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Citation for published version (APA):

DOI:
10.1002/anie.199709691

Document status and date:
Published: 01/01/1997

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
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Crystal Engineering of Melamine–Imide Complexes; Tuning the Stoichiometry by Steric Hindrance of the Imide Carbonyl Groups**

Ronald F. M. Lange, Felix H. Beijer, Rint P. Sijbesma, Rob W. W. Hooft, Huub Kooijman, Anthony L. Spek, Jan Kroon, and E. W. Meijer*

The proposed infinite, two-dimensional lattice, formed by complexation of melamine with cyanuric acid through triple hydrogen bonds,[1] has been a unique inspiration to supramolecular chemists.[2] Various model studies have been performed to mimic this triple hydrogen bond formation.[3-8] Whitesides et al. reported the formation of a well-defined complex of six melamine and six cyanuric acid derivatives, linked together by 36 hydrogen bonds.[3] Using substituted melamines and barbituric acid derivatives, they were also able to prepare molecular tapes, crinkled tapes, and rosettes.[4] A variation of the linear tape was described by Lehn et al.[5] Furthermore, helical[6] and tube-like[7] nanostructures are formed by complexation of dialkyl-substituted melamines with a diimide, whereas Rebek et al. reported on a trisamide which could act as a molecular “tool chuck” for melamine.[8] Until now, only two crystalline complexes containing melamine have been reported in literature.[9]

Here, we present the formation of supramolecular 1:1, 1:2, and 1:3 complexes of melamine with imides. We show that the availability for hydrogen bonding of the carbonyl groups in the imide is strongly influenced by subtle differences in its molecular structure. The result that the stoichiometry of the supramolecular complexes can be tuned represents a distinct step forward towards crystal engineering.[10]

Cocrystallization of melamine with succinimide from water or DMSO in a molar ratio between 1:10 and 1:1 resulted in the formation of a supramolecular 1:1 complex of melamine and succinimide. When a molar excess of melamine was used, crystals of pure melamine were formed together with crystals of the 1:1 complex. X-ray analysis[11] of the complex revealed a 1:1 sheetlike structure (Figure 1). In both molecules, every donor and acceptor site available for hydrogen bonding is used. Surprisingly, when glutarimide was crystallized with melamine from water or DMSO in melamine:imide ratios between 1:10 and 1:2, a 1:2 complex of melamine and glutarimide was obtained. X-ray analysis[12] showed a 1:2-herringbone structure (Figure 2). In this complex, one of the four carbonyl acceptor sites of the imide is not involved in hydrogen bonding. Therefore, by masking two of the four carbonyl acceptor sites of an imide, it should be possible to obtain a 1:3 cocrystal with melamine. To verify this hypothesis, we co-crystallized melamine with a variety of imides (adipimide, 2,3-diphenylmaleimide, pthalimide, diphenylmaleimide, and 1,8-naphthalimide) in various ratios of DMSO, DMF, ethanol, or NMP as solvent. However, crystallization did not result in single crystals of the desired 1:3 melamine–imide complex. This is possibly due to the large solubility difference between the imides and melamine.[13]

However, cocrystallization of melamine with the water-soluble 1-N-propylthymine from water or 96% ethanol in initial

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[1] The analog of 1 lacking the crown ethers, Boc-(L-L-L-F)-OMe, was inactive in the same bilayer experiment but led to perturbations in bilayer stability.


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molar ratios between 1:2 and 1:5 resulted indeed in the crystallization of the desired 1:3 melamine-imide complex. X-ray analysis\(^\text{[14]}\) showed a 1:3 \(C_3\)-symmetrical structure with disordered propyl groups and small quantities of disordered solvent in infinite channels perpendicular to the plane of molecules (Figure 3).

The crystal structures of the complexes show that all hydrogen-bond lengths and angles agree well with values in other melamine complexes\(^\text{[4, 5, 9]}\) and support the triple hydrogen-bond motif. In the 1:1 melamine-succinimide crystal structure the molecules are paired through three anti-parallel hydrogen bonds (Figure 1).\(^\text{[15a]}\) Two independent pairs are present in the unit cell, and a two-layer zigzag sheet is formed. Intermolecular hydrogen bonds within the two-layer zigzag sheet connect the different pairs parallel to the \(a, c\) plane (Figure 1). No hydrogen bonding occurs between different two-layer zigzag sheets along the \(b\) axis. Detailed analysis of this complex crystal structure reveals that each succinimide molecule uses all four H-bond acceptor sites and its H-bond donor site, while melamine uses three H-bond acceptor and all its six H-bond donor sites. This results in a 1:1 complex with seven donors and seven acceptors per pair.

In the 1:2 melamine-glutarimide crystal structure, each melamine molecule is connected to two glutarimide molecules by three anti-parallel hydrogen bonds.\(^\text{[15b]}\) These units, located on a crystallographic twofold rotation axis, are connected in a one dimensional hydrogen-bonded chain, forming an \(x\)-network in which the arrangement of the molecules resembles a herringbone structure. No specific interactions between the \(x\)-networks are detected. All molecules in the complex leave one of their H-bond acceptor sites unused. Assuming that one of the four imide carbonyl acceptor sites is not available due to steric hindrance, it is obvious that a 1:2 stoichiometry gives an optimal balance of donor and acceptor sites.

In the 1:3 melamine-\((1-N\text{-propylthymine})\) crystal structure four molecules are connected by nine H-bonds to form a planar \(C_3\)-symmetrical structure.\(^\text{[15c]}\) Here, two carbonyl acceptor sites are not used, because they are masked by the methyl and the \(N\)-propyl group. This 1:3 arrangement of molecules around melamine resembles the hydrogen-bonding motif of the cyano-uric acid-melamine lattice.

These results show that it is possible to influence the ratio of the components of the complex of melamine with succinimide (1:1), glutarimide (1:2), and 1-N-propylthymine (1:3). The availability of the imide carbonyl acceptor sites affords a handle to tune the supramolecular crystal structure with melamine. Because of the hydrophobic interactions, water seems to be the best medium from which the different crystals can be grown. The 1:3 melamine-imide structure is consistent with the arrangement of cyano-uric acid around melamine in the 1:1 complex.
plex of melamine and cyanuric acid.[11] It also supports the uncovering assembly rules that govern the crystallization of a restricted group of related complexes is a useful approach to the design of crystalline solids.[10–13] Further research to extend these new insights into the formation of supramolecular lattices is in progress.

**Experimental Section**

Typical procedure for the cocryrtallization of melamine and succinimide: melamine (94.1 mg, 0.79 mmol) and succinimide (78.7 mg, 0.79 mmol) were dissolved in water (5 mL) under reflux and slowly cooled to ambient temperature. After filtration 136.9 mg (0.61 mmol, yield 77%) of the [2:2] melamine-succinimide cocrystals were obtained. The 1:3 melamine–glutarimide and the 1:3 melamine–(1-N-propylthiophene) complexes were obtained in a similar manner.

Received: October 4, 1996 [29614E]

German version: Angew. Chem. 1997, 105, 1066–1068

**Keywords:** crystal engineering, hydrogen bonds, imides, supramolecular chemistry


[11] Crystal data for 1:1 melamine-succinimide: C,NH, C,HNO, M, = 225.21 g mol⁻¹, colorless, block-shaped crystal (0.2x0.2x0.5 mm), monoclinic, space group P2₁/c (no. 14), a = 10.1648(8), b = 14.0935(6), c = 4.158(6) Å, β = 106.25(2)°, V = 1999(2) Å³, Z = 8, ρcalc = 1.496(1) g cm⁻³, F(000) = 944, µ(CuKα) = 9.4 cm⁻¹. Of 1877 reflections measured, R = 0.050, 3.1°≤θ≤75° for 12674 reflections. T = 295 K, CuKα radiation, Ni filter, R = 0.1481 Å on an Enraf-Nonius CAD4-F diffractometer in a sealed tube. Data were corrected for Lp effects, extinction, and for a linear instability of 2% in three reference reflections during 50 h of X-ray exposure time, no absorption correction applied. The structure was solved by automated direct methods (SHELXTL). Refinement on F2 was carried out by full-matrix least-squares techniques (SHELXL96); final R value 0.047, wR = 0.11, S = 1.07, for 690 reflections with 0.0<0<37.5°, a scan, T = 100 K, MoKα, graphite monochromator, λ = 0.71073 Å on an Enraf-Nonius CAD4 Turbo diffractometer on rotating anode. Data were corrected for Lp effects and for a linear decay of 4% of three reference reflections during 50 h of X-ray exposure time. No absorption correction was applied. The structure was solved by automated direct methods (SHELXL96). Refinement on F2 was carried out by full-matrix least-squares techniques (SHELXL86); no observation criterion was applied during refinement. The R-propyl moiety is disordered over four positions, five of which are generated by space-group symmetry. The occupancy ratio of the two unique conformations was included as a parameter. Hydrogen atoms were located on the unit cell contains a channel parallel to the c axis and passing through the origin, filled with disordered solvent (probably water). This density was modeled by introducing two partially occupied oxygen sites in the channel. Hydrogen atoms were located on a difference Fourier map and subsequently included in the refinement. All non-hydrogen atoms were refined with anisotropic thermal parameters except for the carbon atoms in the disordered R-propyl moiety. Hydrogen atoms were refined with a fixed isotropic thermal parameter related to the value of the equivalent isotropic displacement parameter of their carrier atoms by a factor of 1.5 for the methyl, disordered methylene, and amine hydrogen atoms, and by a factor of 2 for the other hydrogen atoms. Refinement was carried out to F = 0.179, w = 1/[F²(F²)] = 0.4843P² + 1.81P[R]. R = 0.065 for 690 reflections with I > 2σ(I), S = 1.07 for 113 parameters. A final difference Fourier showed no residual density outside −0.25 and 0.25 e Å⁻³. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-106114. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax int. code +1223)363-0393; e-mail: deposit@ccdc.cam.ac.uk.

[12] a) The NH – O hydrogen bond are of comparable length (3.12(2), 3.048(2), 3.120(2), and 3.150(2) Å), while the NH – N hydrogen bond is shorter (2.812(2) and 2.814(2) Å). The hydrogen bonds connecting the pairs range from 2.913(2) to 3.054(2) Å. b) The length of triple anti-parallel hydrogen bonds is the same within 0.063 Å (2.941(1), 2.961(1), and 3.001(1) Å), while the other hydrogen bond is somewhat longer (3.089(1) Å). c) The triple anti-parallel hydrogen bonds range from 2.881(1) Å (NH…N distance) to 2.876(5) Å.


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