

Synthesis and Reactivity of Cationic Gallium(I) [12]Crown-4 Complexes

Jeremy L. Bourque, Robert A. Nanni, Mark C. Biesinger, and Kim M. Baines*

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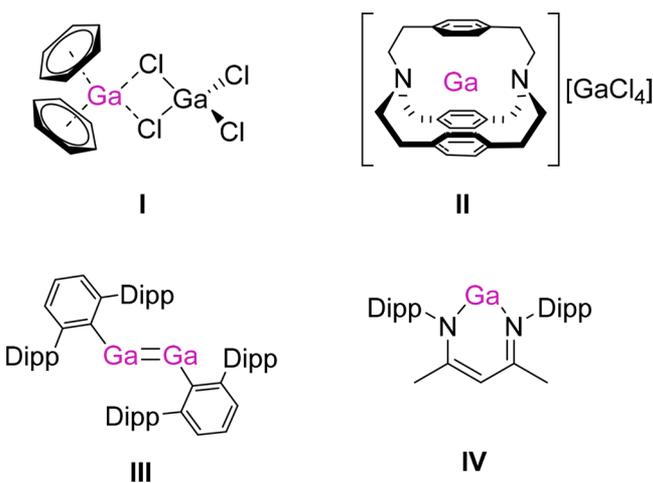
ABSTRACT: The synthesis and reactivity of a gallium(I) cationic complex using [12]crown-4 as a stabilizing ligand were explored. The synthesis of $[\text{Ga}(\text{[12]crown-4})][\text{GaCl}_4]$ was achieved in one step from commercially available starting materials. Anion exchange was utilized to replace the reactive tetrachlorogallate anion for the perfluorophenylborate anion. $[\text{Ga}(\text{[12]crown-4})][\text{B}(\text{C}_6\text{F}_5)_4]$ was analyzed using XPS, which allowed for the classification of the gallium(I)-crown ether complex as electron-deficient. Reactions of the gallium(I)-crown ether complex with Cp^*K and cryptand[2.2.2] demonstrated the facile synthesis of a known gallium(I) compound as well as the generation of new gallium(I) complexes, highlighting the use of the gallium(I)-crown ether complex as an effective starting material for new gallium(I) complexes.



INTRODUCTION

The chemistry of low valent gallium compounds (Chart 1)¹ is of much interest because of the potential of the compounds to

Chart 1. Examples of Gallium(I) Compounds¹ (II = $[\text{Ga}(\text{prismand})][\text{GaCl}_4]$; Dipp = 2,6-diisopropylphenyl; IV = $\text{GaNacNac}^{\text{Dipp}}$)



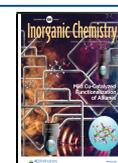
be utilized as alternatives to transition metal catalysts. Some transition metals are expensive, have low natural abundances, and are toxic, which impacts their use in industrial processes.² Like transition metals, gallium(I) compounds can undergo oxidative addition reactions with H–E bonds (where E = H, SnPh₃, NEt₂, PPh₂, OH, OEt), insertion chemistry with H₂ and NH₃, as well as cycloaddition reactions with alkenes.³ This varied reactivity is a consequence of the ambiphilic nature of gallium(I), with its empty *p*-orbital and lone pair of electrons, which enables the Group 13 element to act as both a Lewis acid and a Lewis base.⁴ For example, $[\text{Ga}(\text{C}_6\text{H}_5\text{F})_2][\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$

$[\text{CF}_3)_3)_4]$ ⁵ has been shown to be an effective catalyst for the polymerization of isobutylene where the ambiphilicity of the gallium(I) center is critical for the reactivity.^{6,7} Gallium(I) cations have also been used as catalysts *in situ*. Ultrasonic activation of gallium metal, silver triflate, [18]crown-6, and 1,4-dioxane gave a gallium(I) species, the presence of which was confirmed by ⁷¹Ga NMR spectroscopy. While the complex was not isolated (*vide infra*), it was proposed to be the active catalyst for carbon–carbon bond forming reactions between allyl or allenyl boronic esters and acetals, ketals, or amins.⁸

Despite the promise of gallium(I) reagents as catalysts, gallium(I) complexes, including the materials used to synthesize them, are often unstable toward donor solvents or have variable composition, limiting the scope of their chemistry. For example, “GaI”⁹ has a variable composition which depends on the reaction time used in its preparation.¹⁰ Although gallium(I) cations are present in “GaI”, gallium(II) or gallium(III) compounds are often isolated from reactions using this starting material.^{10,11} Furthermore, “GaI” decomposes or disproportionates upon exposure to donor solvents such as ether and THF.⁹ When Ga₂Cl₄, which contains a gallium(I) cation and a tetrachlorogallate(III) anion ($[\text{Ga}][\text{GaCl}_4]$),¹² is used as a starting material for the synthesis of gallium(I) complexes, comproportionation reactions are common.^{13–16} Although Crossing’s reagent, $[\text{Ga}(\text{C}_6\text{H}_5\text{F})_2][\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$, and derivatives with different arene ligands on the gallium(I) center⁵ or counterions⁷ can be used as sources of gallium(I) for synthesis and catalysis, the stability of

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$[\text{Ga}(\text{C}_6\text{H}_5\text{F})_2][\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$ in donor solvents has not been described.¹⁷ A study of the composition and structural chemistry of gallium(I) triflate has recently been published; a mixture of mixed-valence complexes including Ga-arene, Ga-OTf complexes, and a naked Ga^+ has been identified.¹⁸ Finally, the synthesis of pentamethyldiethylenetriamine (PMDTA) coordinated Ga(I) cation, $[(\text{Ga}(\text{PMDTA}))][\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$, has been reported; however, the limited lifetime of the complex at room temperature may limit its use as a starting material for Ga(I) complexes.¹⁹

The development of novel gallium(I) catalysts and reagents that are easily synthesized using commercially available ligands and are stable toward a wide range of solvents is desirable and may facilitate the use of gallium(I) complexes in main group catalysis. We have recently explored the synthesis of crown ether-stabilized low valent Group 14 complexes²⁰ as well as cryptand-stabilized gallium complexes^{13,21} and now report on the use of crown ethers as a stabilizing ligand in gallium(I) chemistry.

There are only a few reports of gallium(I)-crown ether complexes in the literature. The synthesis and characterization of $[\text{Ga}([\text{18}]\text{crown-6})(\text{C}_6\text{H}_5\text{F})_2][\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$ has been described.²² The crystal structure, while of poor quality, reveals the complexation of a gallium(I) cation within [18]crown-6, along with coordination of the gallium(I) cation by fluorobenzene molecules both above and below the plane of the crown ether. More recently, the synthesis and structural characterization of $[\text{Ga}([\text{18}]\text{crown-6})][\text{OTf}]$ has been reported.¹⁸ In this complex, the triflate anion is tightly bound to the gallium which leads to a weakening of the gallium-crown ether interactions. The $[\text{Ga}([\text{12}]\text{crown-4})][\text{GaCl}_4]$ complex has been synthesized, and the molecular structure has been determined; however, the reactivity was not studied, and the work was not published in a peer-reviewed journal.²³

Herein, we describe the facile synthesis of two gallium(I) complexes of [12]crown-4 and the reactivity of the $[\text{Ga}([\text{12}]\text{crown-4})]^+$ cation toward donor ligands, demonstrating its versatility as a source of gallium(I).

RESULTS AND DISCUSSION

Reactions between $[\text{Ga}][\text{GaCl}_4]$ and [12]crown-4 in a 1:1 ratio in toluene resulted in the rapid formation of a precipitate and conversion to a single product, as determined by a singlet observed in the ^1H NMR spectrum of the precipitate dissolved in CD_3CN . ESI-MS data of the solid indicated the presence of $[\text{Ga}([\text{12}]\text{crown-4})]^+$ ($m/z = 245$). ^{71}Ga NMR spectra of the reaction mixture revealed two signals: a relatively sharp signal at +251 ppm, which was assigned to the tetrachlorogallate(III) anion ($[\text{GaCl}_4]^-$) on the basis of chemical shift and line width²⁴ and a broad signal at -471 ppm. The ^{71}Ga chemical shift of gallium(I) cations is typically observed in the range of -600 to -800 ppm,^{5,24} however, a gallium(I) complex with three PPh₃ ligands, $[\text{Ga}(\text{PPh}_3)_3]^+$, has a ^{71}Ga NMR chemical shift of -144 ppm,⁵ and thus, a chemical shift of -471 ppm is not unreasonable for $[\text{Ga}([\text{12}]\text{crown-4})]^+$. Single crystals suitable for X-ray crystallography were obtained; the molecular structure of $[\text{Ga}([\text{12}]\text{crown-4})][\text{GaCl}_4]$, **1** (Figure 1) was confirmed by X-ray diffraction.

The solid-state structure of **1** is remarkable for several reasons. Similar to the structure of the isoelectronic Ge(II)²⁺ [12]crown-4 complex,^{20b} the cation is not centered within the [12]crown-4 cavity; it is displaced from the plane of the four oxygen atoms by 1.4734(7) Å. The bond lengths between the

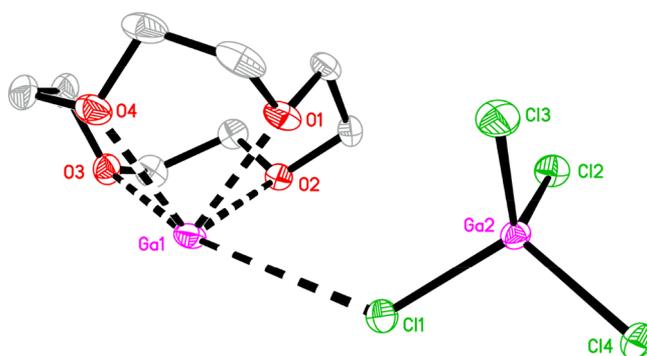


Figure 1. Displacement ellipsoid plot of **1**. Ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths and angles (Å, deg): Ga1–O1 2.3599(11), Ga1–O2 2.5041(13), Ga1–O3 2.3789(11), Ga1–O4 2.5008(13), Ga1⋯Cl1 3.5937(9); O1–Ga1–O2 68.12(3), O1–Ga1–O3 102.21(3).

gallium atom and the oxygen atoms vary quite substantially, from 2.3599(11) Å (Ga1–O1) to 2.5041(13) Å (Ga1–O2), a difference of greater than 0.14 Å and alternate in length around the ring. The alternation of short and long bond distances to oxygen in **1** is analogous to the structure of a related tetra-aza macrocyclic complexed Ge(II) dication²⁵ and may be a consequence of interactions between the $[\text{GaCl}_4]^-$ anion and the gallium(I) cation.

Preliminary reactivity studies of **1** revealed that the chemistry of the $[\text{GaCl}_4]^-$ anion obscured that of the $[\text{Ga}([\text{12}]\text{crown-4})]^+$ cation. For example, the reaction of **1** with tris(pentafluorophenyl)borane ($\text{B}(\text{C}_6\text{F}_5)_3$, BCF) appeared to give $[\text{Ga}([\text{12}]\text{crown-4})][\text{ClB}(\text{C}_6\text{F}_5)_3]$, where the strongly Lewis acidic borane abstracted a chloride anion from the tetrachlorogallate anion. An attempt to oxidize the gallium(I) center of **1** using methyl iodide did not proceed as expected; halide scrambling in the $[\text{GaCl}_4]^-$ anion was detected by ESI-MS. As the anion was observed to mask the reactivity of the $[\text{Ga}([\text{12}]\text{crown-4})]^+$ cation, anion exchange reactions were explored to replace the reactive tetrachlorogallate with a less reactive anion.

The reaction of TMSOTf and **1** was performed; however, no reaction was observed at room temperature, as shown by ^{71}Ga NMR spectroscopy. When a mixture of excess TMSOTf and **1** was heated at 60 °C, the signal assigned to the $[\text{Ga}([\text{12}]\text{crown-4})]^+$ cation disappeared from the ^{71}Ga NMR spectrum; however, the signal for the $[\text{GaCl}_4]^-$ anion remained. Anion exchange reactions using simple ionic reagents such as NaBPh_4 and NMe_4BPh_4 were attempted, but mixtures of the $[\text{GaCl}_4]^-$ and $[\text{BPh}_4]^-$ anions were obtained in all reactions. Given the lack of success in exchanging the anion of **1**, anion exchange reactions of the $[\text{Ga}][\text{GaCl}_4]$ starting material were explored. The reaction of NaBPh_4 with $[\text{Ga}][\text{GaCl}_4]$ resulted in the formation of crystals of $\text{Na}[\text{GaCl}_3\text{Ph}]$ (**2**) (Figure S16). BPh_3 was detected as a byproduct in the ^{11}B NMR spectrum of the crude reaction mixture. The mechanism for the formation of $\text{Na}[\text{GaCl}_3\text{Ph}]$ is unknown, but a modified Wheland intermediate is postulated to form, giving the free borane and **2**.

Silylium cations ($[\text{R}_3\text{Si}]^+$) have been known for several decades²⁶ and have been used as halide abstraction agents for main group halides.²⁷ Thus, the reaction of **1** with $[(\text{Et}_3\text{Si})_2(\mu\text{-H})][\text{B}(\text{C}_6\text{F}_5)_4]$ ²⁸ was performed in fluorobenzene. A white precipitate was observed within minutes and examined using

multinuclear NMR spectroscopy, ESI-MS, and X-ray crystallography following isolation. The ^1H NMR spectrum of the solid in CD_3CN revealed a singlet with a chemical shift at 3.85 ppm similar to that of **1** (3.82 ppm). A signal assigned to the $[\text{GaCl}_4]^-$ anion was not observed in the ^{71}Ga NMR spectrum of the product. A signal which could be assigned to the gallium(I) cation was also not observed in the ^{71}Ga NMR spectrum of the product; however, the relaxation rates of ^{71}Ga nuclei are often fast which leads to significant broadening of the signals. The ESI mass spectrum of the solid indicated that the $[\text{Ga}(\text{[12]crown-4})]^+$ cation was present, as a signal with a mass to charge ratio of 245 was observed. Furthermore, a signal in the negative ion ESI mass spectrum corresponding to $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (m/z 678) was observed. This allowed for the assignment of the product as $[\text{Ga}(\text{[12]crown-4})][\text{B}(\text{C}_6\text{F}_5)_4]$ (**3**); the formulation of the salt was confirmed using X-ray crystallography (Figure 2). We propose that the mechanism of

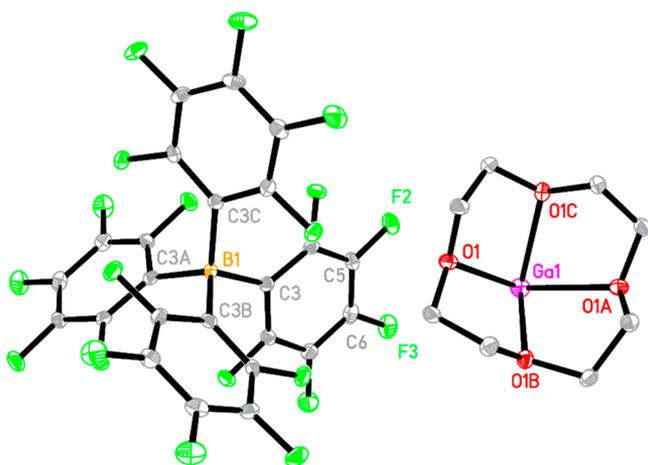
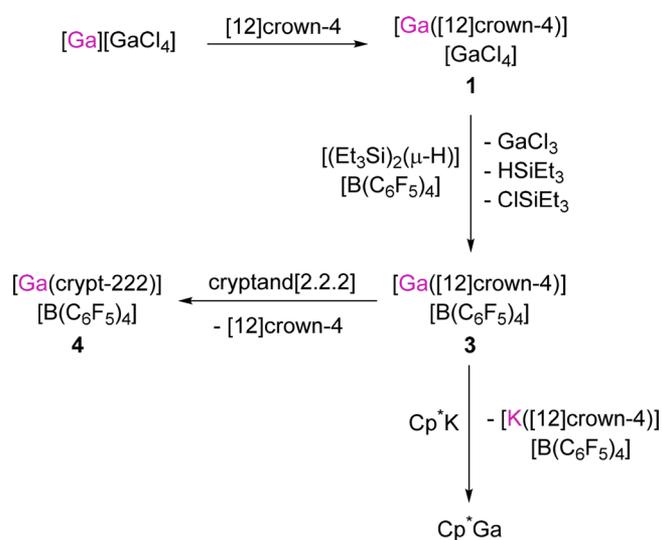


Figure 2. Displacement ellipsoid plot of **3**. Ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths and angles (Å, deg): Ga1–O1 2.4122(9), B1–C3 1.6617(11), Ga1...F2 3.4923(8), Ga1...F3 3.8518(10), Ga1...C5 3.9747(11), Ga1...C6 4.1431(12); O1–Ga1–O1A 106.50(4), O1–Ga1–O1B 69.02(2). The crown ether sits on the 4 axis. The oxygen atoms are equivalent by symmetry, and the equivalent positions are given by $x, y, z; y, -x+1/2, z; -x+1/2, -y+1/2, z; -y+1/2, x, z$.

the transformation of **1** to **3** involves the abstraction of a chloride ligand by the $[(\text{Et}_3\text{Si})_2(\mu\text{-H})]^+$ cation from the tetrachlorogallate anion, giving 1 equiv of Et_3SiH , Et_3SiCl , and GaCl_3 , all of which are volatile or soluble in nonpolar organic solvents. This allows for the simple isolation and purification of the new salt, $[\text{Ga}(\text{[12]crown-4})][\text{B}(\text{C}_6\text{F}_5)_4]$, **3**, by removal of the volatiles under vacuum and trituration with nonpolar solvents (Scheme 1).

When comparing the structural metrics of **1** to those of **3**, several differences were noted. First, the gallium–oxygen bond lengths of **3** are comparable to the shortest Ga–O distances observed in **1** (**1**: 2.3599(11) Å–2.5041(13) Å; **3**: 2.4122(9) Å), suggesting that the gallium cation is closer to the center of the [12]crown-4 molecule in **3**. This is corroborated by the distance of the gallium center above the plane of the oxygen atoms, which is 1.4734(7) Å for **1** compared to 1.4433(10) Å for **3**. Despite the weakly coordinating nature of the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion in **3**, contacts between the gallium cation and F2, F3, C5, and C6 of the anion are observed in the solid state (Ga1–F2, 3.492 Å; Ga1–F3, 3.852 Å); however, the

Scheme 1. Reactivity of **1** and **3**



contacts are longer than the sum of the van der Waal's radii (Ga: 1.87; F: 1.47).²⁹

Complex **3** was characterized using X-ray photoelectron spectroscopy (XPS), and the data were compared to the data of related gallium complexes using a Wagner plot.^{21a} The portion of the plot containing electron-rich gallium complexes is in the upper right corner (gallium(I) compounds), whereas the bottom left portion is where electron-deficient compounds are found (gallium(III) complexes). The central area contains data of compounds of intermediate electron density (gallium(II) compounds). In the Wagner plot, the data for **3** are plotted along with compounds with an unambiguously assigned oxidation number representing the three possible oxidation numbers for gallium (Figure 3).

As shown in Figure 3, **3** is found in the region of the Wagner plot typical of gallium(III) compounds. Notably, $[\text{Ga}(\text{prismand})][\text{OTf}]$ is found in the same region. The donor strength of the neutral crown ether in **3** can be considered to

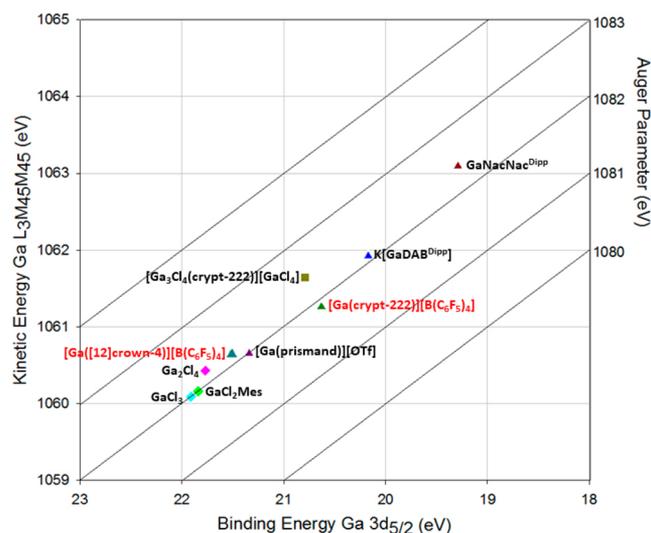


Figure 3. Wagner plot of representative Ga(I) (triangles), mixed valent Ga (squares), and Ga(III) (diamonds) compounds, $[\text{Ga}(\text{[12]crown-4})][\text{B}(\text{C}_6\text{F}_5)_4]$ (**3**), and $[\text{Ga}(\text{crypt-222})][\text{B}(\text{C}_6\text{F}_5)_4]$ (**4**). (DAB^{Dipp} = $[(\text{CH}_2)_2(\text{N}(\text{Dipp}))_2]^{2-}$; Dipp = 2,6-diisopropylphenyl).

be quite weak in comparison to covalently bound ligands in gallium(I) species such as in GaNacNac^{DIPP} (IV, Chart 1). In addition, **3** has a cationic gallium(I) center, further decreasing the electron density at gallium. While GaNacNac^{DIPP} is found in the electron-rich portion of the Wagner plot and has been used as a Lewis base, the gallium(I) cation of **3** may not react in a similar fashion, as its position on the Wagner plot indicates that its chemistry will be more similar to that of Lewis acidic gallium(III) compounds. Without these experimental data, it would be unclear as to the electronic nature of **3**; the use of XPS enables an understanding of the potential reactivity of **3**. Given the electron-deficient nature of **3**, its reactivity with donor molecules was explored.

Computational Analysis of [Ga([12]crown-4)]⁺. Computational analyses were performed to further assist in the understanding of the electronic structure of the [Ga([12]crown-4)]⁺ cation in **3**. The frontier molecular orbitals were calculated and visualized from a geometry-optimized structure of the cation. As shown in Figure 4, the HOMO of the cation

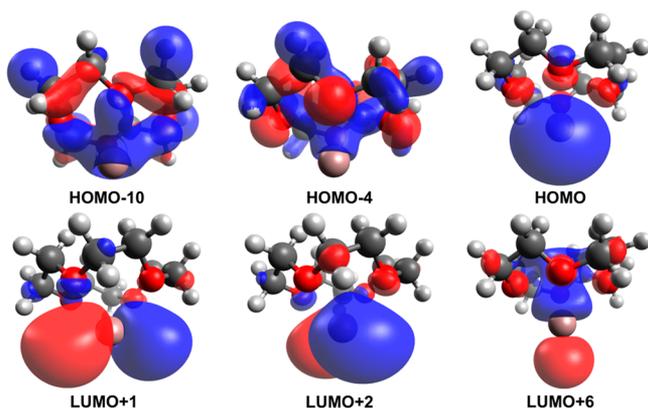


Figure 4. Calculated frontier molecular orbitals for [Ga([12]crown-4)]⁺ at the UM062X/6-311+G(2d,p) level of theory (isovalue = 0.03).

was found to correlate to the lone pair on gallium, and the LUMO+1 and LUMO+2 were found to correlate to the empty p orbitals on gallium. The bonding interactions between the oxygen atoms of the [12]crown-4 ligand and the gallium(I) cation were found to correspond to the HOMO–10 and HOMO–4, whereas the antibonding interaction was found to be the LUMO+6.

Natural bond orbital (NBO) calculations were performed to explore the Lewis structure of [Ga([12]crown-4)]⁺. The natural charge on the gallium(I) center was found to be 0.841, indicating that the +1 overall charge of the cation is primarily located at the gallium center with a small fraction of the charge located on the [12]crown-4 ligand (0.159). The Wiberg bond indices (WBIs) between the gallium and oxygen atoms were calculated and found to be small; each gallium–oxygen interaction had a WBI of 0.071, totalling to 0.284 for all four Ga–O bonds. The low bond order for the gallium–crown ether interaction reaffirms that the [12]crown-4 ligand offers weak stabilization to the gallium(I) cation and that the nature of the interaction between the gallium cation and the crown ether is mostly electrostatic. Examination of the orbitals in the NBO calculation reveals that the gallium–oxygen interactions are not classified as bonding; the lone pair on gallium has 97.6% s character. The weak interaction between the gallium and the crown ether involves a p type orbital at gallium. The

lone pairs on the oxygen atoms are not located in sp³ hybrid orbitals but rather in one sp² hybrid orbital and one p type orbital with 95.9% p character.

To complement the above analysis, time-dependent DFT (TD-DFT) calculations were conducted. The lowest energy excitations were found to exclusively arise from the lone pair of electrons on the gallium(I) cation, and the lowest allowed transition had an excitation energy of 6.10 eV (1 eV/molecule = 96.485 kJ/mol). The destination orbitals for the exciton were found to be one of the two empty p type orbitals on gallium with a probability of 95.2% for either the LUMO+1 or LUMO+2. Although lower energy electron excitations exist, they were found to be forbidden transitions. The lowest energy-allowed transition was significantly greater in energy than the excitation energies reported for gallium(I) complexes that undergo small molecule activation.³⁰ Thus, with both the computational and XPS data suggesting that the lone pair on the gallium center in [Ga([12]crown-4)]⁺ may not be able to undergo oxidative addition due to the contraction of the lone pair into an s type orbital and the large HOMO–LUMO+1 gap, the reactivity of **3** with Lewis bases and its potential use as a donor–solvent stable gallium(I) starting material were investigated.

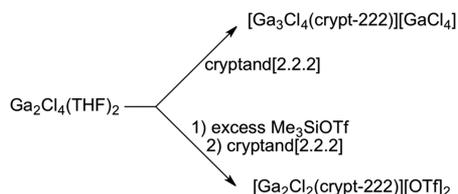
Reactivity of [Ga([12]crown-4)]B(C₆F₅)₄, **3.** Unlike “GaI” and [Ga][GaCl₄], **1** and **3** are stable in Et₂O, THF, and acetonitrile. In fact, **3** was found to have appreciable solubility only in acetonitrile. As such, it was envisioned that **3** could act as a donor–solvent stable source of gallium(I). Thus, we investigated the use of **3** to improve the synthesis of useful gallium(I) compounds and to generate gallium(I) complexes that could not be readily synthesized from “GaI” or [Ga][GaCl₄].

Cp*Ga is an important two electron ligand in transition metal chemistry and has been synthesized previously using three different methods: the metastable GaCl was reacted with Cp*Li at low temperature,³¹ “GaI” was reacted with Cp*K,³² or a gallium(III)–Cp* complex with halide ligands was synthesized and subsequently reduced to the gallium(I) species using potassium metal.³³ When **3** and Cp*K were combined in fluorobenzene at room temperature, the major product was identified as Cp*Ga in approximately a 6:1 ratio of Cp*Ga to an unknown Cp* species as determined by ¹H NMR spectroscopy (assuming that the unknown species has only one Cp* ligand). When the mixture was analyzed using ⁷¹Ga NMR spectroscopy, a signal was observed at –648 ppm, which is consistent with the ⁷¹Ga chemical shift reported for Cp*Ga (–653 ppm).³¹ Mass spectral data were also consistent with the formation of Cp*Ga; a signal at *m/z* 204 was observed in the mass spectrum, consistent with previous results.³¹ Thus, **3** is an effective starting material for the generation of Cp*Ga (Scheme 1). The yield of Cp*Ga was 83% as determined by ¹H NMR spectroscopy, using triethylsilane, HSiEt₃, as an internal standard which compares well to literature values (isolated yields of 52% and 70% have been reported^{32,33}). Cp*Ga was also isolated on a small scale, giving a yield of 73%, simply by removing insoluble byproducts by filtration in benzene. As the use of flammable alkali metals and a metastable gallium(I) reagents that must be used in a cooling bath are avoided using this method, the synthesis of known gallium(I) complexes including Cp*Ga using **3** demonstrates the potential for **3** to be used as a well-defined gallium(I) source.

Previous attempts to synthesize a single gallium(I) cation encapsulated within cryptand[2.2.2], analogous to the

germanium(II) dication derivative,³⁴ failed. The reaction between Ga₂Cl₄ and cryptand[2.2.2] in toluene led to the formation of insoluble solids of variable composition. When “GaI” was used as a starting material, insoluble products were also formed. Products could only be isolated when Ga₂Cl₄(THF)₂¹⁴ was used as a starting material. In this case, mixed valent and gallium(II) species were obtained (Scheme 2).¹³

Scheme 2. Synthesis of Previously Reported Multinuclear Gallium Cations Stabilized by Cryptand[2.2.2]¹³



When cryptand[2.2.2] was added to **1**, the results of the experiments were not reproducible, most likely a consequence of the reactive [GaCl₄][−] anion in **1**. Therefore, reactions between **3**, with the less reactive B(C₆F₅)₄ counterion, and cryptand[2.2.2] in acetonitrile were attempted. Notably, the traditional gallium(I) starting materials, “GaI” and [Ga]-[GaCl₄], are not stable in acetonitrile. After removing the solvent from the reaction mixture and triturating the resultant solid, the product was identified as [Ga(crypt-222)][B(C₆F₅)₄], **4**, by NMR spectroscopy, ESI-MS, and X-ray crystallography (Scheme 1). The compound exhibited a signal in the ⁷¹Ga NMR spectrum at −600 ppm, consistent with the formation of a gallium(I) cation. The ⁷¹Ga chemical shift of **4** is similar to what was reported by Crossing for [Ga(arene)_x]⁺ cations,⁵ although shifted downfield by approximately 100 ppm. The crystal structure of **4** (Figure 5) was obtained, confirming the formula of the salt and the presence of a gallium(I) cation encapsulated within a molecule of cryptand[2.2.2].

Complex **4** crystallized in the P-1 space group with two formula units in the asymmetric unit. As a result, there is a

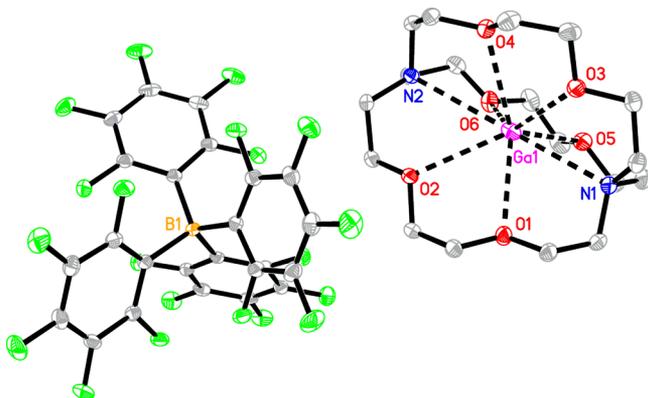


Figure 5. Displacement ellipsoid plot of **4**. Ellipsoids are drawn at the 50% probability level, and hydrogen atoms and the second formula unit are omitted for clarity. Selected bond lengths and angles (Å, deg): Ga1–N1 2.9218(14), Ga1–N2 3.1242(14), Ga1–O1 2.8418(15), Ga1–O2 2.9081(12), Ga1–O3 2.7709(14), Ga1–O4 2.9177(14), Ga1–O5 2.8037(14), Ga1–O6 2.8510(13); N1–Ga1–N2 179.53(3).

significant range observed for the Ga–N bond lengths (2.9218(14) to 3.1242(14) Å) and the Ga–O bond lengths (2.7709(14) to 2.9177(14) Å) in both [Ga(crypt-222)]⁺ cations in the asymmetric unit. The N–Ga–N bond angles were found to be approximately 180° (179.53(3)° and 178.70(3)°), and the gallium(I) cation is located approximately in the center of the macrocycle in both formula units.

As with **3**, the cation of **4** was analyzed computationally using a geometry-optimized structure of *D*₃ symmetry. The frontier molecular orbitals of the [Ga(crypt-222)]⁺ cation demonstrated that, analogous to [Ga([12]crown-4)]⁺, the HOMO is the gallium-centered lone pair. The HOMO–2 corresponds to a bonding interaction between the nitrogen atoms and the gallium center, and the HOMO–16 corresponds to a bonding interaction between the oxygen atoms and the gallium cation. The LUMO and LUMO+1 correspond to the empty p-type orbitals on gallium, although due to the three-dimensional stabilization imparted by the cryptand, they are distorted from idealized p orbitals (Figure 6). Similar p type orbitals are also observed for the LUMO+4

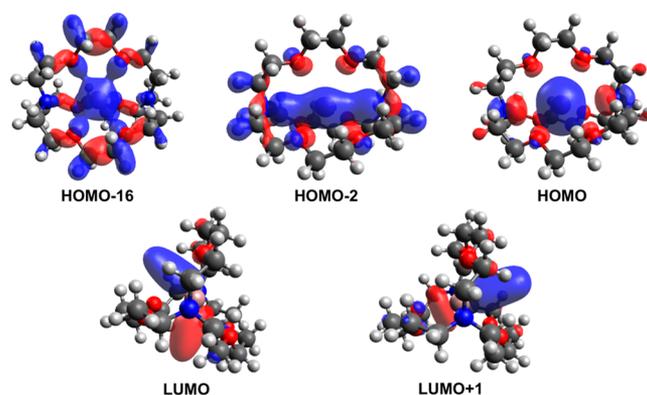


Figure 6. Calculated frontier molecular orbitals for [Ga(crypt-222)]⁺ at the UM062X/6-311+G(2d,p) level of theory (isovalue = 0.03).

and LUMO+5 orbitals. NBO calculations were performed on the [Ga(crypt-222)]⁺ cation, and the lone pair on the gallium center was located in an s orbital, with 100% s character. The lone pairs on the nitrogen atoms were primarily of p character, with 84.2% p and 15.7% s character. The oxygen atom lone pairs were similar in electronic structure to those in the cation of **3**, where one lone pair is located in an sp²-like orbital and another in a p orbital, with 57.8% and 99.8% p character for the two orbitals, respectively. The natural charge on the gallium(I) cation was found to be 0.666, which is slightly lower than the charge on the gallium(I) cation in [Ga([12]crown-4)]⁺ (0.841). This is expected with the greater number of donor atoms provided by the cryptand in comparison to [12]crown-4, lowering the charge localized on the gallium center. TD-DFT calculations demonstrated that, similar to [Ga([12]crown-4)]⁺, the lowest allowed electronic transition of the [Ga(crypt-222)]⁺ cation is from the HOMO to the LUMO or the LUMO+4, with the energy required for the transition being 5.41 eV. The calculated lowest energy transition of [Ga(crypt-222)]⁺ is approximately 0.7 eV lower in energy compared to that of [Ga([12]crown-4)]⁺ (6.10 eV), demonstrating that stronger electron donation from the ligand to the gallium(I) cation increases the potential for reactivity.

XPS data were obtained on compound **4** to compare the data to those of the starting material, **3**, as well as other

gallium-cryptand complexes (Table 1 and Figure 3). In comparing to the Ga 3d_{5/2} binding energy of the cryptand

Table 1. Summary of XPS Data for Representative Ga Complexes and 3 and 4^a

compound	Ga 3d _{5/2} (eV)	Ga 2p _{3/2} (eV)	Ga L ₃ M ₄₅ M ₄₅ (eV)	Auger parameter (eV)
GaNacNac ^{Dipp} , IV	19.29	1117.50	1063.09	1082.38
K[GaDAB ^{Dipp}]	20.17	1118.02	1061.92	1081.84
[Ga(prismand)] [OTf]	21.34	1119.31	1060.65	1081.99
[Ga ₃ Cl ₄ (crypt-222)] [GaCl ₄]	20.79	1118.51	1061.64	1082.43
GaCl ₃	21.91	1119.85	1060.09	1082.00
GaCl ₂ Mes	21.84	1120.10	1060.16	1082.00
Ga ₂ Cl ₄	21.77	1119.54	1060.43	1082.00
[Ga([12]crown-4)] [B(C ₆ F ₅) ₄], 3	21.51	1119.23	1060.64	1082.15
[Ga(crypt-222)] [B(C ₆ F ₅) ₄], 4	20.63	1118.49	1061.26	1081.89

^aThe Ga 3d_{5/2} and Ga 2p_{3/2} are photoelectron emissions and are expressed as binding energy; the Ga L₃M₄₅M₄₅ is an Auger emission and is expressed as kinetic energy. The Auger parameter is the sum of the Ga 3d_{5/2} and Ga L₃M₄₅M₄₅ energies.

complex 4 with that of the crown ether complex 3, the cryptand[2.2.2] complex possesses a gallium center with more electron density, as revealed by the decrease of approximately 1 eV in the Ga 3d_{5/2} binding energy, and a similar increase in the Ga L₃M₄₅M₄₅ Auger kinetic energy. The Ga 3d_{5/2} binding energy of 4 is also very close to what was observed previously for other gallium(II)-cryptand complexes,^{21a} again supporting the conclusion that cryptand[2.2.2] is a stronger donor toward the gallium(I) cation and the electronic nature of the gallium(I) cation 4 is more electron-rich than 3.

The addition of [15]crown-5 to [Ga][GaCl₄] was also examined. On the basis of ESI MS and ¹H NMR spectroscopic analysis, a mixture of three products was consistently obtained (ratio 1:0.14:0.08 assuming one crown ether for each complex). The products were separated with considerable effort by fractional crystallization; however, only the minor products of the reaction could be crystallized and were identified by X-ray diffraction as [GaCl₂([15]crown-5)][GaCl₄] (6) and [Ga₂Cl₃([15]crown-5)(CH₃CN)][Ga₂Cl₆]_{0.5} (7) (see the Supporting Information). The structure of [Ga₂Cl₃([15]crown-5)(CH₃CN)][Ga₂Cl₆]_{0.5} is interesting in that it is a rare example of a Ga(I) cation acting as both a Lewis acid and a Lewis base. The major product of the reaction is tentatively identified, on the basis of ¹H and ⁷¹Ga NMR spectroscopy and ESI mass spectrometry, as [Ga([15]crown-5)][GaCl₄]. Due to the difficult separation procedure, the reactivity of this system was not explored further.

CONCLUSIONS

Herein, we report the use of a commercially available ligand, [12]crown-4, for the facile complexation of gallium(I) cations from [Ga][GaCl₄]. Comproportionation, a common decomposition reaction for [Ga][GaCl₄], did not occur, allowing for the isolation of [Ga([12]crown-4)][GaCl₄], 1. 1 is a gallium(I) complex which is stable toward donor solvents. The subsequent anion exchange reaction of 1 with [(Et₃Si)₂(μ-H)][B(C₆F₅)₄] allowed for the removal of the reactive [GaCl₄]⁻ anion, to give 3. The chemical state of 3, as revealed

by XPS, indicated the Lewis acidic nature of the cation, which was corroborated by computational analysis. The synthesis of Cp*Ga and 4 from 3 demonstrates how 3 may be utilized as a gallium(I) starting material that does not decompose or undergo disproportionation upon exposure to donor solvents and the ability of 3 to act as a versatile gallium(I) source that can complement the existing starting materials for gallium(I) chemistry.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c01801>.

General experimental details, descriptions of experiments, NMR spectra of compounds 1, 3, and 4, X-ray crystallographic details for all, thermal ellipsoid plots of 2, 6, and 7, computational details, and Cartesian coordinates of calculated compounds (PDF)

Accession Codes

CCDC 1947855–1947860 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

Kim M. Baines – Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7; orcid.org/0000-0001-6515-5749; Email: kbaines2@uwo.ca

Authors

Jeremy L. Bourque – Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7
 Robert A. Nanni – Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7
 Mark C. Biesinger – Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7; Surface Science Western, University of Western Ontario, London, Ontario, Canada N6G 0J3

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c01801>

Author Contributions

J.L.B. and R.A.N. performed all the experimental work. J.L.B. performed the computations. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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