Polyhedron 102 (2015) 705–710

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

1-(1,3-Benzothiazol-2-ylsulfanyl)propan-2-olate anion as a potential multifunctional ligand in aluminum complexes

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ARTICLE INFO

Article history:
Received 26 September 2015
Accepted 27 October 2015
Available online 3 November 2015

Keywords:
Aluminum
1-(1,3-Benzothiazol-2-ylsulfanyl)propan-2-ol
Multifunctional ligands
Ring opening polymerization
Group 13 metals

ABSTRACT

1-(1,3-Benzothiazol-2-ylsulfanyl)propan-2-ol ($C_{10}H_{10}NS_2OH$, LH) was used as a multifunctional ligand in reactions with aluminum trialkyls R_3Al ($R = {}^iBu$, Et, ${}^tBu$). The reactions at 1:1 M ratio of reagents proceeded with formation of dimeric $(R_2AlL)_2$ ($R = {}^iBu$, Et) complexes with a central Al_2O_2 ring, whereas in a presence of an excess of R_3Al the compounds $[(R_2Al)(R_3Al)L]_2$ ($R = {}^iBu$, Et) with the central Al_2O_2 ring and R_3Al molecules coordinated to nitrogen atoms were obtained. ${}^iBu_3Al$ reacted with the LH yielding monomeric complex ${}^tBu_2AlL$ independently on the molar ratio of reagents. In the compound, Al coordinates to the nitrogen atom to form intramolecular sp^2-N donor bonding. The compounds $[({}^iBu_2Al)({}^iBu_3Al)L]_2$ (**1**), $(Et_2AlL)_2$ (**2**) and ${}^tBu_2AlL$ (**3**) were synthesized as pure compounds and characterized. Among four heteroatoms of the ligand, only the oxygen and nitrogen atoms can form bonds with aluminum atoms, whereas two sulfur atoms are non-coordinative. The compounds **1** and **2** are active as an initiator of the ε-caprolactone polymerization.

1. Introduction

Multifunctional ligands containing at least three coordinating heteroatoms have potential abilities to form a variety of complexes with group 13 metals with various coordination mode. In the complexes, the ligands play a role of chelates or are the bridges between metallic centers [1]. There are numerous reports on catalytic activities of the complexes toward ring-opening polymerization of cyclic esters [2]. Group 13 metal complexes with multifunctional ligands are precursors of nanoparticles and thin films of metal oxides [3]. Multifunctional ligands are also good candidates for the construction of coordination polymers and metal organic frameworks that display rich structural diversity [4].

Recently, we have found that the structure of the reaction products of trialkylaluminum with 2-mercaptobenzoksazole, as potentially trifunctional ligand, depends strongly on the presence and strength of Lewis base [5]. Pursuing our continuing interest in complexes of group 13 trialkyls with multifunctional ligands [1l,n,o;5], here we report structural investigations of alkylaluminum complexes with 1-(1,3-benzothiazol-2-ylsulfanyl)propan-2-olate anion (L) that can be regarded as tetrafunctional ligand.

2. Results and discussion

Treatment of the 1-(1,3-benzothiazol-2-ylsulfanyl)propan-2-ol (LH) with two equivalents of ${}^iBu_3Al$ in OEt_2, followed by crystallization from n-C_6H_{14} solution at 10 °C, afforded a crystalline compound, whose characterizing data are consistent with the dimeric species $[({}^iBu_2Al)({}^iBu_3Al)L]_2$ (**1**) (Scheme 1).

The compound was characterized by NMR spectroscopy and elemental analysis. The molecular structure was determined on the basis of an X-ray diffraction study and is shown in Fig. 1. Data collection and structure analyses are listed in Table 1S (see Supplementary data). The molecular studies showed that the centrosymmetric molecule of **1** consists of a central four-membered Al_2O_2 ring. The molecule is composed of two monoanionic 1-(1,3-benzothiazol-2-ylsulfanyl)propan-2-olate ligands, two four-coordinate aluminum atoms and four ${}^iBu$ groups bonded to the aluminum atoms. Moreover, two ${}^iBu_3Al$ molecules are coordinated to the two nitrogen atoms.

Although there are reports on the presence of metal–sulfur coordinative bonds in the complexes with (OSSO) and (ONSO) multidentate ligands [2f,6], however the sulfur atoms in the 1-(1,3-benzothiazol-2-ylsulfanyl)propan-2-olate ligands are non-coordinating. The central Al_2O_2 ring of the molecule of **1** is similar to that of typical alkoxides of group 13 metal alkyls obtained in reactions of R_3M ($R = Me$, Et, ${}^iBu$; $M = Al$, Ga) with monoalcohols.

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http://dx.doi.org/10.1016/j.poly.2015.10.048
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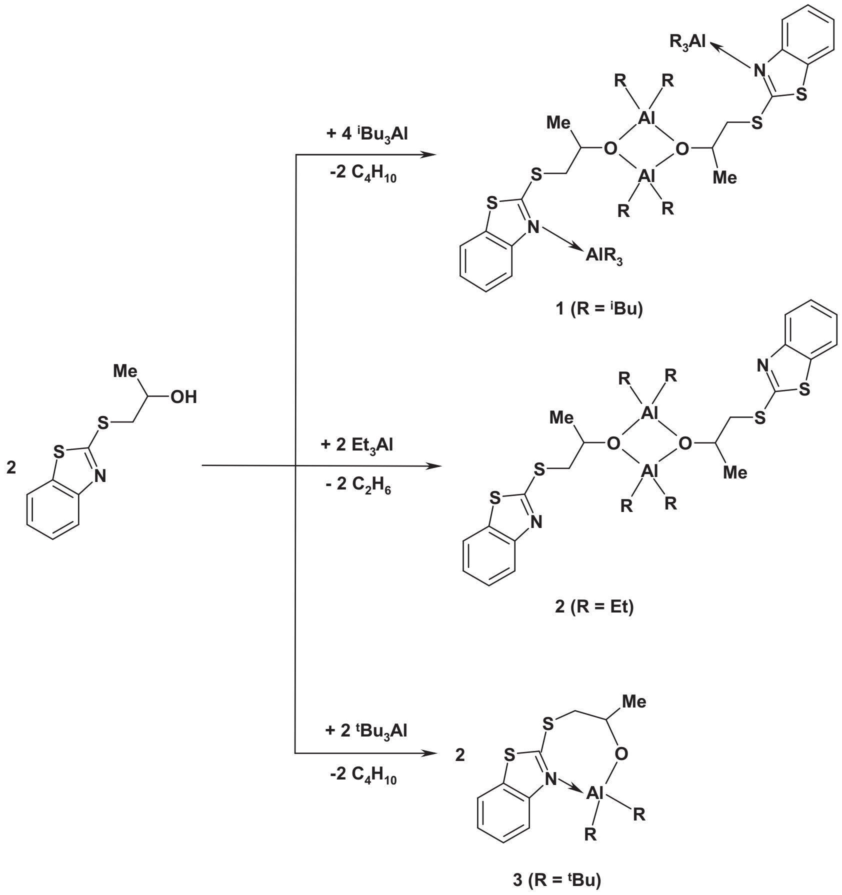

Scheme 1. Reactions of 1-(1,3-benzothiazol-2-ylsulfanyl)propan-2-ol with aluminum trialkyls.

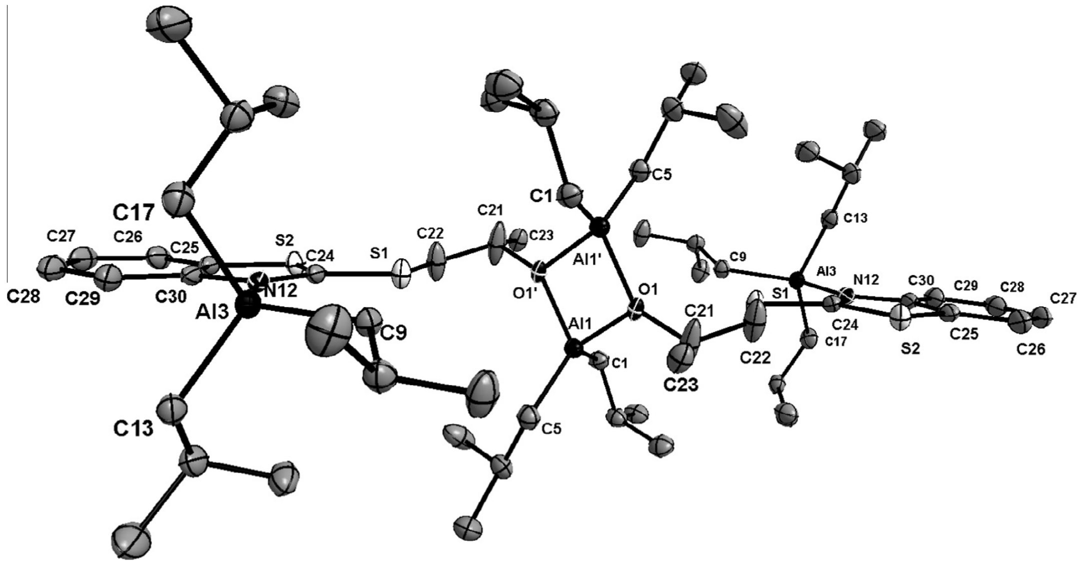

Fig. 1. Molecular structure of (**1**). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Al(1)′–O(1)′ 1.866(2), N(12)–Al(2) 2.081(2), C(22)–S(1) 1.800(3), C(24)–S(1) 1.738(3), C(24)–N(12) 1.322(3), C(5)–Al(1) 1.970(3), O(1)′–Al(1) 1.864(2), Al(1)′–O(1)–Al(1) 99.8(1), O(1)′–Al(1)–O(1) 80.2(1).

The Al–O bond distances range from 1.864(2) to 1.866(2) Å, somewhat more than the Al–O distance found in [Me$_2$Al(μ-*l*-mentholate)]$_2$ [1.835(3)–1.847(3) Å], in [^{i}Bu$_2$Al(μ-*l*-mentholate)]$_2$ [1.828(7)–1.847(8) Å] or in the [Me2Al(μ-l-borneolate)]2 [1.829(5)–1.861(5) Å] [7]. On the other hand, Al–O bond lengths in **1** are almost the same as those of [Me$_2$Al(μ-2-allyl-6-methylphenoxide)]$_2$ [1.859(3)–1.862(3) Å] [8].

The coordination geometry around the Al(1) atom is distorted from tetrahedral geometry. The internal Al(1)′–O(1)–Al(1) [99.8(1)°] and O(1)′–Al(1)–O(1) [80.2(1)°] angles are consistent with