m41.p40

On the role of noncovalent interactions on the structure of metal thiolate complexes

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Keywords: metal complexes, noncovalent interactions, thiolates, database analysis

The chemistry of five-coordinate aluminum complexes has an extensive literature and the significance of the fifth coordinate site for aluminum-based reagent/catalyst function and/or selectivity is gradually emerging. However, the identity of both active centers and transition-state structures remains often elusive. Detailed structural information concerning the extent of coordination and association in alkylaluminum complexes as well as the magnitude of the donor–aluminum interaction in five-coordinate species are crucial in understanding their physical behavior and chemical reactivity. In this regard, investigations based on the dialkylaluminum chelate complexes derived from donor-functionalized alcohols or unsaturated bifunctional O,X-H proligands, i.e., [R2Al(O,X)]n-type complexes, have appeared particularly fruitful. Recently, our group has reported the results concerning the relationship between intra- and intermolecular forces resulting from donor–acceptor and hydrogen-bonding interactions using group 13 chelate complexes.[1]
We report herein on structure investigations of alkylaluminum compounds derived from methyl thiosalicylate. The structural analysis relevaled that the intermolecular S···C(π) interaction between the Al–S thiolate units and the π-surface of the ester functionality can compete with the putative sulfur–aluminum hypercoordinate bond. Thus, in order to verify the significance of the M-S…C(π) interaction between the M-S-C thiolate sulfur and the carbonyl carbon atom as a novel intramolecular force, we have performed detailed structural analysis of intramolecular contacts for the various type of metal thiolate complexes retrieved from the Cambridge Structural Database.

[1] J. Lewiński, J. Zachara, K. B. Starowieyski, Z. Ochal, I. Justyniak, T. Kopec´, P. Stolarzewicz, M. Dranka, *Organometallics*, **2003**, *22*, 3773.