# A simple synthesis for donor-stabilized $Ga_2I_4$ and $Ga_3I_5$ species and the X-ray crystal structure of $Ga_3I_5·3PEt_3$

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**The reaction of 'GaI' synthesized by ultrasonic irradiation of gallium and diiodine in the presence of phosphanes leads to new gallium subhalides in which gallium–gallium bonds are involved.**

The molecular chemistry of the heavier low-valent group 13 elements has gained special interest during recent years.[1] One reason for this rapid development is the cryochemical preparation method in which the high-temperature molecules AlX and GaX (X = Cl, Br, I) are trapped in suitable cooled solvents.[2] By this method donor-stabilized $Al_4I_4$[2] and $Ga_8I_8$[3] compounds can be synthesized.

A much more convenient starting material for many low-valent gallium species is $Ga_2Cl_4$, which consists of $Ga^+GaCl_4^-$ ions in the solid[4] as well as in the molten state.[5] By addition of arenes a series of $Ga^+$–arene compounds with interesting Ga–$\pi$ interactions has been prepared.[6] On the other hand geniune gallium(II) species with Ga–Ga bonds are formed by addition of special donor compounds. $Ga_2Cl_4·2$dioxane[7] was the first prominent example which was followed by the analogous bromides and very recently by two examples of donor-stabilized $Ga_2I_4$ compounds.[3,8] Here we present a new route to low-valent donor-stabilized, gallium iodides, based on a method described by Green *et al.*, in which pale green 'GaI' is formed from a reaction of gallium with iodine in toluene under ultrasonic conditions at *ca.* 35 °C;[9] however, no definite species have, as yet, been isolated.

On treating 'GaI' in toluene with $PEt_3$ at −78 °C a yellow solution was obtained which exhibited $^{31}P$ NMR signals at $\delta$ −24 and −8 (doublet, triplet, coupling constants of 35 Hz) and a singlet at $\delta$ −20, which provides evidence for new molecular species.

The solid metallic residue was analyzed to be elemental gallium. This means that the soluble compound cannot be a pure GaI species since the amount of gallium and iodine was originally 1 : 1.

When the yellow solution was concentrated two new species could be isolated. The first was obtained as a white solid at −78 °C. The white powder can be recrystallized from toluene to provide colourless crystals. X-Ray analysis indicates the formation of $(GaI_2·PEt_3)_2$ **1**, the third example of donor-stabilized $Ga_2I_4$, $Ga_2I_4·2AsEt_3$ **2**[8] and $Ga_2I_4·2NEt_3$ **3**[3] having been characterized very recently.

These iodides exhibit the expected structure with tetrahedrally coordinated gallium atoms and gallium–gallium bonds, Fig. 1.

The gallium–gallium distances are nearly identical for **1** [243.6(2) pm] and **2** [242.8(2) pm] but are shorter than in **3** [249.8(7) pm]. These changes in bond length may be explained with a decrease of donor strength in the series $NEt_3 \rightarrow PEt_3 \rightarrow AsEt_3$. This interpretation is based on an increase of the I–Ga–I bond angle in the same direction [**3**, 101.83(5)°, **1** 107.64(4)°; **2**, 109.0(1)°], which demonstrates that a weaker donor bond is in line with a more $sp^2$-like geometry at the Ga atom.[10]

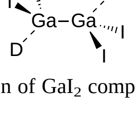


**Fig. 1** Schematic presentation of $GaI_2$ compounds (D = donor group)

However, steric interaction may also influence the Ga–Ga distance since $Ga_2I_4·2PPh_3$ **4**, which has been synthesized by ultrasonic treatment of 'GaI' with $PPh_3$ exhibits a Ga–Ga distance of 244.4(2) pm.

The second compound isolated from the yellow solution is $Ga_3I_5·3PEt_3$ **5** and its molecular structure is shown in Fig. 2. It is the first neutral compound containing a $Ga_3$ unit (similar to $B_3F_5$[11]).

In **5** a $Ga^I$ centre is the bridging entity for two $Ga^{II}$ units with Ga–Ga distances of 245.1(1) and 246.0(1) pm. As expected, the Ga–I distances in the terminal $GaI_2$ units [261.0(1) pm], are shorter than for the central GaI [262.7(1) pm], a fact which is in line with the larger size of $Ga^I$ relative to $Ga^{II}$. The same argument is valid for the corresponding Ga–P distances: 242.7(3) and 240.5(3) pm. More unexpected are the $^{31}P$ NMR shifts in comparison with that of uncoordinated $PEt_3$ ($\delta$ −19). The shifts of the $PEt_3$ groups at the $Ga^{II}$ centers are observed at $\delta$ −24 and of $PEt_3$ at the central $Ga^I$ unit at $\delta$ −8. Owing to the more positively polarized P atom coordinated to $Ga^I$ ($\delta$ −8) and to a more tetrahedral like geometry at phosphorus [sum of C–P–C bond angles is 310.3(13)° cf. 320.5(7)° for terminally coordinated $PEt_3$ ligands] a stronger donor bonding from $PEt_3$ to $Ga^I$ than to $Ga^{II}$ is concluded.

The overall reaction pathway may be described by Scheme 1. This scheme demonstrates the easy synthesis of donor-

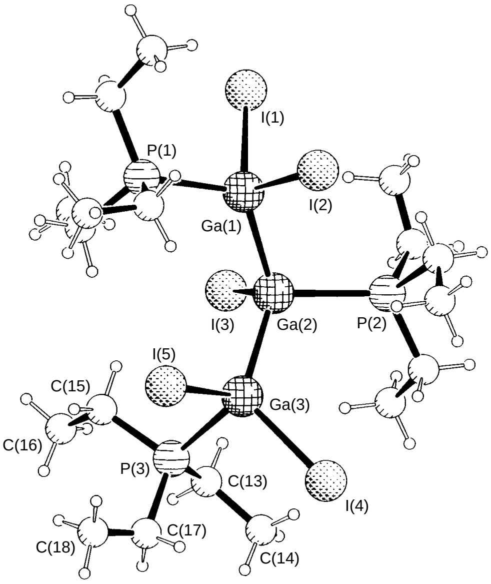
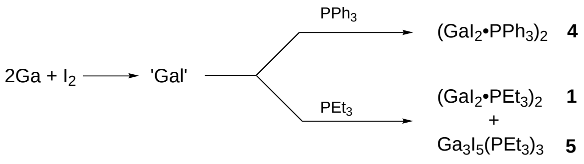


**Fig. 2** Perspective view of the molecular structure of $Ga_3I_5(PEt_3)_3$ **5**. Selected bond lengths (pm) and angles (°): Ga(1)–Ga(2) 245.1(1), Ga(2)–Ga(3) 246.0(1), Ga(1)–I(1) 260.1(1), Ga(2)–I(3) 262.7(1), Ga(3)–I(4) 260.8(1), Ga(1)–P(1) 240.4(3), Ga(2)–P(2) 242.7(3); Ga(1)–Ga(2)–Ga(3) 121.9(1), Ga(2)–Ga(1)–I(1) 117.76(5), Ga(2)–Ga(1)–I(2) 109.34(5), I(1)–Ga(1)–I(2) 107.23(5), P(1)–Ga(1)–Ga(2) 121.85(8), P(2)–Ga(2)–I(3) 98.76(8).



**Scheme 1** Overall reaction pathway

stabilized low-valent gallium iodides, although it does not explain the reaction pathway. However, the results presented here are a strong encouragement to apply this simple synthetic method, besides co-condensation techniques, in order to prepare uncoordinated gallium subhalides.

## Footnotes and References

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† $(GaI_2{\cdot}PPh_3)_2$ **4**: colourless crystals, *ca*. 30% yield, $^{31}P$ NMR: $\delta$ −18.23 (s). $(GaI_2{\cdot}PEt_3)_2$ **1**: colourless crystals, 22% yield, $^{31}P$ NMR: $\delta$ −20.09 (s). $Ga_3I_5(PEt_3)_3$ **5**: yellow crystals, 33% yield, $^{31}P$ NMR: $\delta$ −8.38 (t, *J* 35 Hz), −24.05 (d, *J* 35 Hz).

‡ *Crystal data*: STOE STADI IV diffractometer, Mo-K$\alpha$ radiation, $T$ = 200 K. All structures have been solved by direct methods and refined by full-matrix least squares on $F^2$. Programs used: SHELXL-93 and SHELXS.

$(GaI_2{\cdot}PEt_3)_2$ **1**: monoclinic, space group $P2_1/n$, $a$ = 10.034(2), $b$ = 11.857(2), $c$ = 10.763(2) Å, $\beta$ = 92.60(2)°, $U$ = 1279.2(4) Å$^3$, $Z$ = 4, $D_c$ = 2.293 g cm$^{-3}$, $\mu$ = 70.51 cm$^{-1}$, $F(000)$ = 812. The structure analysis was based on 4311 reflections ($2\theta_{max}$ 49.98°), observed 2044 [$F > 4\sigma(F)$], 94 parameters. Absorption correction (min., max. transmission 0.47, 0.73). Final residuals: $R$ = 0.068, $R_w$ = 0.180.

$(GaI_2{\cdot}PPh_3)_2$ **4**: monoclinic, space group $C2/c$, $a$ = 14.271(3), $b$ = 15.964(3), $c$ = 17.310(3) Å, $\beta$ = 95.16(3)°, $U$ = 3927.7(14) Å$^3$, $Z$ = 8, $D_c$ = 1.981 g cm$^{-3}$, $\mu$ = 46.21 cm$^{-1}$, $F(000)$ = 2200. The structure analysis was based on 4141 reflections ($2\theta_{max}$ 49.98°), observed 2187 [$F > 4\sigma(F)$], 199 parameters. Final residuals: $R$ = 0.038, $R_w$ = 0.081.

$Ga_3I_5(PEt_3)_3$ **5**: orthorhombic, space group $Pna2_1$, $a$ = 13.961(3), $b$ = 12.550(3), $c$ = 21.080(4) Å, $U$ = 3693.3(13) Å$^3$, $Z$ = 4, $D_c$ = 2.155 g cm$^{-3}$, $\mu$ = 64.89 cm$^{-1}$, $F(000)$ = 2224. The structure analysis was based on 6255 reflections ($2\theta_{max}$ 55.02°), observed 3728 [$F > 4\sigma(F)$], 264 parameters. Absorption correction (min., max. transmission 0.0125, 0.0517). Final residuals: $R$ = 0.036, $R_w$ = 0.074. CCDC 182/610.

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