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Letters

A novel supramolecular assembly of 3,5-dinitro-4-methylbenzoic acid and *trans*-1,2-bis(4-pyridyl)ethene

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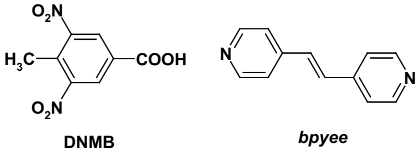
Abstract—A novel organic assembly, formed between 3,5-dinitro-4-methylbenzoic acid and *trans*-1,2-bis(4-pyridyl)ethene under hydrothermal conditions in the presence of Pr(III) and a layered structure obtained by direct co-crystallization of the reactants at ambient conditions is reported. The structures of the complexes were established, unambiguously, by single crystal X-ray diffraction methods.

The design and synthesis of supramolecular assemblies[1,2] employing hydrogen bonds is a 'facile' route for the creation of novel and exotic architectures such as honeycomb, diamondoid and laddranes, etc.[3–6] Co-crystallization of the reactants, under ambient conditions, is a technique often employed to synthesize complexes.[7,8]

In recent times, syntheses of coordination assemblies by hydrothermal methods (at high temperature and pressure) have become popular due to the successful syntheses of many organic–inorganic hybrid assemblies with rigid networks.[9–12] In fact, such assemblies are otherwise not available following conventional synthetic routes. Also, sometimes, employment of the drastic conditions leads to the formation of unusual products, which are quite different from the products obtained, when the reactions were performed under ambient conditions.

Nevertheless, the synthesis of supramolecular assemblies through hydrothermal methods using organic compounds alone have not been thoroughly explored, although its effect was demonstrated in the preparation and elucidation of the supramolecular assembly between cyanuric acid and melamine.[13] In this letter, we report an exotic supramolecular assembly that has been isolated from the hydrothermal reaction of 3,5-dinitro-4-methylbenzoic acid and *trans*-1,2-bis(4-pyridyl)ethene in the presence of Pr(III) and compare it with the assembly obtained from the co-crystallization carried out under ambient conditions.

In our recent experiments[14] to evaluate the ability of Pr(III) to aid construction of novel supramolecular assemblies, we noted that 4,4′-bipyridine and 1,2-bis(4-pyridyl)ethane did not form any dative bonds with Pr(III) but remained as guests in the channels being created by 3,5-dinitro-4-methylbenzoic acid (**DNMB**) and Pr(III).



DNMB ***bpyee***

Thus, we performed a hydrothermal reaction of 3,5-dinitro-4-methylbenzoic acid (**DNMB**) and *trans*-1,2-bis(4-pyridyl)ethene (***bpyee***) in the presence of Pr(III) to obtain a complex of **DNMB** and Pr(III) with ***bpyee*** being inserted as guest molecule.[15] In contrast, and to our surprise, crystal structure determination[16] revealed that a 2:1 adduct of **DNMB** and ***bpyee***, had formed along with water molecules in the crystal lattice.[17] We label this adduct $2(C_8H_5N_2O_6):(C_{12}H_{12}N_2):4(H_2O)$, as **1** and its asymmetric unit is shown in Figure 1.

Three-dimensional crystal structure analysis of **1**, revealed a sandwich type architecture as shown in

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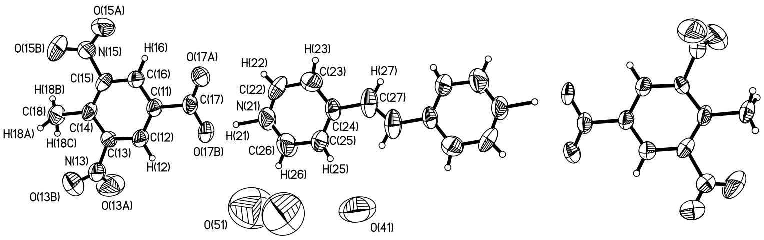

Figure 1. ORTEP drawing of the asymmetric unit in the crystal lattice of **1**.

Figure 2a. It is clearly known from further analysis that this is a result of sandwiching of **DNMB** molecules between the layers of ***bpyee***. In the three-dimensional arrangement, adjacent units are indeed held together by water molecules as shown in Figure 2b.

In this adduct, however, the recognition pattern between **DNMB** and ***bpyee***, as shown in Figure 2c, is very similar to the known interaction between acids and aza compounds with the formation of a supermolecule through a cyclic coupling between the carboxylate of **DNMB** and the hetero N-atom and CH groups of ***bpyee***. The hydrogen bond distances[18] in this coupling are 1.37 and 2.63 Å, respectively, corresponding to $N–H^+\cdots O^-$ and $C–H\cdots O$. Other characteristics of the hydrogen bonds of **1** are given in Table 1.

In a further exploration, we noted that a hydrothermal reaction between **DNMB** and ***bpyee*** alone did not yield a product[19] similar to **1**, suggesting the pivotal role of Pr(III) for the formation of **1** in addition to the drastic conditions.

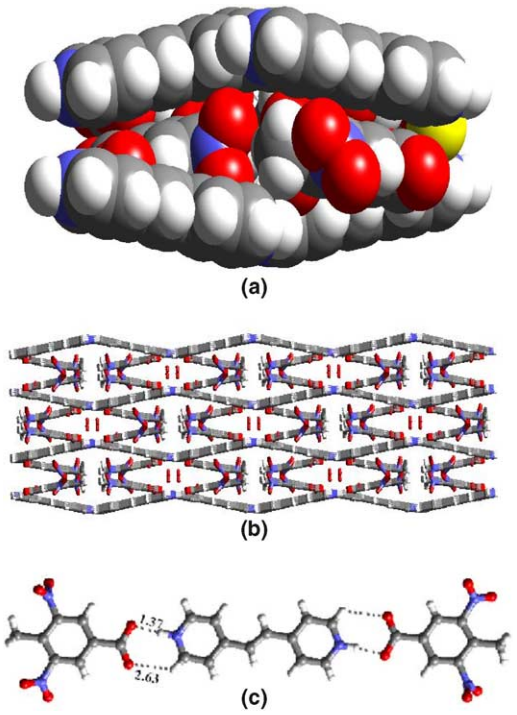

Figure 2. (a) Three-dimensional arrangement of **DNMB** and ***bpyee*** molecules in **1**. (b) Arrangement of adjacent supermolecules of **DNMB** and ***bpyee***. (c) Recognition pattern between **DNMB** and ***bpyee*** in the adduct **1**, forming a cyclic hydrogen bond coupling.

However, co-crystallization of **DNMB** and ***bpyee*** without Pr(III), at ambient conditions, by dissolving in hot methanol followed by slow-evaporation gave an adduct, **2**,[16,20] in a 2:1 composition bearing a formula unit $2(C_8H_6N_2O_6):(C_{12}H_{10}N_2)$, but with an entirely different three-dimensional structure to that observed in **1** thus, further confirming the influence of the Pr(III) species in the formation of the unusual assembly observed in **1**. The asymmetric unit of **2** is shown in Figure 3.

The adduct **2** gave stacked, corrugated layers of supermolecules formed between **DNMB** and ***bpyee***. This arrangement is shown in Figure 4a. In a typical layer, the reactants interact with each other through the formation of a strong $N–H\cdots O$ hydrogen bond formed between –COOH and the hetero N-atom as shown in Figure 4b. The adjacent supermolecules are held together by $C–H\cdots O$ hydrogen bonds with $H\cdots O$ distances of 2.63 and 2.69 Å (Table 1).

In order to substantiate further, the differences between the hydrothermal and ambient conditions, co-crystallization of **DNMB** and 1,2,-bis(4-pyridyl)ethane (an analogue of ***bpyee***), under similar conditions to those employed for the preparation of **2**, gave an adduct, **3**[16,21,22] (Fig. 5) in a 2:1 ratio having the structural formula as $2(C_8H_6N_2O_6):(C_{12}H_{12}N_2)$. In fact, adduct **3** is *iso*-structural with **2** in all aspects. The packing analysis is represented in Figure 6.

It is evident from Figure 6a that adduct **3** is also a stacked, layered structure like **2**, except that the layers are planar rather than corrugated. In a typical layer, the reactants form a supermolecule through the formation of strong $O–H\cdots N$ hydrogen bonds as shown in Figure 6b. However, unlike in **2**, the adjacent units are held together by numerous $C–H\cdots O$ hydrogen bonds with $H\cdots O$ distances in the range of 2.45–2.74 Å (Table 1). Such a similarity between the adducts **2** and **3** suggests that the basic recognition and topological arrangements remain unaffected under ambient conditions.

However, a comparison of the adducts **1**–**3** suggests that even though the basic recognition pattern is almost similar, variations in the conditions such as high temperature, pressure and the presence of metal ions lead to the formation of a novel assembly in the adduct **1**.

Thus, it can be concluded that it is possible to obtain varied architectures of organic supramolecular complexes influenced by metal ions and/or performing reactions under drastic conditions, for example

Table 1. Characteristics of the hydrogen bonds observed in complexes **1**–**3**

	1			**2**			**3**		
O–H···N				1.53	2.53	168	1.30	2.51	165
N^+–H···O^-	1.37	2.62	170						
C–H···O	2.40	3.27	170	2.39	3.32	165	2.45	3.37	163
	2.63	3.19	132	2.59	3.55	165	2.50	3.12	123
	2.66	3.34	147	2.63	3.49	176	2.53	3.38	147
	2.69	3.58	162	2.63	3.57	157	2.61	3.39	141
	2.81	3.57	142	2.69	3.32	129	2.62	3.45	148
	2.85	3.74	160	2.69	3.49	143	2.68	3.37	131
	2.87	3.68	146	2.77	3.43	127	2.69	3.50	151
							2.74	3.56	137
							2.74	3.60	151
							2.76	3.64	157

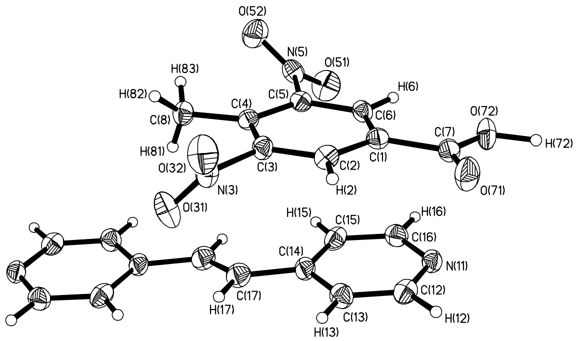

Figure 3. Molecular structure of complex **2**.

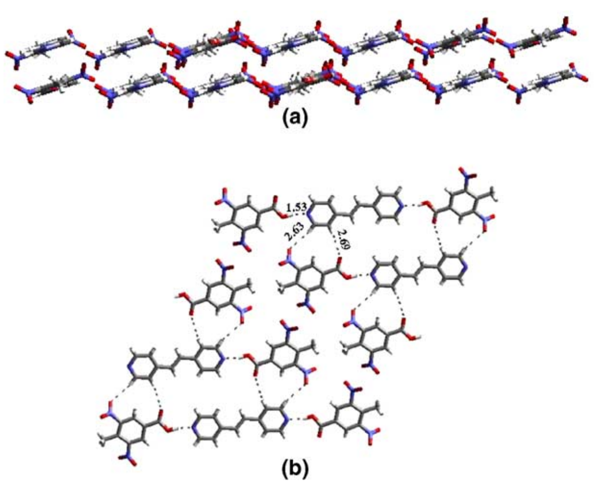

Figure 4. (a) Three-dimensional arrangement in the form of stacked, corrugated layers observed in the crystal structure of adduct **2**. (b) Arrangement of supermolecules in a typical corrugated layer.

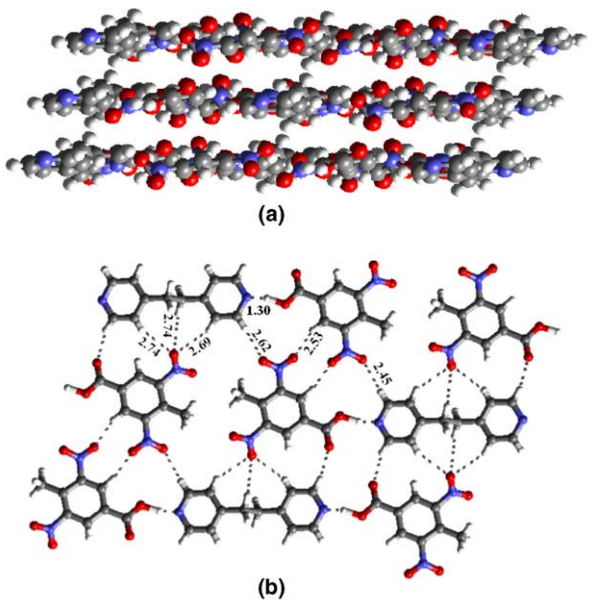

Figure 6. (a) Three-dimensional arrangement of **DNMB** and 1,2,-bis(4-pyridyl)ethane in the crystal structure of adduct **3**, in the form of planar layers. (b) Two-dimensional arrangement of the supermolecules.

hydrothermal synthesis. Such network structures would be of interest from synthetic aspects as well as application studies. To rationalize the substantial effect, a large number of experimental evidence is warranted. For this purpose, several experiments are in progress towards understanding the role of Pr(III) and also other lanthanide ions as well as transition metal ions in order to obtain more exotic and tailor-made architectures.

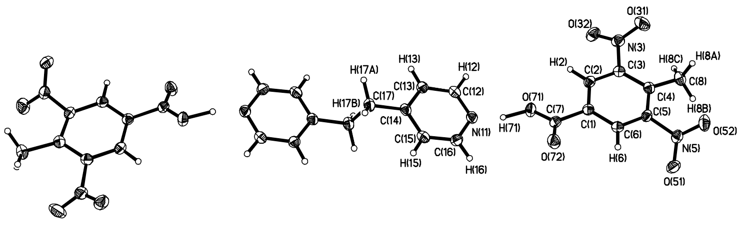

Figure 5. ORTEP drawing of complex **3**.

Acknowledgements

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2005.02.070.

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15. To an aqueous solution (15 mL) of praseodymium acetate hydrate (0.159 g, 0.5 mmol), was added 3,5-dinitro-4-methylbenzoic acid (0.113 g, 0.5 mmol) with stirring, followed by *trans*-1,2-bis(4-pyridyl)ethene (0.091 g, 0.5 mmol). The mixture was transferred into a Teflon-lined stainless-steel autoclave of 23 mL capacity, under autogenous pressure and heated to 160 °C for 24 h. The colourless needles obtained were washed with distilled water and dried at room temperature.
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17. Crystal data for **1**: $2(C_8H_5N_2O_6)$:$1(C_{12}H_{12}N_2)$:$4(H_2O)$, M = 698.52, monoclinic, space group *C* 2/*c*, $a = 20.377(8)$, $b = 10.583(4)$, $c = 16.011(6)$ Å, $\beta = 116.47(1)°$, $U = 3091.00(2)$ Å^3, $D_c = 1.501$ g cm^{-3}, $T = 293(2)$ K, Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ A) for $Z = 4$, $R = 0.0736$, CCDC 236450.
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19. We carried out several co-crystallization experiments of **DNMB** and ***bpyee*** by hydrothermal methods at different temperatures varying from 120 °C to 160 °C at an interval of 10 °C and also varying the ratios of the reactants (1:1, 1:2 and 2:1). However, in each case, the products obtained did not yield any single crystals and the residues were not crystalline as was confirmed by powder X-ray diffraction patterns. Furthermore, the patterns are totally different than observed for the crystals of **1**. However, from the IR spectra (see Supplementary data), it appears that the product could be an adduct of **DNMB** and ***bpyee*** without deprotonation of **DNMB**.
20. Crystal data for **2**: $2(C_8H_6N_2O_6)$:$1(C_{12}H_{10}N_2)$, M = 634.52, triclinic, space group $P\bar{1}$, $a = 8.232(3)$, $b = 8.421(4)$, $c = 11.014(4)$ Å, $\alpha = 95.57(7)$, $\beta = 116.47(1)°$, $\gamma = 116.05(6)°$, $U = 681.7(5)$ Å^3, $D_c = 1.546$ g cm^{-3}, $T = 140(2)$ K, Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ A) for $Z = 1$, $R = 0.0488$, CCDC 236449.
21. Crystal data for **3**: $2(C_8H_6N_2O_6)$:$1(C_{12}H_{12}N_2)$, M = 636.53, triclinic, space group $P\bar{1}$, $a = 7.267(3)$, $b = 9.847(4)$, $c = 10.433(4)$ Å, $\alpha = 77.97(5)$, $\beta = 76.64(5)°$,

$\gamma = 77.29(5)°$, $U = 698.7(4)$ Å^3, $D_c = 1.513$ g cm^{-3}, $T = 140(2)$ K, Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ A) for $Z = 1$, $R = 0.0382$, CCDC 236448.

22. Under hydrothermal conditions, the reactants in the presence of Pr(III) were found to be yield a coordination polymer (see Ref. 14).