Cyclopentadienylaluminum donor–acceptor complexes – Molecular and supramolecular structure

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Abstract

Lewis acid–base complexes of cyclopentadienylaluminum derivatives Me_xCp_{3-x} Al ($x = 0–2$) and trimethylaluminum with selected aromatic amines (L): dmap = 4-dimethylaminopyridine, py–Me = 4-methylpyridyne, were synthesized and characterized by ^{1}H, ^{13}C, ^{27}Al NMR: $Cp_3Al \cdot dmap$ (**1**), $Cp_3Al \cdot py–Me$ (**2**), $MeCp_2Al \cdot dmap$ (**3**), $MeCp_2Al \cdot py–Me$ (**4**), $Me_2CpAl \cdot dmap$ (**5**), $Me_2CpAl \cdot py–Me$ (**6**), $Me_3Al \cdot py–Me$ (**7**). ^{1}H NMR studies of **3**–**6** revealed small amounts of the ligand redistribution products. The crystal structures of **1**, **2** and **3** were determined by single X-ray diffraction studies. The compounds **1**, **2** and **3** are monomeric with Cp ligands bonded to the aluminum center in $\eta^1(\sigma)$, $\eta^1(\pi)$ manner. The change of Cp–Al bond character from $\eta^1(\pi)$ to $\eta^1(\sigma)$ was found to reasonable correlate with the aromaticity of Cp^- ligand described by HOMA index. Analysis of close intra- and intermolecular contacts showed presence of $CH \cdots \pi$ interactions leading to the formation of 2-D supramolecular networks. It was found that these interactions impact on the coordination sphere of aluminum and the conformation of Cp ring.
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1. Introduction

Despite the fact that cyclopentadienylaluminum compounds have been under investigation for many years [1,2] very few cyclopentadienylaluminum complexes with Lewis bases have been described [3–5]. To the best of our knowledge only one crystal structure of a donor–acceptor compound, $Cp_3Al \cdot CN^tBu$, containing unsubstituted Cp ligand was determined so far. The examples of organoaluminum donor–acceptor complexes with pentamethylcyclopentadienyl (Cp^*) ligand are also scant [5–7]. Unlike d- and f-block metals, the cyclopentadienyl compounds of the main group metals, especially aluminum, in the absence of accessible d valence orbitals display high flexibility in Cp-ring coordination as a result of the small energy barrier between different haptotropes ($\eta^1 \leftrightarrow \eta^5$). It has been reported that the bonding mode of Cp–Al strongly depends

on steric and electronic factors introduced by other ligands bonded to the metal center [2]. Thus the changes in the metal surrounding should be reflected in the bonding mode of Cp–Al providing additional information about the character of the metal center, particularly its acidity.

Nevertheless, one can remember that the shape of compounds in the solid state strongly depends on the weak molecular forces. The electronic structure of Cp ligands makes these rings serving simultaneously as potential CH donors and acceptors in weak $CH \cdots \pi$ interactions. The role of this bonds between soft acids CH and soft base π systems such as cyclopentadienyl and pyridyne ring was for example reviewed recently by Nishio [8] and its statistical evaluation for transition metal compounds was presented by Braga et al. [9].

In the last few years we have synthesized and structurally evaluated many cyclopentadienylaluminum derivatives. Continuing this interest we have investigated cyclopentadienylaluminum adducts with aromatic amines to characterize the factors determining the structure of

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the aluminum coordination sphere, particularly the Cp-ring coordination mode. On the other hand, the reactivity of Group 13 metals derivatives towards amines to form donor–acceptor adducts is especially interesting due to possible material science applications of products [10].

Herein, we describe the series of seven novel donor–acceptor complexes formed by Cp_3Al, $MeCp_2Al$, Me_2CpAl and Me_3Al and obtained in reactions with aromatic amines: 4-dimethylaminopyridyne (dmap) and 4-methyl-pyridyne (py–Me). The properties of the **1**–**7** complexes in solution were analyzed according to the NMR spectra. The crystal structures of three of them (**1**–**3**) were determined by single crystal X-ray diffraction studies. The comprehensive analysis of structural parameters with special emphasis on the Cp-ring aromaticity and the Cp–Al bond mode was performed. Examination of intra- and intermolecular contacts allowed to determine the supramolecular structure and to show for the first time the role of CH···π interactions in cyclopentadienylaluminum compounds.

2. Experimental

2.1. General remarks

All synthesized compounds **1**–**7** are air and moisture sensitive. They were prepared and manipulated under an argon atmosphere using standard Schlenk techniques. Solvent was distilled over potassium benzophenone ketyl. $MeCl_2Al$ (as 1.0 M solution in hexane), Me_2ClAl, Me_3Al, 4-dimethylaminopyridine were purchased from Aldrich and used without further purification. 4-Methylpyridine (Aldrich) was distilled under argon over dry molecular sieves (4 Å) before use. Aluminum trichloride (Aldrich) was sublimed before use. CpNa was synthesized in the reaction of freshly distilled cyclopentadiene with sodium in xylene. Cp_3Al was synthesized by the modification of method given in the literature [11] from $AlCl_3$ and NaCp (molar ratio 1:3.6) in toluene reflux for 2 days. Purity of Cp_3Al was confirmed by NMR [12]. $MeCp_2Al$ and Me_2CpAl were prepared from $MeCl_2Al$, Me_2ClAl and CpNa in toluene. NMR spectra were recorded on Varian-Mercury (^{1}H – 400.09 MHz, ^{13}C – 100.60 MHz, ^{27}Al – 104.25 MHz) using d_6-benzene solutions. All chemical shifts are reported in ppm and referenced to solvent (^{1}H, ^{13}C) or $Al(OH)_6^{3+}$ (^{27}Al, external reference, $\delta = 0.0$ ppm).

2.2. Synthesis of $Cp_3Al \cdot dmap$ (1)

A solution of dmap (0.30 g, 2.5 mmol) in toluene was added by syringe to a stirred solution of Cp_3Al (0.55 g, 2.5 mmol) in 50 ml of toluene cooled at −20 °C. The reaction mixture was warmed to room temperature and stirred for additional 1 h, then concentrated to approximately 20 ml and left to crystallize at −5 °C. Slightly orange crystals of **1** were obtained with 67% yield (0.57 g). ^{1}H NMR (C_6D_6): δ 1.79 (s, 6H, NMe_2), 5.29 (m, 2H, C(3)–H), 6.38 (s, 15H, Cp), 7.15 (m, 2H, C(2)–H). ^{13}C NMR (C_6D_6): δ 38.0 (NMe_2), 105.0 (C(3)), 114.0 (Cp), 145.9 (C(2)), 155.1 (C(4)). ^{27}Al NMR (C_6D_6): δ 122.2 ($\omega_{1/2} = 1424$ Hz). Anal. Calc. for $C_{22}H_{25}AlN_2$: C, 76.72; H, 7.32; Al, 7.83. Found: C, 76.02; H, 7.11; Al, 7.42%.

2.3. Synthesis of $Cp_3Al \cdot py–Me$ (2)

A solution of py–Me (0.24 ml, 2.5 mmol) was added by syringe to a stirred solution of Cp_3Al (0.55 g, 2.5 mmol) in 50 ml of toluene cooled at −20 °C. The reaction mixture was warmed to room temperature and stirred for additional 1 h, then concentrated to approximately 40 ml and left to crystallize at −5 °C. Colorless crystals of **2** were obtained with 80% yield (0.62 g). ^{1}H NMR (C_6D_6): δ 1.36 (s, 3H, Me), 5.96 (m, 2H, C(3)–H), 6.25 (s, 15H, Cp), 7.16 (m, 2H, C(2)–H). ^{13}C NMR (C_6D_6): δ 20.7 (Me), 114.1 (Cp), 124.1 (C(3)), 146.3 (C(4)), 153.8 (C(2)). ^{27}Al NMR (C_6D_6): δ 122.6 ($\omega_{1/2} = 1337$ Hz). Anal. Calc. for $C_{21}H_{22}AlN$: C, 79.97; H, 7.03; Al, 8.55. Found: C, 78.94; H, 6.98; Al, 8.32%.

2.4. Synthesis of $MeCp_2Al \cdot dmap$ (3)

The compound **3** was prepared by a method analogous to that for compound **1** using $MeCp_2Al$ (0.44 g, 2.6 mmol) and dmap (0.31 g, 2.6 mmol). The product **3** crystallized from toluene at −5 °C as a colorless solid. Yield 62% (0.47 g). ^{1}H NMR (C_6D_6): δ −0.64 (s, 3H, AlMe), 1.86 (s, 6H, NMe_2), 5.38 (m, 2H, C(3)–H), 6.46 (s, 10H, Cp), 7.45 (m, 2H, C(2)–H). ^{13}C NMR (C_6D_6): δ −13.5 (AlMe), 38.0 (NMe_2), 105.2 (C(3)), 113.2 (Cp), 146.0 (C(2)), 154.9 (C(4)). ^{27}Al NMR (C_6D_6): δ 119.8 ($\omega_{1/2} = 7624$ Hz). The sample reveals peaks due to contamination by ca. 10% **1** and ca. 10% **5**. Anal. Calc. for $C_{18}H_{23}AlN_2$: C, 73.44; H, 7.88; Al, 9.17. Found: C, 73.21; H, 7.63; Al, 9.08%.

2.5. Synthesis of $MeCp_2Al \cdot py–Me$ (4)

The compound **4** was prepared by a method analogous to that for compound **2** using $MeCp_2Al$ (0.44 g, 2.6 mmol) and py–Me (0.25 ml, 2.6 mmol). The product **4** crystallized from toluene at −5 °C as a colorless solid. Several attempts to obtain crystals of **4** suitable for X-ray study failed. Yield 54% (0.37 g). ^{1}H NMR (C_6D_6): δ −0.74 (s, 3H, AlMe), 1.47 (s, 3H, Me), 6.10 (m, 2H, C(3)–H), 6.32 (s, 10H, Cp), 7.58 (m, 2H, C(2)–H). ^{13}C NMR (C_6D_6): δ −13.5 (AlMe), 20.7 (Me), 113.2 (Cp), 124.7 (C(3)), 146.2 (C(4)), 152.9 (C(2)). ^{27}Al NMR (C_6D_6): δ 132.1 ($\omega_{1/2} = 7242$ Hz). The sample reveals peaks due to contamination by ca. 5% **2** and ca. 5% **6**. Anal. Calc. for $C_{17}H_{20}AlN$: C, 76.95; H, 7.60; Al, 10.17. Found: C, 76.34; H, 7.11; Al, 10.27%.

2.6. Synthesis of $Me_2CpAl \cdot dmap$ (5)

A solution of dmap (0.22 g, 1.8 mmol) in toluene was added by syringe to a stirred solution of Me_2CpAl (0.25 g, 1.8 mmol) in 50 ml of toluene cooled at −20 °C.

The reaction mixture was warmed to room temperature and stirred for additional 1 h. Then the solvent was evaporated to give yellow oil. The quantitative yield was 0.47 g. ^{1}H NMR (C_6D_6): δ −0.32 (s, 6H, AlMe$_2$), 1.97 (s, 6H, NMe$_2$), 5.52 (m, 2H, C(3)–H), 6.37 (s, 5H, Cp), 7.68 (m, 2H, C(2)–H). ^{13}C NMR (C_6D_6): δ −9.4 (AlMe$_2$), 38.1 (NMe$_2$), 105.9 (C(3)), 112.5 (Cp), 146.0 (C(2)), 155.1 (C(4)). ^{27}Al NMR (C_6D_6): δ 148.6 ($\omega_{1/2} = 6984$ Hz). The sample reveals peaks due to contamination by ca. 10% **3** and ca. 10% Me$_3$Al(dmap) [13]. Anal. Calc. for C$_{15}$H$_{24}$AlN$_2$: C, 69.47; H, 9.33; Al, 10.40. Found: C, 69.12; H, 9.03; Al, 10.14%.

2.7. Synthesis of Me$_2$CpAl · py–Me (6)

A solution of py–Me (0.18 ml, 1.8 mmol) was added by syringe to a stirred solution of Me$_2$CpAl (0.25 g, 1.8 mmol) in 50 ml of toluene cooled at −20 °C. The reaction mixture was warmed to room temperature and stirred for additional 1 h. Then the solvent was evaporated to give yellow oil. The quantitative yield was 0.42 g. ^{1}H NMR (C_6D_6): δ −0.35 (s, 6H, AlMe$_2$), 1.46 (s, 3H, Me), 6.12 (m, 2H, C(3)–H), 6.38 (s, 5H, Cp), 7.79 (m, 2H, C(2)–H). ^{13}C NMR (C_6D_6): δ −9.3 (AlMe$_2$), 20.6 (Me), 112.4 (Cp), 125.1 (C(3)), 146.4 (C(4)), 152.7 (C(2)). ^{27}Al NMR (C_6D_6): δ 154.4 ($\omega_{1/2} = 6898$ Hz). The sample reveals peaks due to contamination by ca. 10% **4** and ca. 10% **7**. Anal. Calc. for C$_{14}$H$_{21}$AlN: C, 73.01; H, 9.19; Al, 11.72. Found: C, 72.32; H, 8.94; Al, 11.20%.

2.8. Synthesis of Me$_3$Al · py–Me (7)

A solution of py–Me (0.20 ml, 2.0 mmol) was added by syringe to a stirred solution of Me$_3$Al (0.14 g, 2.0 mmol) in 20 ml of toluene cooled at −20 °C. The reaction mixture was warmed to room temperature and stirred for additional 1 h. Then the solvent was evaporated to give a white solid. The quantitative yield was 0.33 g. ^{1}H NMR (C_6D_6): δ −0.17 (s, 6H, AlMe$_3$), 1.50 (s, 3H, Me), 6.18 (m, 2H, C(3)–H), 8.03 (m, 2H, C(2)–H). ^{13}C NMR (C_6D_6): δ −7.7 (AlMe$_3$), 20.6 (Me), 125.8 (C(3)), 146.4 (C(4)), 152.8 (C(2)). ^{27}Al NMR (C_6D_6): δ 169.1 ($\omega_{1/2} = 6476$ Hz). Anal. Calc. for C$_9$H$_{16}$AlN: C, 65.43; H, 9.76; Al, 16.33. Found: C, 64.92; H, 9.21; Al, 15.97%.

2.9. Synthesis of Me$_3$Al · dmap (8)

The synthesis was carried out according to procedure described previously [13]. Obtained ^{1}H NMR and ^{13}C NMR spectra were consistent with the literature data. ^{27}Al NMR (C_6D_6): δ 171.8 ($\omega_{1/2} = 6296$ Hz).

2.10. X-ray structure determination

Single crystals of **1–3** were placed in thin-walled capillaries (Lindemann glass) in an inert atmosphere. It should be mentioned that several crystallizations of **1** gave weakly diffracting, low quality crystals. The measurements were performed on a Kuma KM4CCD κ-axis diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 173(2) K. The measured intensities were processed with the Lorentz and polarization effects and crystal decomposition. To improve the data for **1** the absorption correction based on symmetry-related intensities was also applied. The structures were solved by direct methods using the SHELXS-97 program [14], and refined by the full-matrix least-squares method against F^2 (SHELXL-97) [15]. In all cases all non-hydrogen atoms were anisotropically refined. The positions and isotropic displacement parameters of H atoms attached to cyclopentadienyl C(1), C(6) and C(11) atoms were refined freely with U_{iso}(H) = 1.2 × [U_{eq}(C)]. The remaining H atoms were positioned geometrically and refined using a riding model with U_{iso}(H) = 1.2 × [U_{eq}(C)] or 1.5 × [U_{eq}(C)] in the case of Me groups. The methyl groups bonded to pyridine ring in **2** and bonded to the Al atom in **3** were modeled as an idealized disordered rotating groups with refined occupancy factors for the major conformer of 0.69(2) and 0.78(2), respectively. The crystal and structure refinement details are presented in Table 1. The geometrical parameters for structural analysis were calculated using the Platon package [16].

2.11. Cambridge structural database search

The collections of structural data were obtained through systematic searches of the 5.26 version (October 2004) of the Cambridge Structural Database (CSD) using CCDC software [17]. The searches were performed for: (i) four-coordinate aluminum complexes comprising unsubstituted Cp ligand(s), (ii) ionic compounds with uncomplexed Cp$^-$ anion. The resulting subsets were sorted and investigated manually. Subsequently, entries showing the following characteristics: the R factor greater than 0.08, an error flag, low bond precision (σ_{C-C} greater than 0.005 Å), and disorder in the Cp region were rejected. The geometrical parameters were extracted using CONQUEST. Details concerning data retrieval from CSD files, list of CSD refcodes with references, selected geometrical parameters are listed in Supporting information.

3. Results and discussion

3.1. Synthesis, solution properties and NMR analysis

The used cyclopentadienylaluminum derivatives Cp$_3$Al, MeCp$_2$Al, and MeCp$_2$Al were obtained in reactions between sodium cyclopentadienine salt and chloroaluminum compounds according to Eq. (1) [18]

$$Me_xCl_{3-x}Al + (3x)NaCp \rightarrow Me_xCp_{3-x}Al + (3x)NaCl \quad (1)$$
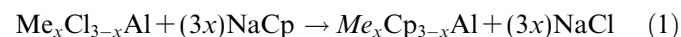
The studied Lewis acid–base complexes **1–8** are formed in the reaction of aluminum alkyls with pyridine derivatives

Table 1
Crystal data, data collection and refinement parameters for compounds **1**–**3**

Compound	**1**	**2**	**3**
Empirical formula	$C_{22}H_{25}AlN_2$	$C_{21}H_{22}AlN$	$C_{18}H_{23}AlN_2$
Formula weight	344.42	315.38	294.36
Radiation	Mo Kα ($\lambda = 0.71073$ Å), graphite-monochromated		
Temperature (K)	173(2)	173(2)	173(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
Z	4	4	2
a (Å)	10.6073(10)	11.803(2)	8.6154(7)
b (Å)	12.6118(10)	8.7530(18)	9.3827(10)
c (Å)	14.6498(12)	17.699(4)	10.4794(9)
α (°)	90	90	95.990(8)
β (°)	109.118(8)	107.92(3)	91.735(7)
γ (°)	90	90	91.820(7)
Volume (Å³)	1851.7(3)	1739.8(7)	841.58(13)
Calculated density (Mg m⁻³)	1.235	1.204	1.162
Absorption coefficient (mm⁻¹)	0.116	0.116	0.116
Reflections collected	14,457	25,824	10,541
Unique reflections, (R_{int})	2723 (0.0547)	3053 (0.0702)	2955 (0.0385)
Data/restraints/parameters	2723/0/237	3053/0/220	2955/0/201
Goodness-of-fit on F^2[a]	1.122	1.115	1.140
Reflections with $I > 2\sigma(I)$	2147	2651	2569
Final R indices ($I > 2\sigma(I)$)[b]	$R_1 = 0.0632$, $wR_2 = 0.1663$	$R_1 = 0.0468$, $wR_2 = 0.1136$	$R_1 = 0.0470$, $wR_2 = 0.0945$
R indices (all data)[b]	$R_1 = 0.0789$, $wR_2 = 0.1836$	$R_1 = 0.0579$, $wR_2 = 0.1218$	$R_1 = 0.0582$, $wR_2 = 0.1005$
Largest difference in peak and hole (e Å⁻³)	+0.566 and −0.388	+0.286 and −0.281	+0.193 and −0.198

[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] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_c|$, $wR_2 = \left\{ \sum \left[w(F_o^2 - F_c^2)^2 \right] \middle/ \sum \left[w(F_o^2)^2 \right] \right\}^{1/2}$.
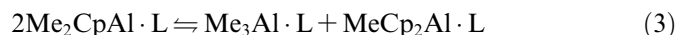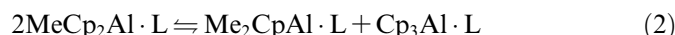
in 1:1 molar ratio (Scheme 1). We chose two simple aromatic amines with comparable steric demands and different basicity which is indicated by pK_a values for Hdmap⁺ and Hpy–Me⁺ of 10.1 and 6.3, respectively [19]. The advantage of using dmap is the fact that its several adducts with aluminum derivatives such as Me_3Al, $^tBu_3Al$, and Cl_3Al were previously structurally characterized [13] and their structures could be compared with the series of presented complexes. The synthesis of adduct **8** was performed to complete the ²⁷Al NMR data, despite it was previously structurally characterized by Schulz et al. [13].

The formation of the adducts **1**–**8** was confirmed by NMR analysis. It should be noted that in the case of all
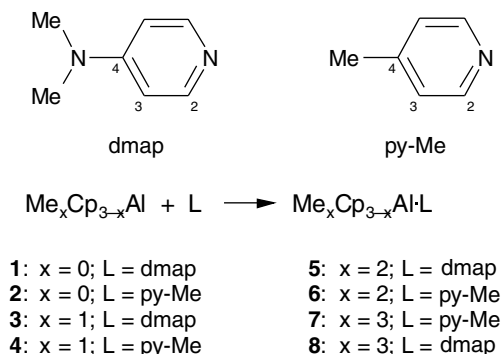
studied cyclopentadienyl derivatives in ¹H, ¹³C NMR spectra Cp hydrogen atoms and carbons atoms appear as a single resonance line as a result of rapid (in the NMR timescale) rotation of the Cp ring on Al atom; this is consistent with the calculated low energy barrier for 1,2-migration of the metal center about Cp ring [2,12,20]. The ¹H, ¹³C NMR spectra of **1**, **2** show signal patterns characteristic for the appropriate amine (dmap or py–Me), and single resonance for Cp ligand bonded to the Al atom. We have found that, in the presence of the studied Lewis bases, compounds $MeCp_2Al$ and Me_2CpAl undergo a partial redistribution reaction according to the equilibria shown in Eqs. (2) and (3)

$$2MeCp_2Al \cdot L \rightleftharpoons Me_2CpAl \cdot L + Cp_3Al \cdot L \qquad (2)$$

$$2Me_2CpAl \cdot L \rightleftharpoons Me_3Al \cdot L + MeCp_2Al \cdot L \qquad (3)$$

Therefore, except of signals for $MeCp_2Al \cdot L$ in the samples of **3**, **4** minor amounts of the ligand redistribution species: $Me_2CpAl \cdot L$ and $Cp_3Al \cdot L$ were observed. The same was observed for adducts **5** and **6**, where approximately 10% of $MeCp_2Al$ and Me_3Al was found. These results are in agreement with the well-known feature of organoaluminum compounds undergoing ligand redistribution reactions in the presence of Lewis bases [21]. For cyclopentadienylmethylaluminum derivatives the ligand redistribution by $MeCp_2Al \cdot L$ to form $Cp_3Al \cdot L$ and $Me_2CpAl \cdot L$ in the presence of ^tBuNC, ^tBuCN, THF

Scheme 1.

1: x = 0; L = dmap
2: x = 0; L = py-Me
3: x = 1; L = dmap
4: x = 1; L = py-Me
5: x = 2; L = dmap
6: x = 2; L = py-Me
7: x = 3; L = py-Me
8: x = 3; L = dmap

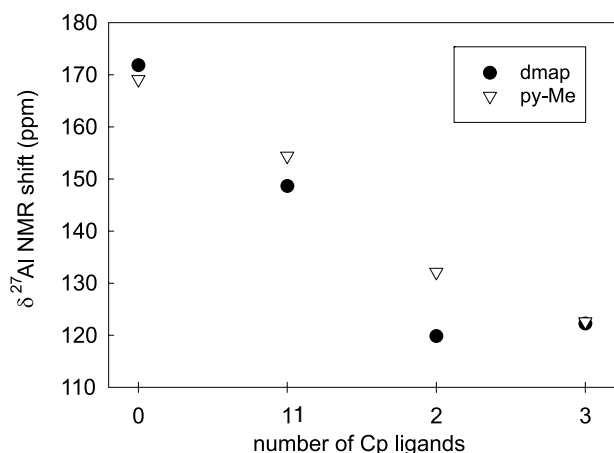$Me_xCp_{3-x}Al + L \longrightarrow Me_xCp_{3-x}Al \cdot L$

Fig. 1. ^{27}Al NMR chemical shift for complexes **1**–**8** as a function of the number of Cp ligands.

and Et$_2$O was reported [3] and analogous behavior for Me$_2$CpAl in THF was also described [22]. It should be emphasized that the uncomplexed MeCp$_2$Al does not redistribute at ambient conditions [3].

All studied compounds **1**–**8** show signal characteristic for four-coordinated Al atom in ^{27}Al NMR consistent with their monomeric structure. We observed that the order of increasing of chemical shift in ^{27}Al NMR is Cp$_3$Al · L <MeCp$_2$Al · L<Me$_2$CpAl · L<Me$_3$Al · L, with exception of **3**, for which the signal at almost the same chemical shift as for **1** was detected (Fig. 1). It shows that the shielding effect of Cp ring is usually stronger than of Me group bonded to the aluminum center and confirms our earlier results where for cyclopentadienylaluminum alkoxides the change of Cp ring on Me group on going from [Cp$_2$Al-μ-OR]$_2$ to [Cp(Me)Al-μ-OR]$_2$, where R = Me, Et, CH$_2^t$Bu,

^{t}Bu, resulted in increase of chemical shift approximately 10 ppm in ^{27}Al NMR [11,23].

3.2. Molecular and crystal structure

The molecular structures of **1**, **2** and **3** are shown in Fig. 2, and selected bond lengths and angles are collected in Table 2. In all compounds the cyclopentadienyl ligands are η^1 bonded to aluminum and the central C$_3$AlN core exhibits slightly distorted tetrahedral geometry. For the detailed discussion of geometrical features in these complexes it is convenient to define a center of gravity of the Cp ring (*Cg*) and use additional parameters such as the distance between *Cg* and perpendicular projection of Al on mean Cp plane, called the ring-slippage. In all compounds one of the Cp rings (denoted as Cp1) is oriented in unique manner and it is directed over the Al–N bond what can be illustrated by the values of *Cg*1–C(1)–Al(1)–N(1) torsion angles equal to 0.4, 12.2 and −0.8° for **1**, **2** and **3**, respectively. Further, the Cp2 rings are directed outwards (*Cg*2–C6–Al1–N1 torsion angles are close to 120°) and show the lowest ring slippages. In **1** and **2** the distinctly highest slippages (greater than 2 Å) show the Cp3 rings and simultaneously they display significantly different orientation in the coordination sphere, i.e. *Cg*3–C11–Al1–N1 torsion angles are 100.5° and 31.5°, respectively. The observed conformation of Cp rings in **1** and **2** is totally different from the reported previously symmetrical structure of Cp$_3$Al · CN^{t}Bu adduct [3] where Cp rings are symmetry related by threefold axis and the relevant torsion *Cg*–C$_{Cp}$–Al–C angle and the ring-slippage are equal to 104.8° and 1.818 Å, respectively.

The Al–N bond length for **1** is 1.951(2) Å and it is 0.05 Å longer than in analogous AlCl$_3$ adduct and 0.04 Å shorter
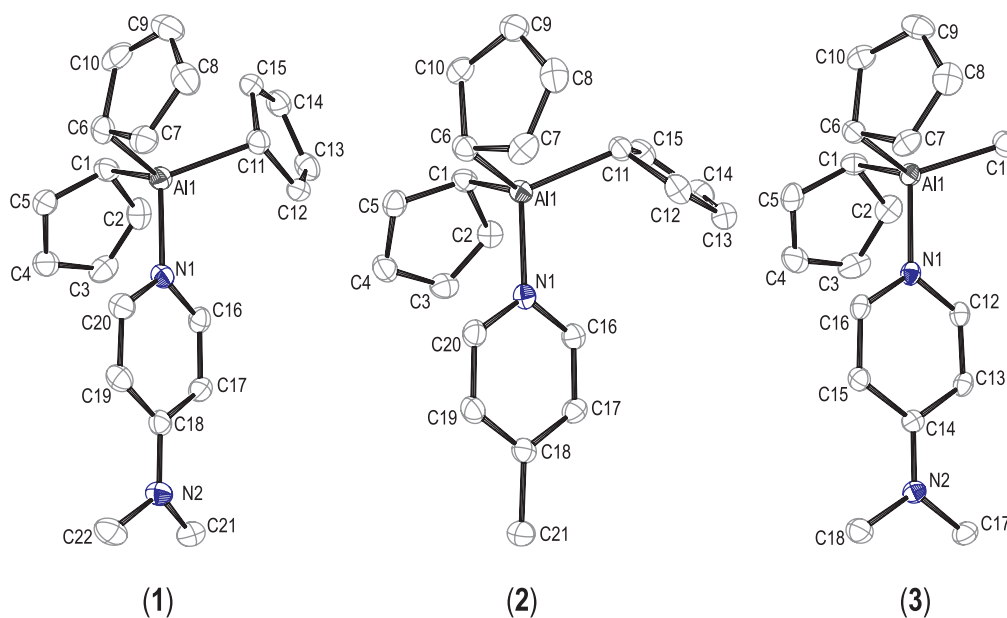

Fig. 2. A view of the molecular structures of complexes **1**–**3** with the atom numbering schemes, showing the differences in their conformations. Displacement ellipsoids are drawn at the 50% probability level and H-atoms are omitted for clarity.

Table 2
Selected bond lengths and valence and torsion angles for **1**–**3**

	1	2	3
Bond lengths (Å)			
Al(1)–N(1)	1.951(3)	1.9531(17)	1.9484(17)
Al(1)–C(1)	2.045(3)	2.040(2)	2.066(2)
Al(1)–C(6)	2.064(3)	2.051(2)	2.080(2)
Al(1)–C(11)	2.047(3)	2.020(2)	1.964(2)
C(1)–C(2)	1.448(5)	1.456(3)	1.448(3)
C(1)–C(5)	1.450(4)	1.454(3)	1.446(3)
C(2)–C(3)	1.370(5)	1.359(3)	1.366(3)
C(3)–C(4)	1.423(5)	1.425(3)	1.415(3)
C(4)–C(5)	1.361(4)	1.361(3)	1.369(3)
C(6)–C(7)	1.448(5)	1.453(3)	1.447(3)
C(6)–C(10)	1.460(3)	1.450(3)	1.451(3)
C(7)–C(8)	1.358(4)	1.364(3)	1.374(3)
C(8)–C(9)	1.407(5)	1.424(3)	1.420(3)
C(9)–C(10)	1.364(5)	1.362(3)	1.371(3)
C(11)–C(12)	1.450(4)	1.465(3)	–
C(11)–C(15)	1.464(4)	1.469(3)	–
C(12)–C(13)	1.357(4)	1.353(3)	–
C(13)–C(14)	1.430(5)	1.437(3)	–
C(14)–C(15)	1.356(4)	1.354(3)	–
Bond angles (°)			
N(1)–Al(1)–C(1)	106.90(12)	106.13(8)	106.25(8)
N(1)–Al(1)–C(6)	105.55(12)	103.72(8)	102.25(7)
N(1)–Al(1)–C(11)	109.48(11)	111.85(8)	108.51(8)
C(1)–Al(1)–C(11)	115.46(14)	111.35(9)	111.84(9)
C(1)–Al(1)–C(6)	107.13(14)	112.02(8)	109.28(8)
C(11)–Al(1)–C(6)	111.76(13)	111.41(8)	117.70(9)
Torsion angles (°)			
N(1)–Al(1)–C(1)–C(2)	−54.7(2)	−42.68(15)	−54.51(14)
N(1)–Al(1)–C(6)–C(7)	63.4(2)	76.15(14)	69.59(13)
N(1)–Al(1)–C(11)–C(12)	43.9(2)	−26.95(17)	–

HOMA= 0.97   0.8 > HOMA> 0.1   HOMA= −0.70

Cp⁻   Cp–Al   CpH

Scheme 2.

than in AlMe₃ one [13]. One can assume that the Cp₃Al moiety shows intermediate acidity, i.e. lower than AlCl₃ and higher than AlMe₃. As a consequence, one can expect that a stepwise exchange of Cp ligands by Me groups should cause the lowering of the aluminum center acidity and the elongation of Al–N bond. On the other hand a similar geometrical effect (Al–N bond elongation) should be observed when decreasing the N-donor basicity as evidenced, in series of AlCl₃ adducts with pyridine derivatives dmap (pK_a 10.1) [19], 2-methylpyridyne (pK_a 6.0) [24] and quinoline (pK_a 4.9) [24] where the Al–N bond lengths change from 1.900(5) to 1.942(4) and to 1.956(4) Å, respectively [13,25]. Unexpectedly, in all studied compounds the donor–acceptor bond lengths are the same within the 3σ despite the lowering of N-donor basicity on going from **1** to **2**, or the replacement of Cp by Me comparing **1** and **3**. Consequently, these changes in Al³⁺ environment are reflected in the region of cyclopentadienyl ligands influencing their bonding mode. The change of Cp–Al bond character from η¹(π) to η¹(σ), described by ring-slippage, causes subtle changes of the ligand geometry, i.e. its electronic structure, which is also closely connected with the degree of π-electron donation from Cp⁻ to Al³⁺. Because the π-electrons are also responsible for the aromatic character of Cp⁻, the variation of ligand aromaticity should be observed (Scheme 2).
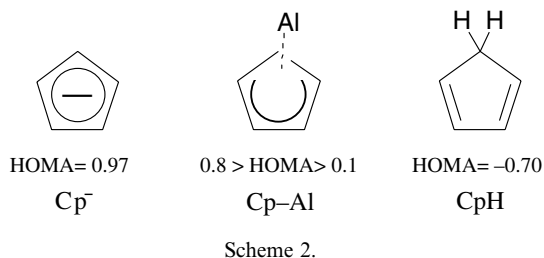
To describe the electronic changes correlated with C–C bond length changes in Cp⁻ ligands, one of the numerous aromaticity indices can be chosen. The geometric HOMA index based on C–C bond length [26] appeared to be the most appropriate for the studied problem, particularly to the results showing the alteration of aromaticity of cyclopentadienyl moieties in different chemical environments [27]. The HOMA index was calculated according to the equation [26]:

$$\text{HOMA} = 1 - \frac{\alpha}{n} \sum_i^n (R_{opt} - R_i)^2$$

where R_i are individual bond lengths taken into the summation, R_{opt} is a optimal value of bond length (Å), assumed to be realized for full aromatic systems (for CC bonds R_{opt} is equal to 1.388 Å), α is a normalization (empirical) constant (for CC bonds $\alpha = 257.7$).

The results for compounds **1**–**3** were gathered with the structural data for other, four-coordinated aluminum complexes to analyze how the acidity of the coordination center influence the differentiation of electronic structure of the ligands exhibiting aromatic character. The structural data were taken from the Cambridge Structural Database [17] and additionally from our recently obtained results [28]. Subsequently, we calculated the HOMA indices for cyclopentadienyl rings in complexes where Cp ligand is η¹ bonded to the aluminum. Among others we found a reasonable correlation between HOMA and the ring-slippage parameter as it is depicted in Fig. 3. The correlation coefficient between these two parameters is equal 0.64. HOMA indices change from 0.8 to 0.1 whereas the slippage increase from 1.2 [η¹(π)] to 2.5 Å [η¹(σ)]. It is worth noting that the lowest aromaticity (HOMA = 0.11) exhibits the Cp3 ring in compound **2**. For comparison, the mean HOMA index for Cp⁻ anion in series of ionic compounds with relatively bulky counter-ions is 0.97 (see Supporting information), while for cyclopenta-1,3-diene [29] is −0.70 (Scheme 2). Generally, the increase of η¹(σ) bound (high slippage) connected with the increase of electron density in the C(1) atom region cause higher participation of the diene form. The conformation of Cp ligands (e.g. ring-slippage) results from the interplay of several factors. For example, we demonstrated previously the impact of steric factors introduced by alkoxy ligands in series of [Cp₂Al(μ-OR)]₂ complexes [11]. On the other hand, the HOMA spread at similar slippage values can be mainly due to diversified acidity of the aluminum center. The effect of bonding mode and metal
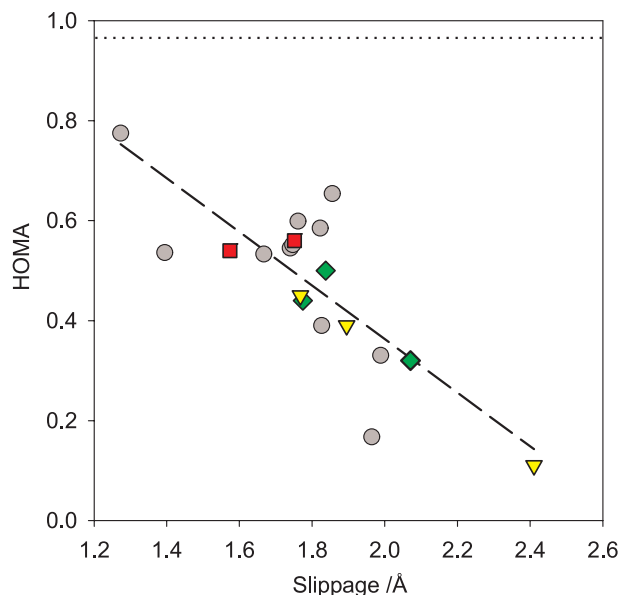
Fig. 3. Plot of HOMA index of cyclopentadienyl ligand vs. ring-slippage parameter in cyclopentadienylaluminum derivatives. Data for compound **1**, **2** and **3** are denoted by diamonds, triangles and squares, respectively. Dotted line points the mean HOMA value of 0.97 for ionic cyclopentadienides.

center acidity on Cp^- aromaticity will be studied in details basing on the whole spectrum of group 13 cyclopentadienyl derivatives and by theoretical calculations on model compounds [30]. Moreover, the significant influence of inter- and intramolecular interactions such as hydrogen bonds must be regarded.

The partial negative charge localized on Cp ligands makes these rings the potential acceptors in $H \cdots \pi$ interactions. The commonly used geometrical parameters characterizing $C–H \cdots \pi$ bonds are collected in Table 3 for compounds **1–3**. In **1** and **2** the intramolecular interactions are observed between Cp2 and Cp3 ligands, where the first ring is a π-acceptor and the C(11)–H(11) group in the second acts as a donor. The $H \cdots Cg$ contacts are equal 2.86 and 2.66 Å, in **1** and **2** respectively. In case of **2** the Cp3 ring is also engaged as an acceptor in $C–H \cdots \pi$ interligand interaction with aryl hydrogen H(16) of py–Me.

The analysis of intermolecular contacts showed the presence of weak $C–H \cdots \pi$ interactions, which are decisive for supramolecular architecture. In compound **1** the main structural unit is a centrosymmetric dimer joined by pair of $C8–H8 \cdots \pi(Cp3)$ bridges. The dimers are linked by $C(19)–H(19) \cdots \pi(Cp2)$ bonds forming wavy layers parallel to the $(10\bar{1})$ plane. The fragment of the layer of the 2-D structure is presented in Fig. 4.

Table 3
Hydrogen-bonding geometry (Å, °)[a]

	$d(H \cdots Cg)$	$\angle C–H \cdots Cg$	$d(C \cdots Cg)$
1			
C(11)–H(11)$\cdots Cg(2)$	2.85(3)	111(2)	3.261(3)
C(8)–H(8)$\cdots Cg(3)^{\#1}$	2.70	153	3.572(4)
C(19)–H(19)$\cdots Cg(2)^{\#2}$	2.98	155	3.862(3)
2			
C(11)–H(11)$\cdots Cg(2)$	2.66(2)	118.2(15)	3.228(2)
C(16)–H(16)$\cdots Cg(3)$	2.79	131	3.486(2)
C(8)–H(8)$\cdots Cg(4)^{\#3}$	2.96	151	3.827(3)
C(17)–H(17)$\cdots Cg(2)^{\#4}$	2.51	154	3.385(2)
C(19)–H(19)$\cdots Cg(3)^{\#5}$	2.57	153	3.447(2)
3			
C(13)–H(13)$\cdots Cg(2)^{\#6}$	2.74	149	3.587(2)
C(17)–H(17B)$\cdots Cg(3)^{\#7}$	2.88	126	3.540(2)
$Cp_3Al \cdot CN^tBu$ [3]			
C(3)–H(3)$\cdots Cg(1)^{\#8}$	2.88	179	3.841(5)

[a] Symmetry transformations: (#1) $1 - x, -y, 1 - z$; (#2) $1/2 - x, 1/2+y, 1/2 - z$; (#3) $2 - x, -1/2+y, 1/2 - z$; (#4) $x, 1 + y, z$; (#5) $x, 1/2 - y, -1/2+z$; (#6) $-1 + x, y, z$; (#7) $-x, 2 - y, 1 - z$; (#8) $-x, 1 - y, -z$.
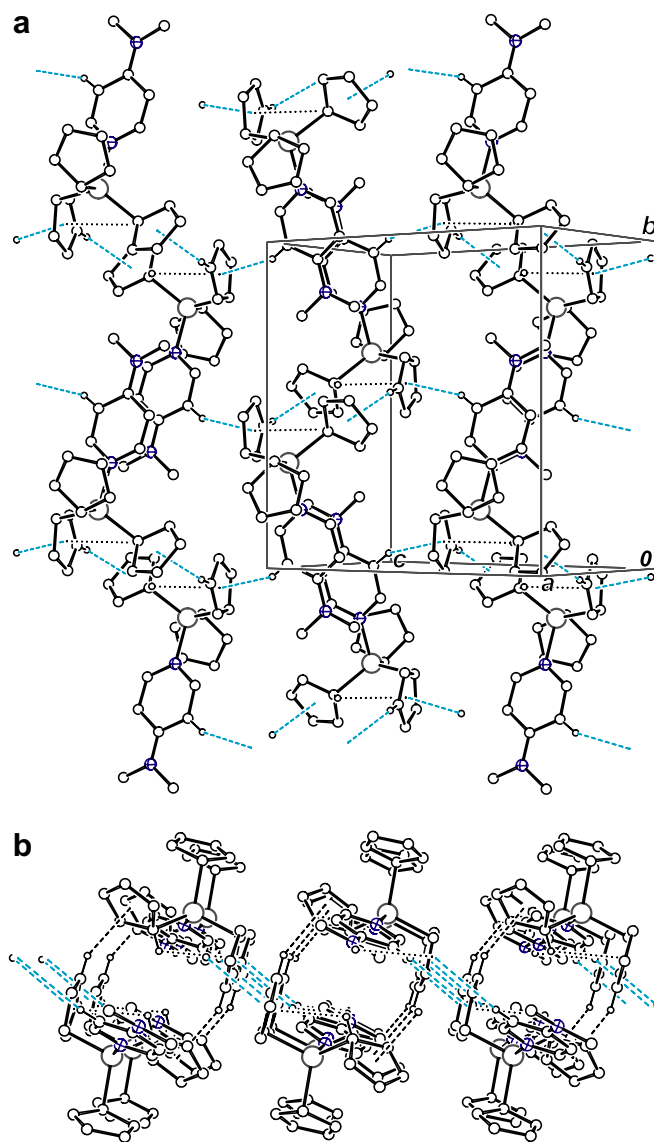

Fig. 4. The 2D hydrogen bonding network in the crystal structure of complex **1**: (a) a view on the $(10\bar{1})$ plane; (b) a side-view showing layer structure.

In crystals of **2** each molecule forms four relatively strong C–H···π links with four neighboring molecules what leads to simple 2-D network lying parallel to the crystallographic plane (100) (Fig. 5a). The weaker interactions between C(8)–H(8) of Cp2 and aromatic ring of py–Me ligand leads to a double-layered structure (Fig. 5b). In the crystal structure of **3** adjacent monomeric molecules are linked by C(13)–H(13)···π(Cp2) interactions into form of infinite chains running along *a* axis. Two parallel chains are further joined by weaker C(17)–H(17B)···π(dmap) interactions forming double-chains (chain of rings), what is depicted in Fig. 6.

We examined the supramolecular structure of $Cp_3Al \cdot CN^tBu$ based on crystal data deposited in CSD (appropriate data are also included in Table 3) [3,17]. $Cp_3Al \cdot CN^tBu$ crystallize in rhombohedral $R\bar{3}$ space group. The molecules are arranged in the layer perpendicular to *c*-axis. Each molecule is surrounded by three others oppositely directed. Adjacent molecules are linked by C–H···π(Cp) intermolecular interactions resulting from engaging of each Cp ligand and each methyl group of CN^tBu ligand (Fig. 7). It should be notified that no significant intramolecular contacts are detected.

We suppose, intra- and intermolecular attractions are key feature responsible for different conformation of Cp3
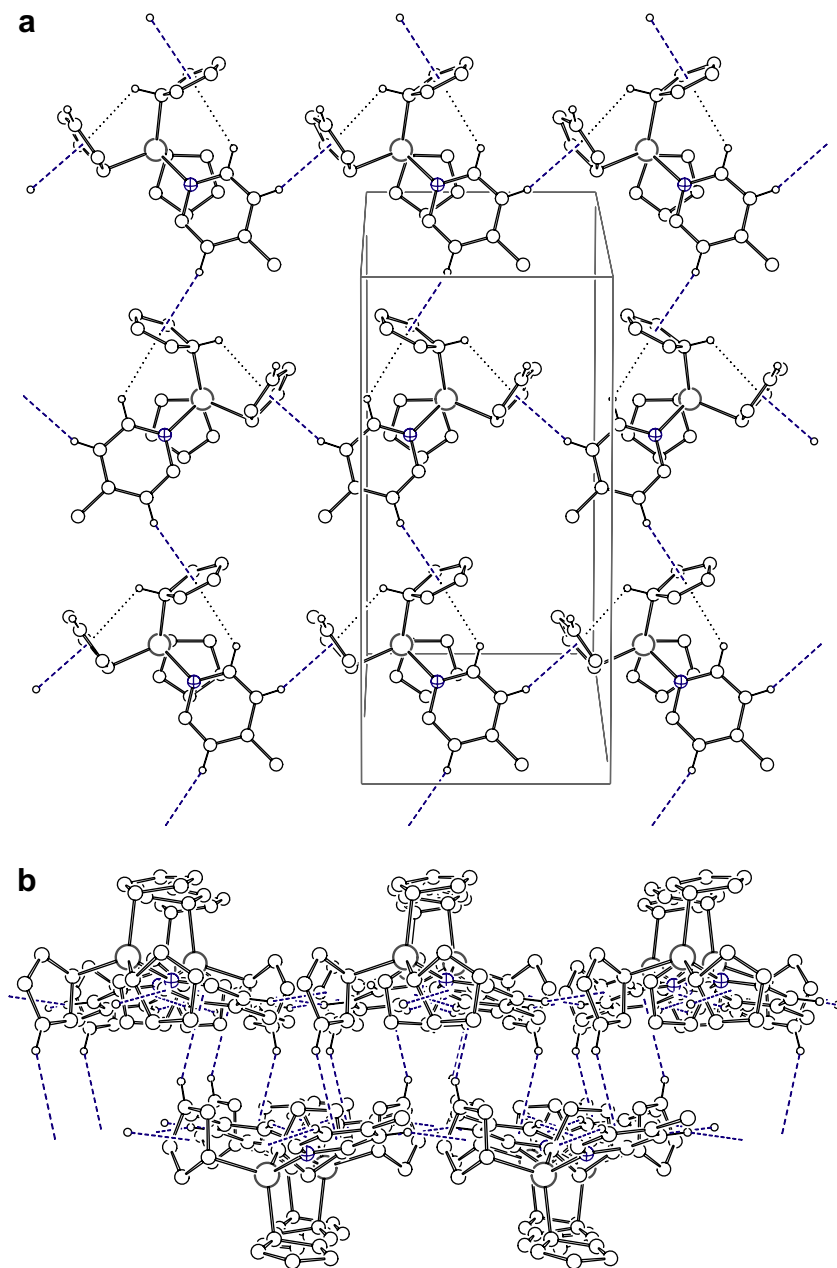

Fig. 5. The hydrogen bonding network in the crystal structure of complex **2**: (a) a view of simple layer parallel to the crystallographic (100) plane; (b) a side-view showing the double-layered structure.
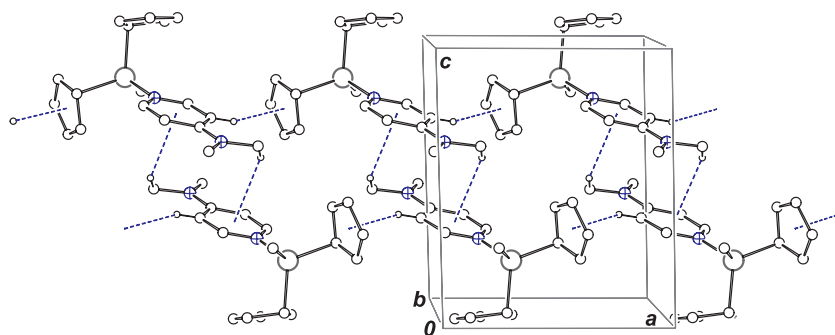
Fig. 6. A view of the crystal structure of complex **3** illustrating the hydrogen-bonded double-chain running along *a*-axis.
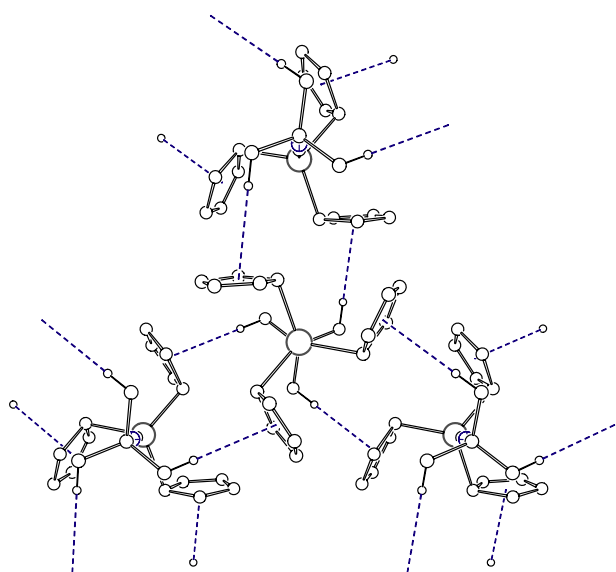

Fig. 7. A part of the hydrogen-bonded 2D network in the crystal structure of $Cp_3Al \cdot CN^tBu$ complex viewed down the threefold axis.[3]

ligand when comparing **1** and **2**. Further, the presence of intramolecular interligand interaction cause the lowering of the aluminum coordination sphere symmetry in our compounds in comparison to $Cp_3Al \cdot CN^tBu$ adduct.

4. Conclusions

The new series of aluminum donor–acceptor complexes with pyridine derivatives have been synthesized. Comparison of the ^{27}Al NMR spectral data showed that stepwise exchange of Cp ligands by Me groups shifts almost monotonically the ^{27}Al NMR signal to lower field. The analysis of Al–N bond length reveals the Cp_3Al and Cp_2AlMe moieties show intermediate acidity between $AlCl_3$ and $AlMe_3$. However, for cyclopentadienylaluminum compounds the alteration of the acidity of Al center is mainly reflected in the region of Al–Cp bonds. It was stated the change of Cp–Al bond character from $\eta^1(\pi)$ to $\eta^1(\sigma)$ correlates with the aromaticity of Cp^- ligand described by HOMA index, albeit the practical use of C–C bond lengths as indicators of metal–Cp interactions is thought to be limited [2]. This effect will be verified on the whole spectrum of data regard-

ing bonding modes in group 13 cyclopentadienyl derivatives and by theoretical calculations on model compounds.

We found intra- and intermolecular attractions play significant role in conformation of Cp ligands. In particular, the presence of intramolecular interligand interactions breaks the symmetry of aluminum coordination sphere. These aspects of influence of weak $CH \cdots \pi$ interaction are of general importance for other Cp complexes of main group metals.

Acknowledgements

Appendix A. Supplementary material

CCDC 614966, 614967 and 614968 contain the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge via http://www.ccdc.cam.a-c.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data (details concerning data retrieval from CSD files, list of CSD refcodes with references, selected geometrical parameters) associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.10.004.

References

[1] (a) For recent reviews of cyclopentadienyl derivatives of main-group metals see: P. Jutzi, N. Burford, Chem. Rev. 99 (1999) 969;
(b) P.J. Shapiro, Coord. Chem. Rev. 189 (1999) 1;
(c) V.N. Sapunov, K. Kirchner, R. Schmid, Coord. Chem. Rev. 214 (2001) 143.
[2] P.H.M. Budzelaar, J.J. Engelberts, J.H. van Lenthe, Organometallics 22 (2003) 1562.
[3] J.D. Fisher, M.-Y. Wei, R. Willett, P.J. Shapiro, Organometallics 13 (1994) 3324.
[4] (a) P.J. Shapiro, A. Vij, G.P.A. Yap, A.L. Rheingold, Polyhedron 14 (1995) 203;

(b) P.J. Shapiro, S.-J. Lee, P. Perrotin, T. Cantrell, A. Blumenfeld, B. Twamley, Polyhedron 24 (2005) 1366.

[5] S. Schulz, F. Thomas, W.M. Priesman, M. Nieger, Organometallics 25 (2006) 1392.

[6] P.E. Romero, W.E. Piers, S.A. Decker, D. Chau, T.K. Woo, M. Parvez, Organometallics 22 (2003) 1266.

[7] A. Ecker, R. Köppe, C. Üffing, H. Schnöckel, Z. Anorg. Allg. Chem. 624 (1998) 817.

[8] M. Nishio, CrystEngComm 6 (2004) 130.

[9] D. Braga, F. Grepioni, E. Tedesco, Organometallics 17 (1998) 2669.

[10] (a) See for example: E.K. Styron, C.H. Lake, S.J. Schauer, C.L. Watkins, L.K. Krannich, Polyhedron 18 (1999) 1595;
(b) J.F. Janik, E.N. Duesler, R.T. Paine, J. Organomet. Chem. 539 (1997) 19;
(c) D.C. Bradley, I.S. Harding, I.A. Maia, M. Motevalli, J. Chem. Soc., Dalton Trans. (1997) 2969.

[11] S. Szumacher, I. Madura, J. Zachara, A.R. Kunicki, A. Cebulski, L. Jerzykiewicz, J. Organomet. Chem. 669 (2003) 64.

[12] J.D. Fisher, P.H.M. Budzelaar, P.J. Shapiro, R.J. Staples, G.P.A. Yap, A.L. Rheingold, Organometallics 16 (1997) 871.

[13] F. Thomas, T. Bauer, S. Schulz, M. Nieger, Z. Anorg. Allg. Chem. 629 (2003) 2018.

[14] G.M. Sheldrick, Acta Crystallogr. A 46 (1990) 467.

[15] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement; Universität Göttingen, Göttingen, Germany, 1997.

[16] (a) A.L. Spek, PLATON, A Multipurpose Crystallographic Tool; Utrecht University, Utrecht, The Netherlands, 2002;
(b) A.L. Spek, Acta Crystallogr. A 46 (1990) C-34.

[17] F.H. Allen, Acta Crystallogr. B 58 (2002) 380.

[18] (a) N. Giannini, S. Cezca, Gazz. Chim. Ital. 28 (1961) 597;
(b) J. Stadelhofer, J. Weidlein, A. Haaland, J. Organomet. Chem. 84 (1975) C1;
(c) W.R. Kroll, W. Naegele, J. Chem. Soc. D 6 (1969) 246;
(d) S. Szumacher, I. Madura, J. Zachara, A.R. Kunicki, J. Organomet. Chem. 690 (2005) 1125.

[19] M.T. Skoog, W.P. Jencks, J. Am. Chem. Soc. 106 (1984) 7597.

[20] T. Gropen, A. Haaland, J. Organomet. Chem. 92 (1975) 157.

[21] (a) See for example: S.J. Obrey, S.G. Bott, A.R. Barron, Organometallics 20 (2001) 5119;
(b) A.P. Shreve, R. Mulhaupt, W. Fultz, J. Calabrese, W. Robbins, S.D. Ittel, Organometallics 7 (1988) 409.

[22] W.R. Kroll, J. Chem. Soc. D 15 (1969) 844.

[23] S. Szumacher, K. Leszczyńska, A.R. Kunicki, I. Madura, J. Zachara, Pol. J. Chem. 79 (2005) 1773.

[24] Dissociation constants of organic acids and bases, in: D.R. Lide (Ed.), CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton, FL, 2005. http://www.hbcpnetbase.com.

[25] L.M. Engelhardt, P.C. Junk, C.L. Raston, B.W. Skelton, A.H. White, J. Chem. Soc., Dalton Trans. (1996) 3297.

[26] (a) T.M. Krygowski, J. Chem. Inf. Comput. Sci. 33 (1993) 70;
(b) T.M. Krygowski, M. Cyrański, Tetrahedron 52 (1996) 10255.

[27] T.M. Krygowski, A. Ciesielski, M. Cyrański, J. Mol. Struct. 374 (1996) 277.

[28] K. Leszczyńska, I.D. Madura, J. Zachara, A.R. Kunicki, unpublished results.

[29] T. Haumann, J. Benet-Buchholz, R. Boese, J. Mol. Struct. 374 (1996) 299.

[30] J. Zachara, I.D. Madura, A.R. Kunicki, in preparation.