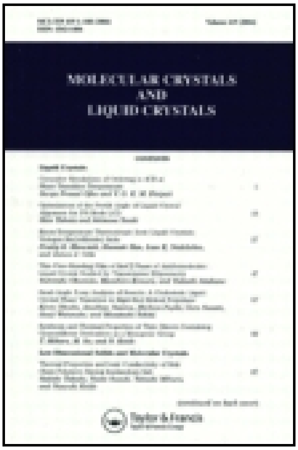

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The Squaramides. A New Family of Host Molecules for Crystal Engineering

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THE SQUARAMIDES. A NEW FAMILY OF HOST MOLECULES FOR CRYSTAL ENGINEERING

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A host guest co-crystallization strategy for crystal engineering has been developed and a library of host molecules has been established. Each molecule possesses a hydrogen bond functionality that leads to the formation of a one-dimensional α-network with a characteristic repeat distance. The squaramides, diamides derived from squaric acid, represent a new entry into this library. They self assemble with repeat distances of about 6.1 Å. This structure of the squaramide derived from 4-aminomethylpyridine is reported along with two of its co-crystals.

Keywords: crystal engineering; supramolecular structure; hydrogen bonding

INTRODUCTION

The science of crystal engineering is still in its formative stages. Like any new field there are two necessary approaches. One approach is concerned with increasing our understanding of the fundamentals. The second approach is directed toward the application of these fundamentals to problems of interest. Crystal engineering is a form a chemical synthesis, meaning that applications of crystal engineering are actually directed chemical syntheses leading to desired supramolecular entities. We would like to believe that we now have enough understanding of the fundamentals to pursue these applications.

One difficulty with crystal engineering that differentiates it from normal chemical synthesis is that a particular molecule crystallizes to give one particular structure. Although one can search for polymorphs one is generally confronted with the fact that there are few or no available options if a single molecule is found to crystallize in a manner at odds with ones

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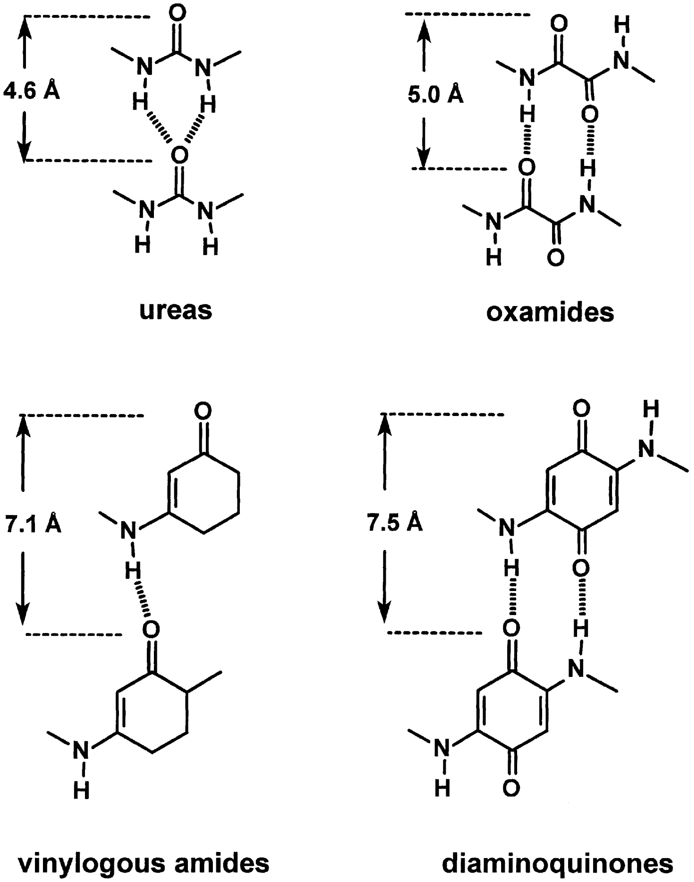


FIGURE 1 A selection of host molecules. Each molecule forms a one-dimensional hydrogen bonded α-network with a characteristic spacing.

designs or desires. This means that if the molecule of interest crystallizes in an "undesirable manner" one must start anew.

An alternate technique to overcume this difficulty is to use more than one molecule from the outset. The co-crystallization of two separate molecules greatly increases the number of readily obtainable crystalline entities. It allows a convergent synthetic approach and lends itself to a combinatorial strategy. It is a valid strategy since the supramolecular goal often does not require the specification of an entire crystal, but instead just some functionality or structure of interest.

Our approach to chemical engineering has been to use a host-guest co-crystal approach [1]. We have previously developed a library of host molecules [2,3], each possessing the requisite hydrogen bond functionality to lead a one-dimensional α-network with a characteristic repeat distance, Figure 1.

We have used these host molecules to design and prepare many different structures of interest. For example we have prepared substituted ureas and oxamides and used them to align various diacetylenes guests in accordance with the structural parameters needed for a 1-4 topochemical polymerization [4,5]. The vinylogous amides have been used to align triacetylenes for a 1-6 topochemical polymerization [6]. Host molecules with pyridine substituents have been used to align metal atoms [7].

As can be seen in Figure 1 our host library contains molecules that span a variety of different distances. We would like to expand the library by adding new molecules that would yield other spacings. One candidate family is the squaramides, diamides of squaric acid, **1,2**.

The squaramides are vinylogous amides with two hydrogen bond donors and two acceptors. We expect them to form a hydrogen bonded α-network, **3**; molecular modeling suggests a repeat distance of about 6 Å. In this paper we report our initial investigations with squaramide **1**.

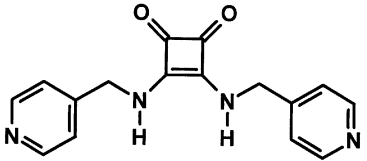
RESULTS AND DISCUSSION

Squaramide, **1**, is easily prepared by mixing diethyl squarate with stoichiometric amounts of 4-aminomethylpyridine. It crystallizes in the space group C2/c with a *b* axis of 6.077 Å. The molecules form an α-network along the C2 axis meaning that the 6.077 Å distance corresponds to the molecular repeat, Figure 2.

Once we established that **1** would indeed self assemble as we anticipated the next step was to attempt to form a host-guest co-crystal. Since **1** is a bipyridine, the obvious guest candidates would include dicarboxylic acids. We expected to form a two-dimensional β-network, **4**, analogous to the many β-networks previously prepared from urea and oxalamide host molecules.

Figure 3 shows the crystal structure of **1** co crystallized with dodecanedioic acid. A β-network is formed. It has P1 layer group symmetry, the twofold axis of the host molecule and the inversion center of the guest have both been lost. The observed repeat distance of 6.055 Å is similar to the repeat distance of 6.077 Å found for the host alone. Although we have the structure of only this one example we would anticipate that other dicarboxylic acids would form similar β-networks with **1**.

One restriction of our host-guest co-crystallization approach is the necessity for the guest molecule to fit within the spacing dictated by the host molecule. If the guest is too big either the co-crystals won't form at all or some alternate network will form. We put host molecule **1** to the test by



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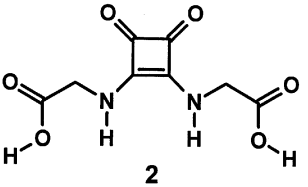

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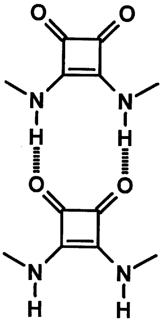

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co-crystallizing it with the transition metal complex, bis(acetylacetonate)-cobalt(II). On paper one can draw a proper β-network, **5**, but a little consideration of molecular sizes indicates that such a structure is quite unlikely since it is doubtful that a Co(acac)$_2$ molecule could be accommodated within in a 6.08 Å spacing.

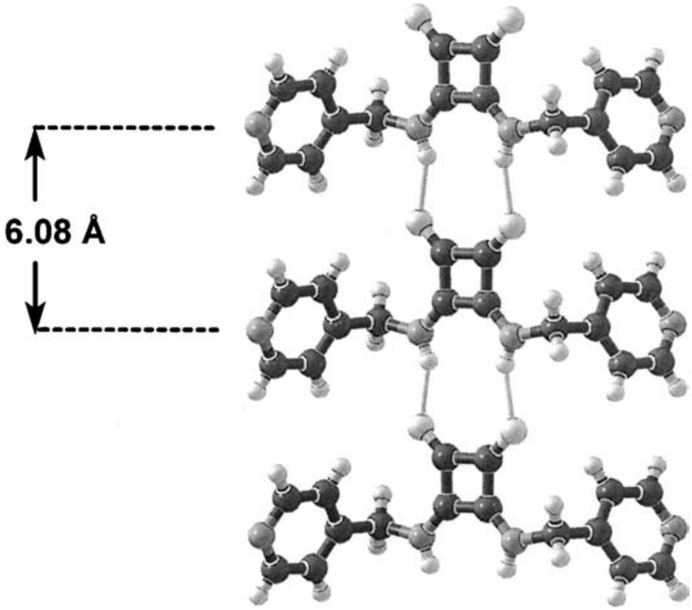
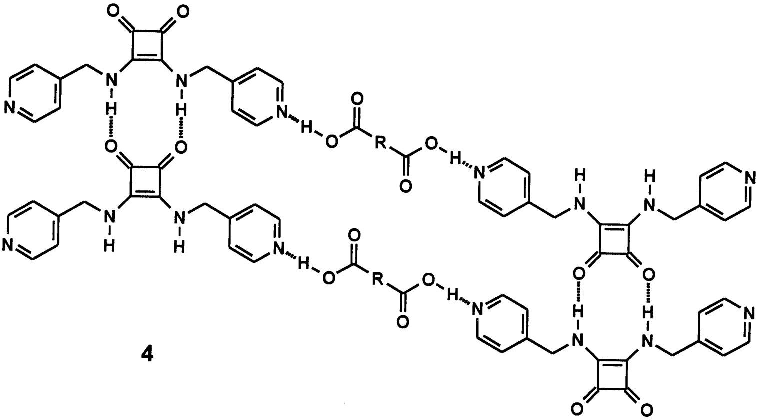


FIGURE 2 The crystal structure of **1** showing the hydrogen bonded α-network.



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Host molecule **1** and Co(acac)$_2$ were dissolved in a methanol water solution and allowed to crystallize. A rather complicated structure with an unanticipated compositions of [Co(acac)$_2$] and **1** in a 3:4 ratio was found, Figure 4.

The primary interaction between **1** and Co(acac)$_2$ is the pyridine-cobalt coordinate bond. These bonds form as anticipated, each Co has axial

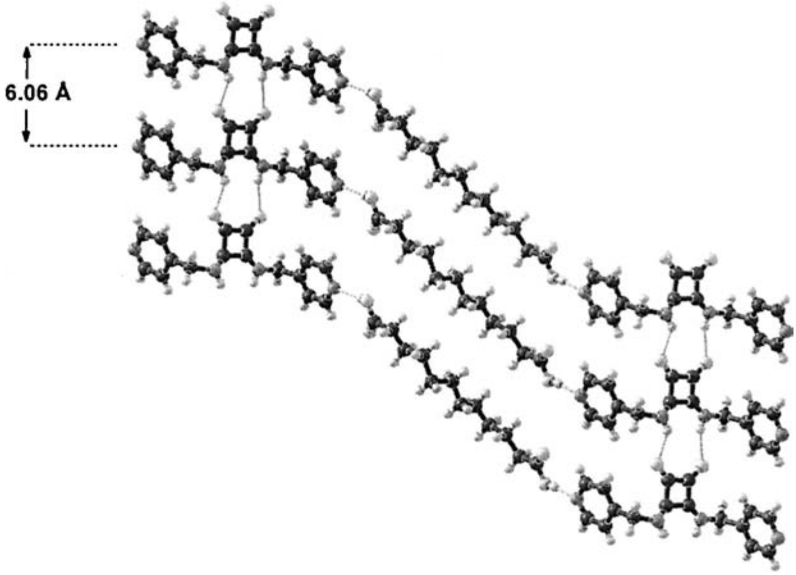

FIGURE 3 The co-crystal of **1** with dodecanedioic acid.

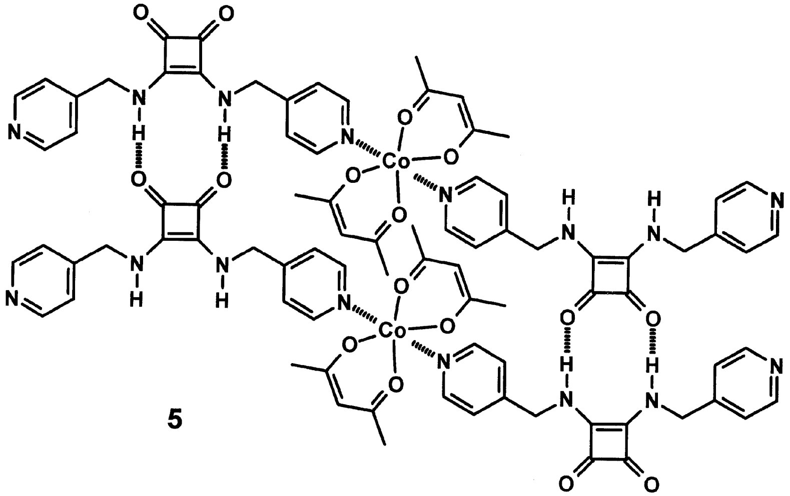

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FIGURE 4 Expected hydrogen bonding (in **5**).

pyridines, but the hydrogen bonds between the squaramides as shown in **5** do not form. There are two different molecular entities in the structure, Figure 5**a** and **b**. The first is a discrete cobalt complex with axial pyridines. One end of each bipyridine is coordinated to the Co atom, the far end is hydrogen bonded to a water molecule of hydration. The second molecular entity is a coordination polymer of the $Co(acac)_2$ and **1** in a 1:1 ratio. These two molecular entities are hydrogen bonded together in a reciprocal manner. The squaramides of the discrete molecule use the amide hydrogen atoms to hydrogen bond to oxygen atoms of the $Co(acac)_2$ of the coordination polymer, Figure 5**c**. The same interaction is found between the squaramide of the polymer and the $Co(acac)_2$ of the discrete molecule. The structure contains considerable open space which is occupied by an indeterminate number of water molecules.

CRYSTALLOGRAPHIC DATA

Compound **1**. a = 28.624(5)Å, b = 6.0789(1)Å, c = 8.145(1)Å, $\beta = 99.04(1)°$, vol = 1399.7(4)Å^3, space group C2/c, Z = 4.

Compound **1** co-crystallized with dodecanedioic acid. a = 6.055(1)Å, b = 8.751(2)Å, c = 13.088(13)Å, $\alpha = 85.72(1)$, $\beta = 84.66(1)°$, $\gamma = 84.25(1)$ vol = 685.2(2)Å^3, space group P1, Z = 1.

$Co(acac)_2$ co-crystallized with **1** in a 3:4 ratio. a = 16.411(2)Å, b = 16.946(2)Å, c = 20.298(3)Å, $\beta = 112.98(1)°$, vol = 5197(1)Å^3, space group $P2_1/c$, Z = 2.

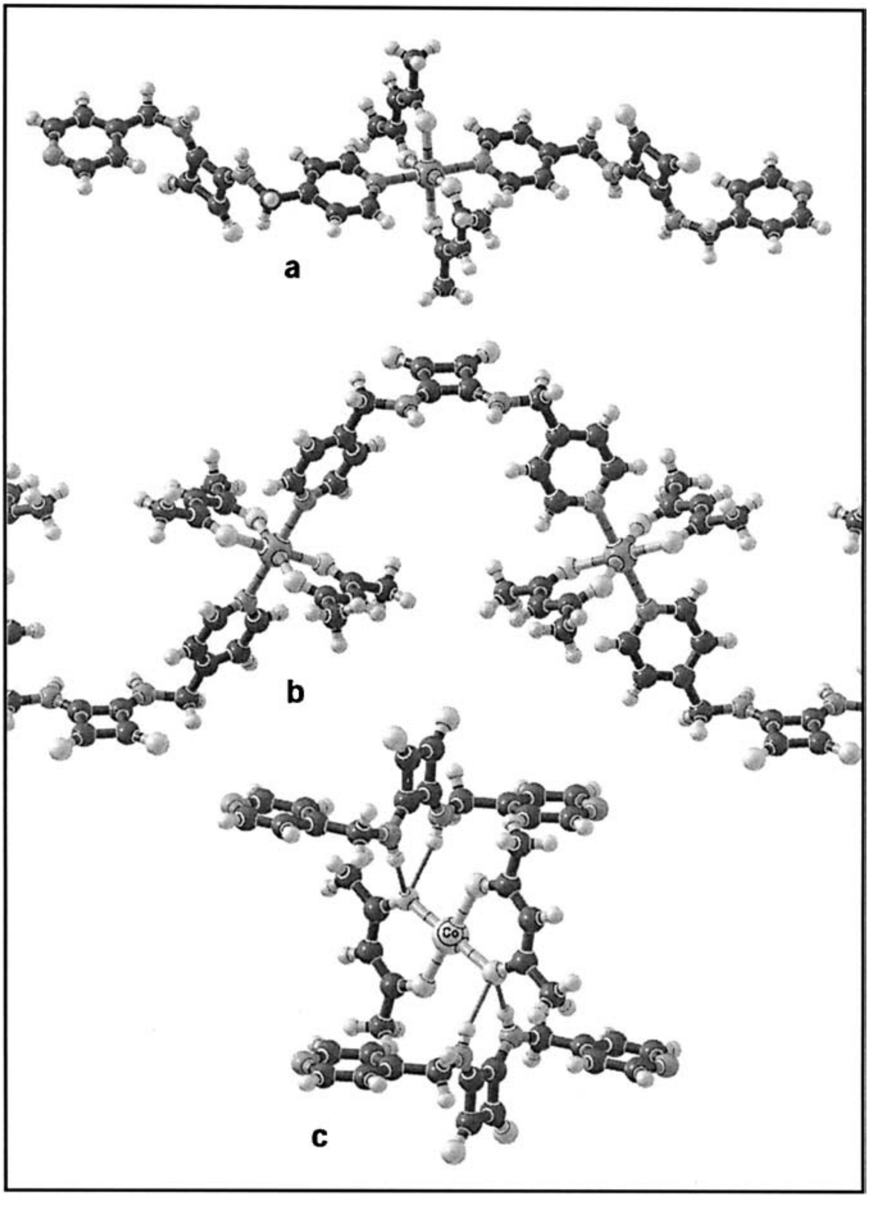

FIGURE 5 The co-crystal of bipyridine **1** with Co(acac)$_2$ contains two distinct molecular entities. The first, **a**, is a simple coordination complex of Co(acac)$_2$ with two axial pyridines. The second molecular entity is a coordination polymer of the bipyridine and Co(acac)$_2$., **b**. These two molecular entities are held together by hydrogen bonds between the squaramides and the oxygen atoms of the coordinated acetylacetonate ligands as shown in **c**.

SUMMARY

Our library of molecular hosts has been expanded by the addition of the squaramides. A characteristic spacing of 6.08 Å can be expected for host guest co-crystals derived from this new family of molecules. Subject of course to the restriction that the guest molecule be compatible in size with the requirements of the host.

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