

Structure of the Cocrystal of 2,2'-Diamino-4,4'-bis(1,3-thiazole) and 4,4'-Bipyridine

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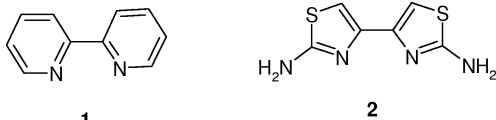
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A new cocrystal based upon 2,2'-diamino-4,4'-bis(1,3-thiazole) and 4,4'-bipyridine has been synthesized and characterized. Self-assembly of this compound in the solid state is likely caused by both hydrogen bonding and π - π stacking, and the network contains large vacant voids.

Key words: 4,4'-Bipyridine, 2,2'-Diamino-4,4'-bis(1,3-thiazole), Cocrystal, π - π Stacking, Hydrogen Bond

Introduction

Cocrystallization reactions provide helpful means for probing the importance and balance between different intermolecular interactions and, thus offer practical guidelines for developing new methodologies in supramolecular synthesis. The role of hydrogen bonding and π - π stacking for these purposes is well established [1,2]. The present determination of the structure of a cocrystal from 4,4'-bipyridine (4, 4'-bipy) and 2,2'-diamino-4,4'-bis(1,3-thiazole) (DABTZ) (Scheme 1) provides a novel two-dimensional polymer involving hydrogen bonding and π - π stacking interactions.



Scheme 1. Formula drawing of compounds **1** and **2**.

Results and Discussion

Attempts to isolate zinc(II), cadmium(II), and lead(II) complexes from a solution containing a mixture of 4,4'-bipyridine (4,4'-bipy) (**1**) and 2,2'-diamino-4,4'-bis(1,3-thiazole) (DABTZ) (**2**) were not successful and a new cocrystal structure [(4,4'-bipy) (DABTZ)], was isolated. This adduct is also produced

from solutions containing only the components of the cocrystals. Other adducts of this type of cocrystal, such as [(bpy) (DABTZ)] and [(bpe) (DABTZ)] (bpy = 1,3-di(4-pyridyl)propane and bpe = 1,2-bis(4-pyridyl)ethene), have recently been prepared in our lab and will be reported in the future. The IR spectrum of the compound shows absorption bands resulting from the skeletal vibrations of aromatic rings in the 1400–1600 cm⁻¹ range. The absorption bands of the -NH₂ groups are observed as a strong band centered at 3075 and 3260 cm⁻¹ and are significantly shifted to the lower frequency region, compared to the free ligand (3270 and 3430 cm⁻¹). The relatively low frequency of the band is indicative of hydrogen bonding. The ¹H NMR spectrum of the DMSO solution of the compound displays four distinct absorption bands at δ = 6.75 (s, H), 7.15 (s, 2H), 7.90 (q, 2H), and 8.40 (q, 2H) ppm assigned to CH- thiazole, NH₂, and the two different protons of **1**, respectively. The ¹³C NMR spectrum of the DMSO solution displays six distinct absorption bands at 102.63, 146.91, 168.71 ppm assigned to the aromatic carbons of **2** and 121.64, 144.81, 151.09 ppm assigned to the aromatic carbons of **1**. There is no difference between the ¹H and ¹³C NMR spectra of the cocrystal and those of the individual components and the spectra are independent on concentration. Single-crystal structure determination of the cocrystal [(4,4'-bipy) (DABTZ)] demonstrates that in the solid state the DABTZ moieties connect

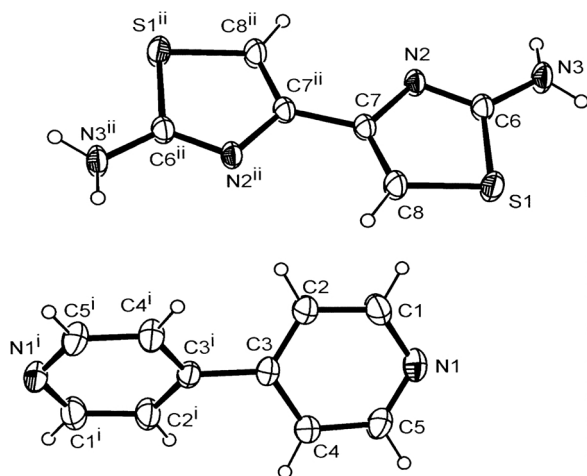


Fig. 1. ORTEP plot of the [(4,4-bipy)(DABTZ)] with ellipsoids of 30% probability. i: $-x, y, -z + 1/2$, ii: $-x + 1/2, -y + 1/2, -z$.

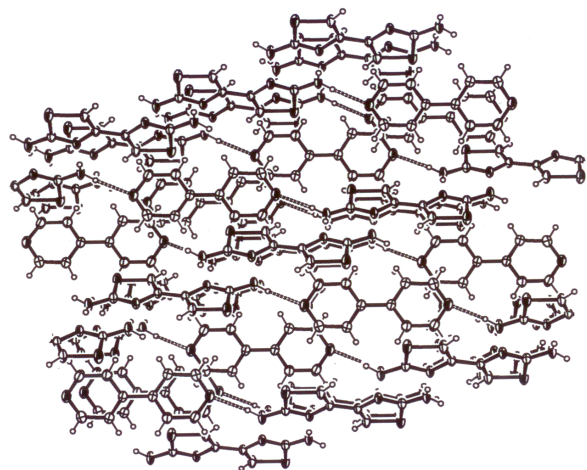


Fig. 2. A packing diagram and showing of the two-dimensional polymer in the [(4,4-bipy)(DABTZ)].

through dimeric self-complementary hydrogen bonds, as well as in a N-H...N hydrogen bond involving one proton of the amine moiety (the hydrogen-bond donor) and a heterocyclic nitrogen atom of DABTZ (the hydrogen-bond acceptor). The other amine proton acts as the hydrogen-bond donor with a heterocyclic nitrogen atom of **1** as the hydrogen-bond acceptor. Consequently the self-complementary hydrogen bonds system grows into a three-dimensional network by packing *via* the hydrogen-bonding interactions and the network contains large vacant voids (Fig. 2).

Table 1. Crystal data and structure refinement for [(4,4-bipy)(DABTZ)].

Empirical formula	C ₁₆ H ₁₄ N ₆ S ₂
Formula weight	354.47
Temperature [K]	298(2)
Wavelength [Å]	0.71073
Crystal system	monoclinic
Space group	C2/c
Unit cell dimensions	$a = 12.630(4) \text{ Å}$ $b = 7.818(2) \text{ Å}$ $c = 17.051(5) \text{ Å}$ $\beta = 93.401(6)^\circ$
Volume [Å ³]	1680.7(8)
Z	4
Density (calculated) [g cm ⁻³]	1.401
Absorption coefficient [mm ⁻¹]	0.327
$F(000)$	736
Crystal size [mm ³]	0.37 × 0.29 × 0.15
Theta range for data collection [°]	2.39 to 25.50
Index ranges	$-15 \leq h \leq 9$, $-8 \leq k \leq 9$, $-20 \leq l \leq 20$
Reflections collected	4421
Independent reflections	1553
Completeness to theta = 25.50°	99.8%
Absorption correction	Multi-scan
Max. and min. transmission	0.9526 and 0.8886
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1553 / 0 / 109
Goodness-of-fit on F^2	1.093
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0466$, $wR2 = 0.1074$
R Indices (all data)	$R1 = 0.0521$, $wR2 = 0.1111$
Largest diff. peak, hole [e·Å ⁻³]	-0.250 and 0.280

Table 2. H-Bonds [Å and °] in the structure of [(4,4-bipy)(DABTZ)].

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠(DHA)	A
N(3)-H(3)	0.848	2.094	2.940	174.50	N(1)
(2 - x, y, 3/2 - z)					
N(3)-H(3)	0.849	2.208	3.057	179.32	N(2)
(2 - x, 1 - y, 1 - z)					

There are both face-to-face and edge-to-face π - π stacking [3–4] interactions between aromatic rings belonging to two different ligands in this network. The thiazole groups of **2** are almost parallel and this parallel array of the planes of the aromatic moieties indicates that these interactions are of the face-to-face “ π -stacking” type [4, 5]. The centroid-centroid distance of thiazole groups is 3.92 Å and the angle between the ring normal and the centroid vectors is 14.99°. There are also edge-to-face π - π stacking interactions between the components **1** and **2** and the slippage distance is 3.65 Å.

Thus two factors, hydrogen bonding and π - π stacking, may control the packing of this cocrystal. The obvious question then is whether the hydrogen bonds have been formed to result in ligand stacking or whether it is the stacking interaction which has imposed a positioning of the donor atoms for forming hydrogen bonding. However, self-assembly of this compound is likely caused by both hydrogen bonding and π - π stacking.

The aromatic rings of **1** are not coplanar but the aromatic rings of coordinated **2** are coplanar, because the dihedral angle between the two rings within **1** is 39.5°, whereas the dihedral angle between the two rings within **2** is only 1.0° (Fig. 1).

An interesting point is that the new cocrystal was obtained from the mixture of **1** and **2** and metal ions such as Zn(II), Cd(II) and Pb(II). This shows that the stabilization of the cocrystal may be at least comparable with metal complexes with these ligands.

Experimental Section

General: IR spectra were recorded as Nujol mulls using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. The microanalysis was carried out using a Heraeus CHN-O-Rapid analyzer. The Melting point was measured on an Electrothermal 9100 apparatus and is uncorrected. ^1H and ^{13}C NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 and 125 MHz, respectively. 2,2'-Diamino-4,4'-bis(1,3-thiazole) was prepared from 1,4-dibromobutane-2,3-dione and thiourea by the method of Erlenmeyer and Überwasser [6].

2,2'-Diamino-4,4'-bis(1,3-thiazole) 4,4'-bipyridine, [(4,4'-bipy) (DABTZ)]

The compound was prepared by dissolving cadmium(II) acetate/zinc(II) acetate/lead(II) acetate (1 mmol) and sodium perchlorate (0.123 g, 1 mmol) in distilled water (10 ml) and adding an ethanolic solution of 2,2'-diamino-4,4'-bis(1,3-thiazole) (0.198 g, 1 mmol) and 4,4'-bipyridine (0.156 g, 1 mmol). The resulting solution was stirred for 2 h at room temperature and then allowed to stand for 10 d at room temperature (*ca.* 25 °C). Brown crystals of the desired product precipitated, which were filtered off, washed with acetone and ether and dried in air (*dec. p.* 210 °C). Yield: 0.177 g, 50%. – IR (KBr): ν = 605 (m), 690 (s), 801 (m), 1040 (w), 1240 (s), 1327 (s), 1525 (vs), 1582 (s), 1646 (s), 2775 (w), 3075 (s), 3260 (s) cm^{-1} . – ^1H NMR ([D₆]-DMSO): δ = 6.75 (s, 1H), 7.15 (b, 2H), 7.90 (q, 2H), and 8.40 (q, 2H). – ^{13}C -{ ^1H } NMR ([D₆]-DMSO): δ = 102.63, 121.64, 144.81, 146.91, 151.09, 168.71. C₁₆H₁₄N₆S₂ (354.47): *calcd.* C 54.16, H 3.94, N 23.69; *found* C 54.70, H 3.40, N 23.50.

Supplementary material

Complete bond lengths and angles, co-ordinates and displacement parameters have been deposited at Cambridge Crystallography Data Centre. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number 274549.

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