

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

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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

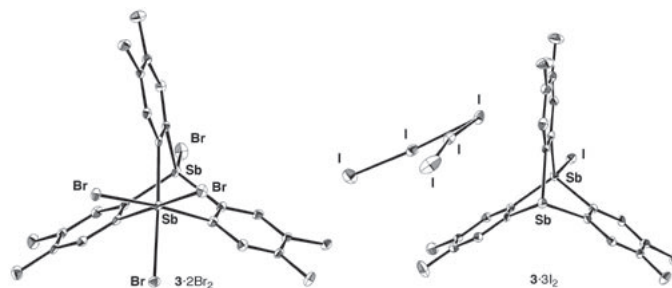
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Structural studies of 9,10-diheteratriptycenes with group 15 elements and their halogen adducts

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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

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

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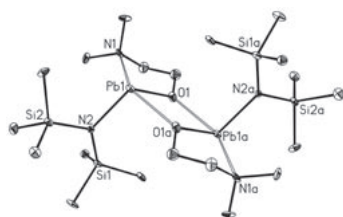
In continuation of our investigations on the relative contributions of different factors to the stabilization of divalent Group 14 compounds [1-5], we report here the synthesis and the results of experimental and theoretical studies of two stable lead(II) complexes $\text{Pb}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2$ (**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.

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Fig. The dimeric structure of 2 in the crystal.



Keywords: lead compounds, intramolecular interactions, X-ray diffraction

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Annealing cattle tibiae: From nano-bio-apatite to geo-apatite

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Biogenic minerals have attracted much attention because of their unusual properties and structural details on many length scales. To elucidate the interrelation of occluded organic material and inorganic crystal properties, we performed X-ray powder diffraction (XRPD), thermogravimetry (TG) and differential scanning calorimetry (DSC) combined with mass spectrometry on cattle tibiae annealed at temperatures up to 1000°C. TG and DSC show that three thermal regimes may be discerned: a) endothermic weight loss up to about 200°C due to dehydration, b) substantial exothermic weight loss up to 550°C due to outgassing of CO, CO₂, N₂, NO, etc., c) slight weight loss above 750°C due to further CO/N₂ etc. outgassing. Strong XRPD line broadening reveals a crystallite size of about 7nm for natural cattle tibia apatite. Narrowing line widths point to substantial crystal growth in the range 400°C -600°C, possibly enabled by relief from organic matter constraints in thermal region b). Le Bail refinement reveals anisotropic reduction of apatite cell volume after loss of organic material, thus confirming the occlusion of organic matter within the apatite structure itself. Above 700°C sharp lines allow perfect Rietveld refinements of the monoclinic apatite structure model in space group *P2₁/b*, comparable to geological apatite samples. Pair distribution function analysis of nano- and annealed apatite permit a comparison of short range P-O-distances.

Keywords: biominerals, annealing, X-ray powder diffraction

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Crystal structures of modified PNA analogues and of cationic diimine Pd(II)-alkyl complex

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Nature provides the best inspiration for development of new materials. Inorganic nucleic acid derivatives and structural mimics are receiving increased attention in recent years. We present four structures of Cu(II) complexes with amino acid substituted Di(2pyridyl) amine ligands which can serve as inorganic analogs of nucleic acids. Two of these structures have interesting intermolecular interactions and will be presented in the poster. In addition, we also present the structure of a monomer synthesized by reacting Pd(II) diimine complex with methyl methacrylate. This complex has been used to synthesize poly(alkene-block-alkene/carbon monoxide) copolymers. Late transition metal based systems have attracted attention recently, due to their lower oxophilicity and relatively high functionality tolerance. Catalytic synthesis of such copolymers is of immense interest as they may have new desirable properties.

Keywords: PNA analogues, synthesis of copolymers, crystal structure

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Coordination abilities of selected cytokinins and CDK inhibitors to transition metal ions

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The compounds bearing 6-benzylaminopurine (Bap) moiety belong to a group of plant growth hormones - called cytokinins (CKs). The CKs represent a group of compounds, which can significantly affect some of physiological functions, e.g. plant cells division, senescence, etc. The substitution of the Bap skeleton at the C2 and N9 positions by suitable side chains may lead to the formation of compounds having the ability to behave as cyclin-dependent kinase inhibitors (CDKIs). The CDKIs belong to the family of protein kinase enzymes responsible for the regulation of the cell cycle. Moreover, some of the CDKIs demonstrate both in vitro and in vivo cytotoxicity against some human cancer cell lines. A few years ago, we have found that the cytotoxicity may be increased after the coordination of both CKs and CDKIs to suitable transition metal ions. Herein, seven X-ray structures of Zn(II), Cu(II), Pd(II) and Pt(II) complexes involving the above-mentioned organic molecules are presented. The coordination ability of CKs and CDKIs can be seen from the following structures: [ZnCl₃(BapH)], [ZnCl₂(Bap)]_n, [CuCl₃(BapH)₂]Cl, [Cu₂(Bap)₄(ClO₄)₂](ClO₄)₂, *trans*-[PdCl₂(Bap)₂], *cis*-[PtCl₂(Bap)₂] and *trans*-[PtCl₂(Bap)₂], where Bap stands for a variously substituted Bap derivative. Generally, it may be concluded that the coordination ability strongly depends on an extent of substitution of Bap skeleton and reaction conditions used during the synthesis such as pH medium, molar ratio of reactants, and solvents used. In vitro cytotoxicity-structure relationship will be also discussed within the framework of the presentation. Financial support of part of this work by the Ministry of Education, Youth and Sports of the Czech Republic (a grant no. MSM6198959218) is gratefully acknowledged.

Keywords: Zn(II), Cu(II), Pd(II) and Pt(II) complexes, 6-benzylaminopurine, cytokinins and CDK inhibitors