

In the case of the bipyridyl ligand (5MeCONHbpy) possessing -NHC(O)Me at 5,5'-positions, of which the orientation is different from -C(O)NH^tBu, the structures of [Ru(5MeCONHbpy)₃]²⁺ drastically depend on the counter ion. The hexafluorophosphate salt, [Ru(5MeCONHbpy)₃](PF₆)₂, yield a bundle structure of one-dimensional chains in which the amide groups connect together with each other via hydrogen bonds. On the other hand, the chloride salt, [Ru(5MeCONHbpy)₃]Cl₂, give layer structures, where the layer of ruthenium complexes link with the chloride layer. Here, the differences in photophysical properties of the ruthenium complexes with amide groups having different orientation will be presented.

Keywords: ruthenium, bipyridine, amide Groups

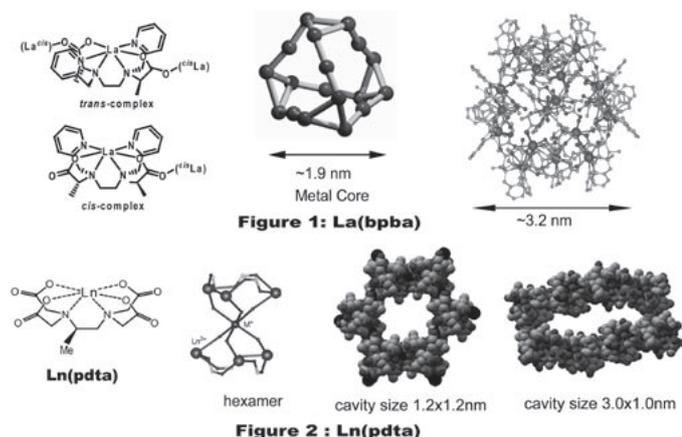
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Supramolecular assemblies of lanthanide clusters with chiral ligands in the crystalline state

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It is well known that the structures of lanthanide-based supramolecular systems are hardly predictable and often quite peculiar. Recently, we found out an unprecedented tetrahedral cage-like lanthanide cluster [La^{III}]₁₈(D-bpba)₁₈(H₂O)₃₆X₁₈ {D-bpba=N,N'-bis(2-pyridylmethyl)-N,N'-1,2-ethanediyl-bis(D-alaninate)} **1**. This octadecameric cluster is built up with twelve cis- and six trans-complexes, including the carboxylate-bridging trinuclear core due to the chiral ligand. Very recently, we found out that the trinuclear core can be easily formed in the chiral M⁺[Ln(pdta)(H₂O)₂] complexes **2** {pdta=propylenediamine-N,N',N',N'-tetraacetate}, leading to the hexameric unit via a central M⁺ ion. The hexameric unit can generate a two-dimensional porous network via the M⁺ ions in the crystalline state. Especially, supramolecular assemblies with 36 units of **2** (M⁺=K⁺, racemic crystal) and 48 units of **2** (M⁺=Na⁺, chiral crystal) generate large cavities (Figure 2). We wish to present and discuss here the details about the crystal structures of lanthanide complexes **1** (X=Cl⁻, Br⁻) and **2** (M⁺=Na⁺, K⁺; Ln=La^{III}, Pr^{III}, Sm^{III}, Eu^{III}, Gd^{III}, Dy^{III}).



Keywords: cluster in coordination complexes, lanthanide coordination, supramolecular assembly

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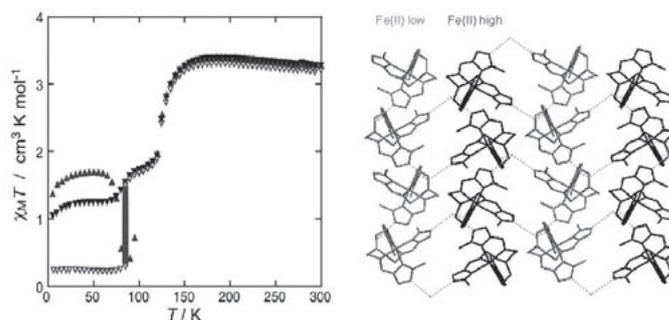
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A problem in the crystal structure of a two-step spin crossover complex

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A spin crossover (SC) complex [Fe^{II}H₃L^{Me}]ClAsF₆ revealed a two-step behavior of HS(High-Spin), (HS + LS)/2, LS(Low-Spin), where H₃L^{Me} denotes the tripod ligand containing three imidazole groups, tris[2-((2-methylimidazol-4-yl)methylidene)amino]ethylamine. The complex exhibited similar cell dimensions at three states. The space group is *P*₂₁/*n* at the HS and LS states and *P*₂₁ at the HS + LS state. The crystal structure consists of a 2D extended network structure constructed by NH...Cl hydrogen bonds, while the anion exists as an isolated counter anion. The complex cation is a chiral species with the C(clockwise) or A(anticlockwise) configuration due to the screw coordination arrangement of the achiral tripod ligand. At 180 and 90 K, there is unique one molecule in the unit cell, in which the A and C enantiomers are related by the symmetry operation to give a racemic crystal. The space group *P*₂₁ at 110 K is a chiral space group, where either of (a combination of C-HS and A-LS) and (a combination of A-HS and C-LS) should exist in a crystal. However, the Flack parameter calculated was 0.5.



Keywords: iron complex, chirality, spin crossover

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Metallasiloxane complexes: Rings and cages

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Our work is mostly focused on the synthesis of new aluminium and rare earth metallasiloxanes and their structural characterization using X-ray crystallography. Several aluminosiloxanes have been prepared by amine-assisted metathesis and condensation reactions between appropriate aluminium compounds and diphenylsilanediol. The reactions proceeded with the condensation of Ph₂Si(OH)₂ to higher siloxanes containing -OSiPh₂OPh₂SiO- and -OSiPh₂(OSiPh₂)Ph₂SiO- units giving anionic or cyclic aluminosiloxanes. The cyclic complex [AlCl(THF){O(Ph₂SiO)₂}]₂ prepared is the first example of a 12-membered cyclic aluminosiloxane. Interactions of Al(Et)₃

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

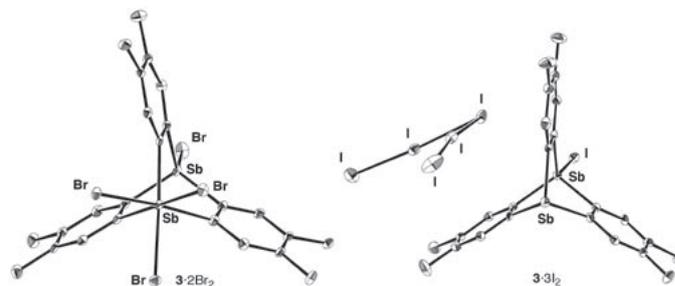
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Structural studies of 9,10-diheteratriptycenes with group 15 elements and their halogen adducts

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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.