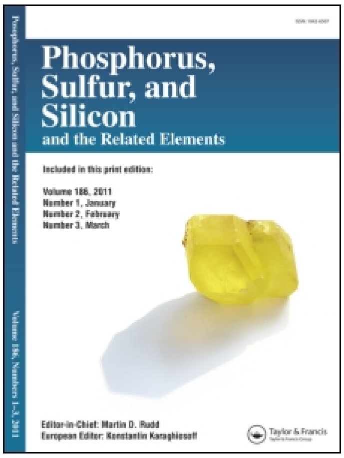

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RING MOLECULES BUILT FROM GAS-UNITS

Gerhard G. Hoffmann[a]
[a] Institut für Anorganische Chemie der Universität Würzburg Am Hubland, Würzburg, FRG

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RING MOLECULES BUILT FROM GaS-UNITS

GERHARD G. HOFFMANN

Institut für Anorganische Chemie der Universität Würzburg Am Hubland,
D-8700 Würzburg, FRG

Different synthetic routes are available for the formation of dihalogeno-(organylthio)gallanes. Some of the most important reactions leading to these compounds are reported.[1-4]

$$2GaI_3 + Me_2S_2 \rightarrow 2I_2Ga(SMe) + I_2 \qquad (1)$$

$$2RGaI_2 + Me_2S_2 \rightarrow I_2Ga(SMe) + I(R)Ga(SMe) + RI \qquad (2)$$

$$RGaHal_2 + R'SH \rightarrow Hal_2Ga(SR') + RH \qquad (3)$$

$$GaHal_3 + Me_3SiSR \rightarrow Hal_2Ga(SR) + Me_3SiHal \qquad (4)$$

Trivalent compounds of gallium are naturally Lewis acids; moreover, in organylthiogallanes a Lewis-base center exists on the sulfur atom. Therefore these molecules have the possibility of both intermolecular and intramolecular Lewis-acid-base interactions, which in the case of intermolecular interactions lead to Lewis-acid-base adducts. The thus formed adducts can be chains or rings of different sizes.

Diiodo(organylthio)gallanes are able to form monomers, dimers, and even trimers of different shapes. These differences in the structure are not only due to the group R on the sulfur atom, because investigations on these compounds in solution (molecular weight determinations, and ^{1}H-n.m.r. spectroscopy) and in the solid state (X-ray-structure determinations) have shown differences in the ring sizes for one and the same molecule as well.

Therefore some ^{1}H-n.m.r. spectroscopic investigations on $I_2Ga(SR)$ compounds ($R = CH_3$, C_2H_5, n-C_3H_7, i-C_3H_7, Ph) are presented and the crystal structures of both, $I_2Ga(SCH_3)$ and $I_2Ga(S\ i$-$C_3H_7)$ are discussed in view of some surprising differences in the structure of these two compounds.

If one reflects upon the chemistry of gallium from the point of view of sulfur chemistry, one will find a striking deficiency. Not much work has been done on this particular field till now. Therefore it is not surprising that there are only very few examples for compounds of gallium, containing an organic sulfur species.[1,2] Nevertheless, in the meantime some interesting and surprising results could be obtained, which are not only due to the fact that the chemistry of gallium is very different from the chemistry of its homologues over a wide range. This fact, however, justifies a special treatment of this element.

Some of the most important reactions, which lead to (organothio)gallanes are summarized below.

In general, the reactions between the gallium trihalides and trimethylsilyl sulfides should lead to all conceivable mono-, bis-, and tris(organylthio)gallanes[3,4] and the corresponding trimethylsilyl halides:

$$GaHal_3 + n(CH_3)_3SiSR \rightarrow (RS)_nGaHal_{3-n} + n(CH_3)_3SiHal \qquad (1)$$

$$Hal = Cl, Br, I; \qquad R = \text{alkyl, aryl}; \qquad n = 1, 2, 3$$

A special method is represented by the redox-reactions between gallium triiodide and organic disulfides[5] which also should yield the (organothio)gallanes and elemental iodine:

$$GaI_3 + R_2S_2 \rightarrow (RS)GaI_2 + ISR \qquad (2)$$

and

$$GaI_3 + RSI \rightarrow (RS)GaI_2 + I_2 \qquad R = CH_3, Ph \tag{3}$$

Starting from organogallium diiodes one primarily should expect the same reactions leading to iodo(organyl)(organylthio)gallanes. The main products of these reactions rather are the diiodo(organyl)(organylthio)gallanes, which are always obtained in more than 50% yield.[5] The iodo(organyl)(organylthio)gallanes are produced only as by-products in less than 30% yield. The complex mechanism of this reaction can be expressed only very inaccurately by

$$2R'GaI_2 + R_2S_2 \rightarrow (RS)GaI_2 + I(R')GaSR + R'I \qquad R = R' = CH_3, Ph \tag{4}$$

and will be discussed in more detail a little later.

In general organogallium halides are able to react with organic sulfur compounds in two different ways. According to the sulfur compounds that are employed, one can force either reaction on the gallium-carbon-bond[6]

$$R'GaHal_2 + RSH \rightarrow Hal_2GaSR + R'H \tag{5}$$

$$Hal = Cl, Br, I; \qquad R' = CH_3, Ph; \qquad R = \text{alkyl, aryl}$$

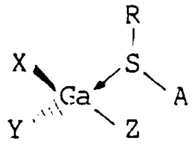
or on the gallium-halogen bond:[7]

$$R'_2GaHal + (CH_3)_3SiSR \rightarrow R'_2GaSR + (CH_3)_3SiHal \tag{6}$$

$$Hal = Cl, Br, I; \qquad R' = CH_3, Ph; \qquad R = \text{alkyl, aryl}$$

All these reactions are Lewis-acid base reactions and will therefore follow a general mechanism. The first step of all these reactions will be a nucleophilic attack of the sulfur compound on the gallium compound:

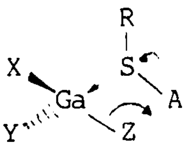
$Ga(X)(Y)Z + RSA \rightleftharpoons$



(7)

X, Y, Z, A, and R: different ligands

This, of course, primarily leads to the corresponding Lewis-acid-base adduct. The next step will either be the back-reaction or a reaction which leads to the (organylthio)gallane and another thermodynamically favored species, like trimethylsilyl halides, elemental iodine and alkanes or arenes; for example:



$\rightarrow Ga(X)(Y)(SR) + AZ$ (8)

X, Y, Z, A and R: different ligands.

In the special case of the reaction between gallium trihalides and trimethylsilyl sulfides,[3,4] one might expect for all three metal halides the formation of mono, bis, and tris(organylthio)gallanes and the corresponding trimethylsilyl halides, if the stoichiometry changes from 1:1 to 1:2 to 1:3. Nevertheless, only the treatment of gallium trichloride with silyl sulfides results in the formation of all these expected products:

$$GaCl_3 + n(CH_3)_3SiSR \rightarrow Cl_{3-n}Ga(SR)_n + n(CH_3)_3SiCl \qquad (9)$$
$$R = \text{alkyl, aryl}; \quad n = 1, 2, 3$$

Gallium tribromide and silyl sulfides react to the dibromo(organylthio)gallanes

$$GaBr_3 + (CH_3)_3SiSR \rightarrow Br_2Ga(SR) + (CH_3)_3SiBr, \quad R = \text{alkyl, aryl} \qquad (10)$$

or, if the silyl sulfide is employed in a twofold or even threefold excess, products of the general composition $Br_3Ga_2(SR)_3$ are formed; this reaction may be formulated as

$$2GaBr_3 + 3(CH_3)_3SiSR \rightarrow Br_3Ga_2(SR)_3 + 3(CH_3)_3SiBr \quad R = \text{alkyl, aryl}. \qquad (11)$$

Gallium triiodide and silyl sulfides afford in all reaction ratios the mono(thiolates) only:

$$GaI_3 + n(CH_3)_3SiSR \rightarrow I_2Ga(SR) + (CH_3)_3SiI + (n-1)(CH_3)_3SiSR \qquad (12)$$
$$R = \text{alkyl, aryl}$$

An explanation for these differences may be found in steric reasons: In the case of gallium triiodide, the equilibrium between educts and adduct may be shifted to the side of the educts because of steric hindrance caused by the bulky iodine atoms. Another explanation could be found in the tendency of the formation of trimethylsilyl halides which is decreasing from trimethylsilyl chloride to trimethylsilyl iodide.

The redox reactions between gallium triiodide and organic disulfides (Equations 2 and 3) always yield the diiodo(organylthio)gallanes; there can be found no influence on this result by the amount of disulfide which is used; this means, it doesn't matter whether the stoichiometry of metal halide to disulfide is raised from 2:1 to 1:1 to 2:3 or even more.[5]

As mentioned before, in the redox reactions between diiodo(organyl)gallanes and organic disulfides (Equation 4) the diiodo(organylthio)gallanes and not the iodo(organyl)(organylthio)gallanes are the main products.[5] This surprising result may be explained as follows:

The first step of this reaction certainly must be the nucleophilic attack of the disulfide on the diiodo(organyl)gallane. Thereby, primarily, the expected Iodo(organyl)(organylthio)gallane and ISR are formed:

$$R'GaI_2 + R_2S_2 \rightarrow I(R')Ga(SR) + ISR \quad R = R' = CH_3, Ph \qquad (13)$$

ISR itself is a very reactive nucleophile and, for examnple, will attack diiodo(organyl)gallane with formation of another iodo(organyl)(organylthio)gallane and elemental iodine:

$$R'GaI_2 + ISR \rightarrow I(R')Ga(SR) + I_2 \qquad R = R' = CH_3, Ph \qquad (14)$$

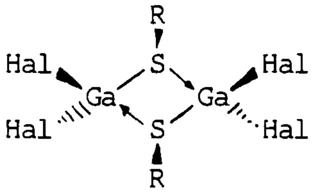
This reaction course easily can be recognized by the color of the reaction mixture. Now, iodine itself may react as a nucleophile and may attack either the educt with formation of gallium triiodide and the corresponding alkyl or aryl iodide:

$$R'GaI_2 + I_2 \rightarrow GaI_3 + R'I \qquad R' = CH_3, Ph \qquad (15)$$

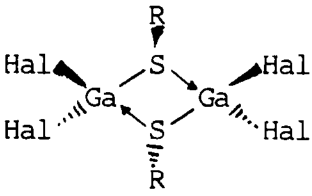
But iodine may attack as well iodo(organyl)(organylthio)gallane, yielding diiodo(organylthio)gallane and alkyl or aryl iodide:

$$I(R')Ga(SR) + I_2 \rightarrow I_2Ga(SR) + R'I \qquad R' = CH_3, Ph \qquad (16)$$

Of course GaI_3 can react with R_2S_2 or ISR as formulated in Equations (2) and (3). Naturally, the thus formed (organylthio)gallanes will not be monomeric, if there are no steric problems to be taken in account. The most simple oligomer certainly is the dimeric species. But even then, there have to be discussed syn- and anti-isomers for the (organylthio)gallium dihalides (if the halide is chloride or bromide, respectively):

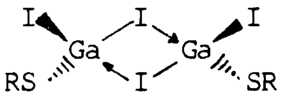


syn

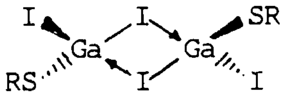


anti

If the halide is iodide, there have to be discussed two more possible isomers: the *cis*- and *trans*-species of iodine-bridged isomers:

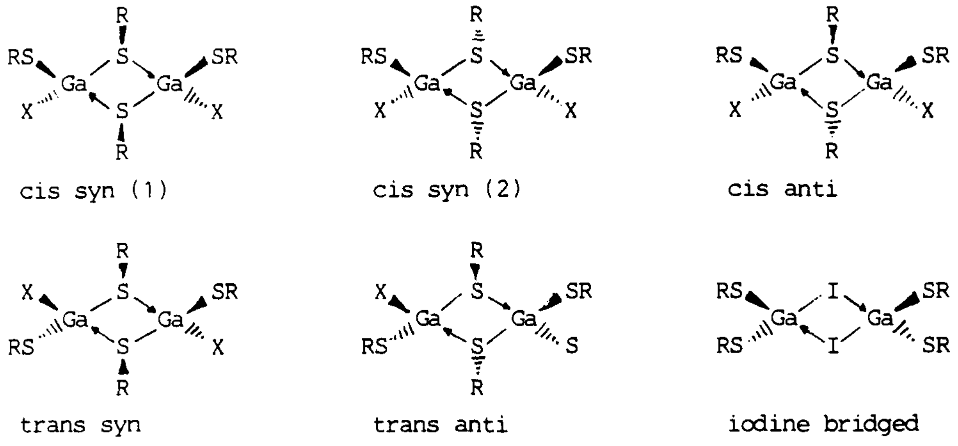


cis



trans

For the bis(organylthio)gallium halides one has to expect five isomers, if the halide is chloride or bromide, and, if the halide is iodide, one has to expect even six isomers: two *cis*-syn-species, one, where the R of the bridged thiolate groups are pointing at the exocyclic thiolate groups, the other, with the R of the bridged thiolate groups pointing at the halogen atoms; one *cis*-anti-species, one *trans*-syn- and one *trans*-anti-species. If the halide is iodide, there has to be discussed one iodine-bridged species as well:


cis syn (1)

cis syn (2)

cis anti

trans syn

trans anti

iodine bridged

R = alkyl; X = Cl, Br, I

FIGURE 1

Which of these isomers could be found?

In benzene solution surprisingly none of them. Osmometric molecular weight determinations have shown the (organylthio)gallium dihalides to be trimeric, except for the derivatives where R equals phenyl or benzyl; these compounds are monomeric, perhaps because of steric hindrance and electronic properties. In contrast, bis(organylthio)gallium halides as well as tris(organylthio)gallanes are oligomeric in benzene solution, except the phenyl and benzyl derivatives, which are monomeric as well.

Nevertheless, an X-ray diffraction study of (methylthio)gallium diiodide has shown this derivative to be dimeric, sulfur-bridged in the crystal. All gallium and sulfur atoms are in-plane and the methyl groups are situated in the anti-position relative to the ring.[8,9]

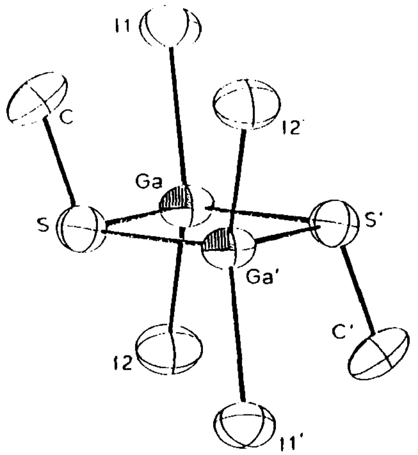


FIGURE 2 ORTEP-plot of the molecular structure of (methylthio)gallium diiodide in the crystal.

This particular structure could also be found for diphenyl(ethylthio)gallane: again, all gallium and sulfur atoms are in-plane and the R (in this case ethyl) groups are situated in the anti-position relative to the ring:[10]

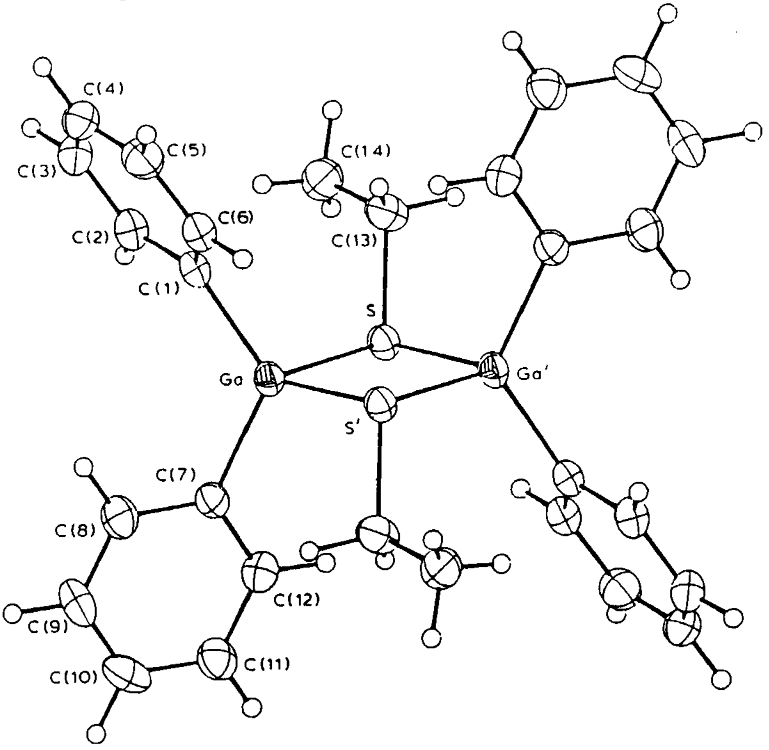


FIGURE 3 ORTEP-plot of the molecular structure of diphenyl(ethylthio)gallane in the crystal.

Now, very recently, we could proof with (*i*-propylthio)gallium diiodide the first example of a "butterfly"-structure of a compound incorporating a tetravalent gallium atom:[11]

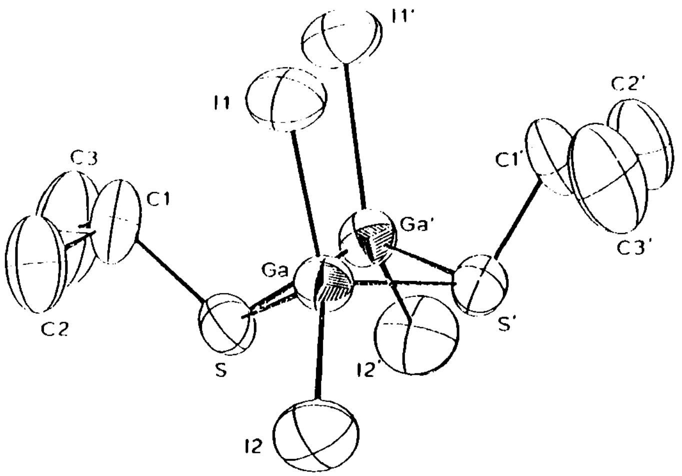


FIGURE 4 ORTEP-plot of the molecular structure of (*i*-propylthio)gallium diiodide in the crystal.

The *i*-propyl groups are situated in the syn-position relative to the now nonplanar four-membered GaSGaS ring. The divergence from the plane is very distinct, 37°.

Some important distances and angles of the three compounds are given in Table I. However, things are even more complicated, if one looks at the ^{1}H-n.m.r. spectra of the (alkylthio)gallium diiodides, where R equals methyl, ethyl and *n*-propyl. At room temperature one will find two different sorts of signals, which are apart from each other about 0.3 to 0.4 ppm. Immediately after dissolving the (organylthio)gallanes, these signals are very sharp; but after a while in solution, they will broaden irreversibly. If temperature is raised, the signals will coalesce, and at about 78°C there remains only one broad-signal group. At low temperatures, the intensity of the signal group at lower field increases, whereas the intensity of the signal group at higher field decreases. At about −78°C there only remains the signal group at lower field.[3,6,8] These phenomena point out that these (alkylthio)gallium diiodides don't have a homogenous structure in solution! Much more discussion is needed of both sulfur-bridged species as well as iodine-bridged species. This is not at all surprising, if one looks at the electronegativities of sulfur and iodine, which almost equal each other. At room temperature, both species are more or less equivalent in solution; at higher temperatures there is a very rapid exchange between these two species and at low temperatures one of these species is favored. This favored species should be the sulfur-bridged one, because the density of charge should be lower on the R group in a sulfur-bridged species than in an iodine-bridged one, and this, however, will cause a down-field shift of the proton-resonance signals of the R groups in the ^{1}H-n.m.r. spectra.

In the case of (*i*-propylthio)- and (phenylthio)gallium diiodide one can find only one signal group which is very sharp.

TABLE I

Bond Lengths (pm) and Bond Angles (°) of $(I_2GaSCH_3)_2$, $(I_2GaS\,i\text{-}C_3H_7)_2$, and $(Ph_2GaSC_2H_5)_2$

$(I_2GaSCH_3)_2$			
Ga—I(1)	249.0(2)	I(1)—Ga—I(2)	115.46(6)
Ga—I(2)	245.0(2)	S—Ga—S′	94.3(1)
Ga—S	234.3(4)	Ga—S—Ga′	85.6(1)
Ga—S′	234.4(4)	Ga—S—C	105.5(5)
S—C	183(2)	Ga′—S—C	103.7(5)
Ga · · · Ga′	318.6(2)		
S · · · S′	343.7(4)		
$(I_2GaS\,i\text{-}C_3H_7)_2$			
Ga—I(1)	248.2(2)	I(1)—Ga—I(2)	114.58(6)
Ga—I(2)	247.9(2)	S—Ga—S′	89.1(1)
Ga—S	232.7(3)	Ga—S—Ga′	84.7(1)
Ga—S′	233.1(3)		
Ga · · · Ga′	313.7(2)		
S · · · S′	326.8(4)		
$(Ph_2GaSC_2H_5)_2$			
Ga—S	237.3(1)	S—Ga—S′	93.58(4)
Ga—S′	238.4(1)	Ga—S—Ga′	86.42(3)
Ga—C(1)	196.4(4)	C(1)-Ga—C(7)	121.2(2)
Ga—C(7)	196.4(4)	S—Ga—C(1)	108.1(1)
S—C(13)	183.8(4)	S—Ga—C(7)	109.0(1)
C(13)—C(14)	148.5(6)	Ga—S—C(13)	106.1(1)
		Ga′—S—C(13)	102.4(1)

This excursion into gallium-sulfur chemistry has only been a very small section; in this short time only a few problems could be mentioned; so, for example, nothing has been told about the reactivity of these compounds.

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