

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.

[1] H. Kherfi, M. Hamadene, A. Guehria-Laïdoudi, S. Dahaoui and C. Lecomte, *Acta Cryst* **2011**, C67, m85-m89. [2] U. Kolitsch, *Acta Cryst.*, **2004**, C60, m129.[3] K. Schwendtner, U. Kolitsch, *Acta Cryst.*, **2004**, E60, m659. [4] F.A. Cotton, E.A. Hillard, C.A. Murillo, H.C. Zhou, *J. Am. Chem. Soc.*, **2000**, 122, 416-417.

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

Tetsuya Suzuki,^a Katsuhide Terada,^b ^aAnalytical & Quality Evaluation Research Laboratories, Pharmaceutical Technology Division, Daiichi Sankyo Co., Ltd., Shinagawa-ku, Tokyo 140-8710, (Japan). ^bDepartment of Pharmaceutics, School of Pharmaceutical Sciences, Toho University. E-mail: suzuki.tetsuya.fb@daiichisankyo.co.jp

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.

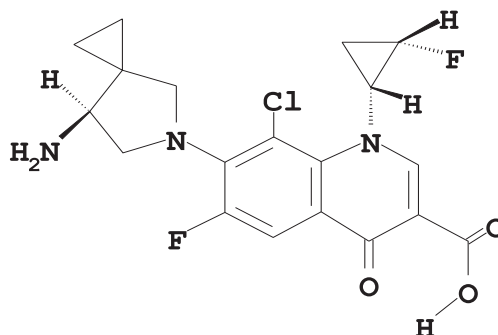


Figure. Chemical structure of sitafloxacin.

Keywords: crystal structure, physicochemical property, pharmaceuticals

MS24.P42

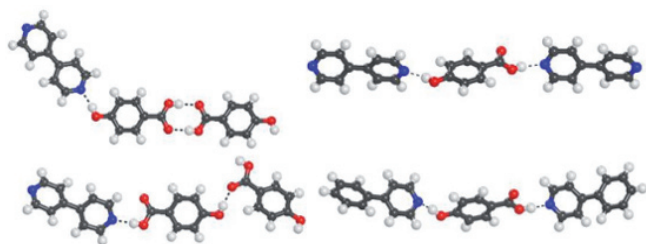
Acta Cryst. (2011) A67, C372-C373

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

Arijit Mukherjee, Gautam R. Desiraja. *Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, (India)*. E-mail: a.mukherjee@sscu.iisc.ernet.in

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].

The structural landscape for the 4,4'-bipyridine–4-hydroxybenzoic acid system consists of two polymorphs and two pseudopolymorphs



[1] H.D. Clarke, K.K. Arora, H. Bass, P. Kavuru, T.T. Ong, T. Pujari, L. Wojtas, M.J. Zaworotko, *Cryst. Growth Des.* **2010**, *10*, 2152-2167. [2] A. Mukherjee, G.R. Desiraju, *Chem. Commun.* **2011**, *47*, 4090-4092. [3] (a) A. Dey, G.R. Desiraju, *CrystEngComm.*, **2006**, *8*, 478-482. (b) G.R. Desiraju, *Angew. Chem., Int. Ed.*, **2007**, *46*, 8342-8356. [4] M.T. Kirchner, L.S. Reddy, G.R. Desiraju, R. K.R. Jetti, R. Boese, *Cryst. Growth Des.*, **2004**, *4*, 701-709.

Keywords: polymorphism, hydrogen bond, crystal engineering.

MS24.P43

Acta Cryst. (2011) **A67**, C373

Compounds of organic molecules and metal halides: structures and properties

Melanie Rademeyer, David C. Liles, Gerhard Overbeek, Stefan Coetzee. *Department of Chemistry, University of Pretoria, Pretoria, (South Africa)*. E-mail: Melanie.rademeyer@up.ac.za

Organic molecules containing amine, carboxylic acid and/or amide functional groups may be combined with inorganic metal halides to form two different types of hybrid materials, both of which are of technological interest and self-assemble at the nano-scale.

When the components are combined as organic cations and perhalometalate anions, the resulting ionic organic-inorganic hybrid material often retains the properties of the individual parts, with the inorganic component potentially contributing mechanical hardness, thermal stability, electronic properties (conductor, semiconductor, insulator) and magnetic properties, while the organic component may add structural diversity and optical properties (fluorescence and luminescence) [1]. Proven applications of these ionic hybrids include light emitting diodes (LED's) [1].

Coordination compounds or coordination polymers are formed when the organic molecules coordinate to the metal atom of the metal halide component. The coordination polymers may be related to metal organic framework materials (MOF's), and contain both organic linkers and inorganic halide linkers, whereas MOF's typically only have organic linkers. Related coordination polymers have been reported to have interesting properties including non-linear optic behaviour and magnetic properties [2].

In the current study the effect of a change in one of the three parameters (organic component, metal atom and halide atom) on the crystal structures, packing and crystal engineering motifs are reported. In addition, the preliminary results of experimental properties, including band gap and electronic conduction, are presented, and compared to the properties calculated employing the software Materials Studio [3].

[1] D.B. Mitzi, K. Chondroudis, C.R. Kagan, *IBM J. Res. & Dev.* **2001**, *45*, 29-45 [2] D.M. Ciurtin, Y.B. Dong, M.D. Smith, T. Barclay, H.C. zur Loye, *Inorg. Chem.* **2001**, *40*, 2825-2834. [3] Accelrys **2010**, *Materials Studio 5.5*.

Keywords: crystal engineering, properties

MS24.P44

Acta Cryst. (2011) **A67**, C373

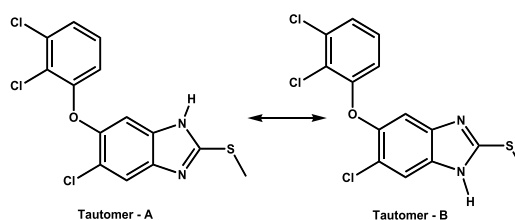
Tautomeric polymorphism in triclabendazole

Srinu Tothadi,^a Ram K. R. Jetti,^b Balakrishna R. Bhogala,^b Asha R. Gorantla,^b Tejender S. Thakur,^a Gautam R. Desiraju,^a ^a*Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, (India)*. ^b*Chemical Research Division, API-R&D, Matrix Laboratories Limited (a Mylan company), Plot No. 34A, Anrich Industrial Estate, Bollaram Village, Jinnaram Mandal, Medak District, Pin No. 502325, A.P., (India)*. E-mail: srinut.iisc@gmail.com

Triclabendazole [1] (TCB), 5-chloro-6-(2,3-dichlorophenoxy)-2-(methylthio)benzimidazole, is a classical veterinary anthelmintic drug active against liver flukes and belongs to the benzimidazole family of anthelmintics. It is known to exhibit polymorphism [2]. Two anhydrides (Form I and II), three solvates and an amorphous form are known. This study reports for the first time the crystal structures of Form I and Form II. The structural features of these crystal forms are interesting in the context of a little known variety of polymorphism, namely tautomeric polymorphism [3] (Scheme 1).

The crystal structure analysis reveals that Form I ($Z' = 2$) is composed of two molecules of tautomer A and Form II ($Z' = 1$) contains a 1:1 tautomeric mixture of A and B (Scheme 1) with the N=C-N-H fragment of the imidazole showing positional disorder (H-N=C-N-H). The polymorphs were also characterized using different solid state techniques (DSC, TGA, PXRD, IR and SSNMR). Based on enthalpy of fusion rule⁴ and infrared rule⁴ Form I and Form II are monotonically related to each other, and Form I is thermodynamically the most stable form. In addition, the tautomeric forms present in Form I and Form II were characterized by variable temperature NMR experiments in DMSO-*d*₆.

Further, to check the existence of the 100% tautomer B of TCB we carried out various co-crystallization experiments with 3,5-dinitrobenzoic acid and 3,5-dinitrosalicylic acid in different solvents and elucidated their crystal structures. In solvated cocrystals of dinitrobenzoic acid (methanol, acetone, acetonitrile and DMF) and dinitrosalicylic acid (methanol and DMF), the TCB molecule exists as a 100% tautomer B. However, in the latter case there is a proton transfer observed from the carboxylic acid to N(1) of the benzimidazole ring. In the absence of a carboxylic acid co-former TCB forms a 1:1 dimethylacetamide/water solvate with tautomer A. The presence of 100% tautomer B in cocrystals/salts of TCB strongly supports tautomeric polymorphism in TCB and confirms the coexistence of both tautomers A and B in Form II. The intriguing structural and thermodynamic features of these tautomorphs will be discussed in detail.



Scheme 1. Two possible tautomeric forms of TCB

[1] Patent US 4197307 [2] (a) M. Kuhnert-Brandstätter, U. Porsche, *Scientia Pharmaceutica (Sci.Pharm)* **1990**, *58*, 55-67. (b) R. K. R. Jetti, O. D. Tyagi, A. R. Gorantla, 2722/CHE/2007. (c) Patent EP 0224249 [3] P. M. Bhatt, G. R. Desiraju, *Chem. Commun.*, **2007**, 2057-2059. [4] A. Burger, R. Ramberger, *Mikrochim. Acta* **1979**, *2*, 273-316, 259-271.

Keywords: crystal engineering, polymorph, drug.