

Hydrogen bonded binary molecular adducts derived from exobidentate N-donor ligand with dicarboxylic acids: Acid···imidazole hydrogen-bonding interactions in neutral and ionic heterosynthons

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ABSTRACT

Four new binary molecular compounds between a flexible exobidentate N-heterocycle and a series of dicarboxylic acids have been synthesized. The N-donor 1,4-bis(imidazol-1-ylmethyl)benzene (bix) was reacted with flexible and rigid dicarboxylic acids viz., cyclohexane-1,4-dicarboxylic acid (H_2chdc), naphthalene-1,4-dicarboxylic acid (H_2npdc) and 1H -pyrazole-3,5-dicarboxylic acid (H_2pzdc), generating four binary molecular complexes. X-ray crystallographic investigation of the molecular adducts revealed the primary intermolecular interactions carboxylic acid···amine (via $O-H\cdots N$) as well as carboxylate···protonated amine (via $N-H^+\cdots O^-$) within the binary compounds, generating layered and two-dimensional sheet type H-bonded networks involving secondary weak interactions ($C-H\cdots O$) including the solvent of crystallization. Depending on the differences in pK_a values of the selected base/acid (ΔpK_a), diverse H-bonded supramolecular assemblies could be premeditated. This study demonstrates the H-bonding interactions between imidazole/imidazolium cation and carboxylic acid/carboxylate anion in providing sufficient driving force for the directed assembly of binary molecular complexes. In the two-component solid form of heterosynthons involving bix and dicarboxylic acid, only H_2chdc exist as cocrystal with bix, while all the other three compounds crystallized exclusively as salt, in agreement with the ΔpK_a values predicted for the formation of salts/cocrystals from the base and acid used in the synthesis of supramolecular solids.

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1. Introduction

Crystal engineering offers a rational approach to the design of materials with new compositions, properties and crystal structures. Much as an organic chemist employs the covalent bond in the design of target molecules, non-covalent bonds can be exploited in the design of supramolecular assemblies [1,2]. Such non-covalent interactions include hydrogen bonding, van der Waals, π - π stacking, and electrostatic interactions. These kind of molecular interactions could be utilized in designing cocrystals, solvates, organic salts, polymorphs and pseudopolymorphs, etc. [3–7], out of which cocrystals are of widespread interest.

Cocrystal [8–10], also referred to as molecular complex, is a homogeneous phase of two or more different components in a stoichiometric composition, and often relies on hydrogen bonded assemblies between neutral molecules. Strong and directional hydrogen bonds have been used in rational strategies to design binary/ternary cocrystals in crystal engineering, materials science,

host-guest inclusion compounds, and pharmaceutical solids [11]. Understanding of highly specific and mutually complementary non-covalent interactions between molecules is the basic aspect in molecular recognition, cocrystallization and supramolecular synthetic chemistry [12]. By the judicious choice of the supramolecular synthons with specific and directional non-covalent connectivity, multidimensional solid state assembly can be generated by the effective close packing of the discrete building blocks [13–15]. Among all the non-bonded interactions, hydrogen bonding has proved to be the most useful and reliable because of its strength and directional properties [16]. Many molecular solids with novel properties have been prepared using hydrogen bonding as the main steering force [17–19]. Molecular cocrystals have been known for a long time, still there is wide scope for further applications and structural studies in this field. In recent years, many premeditated synthesis of binary and ternary cocrystals [20–24] have been reported. Variety of cocrystals with multidimensional topology, based on hydrogen bonded networks can be achieved when a N-heterocycle moiety is allowed to interact with a suitable carboxylic acid [14,25]. The ability of carboxylic acids to readily aggregate through the dimer homosynthon have been observed traditionally in structural chemistry.

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Conformationally flexible ligand 4-bis(imidazol-1-ylmethyl)benzene (bix) has been proved as a suitable building block for designing the coordination polymers of various network topology. It has been employed to fabricate a large number of coordination polymers with a variety of structural diversity from low dimensional entities such as 1D helix, linear threads to high-dimensional supramolecular networks such as 3D interpenetrated networks, metal organic polyrotaxanes; brick-wall type networks, chiral and magnetic Metal–Organic Frameworks. These fascinating structures hold promising applications in the area of non linear optical properties, magnetic properties, gas adsorption ability and catalytic properties [26–32]. Herein, we report synthesis, characterization by various physicochemical methods and a systematic structural examination of the cocrystal/salt resulted from cocrystallization between exobidentate N-heterocycle ligand 1,4-bis(imidazol-1-ylmethyl)benzene (bix) and a series of rigid and flexible dicarboxylic ligands such as cyclohexane-1,4-dicarboxylic acid (H_2chdc), naphthalene-1,4-dicarboxylic acid (H_2npdc) and 1H-pyrazole-3,5-dicarboxylic acid (H_2pzdc). The related primary intermolecular carboxylic acid···amine ($O-H\cdots N$)/carboxylate···protonated amine ($N-H^+\cdots O^-$) interactions and secondary weak molecular interactions including stacking have been investigated by crystallography on these binary cocrystals or organic salts in their supramolecular arrangement.

2. Experimental

2.1. Materials

All the chemicals were purchased from Sigma Aldrich, USA and used without any further purification. All solvents were freshly purified by general distillation process and used as and when required.

2.2. IR, NMR, CHNS and TGA measurements

IR spectra were recorded using KBr pellets on a Perkin–Elmer GX FTIR spectrometer. For each IR spectra 10 scans were recorded at 4 cm^{-1} resolution. 1H NMR spectra for the compounds were recorded on Bruker AX 500 spectrometer (500 MHz) at temperature $25\text{ }^\circ\text{C}$. 1H NMR Spectra was calibrated with respect to TMS and TMS was used as an internal reference for solvents such as d_6 -DMSO. Elemental analysis (CHNS estimation) was done by using the instrument Perkin–Elmer 2400 CHNS/O analyzer. All the TGA spectra were recorded on METTLER TOLEDO STAR SW 7.01.

2.3. X-ray crystallography

The crystallographic data and details of data collection for all the four compounds are given in supplementary information (Table S1). In each case, a crystal of suitable size was selected from the mother liquor and then mounted on the tip of a glass fiber and cemented using epoxy resin. Intensity data for all the six crystals were collected using $Mo\ K\alpha$ ($\lambda = 0.71073\text{ \AA}$) radiation on a Bruker SMART APEX diffractometer equipped with CCD area detector either at 293 K or at 100 K . The data integration and reduction were processed with SAINT [33] software. An empirical absorption correction was applied to the collected reflections with SADABS [34]. The structures were solved by direct methods using SHELXTL [35] and were refined on F^2 by the full-matrix least-squares technique using the SHELXL-97 [36] package. In all compounds all non-hydrogen atoms were refined anisotropically till convergence is reached. Hydrogen atoms attached to the ligand moieties are either located from the difference Fourier map or stereochemically fixed. The diagrams of the crystal structures are generated using

programs ORTEP [37], Mercury 1.4.1 [38] or PLATON [39]. ORTEP diagrams of all four compounds are shown in Fig. 2, and structural drawings of the adducts for better understanding and clarity are incorporated in Supplementary material as Fig. S2. Relevant crystallographic data and selected bond lengths for the molecular adducts are given in Supplementary material as Tables S1 and S2 respectively. Hydrogen bonding interaction with symmetry code and pK_a value data for all four compounds are listed in Table 1 and Table 2 respectively.

2.4. Synthesis of the N-donor ligand

1,4-Bis(imidazol-1-ylmethyl)benzene (bix) was synthesized by following a procedure reported by Abrahams et al. [40]. Re-crystallization of the crude product by dissolving in hot water and keeping at constant temperature $23\text{ }^\circ\text{C}$ yielded white crystalline material. The detailed synthetic procedure for the preparation of ligand bix and its proton NMR spectra is given in Supplementary data as S1 and Fig. S3 respectively.

2.4.1. 1H NMR data for bix

$\delta = 5.163$ (s, 4H; methylene), 6.885(s, 2H; imidazole), 7.715(s, 2H; imidazole), 7.231(s, 4H; aryl ring), 7.731(s, 2H; imidazole) CHN data for bix: calculated (%): C = 61.29; H = 5.15; N = 20.45. Observed (%): C = 60.3; H = 6.21; N = 19.63. IR spectral data: (ν_{max} (cm^{-1})) 3438(b), 3108(m), 2553(w), 2949(m), 1677(m), 1602(w), 1512(s), 1444(s), 1281(s), 1228(s), 1104(m), 1081(s), 1029(m), 919(s), 828(m), 767(m), 708 (m), 665(m).

2.5. Synthesis of molecular complexes

2.5.1. Bix: H_2chdc (CC1)

Bix (0.272 g, 1 mmol) and H_2chdc (0.172 g, 1 mmol) was dissolved separately in 5 ml methanol each and mixed gradually with constant stirring at room temperature in 1 h duration. Five milliliters water was then added to this solution and continued stirring for another three more hours. The clear colorless solution obtained was kept at room temperature for 1 week to get crystals suitable

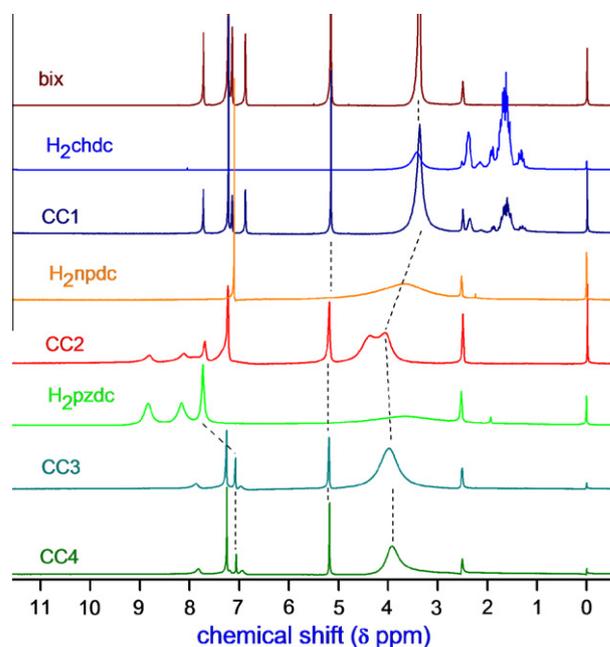


Fig. 1. NMR spectra of CC1, CC2, CC3, CC4 in d_6 -DMSO solvent. The spectra of bix and used dicarboxylic acids are also presented for assessment of signals.

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