

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

The structure consists of infinite files built up from  $\text{Cs}_2\text{O}_{16}$  binuclear entities sharing one face with  $\text{CrO}_6$  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

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### 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 ( $\alpha$ -form and  $\beta$ -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  $\beta$ -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  $\beta$ -form, whereas STFX molecules exist as zwitterionic form in other forms. The protonation in the  $\beta$ -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 ( $\alpha$ -form and monohydrate) is opposite to those of lower solubility ( $\beta$ -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  $\alpha$ -form and monohydrate cause higher standard free energy of a formation that has a close relation with solubility.

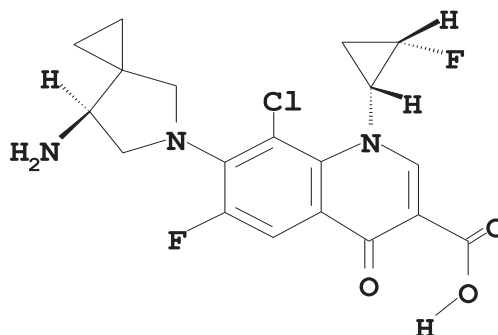


Figure. Chemical structure of sitafloxacin.

**Keywords:** crystal structure, physicochemical property, pharmaceutics

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### 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].