Experimental report

15/09/2015

Proposal: 5-12-309 **Council:** 4/2014

Title: Hydrogen bonding in co-crystals ofcyprodinil

Research area: Chemistry

This proposal is a new proposal

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Samples: Co-crystal Cyprodinil/2-aminopyrimidine
Co-crystal Cyprodinil/maleimide

Instrument	Requested days	Allocated days	From	To
D19	14	2	24/09/2014	29/09/2014

Abstract:

Our co-crystallization studies of the commercial fungicide Cyprodinil show that it forms new co-crystals with 2-aminopyrimide and maleimide as co-formers. As cyprodinil is a low melting material that undergoes phase transformation in storage such high melting cocrystals may of of significant commercial benefit. These co-crystals are formed through moderately strong hydrogen bonds between the co-former and cyprodinil molecules - though hydrogen positions have been only inferred/calculated in our SXD studies. The aim of this experiment will be to accurately determine the hydrogen-bonding patterns in these two agrochemical co-crystals - we believe the first time such a system has been studied using SND. Each co-crystal will be studied at 3 temperatures so that the hydrogen bonding can be modeled using appropriate theoretical models and software.

A co-crystal of the fungicide Cyprodinil with 2-fluorobenzoic acid as co-former was studied in proposal 5-12-309. Data were collected on a large crystal (4,1 x 3,4 x 1,8 mm) at four temperatures, 30, 100, 200, and 298K, in order to study the effect of temperature on the hydrogen bond, which is the main feature in the definition of the crystal packing of this complex, as shown in Fig. 1. Unfortunately, the refinement of the structure at 298K showed a loss in intensity of the reflection used to detect possible changes in the crystal during the experiment. The set of data collected at room temperature led to a poorly refined structure, whose results do not allow model a reliable crystal structure. Unit cell parameters for the structure at 30K are reported in Table 1.

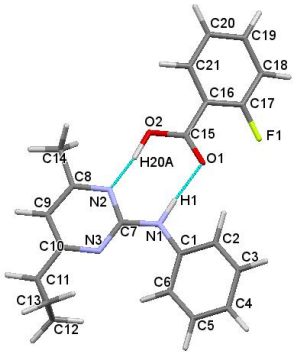

Fig.1. Particular of the crystal packing.

Wavelength	1.1700 Å
Temperature	30K
System	Monoclinic
Space group	$P2_1/n$
a	11.0969(4) Å
b	8.1618(3) Å
c	20.6207(7) Å
β	102.863(3)°
Z	4
V	1820.8(1) $Å^3$

Table 1. Cell parameters at 30K.

The molecules of the fungicide and of the co-former arrange themselves in dimers, formed by the interaction of the amino-pyrimidine part of the Cyprodinil and the carboxylic group of the acid. These dimers are formed by two hydrogen bonds (HBs): one of medium strength between the hydrogen atom of the amino group and the oxygen atom of the carboxylic group; and a strong HB featuring the hydrogen of the hydroxyl group as donor and the nitrogen atom on the pyrimidine ring as acceptor. Thanks to the single crystal neutron diffraction, it is possible to investigate the characteristics of the HB, in particular the shape of the hydrogen thermal ellipsoids. As shown in Fig. 2, the thermal ellipsoid of H20A is elongated along the direction of interaction, suggesting a stronger hydrogen bond than the one involving H1. The lengths of the two hydrogen bonds, together with other relevant bond distances, are reported in Table 2. The dimers are stacked into piles held together by π-π interactions, leading to the formation of a fishtail-like structure, as shown in Fig. 3.

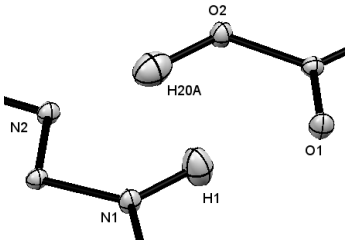

Fig. 2. Thermal ellipsoids.

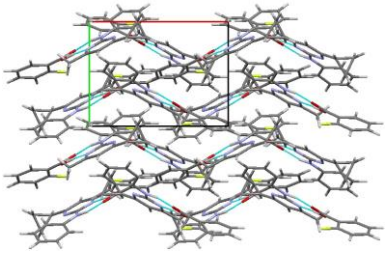

Fig. 3. Crystal packing.

	30K	100K	200K
H1···O1	1.866(2) Å	1.869(2) Å	1.867(3) Å
H20A···N2	**1.505(2) Å**	**1.501(2) Å**	**1.496(3) Å**
N1–H1	1.029(2) Å	1.023(2) Å	1.015(3) Å
O2–H20A	1.098(2) Å	1.096(2) Å	1.096(3) Å
N1···O1	2.885(1) Å	2.880(1) Å	2.871(2) Å
N2···O2	2.595(1) Å	2.589(1) Å	2.584(2) Å

Table 2. Relevant bond distances and lengths of interaction.

The data collected at all temperatures were corrected for the absorption, using the analytical correction with the indexing of the crystal faces. The refinement at 30K was very successful, exhibiting the following R-values: R(int) = 0.0408; R(sigma) = 0.0288; and R1 = 0.0305.