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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)

$$\underset{\mathbf{1a,b}}{\mathrm{GaHal_3}} + \underset{\mathbf{2a-c}}{\mathrm{EtYH}} \longrightarrow \underset{\mathbf{3a-e}}{\mathrm{GaHal_3 \cdot HYEt}} \qquad (1)$$

If the chalcogenol is used in a twofold or threefold excess, the 1:1-adduct is still formed. However, in the ^{1}H 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

[a] Difference of the vibrations of the bonded chalcogen hydrogen to the non-bonded chalcogen hydrogen [4, 7]. [b] Difference of the signals of the bonded chalcogen hydrogen to the non-bonded chalcogen hydrogen, benzene solution. [c] Mp.

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)

$$\mathrm{GaHal_3 \cdot HYEt} \rightleftharpoons \mathrm{GaHal_2(YEt)} + \mathrm{HHal} \qquad (2)$$

to the left side. The hydrohalogenic acid cannot be captured with bases like triethylamine. Instead of this reaction, compounds of the general composition $[\mathrm{NEt_3H}][\mathrm{GaHal_3(YEt)}]$ are formed, which can be identified analytically and by ^{1}H 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 ^{1}H 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}.

[a] For IR data, only the frequencies of the vibration of the chalcogen hydrogen and the interval between 800–200 cm^{-1} are given.

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

Many other thiol- and selenol-adducts of **1a** and **1b** and even $GaCl_3$ and AlI_3 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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