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Novel Motif of Hydrogen Bonds in the Water-assisted Supramolecular Self-assembly of 2-acetylamino-6-methylpyridine-*N*-oxide and Hetero-assembly of 1:1 Co-crystal of *o*-Phenylenediamine with Catechol

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Water assisted supramolecular structures of 2-acetylamino-6-methylpyridine-1-oxide (1) and 1:1 complex of *o*-phenylenediamine with catechol (2) were determined. The crystal structure of 2-acetylamino-6-methylpyridine-1-oxide. H_2O (1), triclinic, $a = 7.1276$ (6), $b = 7.8860$ (6), $c = 8.9938$ (7) Å, $\alpha = 100.143$ (2), $\beta = 91.493$ (2), $\gamma = 110.972$ $(1)^0$, $V = 462.47$ (6) $Å^3$, $Z = 2$, $D_{calc} = 1.323\,mg.m^{-3}$(293°K) reveals a novel centrosymmetric supramolecular assembly that is sustained by water molecules linking the dimers of pyridine-1-oxide through C—H...O, N—H...O, N^+—O^-...H hydrogen bonds. The pyridine rings of the dimers are stacked at 3.473 Å apart, involving π- stacking interactions. Complex (2), $C_6H_8N_2$.—$C_6H_6O_2$. $1/2H_2O$ crystallises in the monoclinic space group *P2/c*: $a = 9.0498(2)$, $b = 5.2275(1)$, $c = 25.0771(2)$ Å, $\beta = 97.71°$, $V = 1175.62(4)$ $Å^3$, $Z = 4$. Refinement led to a final conventional *R* value of 0.041 for 2016 reflections. In these crystals (2), the water molecules lie on the twofold axis and they are linked to the pyrocatechol molecules through an O—H...O hydrogen bond.

Keywords: Water-assisted, self-assembly, supramolecular, hydrogen bonds

INTRODUCTION

Hydrogen bonds play an important role in all biological recognitions and assembly processes [1]. They are widely used for the development of synthetic receptors [2] and for the design of supramolecular crystals [3]. Most of the supramolecular crystals are originated from strong N—H---X and O—H---X (X = O, N) hydrogen bonds. Besides these conventional hydrogen bonds unconventional C—H---O hydrogen bonds are also involved in the formation of supramolecular assembly [4]. The C—H---O hydrogen bonds are much weaker than the traditional hydrogen bonds (X—H---X where X = O or N; C—H---O bond energy is about 10% of a classical hydrogen bond) [5]. This type of hydrogen bonds has weak electrostatic attraction with a moderate degree of directionality. Previous studies on C—H---O hydrogen

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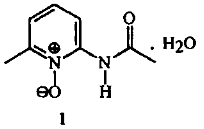
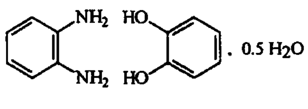
*Corresponding author.

bonding reveals that they play important functional and structural roles in the biological macromolecules including nucleic acids [6], proteins [7] and carbohydrates [8]. More interestingly, water molecules satisfy their incomplete tetrahedral co-ordination through such C—H...O contacts. These C—H---O contacts involving water molecules are observed in large biological molecules *e.g.*, vitamin B_{12} and the enzyme actindin [9]. In contrast to these biological macromolecular systems the study toward the hydrogen bonding interactions through the short unconventional C—H---O contacts in small organic molecules to determine the molecular packing in the crystal is of considerable interest. In our continued research on hydrogen bonds in molecular recognition and supramolecular chemistry, we report here a couple of interesting structures which were accidentally prepared from water-incorporation in the supramolecular crystals of the following systems. In our highly functionalised polar 2-(*N*-acetyl)-6-methylpyridine-*N*-oxide **1**, a simple molecule of biological significance which provides such an extraordinary example where all the weak forces like π-stacking, C—H...O, X—H...X(X = O *or* N) hydrogen bonding interactions and water encapsulation *via* C—H...O contacts *etc.*, are involved to devise a supramolecular assembly of the dimeric entity. We also report here the hetero-assembling complementarity of diamine/diol motif **2** where water molecules lie on the two fold axis and bridge catechol as well as diamine molecules through O—H...O and O—H...N hydrogen bonds. Thus the crystals having strong hydrogen bonding polar groups in simple molecules can give rise to interesting self-or hetero-assembly with water assisted hydrogen bonds.



1



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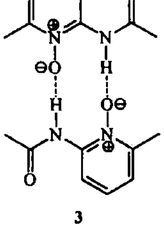

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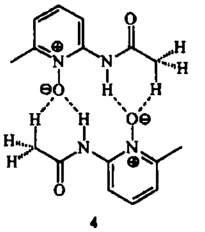

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RESULTS AND DISCUSSION

Water Assisted Supramolecular Self-assembly

A view of the crystal structure of **1** is shown in both Figures 1 and 2. Figure 1 gives the numbering scheme of the molecule and Figure 2 is the packing diagram of the molecules down '*a*' axis,

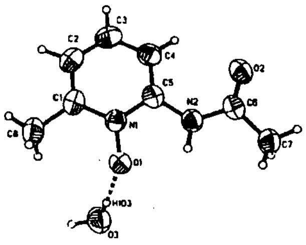

FIGURE 1 ORTEP diagram of **1** showing 50% probability displacement ellipsoids and the atom-numbering scheme.

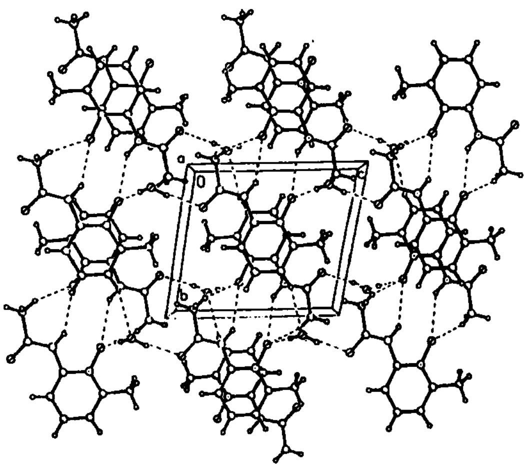

FIGURE 2 Packing of the molecules down '*a*' axis.

showing the hydrogen bonding scheme. The pyridine ring consisting of C1, C2, C3, C4, C5 and N1 is planar. The atoms N2, C6, O2 and C7 also lie in a plane. The dihedral angle between these two planes is 6.05°(6). Figures 3 and 4 show the packing diagram of the molecules down *'b'* and *'c'* axis respectively. More surprisingly, the compound **1** having two point hydrogen bonding sites exhibits the dimeric structure **4** instead of the other hypothetically possible form **3**. This may be due to the formation of stable six membered hydrogen bonding arrangements in **4** and also may be due to less N-oxide dipole repulsion in **4** compared to **3**. Thus **4** may be thermodynamically more stable than **3**. The dimeric form **4** gives a centrosymmetric arrangement by weak N—H---O and C—H---O hydrogen bonds and in the six membered hydrogen bonding arrangements the distances of N2H1---O1 and C7HC---O1 are 2.543 and 2.400 Å at an angle of 145.45 (1.71)^0 and 162.26 (2.76)^0 respectively. These dimers are linked by O—H---O and C—H---O intermolecular hydrogen bonds involving water molecule to form layers almost parallel to (4 −1 1) planes. Dimers are also linked by water molecule by O—H---O hydrogen bonds and the pyridine rings are stacked at 3.473 Å apart, an optimum arrangement for π-π stacking interactions [Fig. 2]. In order to minimize intersheet pyridine *N*-oxide-pyridine *N*-oxide repulsion, successive molecules in the stack are related not by translation but by inversion.

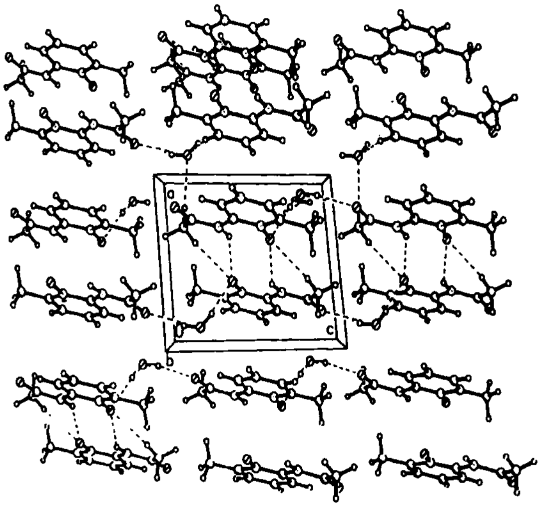

FIGURE 3 Packing of the molecules down *'b'* axis.

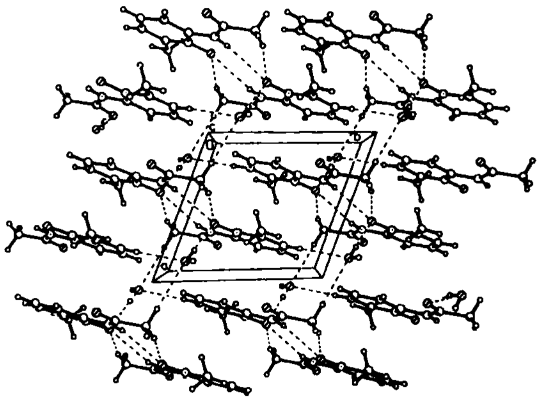

FIGURE 4 Packing of the molecules down *'c'* axis.

It is well known that the preferred hydrogen bond co-ordination of the water molecule is tetrahedral or planar trigonal [10]. In the present case, water molecules are in tetrahedral environment where one water hydrogen atom is bonded to O1 atom of pyridine *N*-oxide group [O3H1---O1 = 1.950Å; 174.04(2.77)^0] and the other is bonded to O2 atom of the amide functionality [O3H2---O2 = 2.042Å; 168.97(3.13)^0] in a layer. Simultaneously the O3 atom of that water molecule accepts two hydrogens donated by C7HA[C7HA---O3 = 2.508Å; 177.41(3.37)^0] of the amide methyl group and C2H2[C2H2---O3 = 2.466Å; 161.55(1.89)^0] of the stacked pyridine ring of the other layer successively. Water molecules thus bridge the two layers and repeat such hydrogen bonding arrangements to create a supramolecular assembly in Figure 2.

Interestingly, in this assembly C8H's of the CH_3 group are not involved in hydrogen bonding despite of their sufficient acidity. Participation of the amide methyl group but not the methyl group attached to pyridine ring in the formation of hydrogen bonds may thus be due to comparatively greater acidity of the hydrogens of amide CH_3 than ring CH_3. These C—H---O interactions in the present study therefore may be either due to the more acidity of C—H protons or may arise owing to the geometrical constraints imposed by other contacts.

Water Assisted Supramolecular Hetero-assembly

We have crystallised catechol and *o*-phenylenediamine (1:1) and in the crystal structure, the asymmetric unit consists of one molecule each of *o*-phenylenediamine, catechol and water giving rise to a hemihydrate hetero-complex. Figure 5 gives the numbering scheme of the molecule and Figures 6 and 7 indicate the packing diagram of the heteroassembly down '*b*' and '*c*' axis respectively.

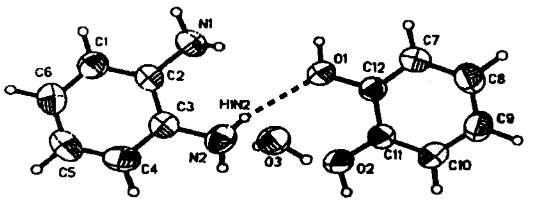

FIGURE 5 ORTEP diagram of the complex 2 showing 50% probability displacement ellipsoids and the atom-numbering scheme.

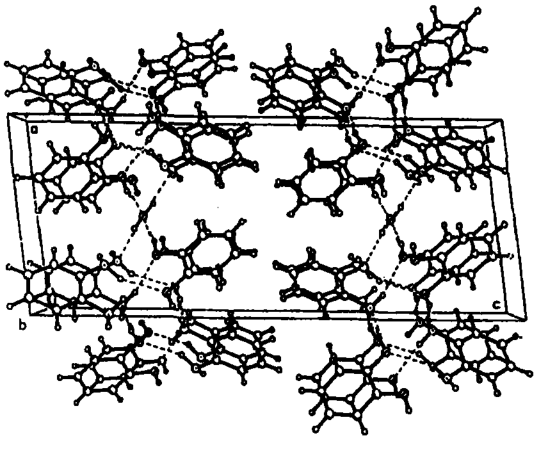

FIGURE 6 Packing diagram of complex 2 down '*b*' axis.

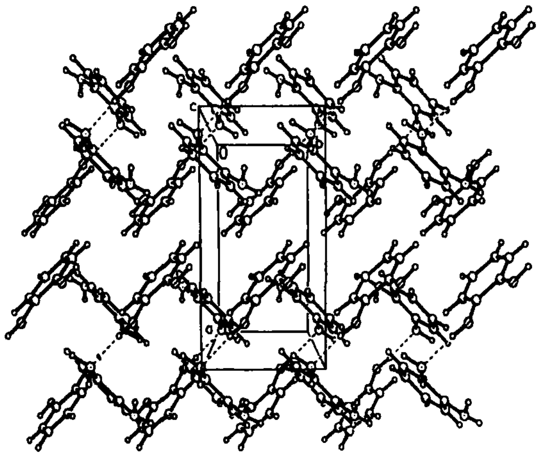

FIGURE 7 Packing diagram of complex 2 down '*c*' axis.

In the crystal $C_6H_8N_2$—$C_6H_6O_2$. $1/2H_2O$, the water molecules lie on the twofold axis and they are linked to the catechol molecules through an O_2—H1...O3 hydrogen bond [1.799 Å, 168.00(2.11)^0]. The diamine molecules are connected similarly to the water molecules by O_3—H1...N2 (6) [1.954 Å, 164.32(1.84)^0] hydrogen bonds. As the hydrogen bondings between diol and diamine molecules are concerned, it is observed that they involve N—H...O hydrogen bonds [N2—H1...O1 = 2.325 Å, 154.10(1.89)^0 and N1—H2...O2(2) = 2.365 Å, 150.41(1.72)^0].

This hydrogen bonded network forms a supramolecular structure around the two-fold axis. The neighbouring molecular assemblies are interlinked by O1—H1...N1 (3) hydrogen bonds [1.892 Å, 168.77(2.01)^0]. Both the nitrogen atoms and water oxygen atoms exhibit full tetracoordination due to hydrogen bonding arrangements. The hydrogen bonded assembly in this structure is significantly different from the supramolecular helicate structures observed for the 1:1 complex of *trans*-1, 2-diamino cyclohexane and (1S, 2S)-*trans*-1, 2-cyclohexane diol, [13] and also different from the supramolecular assembly of linear diamine and diol [14] which may be due to the presence of water molecules. The C—N, C—O and C—C lengths in the structure agree with the reported values [15]. Interestingly, the dihedral angle between the mean planes through the diamine and diol moieties is 25.87(3)^0. The diamine and diol associated molecules translated one unit cell along the '*b*' direction are stacked stepwise without any π-π stacking interactions with minimum short contacts for C1 ... C4[3.662(2) Å] and C7...C10[3.543(2) Å]. The herringbone motif found in the crystal is shown in Figure 7 which is usually observed in lower aromatics like benzene, naphthalene [16] *etc.*

EXPERIMENTAL

The title compound **1** was prepared from 2-(*N*-acetyl)-6-methylpyridine by reaction with 48% H_2O_2 in glacial acetic acid at 80°C. Single crystals were obtained by slow evaporation of chloroform solution of the compound. Single crystals for the heteroassembly **2** were grown by slow evaporation of 1:1 mixture of *o*-phenylenediamine and catechol in a chloroform solution.

^{1}H NMR ($CDCl_3$, 300 MHz) of compound **1**: δ(ppm): 10.19[s, 1H, NH (Pyr amide), 8.30(*d*, 1H, $J = 9$ Hz), 7.24 (*t*, 1H, $J = 9$ Hz), 6.96 (*d*, 1H, $J = 9$ Hz), 2.56 (*s*, 3H), 2.30 (*s*, 3H).

^{1}H NMR ($CDCl_3$, 200 MHz) of complex **2**: δ(ppm): 6.88–6.72 (m, 8H), 2.74 (bs, 6H).

X-ray Structure Analysis

The supramolecular assemblies of both structures **1** and **2** are presented in Figures 2–4 and 6–7. A summary of crystallographic data are given in Table I, while Table II contain the atomic coordinates and equivalent isotropic displacement for both. Table III represents the bond lengths and bond angles while Table IV represents the hydrogen bond parameters for compound **1** and complex **2**. It is clearly visible

TABLE I Crystal data and structure refinement for compound **1** and complex **2**

	Compound **1**	Complex **2**
Empirical formula	C8H12N203	C12H15N2O2.50
Formula weight	184.20	227.26
Wavelength Å	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	*P*-1	*P*2/c
Unit cell dimensions (Å)		
a	7.1276(6)	9.0498(2)
b	7.8860(6)	5.2275(10)
c	8.9938(7)	25.0771(2)
α	100.143(2)	90
β	91.493(2)	97.71
γ	110.972(1)	90
Volume Å^3	462.47(6)	1175.62(4)
Z	2	4
Density (calculated)	1.323 mg/m^3	1.284 mg/m^3
Absorption coefficient	0.102 mm^{-1}	0.091 mm^{-1}
F(000)	196	484
Reflections collected	3032	7110
Independent reflections	2045 [R(int) = 0.0178]	2692 [R(int) = 0.0237]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.055	1.057
Final R indices [I > 2sigma(I)]	R1 = 0.0459, wR2 = 0.1306	R1 = 0.0411, wR2 = 0.0959
R indices (all data)	R1 = 0.0596, wR2 = 0.1429	R1 = 0.0601, wR2 = 0.1066
Largest diff. peak and hole	0.176 and − 0.181 e.A^{-3}	0.158 and − 0.113 e.A^{-3}

TABLE II Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($A^2 \times 10^3$). U(eq) is defined as one third of the orthogonalized U_{ij} tensor

	x	*Y*	*z*	*U*(eq)
Compound 1				
O(1)	3817(2)	7851(1)	3853(1)	54(1)
O(2)	2022(2)	7298(2)	8847(1)	72(1)
O(3)	1231(3)	8633(2)	1887(2)	76(1)
N(1)	3121(2)	6237(2)	4296(1)	44(1)
N(2)	3127(2)	8003(2)	6610(1)	47(1)
C(1)	2808(2)	4625(2)	3290(2)	49(1)
C(2)	2100(2)	2982(2)	3794(2)	57(1)
C(3)	1678(2)	2956(2)	5274(2)	58(1)
C(4)	1975(2)	4584(2)	6279(2)	53(1)
C(5)	2720(2)	6237(2)	5773(2)	44(1)
C(6)	2702(2)	8451(2)	8067(2)	49(1)
C(7)	3099(3)	10459(3)	8615(2)	61(1)
C(8)	3251(4)	4764(3)	1702(2)	66(1)
For complex 2				
O(1)	1403(1)	3317(3)	7938(1)	75(1)
O(2)	3130(1)	7177(2)	7750(1)	70(1)
O(3)	5000	847(3)	7500	54(1)
N(1)	534(2)	− 708(3)	6894(1)	56(1)
N(2)	2664(2)	3174(3)	6808(1)	62(1)
C(1)	724(2)	− 1942(3)	5964(1)	56(1)
C(2)	1162(1)	− 389(3)	6404(1)	45(1)
C(3)	2154(1)	1617(3)	6357(1)	48(1)
C(4)	2681(2)	1981(3)	5864(1)	62(1)
C(5)	2229(2)	411(4)	5429(1)	68(1)
C(6)	1247(2)	− 1550(4)	5478(1)	65(1)
C(7)	2357(2)	3374(3)	8891(1)	54(1)
C(8)	3270(2)	4523(4)	9312(1)	63(1)
C(9)	4149(2)	6565(4)	9213(1)	64(1)
C(10)	4133(2)	7475(3)	8693(1)	54(1)
C(11)	3219(1)	6346(3)	8271(1)	47(1)
C(12)	2317(1)	4281(3)	8372(1)	48(1)

TABLE III Bond lengths (Å) and bond angles (deg)

Compound 1	
O(1)—N(1)	1.327(2)
O(2)—C(6)	1.217(2)
N(1)—C(1)	1.366(2)
N(1)—C(5)	1.367(2)
N(2)—C(6)	1.367(2)
N(2)—C(5)	1.386(2)
C(1)—C(2)	1.374(2)
C(1)—C(8)	1.485(2)
C(2)—C(3)	1.374(3)
C(3)—C(4)	1.377(2)
C(4)—C(5)	1.383(2)
C(6)—C(7)	1.492(2)
O(1)—N(1)—C(1)	120.45(12)
O(1)—N(1)—C(5)	118.25(11)
C(1)—N(1)—C(5)	121.30(13)
C(6)—N(2)—C(5)	126.72(13)
N(1)—C(1)—C(2)	118.71(14)
N(1)—C(1)—C(8)	117.3(2)
C(2)—C(1)—C(8)	123.97(14)
C(3)—C(2)—C(1)	120.7(2)
C(2)—C(3)—C(4)	120.3(2)

TABLE III (Continued)

Compound 1	
C(3)—C(4)—C(5)	118.8(2)
N(1)—C(5)—C(4)	120.17(13)
N(1)—C(5)—N(2)	112.64(13)
C(4)—C(5)—N(2)	127.19(14)
O(2)—C(6)—N(2)	122.58(14)
O(2)—C(6)—C(7)	122.66(14)
N(2)—C(6)—C(7)	114.75(14)
Complex 2	
O(1)—C(12)	1.371(2)
O(2)—C(11)	1.369(2)
N(1)—C(2)	1.430(2)
N(2)—C(3)	1.419(2)
C(1)—C(6)	1.381(2)
C(1)—C(2)	1.385(2)
C(2)—C(3)	1.396(2)
C(3)—C(4)	1.396(2)
C(4)—C(5)	1.383(2)
C(5)—C(6)	1.373(3)
C(7)—C(12)	1.381(2)
C(7)—C(8)	1.388(2)
C(8)—C(9)	1.374(2)
C(9)—C(10)	1.385(2)
C(10)—C(11)	1.385(2)
C(11)—C(12)	1.397(2)
C(6)—C(1)—C(2)	121.4(2)
C(1)—C(2)—C(3)	119.40(12)
C(1)—C(2)—N(1)	120.78(13)
C(3)—C(2)—N(1)	119.69(13)
C(2)—C(3)—C(4)	118.56(13)
C(2)—C(3)—N(2)	120.46(13)
C(4)—C(3)—N(2)	120.91(14)
C(5)—C(4)—C(3)	121.2(2)
C(6)—C(5)—C(4)	119.9(2)
C(5)—C(6)—C(1)	119.5(2)
C(12)—C(7)—C(8)	120.5(2)
C(9)—C(8)—C(7)	119.85(14)
C(8)—C(9)—C(10)	120.30(14)
C(9)—C(10)—C(11)	120.2(2)
O(2)—C(11)—C(10)	123.16(13)
O(2)—C(11)—C(12)	117.24(12)
C(10)—C(11)—C(12)	119.59(12)
O(1)—C(12)—C(7)	123.95(13)
O(1)—C(12)—C(11)	116.42(12)
C(7)—C(12)—C(11)	119.61(12)

TABLE IV Hydrogen bond parameters (Å, ⁰)

D—H...A	H...A	D...A	D—H...A
Compound 1			
O3—H1O3...O1(0)	1.950(.032)	2.817(.002)	174.04(2.77)
	1.882		173.82(**)
N2—H1N2...O1(0)	2.052(.019)	2.531(.002)	112.10(1.49)
	2.006		108.61(**)
C4—H4...O2(0)	2.247(.018)	2.849(.002)	121.10(1.44)
	2.179		117.96(**)
O3—H2O3...O2(1)	2.042(.034)	2.898(.002)	168.97(3.13)
	1.972		168.57(**)
N2—H1N2...O1(2)	2.543(.018)	3.322(.022)	145.45(1.71)
	2.436		143.69(**)
C7—H7C...O1(2)	2.400(.032)	3.276(.002)	162.26(2.76)
	2.237		160.91(**)
C2—H2...O3(3)	2.466(.023)	3.382(.002)	161.55(1.89)
	2.344		160.56(**)
C7—H7A...O3(5)	2.508(.042)	3.445(.003)	177.41(3.37)
	2.365		177.25(**)

**Values normalized following G. A. Jeffrey and L. Lewis, Carbohydr. Res. (1978), 60, 179; R. Taylor, O. Kennard, Acta Cryst. (1983). B39, 133.

Equivalent positions: (0) x, y, z (1) $x, +y, +z-1$ (2) $-x+1, -y+2, -z+1$ (3) $x, +y-1, +z$ (4) $-x, -y+1, -z+1$ (5) $-x, -y+2, -z+1$.

TABLE IV (Continued)

D—H...A	H...A	D...A	D—H...A
Complex **2**			
N2—H1N2...O1(0)	2.325(.023)	3.196(.002)	154.10(1.89)
N1—H2N1...O2(2)	2.365(.019)	3.162(.002)	150.41(1.72)
O1—H1O1...N1(3)	1.892(.022)	2.806(.002)	168.77(2.01)
O2—H1O2...O3(4)	1.799(.023)	2.687(.002)	168.00(2.11)
O2—H1O2...O3(5)	1.799(.023)	2.687(.002)	168.00(2.11)
O3—H1O3...N2(6)	1.954(.019)	2.824(.002)	164.32(1.84)

Equivalent positions: (0) x, y, z (1) $-x, +y-1, -z+1/2+1$ (2) $x, +y-1, +z$ (3) $-x, +y, -z+1/2+1$ (4) $x, +y+1, +z$ (5) $-x+1, +y+1, -z+1/2+1$ (6) $-x+1, +y, -z+1/2+1$.

from the self-assembled structure of compound **1**, two molecules are sustained through six-membered intermolecular hydrogen bonding arrangements where amide methyl hydrogens (sp^3-hybridised) and pyridine ring hydrogens (sp^2 hybridised) as the participants for C—H...O interactions are of keen interest. Water molecules tetrahedrally bridge the two layers and repeat the same arrangements to provide the supramolecular structure.

Complex **2** crystallizes in the centrosymmetric space group *P*2/*c* with four formula units of complex in the unit cell (Tab. I). Crystal data for compound **1** were collected on SMART CCD area detector diffractometer using graphite monochromator Mo-K_α radiation ($\lambda = 0.71073$ Å). The data were reduced using the program SAINT and the structure was solved by direct methods using SHELXTL software package. The structure of complex **2** was solved by direct methods and refined by full-matrix least-squares techniques. All hydrogen atoms were located from a difference Fourier map and refined isotropically. Data were collected on SMART detector and cell refinement and data reduction were done using SAINT program. SHELXTL program was used for structure refinement for complex **2**.

CONCLUSION

Our observations on these simple molecules emphasize that (a) smaller structural units within which hydrogen bonding information is encoded, do not necessarily arrange themselves in the crystal in the conventional and predictable way, (b) C—H...O interactions like other interactions such as X—H...X (X = N, O) and π-stacking interactions play both structural and functional role to provide a refine packing mode of the crystal, (c) water molecules can act as a bridging ligand.

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