

Investigations on the interaction of dichloroaluminum carboxylates with Lewis bases and water : an efficient road toward oxo- and hydroxoaluminum carboxylate complexes.

Autorzy

Wojciech Bury
Elżbieta Chwojnowska
Iwona Justyniak
Janusz Lewiński
Aneta Affek
Ewa Zygadło-Monikowska
Joanna Bąk
Zbigniew Florjańczyk

Rok wydania

2012

Czasopismo

Inorganic Chemistry

Numer woluminu

51

Strony

737-745

DOI

10.1021/ic2023924

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

A series of dichloroaluminum carboxylates $[\text{Cl}_2\text{Al}(\text{O}_2\text{CR})]_2$ (where $\text{R} = \text{Ph}$ (1a), tBu (1b), CHCH_2 (1c) and $\text{C}_{11}\text{H}_{23}$ (1d)) were prepared and extended investigations on their structure and reactivity toward various Lewis bases and H_2O performed. Compounds $[\text{Cl}_2\text{Al}(\text{O}_2\text{CR})]_2$ and their adducts with Lewis bases show a large structural variety, featuring both molecular and ionic forms with different coordination numbers of the metal center and various coordination modes of the carboxylate ligand. Upon addition of a Lewis base of moderate strength the molecular form $[\text{Cl}_2\text{Al}(\text{O}_2\text{CR})]_2$ equilibrates with new ionic forms. In the presences of 4-methylpyridine the six-coordinate Lewis acid–base adducts $[\text{Cl}_2\text{Al}(\lambda^2\text{-O}_2\text{CR})(\text{py-Me})_2]$ [$\text{R} = \text{Ph}$ (3a), tBu (3b)] with a chelating carboxylate ligand were formed. The reactions of 1a, 1b, and 1d with 0.33 equiv of H_2O in THF-toluene solution lead to oxo carboxylates $[(\text{Al}_3\text{O})(\text{O}_2\text{CR})_6(\text{THF})_3][\text{AlCl}_4]$ [where $\text{R} = \text{Ph}$ (4aTHF), tBu (4bTHF), and $\text{C}_{11}\text{H}_{23}$ (4dTHF)] in high yield. The similar reaction of 1c in tetrahydrofuran (THF) afforded the chloro(hydroxo)aluminum acrylate $[(\text{ClAl})_2(\text{OH})(\text{O}_2\text{CC}_2\text{H}_3)_2(\text{THF})_4][\text{AlCl}_4]$ (5), while the hydrolysis of 1b in MeCN lead to the hydroxoaluminum carboxylate $[\text{Al}_2(\text{OH})(\text{O}_2\text{CtBu})_2(\text{MeCN})_6][\text{AlCl}_4]_3$ (6). All compounds were characterized by elemental analysis, ^1H , ^{27}Al NMR, and IR spectroscopy, and the molecular structure of 1a, 3a, 3b, 4aTHF, 4bTHF, 4bpy-Me', 5, and 6 were determined by single-crystal X-ray diffraction. The study provides a platform for testing transformations of secondary building units in Al-Metal–Organic Frameworks toward H_2O and neutral donor ligands.

Adres publiczny

<http://dx.doi.org/10.1021/ic2023924>

Strona internetowa wydawcy

<https://www.acs.org/content/acs/en.html>

Plik został wygenerowany dnia 2026-06-28 08:30:29

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