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A new lanthanide-organic framework (LOF) based on a long (21.2Å) and rigid bid-Gd complex synthon (complex 1) and carbonate anion spacers was discovered. Complex 1 is comprised of two Gd³⁺ ions complexed with a pyridine tetracarboxylate ligand and a bridging linear 1,4-diethynylbenzene unit. Two water molecules are coordinated to each Gd ion in order to satisfy its high coordination number. Carbonate anions are coordinated to the Gd³⁺ ions linking between two synthons, resulting in the construction of two network types (type A and B). All three oxygen atoms of the carbonate anion are utilized in its function as a spacer between two synthons (complex 1) in the networks. In addition, the carbonate anions also serve as acceptors for hydrogen bonding (O-H...O), with water molecules coordinated to Gd³⁺ ions in both the networks. While all the synthons adopt a planar conformation in network A, they are backed alternately in plane and vertical conformation in network B. Auxiliary Na⁺ ions and water molecules are positioned around the carbonate ions and connect between the networks. Overall, in this new LOF the synthons are packed in criss-cross fashion and tethered by carbonate spacers, creating a crystal lattice perforated by 10.6 × 15.6Å and 18.6 × 15.6Å wide-open channels.

Keywords: supramolecular assembly, gadolinium complexes, crystal design.

MS24.P39

Acta Cryst. (2011) A67, C371

Synthesis and Crystal Structure of a Two-Dimensional Di-Aqua Pyromellitate Strontium(II) Complex: [Sr₂{(OOC)₂-C₆H₂(COOH)₂}(H₂O)₂]_n

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In recent years, metal-organic coordination polymers have attracted considerable attention and been rapidly developed due to their fascinating molecular topologies and crystal-packing motifs along with potential applications as smart optoelectronic, magnetic, and porous materials[1–2]. These specific features are due to the carboxylate group which acts as a linker between inorganic moieties and to the flexible or relatively rigid carbon backbone, which gives a modular nature to the resulting MOFs[3-5]. Most of the bridging ligands used in construction of the porous MOFs are rigid such as benzene-polycarboxylate. Benzene-1,2,4,5-tetracarboxylic acid (H₄BTC) is an important carboxylate ligand as it has multiple coordinating modes. Moreover, the various coordination geometry of metal ions and the four carboxylic groups of (H₄BTC) completely or partially deprotonated, have led to the generation of products containing 1D chains, 2D layers and three-dimensional packings[7].

We report here the synthesis and structure of a novel alkaline-earth metal benzene-tetracarboxylate complex [Sr₂{(OOC)₂-C₆H₂(COOH)₂}(H₂O)₂]_n. The asymmetric unit consists of two Sr(II) cations, two pyromellitate dianions (H₂BTC)²⁻ and two aqua ligands. The two independent [H₂BTC]²⁻ ligands adopt different coordination mode. They are heptadentate and octadentate and coordinate to five and six metals centers respectively. The coordination polyhedra around

the two Sr atoms can be described as a distorted monocapped square antiprism and a distorted dodecahedron respectively. Among all the nine coordinated oxygen atoms, one come from one coordinated water molecule and the remaining from six [H₂BTC]²⁻ dianions ligands while the eight oxygen atoms around the second metal center belong to one coordinated water molecule and five [H₂BTC]²⁻ dianions ligands.

Each strontium atom is linked to two Sr metals through μ_{oxo} bridges leading to the formation of an infinite zigzag chains of one-edge sharing SrO₉/SrO₈ polyhedra. The chain running parallel to the a axis are further connected through pyromellitate ligands resulting in a two-dimensional network. The crystal structure is further stabilized by hydrogen bonds between chains, involving the four acid groups and the two coordination water molecules as donors.

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Keywords: Coordination polymers, pyromellitate, strontium

MS24.P40

Acta Cryst. (2011) A67, C371-C372

Synthesis and structural study at 100K of a new double metal oxalate Cs₂Cr(C₂O₄)₂(H₂O)₄

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In the course of our studies dealing with oxalate-based bimetallic compounds potentially leading to Metal-organic-frameworks (MOFs) and Coordination polymers (CPs), we have obtained single crystals of [M_xCr(C₂O₄)₂(H₂O)_y]_n. When M=Rb⁺, a new supramolecular isomer RbCr(C₂O₄)₂(H₂O)₂]_n has revealed a 3D extended framework built up from layers containing bi-polyedra surrounding Rb and Cr respectively [1].

This structure is completely different from the previously known^[2]. When M=Cs⁺, and replacing RbCl by a caesium salt in the same synthesis conditions and mixture, including a Cr³⁺ starting salt, few pink prismatic crystals studied by XRD at 100K, brought out a polymeric structure corresponding to a tetraaqua complex, with x=2, owing to the fact that the transition metal has been reduced during synthesis process leading to the unexpected dication Cr²⁺.

This poly[tetraaquad-μ₆-oxalato]chromium(II)dicaesium(I)] is isotypic with Cs₂M(C₂O₄)₂.4H₂O (M=Mg(II); Co(II)) [3], [4]. It belongs to C2/c space group, with a=16.1880(4)Å; b=7.3212(2)Å; c=13.5268(3)Å; β=128.3640(10)°.

The asymmetric unit contains one unique Cs atom, one Cr atom, one oxalate dianion and two water molecules. Only the Cr(II) atom is located on a special position (O y ¼). The nine-coordinated caesium atom is surrounded by six oxalate ligands involving all their donor atoms. One O atom of each functional group chelates to the central alkali in a typical five-membered ring. The coordination sphere is completed by the two independent water molecules. The nearly regular CrO₄(H₂O)₂ octahedron consists of four O atoms from two dianions in a η⁴-chelation and two O atoms from two equivalent water molecules in *cis* position. Consequently, the oxalato ligand is bis-bidentate,

bridging the alkali and Cr(II) and forming five-membered rings with each central atom.

The structure consists of infinite files built up from Cs_2O_{16} binuclear entities sharing one face with CrO_6 octahedra, running along [10 $\bar{1}$] direction, and interconnected by the bis-bidentate oxalate ions. In the overall 3D framework, within $\text{Cs}_2\text{CrO}_{19}$ bimetallic groups, the Cr(II) octahedron shares three vertex with each of the two neighbouring Cs polyhedra. The medium observed H-bonds occur between water molecules as well as between the aqua and oxalato ligands and participate to the supramolecular extension of the framework.

In the serie, only few homometallic carboxylate compounds containing the chromium II, have been reported in literature [4] and the investigated compound could be the first bimetallic dicarboxylate including Cr(II), obtained in crystalline solid state.

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Key-words: supramolecular structure, chromium II, oxalato-bridged bimetallic polymer.

MS24.P41

Acta Cryst. (2011) A67, C372

The crystal structure-physicochemical property relationship of sitafloxacin

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Sitafloxacin (STFX) is a new fluoroquinolone antibiotic which was recently put on the market in Japan and several Asian countries. Two anhydrides (α -form and β -form) and three hydrates (hemihydrate, monohydrate and sesquihydrate) of STFX have been found so far. Physicochemical properties (hygroscopicity, photostability and solubility) of these crystalline forms were investigated and correlated with the structure of each crystalline form.

Sesquihydrate showed approximately 2% weight change between 1% and 90% relative humidities (RHs). Weight changes of hemihydrate and monohydrate were very slight. Anhydrides did not show weight changes. In sesquihydrate, two STFX molecules and four water molecules are contained in an asymmetric unit and STFX molecules form a channel structure where water molecules exist. This particular structure may cause non-stoichiometric hydration. Contrary to sesquihydrate, water molecules in a monohydrate are located in well-defined and isolated crystallographic sites. The difference of the structure of crystallographic sites where water molecules exist causes different moisture sorption-desorption profiles between sesquihydrate and monohydrate. Unfortunately, the crystal structure of hemihydrate has not been determined

The β -form exhibited significantly severer photodegradation than the other four forms under the irradiation of a D65 lamp. STFX molecules exist in non-ionic form in the β -form, whereas STFX molecules exist as zwitterionic form in other forms. The protonation in the β -form allowed intramolecular hydrogen bonding that caused a red shift on the solid-state UV spectrum. This red shift caused greater absorption of photoenergy and consequent degradation under the irradiation of a D65 lamp.

Solubility is also affected by the crystalline structure: torsion at the quinolone ring of crystalline forms of higher solubility (α -form and monohydrate) is opposite to those of lower solubility (β -form and sesquihydrate). Standard free energy of the formation of STFX molecule with each torsion was estimated by DFT (density functional theory) calculation. It is suggested that the torsion observed in α -form and monohydrate cause higher standard free energy of a formation that has a close relation with solubility.

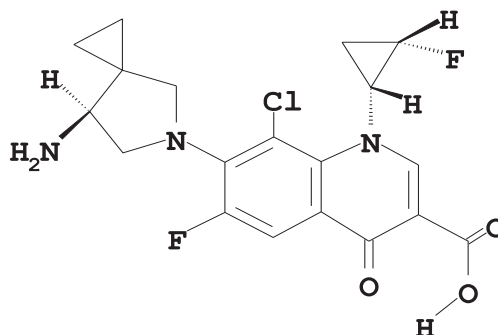


Figure. Chemical structure of sitafloxacin.

Keywords: crystal structure, physicochemical property, pharmaceuticals

MS24.P42

Acta Cryst. (2011) A67, C372-C373

Synthon polymorphism and pseudopolymorphism in co-crystals. The 4,4'-bipyridine – 4-hydroxybenzoic acid structural landscape

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The study of co-crystals is an important part of crystal engineering and it is believed that co-crystals are less prone to polymorphism than monocomponent crystals. The matter of synthon polymorphism is more quantifiable because it involves enumerating structures that contain different synthons in different polymorphs. There are 38 co-crystals reported to be polymorphic but only three among them show synthon polymorphism [1]. In this context, we have found synthon polymorphs of the 1:2 co-crystal of 4,4'-bipyridine and 4-hydroxybenzoic acid [2]. In these polymorphs, the phenolic (Form 1) and carboxyl OH groups (Form 2) of the acid are respectively hydrogen bonded to the pyridine N-atom. Form 1 is the more stable polymorph. The structures of the two forms reflect the interplay of close packing and intermolecular interactions in organic crystals; it is clear that such interplay between geometrical and chemical factors is one of the important reasons for the existence of polymorphs [3]. These forms are obtained with slight changes in the crystallization conditions. This shows that they are energetically comparable. Our results invoke the question as to whether the chemical and geometrical models are related to one another and if the basis for the chemical model actually arises from the geometrical model itself. In addition, the 2:1 co-crystal pseudopolymorph (Form 3) is found within the same structural landscape with the structural roles of the two bipyridine N-atoms being quite distinct. The difference between these roles is exploited in obtaining the 2:1 co-crystal of 4-phenylpyridine and 4-hydroxybenzoic acid (Form 4) which forms a part of the extended structural landscape. This more broadened definition of the structural landscape, to include slightly different chemical substances, is believed to be advantageous [4].