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,[10] has been a unique inspiration to supramolecular chemists. Various model studies have been performed to mimic this triple hydrogen bond formation. 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.[13] Using substituted melamines and barbituric acid derivatives, they were also able to prepare molecular tapes, crinkled tapes, and rosettes.[14] A variation of the linear tape was described by Lehn et al.[15] Furthermore, helical[16] and tube-like[17] nanostructures are formed by complexation of dialkyl-substituted melamines with a dimide, whereas Rebek et al. reported on a trisside which could act as a molecular “tool chuck” for melamine.[18] Until now, only two crystalline complexes containing melamine have been reported in literature.[19]

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 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 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, phthalimide, diphenylphthalimide, 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-propylmelamine from water or 96% ethanol in initial

---

**The authors acknowledge the fruitful discussions with many colleagues at DSM Research and the University of Eindhoven. Dr. B. Coussens is acknowledged for her contributions in molecular modeling.

---


---

**COMMUNICATIONS**


Figure 1. X-ray crystal structure of the 1:1 complex between melamine and succinimide (PLUTON plot).
molar ratios between 1:2 and 1:5 resulted indeed in the crystallization of the desired 1:3 melamine–imid complex. X-ray analysis\(^{14}\) 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\(^{4,5,9}\) 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).\(^{15a}\) 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.\(^{15b}\) 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-propylthymine) crystal structure four molecules are connected by nine H-bonds to form a planar C\(_3\)-symmetrical structure.\(^{15c}\) 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 cyanuric 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–imid structure is consistent with the arrangement of cyanuric acid around melamine in the 1:1 com-
plex of melamine and cyanuric acid.[11] It also supports the 1:3
complexation of melamine with an alternating copolymer of
maleimide and styrene, in which the polymer backbone is
presumed to mask two carbonyl acceptor sites of the maleimide.[16]

The present results suggest that uncovering assembly rules that
govern the crystallization of a restricted group of related com-
plexes 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 cocrysalization of melamine and succinimide: melamine
(9 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,
the formation of supramolecular lattices is in progress.

Received: October 4, 1996 [29641E]
German version: Angew. Chem. 1997, 109, 1006 – 1008

Keywords: crystal engineering; hydrogen bonds; imides; supramolecular chemistry

Chem. 1962, 28, 273; b) A Finkel'shtein, O S. Rukhovich, Zh. Prakt. Spektro-
trakt. 1983, 38, 327.

Chemistry, VCH, Weinheim, 1995; b) G R Desiraju, The Crystal as a Supramolec-
ular Phenomenon, Wiley, 1996; c) D Pilip, J F Stoddart, Angew. Chem. 1996, 109,


5473; b) A J Zerewinski, G M Whitesides, ibid. 1994, 116, 4298; c) A J
Mathias, E E Simanek, A J Zerewinski, C T Seto, G M Whitesides, ibid
1994, 116, 4316; e) J P Mathias, E E Simanek, G M Whitesides, ibid. 1994,
116, 4326.


117, 6130.


1250; b) M M. Chowdhry, D M. P Mingos, A J P. White, D J Williams,

1995, 34, 2328; b) J D Dunitz, Pure Appl. Chem. 1991, 63, 171; c) M C Ettie,

[11] Crystal data for 1:1 melamine–succinimide: C6H6N3·C6H6N3·M1 =
225.21 g mol–1, colorless, block-shaped crystal (0.1 x 0.2 x 0.5 mm),
hexagonal, space group P63/m (no. 176), a = 17.212(2) Å, c = 6.3697(5) Å,
V = 1634(2) Å3, Z = 2, p(MoKα) = 1.28 g cm–3, F(000) = 672, µ(MoKα) =
1.0 cm–1. All data, where relevant, are given without disturbed solvent con-
tribution (side infia). Of 4825 reflections measured, 1506 were independent;
R1 = 0.14, (I > 2σ(I), α scan, T = 100 K, MoKα, radiation, graphite
monochromator, λ = 0.71073 Å) on an Enraf-Nonius CAD-4 Turbo diffrac-
tometer on rotating anode. Data were corrected for Lp effects and for a linear
decay of 4% of three reference reflections during 59 h of X-ray exposure time;
no absorption correction was applied. The structure was solved by automated
direct methods (SHELX86). Refinement on F2 was carried out by full-matrix
least-squares techniques (SHELX86); no observation criterion was applied
during refinement. All hydrogen atoms were refined with anisotropic thermal
parameters except for the carbon atoms in the disordered V-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. Refine-
ment converged at R1 = 0.179, wR2 = 1.0483P2 + 1.81P, R1 = 0.063 for
690 reflections with I > 2σ(I), S = 1.07 for 113 parameters. A final difference
Fourier showed no residual density outside −0.26 and 0.28 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 suppl supplemental
publication no. CCDC-100114. Copies of the data
can be obtained free of charge on application to The Director, CCDC, 12
Union Road, Cambridge CB21E2Z, UK (fax info. code +(+44)1223)363-033;
e-mail: deposit@chemcrys.cam.ac.uk).

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. The length of triple anti-parallel hydrogen bonds is the same within
0.063 Å (2.941(1), 2.961(1) and 3.005(1) Å), while the other hydrogen bond is
somewhat longer (3.095(1) Å). c) The three triple anti-
parallel hydrogen bonds range from 2.881(6) Å (NH · · · N) to 2.867(5)
and 2.881(1) Å (NH · · · O) distance.

Symp. 1996, 102, 301.