

A simple synthesis for donor-stabilized Ga_2I_4 and Ga_3I_5 species and the X-ray crystal structure of $\text{Ga}_3\text{I}_5\cdot 3\text{PET}_3$

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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 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) are trapped in suitable cooled solvents.² By this method donor-stabilized $\text{Al}_4\text{I}_4^{2-}$ and $\text{Ga}_8\text{I}_8^{3-}$ compounds can be synthesized.

A much more convenient starting material for many low-valent gallium species is Ga_2Cl_4 , which consists of $\text{Ga}^+\text{GaCl}_4^-$ ions in the solid⁴ as well as in the molten state.⁵ By addition of arenes a series of Ga^+ -arene compounds with interesting $\text{Ga}-\pi$ interactions has been prepared.⁶ On the other hand genuine gallium(II) species with $\text{Ga}-\text{Ga}$ bonds are formed by addition of special donor compounds. $\text{Ga}_2\text{Cl}_4\cdot 2\text{dioxane}$ 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 $(\text{GaI}_2\cdot\text{PET}_3)_2$ **1**, the third example of donor-stabilized Ga_2I_4 , $\text{Ga}_2\text{I}_4\cdot 2\text{AsEt}_3$ **2**⁸ and $\text{Ga}_2\text{I}_4\cdot 2\text{NET}_3$ **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 $\text{NET}_3 \rightarrow \text{PET}_3 \rightarrow \text{AsEt}_3$. This interpretation is based on an increase of the $\text{I}-\text{Ga}-\text{I}$

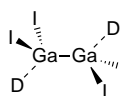


Fig. 1 Schematic presentation of GaI_2 compounds ($\text{D} = \text{donor group}$)

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

However, steric interaction may also influence the $\text{Ga}-\text{Ga}$ distance since $\text{Ga}_2\text{I}_4\cdot 2\text{PPh}_3$ **4**, which has been synthesized by ultrasonic treatment of 'GaI' with PPh_3 exhibits a $\text{Ga}-\text{Ga}$ distance of 244.4(2) pm.

The second compound isolated from the yellow solution is $\text{Ga}_3\text{I}_5\cdot 3\text{PET}_3$ **5** and its molecular structure is shown in Fig. 2. It is the first neutral compound containing a Ga_3 unit (similar to $\text{B}_3\text{F}_5^{11}$).

In **5** a Ga^{I} centre is the bridging entity for two Ga^{II} units with $\text{Ga}-\text{Ga}$ distances of 245.1(1) and 246.0(1) pm. As expected, the $\text{Ga}-\text{I}$ 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 $\text{Ga}-\text{P}$ 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 $\text{C}-\text{P}-\text{C}$ 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-

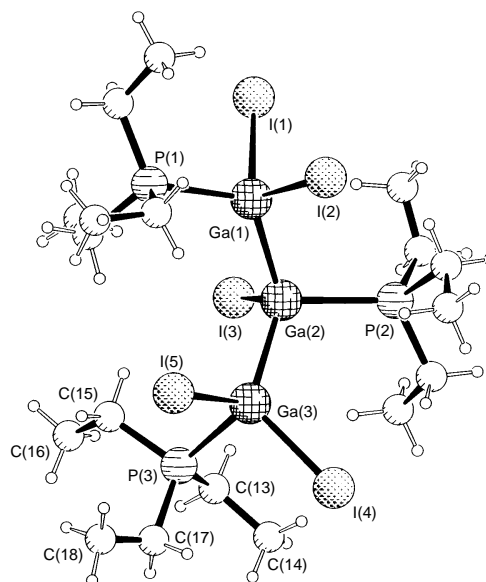
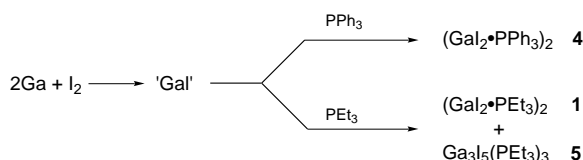


Fig. 2 Perspective view of the molecular structure of $\text{Ga}_3\text{I}_5(\text{PET}_3)_3$ **5**. Selected bond lengths (pm) and angles (°): $\text{Ga}(1)-\text{Ga}(2)$ 245.1(1), $\text{Ga}(2)-\text{Ga}(3)$ 246.0(1), $\text{Ga}(1)-\text{I}(1)$ 260.1(1), $\text{Ga}(2)-\text{I}(3)$ 262.7(1), $\text{Ga}(3)-\text{I}(4)$ 260.8(1), $\text{Ga}(1)-\text{P}(1)$ 240.4(3), $\text{Ga}(2)-\text{P}(2)$ 242.7(3); $\text{Ga}(1)-\text{Ga}(2)-\text{Ga}(3)$ 121.9(1), $\text{Ga}(2)-\text{Ga}(1)-\text{I}(1)$ 117.76(5), $\text{Ga}(2)-\text{Ga}(1)-\text{I}(2)$ 109.34(5), $\text{I}(1)-\text{Ga}(1)-\text{I}(2)$ 107.23(5), $\text{P}(1)-\text{Ga}(1)-\text{Ga}(2)$ 121.85(8), $\text{P}(2)-\text{Ga}(2)-\text{I}(3)$ 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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† $(\text{GaI}_2\bullet\text{PPh}_3)_2$ **4**: colourless crystals, ca. 30% yield, ^{31}P NMR: $\delta -18.23$ (s). $(\text{GaI}_2\bullet\text{PEt}_3)_2$ **1**: colourless crystals, 22% yield, ^{31}P NMR: $\delta -20.09$ (s). $\text{Ga}_3\text{I}_5(\text{PEt}_3)_3$ **5**: yellow crystals, 33% yield, ^{31}P NMR: $\delta -8.38$ (t, J 35 Hz), -24.05 (d, J 35 Hz).

‡ *Crystal data*: STOE STADIIV diffractometer, Mo-K α 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.

$(\text{GaI}_2\bullet\text{PEt}_3)_2$ **1**: monoclinic, space group $P2_1/n$, $a = 10.034(2)$, $b = 11.857(2)$, $c = 10.763(2)$ Å, $\beta = 92.60(2)^\circ$, $U = 1279.2(4)$ 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 ($2\theta_{\text{max}} 49.98^\circ$), observed 2044 [$F > 4\sigma(F)$], 94 parameters. Absorption correction (min., max. transmission 0.47, 0.73). Final residuals: $R = 0.068$, $R_w = 0.180$.

$(\text{GaI}_2\bullet\text{PPh}_3)_2$ **4**: monoclinic, space group $C2/c$, $a = 14.271(3)$, $b = 15.964(3)$, $c = 17.310(3)$ Å, $\beta = 95.16(3)^\circ$, $U = 3927.7(14)$ 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 ($2\theta_{\text{max}} 49.98^\circ$), observed 2187 [$F > 4\sigma(F)$], 199 parameters. Final residuals: $R = 0.038$, $R_w = 0.081$.

$\text{Ga}_3\text{I}_5(\text{PEt}_3)_3$ **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 ($2\theta_{\text{max}} 55.02^\circ$), 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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