Unprecedented Coordination Mode Variation of Group 13 Metal–Alkyl Compounds Derived from Methyl Thiosalicylate

Janusz Lewiński,*[a] Wojciech Bury,[a] Tomasz Kopeć,[a] Ewa Tratkiewicz,[a] Iwona Justyniak,[b] and Janusz Lipkowski[b]

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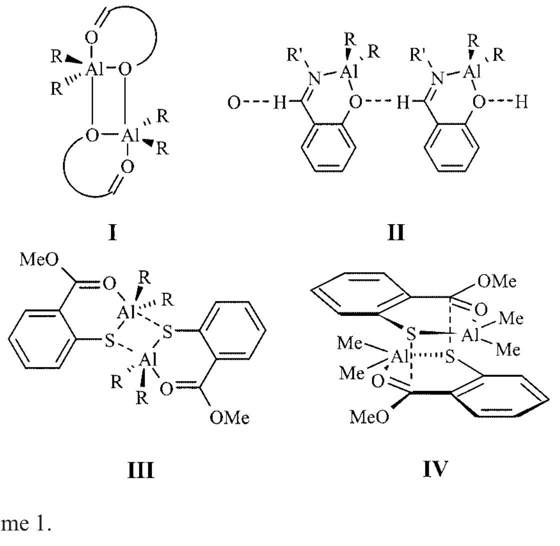
The X-ray structure analysis of the alkylaluminum and -indium compounds derived from methyl thiosalicylate, $Me_2Al(SC_6H_4\text{-}2\text{-}CO_2Me)$ and $[Me_2In(\mu\text{-}SC_6H_4\text{-}2\text{-}CO_2Me)]_2$, revealed that the intermolecular S···C(π) interaction between the Al–S thiolate units and the ester π-surface can effectively compete with the hypercoordinate sulfur–metal dative bond. The former compound exists as the noncovalently bonded dimer involving the thiolate sulfur atom and the electrophilic carbon atom of the ester functionality, whereas the indium complex is a five-coordinate dimer with the $In_2(\mu\text{-}S)_2$ central core.

Introduction

The chemistry of five-coordinate aluminum complexes has an extensive literature[1] and the significance of the fifth coordinate site for aluminum-based reagent/catalyst function and/or selectivity is gradually emerging.[2] In spite of many contributions in this area, less direct information has been gleaned about the nature of bonding, stability, and reactivity of this class of compounds, and the identity of both active centers and transition-state structures remains elusive.[3] Therefore, detailed structural information concerning the extent of coordination and association in alkylaluminum complexes as well as the magnitude of the donor–aluminum interaction in five-coordinate species are crucial in understanding their physical behavior and chemical reactivity. In this regard, investigations based on the dialkylaluminum chelate complexes derived from donor-functionalized alcohols or unsaturated bifunctional O,X-H proligands, i.e., $[R_2Al(O,X)]_n$-type complexes, have appeared particularly fruitful.[4] Recently, our group has reported the results concerning the relationship between intra- and intermolecular forces resulting from donor–acceptor and hydrogen-bonding interactions using group 13 chelate complexes.[5] For instance, we have demonstrated that in the solid state dialkylaluminum chelate complexes have a tendency to form $[R_2Al(\mu\text{-}O,O')]_2$-type adducts with five-coordinate metal centers (Scheme 1, structure **I**) with the intermolecular Al–O distance varying from ca. 2.05 Å to the van der Waals surface (i.e., over 3.5 Å).[4f] Conversely, the structure investigations of the group 13 chelate complexes with salicylideneiminate anion (saldR′) revealed that the crystal structure of $R_2M(saldR')$ (M = Al or Ga) complexes is determined by distinct intermolecular hydrogen-bond motifs (structure **II**), while the indium analogue formed a five-coordinate dimer with $In_2(\mu\text{-}O)_2$ bridges in the solid state.[5a,5b] As an extension of this work, we report herein on structure investigations of alkylaluminum and -indium compounds derived from methyl thiosalicylate, which revealed that the intermolecular S···C(π) interaction between the Al–S thiolate units and the π-surface of the ester functionality (structure **IV**) can compete with the putative sulfur–aluminum hypercoordinate bond (structure **III**).



I **II**

III **IV**

Scheme 1.

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[a] Department of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland
E-mail: lewin@ch.pw.edu.pl
[b] Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44, 01-224 Warsaw, Poland

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Results and Discussion

The reaction of Me_3Al with methyl thiosalicylate in an equimolar ratio results in the quantitative formation of $Me_2Al(SC_6H_4\text{-}2\text{-}CO_2Me)$ (**1**). The resulting complex has been characterized in solution by NMR spectroscopy and molecular weight measurements (see Exp. Sect.), and in the solid state its structure has been determined by X-ray crystallography. Compound **1** exists as a monomer in solution and crystallizes as a noncovalently bonded dimer (Figure 1). The monomeric units of **1** consist of the tetrahedral aluminum center. The salient structural feature of **1** is the conformation of the chelate-ring system S(1)–C(3)–C(8)–C(9)–O(1)–Al(1), which highly deviates from planarity with a puckering amplitude $Q = 0.579(2)$ Å.[6] This deformation is realized by the bending on the sulfur atom, while the metal–ester linkage remains essentially planar; the torsion angles Al(1)–S(1)–C(3)–C(8) and Al(1)–O(1)–C(9)–C(8) are equal to 30.3(3)° and 1.2(4)°, respectively. The ester group is rotated relative to the phenyl ring with an O(1)–C(9)–C(8)–C(3) torsion angle of 23.9(4)°. Most strikingly, the analysis of the crystal-packing patterns of **1** shows notably short intermolecular S···C(π) [3.379(3) Å] distances between a pair of adjacent molecules that represents a type of weak attractive interaction of the sulfur atom to the π-system of the ester group. The observed S···C(π) distance remains significantly below the sum of the van der Waals radii,[7,8] and should be considered as denoting a bonding interaction. This assumption is further supported by the relative orientation of the thiolate and ester groups: the S···C=O angle is 88.7°, and both the Al–S···C(π) and the C–S···C(π) angles are close to the tetrahedral values indicating that the sulfur sp^3 lone pair is oriented approximately perpendicular to the ester group.

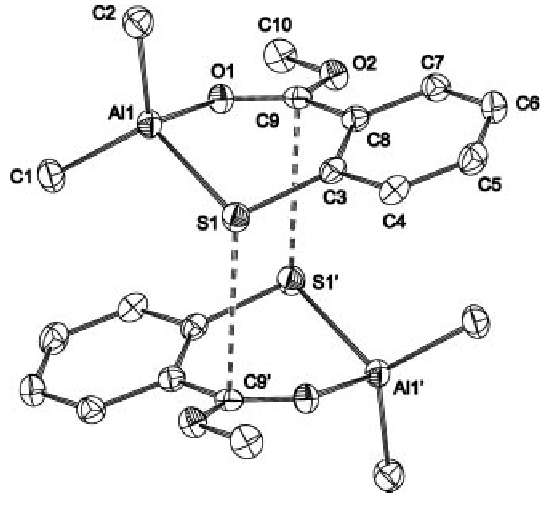

Figure 1. Molecular structure of **1** with thermal ellipsoids drawn at the 40% probability; hydrogen atoms are omitted for clarity.

The structural motif for **1** is surprising as both the participation of thiolate ligands in the formation of the $R_2Al(\mu\text{-}SR')_2AlR_2$ bridges and the Lewis acid properties of the metal center in tetrahedral dialkylaluminum chelate complexes are well recognized.[1] We have previously determined the following order for the Lewis acidity of the group 13 metal centers in the four-coordinate $R_2M(O,O')$ complexes: In ≥ Al > Ga,[4c] and it was of interest to see which type of coordination mode would be adopted by the alkylindium derivative of methyl thiosalicylate. The reaction of Me_3In with the pro-ligand results in the formation of $[Me_2In(\mu\text{-}SC_6H_4\text{-}2\text{-}CO_2Me)]_2$ (**2**) which is found to exist as a monomer/dimer equilibrium based on solution molecular weight studies (calcd. for dimeric **2** 623.72, found 530). A similar equilibrium was observed for dimethylindium acetylacetonate complex,[9] while the related dimethylindium complexes supported by methyl salicylate[4c] or *N*-phenylsalicylideneimine[5a] occurred exclusively in the dimeric form in benzene solution.

The X-ray crystallographic analysis revealed that in contrast to the aluminum complex **1**, the indium derivative **2** adopts the five-coordinate motif with the $In_2(\mu\text{-}S)_2$ central core (see Figure 2). The conformation of the chelate-ring system S(1)–C(3)–C(8)–C(9)–O(1)–In(1) is even more pleated than the related heterocyclic ring in **1** [with a puckering amplitude $Q = 0.922(3)$ Å]. The In–S distances are dissimilar [2.561(5) and 2.853(2) Å], with that in the equatorial position being 0.292 Å shorter. The In(1)–O(1) distance of 2.452(4) Å is longer than the corresponding linkage in the related five-coordinate dimer derived from methyl salicylate, $[Me_2In(\mu\text{-}OC_6H_4\text{-}2\text{-}CO_2Me)]_2$ [2.165(4) Å].[4c] Thus, the five-coordinate dimeric motif observed for **2** demonstrates that group 13 metal–alkyl compounds supported by the monoanionic methyl thiosalicylate ligand are capable of aggregating through dative bridging bonds between the metal center and the thiolate group.

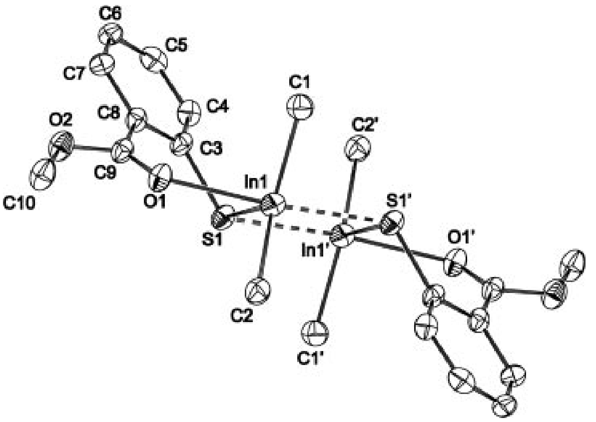

Figure 2. Molecular structure of **2** with thermal ellipsoids drawn at the 40% probability; hydrogen atoms are omitted for clarity.

Conclusions

In conclusion, the reported results clearly indicate that for the methylaluminum complex supported by the methyl thiosalicylate ligand the structure of type **IV** is preferred over the adduct of type **III** with the dative bond between the thiolate sulfur atom and the aluminum five-coordinate site. To the best of our knowledge, this is the first report on the competition of the intermolecular $n\rightarrow\pi^*$ interaction, involving the thiolate sulfur atom and the electrophilic carbon atom of the ester functionality, with the hypercoordinate bond in metal complexes and opens up an interesting area for further studies. Studies of both the relationship between the hypercoordinate bonds in the group 13 metal–alkyl complexes and noncovalent interactions, and the significance of the intermolecular $S\cdots C(\pi)$ interaction between M–S thiolate units and the π-surface of the carbonyl functionality in various systems are in progress.

Experimental Section

General Remarks: All reactions were carried out under dry nitrogen using standard Schlenk techniques. Solvents were dried and distilled prior to use. NMR spectra were recorded with a Varian Mercury 400 spectrometer.

$\mathrm{Me_2Al(SC_6H_4\text{-}2\text{-}CO_2Me)}$ (1): $\mathrm{AlMe_3}$ (0.312 g, 4.32 mmol) was added to a solution of methyl thiosalicylate (0.727 g, 4.32 mmol) in hexane (7 mL) at –78 °C. After the addition was completed, the reaction mixture was allowed to warm to room temperature and a pale yellow solid precipitated. The product was dissolved under heating to 40 °C and yellow block-shaped crystals were obtained at 0 °C. Yield: 0.934 g (96%). $\mathrm{C_{10}H_{13}AlO_2S}$ (224.24): calcd. C 53.32, H 6.26, S 14.23; found C 53.07, H 6.32, S 14.11; molecular weight studies: calcd. 224.24, found 238. ^{1}H NMR (200 MHz, $\mathrm{C_6D_6}$): δ = –0.17 (s, 6 H, $\mathrm{AlCH_3}$), 2.88 (s, 3 H, $\mathrm{OCH_3}$), 6.51–7.68 (m, 4 H, Ar) ppm. ^{13}C NMR (50 MHz, $\mathrm{C_6D_6}$): δ = –8.3, 55.0, 123.2, 123.8, 132.7, 134.8, 137.3, 152.1, 175.9 (C=O) ppm. ^{27}Al NMR (104 MHz, $\mathrm{C_6D_6}$): δ = 158 ppm.

$\mathrm{Me_2In(\mu\text{-}SC_6H_4\text{-}2\text{-}CO_2Me)}$ (2): The reaction was carried out according to the same procedure as described for **1**, using $\mathrm{InMe_3}$ (0.141 g, 0.89 mmol) and methyl thiosalicylate (0.152 g, 0.89 mmol) in toluene (7 mL). Colorless block-shaped crystals were obtained from a toluene/hexane solution at –20 °C after 24 h. Yield 0.27 g (98%). $\mathrm{C_{20}H_{26}In_2O_4S_2}$ (624.19): calcd. C 38.49, H 4.20, S 10.27; found C 38.12, H 4.11, S 9.98. ^{1}H NMR (200 MHz, $\mathrm{C_6D_6}$): δ = 0.42 (s, 6 H, $\mathrm{InCH_3}$), 3.17 (s, 3 H, $\mathrm{OCH_3}$), 6.67–7.64 (m, 4 H, Ar) ppm. ^{13}C NMR (50 MHz, $\mathrm{C_6D_6}$): δ = –2.9, 52.5, 124.4, 129.6, 131.8, 132.2, 136.7, 143.7, 172.0 (C=O) ppm.

X-ray Crystallographic Study: A single crystal of **1** and **2** suitable for X-ray diffraction studies was placed in a thin-walled capillary tube (Lindemann glass 0.5 mm) under an inert gas. The tube was plugged with grease, then flame-sealed and mounted on a goniometer head. **1:** Triclinic, space group $P\bar{1}$ (no. 2), a = 8.4030(4), b = 8.6340(6), c = 9.9590(5) Å, α = 88.776(4), β = 66.253(3), γ = 62.170(3)°, V = 572.34(6) Å^3, Z = 2, $F(000)$ = 236, $D_{\mathrm{calcd.}}$ = 1.301 g m^3, T = 150(2) K. **2:** Monoclinic, space group $P21/c$ (no. 14), a = 8.1080(17), b = 13.151(3), c = 11.423(2) Å, β = 108.0.94(15)°, V = 1157.8(4) Å^3, Z = 4, $F(000)$ = 759, $D_{\mathrm{calcd.}}$ = 2.198 g m^3, T = 150(2) K. Nonius Kappa-CCD diffractometer, $\mu(\mathrm{Mo}\text{-}K_\alpha)$ = 4.19 mm^{-1}. The structures of **1** and **2** were solved by direct methods using the SHELXS-97[10] program and were refined by full-matrix least squares on F^2 using the program SHELXL-97.[11] Refinement converged at R_1 = 0.0514, wR_2 = 0.1185 for all data and 130 parameters [R_1 = 0.0443, wR_2 = 0.1145 for 1600 reflections with $I_o > 2\sigma(I_o)$], GOF = 1.07 for **1**; R_1 = 0.0514, wR_2 = 0.1185 for all data and 130 parameters [R_1 = 0.0443, wR_2 = 0.1145 for 1600 reflections with $I_o > 2\sigma(I_o)$], GOF = 1.053 for **2**. CCDC-240417 (**1**) and -240418 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information: Selected bond lengths and angles in **1** and **2** (see footnote on the first page of this article).

Acknowledgments

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