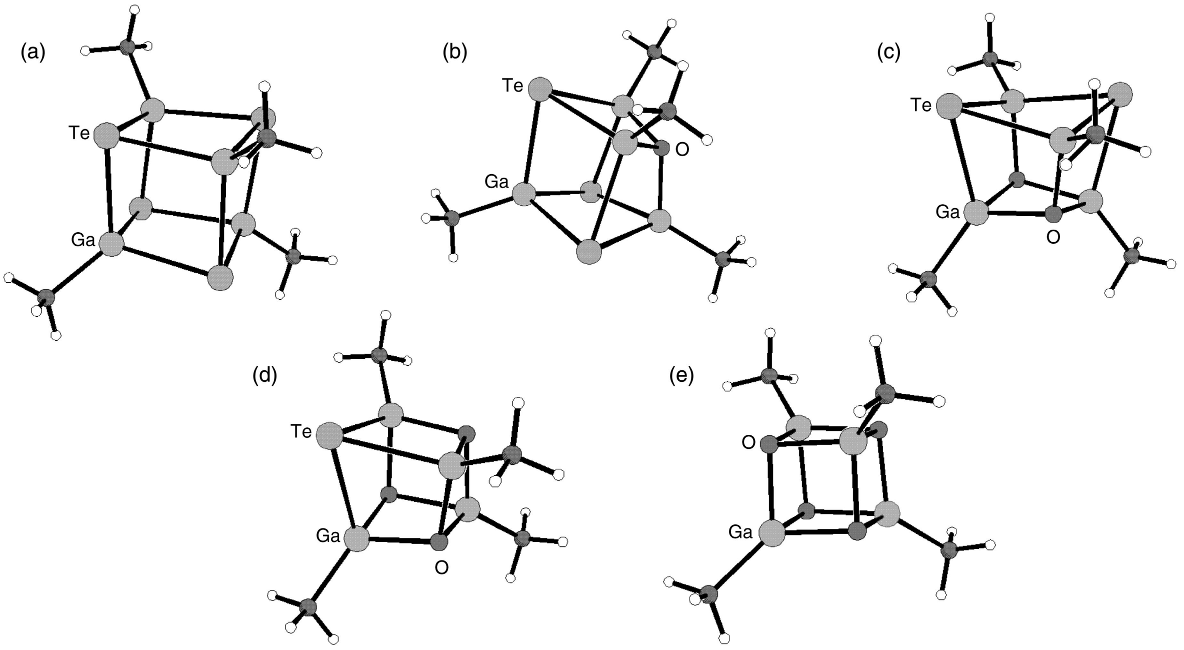

Fig. 1 Structures calculated using the B3LYP/Stuttgart level of DFT theory for (a) $[MeGa(\mu_3\text{-}Te)]_4$, (b) $[Me_4Ga_4(\mu_3\text{-}Te)_3(\mu_3\text{-}O)]$, (c) $[Me_4Ga_4(\mu_3\text{-}Te)_2(\mu_3\text{-}O)_2]$ (1st order saddle point), (d) $[Me_4Ga_4(\mu_3\text{-}Te)(\mu_3\text{-}O)_3]$ (transition-state), and (e) $[MeGa(\mu_3\text{-}O)]_4$. Severe distortion of the gallium chalcogenide cubane core is observed for the oxide species relative to the sulfide structure.

these isolable oxo-cubanes were not prepared by Te/O exchange reactions. The lack of evidence for the formation of either $[R_4Ga_4(\mu_3\text{-}O)_3(\mu_3\text{-}Te)]$ or $[RGa(\mu_3\text{-}O)]_4$ in the reactions described above, suggests that they are not formed, or are unstable with respect to cage expansion. In an attempt to investigate this possibility, we have investigated the stability of $[R_4Ga_4(\mu_3\text{-}O)_x(\mu_3\text{-}Te)_{4-x}]$ (x = 0–4) using density functional theory (DFT) using B3LYP methods[9] and Stuttgart RLC ECP[10] basis sets/pseudopotentials.¶ We have shown that calculations at this level successfully reproduce structural features for the heavier chalcogenide compounds.[2] To reduce computational time, the *tert*-butyl groups on the periphery of the gallium chalcogenide cubane were replaced with methyl groups. We have previously shown, experimentally, that the alkyl substituent does not influence the cubane geometries.[4]

The calculated structures for $[Me_4Ga_4(\mu_3\text{-}Te)_x(\mu_3\text{-}O)_{4-x}]$ (x = 0–4) are shown in Fig. 1; selected structural parameters are given in Table 1. The calculated parameters for $[MeGa(\mu_3\text{-}E)]_4$ (E = O, Te) compare favorably to X-ray structural data.[4–6] In considering the mixed cubanes, the Ga–E–Ga and E–Ga–E angles become more distorted following each subsequent Te/O exchange due to the large difference in the ionic radii of O^{2-} (1.40 Å) *versus* Te^{2-} (2.21 Å).

Frequency calculations were performed, using STP conditions, to determine selected thermochemical properties for the optimized mixed cubanes. The energetics for each exchange reaction (Table 2) were determined to be similar for each step indicating that each sequential exchange is an isolated reaction. Further, the entropy change is small in magnitude and (since isolated O and Te atoms were used as reactant and product) corresponds to the degree of cage distortion within the cubane molecules. For example, the magnitude of $\Delta S°$ is relatively small for the first exchange, but increases with subsequent exchanges, see Table 2. The $\Delta S°$ for the last step of the oxygen exchange series is largely negative, which indicates a release of cage distortion from the $[Me_4Ga_4(\mu_3\text{-}Te)(\mu_3\text{-}O)_3]$ species to the $[MeGa(\mu_3\text{-}O)]_4$ compound; this is immediately apparent by comparing the calculated structures for these compounds (Table 1, and Figs. 1d–e).

The galloxane hexamer structure, $[MeGa(\mu_3\text{-}O)]_6$, that was calculated to convergence using DFT (using B3LYP/Stuttgart for Ga and O and the 6-31G** basis set for C and H) is significantly more stable than the oxo-cubane. The $\Delta G°$ of eqn. (3) was calculated as 1260 kJ mol^{-1}.

$$3[MeGa(\mu_3\text{-}O)]_4 \longrightarrow 2[MeGa(\mu_3\text{-}O)]_6 \qquad (3)$$

The calculated structure for $[\mathrm{MeGa}(\mu_3\text{-O})]_4$ seems reasonable based on low cubane distortion, and thermodynamic predictions indicate that the O/Te exchange reactions should proceed much more readily than either of the sulfur or selenium exchanges.[2] The experimental observations described above, however, suggest there must be a kinetic barrier and/or a more thermodynamically accessible product (*e.g.*, larger galloxane cages) that precludes the full oxide exchange to yield $[\mathrm{RGa}(\mu_3\text{-O})]_4$. This is not unreasonable since the mixed telluride-oxide intermediate species are highly distorted and possess a flat potential energy surface that would allow rearrangement pathways. Although a stable structure for $[\mathrm{Me_4Ga_4}(\mu_3\text{-Te})_3(\mu_3\text{-O})]$ was calculated (Fig. 1b), no global minimum was found for the $[\mathrm{Me_4Ga_4}(\mu_3\text{-Te})_2(\mu_3\text{-O})_2]$ species (Fig. 1c). For this latter compound, one imaginary frequency was calculated for the minimized structure indicating a 1st order saddle point. Since the eigenvalues of the Hessian also contained a single negative value, a structure slightly lower in energy could be obtained by manipulating the current Z-matrix variables. For the $[\mathrm{Me_4Ga_4}(\mu_3\text{-Te})(\mu_3\text{-O})_3]$ species a 1st order saddle point, also containing a single negative Hessian eigenvalue, was eventually reached. The 3D potential energy surface for both the $[\mathrm{Me_4Ga_4}(\mu_3\text{-Te})_2(\mu_3\text{-O})_2]$ and $[\mathrm{Me_4Ga_4}(\mu_3\text{-Te})(\mu_3\text{-O})_3]$ structures were significantly smoother than any other mixed cubane structures we have investigated,[2] suggesting that these intermediate structures would rearrange to more sterically-favored structures on the pathway to a final geometry slightly lower in energy.

On the basis of a combination of experimental and theoretical studies, we propose that the reaction of $[\mathrm{RGa}(\mu_3\text{-Te})]_4$ with O_2, SO_2 or SeO_2 results in a series of stepwise O/Te exchange reactions. Instability of $[\mathrm{Me_4Ga_4}(\mu_3\text{-Te})(\mu_3\text{-O})_3]$, due to the difference in covalent radii between oxygen and tellurium, and hence the cage's distorted structure, leads to cage cleavage and subsequent exchanges result in formation of larger cages depending on substituent.

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Notes and references

§ $[({}^t\mathrm{Bu})_4\mathrm{Ga_4}(\mu_3\text{-O})(\mu_3\text{-Te})_3]$ (**1**). EI-MS (*m*/*z*, %): 849 ($\mathrm{M^+} - {}^t\mathrm{Bu}$, 100), 792 ($\mathrm{M^+} - 2{}^t\mathrm{Bu}$, 10), 57 (${}^t\mathrm{Bu}$, 100). ^{1}H NMR ($\delta$, C_6D_6): 1.04 [9H, s, $\mathrm{C(C}H_3)_3$], 0.95 [27H, s, $\mathrm{C(C}H_3)_3$]. ^{13}C NMR (δ, C_6D_6): 28.0 [$\mathrm{C(}C\mathrm{H_3)_3}$], 27.9 [$C\mathrm{(CH_3)_3}$].

$[({}^t\mathrm{Bu})_4\mathrm{Ga_4}(\mu_3\text{-O})_2(\mu_3\text{-Te})_2]$ (**2**). EI-MS (*m*/*z*, %): 737 ($\mathrm{M^+} - {}^t\mathrm{Bu}$, 40), 57 (${}^t\mathrm{Bu}$, 100). ^{1}H NMR ($\delta$, C_6D_6): 1.14 [18H, s, $\mathrm{C(C}H_3)_3$], 1.06 [18H, s, $\mathrm{C(C}H_3)_3$]. ^{13}C NMR (δ, C_6D_6): 27.0 [$\mathrm{C(}C\mathrm{H_3)_3}$], 26.9 [$C\mathrm{(CH_3)_3}$].

$[(\mathrm{Et_2MeC})_4\mathrm{Ga_4}(\mu_3\text{-O})(\mu_3\text{-Te})_3]$ (**3**). EI-MS (*m*/*z*, %): 933 ($\mathrm{M^+} - \mathrm{Et_2MeC}$, 100).

$[(\mathrm{Et_2MeC})_4\mathrm{Ga_4}(\mu_3\text{-O})_2(\mu_3\text{-Te})_2]$ (**4**). EI-MS (*m*/*z*, %): 821 ($\mathrm{M^+} - \mathrm{Et_2MeC}$, 60).

$[(\mathrm{Et_2MeC})\mathrm{Ga}(\mu_3\text{-O})]_6$ (**5**). EI-MS (*m*/*z*, %): 995 ($\mathrm{M^+} - \mathrm{Et}$, 100), 939 ($\mathrm{M^+} - \mathrm{Et_2MeC}$, 40). ^{1}H NMR ($\delta$, C_6D_6): 1.57 [24H, q, J(H–H) = 7.4 Hz, $\mathrm{C}H_2\mathrm{CH_3}$], 1.10 [18H, s, $\mathrm{C(C}H_3)_2$], 1.03 [36H, t, J(H–H) = 7.4 Hz, $\mathrm{CH_2C}H_3$].

¶ Calculations utilized non-local, gradient corrected density functional theory. For the telluride containing molecules, relativistic effects are non-trivial and were indirectly incorporated into the calculations using quasirelativistic effective core potentials (ECPs) which have been derived from relativistic atomic calculations. The Stuttgart RLC ECP basis set featured single first d and p polarization functions as well as diffuse functions. Electron correlation effects were taken into account by using Becke's three-parameter hybrid gradient-corrected correlation function (B3LYP). This functional was used for all geometry optimizations and subsequent Hessian calculations, as well as for thermodynamic calculations. All geometries were optimized using analytical gradient techniques and the stationary points characterized by harmonic vibrational analysis, accomplished *via* numerical differentiation of the analytical first derivatives. The Gaussian 99 program was used throughout for all single point energy calculations, geometry optimizations, and Hessian calculations.[11]

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