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

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Streszczenie

A series of dichloroaluminum carboxylates [Cl2Al(O2CR)]2 (were R = Ph (1a), tBu (1b), CHCH2 (1c) and C11H23 (1d)) were prepared and extended investigations on their structure and reactivity toward various Lewis bases and H2O performed. Compounds [Cl2Al(O2CR)]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 [Cl2Al(O2CR)]2 equilibrates with new ionic forms. In the presences of 4-methylpyridine the six-coordinate Lewis acid–base adducts [Cl2Al(λ2-O2CR)(py-Me)2] [R = Ph (3a), tBu (3b)] with a chelating carboxylate ligand were formed. The reactions of 1a, 1b, and 1d with 0.33 equiv of H2O in THF-toluene solution lead to oxo carboxylates [(Al3O)(O2CR)6(THF)3] [AlCl4] [where R = Ph (4aTHF), tBu (4bTHF), and C11H23 (4dTHF)] in high yield. The similar reaction of 1c in tetrahydrofuran (THF) afforded the chloro(hydroxo)aluminum acrylate [(ClAl)2(OH)(O2CC2H3)2 (THF)4][AlCl4] (5), while the hydrolysis of 1b in MeCN lead to the hydroxoaluminum carboxylate [Al2(OH)(O2CtBu)2(MeCN)6][AlCl4)3] (6). All compounds were characterized by elemental analysis, 1H, 27Al 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 H2O and neutral donor ligands.

Adres publiczny

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