

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

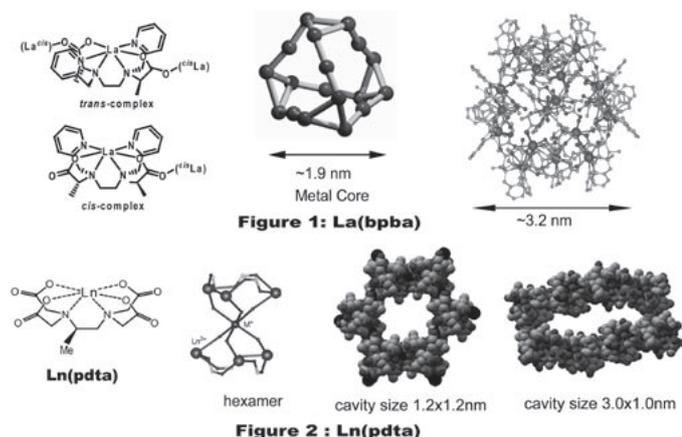
P07.04.41

Acta Cryst. (2008). A64, C411

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

P07.04.42

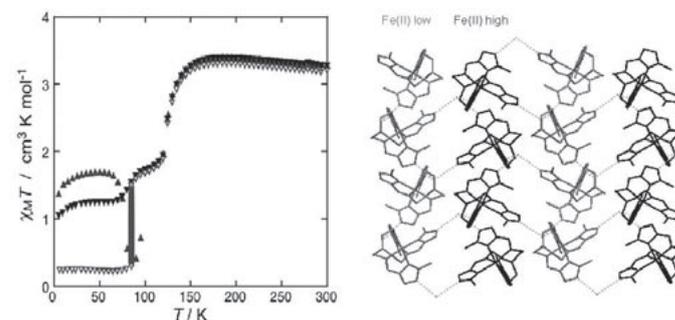
Acta Cryst. (2008). A64, C411

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

P07.06.43

Acta Cryst. (2008). A64, C411-412

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