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Aluminum, gallium and indium thiobenzoates: synthesis, characterization and crystal structures

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Aluminum, gallium and indium thiobenzoates: synthesis, characterization and crystal structures

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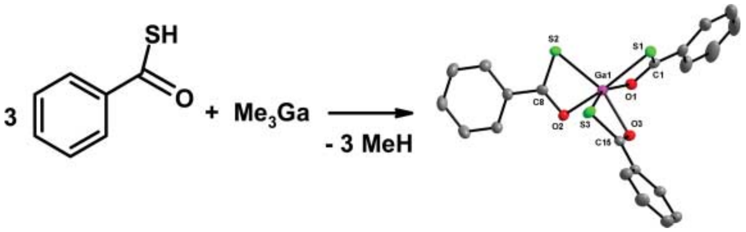
Compounds $R_2M[S(O)CPh]$ [where R = ^{t}Bu, M = Al (**1**); R = ^{t}Bu, M = Ga (**2**); R = Me, M = Ga (**3**)] have been synthesized in reactions of R_3M with thiobenzoic acid in a 1:1 molar ratio of reagents. The reaction of Me_3Ga with three equivalents of thiobenzoic acid yielded the compound $Ga[S(O)CPh]_3$ (**4**), in which thiobenzoate moieties act as bidentate SO ligands. In the presence of Et_3N, $InCl_3$ reacted with thiobenzoic acid with formation of an ionic compound $\{In[S(O)CPh]_4\}^-(HNEt_3)^+$ (**5**). The thiobenzoate ligands are bonded with the metallic center via the sulfur atoms only. The compounds **4** and **5** have been structurally and thermally studied. The thermal decomposition pathways of compounds **4** and **5** are proposed.



Keywords: aluminum; gallium; indium; thiobenzoic acid; thermogravimetry

1. Introduction

Over the last two decades, significant attention has been focused on group 13 elements, particularly Ga and In, with sulfur ligands due to their relevance as metal precursors for metal sulfides,[1–15] biologically active compounds [16–18] and catalysts for polymerization.[19,20] Among these complexes, gallium and indium dithiocarbamates and dithiocarboxylates have been reported as source precursors for metal sulfide thin films and nano particles.[1,7–9,12–14] In contrast to the numerous literature data consisting of characterization and applications of gallium and indium dithiocarbamates and dithiocarboxylates, the number of reports on group 13 thiocarboxylates is sparse. Dialkyl aluminum-, gallium and indium thioacetates published in 1971 by Weidlein [21] are the first thiocarboxylates. They were obtained by the reaction of the trialkyls

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*Corresponding author. Email: ziemk@ch.pw.edu.pl with equivalent amounts of thiocarboxylic acid. On the basis of spectroscopic data the structure of dimethyl aluminum thioacetate was proposed as a dimer with the central eight-membered $Al_2O_2C_2S_2$ ring skeleton, whereas the corresponding Ga and In derivatives were monomeric with four-membered MSCO rings.

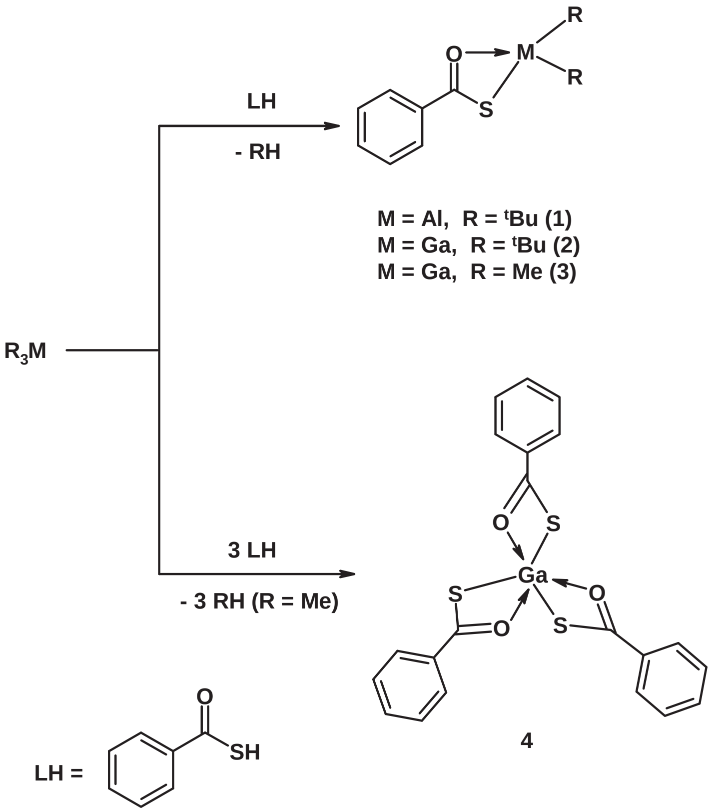
According to our knowledge, there are several structurally characterized group 13 thiocarboxylates. The first example of a structurally characterized gallium thiocarboxylate compound is methylgallium tioacetate $Ga(SCOMe)_2Me(dmpy)$ (where dmpy = 3,5-dimethylpyridine) obtained in the reaction of Me_3Ga with thioacetic acid in the presence of dmpy.[15] In the solid state, the Ga center is tetrahedrally coordinated by two S atoms, one C atom from the methyl group and one N atom from neutral dmpy. The X-ray structural determination of diethylindium thioacetate showed the polymeric complex $[Et_2In(SCOCH_3)]_n$, in which the thioacetate ligand chelates through both S and O atoms and the O atom is also bridging two In centers, resulting in five-coordinate metal centers.[22] The second structurally characterized indium compound is the ionic complex $[Hdmpy]^+[In(SCOCH_3)_4]^-$, synthesized by the reaction of Et_3In with an excess of thioacetic acid followed by addition of dmpy.[2] The molecular structure of the compound shows that the In center is tetrahedrally coordinated by four monodentate S-bonded thioacetic ligands. Similarly, reactions of $InCl_3$ with thiobenzoic acid in the presence of Et_3N proceeded with formation of $(Et_3NH)[In(SC(O)Ph)_4]\cdot H_2O$ [23] and $(Et_3NH)[In(SC(O)Ph)_4]$.[24]

Following our interest on group 13 carboxylates,[25,26] benzoxaborolates [27] and amidates,[28,29] herein, we report the synthesis and structures of aluminum, gallium and indium thiobenzoates. We show that reactions of R_3M ($R = {}^tBu$, Me; M = Al, Ga) with thiobenzoic acid in a 1:1 molar ratio proceed with formation of monomeric $R_2M[S(O)CPh]$ complexes, whereas in the reaction of Me_3Ga with thiobenzoic acid in a 1:3 molar ratio the product $Ga[S(O)CPh]_3$ was formed. We reinvestigated the compound $(Et_3NH)[In(SC(O)Ph)_4]$, reported by Nöth and Gupta in 1996,[24] to characterize it structurally and thermally and deposit crystal data in the Cambridge Crystallographic Data Centre.

2. Results and discussion

The treatment of thiobenzoic acid with one molar equivalent of R_3M produces the compounds $R_2M[S(O)CPh]$ (where $R = {}^tBu$, M = Al (**1**); $R = {}^tBu$, M = Ga (**2**); R = Me, M = Ga (**3**)) as shown in Scheme 1. The pure compounds, obtained as yellow liquids after distillation from the post-reaction mixtures, were examined by NMR spectroscopy and molecular weight measurements. In the ^1H NMR spectra, integration ratios of signals of aromatic protons and protons of alkyl groups bonded to metal atoms, indicate one aromatic ring per two R groups. According to molecular weight measurements, thiobenzoates **1**–**3** are monomeric, which is in contrast to dimeric dialkylaluminum and -gallium carboxylates.[30–32] Based on NMR spectra and molecular weight measurements, compounds **1**–**3** consist of a metal atom bonded to two alkyl groups and thiobenzoate moiety acting as a bidentate OS ligand.

We found that in the presence of an excess of thiobenzoic acid $^tBu_3M$ (M = Al, Ga) reacts only with one equivalent of the acid to form **1** and **2** complexes, whereas the reaction of Me_3Ga with three equivalents of thiobenzoic acid leads to a formation of the crystalline compound $Ga[S(O)CPh]_3$ (**4**) (Scheme 1). The molecular and crystal structure of the compound was determined on the basis of X-ray diffraction studies and is shown in Figures 1 and 2, respectively. The crystal data as well as the details of the data collection and refinement are listed in Table 1. A molecule of **4** consists of a central hexacoordinate gallium atom bonded to three thiobenzoate moieties acting as bifunctional SO ligands and differing in bond lengths and angles from each other. The coordination sphere geometry of the gallium atom is a distorted tetragonal



Scheme 1. Reactions of thiobenzoic acid with R_3M (R = Me, ^{t}Bu; M = Al, Ga).

bipyramidal geometry. Values of the following angles are similar: S(1)–Ga(1)–(O2) 157.45 (4), O(1)–Ga(1)–S(3) 156.39(4) and O(3)–Ga(1)–S(2) 160.45(4). It indicates that not only can the O(3) and S(2) atoms occupy the axial positions of the bipyramid, but also S(1) and O(2) as well as O(1) and S(3) atoms can be regarded as atoms in the axial positions of the bipyramid. In comparison with $Ga(SCOMe)_2Me(dmpy)$ the only structurally characterized gallium thiocarboxylate,[15] the Ga–S bonds in **4** [2.371(1)–2.380(1) Å] are about 0.1 Å longer than in those compounds. The sums of the angles about the C(1), C(8) and C(15) atoms Σ(C) 360.0° show a sp^2 hybridization of these atoms. Four-membered GaSCO rings are twisted in relation to aromatic rings, which is manifested by torsional angles C(3)–C(2)–C(1)–O(1) − 7.6(3), C(7)–C(2)–C(1)–S(1) − 8.1(3), S(2)–C(8)–C(9)–C(14) 6.4(3), O(2)–C(8)–C(9)–C(10) 5.9(3), C(23)–C(16)–C(15)–O(3) 175.5(2), C(17)–C(16)–C(15)–S(3) − 179.3(2).

The ionic compound $\{In[S(O)CPh]_4\}^-[HN(C_2H_5)_3]^+$ (**5**) was synthesized in the reaction of $InCl_3$ with thiobenzoic acid in the presence of Et_3N (Scheme 2). The ^1H NMR spectrum of **5** reveals three multiplets of aromatic protons at 8.08, 7.46 and 7.34 ppm, quartet and triplet at 3.24 and 1.21 of ethyl group protons. On the basis of the integration ratio of the aromatic protons and the ethyl group protons, we found that in the molecules there are four thiobenzoate moieties per one molecule of NEt_3.

The molecular structure of **5** depicted in Figure 3 is similar to that reported in [24]. The crystal data as well as the details of the data collection and refinement are listed in Table 1. S–C–O angles in monodentate thiobenzoate ligands in **5** [from 121.1(1) to 122.8(1)°] are significantly bigger than those in bidentate ligands in **4** [from 116.5(1)° to 116.9(1)°]. Very probably, it is

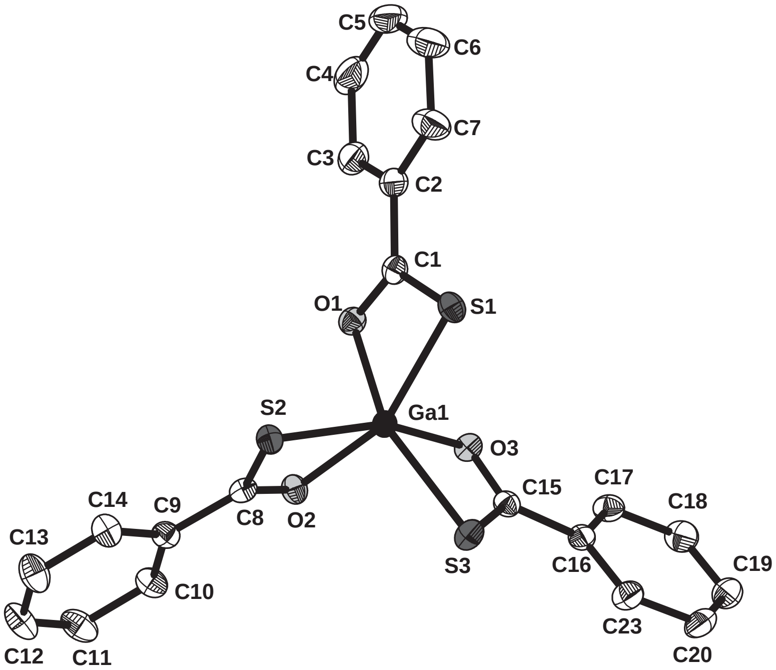


Figure 1. Molecular structure of $C_{21}H_{15}GaO_3S_3 \cdot H_2O$ (**4**·H_2O) with atomic displacement parameters set at the 50% level. Hydrogen atoms and water molecules have been omitted for clarity. For selected interatomic distances, angles and torsional angles see Supporting information (Figure 1S).

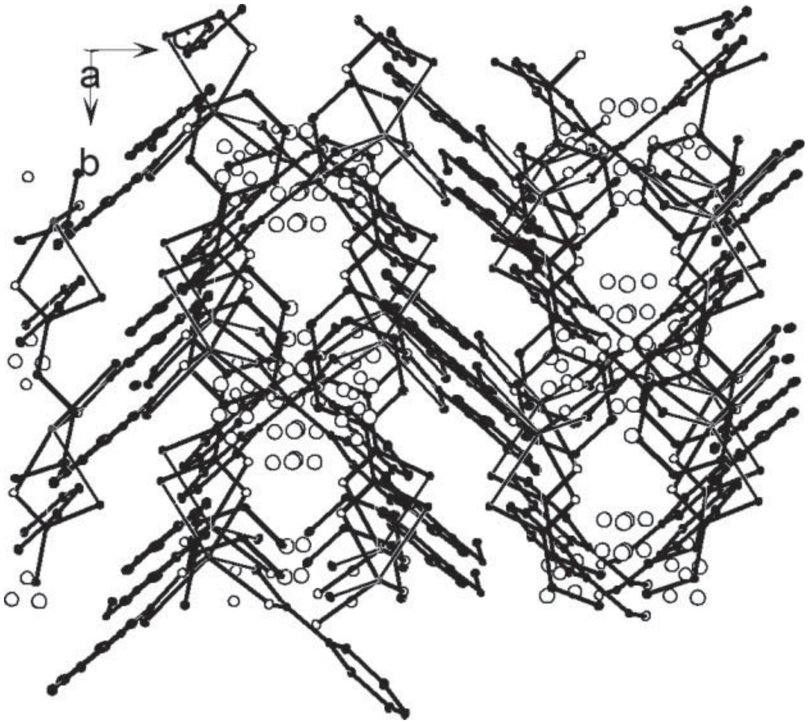
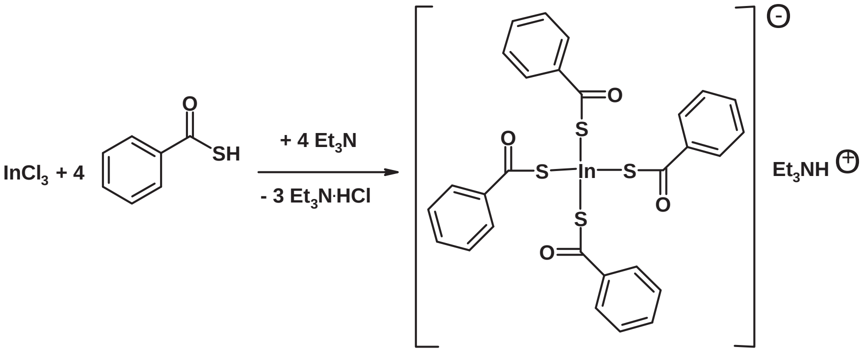


Figure 2. Molecular packing of **4** drawn along *a* axis. Circles represent disordered molecules of water. H atoms have been omitted for clarity.

Table 1. Crystal data and data collection parameters for **4**·H_2O and **5**.

	4·H_2O	**5**
Empirical formula	$C_{21}H_{15}GaO_3S_3\cdot H_2O$	$[C_{28}H_{20}InO_4S_4]^-\cdot[HN(C_2H_5)_3]^+$
Formula weight	497.23	765.70
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P1\ 21/n1$
a(Å)	23.7175(4)	11.6532(6)
b(Å)	11.5723(1)	19.936(1)
c(Å)	19.2640(3)	14.5531(7)
α(°)	90	90
β(°)	117.399(2)	92.848(2)
γ(°)	90	90
V(Å^3)	4694.2(1)	3376.8(3)
Z	8	4
D_{calc}(g cm^{-3})	1.407	1.506
Absorption coefficient (mm^{-1})	1.462	0.986
F(000)	2016	1568
Crystal size (mm)	0.20 × 0.15 × 0.10	0.12 × 0.14 × 0.17
Θ range for data collection (°)	1.7398–28.6580	2.29–26.00
Index ranges	$-28 \le h \le 28$, $-14 \le k \le 14$, $-23 \le l \le 23$	$-14 \le h \le 14$, $-24 \le \mathrm{k} \le 24$, $-17 \le \mathrm{l} \le 17$
Reflections collected	43,971	54,584
Independent reflections	4332 [$R_{int} = 0.0238$]	6637 [$R_{int} = 0.0305$]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4332/0/282	6637/0/404
Goodness-of-fit on F^2	1.062	1.067
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0254$, w$R_2 = 0.0633$	$R_1 = 0.0201$, w$R_2 = 0.0454$
R indices (all data)	$R_1 = 0.0285$, w$R_2 = 0.0656$	$R_1 = 0.0251$, w$R_2 = 0.0474$
Max/min of residual electron density	0.813 and −0.408	0.492 and −0.231



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Scheme 2. Reaction of thiobenzoic acid with $InCl_3$.

caused by a lack of a strain in the monodentate ligands. The lack of strain is also demonstrated by torsion of planes consisting of O(2), C(8), S(2) and O(3), C(15), S(3) and O(4), C(22) S(4) atoms in relation to the proper aromatic rings. In comparison with the torsion of GaSCO planes in relation to the aromatic rings in **4** [from 0.7(2)° to 8.1(3)°], the proper torsion angles in **5** are significantly bigger [from 9.8(1)° to 21.4(2)°]. The only exception is the O(1)–C(1)–C(2)–C(3)

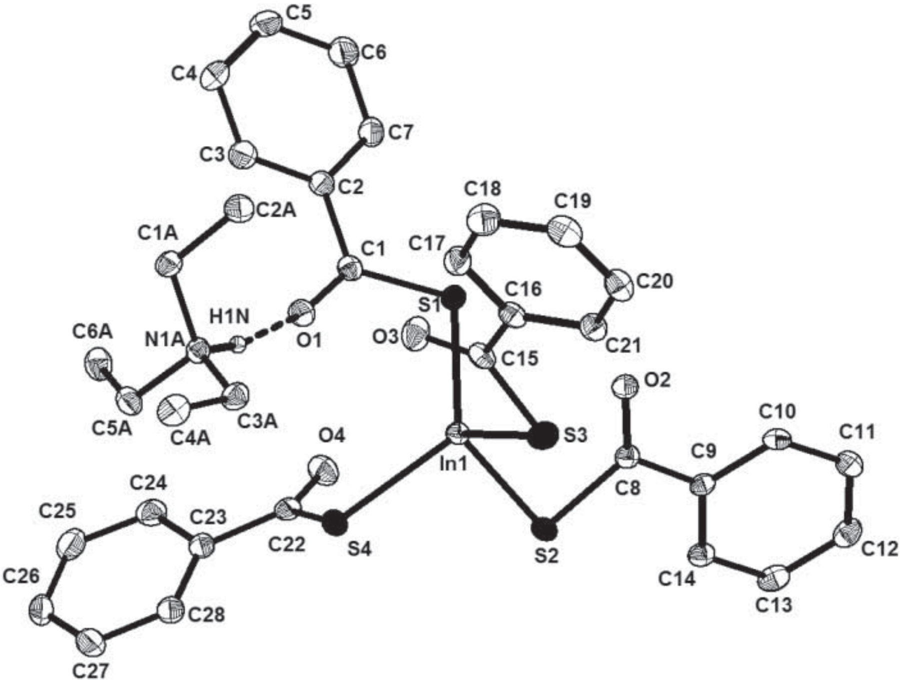


Figure 3. Molecular structure of $[C_{28}H_{20}InO_4S_4]^- \cdot [HN(C_2H_5)_3]^+$ (**5**) with atomic displacement parameters set at the 50% level. Hydrogen atoms (besides the hydrogen atom bonded to the nitrogen atom) have been omitted for clarity. For selected interatomic distances, angles and torsional angles see Supporting information (Figure 2S).

torsion angle [5.8(2)°], which is comparable with those of compound **4**. Very probably, presence of the O(1)H(1N)–N(1A) hydrogen bond introduced more steric strain.

The views along *a* and *c* axes demonstrate a laminar crystal structure of **5** (for the view along *c* axis see Figure 4(a)); however the intramolecular atom distances that are roughly estimated as 10 Å (Figure 4(b)) indicate no bonds between layers. The view along *b* axis shows channels, in which intramolecular atom distances are approximately from 7 to 10 Å (Figures 5(a) 5(b)). Recently, group 13 carboxylates have been attracting attention owing to their usefulness as metal organic frameworks (MOFs). Although pore sizes of **5** and known MOFs like MIL-53 (channel dimensions of 8.5 × 8.5 Å^2) [33] and WUT-1 (cavities of 6.2 and 10.4 Å diameters) [34] are similar, it is difficult to consider compound **5** as a potential MOF.

The thermogravimetric (TG) curve of complex **5** in argon atmosphere was considered to decompose in two steps (Figure 6) (Scheme 3). The first step of decomposition occurred between 180°C and 250°C, where 63.80% of the initial mass was lost. This step was attributed to the loss of Et_3N, three molecules of C_6H_5CO and one C_6H_6 (theoretical 64.61%). The last step of decomposition indicated a loss of 7.78% of the initial mass. This corresponded to the expulsion of C(O)S (theoretical 7.83%). The residue obtained afterwards (28.42%) gave a non-stoichiometric composition InS_3 (theoretical 27.54%). The thermogravimetric curve of complex **4** indicated decomposition as a multistep process (Figure 7) (Scheme 4). The first two steps occurred between room temperature and 200°C and corresponded to a loss of solvents and water. In the next steps, between 200°C and 500°C, three moieties of C_6H_5CO corresponding to the loss of 59.45% of the initial mass were eliminated (theoretical 59.85%). Similar to the decomposition of **5**, the residue after decomposition of **4** manifests a non-stoichiometric composition GaS_3.

In conclusion, this work presents the synthesis and characterization of group 13 thiobenzoates. The compounds $R_2M[S(O)CPh]$ [where R = ^{t}Bu, M = Al (**1**); R = ^{t}Bu, M = Ga (**2**);

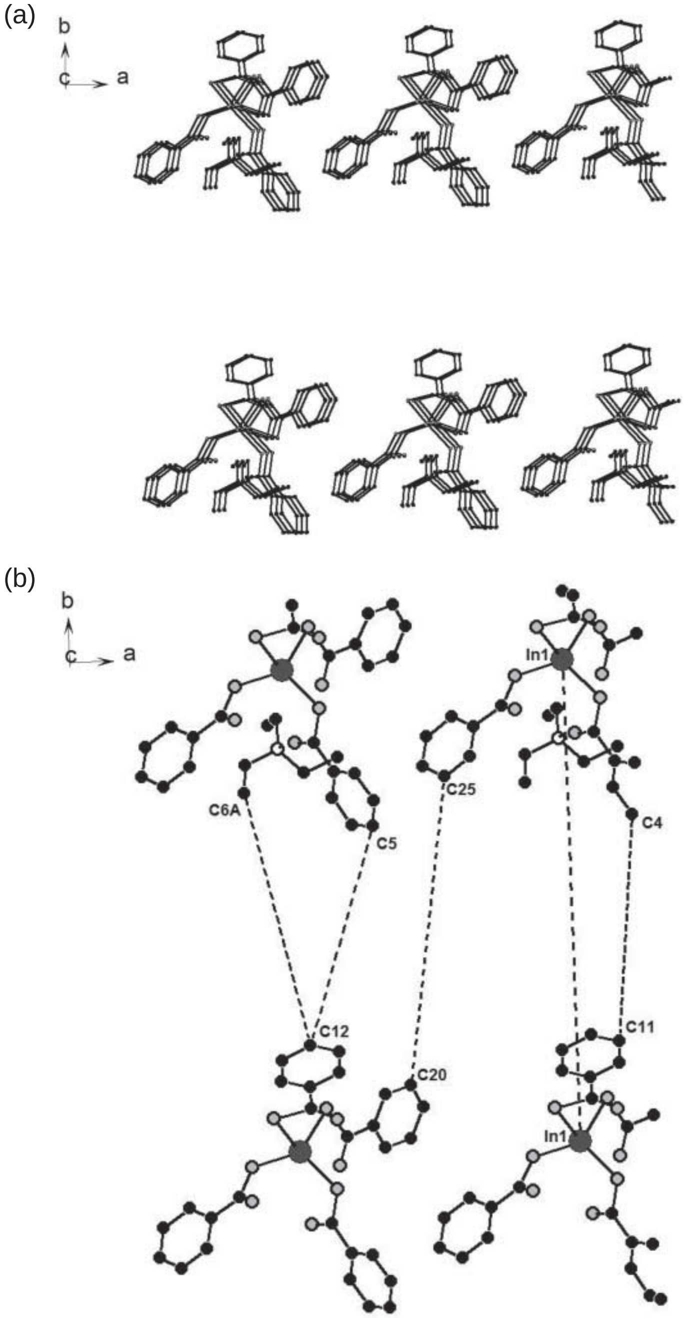


Figure 4. Crystal structure of **5**. (a) View along the *c* axis showing laminar structure of the compound. (b) Intermolecular atom distances (Å) between layers: C(6A)–C(12) 13.49, C(5)–C(12) 10.59, C(25)–C(20) 13.20, In–In 19.93, C(4)–C(11) 10.71.

R = Me, M = Ga (**3**)] are liquids. Molecular weight measurements revealed the monomeric structure of the compounds. The reaction of Me_3Ga with three equivalents of thiobenzoic acid led to a formation of the crystalline compound $Ga[S(O)CPh]_3$ (**4**), whereas the ionic compound $\{In[S(O)CPh]_4\}^-[HN(C_2H_5)_3]^+$ (**5**) was synthesized in the reaction of $InCl_3$ with thiobenzoic

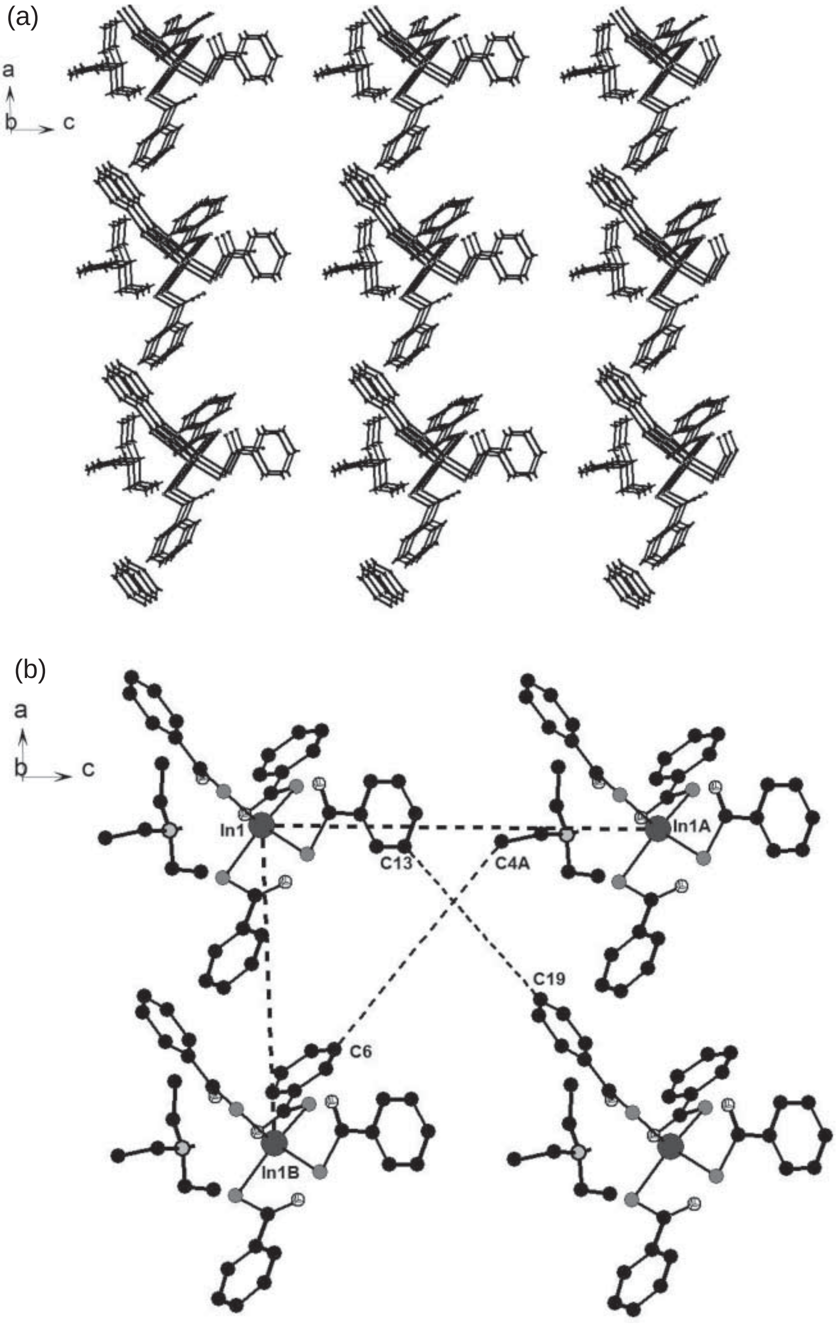


Figure 5. Crystal structure of **5**. (a) View along the *b* axis showing channel structure of the compound. (b) Intermolecular atom distances (Å) estimating a channel size: In(1)–In(1A) 14.55, In(1)–In(1B) 11.65, C(4A)–C(6) 10.32, C(13)–C(19) 7.75.

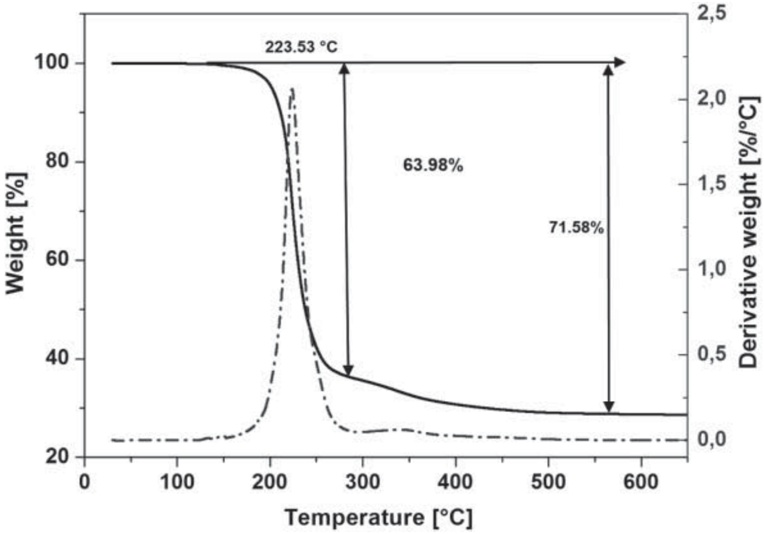


Figure 6. DSC (dashed line) and TGA (solid line) curves of compound **5**.

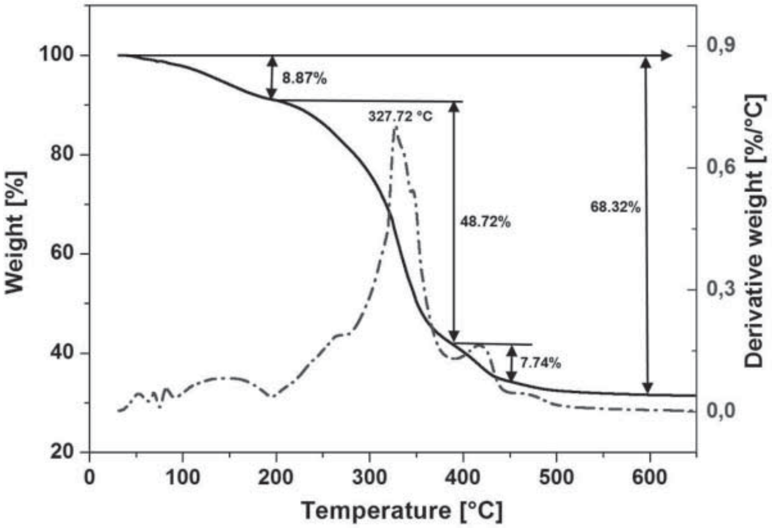


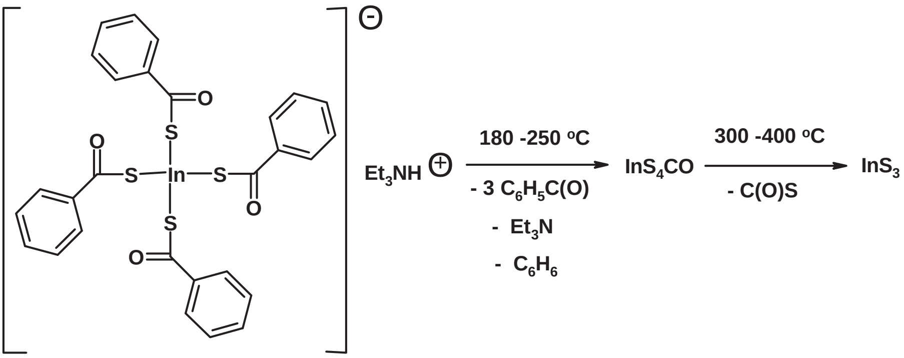
Figure 7. DSC (dashed line) and TGA (solid line) curves of compound **4**.

acid in the presence of Et_3N. An analysis of the crystal structure showed that compound **5** can be considered as a porous material, probably a potential MOF.

3. Experimental

3.1. *Materials and instrumentation*

All manipulations were carried out using standard Schlenk techniques under inert gas atmosphere. Solvents (n-C_6H_{14} and C_6H_6) were distilled over the blue benzophenone-K complex,



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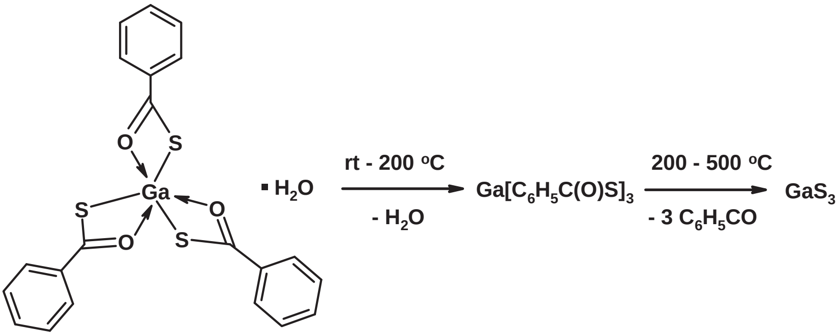
Scheme 3. The decomposition pathways of compound **5**.



Scheme 4. The decomposition pathways of compound **4**.

whereas CH_2Cl_2 was distilled over P_2O_5. ^{t}Bu$_3$Al·OEt$_2$ and ^{t}Bu$_3$Ga were synthesized as described in the literature.[35,36] ^{1}H and ^{13}C NMR spectra were obtained on a Mercury-400BB spectrometer. Chemical shifts were referenced to the residual proton signals of $CDCl_3$ (7.26 ppm). ^{13}C NMR spectra were acquired at 100.60 MHz (standard: chloroform $^{13}CDCl_3$, 77.20 ppm). Hydrolysable ^{t}Bu groups for compound **1** were determined by hydrolysis of the compound (0.2 g) under argon using HNO_3 solution (10% concentrated, 5 cm^3) and measurement of the volume of C_4H_{10}. Subsequently, the sample was transformed into Al_2O_3 by mineralization and the obtained white solid was dissolved in a diluted water solution of HNO_3. The content of aluminum was determined by complexation of Al^{3+} cations with versenate anions using an excess of the titrated solution of calcium disodium versenate. Then the excess of calcium disodium versenate was titrated by $FeCl_3$ according to the procedure described in [37,38]. Elemental analyses of compounds **4** and **5** were performed using a Perkin-Elmer 2400 analyzer. Molecular weights were measured by the cryoscopic method in benzene solutions.

3.2. *Synthesis of $R_2M[S(O)CPh]$ [$R = {}^t$Bu, $M =$ Al (1); $R = {}^t$Bu, $M =$ Ga (2); $R =$ Me, $M =$ Ga (3)]: general procedure*

A solution of R_3M (5 mmol) in CH_2Cl_2 (10 cm^3) was injected into a solution of thiobenzoic acid (0.690 g; 5 mmol) in CH_2Cl_2 (10 cm^3) at −76°C. The reaction mixture was allowed to warm slowly to room temperature. Then the post-reaction mixture was placed in a glass apparatus for distillation. The pressure was slowly reduced to 10^{-2} Torr to distill off solvents. Subsequently, the flask was wrapped up with a heating belt and temperature was slowly increased up to the moment of beginning of compound deposition on the condenser. The distillate was obtained as solution of the yellow product (**1**–**3**) in solvent. The pure product was isolated in the second distillation off a solvent from the flask at the temperature of 5°C within 2 h under vacuum (10^{-2} Torr).

3.3. $^{t}Bu_2Al[S(O)CPh]$ (1)

Yield 80%. ^{1}H NMR ($CDCl_3$) δ: 8.24 (2H, m, H_{aromat}), 7.70 (1H, m, H_{aromat}), 7.51 (2H, m, H_{aromat}), 1.05 [18H, s, $(CH_3)_3CAl$] ppm. ^{13}C NMR ($CDCl_3$) δ: 221.98 [C(O)S], 135.60, 129.68, 129.11, 128.61 (C_{aromat}), 29.20 [$(CH_3)_3CAl$], 16 [$(CH_3)_3CAl$, broad] ppm. Elemental anal. Found: Al, 9.40; hydrolyzable ^{t}Bu groups, 41.39; Calcd for $C_{15}H_{23}AlOS$: Al, 9.71; ^{t}Bu, 41.01 wt.%. Molecular weight Found: 268; Calcd for $^tBu_2Al[S(O)CPh]$: 278 g mol^{-1}.

3.4. $^{t}Bu_2Ga[S(O)CPh]$ (2)

Yield 85%. ^{1}H NMR ($CDCl_3$) δ: 8.16 (2H, m, H_{aromat}), 7.63 (1H, m, H_{aromat}), 7.46 (2H, m, H_{aromat}), 1.19 [18H, s, $(CH_3)_3CGa$] ppm. ^{13}C NMR ($CDCl_3$) δ: 219.58 [C(O)S], 136.76, 134.26, 128.46, 128.33 (C_{aromat}), 29.36 [$(CH_3)_3CGa$], 27.26 [$(CH_3)_3CGa$] ppm. Molecular weight Found: 315; Calcd for $^tBu_2Ga[S(O)CPh]$: 321 g mol^{-1}. Anal. Found: C, 60.05, H, 7.95; Calcd. for $C_{15}H_{23}GaOS$: C, 60.44; H, 7.72 (wt%).

3.5. $Me_2Ga[S(O)CPh]$ (3)

Yield 78%. ^{1}H NMR ($CDCl_3$) δ: 8.12 (2H, m, H_{aromat}), 7.63 (1H, m, H_{aromat}), 7.45 (2H, m, H_{aromat}), 0.21 (6H, s, CH_3Ga) ppm. ^{13}C NMR ($CDCl_3$) δ: 218.81 [C(O)S], 134.41, 129.21, 128.56, 128.33 (C_{aromat}), -2.60 (CH_3Ga) ppm. Molecular weight Found: 248; Calcd for $Me_2Ga[S(O)CPh]$: 237 g mol^{-1}. Anal. Found: C, 45.25, H, 4.92; Calcd. for $C_9H_{11}GaOS$: C, 45.61; H, 4.65 (wt%).

3.6. Synthesis of $Ga[S(O)CPh]_3$ (4)

A solution of Me_3Ga (0.575 g, 5 mmol) in CH_2Cl_2 (10 cm^3) was injected into a solution of thiobenzoic acid (2.208 g; 16 mmol) in CH_2Cl_2 (20 cm^3) at -76°C. The reaction mixture was allowed to warm slowly to room temperature. The solvent was distilled off from the post-reaction mixture under vacuum, yielding a light yellow solid of **4**. *n*-Hexane (5 cm^3) was added to the solid to form a suspension. Methylene dichloride was slowly injected dropwise to dissolve the solid. Pure compound **4**$\cdot H_2O$ was obtained after crystallization from the *n*-C_6H_{14}-CH_2Cl_2 solution containing 10 mmol of water at 7°C (Yield: 1.390 g, 2.8 mmol, 56%).

^{1}H NMR ($CDCl_3$) δ: 8.14 (2H, m, H_{aromat}), 7.63 (1H, m, H_{aromat}), 7.46 (2H, m, H_{aromat}), 4.60 (broad, H_2O) ppm. ^{13}C NMR ($CDCl_3$) δ: 212.33 [C(O)S], 135.19, 134.64, 129.40, 128.32 (C_{aromat}) ppm. FTIR: $\nu = 3056.6$, 2917.8, 2842.6, 1594.8, 1457.9, 1421.3, 1309.4, 1228.4, 1174.4, 970.0, 773.3, 707.7, 678.8, 649.9, 590.11 cm^{-1}. Mp.: 86–90°C. Anal. Found: C, 50.56, H, 3.62; Calcd. for $C_{21}H_{17}GaO_4S_3$: C, 50.68; H, 3.42 (wt%).

3.7. Synthesis of $\{In[S(O)CPh]_4\}^-[HN(C_2H_5)_3]^+$ (5)

Compound **5** was synthesized by a similar method as described in [24]. A solution of thiobenzoic acid (1.173 g, 8.5 mmol) in 7 cm^3 of benzene was injected into a suspension of $InCl_3$

(0.443 g, 2 mmol) in 15 cm^3 of benzene consisting of Et_3N (0.909 g, 9 mmol). The reaction mixture became transparent; afterwards a light yellow solid precipitated. The solid was separated by filtration, dried under vacuum, washed by 5 cm^3 of CH_3OH and dried again. A crystalline solid of the pure compound **5** was obtained from an n-C_6H_{14}-CH_2Cl_2 solution (for preparation of the solution see Section 3.6) at 10°C. (Yield: 1.072 g, 70%.) Mp.: 136–139°C (literature data [24]: 118–119°C). ^1H NMR ($CDCl_3$) δ: 8.08 (8H, m, H_{aromat}), 7.46 (4H, m, H_{aromat}), 7.34 (8H, m, H_{aromat}), 3.24 (6H, q, $C\underline{H}_3CH_2N$), 1.21 (9H, t, $C\underline{H}_3CH_2N$). ^{13}C NMR ($CDCl_3$) δ: 203.40 C(O)S, 139.37, 132.33. 128.71, 127.88 (C_{aromat}), 46.94 (CH_3CH_2N), 8.71 (CH_3CH_2N) ppm. FTIR: $\nu = 3093.3$, 3062.5, 1598.7, 1569.8, 1444.4, 1396.2, 1303.7, 1199.5, 1164.8, 1074.2, 1024.0, 919.9, 908.3, 835.0, 771.4, 686.5, 648.0 cm^{-1}. Anal. Found: C, 52.90, H, 4.92; Calcd. for $C_{34}H_{36}InNO_4S_4$: C, 53.28; H, 4.70 (wt%).

3.8. *Crystallographic data*

Single crystal data for **4** and **5** were collected at 100 (2) K using graphite monochromated Mo/Kα radiation ($\lambda = 0.7107$ Å). Experiments were performed on an Xcalibur Opal CCD k-axis (Oxford Diffraction) and a Bruker D8 VENTURE system equipped with a TRIUMPH monochromator, respectively. The CrysAlis^{Pro} program [39] was used for data collection of **4**, cell refinement, data reduction and the empirical absorption corrections using spherical harmonics, implemented in a multi-scan scaling algorithm. The structure was solved using direct methods and refined with the full-matrix least-squares technique using the SHELXS97 and SHELXL97 programs, respectively,[40] both implemented in the OLEX2 program.[41]

The residual map of electron density showed that apart from the main molecule **4**, a disordered solvent molecule should have also been considered in the crystal structure. Following the reaction mechanism, selection of solvents and their potential impurities, for example a water molecule, traces of dichloromethane, hexane or even hydrogen chloride could be taken into account as a solvent molecule in the crystal structure. The best model was obtained with one water molecule disordered in seven positions, refined isotropically with no hydrogen atoms attached. However this choice should be regarded as arbitrary. The atomic scattering factors were taken from the International Tables. [42]

The structure of **5** was solved and refined using the Bruker SHELXTL Software Package and the SHELXL-2013 (Sheldrick, 2013) program.

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Disclosure statement

No potential conflict of interest was reported by the authors.

Supplemental data

Supplemental data for this article can be accessed at 10.1080/17415993.2015.1025073

References

[1] Ghoshal S, Jain VK, Dutta DP, Phadnis PP, Nethaji M. Gallium and indium dithiocarboxylates: Synthesis, spectroscopic characterization and structure of [MeGa(S_2Ctol)$_2$]. J Organomet Chem. 2006;691:5838–5844.

[2] Shang G, Kunze K, Hampden-Smith MJ, Duesler EN. Low-temperature chemical vapor deposition of indium sulfide thin films using a novel single-source indium thiocarboxylate compound as precursor. Chem Vap Deposition. 1996;2:242–244.

[3] MacInnes AN, Cleave WM, Barron AR, Power MB, Hepp AF. Metal–Organic chemical vapour deposition of polycrystalline tetragonal indium sulphide (InS) thin films. Adv Mater Opt Electron. 1992;1:229–233.

[4] Barron AR. Oxide, chalcogenide and related clusters of aluminum, gallium and indium. Comments Inorg Chem. 1993;14:123–153.

[5] Nomura R, Konishi K, Matsuda H. Single-source organometallic chemical vapour deposition process for sulphide thin films: introduction of a new organometallic precursor $\mathrm{Bu^nIn(SPr^i)_2}$ and preparation of In_2S_3 thin films. Thin Solid Films. 1991;198:339–345.

[6] MacInnes AN, Power MB, Barron AR. Chemical vapor deposition of gallium sulfide: phase control by molecular design. Chem Mater. 1993;5:1344–1351.

[7] Haggata SW, Malik MA, Melevalli M, O'Brien P. Synthesis and characterization of some mixed alkyl thiocarbamates of gallium and indium, precursors for III/VI materials: the x-ray single-crystal structures of dimethyl- and diethylindium diethyldithiocarbamates. Chem Mater. 1995;7:716–724.

[8] O'Brien P, Otway DJ, Walsh JR. Novel precursors for the growth of α-In_2S_3: trisdialkyldithiocarbamates of indium. Thin Solid Films. 1998;315:57–61.

[9] Sivagurunathan GS, Ramalingam K, Rizzoli C. Continuous shape measure of electronic effect free steric distortions in tris(dithiocarbamato)indium(III): synthesis, spectral, electrochemical, single crystal X-ray structural investigations and BVS calculations on tris(dithiocarbamato)indium(III) complexes. Polyhedron. 2014;72:96–102.

[10] Ghoshal S, Kushwah NP, Pal MK, Jain VK, Nethaji M. Tris(dithiocarboxylato)indium(III): thermal studies and crystal structure of [In(S_2Ctol)$_3$]. J Chem Sci. 2008;120:305–308.

[11] Lazell M, O'Brien P, Otway DJ, Park J-H. Oxide, chalcogenide and related clusters of aluminum, gallium and indium. J Chem Soc, Dalton Trans. 2000;4479–4486.

[12] Keys A, Bott SG, Barron AR. Single source molecular precursors for the deposition of III/VI chalcogenide semiconductors by MOCVD and related techniques. Chem Mater. 1999;11:3578–3587.

[13] Haggata SW, Malik MA, Motevalli M, O'Brien P, Knowles JC. Synthesis and characterization of some mixed alkyl thiocarbamates of gallium and indium, precursors for III/VI materials: the X-ray single-crystal structures of dimethyl- and diethylindium diethyldithiocarbamates. Chem Mater. 1995;7:716–724.

[14] Afzaal M, Malik MA, O'Brien P. Indium sulfide nanorods from single-source precursor. Chem Commun. 2004;334–335.

[15] Shang G, Hampden-Smith MJ, Duesler EN. Synthesis and characterization of gallium thiocarboxylates as novel single-source precursors to gallium sulfide thin films by aerosol-assisted CVD. Chem Commun. 1996; 1733–1734.

[16] da Silva JG, Pergigão CCH, Speziali NL, Beraldo H. Chalcone-derived thiosemicarbazones and their zinc(II) and gallium(III) complexes: spectral studies and antimicrobial activity. J Coord Chem. 2013;66:385–401.

[17] Lessa JA, Soares MA, dos Santos RG, Mendes IC, Salum LB, Daghestani HN, Andricopulo AD, Day BW, Vogt A, Beraldo H. Gallium(III) complexes with 2-acetylpyridine-derived thiosemicarbazones: antimicrobial and cytotoxic effects and investigation on the interactions with tubulin. Biometals. 2013;26:151–165.

[18] Ferreira IP, de Lima GM, Paniago EB, Takahashi JA, Pinheiro CB. Synthesis, characterization, and biocide activity of new dithiocarbamate-based complexes of In(III), Ga(III), and Bi(III) – Part III. J Coord Chem. 2014;67:1097–1109.

[19] Nakata N, Saito Y, Ishii A. Neutral methyl and cationic aluminum complexes supported by a trans-1,2-cyclooctanediyl-bridged [OSSO]-type bis(phenolato) ligand: synthesis, structures, and use in catalysis for propylene oxide polymerization. Organometallics. 2014;33:1840–1844.

[20] Postigo L, Maestre MD, Mosquera MEG, Cuenca T, Jimenez G. Aminoarenethiolate aluminum complexes: synthesis, characterization, and use in L-Lactide polymerization. Organometallics. 2013;32:2618–2624.

[21] Weidlein J. Über dialkylaluminium-, -gallium- und -indium- thiocarboxylate. J Organomet Chem. 1971;32:181–194.

[22] Hausen HD, Guder HJ. Dialkylindium-thioacetate $R_2InOSCCH_3$ ($R = CH_3, C_2H_5$), darstellung, eigenschaften und struktur. J Organomet Chem. 1973;57:243–253.

[23] Lin M, Loh KP, Deivaraj TC, Vittal JJ. Heterogeneous reaction route to CuInS2 thin films. Chem Commun. 2002;1400–1401.

[24] Singh P, Bhattacharya S, Gupta VD, Nöth H. Structural studies on indium and tin thiobenzoates. Chem Ber. 1996;129:1093–1098.

[25] Ziemkowska W, Cyrański M, Kunicki A. Alkylaluminum derivatives of diphenic acid: novel aluminium carboxylates. Inorg Chem. 2009;48:7006–7008.

[26] Ziemkowska W, Jaśkowska E, Madura I, Zachara J, Zygadło-Monikowska E. Synthesis and structure of diethylaluminum malonate: an unusual hexanuclear aluminum complex with malonate trianion ligands. J Organomet Chem. 2012;713:178–181.

[27] Jaśkowska E, Justyniak I, Cyrański MK, Adamczyk-Woźniak A, Sporzyński A, Zygadło-Monikowska E, Ziemkowska W. Benzoxaborolate ligands in group 13 metal complexes. J Organomet Chem. 2013;732:8–14.

[28] Ziemkowska W, Kochanowski J, Cyrański MK. Synthesis, structures and ϵ-caprolactone polymerization activity of aluminum N,N'-dimethyloxalamidates. J Organomet Chem. 2010;695:1205–1209.

[29] Ziemkowska W, Jaśkowska E, Zygadło-Monikowska E, Cyrański MK. Reactions of group 13 metal trialkyls with oxamides. J Organomet Chem. 2011;696:2079–2085.

[30] Bethley CE, Aitken CL, Harlan CJ, Koide Y, Bott SG, Barron AR. Structural characterization of dialkylaluminum carboxylatyes: model for carboxylate alumoxanes. Organometallics. 1997;16:329–341.

[31] Keys A, Barbarich TJ, Bott SG, Barron AR. *tert*-Butyl compounds of gallium. J Chem Soc Dalton Trans. 2000;577–588.

[32] Dickie DA, Choytun DD, Jennings MC, Jenkins HA, Clyburne JAC. A structural study of dimethylaluminum carboxylate and hydrazonato complexes. J Organomet Chem. 2004;689:2186–2191.

[33] Loiseau T, Serre C, Huguenard C, Fink G, Taulelle F, Henry M, Bataille T, Férey G. A rationale for the large breathing of the porous aluminum terephthalate (MIL-53) upon hydration. Chem Eur J. 2004;10:1373–1382.

[34] Sokołowski K, Bury W, Justyniak I, Fairen-Jimenez D, Sołtys K, Prochowicz D, Yang S, Schröder M, Lewiński J. Permanent porosity derived from the self-assembly of highly luminescent molecular zinc carbonate nanoclusters. Angew Chem Int Ed. 2013;52:13414–13418.

[35] Uhl W. Die Reaktion des tert.Butyl-lithiums mit Aluminiumtribromid; Molekülstrukturen von $[HAl(CMe_3)_2]_3$ und $[LiHAl(CMe_3)_3]_2$. Z Anorg Allg Chem. 1989;570:37–53.

[36] Kovar RA, Derr H, Brandau D, Callaway JO. Preparation of organogallium compounds from organolithium reagents and gallium chloride. Infrared, magnetic resonance, and mass spectral studies of alkylgallium compounds. Inorg Chem. 1975;14:2809–2814.

[37] Marczenko Z. Odczynniki organiczne w analizie nieorganicznej. Warszawa: PWN; 1959, polish edition.

[38] Milner WG, Woodhead JL. The determination of alumina in silicates (Rocks and Refractories). Anal Chim Acta. 1955;12:127–137.

[39] CrysAlis^{Pro}, Agilent Technologies. Version 1.171.35.19 (release 27-10-2011 CrysAlis171.NET), Santa Clara, CA; 2011.

[40] Sheldrick GM. A short history of SHELX. Acta Cryst. 2008;A64:112–122.

[41] Dolomanov OV, Bourhis LJ, Gildea RJ, Howard JAK, Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. J Appl Cryst. 2009;42:339–341.

[42] Wilson A J C, editor. International tables for crystallography. Dordrecht: Kluwer; 1992, Vol.C.