

Urea–picoline *N*-oxide (4 : 2) cocrystal: an unusual channel inclusion compound

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The crystal structure of urea–picoline *N*-oxide cocrystal reveals urea channel formation in which two independent picoline *N*-oxide molecules are stacked with their charge-transfer axes aligned approximately at 60° toward the crystallographic *b*-axis.

In the classical urea inclusion compounds^{1–3} the host structure comprises an extensive hydrogen-bonded array of urea molecules, giving rise to parallel chains (with an internal diameter of 5.3–5.7 Å) within which the guest molecules are densely packed. The X-ray structural characterisation confirmed that the vast majority of urea inclusion compounds are incommensurate, that is no small integers *m* and *n* exist to satisfy $mc_h = nc_g$, where c_h and c_g are the host and guest repeat distance along the channel axis. Unusual inclusion compounds are formed by urea and sebaconitrile⁴ (6 urea : 1 guest) and undecane-2,10-dione (9 urea : 1 guest),⁵ in which additionally hydrogen-bond interactions appear between the host and the guest molecules. Urea also forms many inclusion compounds with the incorporation of other molecular species as additional building blocks of their hydrogen-bonded host lattices as for example halides and pseudohalides, planar oxoanions, dihydrogen orthoborate $\text{BO}(\text{OH})_2$ and allophanate ion $\text{NH}_2\text{CONHCO}_2^-$, spirocyclic pentaborate anion $[\text{B}_5\text{O}_6(\text{OH})_4]^-$, and tetra-*n*-propylammonium halides.⁶ Thus far, with the exception of urea inclusion complexes with trioxane,⁷ undecan-5-one⁸ and with certain short-chain α,ω -dihaloalkanes and dicarboxylic acids,⁹ virtually all urea inclusion compounds are incommensurate, where the repeat distance of host and guest along the channel is a common factor, and the guest molecules pack within van der Waals contact of each other. In some cases, particularly at low temperatures, the host structure becomes slightly distorted from the conventional hexagonal tunnel structure, but the repeat length along the channel axis is uniformly close to the standard value of 11.0 Å.² If a guest species cannot be accommodated by the conventional hexagonal channel, it is ordinarily not included within urea,¹⁰ and either separate phases or specific cocrystals¹¹ are formed. Recent reviews^{12,13} summarise the present level of understanding of the structural and dynamic properties of urea and thiourea channel inclusion compounds.

We now report the X-ray single crystal structure† of a novel channel inclusion compound formed by urea and picoline *N*-oxide molecules (4 urea : 2 guest). Nice transparent rectangular plates of significant sizes were obtained by the slow evaporation method from a methanol solution of urea and picoline *N*-oxide (T_m 146–148 °C).‡ The crystal structure comprises two independent picoline *N*-oxide molecules, each lying on a mirror plane, and four independent urea molecules forming host channels in which the guests are imbedded. The IR spectra§ of the crystal are qualitatively different from the spectra of the substituents and reflect the formation of a hydrogen-bonded network, substantially different from that in the urea crystal. The splitting of the ring C–C and C–H modes in the regions 1450–1500 cm^{-1} , 1150–1250 cm^{-1} , 1000–1050 cm^{-1} and 750–760 cm^{-1} , as well as of the CH_3 stretching and deformation modes (3000–3130 cm^{-1} and 1370–1460 cm^{-1}), reflects the presence of two independent picoline *N*-oxide molecules. On the other hand, the significant changes (band broadening, multiplication and wavenumber shift) observed in the regions of

νNH_2 and δNH_2 modes (3450–3000 and 1600–1700 cm^{-1}) are consequential to the hydrogen-bond specification in the new channel arrays. However, the most spectacular changes are observed in the region 750–500 cm^{-1} , where several new bands appear, each of which is doubly split. This region is not well understood now and requires further investigation, but it very probably has something to do with the formation of hydrogen bonds toward the picoline O21 oxygen atom.

The 1D hydrogen-bonded arrays are extended explicitly through $\text{N}-\text{H}_{\text{syn}}\cdots\text{O}=\text{C}$. Each pair of urea molecules assigned as U1–U3 and U2–U4 (related *via* screw rotation along the *z*-axis) form hydrogen-bonded ring motifs $R_2^2(8)$ which are further propagated to form molecular tapes running along the *a*-crystallographic axis. Distortions from planarity allow for mutual topological, geometrical and sterical adaptation and recognition of the hydrogen-bond donor and acceptor sites, left unused in the tape formation, in order to zip each two neighbouring tapes at $1/2a$, $3/2a$, $5/2a$, *etc.* *via* four $\text{N}-\text{H}_{\text{anti}}\cdots\text{O}$ bonds with the resultant formation of a strongly folded 2D hydrogen-bond arrangement of the host lattice (see Chart 1a).

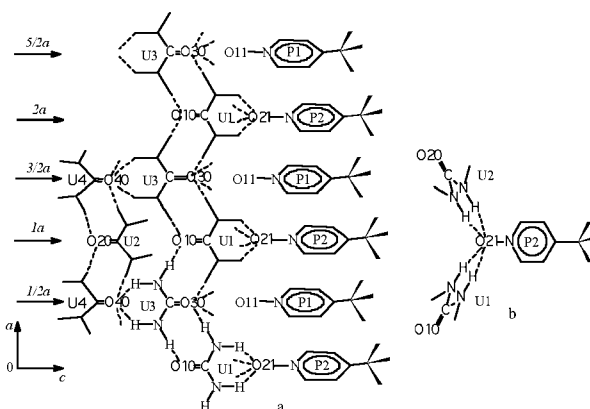


Chart 1

The dihedral angle between the zipped tapes is *ca.* 120°. The fourfold accessibility of O30 and O40 for hydrogen bonds is a rare phenomenon, so far noted only in urea crystals. This fact suggests that the two electron pairs on the urea oxygen are delocalised on a cone surface. The four hydrogen bonds toward the urea O30 and O40 adapt a pyramidal configuration. The other two oxygens O10 and O20 from U1 and U2 are imbedded in the tapes and are not accessible for additional hydrogen bonds.

The two independent picoline *N*-oxide molecules assigned as P1 and P2 are stacked in the host channels of urea with a repeat distance of 3.55 Å between the aromatic ring planes and densely fill the empty space. However, the bound mechanism toward the host lattice is diverse for the guests P1 and P2. Four $\text{N}-\text{H}_{\text{anti}}$ donors from U1 and U2 project the O21 atoms located on P2 in order to form four hydrogen bonds with a pyramidal configuration (see Chart 1b). The dihedral angle between the planes of two pairs of hydrogen bonds toward O21, donated by U1 and U2 is 120°. Thus, each two neighbouring tapes are hinged on the P2 molecules at $1a$, $2a$, $3a$ *etc.*, completing the 3D hydrogen-bonded network (Chart 1 and Table 1). The three-dimensional

Table 1 Hydrogen bond geometries and hydrogen bond patterns in urea picoline *N*-oxide (4:2) cocrystal

Hydrogen bonds	D—H...A/ Å	H...A/ Å	Symmetry operator
host interactions			
U1–U3 tape			
N30–H1(N30)...O10	2.920(9)	2.05(4)	x, y, z $2 - x, y, z$
N10–H1(N10)...O30	2.991(9)	2.04(8)	x, y, z
U2–U4 tape			
N20–H1(N20)...O40	3.016(9)	2.17(4)	x, y, z
N40–H1(N40)...O20	2.926(9)	2.12(4)	x, y, z $2 - x, y, z$
U3–U4 intertape			
N40–H2(N40)...O30	3.021(5)	2.15(4)	$x, -1 + y, z$ $1 - x, -1 + y, z$
N30–H2(N30)...O40	2.969(5)	2.15(4)	$1 - x, 2 - y, -5 + z$
host-guest interactions			
N20–H2(N20)...O21	2.994(5)	2.24(3)	x, y, z $2 - x, y, z$
N10–H2(N10)...O21	2.994(5)	2.25(4)	x, y, z $2 - x, y, z$

crystal structure can be considered as consisting of urea channels running along the *a*-axis, in which the P2 molecules are hydrogen-bond fixed perpendicularly to the urea chains, padlocking large cavities where the other guests P1 are simply trapped. Despite the similar geometry of both guest molecules, the topology of the host lattice dictates different including mechanism and the P1 molecules intercalate (at 1/2*a*, 3/2*a* etc.) between the P2 molecules residing the empty spaces in between. The acceptor site O11 on the P1 molecule is imbedded in the O10 and O20 electron rich environment, lacking free hydrogen-bond donors. However, neither the repulsive forces between the P1 guests and U host lattice nor the dipole–dipole interactions between the P1 and P2 are strong enough to overcome the hydrogen bond interactions confining the cavity size. So, the P1 molecules, though not specifically bonded to the host, are only free to some librational motions. The sublimation process in the temperature range 100–140 °C may be explained with a partial breaking of the hydrogen bond lattice and leaving of the P1 molecules. As a result of this unusual channel inclusion mechanism, both guest molecules P1 and P2 are aligned almost in the same way in the host lattice (see Fig. 1). Their charge-transfer (CT) axes are directed approximately at 60° toward the

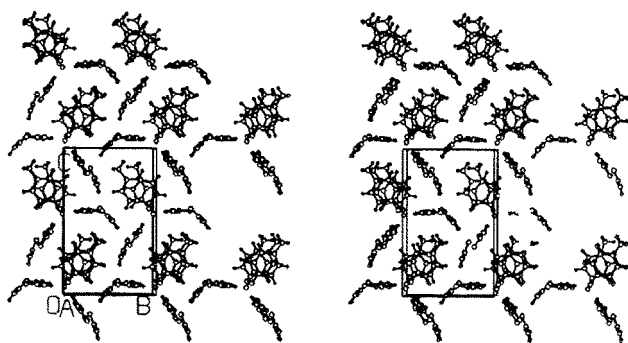


Fig. 1

optical *b*-axis, which is very close to the optimal molecular orientation for bulk phase-matching in the *mm2* space group.¹⁴ The crystal passes positively a second harmonic generation test yielding a signal 1.5 times higher than that of urea.

Notes and references

† *Crystal data*: C₈H₁₅O₃N₅, *M_r* = 229.24 g mol⁻¹, white prism, (0.60 × 0.50 × 0.30 mm), orthorhombic, space group *Pmc*2₁ (no. 26) *a* = 7.09(3), *b* = 10.065(3), *c* = 16.267(4) Å, *V* = 1162(6) Å³, *Z* = 4, *D_c* = 1.311 Mg m⁻³, *T* = 297 K, *F*(000) = 488, μ(*Mo*-Kα) = 0.096 mm⁻¹; 3055 measured reflections (20.28 < 2θ < 47.14°), 1649 unique reflections (*R_{int}* = 0.017); refinement on *F* for 1139 observed reflections (*I* > 2.00 σ(*I*)), and 210 variable parameters, *R* = 0.043, *wR* = 0.048. CCDC 182/1306. See <http://www.rsc.org/suppdata/cc/1999/1527/> for crystallographic data in .cif format.

‡ The crystal sublimates at temperatures higher than 100 °C and melts at 146–148 °C. At 170 °C it starts to boil.

§ Solid state IR spectra were measured on a Nicolet FT-IR spectrometer as Nujol mulls.

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- 14 Bulk-phase matching is defined by the angle α between the CT axis and the principle dielectric axis. For more information see: J. Zyss and J. L. Oudar, *Phys. Rev.*, 1982, **A26**, 2028; J. Zyss and D. S. Chemla, in *Nonlinear Optical Properties of Organic Molecules and Crystals*, vol. 1, ed. D. S. Chemla and J. Zyss, 1987, Academic Press. For optimal molecular orientations and phase-matching configurations see Figure 16 and Table XIV therein.

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