

with $\text{Ph}_2\text{Si}(\text{OH})_2$ yielded a new molecular aluminopolysiloxane $[\text{Al}(\text{OH})_4][(\text{Ph}_2\text{SiO})_2\text{O}]_4$, in which there is framework of five annelated eight-membered rings, an $\text{Al}_4(\text{OH})_4$ eight-membered ring lies in the centre of the structure. The idea of cleavage of cyclic siloxane frameworks by the Lewis acid AlCl_3 was applied to the cyclic tetrameric siloxane, in refluxing THF conditions, which resulted in the formation of the spirocyclic aluminosiloxane $[\text{Al}_3\{\text{O}(\text{Ph}_2\text{SiO})_2\}_2\text{Cl}_5]$. This is a first example of an unprecedented siloxane ring shrinkage, which has not been reported to date. The spirocyclic aluminosiloxane is also a very promising building block for fabrication of oligomeric and polymeric aluminosiloxane structures. On reacting AlCl_3 with the silsesquioxane trisilanol ligand a new anionic aluminosilsesquioxane $[\text{HNET}_3][\text{Al}\{\text{C}(\text{C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{11}(\text{OH})\}_2]$ was isolated. This complex contains two unreacted hydroxyl functionalities that makes it particularly attractive as a molecular model for natural aluminosilicates (zeolites) and as a precursor for novel heterometallic metallasilsesquioxanes.

Keywords: cage molecules, silicon compounds, metal-organic compounds

P07.05.45

Acta Cryst. (2008). A64, C412

Structures of tris{[(hydroxymethyl)aminomethane]5-bromosalicylideneaminato}diorganotin complexes

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Tris(hydroxymethyl)aminomethane and its derivatives are known to display a variety of biological activities such as antibiotic, anticancerous, antihistamine, antifungal, anti-inflammatory and many others. Tris{[(hydroxymethyl)aminomethane]5-bromosalicylideneaminato}dimethyltin(IV), **C1** and tris{[(hydroxymethyl)aminomethane]5-bromosalicylideneaminato}diphenyltin(IV), **C2** were prepared and their X-ray structures were determined. The X-ray structure of **C1** crystallises in the monoclinic, $P2_1/n$ space group with the unit cell parameter, $a = 18.9301(4) \text{ \AA}$, $b = 8.8951(2) \text{ \AA}$, $c = 19.8873(4) \text{ \AA}$ and $\beta = 114.0750(10)^\circ$. Its molecular structure shows that the ligand, tris{[(hydroxymethyl)aminomethane]5-bromosalicylideneaminato} is tridentate in which the two phenolic oxygen and an imino nitrogen atoms are involved in coordination with the tin atom. It is a dimeric structure with coordination involving one of the hydroxylmethyl groups forming a central Sn_2O_2 stannoxane ring. On the other hand, the X-ray structure of **C2** is monomeric, probably due to the steric effect as a result of the presence of bulky phenyl organic groups. The ligand in **C2** is also tridentate in which the two phenolic oxygen, one imino nitrogen atom and two phenyl rings are involved in coordination with the tin atom. **C2** crystallises in the triclinic, $P\bar{1}$ space group with the unit cell parameter, $a = 8.7156(2) \text{ \AA}$, $b = 10.0110(3) \text{ \AA}$, $c = 14.8031(4) \text{ \AA}$ and $\alpha = 104.6800(10)^\circ$, $\beta = 102.668(6)^\circ$, $\gamma = 113.2300(10)^\circ$.

Keywords: diorganotin, tridentate, X-ray crystal structure

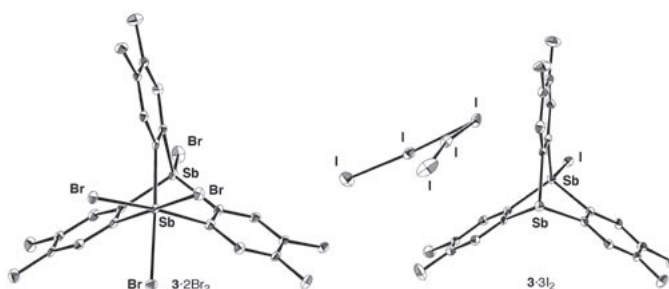
P07.05.46

Acta Cryst. (2008). A64, C412

Structural studies of 9,10-diheteratriptycenes with group 15 elements and their halogen adducts

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9,10-Diheteratriptycenes have intriguing characters because two heteroatoms of their bridgehead positions have various structural possibilities such as pyramidal, tetrahedral, and octahedral forms. In this study, 9,10-diphosphatriptycene **1**, 9-phospha-10-stibatriptycene **2**, and 9,10-distibatriptycene **3** and their halogen adducts were newly synthesized and their molecular structures were investigated by X-ray crystallography and NMR spectroscopy. The bromine adduct **3_2Br₂** forms an intramolecular salt composed of a tetracoordinate stibonium cation and a hexacoordinate stiborate anion in the crystalline state. On the other hand, the iodine adduct **3_3I₂**, which was obtained by the reaction with excess of iodine, shows an intermolecular salt composed of an iodostibonium ion and I_5^- ion. The bromine and iodine adducts showed the occurrence of a topomerization process in CD_2Cl_2 solution, respectively. We will discuss about the mechanism of the process and structures of the other halogenated adducts in the crystalline state and in their solution.



Keywords: molecular structure, X-ray crystal structure analysis, NMR spectroscopy

P07.05.47

Acta Cryst. (2008). A64, C412-413

New stable lead(II) complexes with intramolecular coordination: Experimental and theoretical study

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In continuation of our investigations on the relative contributions of different factors to the stabilization of divalent Group 14 compounds [1-5], we report here the synthesis and the results of experimental and theoretical studies of two stable lead(II) complexes $\text{Pb}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2$ (**1**) and $(\text{SiMe}_3)_2\text{NPbOCH}_2\text{CH}_2\text{NMe}_2$ (**2**). The molecular structures of these compounds were studied by NMR, IR and Raman spectroscopy both in solution and solid state as well as X-ray diffraction analysis in the crystal. The electronic structures of **1** and **2** were studied by quantum-chemical calculations within the DFT approach. The reactivity, conformational peculiarities and dynamic behavior in solution of the investigated compounds are discussed.