Beyond Oxidation States: Distinguishing Chemical States of Gallium in Compounds with Multiple Gallium Centers

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ABSTRACT: The electronic structures of a series of gallium complexes are examined using X-ray absorption spectroscopy (XAS) in combination with ab initio calculations. The chemical states of Ga are strongly affected by the ligands and the bonding environment. For complexes containing multiple gallium sites, we demonstrate that XAS can identify the chemical state of each unique gallium center. A reliable understanding of the chemical nature of the core element in a coordination complex with strong core–ligand interaction can be obtained only when both experimental and theoretical approaches are combined.

INTRODUCTION

Characterizing the chemical state of a coordination complex greatly facilitates predictions of reactivity. Despite this, direct experimental measurements of the chemical state of an element are not routinely performed on coordination complexes; rather, the reactivity is predicted using valence number (the number of electrons involved in bonding) or the oxidation number (obtained by heterolytically cleaving all bonds to the atom of interest and giving the electrons to the atom with the higher electronegativity, followed by counting the number of remaining electrons) of the element of interest. Although these formalisms are widely used in coordination complexes with multiple core elements and in cases in which interatomic charge transfer between the elements is possible, the assignment of valence or oxidation numbers can be ambiguous. A case in point is gallium, in which the assigned oxidation and/or valence numbers can be uncertain. The task becomes increasingly complicated if a complex contains more than one gallium center and more important as the role of gallium complexes in small molecule activation and catalysis develops. Thus, it is desirable to establish a measure of the chemical state of gallium in a complex that can be obtained experimentally and will provide accurate insights into the reactivity.

Solid-state nuclear magnetic resonance (SSNMR) spectroscopy is one tool that has been utilized to probe the nature of the element of interest in a wide range of compounds with quadrupolar nuclei. SSNMR parameters provide useful information about the oxidation number and the coordination environment at the element of interest. SSNMR spectroscopy has been successfully applied to the study of fundamentally important gallium halides and has been used to characterize the two unique gallium centers in Ga[GaCl₄]₉,10 to characterize the metal–metal bonds in Ga₂Cl₄L₂ (L = ligand),11 and to assess the composition of “GaI”, which contains gallium in multiple environments and assigned oxidation numbers.12,13 While SSNMR is becoming an increasingly popular tool for obtaining oxidation states of coordination compounds, techniques that provide direct insight into the valency of the element of interest are desired.

The reactivity of a core element in a complex is directly dependent on the electron density in the HOMO and the LUMO. A direct measurement of the electron density using, for example, X-ray photoelectron spectroscopy (XPS) or X-ray absorption spectroscopy (XAS) provides deep insights into the chemical state of the element in a compound. Recently, XPS has been employed to study the chemical states of molecular Ga compounds.14 Changes in Ga electron density are measured by the degree of shift in the core electron binding energy, e.g., Ga 3d and Ga 2p. In combination with the core levels of Ga as well as the LMM Auger profile [“LMM” denotes the Auger transition using typical X-ray notation; i.e., L represents the core level hole, the first M represents the relaxing electron’s initial state, and the second M represents the emitted electron’s initial state (details can be found in ref 14)], the chemical states of a series of molecular Ga compounds were identified using chemical speciation or Wagner plots. XPS is a straightforward, readily accessible technique that can be used to assess the Ga
chemical state for compounds possessing single Ga centers. For multivalent Ga complexes, the technique lacks the resolution to distinguish between different Ga environments because of the instrumental resolution limit. In addition, XPS probes shifts in the core level electron binding energy, and this is only indirectly related to the change in the valency of the element.

Alternatively, XAS is a nondestructive, direct probe of the electron density of unoccupied states. During an XAS measurement, a core electron of Ga is excited to a previously unoccupied electronic state. The spectral profile is dependent on the binding energy of the core electron, as well as the energy and density of the unoccupied molecular orbitals local to the absorption site. In addition, the theory of XAS is reasonably well-established, and experimental XAS can be rationalized using theoretical models that are readily available, such as FEFF, StoBe, or FDMNES. Although XAS is widely applied to solid-state materials, the use of XAS to study the chemical nature of organometallic or coordination compounds remains unexplored. However, this valuable technique can provide information that other techniques cannot. For example, we have reported an XAS study on a series of Ge-based coordination complexes. By measurement of the XAS in combination with FEFF calculations, Ge compounds with assigned oxidation numbers of +2 and +4 can be distinguished, and the degree of ionicity of the compounds can be obtained. The preliminary study demonstrated the feasibility of XAS in analyzing the chemical nature of coordination compounds of main group elements with different oxidation numbers.

In this work, Ga K-edge XAS was performed to examine the chemical states of several Ga complexes, from relatively common compounds such as Ga[GaCl₄] and Ga₂Cl₄(1,4-dioxane)₂ to novel macrocycle-stabilized Ga complexes such as [Ga(prismand)][GaCl₄], [Ga₂Cl₂(crypt-222)][OTf]₂, and [Ga₃Cl₄(crypt-222)][GaCl₄]. The structures of these compounds are shown in Figure 1. All Ga complexes investigated here contain more than one Ga center in their structures. In a K-edge XAS spectrum, the 1s electron of Ga is excited to a previously unoccupied electronic state of p symmetry. Ab initio calculations utilizing FDMNES and SIESTA code were performed to rationalize the experimental results with a qualitative analysis of the charge density at each Ga site in the compounds.

### EXPERIMENTAL SECTION

All Ga complexes were synthesized according to previously published protocols, and their chemical and crystal structures were confirmed using NMR and single-crystal X-ray diffraction (XRD). XAS experiments were performed at beamline BL01C1 at the National Synchrotron Radiation Research Centre (NSRRC) of Taiwan and at the hard X-ray microanalysis beamline (HXMA, BL01ID-1) of the Canadian Light Source. The samples were pressed into thin pellets and sealed with Kapton tape. To minimize degradation, the samples were prepared inside a N₂-filled glovebox and transferred under N₂ to the synchrotron facility. XAS spectra were recorded by positioning the sample under the incident X-ray beam. As the X-ray energy was gradually tuned across the Ga K edge, the incident photon intensity (I₀) was recorded using an ion chamber that was placed in front of the sample, and the emitted X-ray fluorescence from the sample was collected using a multielement Ge detector. For each sample, multiple scans were conducted on multiple spots to check for beam damage. No obvious spectral profile change was observed during the measurements. All spectra are normalized to incident photon intensity I₀.

The experimental XAS spectra were compared with those calculated using the FDMNES code. The experimental single-crystal XRD data of the compounds and the highly accurate finite difference method (FDM) were used to calculate the XAS spectra near the absorption edge. Calculations of the spectra far above the edge were performed using the computationally inexpensive Green’s function method. The switch between the two computational methods occurred somewhere between 25 and 35 eV above the absorption edge, at a point where both methods produced the same result, within the expected error.

The net electric charge of the Ga sites was calculated using density functional theory (DFT) with the SIESTA code based on the empirical crystal structures. Ultrasoft norm-conserving pseudopotentials, double-ζ basis sets with polarization orbitals, the Perdew–Burke–Emzerhof exchange-correlation functional, and the basis-set-independent Voronoi method were utilized for the determination of atomic charges.

### RESULTS AND DISCUSSION

We first focus our discussion on the complexes possessing two Ga centers with different oxidation numbers [Ga(I) and Ga(III)], namely, [Ga(prismand)][GaCl₄] and Ga[GaCl₄]. The XAS spectrum of [Ga(prismand)][GaCl₄] contains two sharp peaks (labeled A and B, indicated with vertical dashed lines in Figure 2) at 10369 and 10372 eV, respectively, which can be attributed to different Ga centers exhibiting distinct chemical states. The energy position of peak B is the same as that of ionic compound Na[GaCl₄] (Figure 2), which allows the assignment of peak B in the XAS spectrum of [Ga(prismand)][GaCl₄] to the tetrachlorogallate anion. Peak A, on the other hand, appears at a lower energy, indicating the Ga center at that site has a higher electron density (i.e., a lower

![Figure 1. Chemical structures of the Ga complexes.](image)

![Figure 2. Ga K-edge XAS spectra of [Ga(prismand)][GaCl₄] and Ga[GaCl₄] in comparison with that of Na[GaCl₄].](image)
tetrachlorogallate anion demonstrate that the XAS spectral features are dominated by the short-range chemical environment; because the tetrachlorogallate sites in Ga[GaCl₄] and [Ga(prismand)][GaCl₄], as well as that of the simple salt, NaGaCl₄, exhibit only minor differences because of the different cations [Ga⁺, Na⁺, or [Ga(prismand)]⁺], these minor differences mostly occur well above the absorption edge (i.e., above 10375 eV). More importantly, the calculated position of peak A in [Ga(prismand)][GaCl₄] appears at an energy slightly lower than the corresponding peak for Ga[GaCl₄], and the intensity of peak A in [Ga(prismand)][GaCl₄] relative to the intensity of peak B is noticeably greater compared to the intensities of the analogous peaks in Ga[GaCl₄].

X-ray absorption spectra, measured in fluorescence mode, often suffer from self-absorption, wherein X-rays emitted during the absorption process are re-absorbed by the sample and do not reach the fluorescence detector. A few strategies have been suggested to correct for self-absorption; however, removing the influence of self-absorption from a measured spectrum without introducing artifacts is very challenging. In our case, Ga is the only heavy element present, and the background absorption from the other light elements is approximately constant throughout the Ga K-edge measurement range employed. In this situation, the full expression for self-absorption, which is complicated, can be reduced to that shown in eq 1.

$$I(E) = \frac{A \mu_{Ga}(E)}{\mu_{Ga}(E) + B}$$

where $\mu_{Ga}(E)$ is the true absorption of Ga at excitation energy $E$, $I(E)$ is the measured absorption intensity at excitation energy $E$, $A$ is the product of the fluorescence rate for Ga K-edge emission, as well as various experimental factors such as detector efficiency, and $B$ is the sum of the background absorption from the other elements and the total absorption at the fluorescence energy, $E_F$. Despite the simple form of eq 1, it is difficult to invert this equation to obtain $\mu_{Ga}(E)$ because some situations will result in division by values close to zero. Instead, linear fitting with the measured spectrum was employed to determine values of $A$ and $B$ that result in a “calculated with self-absorption” spectrum based on $\mu_{Ga}(E)$ obtained from FDMNES (the calculated spectrum). The resulting calculated spectra with and without self-absorption are shown along with the measured spectra in Figure 4. Self-absorption reduces the relative intensity of peak A relative to that of peak B in [Ga(prismand)][GaCl₄], resulting in a rather good agreement with the measured XAS spectrum. However, self-absorption alone does not sufficiently decrease the intensity of peak A relative to that of peak B in Ga[GaCl₄], unless the ratio of cationic to anionic Ga (nominally 1:1) is reduced to 1:3. Thus, for the self-absorption-corrected spectrum, we show only that using a 1:3 ratio of cationic to anionic Ga for Ga[GaCl₄] in Figure 4.

Our interpretation of the XAS data of [Ga(prismand)][GaCl₄] and Ga[GaCl₄] is consistent with the previous XPS results, as it was postulated that although both [Ga(prismand)][GaCl₄] and Ga[GaCl₄] contain a gallium(I) center, the gallium(I) cations are not as rich in electrons as one would expect on the basis of the assigned oxidation number and the fact that the Ga(I) cation in Ga[GaCl₄] is more electron deficient than that in [Ga(prismand)][GaCl₄]. Therefore, the reduction of the Ga(I):Ga(III) ratio necessary for the calculated spectrum of Ga[GaCl₄] to match the measured one may in fact be a consequence of the relative electron deficiency, rather than the absence, of Ga(I) sites in comparison to Ga(III) sites. We then turn to examine the Ga complexes that contain two Ga centers of purportedly the same oxidation number and
similar coordination environments: \([ \text{Ga}_2\text{Cl}_4(\text{crypt-222})][\text{OTf}]_2\) and \([ \text{Ga}_2\text{Cl}_4(1,4\text{-dioxane})]_2\). Although the two gallium cores of \([ \text{Ga}_2\text{Cl}_4(\text{crypt-222})][\text{OTf}]_2\) are nonequivalent in the solid state, the local structures of the Ga atoms are identical, with the same bonding arrangement: each Ga is bonded to a nitrogen, chlorine, and a second Ga in a plane, with two oxygens in axial positions above and below the plane with only one being within bonding distance.\(^{19}\) Two crystal structures have been reported for \([ \text{Ga}_2\text{Cl}_4(1,4\text{-dioxane})]_2\),\(^{20,34}\) however, in our study, a new polymorph was obtained using modified recrystallization conditions.\(^{35}\) In the new polymorph, each gallium is pseudo-five-coordinate, being linked to a strongly bound 1,4-dioxane molecule, in addition to two chlorines and a gallium, and a more weakly bound bridging dioxane fragment. Thus, the pseudo-five-coordinate environment of the gallium centers in \([ \text{Ga}_2\text{Cl}_4(1,4\text{-dioxane})]_2\) is similar to the coordination environment of the Ga in \([ \text{Ga}_2\text{Cl}_4(\text{crypt-222})][\text{OTf}]_2\), with bond lengths to distal oxygen atoms of 2.631(1) and 2.424(2) Å, respectively, as shown in \textbf{Figure 5}.

\[
\text{Ga}_2\text{Cl}_4(\text{crypt-222}) \quad \text{Ga}_2\text{Cl}_4(1,4\text{-dioxane})_2
\]

\textbf{Figure 5}. Local structures of pseudo-five-coordinate Ga sites in \([ \text{Ga}_2\text{Cl}_4(\text{crypt-222})][\text{OTf}]_2\), (only the cation is shown; the OTf is omitted) and \([ \text{Ga}_2\text{Cl}_4(1,4\text{-dioxane})]_2\).

\[
\text{Ga}_2\text{Cl}_4(\text{crypt-222}) \quad \text{Ga}_2\text{Cl}_4(1,4\text{-dioxane})_2
\]

\textbf{Figure 6} shows the Ga K-edge XAS spectra of \([ \text{Ga}_2\text{Cl}_4(\text{crypt-222})][\text{OTf}]_2\) and \([ \text{Ga}_2\text{Cl}_4(1,4\text{-dioxane})]_2\). Both complexes exhibit a broad peak in their XAS spectra: \([ \text{Ga}_2\text{Cl}_4(1,4\text{-dioxane})]_2\) exhibits a low-energy shoulder, while \([ \text{Ga}_2\text{Cl}_4(\text{crypt-222})][\text{OTf}]_2\) exhibits a high-energy shoulder. Compared to the XAS spectrum of \([ \text{Ga}_2\text{Cl}_4]\) (in which a shoulder was related to a different Ga site), one might be tempted to attribute these features to multiple Ga sites. However, the calculated (FDMES) spectra reveal that this is not the case: calculated and experimental spectra all emphasize that a single Ga site, especially one in a covalent environment, can exhibit considerable fine structure in an XAS spectrum, rather than a single sharp spectral feature. The calculated XAS spectrum of \([ \text{Ga}_2\text{Cl}_4(\text{crypt-222})][\text{OTf}]_2\) is in good agreement with the measured spectrum, especially after simulating the effect of self-absorption in the calculated spectrum. The agreement for \([ \text{Ga}_2\text{Cl}_4(1,4\text{-dioxane})]_2\) is not as good, although the main features are present in both: a weak low-energy shoulder near 10370 eV, a main peak, and a weak high-energy shoulder above 10374 eV. The discrepancy observed between calculated and measured spectra occurs because \([ \text{Ga}_2\text{Cl}_4(1,4\text{-dioxane})]_2\) measured in this work has a high crystal symmetry (space group \(Pm\overline{3}m\)), with only one crystallographically unique Ga site.\(^{35}\) This is in contrast to \([ \text{Ga}_2\text{Cl}_4(\text{crypt-222})][\text{OTf}]_2\), in which the two Ga sites, while sharing the same local chemical environment, are crystallographically inequivalent because of a difference in long-range order. In practice, including these two almost identical Ga sites in the calculated XAS spectrum of \([ \text{Ga}_2\text{Cl}_4(\text{crypt-222})][\text{OTf}]_2\) produces a reasonable approximation of the anharmonic disorder, which is present in the measured spectrum. Because the approximation of anharmonic disorder is lacking in the calculated XAS spectrum for \([ \text{Ga}_2\text{Cl}_4(1,4\text{-dioxane})]_2\) features in this spectrum are visibly more narrow than those in the measured spectrum. Nevertheless, as noted above, the three main spectral features (low-energy shoulder, main peak, and high-energy shoulder) are present in both measured and calculated spectra.

It appears, however, that the main resonance of the cryptand complex, \([ \text{Ga}_2\text{Cl}_4(\text{crypt-222})][\text{OTf}]_2\), is located between the two peaks of either \([ \text{Ga}_2\text{Cl}_4]\) or \([ \text{Ga-(prismand)}][\text{GaCl}_4]\) \{the peak positions of \([ \text{Ga-(prismand)}][\text{GaCl}_4]\) are marked by lines A and B in \textbf{Figure 6}\}. Compared to the single Ga isolated in a prismatic cage, the chloride that is bonded to Ga in \([ \text{Ga}_2\text{Cl}_4(\text{crypt-222})][\text{OTf}]_2\) withdraws electron density from the Ga, making it less electron rich than the Ga(I) core in \([ \text{Ga-(prismand)}][\text{GaCl}_4]\) but not as electron deficient as the Ga core in \([ \text{GaCl}_4]\)^{−}, and thus, the main absorption appears at an energy between those that have been attributed to Ga(I) and Ga(III) and allows us to assign an oxidation number of Ga(II) to the gallium cores in the complex.

When the cryptand cage is replaced by the dioxane ligands, the main resonance further shifts to a higher energy. The trend is similar to our previous XPS observation, that the chemical state of the Ga in \([ \text{Ga}_2\text{Cl}_4(1,4\text{-dioxane})]_2\) is slightly more electron deficient than that of \([ \text{Ga}_2\text{Cl}_4(\text{crypt-222})][\text{OTf}]_2\).\(^{14}\) As is evident in the Ga K-edge XAS, the absorption for \([ \text{Ga}_2\text{Cl}_4(1,4\text{-dioxane})]_2\) shares the same energy onset as that of \([ \text{Ga}_2\text{Cl}_4(\text{crypt-222})][\text{OTf}]_2\), indicating the gallium in the dioxane complex has the same chemical state as in the cryptand complex and, thus, is a Ga(II) compound; differences at higher energies, including the energy of the maximal absorption feature, are due to a different distribution of unoccupied Ga states in the two compounds. With an additional electro-negative chloride ligand on the Ga core, the main absorption peak shifts to a higher energy. Furthermore, as is evident from the broadness of the signal, the interaction between the Ga core and the dioxane ligand is stronger than the interaction of Ga with the cryptand ligand. A recent study of the Ga-modified zeolites using Ga K-edge XAS revealed that the changes in the identity and number of Ga nearest neighbors can give rise to changes in XAS spectra that exhibit a similar trend caused by oxidation number variation, so that the commonly interpreted spectral evidence of reduction of Ga(III) to Ga(I) during catalysis is not always accurate.\(^{30}\) This again supports our hypothesis that predicting the chemical nature of the core...
element in a coordination complex using oxidation number formalism is not always reliable.

Lastly, we examine an interesting complex containing four unique gallium centers, [Ga3Cl4(crypt-222)][GaCl4]. Multiple bonding descriptions were proposed on the basis of calculations, some of which suggested the presence of a Ga(0) core within in the cryptand. Figure 7 shows the XAS spectrum of this compound. Again, the calculated XAS spectrum is in good agreement with our measurements; albeit, the calculations do predict a weak shoulder in the pre-edge (indicated by the arrow in Figure 7) that is not observed in our measurements. Because the predicted feature is at energies lower than the remaining features of the spectrum, it is tempting to ascribe this feature to a Ga(0) site. However, our measured spectrum suggests that the LUMO is at energies considerably smaller than the oxidation number, the Voronoi net charges are functional theory. Although the Voronoi net charges are much more localized than the atomic charge. The color of the data markers in panel b matches the calculated atomic charge. The color of the data markers in panel b matches the calculated atomic charge.

![Figure 7. Experimental and calculated Ga K-edge XAS spectra of [Ga3Cl4(crypt-222)][GaCl4] shown at the top. Below that, the calculated contribution from the sum of the Ga sites within the cryptand [labeled Ga3Cl4(crypt-222), solid orange line] is directly compared to the calculated spectrum of [Ga3Cl4(crypt-222)][OTf]4 (dotted brown line). Finally, the calculated spectrum from each Ga site in [Ga3Cl4(crypt-222)][GaCl4] is shown independently.](Image)

![Figure 8. (a) First derivatives of the measured Ga K-edge XAS spectra. The features that correlate with oxidation numbers are marked with asterisks. (b) Plot of the energies of these features (relative to the metallic Ga onset of 10367 eV) in comparison with the calculated atomic charge.](Image)
as Ga(I) in Ga[GaCl₄] has a relatively high Voronoi charge [similar to that of Ga(III)] and a high energy of the first-derivative maximum [similar to that of Ga(II)]. This further reinforces the fact that experimental and theoretical approaches should be combined when attempting to classify systems with significant core–ligand interaction.

## CONCLUSIONS

In conclusion, XAS is a facile, nondestructive spectroscopic technique that can be employed to investigate coordination complexes with multiple cores of the same element. When XAS measurements are supported by the appropriate calculations, or suitable reference spectra, in-depth analysis of the chemical environment of the cores can be performed. Macrocyclic ligands allow effective isolation of cationic Ga₃ as demonstrated by [Ga(prismand)][GaCl₄] and [Ga₂Cl₄(crypt-222)][OTf]₂.

The former clearly contains features of a mixed valent complex [Ga(II)/(III)], and the latter is assigned as a Ga(II) species. Our combined theoretical and experimental approach allows us to unambiguously determine the number of components present in XAS and to provide a qualitative assessment of the chemical state (oxidation number) of each Ga core, even for compounds that exhibit significant core–ligand interactions, such as Ga[GaCl₄] and Ga₂Cl₄(1,4-dioxane)₂, that frustrate their analysis by XPS. We have also found that cryptand-coordinated Ga sites in [Ga₂Cl₄(crypt-222)][GaCl₄] exhibit Ga(II)-like features. A comprehensive approach using XAS to investigate the chemical states of coordination complexes can also be easily extended to the study of a variety of inorganic coordination complexes and organometallic compounds to gain valuable insights into their reactivity.

## ASSOCIATED CONTENT

*Supporting Information*

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b03083.

Crystal structure of Ga₃Cl₄(1,4-dioxane)₂, detailed crystallographic data, and procedures for data collection and processing (PDF)

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The authors declare no competing financial interest.

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1. In this paper, we distinguish between oxidation numbers, assigned using the standard formalism, and chemical states, the experimentally determined physical state of an atom in a complex. We do not use the term oxidation state to avoid ambiguity.


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(35) Ga2Cl4(1,4-dioxane), was synthesized according to ref 20 and was recrystallized from a solution of toluene and 1,4-dioxane in a 3:1 ratio at −20 °C. Crystallographic data can be found in the Supporting Information.