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[GaX₂(dmpe)₂][GaX₄] (X = Cl, Br, I): A Synthetic, Solid State and Computational Study

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Abstract

Derivatives of [GaX₂(dmpe)₂][GaX₄] (X = Cl, Br, I) were prepared and characterized. The salts contain a cation involving two diphosphine ligands bound to GaX₂⁺, imposing a pseudo-octahedral geometry at gallium. A variety of possible structural alternatives for the equimolar combination of GaX₃ and dmpe have been computationally modelled and shown to be energetically similar to the observed cations, indicating potential fluxionality in the system and are in agreement with spectroscopic characterization.

Key words

synthesis, characterization, gallium, phosphine ligands, structure

Introduction

The coordination chemistry of the *p*-block elements is superficially developed in comparison to that of the transition metals. Bonding models for transition metal complexes invoke the use of *d*-orbitals, while the valence *d*-orbitals at *p*-block centres are considered to be too diffuse and too high in energy to allow for sufficient overlap with ligand orbitals. Consequently, bonding

environments for mono-, di-, tri- and tetra-coordinate *p*-block centres are adequately described using *s*- and *p*-orbitals. Nevertheless, hypervalent environments involving five and six electron pairs around the *p*-block centre are observed for many *p*-block elements, including examples of complexes involving L-type ligands. The chemistry of aluminum and gallium are most developed in this context,¹⁻⁵ and the presence of a cationic charge naturally enhances the Lewis acidity of the acceptor site, which we have exploited to realize examples of phosphine and pyridine complexes of pnictogen centres (Group 15) and tetrael centres (Group 14).⁶⁻⁹

While reports of solid state structures for phosphine complexes of gallium are relatively rare,¹⁰ Levason *et al.* revealed structural diversity for diphosphine complexes of gallium,⁵ including a neutral complex of a diphosphine ligand bound to two GaCl₃ acceptors **1**, an *o*-benzodiphosphine ligand chelating a GaCl₂⁺ acceptor **2** and two *o*-benzodiphosphine ligands chelating a GaX₂⁺ acceptor **3** to give a distorted octahedral environment for gallium. The observed structures have been rationalised on the basis of the electronic and steric features of the diphosphine ligand, and with the expectation that a four coordinate tetrahedral environment is favoured for gallium. We now report that reactions of gallium(III) halides with the prototypical ligand 1,2-bis(dimethylphosphino)ethane (dmpe) preferentially form derivatives of [GaX₂(dmpe)₂][GaX₄] (X = Cl, Br, I). The solid state structures of the [GaX₂(dmpe)₂]⁺ cations **4** are analogous to derivatives of **3**, despite the absence of a preorganized structure for chelation that is present in an *o*-benzodiphosphine ligand. Moreover, the [GaX₂(dmpe)₂]⁺ cations are analogous to the structures observed for the cation in [AlCl₂(dmpe)₂] **5** [AlCl₄].³ Spectroscopic and structural characterization of these complexes are reported together with computational insights into the structural preferences.

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Experimental

All reactions were carried out in a MBraun glove box under an N₂ atmosphere. Solvents were dried over CaH₂ or Na/Benzophenone and stored over 4 Å molecular sieves unless otherwise specified. Deuterated solvents were purchased from Aldrich and stored over molecular sieves for 24 hours prior to use. Anhydrous GaCl₃, GaBr₃, and GaI₃ were purchased from Sigma-Aldrich and used as received. 1,2-bis(dimethylphosphino)ethane (dmpe) was purchased from Strem Chemicals and used as received.

Solution ¹H, ¹³C, and ³¹P NMR spectra were collected at room temperature on a Bruker Avance 360 (8.4 T) and Bruker Avance 500 (11.7 T) NMR spectrometers. Chemical shifts are reported in ppm relative to trace protonated solvent (¹H), perdeuterated solvent (¹³C), or an external reference standard (³¹P, 85% H₃PO₄). NMR spectra of reaction mixtures were obtained by transferring an aliquot of the bulk solution to a 5 mm NMR tube, which was then capped and sealed with Teflon tape.

Infrared spectra were collected on samples using ATR using a Perkin-Elmer Frontier FT-IR spectrometer. Peaks are reported in wavenumbers (cm⁻¹) with intensities (strong, medium, weak) in parentheses, relative to the most intense peak. Melting points were obtained on samples sealed in glass capillaries under dry nitrogen using an Electrothermal apparatus. Elemental analyses were performed on selected compounds by Canadian Microanalytical Services Ltd., Delta, British Columbia, Canada.

Unless otherwise stated, crystals for single crystal X-ray diffraction studies were obtained by vapor diffusion at room temperature or from slow diffusion of a layered non-solvent into a saturated solution of the compound at -35°C. Single crystal X-ray diffraction data were collected on a Bruker D8/APEX II CCD diffractometer. All structures were solved by direct methods and

refined by full-matrix least squares on F^2 (*SHELXL-97 or SHELXL-2013*).¹¹ All non-hydrogen atoms were refined anisotropically while hydrogen atoms were assigned positions based on the sp^2 or sp^3 hybridization geometries of their attached carbons. Crystallographic information files have been deposited in the Cambridge Structural Database (CSD) with numbers 1500491 and 1500492 for $[\text{GaBr}_2(\text{dmpe})_2][\text{GaBr}_4]$ and $[\text{GaCl}_2(\text{dmpe})_2][\text{GaCl}_4]$ respectively.

Quantum chemical calculations were carried out using Gaussian 09. See Supporting Information for complete citation and coordinates of optimized geometries.

General Preparation of $[\text{GaX}_2(\text{dmpe})_2][\text{GaX}_4]$:

GaX_3 (1.00 mmol) was dissolved in CH_2Cl_2 (5 mL) to form a colourless solution. To this was added $\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2$ (dmpe) (167 μL , 1.00 mmol) which caused the immediate precipitation of a colourless solid. The reaction was stirred for 2 h at room temperature and the solid isolated by removal of the solvent under reduced pressure and washing with Et_2O . Colourless crystals suitable for structural analysis were obtained by layering 3 mL of a CH_2Cl_2 solution with 0.5 mL Et_2O and standing in a -35°C freezer.

X = Cl: Yield: 0.292 g (89%): ^1H NMR, ppm (CD_2Cl_2 , 295 K): δ = 1.40 (s, [24H], CH_3), 1.89 (s, [8H], CH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR, ppm (CD_2Cl_2 , 295 K): δ = -35.8 (br s). ^{13}C NMR, ppm (CD_2Cl_2 , 295 K): δ = 10.1 (s, CH_3), 21.8 (s, CH_2); IR ATR, cm^{-1} , (relative intensities): 2911 (w), 1418 (s), 1291 (m), 947 (s), 929 (s), 900 (m), 868 (m), 841 (m), 755 (m), 718 (m); Anal. Calc. for $\text{C}_{12}\text{H}_{32}\text{Ga}_2\text{Cl}_6\text{P}_4$ (%): C, 22.09; H, 4.94. Found for crystalline sample with yield of 0.091g: C, 21.83; H, 4.96.

X = Br: Yield: 0.405 g (88%). ^1H NMR, ppm (CD_2Cl_2 , 295 K): δ = 1.38 (s, [24H], CH_3), 1.89 (s, [8H], CH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR, ppm (CD_2Cl_2 , 295 K): δ = -39.4 (br s). ^{13}C NMR, ppm (CD_2Cl_2 , 295

K): $\delta = 10.0$ (s, CH₃), 21.6 (s, CH₂); IR ATR, cm⁻¹, (relative intensities): 2966 (w), 1416 (m), 1291 (w), 951 (s), 929 (s), 899 (w), 868 (s), 775 (w), 753 (w), 721 (w). Anal. Calcd. for C₁₂H₃₂Ga₂Br₆P₄ (%): C, 15.68; H, 3.51. Found for crystalline sample with yield of 0.154g: C, 15.48; H, 3.52.

X = I: Yield: 0.506 g (84%). ¹H NMR, ppm (CD₂Cl₂, 295 K): $\delta = 1.33$ (s, [24H], CH₃), 1.91 (s, [8H], CH₂). ³¹P{¹H} NMR, ppm (CD₂Cl₂, 295 K): $\delta = -41.5$ (br s). ¹³C NMR, ppm (CD₂Cl₂, 295 K): $\delta = 9.2$ (s, CH₃), 21.3 (s, CH₂); IR, ATR, cm⁻¹, (relative intensities): 2961 (m), 2880 (m), 1403 (m), 1291 (s), 1230 (w), 1123 (w) 951 (s), 908 (s), 866 (s), 770 (m).

Results

Treatment of GaCl₃, GaBr₃ or GaI₃ with 1 equiv. of 1,2-*bis*(dimethylphosphino)ethane (dmpe) in CH₂Cl₂ at ambient temperature over 1 h led to the formation of colourless precipitates in high yields (**Scheme 1**). The solids have been characterized as the salts [GaX₂(dmpe)₂][GaX₄]. The ³¹P NMR signal for each complex (X = Cl, -36.2 ppm; X = Br, -39.4 ppm; X = I, -41.0 ppm) appears as a sharp, well resolved singlet as the only signal, shifted downfield relative to the free ligand (-49 ppm). The chloride derivative is the most downfield-shifted, and the iodide derivative is least shifted, consistent with the relative electronegativities of the halogens. The ¹H NMR spectra exhibit only slight downfield shifts (1.78 ppm and 3.23 ppm), for the methyl and methylene protons respectively, relative to the free ligand (1.43 and 3.02 ppm).

Scheme 1: Synthesis of [GaX₂(dmpe)₂][GaX₄] ionic salts.

The chloride and bromide derivatives crystallize in the *Pbca* and *P-1* space groups, respectively. In the solid state, the cations $[\text{GaCl}_2(\text{dmpe})_2]^+$ and $[\text{GaBr}_2(\text{dmpe})_2]^+$ (Figure 1) show the gallium centre adopting a distorted octahedral geometry with the halogen atoms adopting a *trans*-configuration. The cations are structurally analogous to the previously reported **3**⁵ and **5**.³ For $[\text{GaCl}_2(\text{dmpe})_2][\text{GaCl}_4]$, the Ga1-Cl bond lengths range between 2.369(1) Å and 2.393(1) Å, which are greater than the sum of the covalent radii for Ga and Cl ($\Sigma_{\text{CR}} = 2.23$ Å). In the cation of $[\text{GaBr}_2(\text{dmpe})_2][\text{GaBr}_4]$, Ga1-Br1 [2.6249(4) Å] and Ga1-Br2 [2.4896(5) Å] are much longer than the sum of the covalent radii (Ga-Br $\Sigma_{\text{CR}} = 2.38$ Å), likely due to the lower electrophilicity at gallium compared to that in the chloride derivative. The Ga1-P bonds range from 2.467(1) Å to 2.516(1) Å for $[\text{GaCl}_2(\text{dmpe})_2][\text{GaCl}_4]$ for the two molecules in the unit cell, and range from 2.4872(8) Å to 2.5206(9) Å for $[\text{GaBr}_2(\text{dmpe})_2][\text{GaBr}_4]$, all of which are longer than the sum of the covalent radii (Ga-P $\Sigma_{\text{CR}} = 2.35$ Å), which is rationalized by the *trans*-influence of the phosphine ligands.¹² The shortest cation-anion contact in either complex is a H---X interaction of 2.873 Å, indicating the complex is best described as a tetraphosphine complex of a GaX_2^+ cation with a GaX_4^- counteranion. Similar structural features are present in $[\text{GaI}_2(\text{dmpe})_2][\text{GaI}_4]$, although the data was insufficient to provide for reliable bond length analysis.

Figure 1: Structural views of the cations in $[\text{GaX}_2(\text{dmpe})_2][\text{GaX}_4]$ ($\text{X} = \text{Cl}, \text{Br}$) in the solid state.

DFT calculations at the PBE/PBE/6-311g+(d,p) level of theory provide optimized geometrical parameters for the cations in the gas phase that are in good agreement with those observed in the solid-state structures of $[\text{GaCl}_2(\text{dmpe})_2][\text{GaCl}_4]$ and $[\text{GaBr}_2(\text{dmpe})_2][\text{GaBr}_4]$ (Table 1). The calculated Ga-P bond lengths are, on average, 0.069 Å longer in the gas phase structures. This may be partially due to the long interior H---X contacts with the aliphatic backbone of dmpe in the solid state, which is not modelled in the gas phase. Images of the HOMO and LUMO of $[\text{GaBr}_2(\text{dmpe})_2]^+$ are presented in **Figure 2**. The HOMO is primarily based on the phosphorus centre, with major contribution from the now bonding orbital containing what were previously the lone pairs on the phosphorus atoms, and the LUMO is primarily gallium-based. Natural Bond Order (NBO) partial charges and Wiberg Bond Indices (WBI) computed for $[\text{GaCl}_2(\text{dmpe})_2]^+$ and $[\text{GaBr}_2(\text{dmpe})_2]^+$ are listed in **Table 2**. The partial positive charge located on gallium in the cation are small compared to that on the phosphorus centre, indicating significant delocalization of charge into the dmpe ligands. The chloride derivative has slightly more positive charge on gallium, rationalized by the higher negative charge located on the chlorine atoms in

[GaCl₂(dmpe)₂]⁺. In both cases, the WBIs show that the Ga-P bonding is essentially the same, and is significantly less than unity, implying some ionic character for the Ga-P bonds.

Table 1: Selected experimental solid-state and calculated gas-phase structural parameters for the cations in [GaCl₂(dmpe)₂][GaCl₄] and [GaBr₂(dmpe)₂][GaBr₄]

	[GaCl ₂ (dmpe) ₂][GaCl ₄]	[GaBr ₂ (dmpe) ₂][GaBr ₄]
Avg. Ga-P (Å)	2.489(1) [2.555]	2.5011(9) [2.553]
Avg. Ga-X in cation (Å)	2.385(1) [2.421]	2.5572(5) [2.601]
Avg. <i>cis</i> -P-Ga-P (°)	90.02(4) [90.0]	89.96(4) [90.1]
Avg. <i>trans</i> -P-Ga-P (°)	177.49(4) [180.0]	176.66(3) [177.8]
Avg. X-Ga-X in cation (°)	179.61(4) [180.0]	177.57(2) [179.8]

Figure 2: Gas-phase structures of the cations in $[\text{GaCl}_2(\text{dmpe})_2][\text{GaCl}_4]$ and $[\text{GaBr}_2(\text{dmpe})_2][\text{GaBr}_4]$, along with the HOMO (left) and LUMO (right) of $[\text{GaBr}_2(\text{dmpe})_2]^+$

Table 2: NBO partial charges and Wiberg Bond Indices for $[\text{GaX}_2(\text{dmpe})_2]^+$, X = Cl and Br.

	Charge (Ga)	Charge (P)	Charge (X)	WBI (P-Ga)
$[\text{GaCl}_2(\text{dmpe})_2]^+$	0.30	0.98	-0.53	0.56
$[\text{GaBr}_2(\text{dmpe})_2]^+$	0.19	0.98	-0.47	0.56

To assess the thermodynamic factors responsible for formation of $[\text{GaX}_2(\text{dmpe})_2][\text{GaX}_4]$ in the equimolar reactions of GaX_3 with dmpe, Born-Haber-Fajans cycles were constructed for both

$[\text{GaCl}_2(\text{dmpe})_2][\text{GaCl}_4]$ and $[\text{GaBr}_2(\text{dmpe})_2][\text{GaBr}_4]$ using experimentally measured enthalpies of vaporization¹³ (ΔH_{vap}) and sublimation^{14,15} (ΔH_{sub}), calculated ion affinities for GaX_3 , calculated Ga-P bond strengths in the cations, and lattice energies obtained through Volume-Based Thermodynamics¹⁶ calculations, as shown in **Figure 3**. The energy values labeled in **Figure 3** are listed in **Table 3**. Overall, the reactions are exothermic with $\Delta H_{\text{Rxn}} = -431 \text{ kJ mol}^{-1}$ and -376 kJ mol^{-1} for $[\text{GaCl}_2(\text{dmpe})_2][\text{GaCl}_4]$ and $[\text{GaBr}_2(\text{dmpe})_2][\text{GaBr}_4]$, respectively. These values rely heavily on the two largest exothermic components of the reactions, $\Delta H_{\text{Ga-P}}$ and ΔH_{Lat} . If phosphines with less σ -donor character are used, a smaller stabilization results from Ga-P bond formation. Additionally, due to the inverse proportionality of ΔH_{Lat} to the volume of the ions, those ligands which feature larger organic groups are expected to result in lower ΔH_{Lat} and may favor adduct formation. The large lattice energies are needed to overcome the substantial energy required for the ionization of GaX_3 to GaX_2^+ in the Born-Haber-Fajans cycle. This offers insight into the 1:2 reaction of GaX_3 with an *o*-benzodiphosphine in which significant heating was required to effect formation of salts.^{5,17}

Figure 3: Born-Haber-Fajans thermodynamic cycles for the formation of $[\text{GaCl}_2(\text{dmpe})_2][\text{GaCl}_4]$ and $[\text{GaBr}_2(\text{dmpe})_2][\text{GaBr}_4]$ from an equimolar combination of GaX_3 and dmpe .

Table 3: Thermodynamic values for Born-Haber-Fajans cycle in **Figure 3**, corrected using dichloromethane as solvent. All values are in kJ mol^{-1} .

	ΔH_{sub}	ΔH_{vap}	ΔH_{GaX_2}	ΔH_{GaX_4}	$\Delta H_{\text{Ga-P}}$	ΔH_{Latt}	ΔH_{Rxn}
X = Cl	87.1	53.1	351	-179	-514	-369	-431
X = Br	92.5	53.1	314	-152	-464	-366	-376

To provide further insight into the formation of structural alternatives, we have used DFT methods to calculate the reaction enthalpies for the gas phase formation of potential neutral outcomes from the equimolar combination of dmpe and GaX_3 listed in **Scheme 2**. **Scheme 2a** illustrates the coordination of one GaX_3 unit to one phosphorus centre of the dmpe ligand, **1b** illustrates the coordination of GaX_3 units to each of the phosphorus centre of one dmpe ligand and a free dmpe ligand, **1c** illustrates the bidentate coordination of one dmpe to one GaX_3 unit, and **1d** represents the title reaction to form the separated ion pair in the gas phase.

Scheme 2: Neutral outcomes for the equimolar reaction of GaX_3 with dmpe

Table 4: Calculated (solvent-uncorrected) enthalpies for the gas phase equimolar reaction of GaX_3 with dmpe to give the products presented in **Scheme 2**

ΔH_{rxn}	Scheme 2a	Scheme 2b	Scheme 2c	Scheme 2d
X = Cl	-285	-277	-256	-65
X = Br	-260	-253	-229	-35

Table 5: Calculated (solvent-corrected for CH_2Cl_2) enthalpies for the gas phase equimolar reaction of GaX_3 with dmpe to give the products presented in **Scheme 2**

ΔH_{rxn}	Scheme 2a	Scheme 2b	Scheme 2c	Scheme 2d
X = Cl	-317	-311	-314	-342
X = Br	-291	-281	-273	-301

Gas-phase calculations were carried out on both uncorrected gas-phase structures, as well as using the Polarizable Continuum Model (PCM) to account for the influence of dichloromethane solvent. To remain consistent and allow comparison between these methods, all energy values are reported as ΔH_{rxn} of equimolar combinations of the phosphine and gallium halide. In the uncorrected calculations, the formation of all neutral compounds is significantly more exothermic than the formation of the separated cation-anion pair in the gas phase. However, when correction to account for solvent influence, the formation of the separated cation-anion pair is more exothermic than both the solvent-uncorrected values, as well as all of the neutral adducts. Presumably, this is due to the ability of the polar CH_2Cl_2 to stabilize the separated cation-anion pair, and help to dissipate charge density from the cations. In both cases, the exothermicities for the formation of each of the neutral outcomes are similar and, unsurprisingly, do not vary to the same extent when solvent correction is introduced as there is a lessened need of charge dissipation. As the formation

of the neutral compounds are energetically similar to those of the ion pairs, there may be a fluxional nature to these compounds in solution. This is supported by the sharp singlets observed in the ^{31}P NMR, as opposed to the observation of $^{69/71}\text{Ga}$ - ^{31}P spin-spin coupling, indicating the system may be kinetically labile and may undergo exchange processes and/or isomerization. As such, we postulate that the formation of the ionic salts in solution is viable due to the charge dissipation offered by the polar CH_2Cl_2 solvent and their isolation in the condensed phase is made possible by the significantly exothermic lattice energy.

In conclusion, a series of gallium(III) salts with chelating dmpe ligands were prepared and characterized. The salts contain a cation involving two diphosphine ligands bound to GaX_2^+ ($\text{X} = \text{Cl}, \text{Br}$), which impose a pseudo-octahedral geometry at gallium. A variety of possible structural alternatives for the equimolar combination of GaX_3 and dmpe have been shown to be energetically viable through DFT calculations, and are all of similar energy, enabling formation of structural alternatives. Computational studies show that the polar solvent plays a crucial role in the formation of the complexes by dissipating charge. These compounds continue to support the emerging parallels between main group compounds and their transition metal counterparts, and exhibit structural diversity due to their ability to access energetically viable neutral and ionic compounds.

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