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Reactions of alkylalane diolates with water synthesis, characterisation and ε-caprolactone polymerisation activity of novel alane benzopinacolates

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Abstract

1,1,2,2-Tetraphenylethane-1,2-diol (benzopinacole) reacts with R_3Al to yield the trinuclear complexes $\{R_5Al_3[OC(C_6H_5)_2C(C_6H_5)_2O]_2\}$ [where R = Me (**1**), R = Et (**2**)]. Reactions of compounds **1** and **2** with water results in an elimination of R_3Al and formation of unusual binuclear products $\{R_2Al_2(THF)[OC(C_6H_5)_2C(C_6H_5)_2O]_2\}$ [**3** (R = Me), **4** (R = Et)] and a complicated mixture of R_3Al hydrolysis products. Compounds were characterised by spectroscopy and crystal structures of **1**–**3** have been determined by single crystal X-ray diffraction. Binuclear complexes **3** and **4** demonstrate efficient catalytic activity toward ring-opening polymerisation of ε-caprolactone.

Keywords: Aluminium; Benzopinacole; Diols; Hydrolysis; ε-Caprolactone; Ring-opening polymerisation

1. Introduction

Aromatic diolate (biphenolate) complexes of a variety of metals are very effective reagents for enantioselective synthesis like asymmetric nitroaldol reaction [1], catalytic asymmetric Michael reaction [2], hydrophosphonylation of imines [3] and Diels–Alder reactions [4]. An use of the chiral BINOL-aluminium (III) complexes (where BINOL = 2,2′-dihydroxy-1,1′-binaphthyl) was found to be highly effective for the hetero-Diels–Alder reaction of various aldehydes with activated Danishefsky-type dienes [5], asymmetric hydrophosphination of aldehydes [6] and Michael reaction [7–9]. Recently, it has been reported by Lin and co-workers [10–16] that the alkylalane 2,2′-methylenebiphenolates and their derivatives are highly efficient catalysts for polymerisation of cyclic esters and they show excellent catalytic activities toward hydrogen transfer reactions between aldehydes and 2-propanol. In comparison with the BINOLs and 2,2′-methylenebiphenols complexes the catalytic activities of metallane aliphatic diolates are highly unexplored.

Following our work devoted to the synthesis and characterisation of alkylalane diolates [17–19], we become interested in synthesis of the group 13 complexes with diols as potential initiators for the polymerisation of heterocycles. Typical trinuclear complexes of trimethyl-, triethyl- and tri-*iso*-butylaluminium with diols $\{R_5Al_3[diol\text{-}(2H)]_2\}$ and bimetallic complexes $[^tBu_4Al_2[diol\text{-}(H)]_2\}$ with two unreacted hydroxyl groups are inactive toward Lewis bases coordination. We have

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recently reported the reaction of $^{t}Bu_3Al$ with sterically crowded aliphatic diol (2,4-dimethylpentane-2,4-diol) as a route to the unusual dimeric product $\{^{t}BuAl[OC(CH_3)_2CH_2C(CH_3)_2O]\}_2$ with two four-coordinated aluminium atoms [20]. However this product is stable in the presence of Lewis bases and inactive toward ε-caprolactone polymerisation. On the other hand the decreasing strength of Al–O bonds in alkylalane 1,2–catecholates $[R_5Al_3(OC_6H_4O)_2]$ caused by the decreasing basicity of oxygen atoms of aromatic diol units is the reason of the decomposition of alkylalane 1,2-catecholates in the presence of Et_2O, THF and pyridine [21]. In order for an organoaluminium compound to be useful in a polymerisation, it must be able to coordinate a cyclic ester. It implies a complex that is coordinatively unsaturated and/or electron deficient. These qualities can be achieved by employing sterically crowded substituents and chelating ligands [11,14]. Since the polymerisation is considered to be initiated by the insertion of a monomer into Al–X bond (X = O, S, Cl) [14,22,23], our strategy was based on the introduction of phenyl groups into diol units not only as steric hindrances, but also as an electronic factor weakening Al–O bonds. Herein, we report the results of our initial screening of novel alkylalane benzopinacolates as potential initiators for cyclic esters polymerisation.

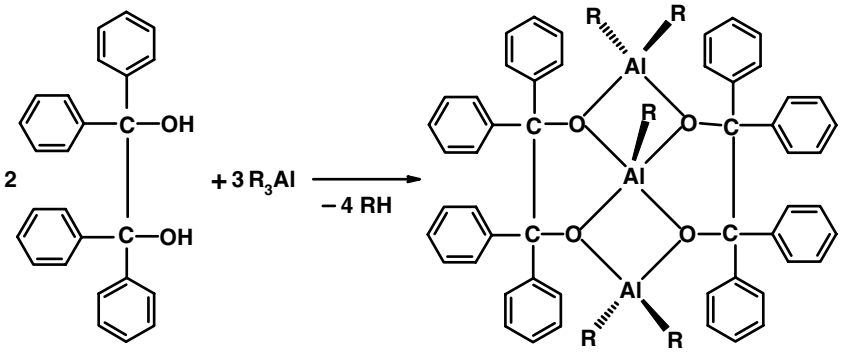
2. Results and discussion

2.1. Synthesis and structural characterisation of trinuclear compounds $\{R_5Al_3[OC(C_6H_5)_2C(C_6H_5)_2O]_2\}$

Reactions of three equivalents of R_3Al with two equivalents of benzopinacole yield trimetallic products $\{R_5Al_3[OC(C_6H_5)_2C(C_6H_5)_2O]_2\}$ [where R = Me (**1**), R = Et (**2**)] with 80 and 75% yields, respectively (Scheme 1).

Product **1** was isolated as colourless X-ray quality crystals after crystallisation from the post-reaction mixture at 15 °C. Compound **2** was obtained after crystallisation from the mixture of dichloromethane–hexane. The molecular structure of compounds **1** and **2** have been determined by X-ray crystallography and are shown in Figs. 1 and 2, respectively; data collection and structure analyses details are shown in Table 1. Two molecules of CH_2Cl_2 are present in the formula unit of **1**. The molecules of **1** and **2** consist of the tetracyclic structures formed from two Al_2O_2 4-membered and two AlO_2C_2 5-membered rings. The central Al(1) aluminium atom is five-coordinate, residing in a distorted square pyramidal geometry with the basal plane consisting of four oxygen atoms of the diol units and the methyl group residing in an apical position. The coordination sphere geometry of the central aluminium atoms is close rather to a square pyramidal structure [i.e., O(2)–Al(1)–O(4) 129.3(2)°, O(1)–Al(1)–O(3) 139.9(2)° in **1** and O(3)–Al(1)–O(1) 130.6(2)°, O(2)–Al(1)–O(4) 138.7(2)° in **2**] then to a trigonal-bipyramidal geometry. The same geometry around the central metal atom was observed for related trinuclear aluminium complexes, consisting of two Al_2O_2 rings and two 5- or 6-membered rings [17,24–28].

The mean Al(1)–O bond distance in **1** (1.868) is equal to the corresponding value observed by Lewiski in methylaluminium acetylacetonate derivative, $[Me_5Al_3(C_6H_{10}O_2)_2]$ (1.870 Å) [25] and longer than this in *tert*-butylaluminium-1,2-catecholdiate, $[^{t}Bu_5Al_3(C_6H_4O_2)_2]$ (1.861 Å) [28]. In comparison with the following mean Al(central)–O bond distances in alkylaluminium complexes with aliphatic diols: $[^{t}Bu_5Al_3(OCH_2CH_2O)_2]$ (1.878 Å) [29]; $\{Me_5Al_3[OC(CH_3)_2CH_2C(CH_3)_2O]_2\}$ (1.876 Å) [17]; $\{Me^{t}Bu_4Al_3[OCH_2C(CH_3)_2CH_2O]_2\}$ (1.877 Å) [26]; the Al(1)–O bond, distance in **1** is significantly shorter. This indicates that **1** differs considerably from the typical aluminium aliphatic diolates. The mean Al(1)–O bond distance in **2**, 1.874 Å, is longer than the



Scheme 1.

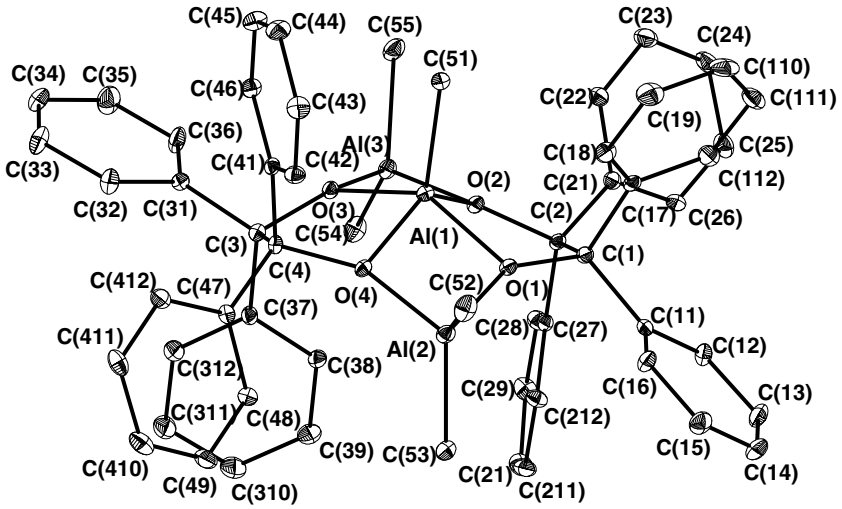


Fig. 1. Molecular structure of $\{Me_5Al_3[OC(C_6H_5)_2C(C_6H_5)_2O]_2\cdot 2CH_2Cl_2\}$ (**1**$\cdot 2CH_2Cl_2$). Thsermal ellipsoids are shown at 10% level and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Al(1)–O(2) 1.835(4), Al(1)–O(4) 1.847(4), Al(1)–O(1) 1.884(4), Al(1)–O(3) 1.904(4), Al(1)–C(51) 1.956(5), Al(2)–O(4) 1.856(4), Al(2)–O(1) 1.857(4), Al(3)–O(3) 1.858(4), Al(3)–O(2) 1.873(4), O(2)–Al(1)–O(4) 129.3(2), O(2)–Al(1)–O(1) 82.7(2), O(4)–Al(1)–O(1) 79.8(2), O(2)–Al(1)–O(3) 81.1(2), O(4)–Al(1)–O(3) 82.7(2), O(1)–Al(1)–O(3) 139.9(2), O(2)–Al(1)–C(51) 110.0(2), O(4)–Al(1)–C(51) 120.6(2), O(1)–Al(1)–C(51) 113.9(2), O(3)–Al(1)–C(51) 106.1(2).

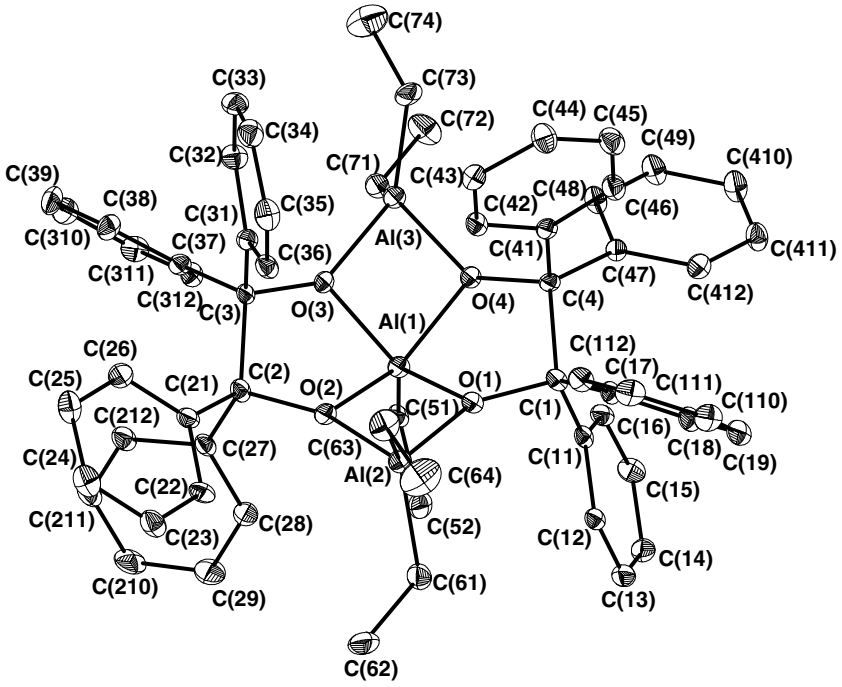


Fig. 2. Molecular structure of $\{Et_5Al_3[OC(C_6H_5)_2C(C_6H_5)_2O]_2\}$ (**2**). Thermal ellipsoids are shown at 10% level, and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Al(1)–O(2) 1.880(5), Al(1)–O(4) 1.891(5), Al(1)–O(1) 1.864(5), Al(1)–O(3) 1.859(5), Al(1)–C(51) 1.944(8), Al(2)–O(1) 1.883(5), Al(2)–O(2) 1.861(5), Al(3)–O(3) 1.886(5), Al(3)–O(4) 1.862(5), O(3)–Al(1)–O(2) 82.8(2), O(1)–Al(1)–O(2) 80.6(2), O(3)–Al(1)–O(4) 80.0(2), O(1)–Al(1)–O(4) 82.7(2), O(3)–Al(1)–O(1) 130.6(2), O(2)–Al(1)–O(4) 138.7(2), O(3)–Al(1)–C(51) 108.9(3), O(1)–Al(1)–C(51) 120.3(3), O(2)–Al(1)–C(51) 114.9(3), O(4)–Al(1)–C(51) 106.2(3).

corresponding value observed in **1** (1.868 Å) and slightly shorter than these in alkylalane aliphatic diolates [17,26,29].

Compound **1** is insoluble in benzene therefore it is not possible to measure a molecular weight in benzene solution. A good solubility of **1** in chloroform and a small solubility in CH_2Cl_2 allow for NMR measurements in a solution. The ^1H NMR spectrum ($CDCl_3$) reveals the signals of two CH_3Al groups *syn* and two CH_3Al groups *anti* (singlets at −0.52 and −1.42 ppm) to the methyl group

Table 1
Crystal data and data collection parameters for **1**–**3**

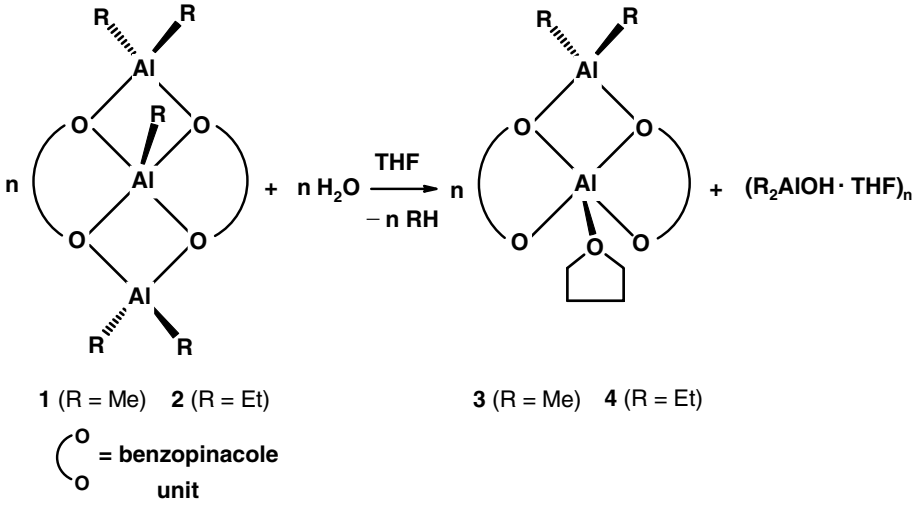
	1·$2CH_2Cl_2$	**2**	**3**·C_4H_8O
Empirical formula	$C_{57}H_{55}Al_3O_4 \cdot 2CH_2Cl_2$	$C_{62}H_{65}Al_3O_4$	$C_{58}H_{54}Al_2O_5 \cdot C_4H_8O$
Formula weight	1054.80	955.08	958.08
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/c$	$P2_12_12_1$
a (Å)	21.031(4)	21.221(4)	12.619(3)
b (Å)	10.937(2)	12.754(3)	17.545(4)
c (Å)	24.134(5)	20.947(4)	23.035(5)
α (°)	90	90	90
β (°)	105.49(3)	114.22(3)	90
γ (°)	90	90	90
V (Å^3)	5349.6(18)	5170.3(18)	5100(2)
Z	4	4	4
D_{calc} (g cm^{-3})	1.310	1.227	1.248
Absorption coefficient (mm^{-1})	0.317	0.122	0.110
$F(000)$	2208	2032	2036
Crystal size (mm)	0.25 × 0.20 × 0.15	0.20 × 0.16 × 0.16	0.25 × 0.25 × 0.20
Θ range for data collection (°)	3.22–22.50	3.19–22.50	3.32–28.74
Index ranges	$-27 \leqslant h \leqslant 27$, $-14 \leqslant k \leqslant 11$, $-32 \leqslant l \leqslant 32$	$-22 \leqslant h \leqslant 22$, $-13 \leqslant k \leqslant 13$, $-20 \leqslant l \leqslant 22$	$-17 \leqslant h \leqslant 16$, $-23 \leqslant k \leqslant 22$, $-30 \leqslant l \leqslant 30$
Reflections collected	31219	30089	48056
Independent reflections	6969 [R_{int} = 0.0854]	6744 [R_{int} = 0.2175]	12,415 [R_{int} = 0.0666]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6949/0/633	6744/0/622	12415/0/631
Goodness-of-fit on F^2	0.957	0.959	0.877
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0683, wR_2 = 0.1561	R_1 = 0.0900, wR_2 = 0.2109	R_1 = 0.0520, wR_2 = 0.1007
R indices (all data)	R_1 = 0.1441, wR_2 = 0.1957	R_1 = 0.1947, wR_2 = 0.2835	R_1 = 0.0994, wR_2 = 0.1173
Largest difference peak and hole (e Å^{-3})	0.468 and −0.474	0.558 and −0.388	0.177 and −0.221

bonded to the central aluminium atom (singlet at −1.14 ppm). The presence of one signal (at 93.43 ppm) of *C*O carbons in the ^{13}C NMR spectrum indicates the equivalence of CO groups. In comparison with following *C*O signals (ppm) of alkylalane aliphatic dioldiates: {^{i}Bu$_5$Al$_3$[OC(CH$_3$)$_2$CH$_2$C(CH$_3$)$_2$O]$_2$} (74.57); {^{i}Bu$_5$Al$_3$[O(CH$_2$)$_4$O]$_2$} (62.98); {^{t}Bu$_5$Al$_3$[O(CH$_2$)$_4$O]$_2$} (64.59) [20]; {^{t}Bu$_5$Al$_3$[O(CH$_2$)$_2$O]$_2$} (61.8) [29]; {Me$_5$Al$_3$[OC(CH$_3$)$_2$CH$_2$C(CH$_3$)$_2$O]$_2$} (74.50) [17]; {^{t}Bu$_4$MeAl$_3$[OCH$_2$C(CH$_3$)$_2$CH$_2$O]$_2$} (74.9) [26]; and in comparison with those of alkylalane dioldiates possessing aromatic rings in the diol units: [Me$_5$Al$_3$(OCH$_2$C$_{12}$H$_8$CH$_2$O)$_2$] (62.98, 61.84); [Et$_5$Al$_3$(OCH$_2$C$_{12}$H$_8$CH$_2$O)$_2$] (63.16, 62.35); [^{i}Bu$_5$Al$_3$(OCH$_2$C$_{12}$H$_8$CH$_2$O)$_2$] (63.30, 62.70) [19]; the *C*O carbon signals of **1** is dramatically shifted downfield, which is caused by withdrawing electron effect of the aromatic rings.

Compound **2** shows better solubility in common organic solvents. Although it is insoluble in hexane and pentane, good solubility was observed in chloroform, dichloromethane and benzene. The ^{13}C NMR spectrum of **2** shows three signals (at 9.88, 9.37 and 8.60 ppm) of AlCH$_2$*C* H$_3$ carbons, which indicates the presence of three kinds of inequivalent Et groups bonded to aluminium atoms. Similarly to compound **1**, the signal of *C*O carbons (at 93.30 ppm) is shifted downfield from those in typical alkylalane dioldiates.

2.2. Reactions of compounds {$R_5Al_3[OC(C_6H_5)_2C(C_6H_5)_2O]_2$} with water

It has been earlier observed that trinuclear aluminium complexes with aliphat1ic diols {R$_5$Al$_3$[diol-(2H)]$_2$} were stable in presence of deoxygenated and dried diethyl ether, THF and pyridine [17–20,26,29]. Unexpectedly, we found that complexes **1** and **2** react with traces of water dissolved in THF to yield unique bimetallic compounds {R$_2$Al$_2$(THF)[OC(C$_6$H$_5$)$_2$C(C$_6$H$_5$)$_2$O]$_2$} [**3** (R = Me), **4** (R = Et)]. The second product is a complicated mixture of alkyl alumoxanes, which presumably is the result of R$_3$Al hydrolysis (Scheme 2). We found that the best method of synthesis of **3** and **4** is to use a water-enriched THF (0.5 mol of H$_2$O per 1 mol of the complex). Compound **3** was isolated from the post-reaction mixture as the precipitation after addition of *n*-hexane. X-ray quality crystals of **3** were obtained from a THF solution at 18 °C. Crystal structure of the compound was determined by X-ray diffraction measurements. A perspective view of the molecule with the atom numbering system is shown in Fig. 3(top).



Scheme 2.

Crystal and structure refinement data are listed in Table 1. Molecules of **3** consist of two aluminium atoms. The five-coordinate Al(1) atom is bonded to four oxygen atoms of the diol units and to the O(5) atom of THF molecule. Besides the THF molecule bonded to the Al(1) atom, one additional molecule of THF is present in the formula unit as a crystalline net stabilising factor. The Al(1)–O(5) bond distance [1.880(2) Å] is within the range of Al(1)–O(diol unit) [1.748(1)–1.934(2) Å] bond distances in the molecules of **3**. The geometry about the Al(1) aluminium atom is a distorted trigonal bipyramid with O(1) and O(3) occupying the axial positions [O(1)–Al(1)–O(3) 162.2(1)°] and O(2), O(4) and O(5) defining the equatorial sites. Five-coordinate organoalanes are popular, however the compounds with aluminium atom bonded to five oxygen atoms are rare. The structures of earlier reported compounds mainly fall into following categories: inorganic products of reactions of aluminium hydroxide, aluminium chloride and triisopropoxide with diols and with other multidentate ligands [31], aluminium alkoxides and sterically crowded aryloxides $[Al_4O(H)(OCH_2CF_3)_{11}]$ [32], $[Al_8(\mu\text{-}O)_2(\mu\text{-}OH)_2(\mu\text{-}O^i\text{-}Bu)_{10}(O^i Bu)_8]$ [33], $\{Al_3[O(c)Hex]_9\}$ [34], $\{[(BHT)Al(OCH_2CH_2OMe)(\mu\text{-}OCH_2CH_2OMe)]_2\}$ (where BHT-H = HOC_6H_2-2,6-$^t Bu_2$-4-Me) [35], boralumoxanes [$^t Bu_4Al_4Ar_4B_2O_8(C_5H_5N)$], [$^t Bu_4Al_4Ar_4B_4O_8$] (where Ar = 2, 6-diisopropylphenyl) [36] and reaction products of sterically crowded alane bisphenolates with benzaldehyde [15,37]. Moreover the Al atoms bonded to five O atoms were found in an alane lithium derivative $[Li_2Al_2(binap)_4\cdot 4thf]$ (where binap = binaphthol-2H) [38] and an aluminium glicolate anionic compound $\{[(C_{16}H_{32}Al_4O_{16})^{4-}]_n 2n(Ba^{2+})\}$ [39].

The four-coordinate Al(2) atom is bonded to two oxygen atoms of the diol units and two methyl groups, which adopt *syn* and *anti* positions with regard to the THF molecule coordinated to the Al(1) atom (Fig. 3, bottom). The presence of two singlets (at −1.06 and −1.85 ppm) of CH_3Al protons in the ^1H NMR spectrum and two signals (at −3.50 and −5.69 ppm) of CH_3Al carbon atoms in the ^{13}C NMR spectrum indicates the inequivalence of methyl groups. The ^{13}C NMR spectrum reveals also two signals (at 92.81 and 87.73 ppm) of two kinds of *C*O carbon atoms of the diol units.

The structure of compound **4** was determined by means of spectroscopic methods and elemental analysis (see Section 3.4).

Generally, a controlled hydrolysis of aluminium trialkyls results in a formation of alkylalumoxanes $[(R)Al(O)]_n$ and $[R_2Al\text{–}O\text{–}AlR_2]_n$ and an evolution of alkanes RH [40]. Barron [41] proved that in the presence of a heteroatom donor ligand (e.g., alkoxide, aryloxide, amide, etc.) the basicity of an aluminium alkyl group is reduced. Therefore, the hydrolysis of a complex $[R_2Al(X)]_n$ produces an alumoxane $[R_2Al\text{–}O\text{–}AlR_2]_n$ and HX, because in the presence of a Broensted acid (H_2O) rather the hydrolytic protonation of the heteroatom X occurs than the protonation of one of the alkyl groups R. According to this observation, in the reaction of the compounds **3** and **4** we expected the protonation of an oxygen atom of a diol moiety and stabilisation of the molecule by formation of O–H···O intramolecular hydrogen bond. An elimination of the molecule of benzopinacole has also been considered as the putative results of the hydrolysis reaction.

Contrary to the expected hydrolysis pathway, water plays herein essentially a role of a factor eliminating of R_3Al molecule from trinuclear compounds **1** and **2**. Presumably, in the presence of phenyl groups in a diol moiety the basicity of both oxygen atoms of diol units and the alkyl groups bonded to aluminium atoms is reduced. The reaction of compounds **1** and **2** with H_2O occurs via

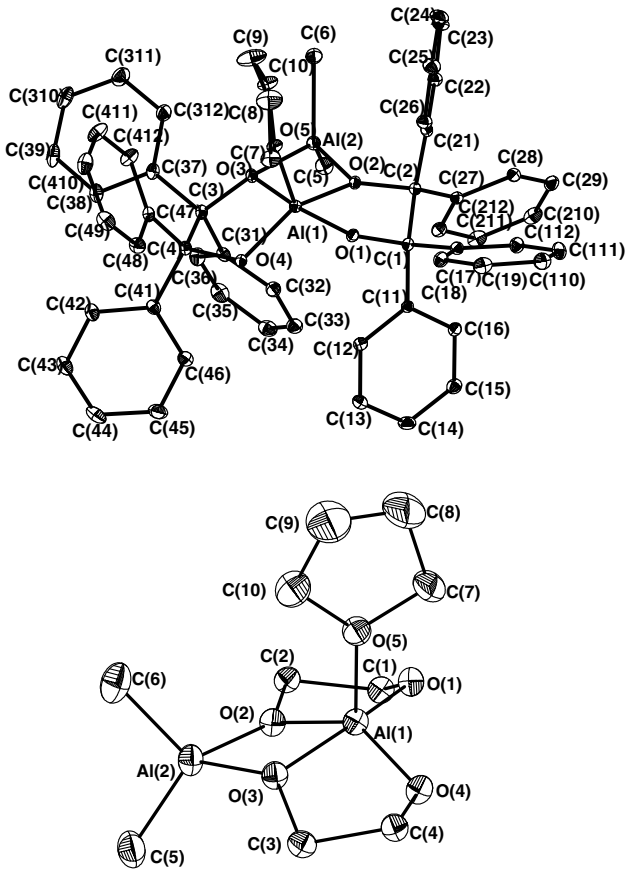


Fig. 3. (top) Molecular structure of $\{Me_2Al_2(THF)[OC(C_6H_5)_2C(C_6H_5)_2O]_2\cdot THF\}$ (**3**·THF). Thermal ellipsoids are shown at 10% level and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Al(1)–O(1) 1.768(2), Al(1)–O(2) 1.865(2), Al(1)–O(3) 1.934(2), Al(1)–O(4) 1.748(1), Al(1)–O(5) 1.880(2), Al(2)–O(2) 1.855(2), Al(2)–O(3) 1.867(2); O(4)–Al(1)–O(1) 103.4(1), O(4)–Al(1)–O(2) 137.6(1), O(1)–Al(1)–O(2) 85.9(1), O(4)–Al(1)–O(5) 108.3(1), O(1)–Al(1)–O(5) 95.4(1), O(2)–Al(1)–O(5) 112.0(1), O(4)–Al(1)–O(3) 85.5(1), O(1)–Al(1)–O(3) 162.2(1), O(2)–Al(1)–O(3) 77.3(1), O(5)–Al(1)–O(3) 96.4(1). (bottom) Co-ordination spheres of Al(1) and Al(2) atoms in $\{Me_2Al_2(THF)[OC(C_6H_5)_2C(C_6H_5)_2O]_2\cdot THF\}$ (**3**·THF). showing that two methyl groups bonded to the Al(2) atom are inequivalent mainly due to their different position to the THF molecule bonded to the Al(1) atom. Thermal ellipsoids are shown at 30% level and eight aromatic rings and hydrogen atoms are omitted for clarity.

protonation of the alkyl group but not of the oxygen atom, similarly to the hydrolysis of aluminium trialkyls. A similar elimination of R_3Al from trinuclear complexes was recently observed during a decomposition of alkylaluminium catecholates $[R_5Al_3(OC_6H_4O)_2]$ [R = Me, Et, ^{I}Bu] in the presence of Lewis bases [21].

2.3. Ring-opening polymerisation (ROP) of ε-caprolactone (ε-CL) initiated by 3 and 4

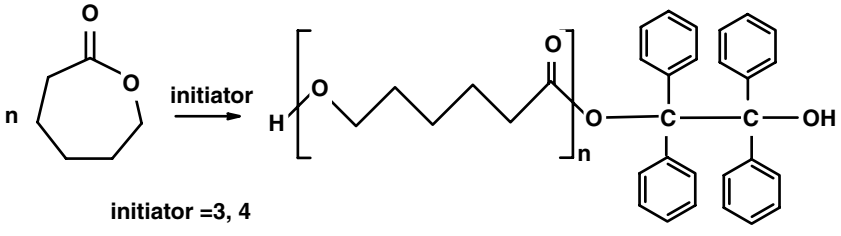
Complexes **1**–**4** were examined for polymerisation activity with ε-CP. Although the trinuclear complexes **1** and **2** are inactive for polymerisation of ε-CL, binuclear compounds **3** and **4** demonstrate ROP of ε-CL (Scheme 3) (Table 2).

The end groups of polycaprolactone (PCL) materials were identified by ^{1}H NMR spectrum (Fig. 4) and MALDI-TOF mass spectroscopy measurements (Fig. 5) to be benzopinacole moiety. The presence of the multiplet at 7.20 ppm in the ^{1}H NMR spectrum of PCL indicates the presence of aromatic protons, which can origin from benzopinacole units only. In the MALDI-TOF MS spectrum the series of peaks with spacing of 114 mass unit (corresponding to the molecular weight of the monomer) was detected. These peaks correspond to the sodium adducts of the polymer chains with the benzopinacolate $OC(C_6H_5)_2C(C_6H_5)_2OH$ end groups. Thus, the diol units in **3** and **4** were incorporated into the polymer chains, consistent with the polymerisation that proceeds by a coordination-insertion mechanism.

According to the MALDI-TOF mass spectrum of the obtained PCL (Fig. 5) there is only one population of peaks, namely coming from the mixture of macromolecules of the structure $\{H[O(CH_2)_5C(O)]_nOC(C_6H_5)_2C(C_6H_5)_2OH\}$.

Although aromatic diolate complexes were described as catalysts of polymerisation (see Section 1), compounds **3** and **4** are the first alkylalane aliphatic diolates demonstrating catalytic activities toward ROP of cyclic esters.

In conclusion, the properties of alane diolates depend on diol moieties. An introduction of phenyl groups as electron withdrawing substituents into the diol moiety allowed for the selective elimination of R_3Al molecule in the reaction with water and formation of the stable binuclear compounds **3** and **4**. Very probably catalytic activity of compounds **3** and **4** in ROP of ε-CL is also the result of the electron withdrawing effect of phenyl groups and the presence of THF molecule coordinate



Scheme 3.

Table 2
Studies of ring-opening polymerisation of ε-CL by complexes **3**·THF and **4**

Entry[a]	Catalyst	Temperature (°C)	Conversion (%)	M_n^b	PDI[b]	ε-CL/Cat.
1	**3**·THF	25	80	16,707	1.48	50
2	**3**·THF	60	100	21,331	1.62	50
3	**4**	60	99	59,119	1.71	100
4	**4**	40	99	32,886	1.57	100
5	**4**	60	100	36,176	1.75	25

[a] Time = 24 h, CH_2Cl_2 solution.
[b] Obtained from GPC analysis and calibrated by polystyrene standard.

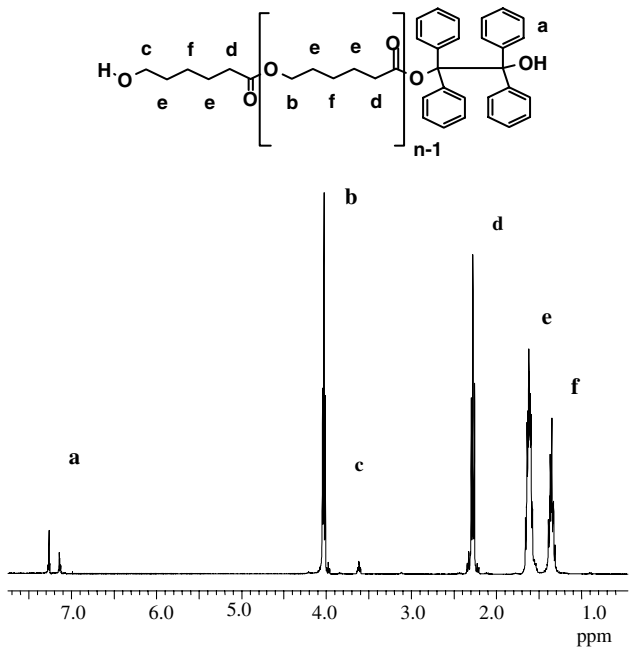


Fig. 4. ^{1}H NMR spectrum ($CDCl_3$) of PCL initiated by compound **4**.

to the aluminium atom, which can be easy exchange into a ε-CL molecule.

Presented herein reaction of trinuclear alane benzopinacolates with water is the first selective partial hydrolysis of alane diolates. Our earlier attempts to hydrolyse selectively complexes of aluminium trialkyls with aliphatic diols failed. Further studies on the influence of electron withdrawing groups on properties of alane diolates will be continued.

3. Experimental

All manipulations were carried out using standard Schlenk techniques under an inert gas atmosphere. The solvents were distilled over a blue benzophenone–K complex. The Me_3Al and Et_3Al were purchased from Aldrich. $^tBu_3Al$ and 1,1,2,2-tetraphenylethane-1,2-diol were synthesised as described in the literature [42,43]. ^{1}H and ^{13}C NMR spectra were run on Mercury-400BB spectrometer. ^{1}H NMR spectra were recorded at 400.09 MHz. Chemical shifts were referenced to the residual proton signals of $CDCl_3$ (7.26 ppm) and CD_2Cl_2 (5.30 ppm). ^{13}C NMR spectra were run at 100.60 MHz (standard: chloroform $^{13}CDCl_3$, 77.20 ppm; dichloromethane $^{13}CD_2Cl_2$, 53.52 ppm). GPC analysis was performed on a Laballiance apparatus equipped with HPLC column jordigel DVB mixed bed, using thf as an eluent. MALDI-TOF mass spectrometry was carried out on KOMPACT MALDI 4 spectrometer (Kratos Analytica). FT-IR spectrum was recorded on a Perkin–Elmer System 2000 instrument. ^{27}Al NMR spectra were excluded from the presentation of the results due to the inadequate quality caused probably by a shield effect of bulky diol units.

3.1. Synthesis of $\{Me_5Al_3[OC(C_6H_5)_2C(C_6H_5)_2O]_2\cdot 2CH_2Cl_2\}$ ($1\cdot 2CH_2Cl_2$)

To a sample (0.230 g, 3.2 mmol) of Me_3Al in 20 cm^3 of Et_2O at −78 °C a solution of 0.732 g (2.0 mmol) of benzopinacole in 30 cm^3 of CH_2Cl_2 was added drop by drop. The reaction mixture was allowed to warm to 18 °C within 2 h. Colourless, X-ray quality crystals of **1**·$2CH_2Cl_2$ were obtained after crystallisation from the post-reaction mixture at 15 °C. Yield: 0.707 g (80%). M.p.: 240–245 °C (dec.).

^{1}H NMR ($CDCl_3$): δ 7.30 −7.06 (40H, m, *H* aromat.), 5.29 (4H, s, CH_2Cl_2), −0.46 (6H, s, $AlCH_3$), −1.09 (3H, s, $AlCH_3$), −1.32 (broadened, 6H, s, $AlCH_3$). ^{1}H NMR (CD_2Cl_2): δ 7.28–7.02 (40H, m, *H* aromat.), 5.30 (4H, s, CH_2Cl_2), −0.52 (6H, s, $AlCH_3$), −1.14 (3H, s, $AlCH_3$), −1.42 (broadened, 6H, s, $AlCH_3$). ^{13}C NMR ($CDCl_3$): δ 143.17, 142.89, 130.49, 130.30, 127.29, 126.96, 126.89, 126.59 (*C* aromat.), 93.31 (*C*O), 53.41 (CH_2Cl_2), −2.27, −5.14 −5.53 ($AlCH_3$). ^{13}C NMR (CD_2Cl_2): δ 143.35, 143.03, 130.56, 130.41, 128.59, 127.38, 127.09, 126.65 (*C* aromat.), 93.43 (*C*O), 53.41 (CH_2Cl_2), −5.30, −5.74 ($AlCH_3$) ppm. IR (Nujol) (cm^{-1}): 1494 (m), 1458 (s), 1446 (s), 1266 (w), 1204 (m), 1168 (w), 1039 (m), 1025 (m), 991 (m), 972 (m), 956 (m), 926 (m), 906 (m), 854 (w), 790 (m), 769 (s), 743 (s), 716 (s), 699 (s), 684 (s), 616 (w), 598 (w), 559 (w). Anal. Found: Al, 8.84; hydrol-

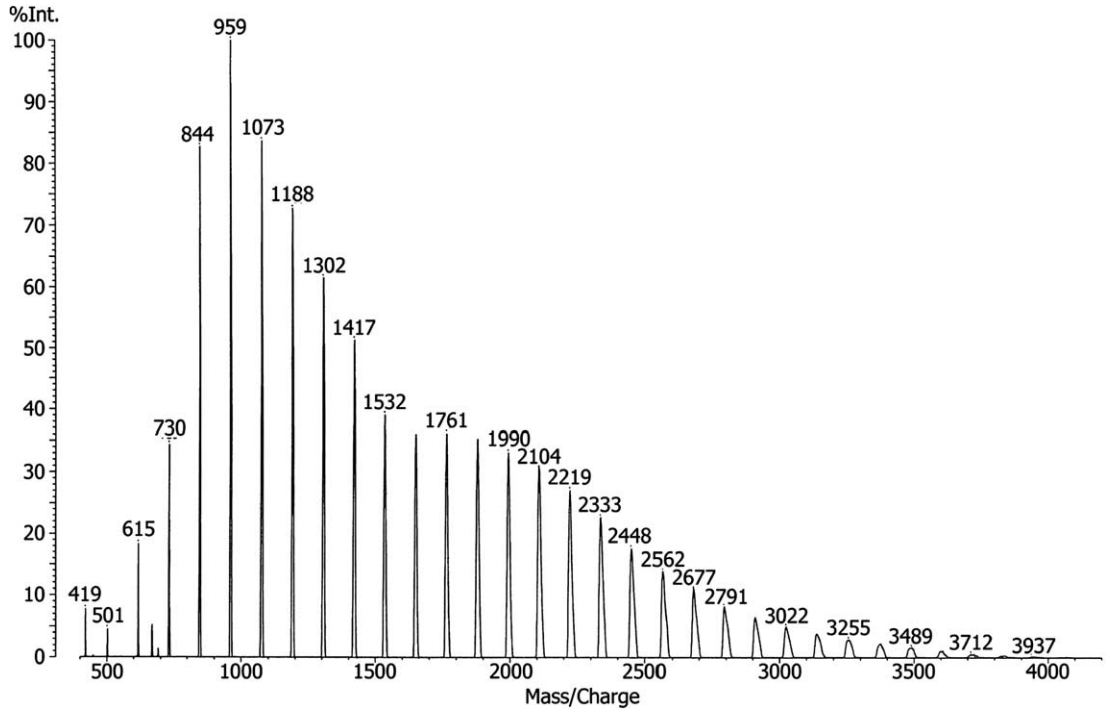


Fig. 5. MALDI-TOF mass spectrum of poly-ε-caprolactone. Mass(m/z) = M[$OC_2(C_6H_5)_4OH$] + M(PCL) + M(Na^+) (where M[OC_2- ($C_6H_5)_4OH$] = 365, M(PCL) = 114, M(Na^+) = 23).

ysable methyl groups, 8.27; {$Me_5Al_3[OC(C_6H_5)_2C(C_6H_5)_2O]_2\cdot 2CH_2Cl_2$} requires Al, 9.16; Me, 8.48 wt%.

3.2. Synthesis of {$Et_5Al_3[OC(C_6H_5)_2C(C_6H_5)_2O]_2$} (2)

Compound **2** was obtained as described in Section 3.1 using Et_3Al (0.365 g, 3.2 mmol) and benzopinacole (0.732 g, 2 mmol). After 24 h all volatiles were removed under vacuum and the resulting white powder was recrystallised from CH_2Cl_2–n-C_6H_{14} at −25 °C. (0.692 g, 75%). X-ray quality crystals were obtained at 5 °C. M.p.: 187 °C (with dec.).

^{1}H NMR ($CDCl_3$): δ 7.32 [8H, d, J(HH) 7.6 Hz, C*H* aromat.], 7.26 [8H, d, J(HH) 7.6 Hz, C*H* aromat.], 7.08 [24H, m, C*H* aromat.], 0.96 [6H, t, $AlCH_2CH_3$], 0.72 [3H, t, $AlCH_2CH_3$], 0.34 [6H, t, $AlCH_2CH_3$], 0.20 [4H, q, $AlCH_2CH_3$], −0.23 [2H, q, $AlCH_2CH_3$], −0.98 [4H, q, $AlCH_2CH_3$]. ^{13}C NMR ($CDCl_3$): δ 143.47, 142.83, 130.35, 130.12, 127.26, 126.94, 126.87, 126.55 [*C* aromat.], 93.30 [*C*O], 9.88, 9.37, 8.60 [$AlCH_2C$ H_3], 3.32, 3.16 [$AlCH_2CH_3$, br] ppm. Anal. Found: Al, 8.89; hydrolysable ethyl groups, 15.39; [$Et_5Al_3(OC(C_6H_5)_2C$-$(C_6H_5)_2O)_2$] requires Al, 8.79; Et, 15.73 wt%.

3.3. Synthesis of {$Me_2Al_2(THF)[OC(Ph)_2C(Ph)_2$-$O]_2\cdot THF$} (3·THF)

A solution of water (0.0045 g, 0.25 mmol) in 15 cm^3 of THF was added dropwise to solid compound **1** (0.528 g, 0.5 mmol) until dissolving. After 24 h the solvent was removed under reduced pressure and the resulting solid was washed two times by 10 cm^3 of n-C_6H_{14}. The white solid was dried under reduced pressure and 0.432 g of **3**·THF was obtained (yield 90%). X-ray quality crystals were obtained from a THF solution at 18 °C. M.p.: 190–192 °C.

^{1}H NMR ($CDCl_3$): δ 7.61–7.00 (40H, m, H aromat.), 3.52 (broadened, 4H, m, CH_2O, THF), 1.45 (4H, m, CH_2, THF), −1.06 (3H, s, $AlCH_3$), −1.85 (3H, s, $AlCH_3$). ^{13}C NMR ($CDCl_3$): δ 151.04, 148.20, 143.25, 131.23, 129.93, 128.60, 127.29, 126.94, 126.46, 126.16, 125.48, 125.27 (*C* aromat.), 92.81, 87.73 (*C*O), 67.98 (CH_2O, THF), 24.53 (CH_2, THF), −3.50, −5.69 ($AlCH_3$) ppm. Anal. Found: Al, 5.40; hydrolysable methyl groups, 2.65; {Me_2Al_2(THF)[$OC(Ph)_2C$ $(Ph)_2O]_2\cdot$ THF} requires Al, 5.64; Me, 3.13 wt%.

3.4. Synthesis of {$Et_2Al_2(THF)[OC(Ph)_2C(Ph)_2O]_2$} (4)

Compound **4** was obtained as described in Section 3.1 using 0.478 g (0.5 mmol) of **2** and 0,0045 g (0.25 mmol) of H_2O in 30 cm^3 of THF. (yield 0.423 g, 86%). ^{1}H NMR ($CDCl_3$): δ 7.64–6.90 (40H, m, *H* aromat.), 3.60 [4H, br m, CH_2O, THF], 1.45 [4H, m, CH_2, THF], 0.85 [3H, t, $AlCH_2CH_3$], 0.09 [3H, t, $AlCH_2CH_3$], −0.61 [2H, q, $AlCH_2CH_3$], −1.33 [2H, q, $AlCH_2CH_3$]. ^{13}C NMR ($CDCl_3$): δ 151.07, 148.36, 142.96, 142.91, 131.03, 130.34, 130.10, 129.81, 128,63, 128.57, 127.51,127.23, 127.05, 126.93, 126.88, 126.53, 126.46,

126.07, 125.37, 125.21 [*C* aromat.], 92.62, 87.78 [*C*O], 68.04 [*C*H_2O, THF], 25.52 [*C*H_2, THF], 9.67, 8.59 [AlCH$_2$*C*H$_3$]. Anal. Found: Al, 5.44; hydrolysable ethyl groups, 5.85; {Et_2Al_2(THF)[OC(Ph)$_2$C(Ph)$_2$O]$_2$} requires Al, 5.92; Et, 6.36 wt%.

3.5. Polymerisation of ε-caprolactone catalysed by 3·THF and 4

Polymerisation reactions were carried out in closed glass ampoules. A solvent (CH_2Cl_2), monomer and initiator solution were added into ampoules successively. The ampoules were kept in thermostat. The reactions were terminated by 5% HCl aq. solution. The resulting polymer was washed for several times and dried in vacuum. In general, ε-CL (2.28 g, 2 mmol) was polymerised by an initiator (for the ratio of ε-CL/cat. see Table 2) in 20 cm^3 of CH_2Cl_2 during 24 h. An approximate conversion yield was obtained as a ratio of the PCL mass to the monomer mass. ^{1}H NMR (see Fig. 4) ($CDCl_3$): δ 7.20 [m, H^a aromat.], 4.03 [m, OCH_2^b], 3.61 [m, HOCH_2^c], 2.28 [m, CH_2^dC(O)], 1.62 [m, CH_2^e], 1.35 [m, CH_2^f] ppm.

3.6. X-ray crystal structure analyses

Crystals of compounds **1**–**3** were mounted in inert oil and sealed in glass capillaries under argon. Determination of the crystal structures of **1**–**3** was performed on a KUMA KM4CCD κ-axis diffractometer with graphite-monochromated Mo Kα radiation. The crystals were positioned at 62 mm from the KM4CCD camera. For compound **1** 460 frames were measured in 1.3° intervals with a counting time of 15 s. For compound **2** 600 frames were measured in 1.5° intervals with a counting time of 35 s. For compound **3** 600 frames were measured in 1.2° intervals with a counting time of 35 s. All of the data were corrected for Lorentz and polarisation effects. No absorption correction was applied. Data reduction and analysis were carried out using the KUMA Diffraction (Wrocław) programs. Structures of the investigated crystals were solved by the Direct methods [44] and refined using the SHELXS/SHELXL computer programs [45]. All hydrogen atoms placed in the calculated positions and their thermal parameters were refined isotropically. Scattering factors were taken from the literature (Tables 6.1.1.4 and 4.2.4.2 [46]).

The structure of **2** is disordered in the peripheral ethyl groups. The disorder involves at least the C(62) atom but also possibly C(64) C(72) and C(74). However the splitting into two atoms almost do not change the final R_{fac}, due to small data/parameter ratio. Instead the procedure causes that one of the split atoms is characterised by very long C–C bonds (e.g. of about 1.65 Å, what is unrealistic). It is the reason why we did not split the atoms, despite of substantial thermal ellipsoids. The disorder may possibly come from the twinning, since the quality of the crystals was not the best one, but the refinement is not better if the twinning procedure is applied.

The X-ray structures were measured in the Crystallography Unit of the Physical Chemistry Laboratory at the Chemistry Department of the University of Warsaw.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC, Nos. CCDC 225428, 225429 and 225430 for **1**, **2** and **3**, 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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