

Cyclopentadienylaluminum thiolates – synthesis and structure

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Abstract

The dicyclopentadienylaluminum thiolates $[\text{Cp}_2\text{Al}(\mu\text{-SR})_2]$, where R = Et (**1**), ⁱPr (**2**), were obtained by reacting Cl_2AlSR with CpNa at the molar ratio 1:2, respectively. Use of CpLi instead of CpNa at the same molar ratio of reagents leads to the formation of cyclopentadienyl(chloro)aluminum thiolates $[\text{Cp}(\text{Cl})\text{Al}(\mu\text{-SR})_2]$, exclusively, where R = Et (**3**), ⁱPr (**4**), ⁱBu (**5**), and ⁿBu (**6**). The compounds were characterized by ¹H, ¹³C, and ²⁷Al NMR spectroscopy. The structures of the compounds **1** and **4** were determined by X-ray crystallography.

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1. Introduction

The organoaluminum compounds containing organic group with chalcogen have been under investigation for many years and reviewed extensively (see for example [1]). Among these compounds aluminum alkoxides have been the most systematically and broadly examined (see for example [2]). Comparing to aluminum alkoxides the chemistry of thiolate derivatives is rather scant [3–17]. The structures of organoaluminum thiolates are diversified and the factors controlling them are not still definitely examined. For example, Me_2AlSMe is dimeric in gas-phase [18], acts as dimer-trimer equilibrium in solution [19] and its crystal structure has shown one-dimensional polymer with MeS groups bridging Me_2Al units to form infinite zig-zag chain [20].

A cyclopentadienyl group is a versatile ligand owing to the bond modes to metal centers [21]. Although the factors concerning its behavior have been under investigation for many years, it still remains lots of unexplored areas. In the past few years, we have been engaged in the

investigation of the chemistry of alkoxy-cyclopentadienylaluminum compounds [22–24]. The correlation between bulkiness of alkoxy group and the CpAl bond mode in $[\text{Cp}_2\text{Al}(\mu\text{-OR})_2]$ have been reported by us recently [25]. To alter the steric and electron factors determining Cp bonding mode in the aluminum complexes we have undertaken the studies on the structure of alkylthiolatodicyclopentadienylaluminum compounds. To our best knowledge there is no evidence about the structure of this class of compounds in the literature.

In this paper, we present the synthesis and the structure of six novel bis[(μ-alkylthiolato)-cyclopentadienylaluminum] compounds. The compounds are characterized by multinuclear NMR spectroscopy and elemental analysis. The crystal structure of $[\text{Cp}_2\text{Al}(\mu\text{-SEt})_2]$ and $[\text{Cp}(\text{Cl})\text{Al}(\mu\text{-S}^i\text{Pr})_2]$ determined by X-ray diffraction methods are also discussed.

2. Experimental

2.1. General remarks

The synthesized compounds are both air and moisture sensitive, so they were prepared and manipulated

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under an argon atmosphere using standard Schlenk techniques. All solvent used (hexane, benzene, and toluene) were dried over benzophenone ketyl. Dichloromethylaluminum were purchased from Aldrich as 1.0 M solution in hexane and used without further purification. Thiols (Aldrich) were distilled under argon over capillar sorbent (dry molecular sieves 4 Å) before use. CpNa was obtained in standard method in the reaction of freshly distilled cyclopentadiene with sodium. CpLi was synthesized from cyclopentadiene and *n*-butyllithium. The alkylthiolatodichloroaluminum compounds were obtained from alkylthiols and dichloromethylaluminum [26]. ^1H , ^{13}C and ^{27}Al NMR spectra were recorded on a Varian-Gemini (^1H – 199.971 MHz, ^{13}C – 50.283 MHz, ^{27}Al – 52.106 MHz) and Varian-Mercury (^1H – 400.09 MHz, ^{13}C – 100.60 MHz, ^{27}Al – 104.25 MHz). The proton chemical shifts were referenced to $\text{C}_6\text{D}_5\text{H}$ ($\delta = 7.15$ ppm) or CHCl_3 ($\delta = 7.28$ ppm), the carbon resonances to C_6D_6 ($\delta = 128$ ppm) or CDCl_3 ($\delta = 78$ ppm) and the ^{27}Al NMR spectra to $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ($\delta = 0$ ppm) in benzene or chloroform. Molecular weight was determined by cryoscopic measurements in benzene. X-ray measurements were performed on a Kuma KM4-CCD κ -axis diffractometer.

2.2. Synthesis of $[\text{Cp}_2\text{Al}(\mu\text{-SEt})_2]$ (1)

Ethylthiolatodichloroaluminum (2.189 g, 13.8 mmol) in 70 mL of hexane was added to solid CpNa (2.485 g, 28.2 mmol). The reaction mixture was stirred for 3 days at room temperature to give clear yellow solution over white residue. The solution was carefully taken out and the residue extracted with two portion (50 mL + 50 mL) of hexane. The combined hexane solution was concentrated to ca. 40 mL and stored at -15 °C to afford the product with 47% yield (1.410 g) as white crystalline solid.

Anal. for $\text{C}_{12}\text{H}_{15}\text{Al}_2\text{S}$, calc. (found): C 66.03% (65.88%), H 6.93% (6.79%), Al 12.36% (12.18%). M_w : 438, calculated for dimer 436.6. ^1H NMR (CDCl_3 , δ , ppm): 1.37 (t, $^3J = 7.6$ Hz, 3H, CH_3), 2.81 (q, $^3J = 7.6$ Hz, 2H, CH_2), 6.12 (s, 10H, C_5H_5). ^{13}C NMR (CDCl_3 , δ , ppm): 16.43 (CH_3), 28.35 (CH_2), 113.32 (C_5H_5). ^{27}Al NMR (CDCl_3 , δ , ppm): 116 ($\omega_{1/2} = 4727$ Hz).

2.3. Synthesis of $[\text{Cp}_2\text{Al}(\mu\text{-S}^i\text{Pr})_2]$ (2)

The solid CpNa (2.301 g, 26.1 mmol) and solution of *iso*-propylthiolatodichloroaluminum (2.130 g, 12.3 mmol) in 70 mL of toluene were combined at room temperature. After that the reaction mixture was stirred for 3 days at ambient temperature to give clear yellow solution over white residue. The solution was carefully decanted and the residue extracted twice with toluene (50 mL + 50 mL). The whole collected solution was concen-

trated to ca. 40 mL and stored at -10 °C to give white solid product with 53% yield.

Anal. for $\text{C}_{13}\text{H}_{17}\text{Al}_2\text{S}$, calc. (found): C 67.21% (66.95%), H 7.38% (7.45%), Al 11.61% (11.91%). M_w : 480, calculated for dimer 464.6. ^1H NMR (C_6D_6 , δ , ppm): 0.97 (d, $^3J = 6.5$ Hz, 6H, CH_3), 3.03 (sept, $^3J = 6.5$ Hz, 1H, CH), 6.19 (s, 10H, C_5H_5). ^{13}C NMR (C_6D_6 , δ , ppm): 26.15 (CH_3), 37.22 (CH), 113.81 (C_5H_5). ^{27}Al NMR (C_6D_6 , δ , ppm): 119.

2.4. Synthesis of $[\text{Cp}(\text{Cl})\text{Al}(\mu\text{-SEt})_2]$ (3)

Ethylthiolatodichloroaluminum (2.239 g, 14.1 mmol) in 70 mL of hexane was added to the solid CpLi (2.167 g, 30.1 mmol) at room temperature. The reaction mixture was stirred for 4 days at ambient temperature to obtain clear light yellow solution over white solid. Attempts to separate the pure product by crystallization failed. A small sample was decanted and dried in vacuo to give light yellow oily liquid. A storage of this compound in hexane at lowered temperature (-10 °C) caused precipitation of white residue, insoluble in common hydrocarbon solvents (e.g. hexane, toluene). Because of the inability to obtain pure compound only the NMR spectra of post-reaction mixture were recorded.

^1H NMR [27] (CDCl_3 , δ , ppm): 1.27 (t, $^3J = 7.6$ Hz, 3H, CH_3), 2.74 (q, $^3J = 7.6$ Hz, 2H, CH_2), 6.32 (s, 5H, C_5H_5); 1.21 (t, $^3J = 7.6$ Hz, 3H, CH_3), 2.61 (q, $^3J = 7.6$ Hz, 2H, CH_2), 6.37 (s, 5H, C_5H_5). ^{13}C NMR (CDCl_3 , δ , ppm): 16.77 (CH_3), 28.04 (CH_2), 113.52 (C_5H_5); 16.86 (CH_3), 29.03 (CH_2), 112.56 (C_5H_5). ^{27}Al NMR (CDCl_3 , δ , ppm): 98 ($\omega_{1/2} = 1823$ Hz).

2.5. Synthesis of $[\text{Cp}(\text{Cl})\text{Al}(\mu\text{-S}^i\text{Pr})_2]$ (4)

The solution of *iso*-propylthiolatodichloroaluminum (2.011 g, 11.6 mmol) in 70 mL of hexane was given to solid CpLi (1.967 g, 27.3 mmol) at ambient temperature. Then the reaction mixture was stirred 6 days. Clear, light yellow solution above white residue was obtained. The solution was taken out and the residue extracted with two portion (50 mL + 50 mL) of hexane. The combined solution was concentrated to ca. 40 mL and crystallized at -15 °C to give product as white solid with 73% yield (1.712 g).

Anal. for $\text{C}_8\text{H}_{12}\text{AlCl}_2\text{S}$, calc. (found): C 47.41% (46.85%), H 5.97% (6.11%), Al 13.31% (14.19%), Cl 17.49% (16.32%). M_w : 399, calculated for dimer 405.4. **4b** ^1H NMR (C_6D_6 , δ , ppm): 1.06 (d, $^3J = 6.6$ Hz, 6H, CH_3), 3.45 (sept, $^3J = 6.6$ Hz, 1H, CH), 6.24 (s, 5H, C_5H_5); (CDCl_3 , δ , ppm) 1.35 (d, $^3J = 6.6$ Hz, 6H, CH_3), 3.46 (sept, 1H, CH), 6.26 (s, 5H, C_5H_5). ^{13}C NMR (C_6D_6 , δ , ppm): 25.72 (CH_3), 41.03 (CH), 113.88 (C_5H_5); (CDCl_3 , δ , ppm): 25.88 (CH_3), 41.03

(CH), 113.56 (C₅H₅). ²⁷Al NMR (C₆D₆, δ, ppm): 97 (ω_{1/2} = 729 Hz); (CDCl₃, δ, ppm): 100 (ω_{1/2} = 1142 Hz).

2.6. Synthesis of [Cp(Cl)Al(μ-SⁱBu)]₂ (5)

The reaction work-up was similar to one described for **4**. CpLi (1.559 g, 21.6 mmol) and of *iso*-butylthiolatodichloroaluminum (1.740 g, 9.3 mmol) were mixed-up together and stirred 3 days to give the product with 65% yield (1.712 g).

Anal. for C₉H₁₄AlCl₂, calc. (found): C 49.88% (50.03%), H 6.51% (6.37%), Al 12.45% (12.24%), Cl 16.36% (15.03%). *M*_w: 441, calculated for dimer 433.4. ¹H NMR (C₆D₆, δ, ppm): 0.76 (d, ³*J* = 6.6 Hz, 6H, CH₃), 1.59 (m, ³*J* = 6.6 Hz, 1H, CH), 2.46 (d, ³*J* = 6.6 Hz, 2H, CH₂), 6.31 (s, 5H, C₅H₅); 0.85 (d, ³*J* = 6.6 Hz, 6H, CH₃), 1.85 (m, 1H, CH), 2.43 (d, ³*J* = 6.6 Hz, 2H, CH₂), 6.30 (s, 5H, C₅H₅); **5c** 0.90 (d, ³*J* = 6.6 Hz, 6H, CH₃), 0.93 (d, ³*J* = 6.6 Hz, 6H, CH₃), 1.85 (m, 2H, CH), 2.48 (dd, 2H, HCH), 2.80 (dd, 2H, HCH), 6.02 (s, 5H, C₅H₅), 6.18 (s, 5H, C₅H₅). ¹³C NMR (C₆D₆, δ, ppm): 21.17 (CH₃), 30.46 (CH), 41.76 (CH₂), 113.94 (C₅H₅); 21.59, 21.74 (CH₃), 30.38, 30.77 (CH), 39.95, 48.55 (CH₂), 113.01, 113.70 (C₅H₅). ²⁷Al NMR (C₆D₆, δ, ppm): 102 (ω_{1/2} = 2111 Hz).

2.7. Synthesis of [Cp(Cl)Al(μ-SⁿBu)]₂ (6)

The reaction work-up was similar to one described for **4**. CpLi (1.599 g, 22.2 mmol) and of *n*-butylthiolatodichloroaluminum (1.638 g, 9.2 mmol) were mixed-up together and stirred 3 days to obtain the product with 69% yield (1.370 g).

Anal. for C₉H₁₄AlCl₂, calc. (found): C 49.88% (49.68%), H 6.51% (6.62%), Al 12.45% (13.16%), Cl 16.36% (15.84%). *M*_w: 424, calculated for dimer 433.4. ¹H NMR (C₆D₆, δ, ppm): 0.72 (t, ³*J* = 7.2 Hz, 3H, CH₃), 1.14 (m, ³*J* = 7.2 Hz, 2H, CH₂), 1.34 (m, ³*J* = 7.2 Hz, 2H, CH₂), 2.67 (t, ³*J* = 7.2 Hz, 2H, CH₂), 6.32 (s, 5H, C₅H₅); **6c** 0.78 (t, ³*J* = 7.2 Hz, 6H, CH₃), 1.10, 1.25 (m, 4H, CH₂), 1.40, 1.60 (m, 4H, CH₂), 2.45 (dt, ²*J* = 12.0 Hz, ³*J* = 7.2 Hz, 2H, HCH), 2.79 (dt, ²*J* = 12.0 Hz, ³*J* = 7.2 Hz, 2H, HCH), 6.03 (s, 5H, C₅H₅), 6.28 (s, 5H, C₅H₅). ¹³C NMR (C₆D₆, δ, ppm): 13.45 (CH₃), 21.64 (CH₂), 33.30 (CH₂), 33.66 (CH₂), 113.91 (C₅H₅); **6c** 13.56 (CH₃), 21.74 (CH₂), 31.46 (CH₂), 33.99 (CH₂), 112.96 (C₅H₅), 113.69 (C₅H₅). ²⁷Al NMR (C₆D₆, δ, ppm): 103 (ω_{1/2} = 2261 Hz).

2.8. X-ray structure determination

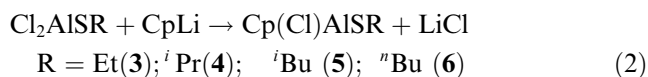
Single crystals of **1** and **4** suitable for X-ray diffraction studies were placed in thin-walled capillaries (Lindemann glass) in an inert atmosphere. The crystallographic data, the summary of data collection and the refinement procedure are presented in Table 1.

In both cases the data were corrected for Lorentz and polarization effects. No absorption correction was applied. The structures were solved by direct methods using SHELXS program [28], completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares method against *F*² (SHELXL [29]). All non-hydrogen atoms were anisotropically refined. The hydrogen atoms were included in calculated positions and refined isotropically except the atoms H(1) and H(6) in **1** and the H(1) atom in **4** where positional parameters were also refined.

3. Results and discussion

3.1. Synthesis

We have found earlier the reaction of series of bis(μ-alkoxy)-dichloroaluminum] complexes with CpNa, at 1:2 molar ratio, respectively, resulted in complete exchange of chlorine for cyclopentadienyl ligands [22,25]. The dicyclopentadienylaluminum thiolates **1–2** were obtained in the analogous reaction with appropriate alkylthiolatodichloroaluminum compounds [Eq. (1)].



The formation of alkylthiolatochlorocyclopentadienylaluminum compounds (**3–6**) exclusively was observed when extent of CpLi was used [Eq. (2)]. The difference in reactivity of pentamethylcyclopentadienyllithium (Cp*Li) and analogous derivatives of the other alkali metals with aluminum compounds was noticed. The reaction of Cp*Li with R₂AlCl gave RAl(Cl)Cp* compounds instead of expected R₂AlCp* [30] while using Cp*K allowed to obtain the R₂AlCp* compounds [31]. We think the difference in reactivity of CpLi in comparison with CpNa results from electronic factors. Both compounds have isomorphous structure [32], however, the cyclopentadienyl-metal bond in CpLi is stronger than in CpNa and CpK, therefore, the nucleophilic ability of Cp⁻ in CpLi is weaker. Our investigations have shown the reaction of CpLi with alkoxydichloroaluminum compounds also leads to partial substitution of chloride by cyclopentadienyl ligands [33].

The formation of compounds **1–6** (Eq. (1)) was affirmed by NMR spectroscopy and elemental analysis (see Section 2). The molar ratio of Cp:SR groups, determined from ¹H NMR spectra was found to be 2:1 for **1–2**, while 1:1 for **3–6**, indicating the formation of Cp₂AlSR and Cp(Cl)AlSR, respectively. The cryoscopic molecular weight measurements show their dimeric

Table 1
Summary of crystal data for compounds **1** and **4**

Compound	1	4
Empirical formula	C ₂₄ H ₃₀ Al ₂ S ₂	C ₁₆ H ₂₄ Al ₂ Cl ₂ S ₂
Formula weight	436.56	405.33
Radiation	Mo K α ($\lambda = 0.71073$ Å), graphite-monochromated	
<i>T</i> (K)	293(2)	100(2)
Crystal system	Triclinic	Tetragonal
Space group	<i>P</i> $\bar{1}$ (No. 2)	<i>I</i> 42 <i>d</i> (No. 122)
<i>Z</i>	1	8
<i>a</i> (Å)	7.7545(8)	11.416(2)
<i>b</i> (Å)	8.7166(7)	11.416(2)
<i>c</i> (Å)	9.6255(8)	31.059(6)
α (°)	103.427(7)	90
β (°)	101.115(8)	90
γ (°)	106.238(8)	90
<i>V</i> (Å ³)	583.99(9)	4048(1)
<i>D</i> _{calc} (Mg m ⁻³)	1.241	1.330
Absorption coefficient (mm ⁻¹)	0.311	0.608
Number of reflections collected	8736	31195
Number of unique reflections (<i>R</i> _{int})	2056 (0.0324)	1791 (0.1279)
Data/restraints/parameters	2056/0/149	1791/0/118
Goodness-of-fit on <i>F</i> ^{2a}	1.084	1.177
Reflections with <i>I</i> > 2 σ (<i>I</i>)	1883	1739
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] ^b	<i>R</i> ₁ = 0.0388, <i>wR</i> ₂ = 0.0847	<i>R</i> ₁ = 0.0345, <i>wR</i> ₂ = 0.0757
<i>R</i> indices (all data) ^b	<i>R</i> ₁ = 0.0430 <i>wR</i> ₂ = 0.0879	<i>R</i> ₁ = 0.0360, <i>wR</i> ₂ = 0.0779
Largest difference peak and hole (e Å ⁻³)	+0.330 and -0.170	+0.291 and -0.284

^a Goodness-of-fit $S = \{[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where *n* is the number of reflections and *p* is the total number of parameters refined.

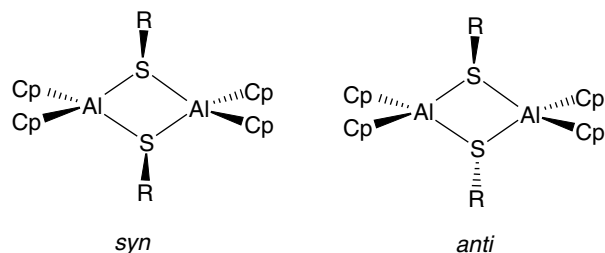
^b $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$, $wR_2 = \{[\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$.

structures (except for **3** which decomposed during crystallization).

3.2. Alkylthiolatodicyclopentadienylaluminum compounds

The ¹H and ¹³C NMR spectra of [Cp₂Al- μ -SEt]₂ (**1**) and [Cp₂Al- μ -S^{*i*}Pr]₂ (**2**) show signal patterns of ethyl and isopropyl groups, respectively, in the high field region and singlets of cyclopentadienyl ligands in the low one. In contrary to alkoxy derivatives, where oxygen atom adopts planar sp² surrounding, the geometry around sulfur bridging atoms in organoaluminum thiolates is clearly pyramidal [7]. This feature leads to formation of *syn*- and *anti*-isomers as depicted on Scheme 1.

The singlet of Cp ligand in the spectra is indicative of the centrosymmetric *anti* isomer. No changes in the character of spectra were observed at temperature lowered up to -50 °C. The *syn* isomer has C₂ symmetry, therefore in that case two signals of Cp ligands should be observed. However, the fast *syn-anti* exchange in NMR time scale for **1** and **2** might be taken into account as well. For example, at ambient temperature in dimeric (μ -alkylthiolato)-dichloroaluminum species we observed *syn-anti* exchange and the presence of both isomers [33]. We think, however, that for bis[(μ -alkylthiolato)-dicyclopentadienylaluminum] compounds the steric hin-



Scheme 1. The *syn*- and *anti*-isomers of [Cp₂Al(μ -SR)]₂.

drance of cyclopentadienyl ligands prevents from dynamic behavior.

Compound **1** crystallizes in triclinic system in *P* $\bar{1}$ space group symmetry. The crystal structure analysis of **1** revealed the presence of thiolato-bridged centrosymmetric dimer, i.e. *anti* isomer (Fig. 1). Selected geometrical data are given in Table 2. The aluminum atom possesses distorted tetrahedral geometry with the small internal S(1)–Al(1)–S(1') angle of 92.31(3)° compensated by angle of 119.7(1)° between cyclopentadienyl ligands. The Al₂(μ -S)₂ central ring is planar with significantly diversified Al–S bond lengths, 2.3251(8) and 2.3597(8) Å. The sulfur atom is clearly pyramidal (sp³) with the S(1) atom moved 0.891(1) Å out of the plane defined by Al(1), Al(1') and C(11) atoms. The angles Cg1–C(1)–Al(1) and Cg2–C(6)–Al(1) (where Cg1 and Cg2 denotes Cp-ring centroids) are equal 107.0(2)° and

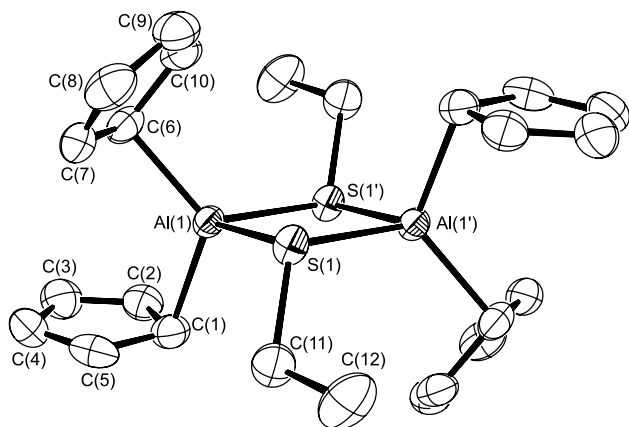


Fig. 1. An ORTEP [37] diagram of $[\text{Cp}_2\text{Al}(\mu\text{-SEt})_2]$ (**1**) showing 50% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 2
Selected structural parameters for compound **1**

Distances (Å)			
Al(1)–S(1)	2.3251(8)	Al(1)···C(2)	2.675(3)
Al(1)–S(1')	2.3597(8)	Al(1)···C(5)	2.708(3)
Al(1)–C(1)	2.012(2)	Al(1)···C(7)	2.682(3)
Al(1)–C(6)	2.004(2)	Al(1)···C(10)	2.687(2)
S(1)–C(11)	1.830(2)		
Angles (°)			
S(1)–Al(1)–S(1')	92.31(3)	C(11)–S(1)–Al(1)	107.27(8)
C(1)–Al(1)–C(6)	119.7(1)	C(11)–S(1)–Al(1')	119.16(8)
C(1)–Al(1)–S(1)	109.60(7)	C(2)–C(1)–Al(1)	100.3(2)
C(6)–Al(1)–S(1)	112.45(7)	C(5)–C(1)–Al(1)	102.2(2)
C(1)–Al(1)–S(1')	99.86(8)	C(7)–C(6)–Al(1)	101.0(2)
C(6)–Al(1)–S(1')	113.55(9)	C(10)–C(6)–Al(1)	101.3(2)
Al(1)–S(1)–Al(1')	87.69(3)		
Torsion angles (°)			
C(2)–C(1)–Al(1)–S(1)	–169.8(1)	C(7)–C(6)–Al(1)–S(1)	–49.0(2)
C(5)–C(1)–Al(1)–S(1)	82.3(2)	C(10)–C(6)–Al(1)–S(1)	59.1(2)
C(2)–C(1)–Al(1)–S(1')	–73.8(2)	C(7)–C(6)–Al(1)–S(1')	–155.3(1)
C(5)–C(1)–Al(1)–S(1')	178.3(2)	C(10)–C(6)–Al(1)–S(1')	–47.2(2)
C(2)–C(1)–Al(1)–C(6)	58.1(2)	C(7)–C(6)–Al(1)–C(1)	81.8(2)
C(5)–C(1)–Al(1)–C(6)	–49.7(2)	C(10)–C(6)–Al(1)–C(1)	170.1(2)

Symmetry transformations used to generate equivalent atoms: 1 – x , 2 – y ,

106.6(2)°, respectively. It shows that both cyclopentadienyl ligands are bonded to the Al atom in $\eta^1(\sigma)$ manner [34], while in the ethoxy derivative $[\text{Cp}_2\text{Al}(\mu\text{-OEt})_2]$ [25] one cyclopentadienyl ligand is $\eta^1(\sigma)$ -bonded and the second one $\eta^1(\pi)$. The $\eta^1(\sigma)$ bond character is also proved by ring-slippage distances [35] equal to 1.760(3) and 1.739(3) Å. The non-bonded Al–C contacts range from 2.68 to 2.71 Å and are so much short that the presence of weak interactions between cyclopentadienyl p-orbitals and the metal center can be assumed. The one cyclopentadienyl is symmetrically positioned towards the central $\text{Al}_2(\mu\text{-S})_2$ ring while the second one is twisted so the C(7) ring atom is located approximately in *trans*

position to the S(1') atom (the appropriate torsion angle C(7)–C(6)–Al(1)–S(1') is equal to $-155.3(1)^\circ$). Therefore, the weak interaction of C(7)···Al causes the lengthening of the *trans*-Al–S(1') bond by 0.035 Å in comparison to Al–S(1) bond. It is indicative of the structural *trans*-effect (*trans*-influence). Similar influence of the Cp orientation on bonds differentiation in the alkoxy or thiolate bridging rings has been also observed by us for other cyclopentadienyl aluminum complexes. This issue will be systematically analyzed and presented separately [36].

The ^{27}Al NMR spectra of **1** and **2** show signals at 116 and 119 ppm, respectively, confirming the presence of four coordinate aluminum atoms in solution. Previously, we have found for (μ -alkoxy)-dicyclopentadienyl-aluminum complexes close relation between ^{27}Al chemical shifts in solution and Cp–Al bond mode in the solid state [25]. Because in the structure of **1** both cyclopentadienyl ligands are $\eta^1(\sigma)$ bonded to aluminum and chemical shifts in **1** and **2** are nearly the same, we suppose that both compounds have the same Cp–Al bond mode.

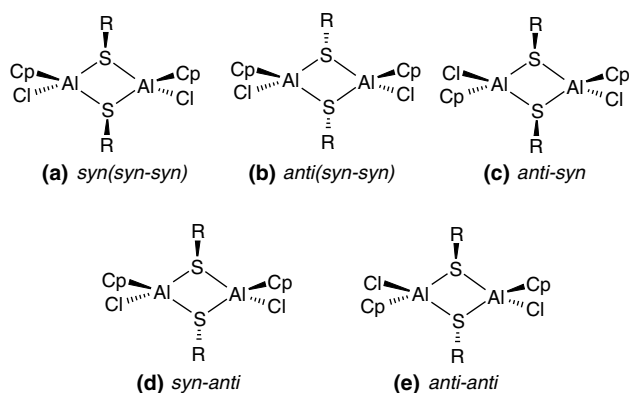
3.3. Alkylthiolatochlorocyclopentadienylaluminum compounds

The pattern of the ^1H and ^{13}C NMR spectra of $[\text{Cp}(\text{Cl})\text{Al}(\mu\text{-SR})_2]$ compounds indicates the presence of geometric isomers. The spectra of the compounds **3–6** show great number of signals of thiolate and Cp groups. However, the integration of the proton signals revealed the 1:1 molar ratios of SR to Cp ligands. One can assume five isomers (Scheme 2) for $[\text{Cp}(\text{Cl})\text{Al}(\mu\text{-SR})_2]$ compounds.

The ^1H NMR spectra of **a**, **b**, **e** isomers have the same character. They show one signal of alkyl group and one signal of cyclopentadienyl ligand. For **e** isomer the methylene protons of the alkyls are diastereotopic. Two singlets of cyclopentadienyl ligands and signals of one alkyl group can be found in ^1H NMR spectrum of **c** isomer and the methylene protons of the alkyls are diastereotopic. The ^1H NMR spectrum of **d** isomer show one singlet of cyclopentadienyl group and signals of two alkyl groups.

The ^1H NMR spectra of reaction mixture containing $[\text{Cp}(\text{Cl})\text{Al}(\mu\text{-SEt})_2]$ (**3**) revealed signal patterns of two isomers at molar ratio 4:1. The character of the spectra exclude **3c** and **3d** isomers. We are not able, however, to assign these signals to proper isomers.

The ^1H and ^{13}C NMR spectra disclose the formation of **4b**. The compound **4** was separated by crystallization and its crystal structure was determined. The X-ray measurements were performed at low temperature because the crystal melted during examination at ambient one. Compound **4** crystallize in $I\bar{4}2d$ space group of tetragonal system. The dimeric molecule of **4** consists of two monomeric

Scheme 2. The postulated isomers of $[\text{Cp}(\text{Cl})\text{Al}(\mu\text{-SR})_2]$ compounds.

species related by crystallographic twofold axis and shows C_2 point group symmetry (Fig. 2).

The aluminum atom exhibits distorted tetrahedral geometry with the largest deviation from ideal geometry being the closure of the internal ring angle $\text{S}(1)\text{--Al}(1)\text{--S}(1')$ to $93.18(4)^\circ$ (Table 3). This is compensated by separating the Cl atom and Cp ligands and thus the $\text{Cl}(1)\text{--Al}(1)\text{--C}(1)$ angle expands to $118.1(1)^\circ$. The $\text{Al}_2(\mu\text{-S})_2$ central bridging ring is bent with the dihedral angle of $23.64(3)^\circ$ between SAIS planes. The geometry around the sulfur atom is clearly pyramidal with S(1) atom perched $0.803(2)$ Å from the plane defined by Al(1), Al(1'), and C(6) atoms. The chlorine atoms and alkyl groups are on the same side of $\text{Al}_2(\mu\text{-S})_2$ central ring thus the molecule adopts *syn-syn* conformation (Fig. 2). This is the first example of *syn* isomer in all structurally characterized dialkylaluminum thiolate complexes [38]. So far the *syn* conformation was only observed for one gallium complex, bis[$(\mu\text{-isopropylthio})\text{-diiodo-gallium}$] [39]. The cyclopentadienyl ligand is $\eta^1(\pi)$ bonded to aluminum atom as the angle $\text{Cg}1\text{--C}(1)\text{--Al}(1)$ and the ring-slippage are equal $95.8(2)^\circ$ and

Table 3

Selected structural parameters for compound **4**

Distances (Å)			
Al(1)–S(1)	2.304(1)	S(1)–C(8)	1.855(3)
Al(1)–S(1')	2.358(1)	Al(1)···C(2)	2.553(4)
Al(1)–C(1)	2.011(4)	Al(1)···C(5)	2.570(4)
Al(1)–Cl(1)	2.132(1)		
Angles ($^\circ$)			
S(1)–Al(1)–S(1')	93.18(4)	Al(1)–S(1)–Al(1')	84.54(4)
C(1)–Al(1)–Cl(1)	118.1(1)	C(8)–S(1)–Al(1)	108.1(1)
C(1)–Al(1)–S(1)	117.6(1)	C(8)–S(1)–Al(1')	107.8(1)
Cl(1)–Al(1)–S(1)	108.24(5)	C(2)–C(1)–Al(1)	93.7(2)
C(1)–Al(1)–S(1')	108.8(1)	C(5)–C(1)–Al(1)	94.6(2)
Cl(1)–Al(1)–S(1')	107.68(5)		
Torsion angles ($^\circ$)			
C(2)–C(1)–Al(1)–Cl(1)	–69.1(2)	C(5)–C(1)–Al(1)–S(1)	–42.9(3)
C(5)–C(1)–Al(1)–Cl(1)	–175.7(2)	C(2)–C(1)–Al(1)–S(1')	167.9(2)
C(2)–C(1)–Al(1)–S(1)	63.7(2)	C(5)–C(1)–Al(1)–S(1')	61.3(2)

Symmetry transformations used to generate equivalent atoms: $x, 1/2 - y, 1/4 - z$.

$1.394(4)$ Å, respectively. Likewise in **1**, short contacts of metal center with C(2) and C(5) atoms are present. The Cp ring is in asymmetrical position to the central core and these weak interactions are in *trans* directions to S(1') and Cl(1) atoms, respectively (the torsion angles $\text{C}(2)\text{--C}(1)\text{--Al}(1)\text{--S}(1')$ and $\text{C}(5)\text{--C}(1)\text{--Al}(1)\text{--Cl}(1)$ are close to 180° , Table 3). It causes the lengthening of Al–S(1') bond of 0.05 Å comparing to Al(1)–S(1) bond alike in case of **1**. The analysis of crystal packing revealed the presence of weak intermolecular interactions of $\text{C--H}\cdots\pi$ type between cyclopentadienyl rings ($\text{H}(1)\cdots\text{Cg}1$ distance of $2.79(1)$ Å, $\text{C}(1)\text{--H}(1)\cdots\text{Cg}1$ angle of $145(1)^\circ$) as shown on Fig. 2. These interactions lead to 3D infinite supramolecular structure.

For compound **5**, based on ^1H NMR spectrum of post-reaction mixture we conclude the presence of three isomers at molar ratio 5:1:1. We were able to assign signal pattern characteristic to **5c** isomer only.

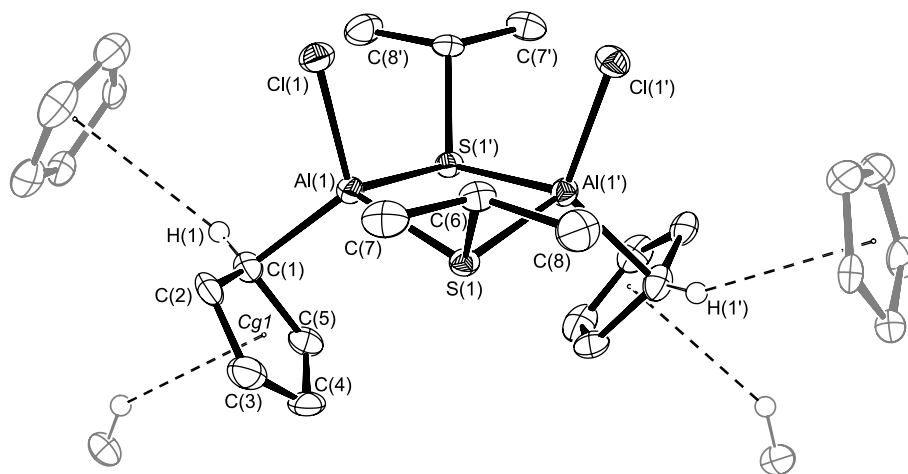


Fig. 2. An ORTEP [37] diagram of $[\text{Cp}(\text{Cl})\text{Al}(\mu\text{-S}^i\text{Pr})_2]$ (**4**) showing 50% probability of thermal ellipsoids. The dashed lines represent $\text{C--H}\cdots\pi$ (Cp) hydrogen bonds. Hydrogen atoms are omitted excluding those involved in the H-bond formation.

The ^1H and ^{13}C NMR spectra of $[\text{Cp}(\text{Cl})\text{Al}(\mu\text{-S}^n\text{Bu})_2]$ **6** recorded from post-reaction mixture, just after synthesis show the formation of two isomers at molar ratio 1:9. The signal pattern of smaller intensities indicates **6c** isomer with characteristic two singlets of cyclopentadienyl ligands and diastereotopic signals of three methylene groups.

The ^{27}Al NMR spectra of **3–6** show chemical shifts in the range 97–103 ppm. It confirms four coordinate aluminum atoms occurrence in the studied compounds. Taking into account the meaningful dependence of aluminum shift from the Cp–Al bonding mode observed in alkoxy derivatives [25], the small differences in chemical shifts of aluminum atoms suggest the presence of $\eta^1(\pi)$ bonds in all examined compounds **3–6**, as was proved for $[\text{Cp}(\text{Cl})\text{Al}(\mu\text{-S}^i\text{Pr})_2]$ **4** by X-ray.

3.4. Discussion

The studies of cyclopentadienylaluminum thiolates show the influence of terminal substituent on bonding mode of cyclopentadienyl ligand to aluminum atom. In $[\text{Cp}_2\text{Al}(\mu\text{-SR})_2]$ compounds both ligands are $\eta^1(\sigma)$ connected to metal center while in $[\text{Cp}(\text{Cl})\text{Al}(\mu\text{-SR})_2]$ ones cyclopentadienyl group is $\eta^1(\pi)$ bonded to aluminum atom. Electronegative chlorine atom in $[\text{Cp}(\text{Cl})\text{Al}(\mu\text{-SR})_2]$, increasing Lewis acidity of metal center, causes stronger donation of cyclopentadienyl ligand electrons to aluminum atom than one in $[\text{Cp}_2\text{Al}(\mu\text{-SR})_2]$. The Al–($\mu\text{-SR}$) bonds are ~ 0.5 Å longer than Al($\mu\text{-OR}$) bonds what causes steric strains weaker in cyclopentadienylaluminum thiolates molecules in comparison to respective alkoxides. Despite the much crowded aluminum atom in aluminum alkoxides than thiolates, one of the cyclopentadienyl rings in $[\text{Cp}_2\text{Al}(\mu\text{-OEt})_2]$ is $\eta^1(\pi)$ connected to aluminum atom but the second one is forced by the ethyl group to have $\eta^1(\sigma)$ CpAl bondage [25], while in $[\text{Cp}_2\text{Al}(\mu\text{-SEt})_2]$ both cyclopentadienyl ligands are $\eta^1(\sigma)$ bonded. Thus more electronegative OR group forces nearer position of cyclopentadienyl ring than SR one. For cyclopentadienylaluminum thiolates alter the thiol order from primary to secondary does not change Cp–Al bond mode while in alkoxy-cyclopentadienylaluminum derivatives the influence of alcohol order was observed [25]. The shorter AlO bond in comparison to AlS one causes proximity and stronger interaction of alkyl group bonded to oxygen on position of cyclopentadienyl ligands. So, further situated alkyl groups in cyclopentadienylaluminum thiolates do not determine the position of cyclopentadienyl ligands.

4. Conclusions

The reactions between Cl_2AlSR and CpLi or CpNa give different products. Use of CpNa reagent leads to

the exchange of both chlorine atoms by cyclopentadienyl ligands, while reaction with CpLi causes the substitution of one chlorine ligand only. We suppose the different reactivity of CpLi in comparison to CpNa results from electronic factors. The synthesized $[\text{Cp}_2\text{Al}(\mu\text{-SR})_2]$ compounds have both cyclopentadienyl rings $\eta^1(\sigma)$ bonded to aluminum atom, while $[\text{Cp}(\text{Cl})\text{Al}(\mu\text{-SR})_2]$ ones $\eta^1(\pi)$. Increasing of covalent radii and change of hybridization of sulfur atom in comparison to oxygen atom in alkoxide analogues, cause decreasing influence of steric factors introduced by SR alkyl groups on molecular structure, particularly on Cp–Al bond mode. However, the comprehensive analysis of the coordination sphere geometry of aluminum showed that the additional weak interactions between carbon atoms of Cp ligands and the metal center are responsible for the symmetry of the $\text{Al}_2(\mu\text{-S})_2$ central bridging ring.

5. Supplementary material

Listings of crystal and refinement data, atomic coordinates, bond distances and angles, thermal parameters for compounds **1** and **4** are available from Cambridge Crystallographic Data Centre, CCDC Nos. 236869 and 236870, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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