

in the Br- and NO₂- derivatives of 1-phenylethanones (1,2). However, when the N atom in these structures is pyramidal, no distant dimers are formed and the N-H...C(aryl) contacts become evident.

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Keywords: hydrogen bonds in organic crystals, small molecules organic, long-range contacts

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The interaction between H-bond and polyhedral network in the polymorphs of aluminium hydroxide

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We have investigated several polymorphs of aluminium hydroxide in the last few years. The most important of these is the structural investigation under pressure of the hydrogen bond (H-bond) in δ -AlOOH, a phase which is a potential water reservoir in cold subducted slabs, transporting water into the lower mantle. Structures of aluminium hydroxides could be characterized as a combination of 0D (D: dimensional) or 1D H-bonding network and 2D or 3D dimensional Al(O, OH)₆ polyhedral network. For example, δ -AlOOH is considered to be a combination of 0D H-bond and 3D polyhedral networks. The H-bond and polyhedral networks are not isolated, but interacted each other via valence sum of the oxygen atoms. For example if we consider a fictitious 1D network consists of 0D H-bond and 0D AlO molecule like: -O-Al-O-H_a...O-Al-O-H_b...O-Al-O-H_c..., where H_a is not able to move independently to acceptor site due to the electrostatic valence principle. This can be considered as a kind of 'ice rule.' In this study, we will present the results of x-ray and neutron diffraction studies for δ -AlOOH, β -AlOOH (boehmite), η -Al(OH)₃ and δ -Al(OH)₃. The last two polymorphs are high pressure modifications of γ -Al(OH)₃ (gibbsite), and their structures had remained unknown for quarter of a century after their discovery. η -Al(OH)₃ has the layered structure like gibbsite, and δ -Al(OH)₃ has the A-site deficient perovskite (ReO₃-type) structure. Although the polymorphs of aluminium hydroxide have a large variety of structures, some features of their phase transitions can be understood by the concept that the H-bonding network interacts with the polyhedral network.

Keywords: hydrogen bonding network, high pressure, aluminium hydroxide

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Rationalizing polymorph stability using hydrogen bonding propensities

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Hydrogen bonding is crucial to structural stability in organic crystals, with impact widely reported in the pharmaceutical industry, and elsewhere [1,2]. Here, in an informatics-based approach, the relative stability of polymorphic structures is assessed based on the hydrogen bonding they exhibit. The implicit connection is made between most probable and energetically favourable interactions. The Logit Hydrogen Bonding Propensity method [3] is used to predict preferences for hydrogen bond formation. The method applies data derived from other known compounds to fit a probability model that creates propensity scores for hydrogen bonding atoms to interact in a crystal structure. This flexible method is parameterized to molecular, chemical and crystal structure descriptors. Once a model is derived, target 2D connectivity information at most is required to calculate propensity predictions specific to that target. In this presentation three contrasting drug-like systems will form an application of the method. The examples are modelled using crystal structure datasets from the Cambridge Structural Database (CSD) [4]. The method is also naturally extendable to use of additional e.g. internal company databases. Focus will be paid to statistical relevance and the influence of the model descriptors, which have physically meaningful interpretations. Relevant feedback into the hydrogen bond prediction from those parameters will also be discussed.

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Keywords: polymorphism, cambridge structural database, hydrogen bonding

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The hydrogen bonds in transition-metal oxalate complexes: Influence of Jahn-Teller distortion

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Single crystals of transition-metal oxalate complexes [M(C₂O₄)₂H₂O: M = Mn(II), Fe(II), Co(II), Ni(II)] were synthesized and analyzed by micro-Raman scattering spectroscopy; the O-H stretching bands of the complexes were located at 3324.7 cm⁻¹ for Mn(II), 3305.5 cm⁻¹ for Fe(II), 3324.6 cm⁻¹ for Co(II) and 3340.2 cm⁻¹ for Ni(II), respectively. The stretching wavenumber of O-H decreases considerably with increasing strength (decreasing length) of the hydrogen bond (Libowitzky 1999), and thus the Raman spectra indicated that Fe(II)-oxalate has the strongest hydrogen bonds among the present complexes. The crystal structure of Fe(II)-oxalate was analyzed using single-crystal X-ray diffraction method and refined to the agreement index R1 = 3.22 % calculated for 595 unique observed reflections. This oxalate crystallizes in the monoclinic system, space group C2/c, with unit cell dimensions of a = 12.011(11), b = 5.557(5), c = 9.920(9), β = 128.53(3), V = 518.0(8), and Z = 4. In the crystal structure, the alternation of oxalate anions [(C₂O₄)²⁻] and Fe(II) ions constitute one-dimensional chain structures parallel to [010]; water molecules (H₂O) form hydrogen bonds to link the chains, where

(H₂O) is essentially part of the crystal structure. Fe(II) ion having electronic configuration [Ar]3d⁶ is in a high-spin state since both H₂O and oxalate anion are weak field ligands (Moore 2004). Hence the electron configuration of Fe(II) ion is somewhat asymmetric that Fe(II)-polyhedron is vertically contracted by Jahn-Teller effect (Burns 1993). Bond-valence analysis (Brown 2002) of the crystal structure of Fe(II)-oxalate suggested that the polyhedral distortion gives rise to the strong hydrogen bond.

Keywords: hydrogen bonding of coordination compounds, Jahn-Teller effect, Raman spectroscopy

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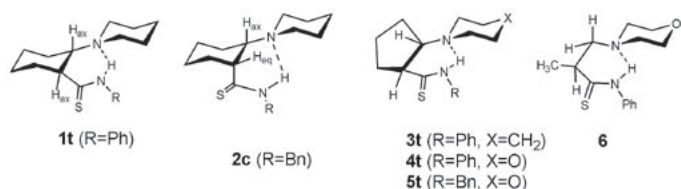
Secondary thioamide group deformations caused by intramolecular hydrogen bond

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Structures of several *b*-aminofunctionalized secondary thioamides capable to form intramolecular hydrogen bond N-H...N have been determined by X-ray diffraction (Scheme 1). Particular attention has been directed to the deformations of the thioamide group caused by steric strain. Out-of-plane deformations of the thioamide group are described in terms of bending (χ_C and χ_N) and twisting (τ) parameters [1]. The X-ray results show that the thioamide group displays high resistance to steric stress which is in this case caused by the intramolecular hydrogen bond and deviations of the thioamide group from planarity are small if any. On the other hand, some sp² bond angles in the thioamide group of the molecules under exploration as well some tetrahedral bond angles in the saturated parts are substantially changed from the ideal values in order to retain the thioamide group planarity.

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Keywords: secondary thioamides, intramolecular hydrogen bond, deformations of the thioamide group

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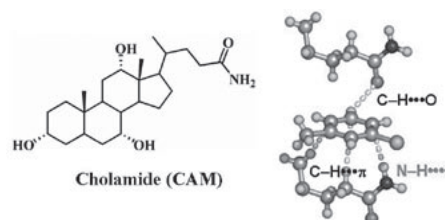
Weak hydrogen bonds in cholamide inclusion crystals with aromatic guests

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Steroidal cholamide (CAM) forms inclusion crystals with more than twenty aromatic compounds in 1:1 or 2:1 host-to-guest molar ratios. The 1:1 crystals have guest-dependent host frameworks, where

weak hydrogen bonds such as N-H/ π , C-H/ π , and C-H/O play a key role in linking the host and guest molecules. The steroidal side-chains involving methyl, methylene, and amide groups serve as the hydrogen bond donors, and aromatic guest molecules serve as the acceptors. Three kinds of such weak hydrogen bonds are visualized by the Hirshfeld surfaces of the guest molecules. Comparisons of the inclusion crystals of CAM and cholic acid (CA) with the same guests clarify a profound effect of the weak hydrogen bonds. In the case of the 1:1 crystals, the N-H/ π hydrogen bonds explain the fact that CAM always employs a β -*trans*-type framework, while CA employs either an α -*gauche*- or β -*trans*-type framework. On the other hand, the 2:1 crystals, termed DCA-type, have only C-H/ π hydrogen bonds. The guest-dependent isomerization of these frameworks is examined in terms of the weak hydrogen bonds as well as compatibilities in size and shape.



Keywords: hydrogen bonding, inclusion compounds, supramolecular chemistry

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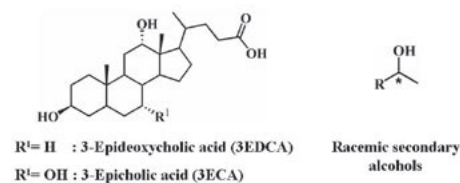
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Chiral recognition for inclusion compounds of 3-epicholic and 3-epideoxycholic acids with alcohols

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Chiral recognition mechanism is still an interesting subject for efficient enantioresolution of racemates by using inclusion crystals. We perform a systematic study on cholic acid derivatives as the host compounds for enantioresolution of various alcohols. So far, we reported that cholamide includes a wide variety of the alcohols and exhibits a specific ability for recognizing (*S*)-2,2-dimethyl-3-hexanol. Moreover, it was found that 3-epicholic and 3-epideoxycholic acids showed efficient enantioresolution towards aliphatic secondary alcohols, such as 2-pentanol, 2-hexanol, 2-heptanol, and so on. The enantioresolution for two stereogenic carbons was ascertained toward (2*R*,3*S*)-3-methyl-2-pentanol (over 95 ee%). Here we describe crystal structures of these inclusion compounds as well as a plausible mechanism for such chiral recognition. The mechanism is based on a four-point location model which demands a disordered structure of the guest molecules in a concaved surface of host channels.



Keywords: chiral recognition, inclusion compounds, supramolecular chemistry