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Hydrogen bonded supramolecular structures of eight organic salts based on 2,6-diaminopyridine, and organic acids

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ABSTRACT

Here anhydrous and hydrated multi-component organic acid-base salts of 2,6-diaminopyridine have been prepared with the organic acids as trichloroacetic acid, 3,5-dinitrobenzoic acid, 5-nitrosalicylic acid, 3,5-dihydroxybenzoic acid, 5-sulfosalicylic acid, m-phthalic acid, naphthalene-1,5-disulfonic acid, and glutaric acid. The eight crystalline compounds were characterized by X-ray diffraction analysis, infrared (IR), melting point (mp), and elemental analysis. Except salt **4**, all structures adopted the hetero $R_2^2(8)$ supramolecular synthon. There were extensive N–H···O/O–H···O/N–H···N/N–H···S hydrogen bonds as well as CH···O, CH–N, CH–π, NH–π, π–π, C–π, Cl–O, and O–O interactions in the supramolecular architectures. The combination of these weak and strong hydrogen bonding associations in the crystal packing led to the formation of the 2D/3D structures.

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1. Introduction

Crystal engineering using multiple interactions, such as electrostatic forces, hydrogen bonding, cation···π interaction, C–H···π, and π···π interactions, is a constantly growing field of research [1]. Multiple hydrogen-bond interactions are widely used in the design of self-assembled structures from organic acid and organic base [2]. The intramolecular, and intermolecular hydrogen bonds are responsible for the construction of several complicated self-assembled structures involving the N-containing compounds and the acidic components [3,4].

Carboxylic acids represent one of the most prevalent functional groups in crystal engineering because they possess the hydrogen bond donor and acceptor with a geometry that facilitates self-association through supramolecular homosynthons *via* centrosymmetric dimer or catemer [5–7]. Furthermore, it is now recognized that carboxylic acids are ideal candidates for multi-component crystals since they form persistent supramolecular heterosynthons with a number of different complementary functional groups such as amine, and aromatic nitrogen etc. For instance, much has been said about the use of carboxyl and pyridyl groups in the design of supramolecular systems [8–13]. Besides the COOH group, the functional groups such as amine, halogen, NO_2, and phenol OH groups are all good groups in forming organic solid through non-covalent interactions [14]. Aminopyridines containing the N, and $-NH_2$ groups have been widely studied to understand the supramolecular synthons existing in their assemblies [15]. Among these supramolecular architectures, however, only a very few reports described the crystals composed of 2,6-diaminopyridine and carboxylic acids [16].

In order to understand the interaction modes 2,6-diaminopyridine have in binding with the organic acids, we began to study the 2,6-diaminopyridine-acids system, also aiming to find the role the weak non-covalent interactions played in forming the final supramolecular frameworks. Thus, in the following, we report the preparation and crystal structures of eight supramolecular compounds assembled *via* nonbonding interactions between carboxylic acids and 2,6-diaminopyridine (L) (Scheme 1). In this study, we got eight organic salts composed of carboxylic acids and 2,6-diaminopyridine, namely (2,6-

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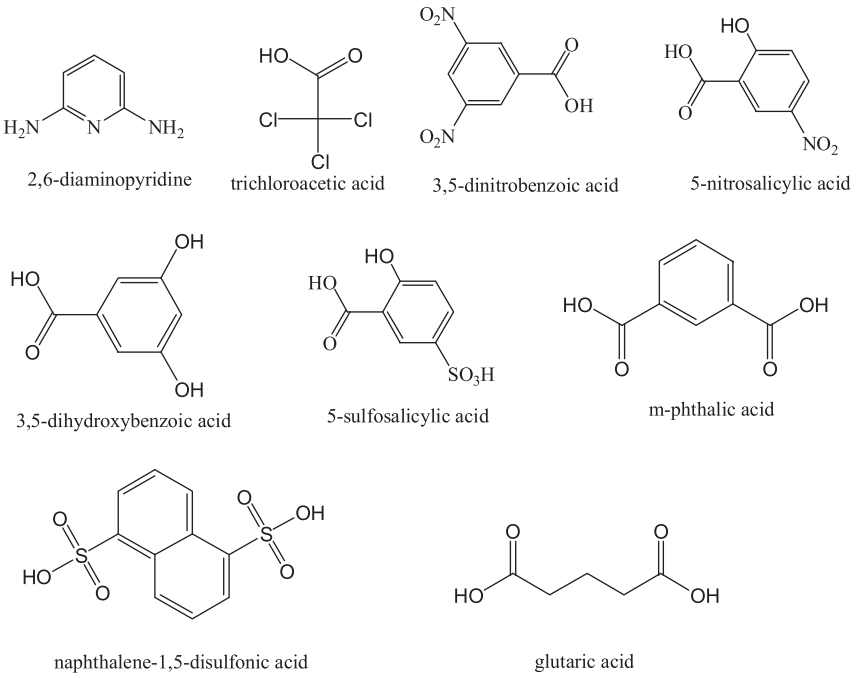

Scheme 1. The building blocks discussed in this paper.

diaminopyridine): (trichloroacetic acid) [(HL^+) · (tca^-), tca^- = trichloroacetate] **(1)**, (2,6-diaminopyridine): (3,5-dinitrobenzoic acid) [(HL^+) · (dna^-), dna^- = 3,5-dinitrobenzoate] **(2)**, (2,6-diaminopyridine): (5-nitrosalicylic acid) [(HL^+) · (nsa^-), nsa^- = 5-nitrosalicylate] **(3)**, (2,6-diaminopyridine): (3,5-dihydroxybenzoic acid) [(HL^+) · ($dhba^-$), $dhba^-$ = 3,5-dihydroxybenzoate] **(4)**, (2,6-diaminopyridine): (5-sulfosalicylic acid): $2H_2O$ [(NH_4^+) (HL^+) · ($5\text{-}ssa^-$) · $2H_2O$, $5\text{-}ssa^-$ = 5-sulfosalicylate] **(5)**, (2,6-diaminopyridine)$_2$: (m-phthalic acid): $2H_2O$ [$(HL^+)_2$ · (mpt^{2-}) · $2H_2O$, mpt^{2-} = m-phthalate] **(6)**, (2,6-diaminopyridine)$_2$: (naphthalene-1,5-disulfonic acid) [$(HL^+)_2$ · (nds^{2-}), nds^{2-} = naphthalene-1,5-disulfonate] **(7)**, and (2,6-diaminopyridine): (glutaric acid) [(HL^+) · ($Hgta^-$), $Hgta^-$ = hydrogenglutarate] **(8)** (Scheme 2).

2. Experimental section

2.1. Materials and physical measurements

The chemicals and solvents used in this work were of analytical grade and available commercially and were used without further purification. The FT-IR spectra were recorded from KBr pellets in range 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Microanalytical (C, H, N, and S) data were obtained with a Perkin–Elmer Model 2400II elemental analyzer. Melting points of new compounds were recorded on an XT-4 thermal apparatus without correction.

2.2. Preparation of the supramolecular compounds

*a. (2,6-Diaminopyridine): (trichloroacetic acid) [(HL^+) · (tca^-), tca^- = trichloroacetate] (**1**)*

2,6-Diaminopyridine (10.9 mg, 0.10 mmol) was dissolved in 3 mL of methanol. To this solution was added trichloroacetic acid (16.4 mg, 0.1 mmol) in 3 mL methanol. Colorless block crystals were obtained after several days by slow evaporation of the solvent (yield: 21 mg, 77.06%). mp 97–98 °C. Elemental analysis: Calc. for $C_7H_8Cl_3N_3O_2$ (272.51): C, 30.82; H, 2.94; N, 15.41. Found: C, 30.77; H, 2.88; N, 15.39. Infrared spectrum (KBr disc, cm^{-1}): 3433w(ν_{as}(NH)), 3325m(ν_s(NH)), 3283w, 3144m, 3036m, 2964m, 1624m, 1594s($\upsilon_{as}(CO_2^-)$), 1555m, 1502m, 1454m, 1405s($\upsilon_s(CO_2^-)$), 1359m, 1312m, 1267m, 1230m, 1177m, 1128m, 1068m, 1020m, 971m, 924m, 876m, 828m, 776m, 730m, 686m, 650m, 623m, 600m.

*b. (2,6-Diaminopyridine): (3,5-dinitrobenzoic acid) [(HL^+) · (dna^-), dna^- = 3,5-dinitrobenzoate] (**2**)*

2,6-diaminopyridine (10.9 mg, 0.10 mmol) was dissolved in 3 mL of methanol. To this solution was added 3,5-dinitrobenzoic acid (21.2 mg, 0.1 mmol) in 8 mL ethanol. Light yellow block crystals were afforded after several days by slow evaporation of the solvent (yield: 22 mg, 68.48%). mp 179–180 °C. Elemental analysis: Calc. for $C_{12}H_{11}N_5O_6$ (321.26): C, 44.82; H, 3.42; N, 21.79. Found: C, 44.76; H, 3.38; N, 21.75. Infrared spectrum (KBr disc, cm^{-1}): 3451s(ν_{as}(NH)), 3339s(ν_s(NH)), 3164m, 2985m, 1645m, 1604s($\nu_{as}(COO^-)$), 1560m, 1528s($\nu_{as}(NO_2)$), 1476w, 1433m, 1390s($\nu_s(COO^-)$), 1357m, 1321s($\nu_s(NO_2)$), 1273m, 1235m, 1194m, 1146m, 1099m, 1056m, 1015m, 972m, 925m, 879m, 835m, 792m, 753m, 712m, 667m, 635m, 613m.

*c. (2,6-Diaminopyridine): (5-nitrosalicylic acid) [(HL^+) · (nsa^-), nsa^- = 5-nitrosalicylate] (**3**)*

2,6-diaminopyridine (10.9 mg, 0.10 mmol) was dissolved in 3 mL of methanol. To this solution was added 5-nitrosalicylic acid (18.3 mg, 0.1 mmol) in 7 mL methanol. Light yellow block crystals were obtained after several days by slow evaporation of the solvent (yield: 24 mg, 82.12%). mp 171–173 °C. Elemental analysis: Calc. for $C_{12}H_{12}N_4O_5$ (292.26): C, 49.27; H, 4.11; N, 19.16. Found: C, 49.23; H, 4.06; N, 19.08. Infrared spectrum (KBr disc, cm^{-1}): 3728s(ν(OH)), 3470s(ν_{as}(NH)), 3364s(ν_s(NH)), 3259m, 3189m, 2934m, 1628m, 1582s($\nu_{as}(COO^-)$), 1530s($\nu_{as}(NO_2)$), 1499m, 1459m, 1420m, 1380s($\nu_s(COO^-)$), 1355m, 1324s($\nu_s(NO_2)$), 1290m, 1249m, 1205m, 1162m, 1111m, 1062m, 1014m, 967m, 923m, 878m, 836m, 794m, 753m, 707m, 662m, 637m, 614m.

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