

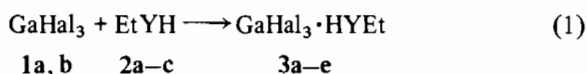
Remarkably Stable Adducts of Gallium Halides with Chalcogenols

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It is well known that chalcogenols react readily with covalent metal halides of both the main group and the auxiliary group elements, with formation of metal chalcogenolates [1, 2]. In these reactions the addition compounds of the chalcogenols to the metal halides can be formulated as intermediates. So far these intermediates could only be isolated and characterized in a very few instances, containing the main group elements [3–6]. The reactions of gallium(III) bromide **1a** or gallium(III) iodide **1b** with the chalcogenols **2a–c** lead in an amazingly simple reaction path to the desired adducts **3a–e** (eqn. 1)



If the chalcogenol is used in a twofold or threefold excess, the 1:1-adduct is still formed. However, in the ¹H NMR spectra (recorded *in situ*) of these mixtures the signals of the chalcogenol hydrogens are shifted towards those of the non-bonded chalcogenol hydrogens. This effect is indicative of a very rapid exchange of the chalcogenol on the metal halide in solution.

Compounds **3a–e** are remarkably stable under normal conditions. They lose neither chalcogenol nor hydrohalogenic acid under reduced pressure. They decompose above 100 °C (Table I), splitting off hydrohalogenic acid, which can be proved both qualitatively and by the aid of differential thermograms.

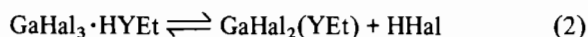
TABLE I. Physical Properties of the Adducts; $\Delta\nu^a$ and $\Delta\delta^b$ Values.

3	Hal	YEt	Decomp. Point (°C)	$\Delta\nu$ (cm ⁻¹)	$\Delta\delta$ (ppm)
a	Br	SEt	115	42	1.80
b	Br	SeEt	51	90	1.94
c	I	OEt	50 ^c	80	1.05
d	I	SEt	120	71	1.74
e	I	SeEt	109	134	2.43

^aDifference of the vibrations of the bonded chalcogen hydrogen to the non-bonded chalcogen hydrogen [4, 7]. ^bDifference of the signals of the bonded chalcogen hydrogen to the non-bonded chalcogen hydrogen, benzene solution.

^cMp.

This extraordinary stability of these adducts may be explained as follows: The coordinative and electronic saturation of the gallium atom prevents the reverse process of eqn. (1); on the other hand, the high reactivity of the hydrohalogenic acid in anhydrous medium displaces the equilibrium in eqn. (2)



to the left side. The hydrohalogenic acid cannot be captured with bases like triethylamine. Instead of this reaction, compounds of the general composition [NEt₃H][GaHal₃(YEt)] are formed, which can be identified analytically and by ¹H NMR spectroscopy.

The adducts **3a–e** are readily soluble in aromatic and halogenated hydrocarbons. They are liquids at room temperature (**3** is a crystalline solid). In the IR spectra of the adducts the absorptions of the chalcogenol hydrogens are observed at much lower frequencies, compared to those of the non-bonded chalcogenol hydrogens. This effect points out a strong metal–chalcogen-interaction. As expected, the shifts of the adducts of **1b** are much stronger than those of the adducts of **1a**. The most polarised band is found for compound **3e** (Table I).

The ¹H NMR spectra of the adducts show clearly a very strong downfield shift for the signals of the chalcogen hydrogens; again the most striking shift is found for compound **3e** (Table II). This also indicates a very strong metal–chalcogen-interaction; therefore, these coordination compounds may also be desig-

TABLE II. Spectroscopic Data of **3a–e**^a.

3a:	¹ H NMR (benzene): δ = 3.23–2.70(s), 2.33(q), 1.13(t); IR (CsI/film): ν = 2488vb, 775w, 734w, 684m, 630m, 576w, 388w, 359m, 300sh, 285sh, 262vb, 233m cm ⁻¹ .
3b:	¹ H NMR (benzene): δ = 2.30(q), 1.40–1.00(s), 0.76(t); IR (CsI/film): ν = 2237vb, 795sh, 750m, 710w, 682m, 538m, 528m, 295sh, 282b, 270sh, 265sh, 230mb cm ⁻¹ .
3c:	¹ H NMR (benzene): δ = 3.46–2.96(s) superposed on 3.33(q), 0.56(t); IR (CsI/nujol): ν = 3520vb, 719m, 695w, 386w, 355w, 245m, 228sh, 211b cm ⁻¹ .
3d:	¹ H NMR (benzene): δ = 2.90(t), 2.30(d of q), 0.76(t); IR (CsI/film): ν = 24.59vb, 770m, 733m, 630b, 558mb, 382w, 354m, 305w, 242b, 215s cm ⁻¹ .
3e:	¹ H NMR (benzene): δ = 2.43(q), 1.83–1.56(s), 0.83 (t); IR (CsI/film): ν = 2193vb, 790m, 748m, 710w, 682m, 538m, 382w, 289m, 230b, 210s cm ⁻¹ .

^aFor IR data, only the frequencies of the vibration of the chalcogen hydrogen and the interval between 800–200 cm⁻¹ are given.

nated as strong protonic acids, which means trihalogeno (monochalcogenolato) gallium acids.

Many other thiol- and selenol-adducts of **1a** and **1b** and even GaCl₃ and AlI₃ could be synthesized.

Experimental

All operations were carried out under nitrogen in dried solvents. To a stirred solution of 1.55 g (5.01 mmol) **1a** or a suspension of 2.25 g (5.00 mmol) **1b** in 10 ml benzene was added a benzene solution of 5.00 mmol **2a–c** at room temperature; there was an initial heat evolution. After stirring for one hour at room temperature, the solvent was evaporated under vacuum. **3c** remained as a colourless solid, **3a, b, d** and **e** as colourless (SEt-compounds) or light yellow (SeEt-compounds) oils. All compounds were dried under high vacuum at room temperature.

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