

# Novel supramolecular organizations in melamine complexes with 4,4'-bipyridyl and silver nitrate

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Received 21 March 2000; accepted 31 May 2000

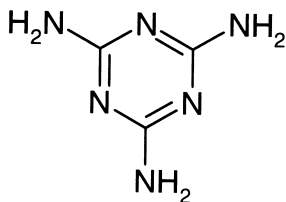
## Abstract

Complexes of melamine with 4,4'-bipyridyl and  $\text{AgNO}_3$  having compositions,  $\text{C}_{10}\text{H}_8\text{N}_2 \cdot 0.5(\text{C}_3\text{H}_6\text{N}_6) \cdot \text{H}_2\text{O}$  and  $[\text{Ag}(\text{C}_3\text{H}_6\text{N}_6)]\text{NO}_3$ , respectively, have been prepared for the first time. A crystallographic investigation has shown unique hydrogen bonding patterns in the two systems. The melamine–4,4'-bipyridyl complex shows a supramolecular organization wherein hydrogen bonding between melamine and water molecules results in tapes. The tapes are connected by hydrogen bonding to 4,4'-bipyridyl giving rise to a rectangular box. In the melamine– $\text{AgNO}_3$  complex, the melamine molecules are bound to  $\text{Ag}^+$  ions forming N–Ag–N chains, giving rise to a helix. The helices are held together by interchain hydrogen bonds. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Supramolecular assemblies; Hydrogen bonds; Melamine complexes

## 1. Introduction

Melamine, **M**, crystallizes as a hydrogen-bonded solid comprising molecular tapes formed by N–H···N hydrogen bonds between the adjacent molecules; the tapes give rise to a sheet structure [1,2].



**M**

Melamine is known to form interesting adducts with heterocyclic compounds and imides. Thus, **M** forms complexes with barbituric acid [3]. Whitesides and coworkers [4–8] have characterized adducts of substituted melamines with barbituric acid derivatives which possess structures involving molecular tapes, crinkled tapes and rosettes. Lehn and co-workers [9,10] have described a variation of the linear tape formed by the adducts of **M**. The formation of supramolecular 1:1, 1:2 and 1:3 complexes of melamine with imides such as succinimide and glutarimide have been studied [11]. In the melamine–succinimide complex, every donor and acceptor site available for hydrogen bonding in the two molecules is used. In this case too, a molecular tape results through the formation of N–H···O and N–H···N bonds. The formation of a robust hydrogen-bonded supramolecular aggregate of **M** with cyanuric acid, **CA**, where the aggregate is stabilized by 18 hydrogen bonds in a cyclic  $\text{CA}_3 \cdot \text{M}_3$  rosette was proposed sometime ago by Mathias et al. [12]. This **M**–**CA** adduct was

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Table 1  
Crystal data for the complexes **1** and **2**

	<b>1</b>	<b>2</b>
Formula	C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> :0.5 (C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> ):H <sub>2</sub> O	[Ag(C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> )]NO <sub>3</sub>
Molecular weight	237.27	296.02
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	P2 <sub>1</sub> /n
<i>a</i> (Å)	18.114(3)	6.692(1)
<i>b</i> (Å)	7.289(1)	11.763(1)
<i>c</i> (Å)	19.342(3)	10.293(1)
$\alpha$ (°)	90	90
$\beta$ (°)	113.05(1)	101.24(1)
$\gamma$ (°)	90	90
Cell volume (Å <sup>3</sup> )	2349.9(6)	794.7(2)
Z	8	4
<i>F</i> (000)	1000	576
<i>d</i> <sub>calc</sub> (mg/m <sup>3</sup> )	1.341	2.474
$\lambda$ (Å)	0.71073	0.71073
$\mu$ (mm <sup>-1</sup> )	0.092	2.533
Crystal size (mm)	0.20 × 0.15 × 0.15	0.35 × 0.30 × 0.20
Diffractometer	Siemens, Smart CCD	Siemens, Smart CCD
<i>T</i> (K)	293 (2)	293 (2)
X-radiation	MoK $\alpha$	MoK $\alpha$
$\theta$ range (°)	2–24	2–24
<i>h</i>	–16 to 20	–7 to 11
<i>k</i>	–8 to 8	–11 to 13
<i>l</i>	–21 to 16	–5 to 11
Total reflection	4696	3231
Non-zero reflection	1689	1141
$\sigma$ -level	3	3
<i>R</i>	0.0568	0.0214
<i>R</i> <sub>w</sub>	0.1056	0.0540
Max. e Å <sup>-3</sup>	0.218	0.235

synthesized recently by the hydrothermal method and the structure of the rosette as well as the three-dimensional channel structure derived from the stacking of the rosette have been described [13].

## 2. Experimental

Single crystals of the 1:2 complex of melamine with 4,4'-bipyridyl containing the water of crystallization, were obtained by slowly evaporating an

aqueous solution containing the two compounds. The composition of this complex, **1**, is C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>:0.5(C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>):H<sub>2</sub>O. Addition of a solution of melamine to a silver nitrate solution gave a white precipitate. The precipitate was kept at 60°C in water for 2 h and cooled down to room temperature (30°C) to obtain single crystals of the melamine·AgNO<sub>3</sub> complex, **2**, of the composition, [Ag(C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>)]NO<sub>3</sub>.

The intensity data of **1** and **2** were collected on the single crystals of both the complexes on a Siemens diffractometer equipped with CCD area detector [14] using MoK $\alpha$  radiation. Important parameters related to data collection and the structures are given in Table 1. The structures were determined and refined using the SHELXTL package [15]. The refinements were uncomplicated and all the non-hydrogen atoms were refined anisotropically. Hydrogen atoms obtained from Fourier maps were refined isotropically. The atomic coordinates of **1** and **2** are listed in Tables 2 and 3, respectively. Selected bond lengths and angles for both the complexes are given in Table 4. The important hydrogen-bond lengths and angles presented in Table 5 were computed using PLATON [16] and the plots of arrangement of molecules are generated using XP package [15].

## 3. Results and discussion

### 3.1. Melamine–4,4'-bipyridyl, **1**

The 1:2 complex of **M** with 4,4'-bipyridyl (**BP**), (C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>:0.5(C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>):H<sub>2</sub>O), **1**, crystallizes in a monoclinic (C2/c) space group (Table 1). The asymmetric unit of **1** is shown in Fig. 1. The structure of **1** shown in Fig. 2 reveals that the melamine molecules are connected to one another through water molecules by forming N–H···O (H···O, 2.16 Å, Table 5) and O–H···N (H···N, 2.08 Å, Table 5) hydrogen bonds giving rise to a molecular tape. The tapes are connected by the **BP** molecules. The **BP** molecules interact with the tapes by forming N–H···N (H···N, 2.13 Å, Table 5) bonds with **M** and O–H···N (H···N, 2.06 Å, Table 5) bonds with the water molecules as can be seen from Fig. 2. Such a hydrogen bonding network results in a rectangular box type structure comprising two molecules each of **M**, **BP** and

Table 2

Atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) of **1**.  $U(\text{eq})$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor

	x	y	z	U(eq)
N(13)	0.0337(2)	0.2034(4)	0.3171(1)	0.039(1)
N(14)	0	0.4899(5)	0.2500	0.041(1)
N(11)	0	-0.0635(6)	0.2500	0.059(1)
C(12)	0.0302(2)	0.3885(5)	0.3132(2)	0.037(1)
C(11)	0	0.1220(6)	0.2500	0.038(1)
N(12)	0.0613(2)	0.4788(5)	0.3784(2)	0.052(1)
C(3)	0.2151(2)	0.3058(4)	0.6885(2)	0.041(1)
N(2)	0.3320(2)	0.3171(4)	0.9287(2)	0.059(1)
C(6)	0.2548(2)	0.3050(4)	0.7715(2)	0.041(1)
C(2)	0.1352(2)	0.2580(5)	0.6507(2)	0.051(1)
N(1)	0.1399(2)	0.3142(4)	0.5311(2)	0.065(1)
C(4)	0.2564(2)	0.3587(5)	0.6443(2)	0.050(1)
C(10)	0.3357(2)	0.2670(5)	0.8079(2)	0.052(1)
C(7)	0.2134(2)	0.3470(5)	0.8162(2)	0.050(1)
C(9)	0.3711(3)	0.2755(5)	0.8850(2)	0.061(1)
C(5)	0.2163(3)	0.3609(5)	0.5675(2)	0.062(1)
C(1)	0.1011(3)	0.2627(5)	0.5740(2)	0.062(1)
C(8)	0.2534(3)	0.3501(5)	0.8931(2)	0.058(1)
O(1)	0.4186(2)	0.3846(4)	1.0843(2)	0.079(1)
H(1)	0.044(3)	0.225(4)	0.547(2)	0.08(1)
H(5)	0.247(2)	0.400(4)	0.539(2)	0.07(1)
H(8)	0.225(2)	0.386(5)	0.924(2)	0.07(1)
H(9)	0.429(3)	0.240(4)	0.910(2)	0.08(1)
H(12B)	0.059(2)	0.602(5)	0.380(2)	0.07(1)
H(2)	0.103(2)	0.221(4)	0.678(2)	0.05(1)
H(7)	0.157(2)	0.377(4)	0.796(2)	0.05(2)
H(12A)	0.080(2)	0.414(5)	0.420(2)	0.06(1)
H(10)	0.369(2)	0.238(4)	0.779(2)	0.06(1)
H(101)	0.396(3)	0.375(6)	1.040(2)	0.09(2)
H(4)	0.314(2)	0.398(5)	0.669(2)	0.07(2)
H(100)	0.427(3)	0.498(7)	1.101(2)	0.12(2)
H(11B)	0.020(2)	-0.116(5)	0.294(2)	0.08(1)

water. In this structure, the two rings of the bipyridyl molecule are not coplanar and form an angle of  $32^\circ$ . The structure of **1** bears close similarity to that of the **BP**-water adduct [17]. Unlike melamine which has hydrogen-bonded tapes of the molecule (Fig. 3a), the crystal structure of the **BP**-water adduct possesses a rectangular box comprising two molecules of **BP** and water (Fig. 3b).

### 3.2. Melamine-AgNO<sub>3</sub>, **2**

The 1:1 complex of **M** with AgNO<sub>3</sub>, [Ag(C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>)]NO<sub>3</sub>, **2**, crystallizes in a monoclinic

Table 3

Atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) of **2**.  $U(\text{eq})$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor

	x	y	z	U(eq)
Ag(1)	0.2058(1)	0.1191(1)	0.8991(1)	0.043(1)
N(1)	0.4020(3)	0.1244(2)	1.1077(2)	0.022(1)
N(7)	0.0699(4)	-0.1094(2)	0.7648(3)	0.027(1)
C(3)	0.4607(4)	0.2249(2)	1.1660(3)	0.023(1)
C(1)	0.3973(4)	0.0374(2)	1.1928(3)	0.022(1)
N(5)	0.4754(4)	0.1660(3)	1.5009(3)	0.036(1)
N(4)	0.3694(5)	-0.0677(2)	1.1407(3)	0.035(1)
O(3)	0.0085(3)	-0.2037(2)	0.7205(2)	0.045(1)
O(2)	0.1267(4)	-0.0378(2)	0.6933(3)	0.051(1)
O(1)	0.0772(3)	-0.0871(2)	0.8851(2)	0.044(1)
N(6)	0.4860(5)	0.3121(3)	1.0886(3)	0.036(1)
C(2)	0.4627(4)	0.1514(2)	1.3720(3)	0.024(1)
N(2)	0.4219(4)	0.0463(2)	1.3239(2)	0.026(1)
N(3)	0.4961(3)	0.2432(2)	1.2978(2)	0.024(1)
H(5B)	0.482(5)	0.232(3)	1.529(4)	0.03(1)
H(6B)	0.484(5)	0.306(3)	1.017(4)	0.04(1)
H(6A)	0.506(6)	0.375(3)	1.118(5)	0.05(1)
H(5A)	0.468(7)	0.104(4)	1.549(5)	0.07(1)
H(4A)	0.346(5)	-0.117(3)	1.192(4)	0.03(1)
H(4B)	0.336(6)	-0.072(4)	1.059(5)	0.05(1)

( $P2_1/n$ ) space group (Table 1). The asymmetric unit of **2** is shown in Fig. 4. In this complex, the melamine molecule gets bonded to the Ag atom through the ring nitrogen, by forming an Ag-N bond (2.29 Å). The coordination number of the Ag atom is two. The structure of **2** is shown in two-dimensions in Fig. 5. The adjacent melamine molecules are connected through Ag-N bonds forming **M**-Ag-**M**-Ag chains. The N-Ag-N bonds in such complexes are generally linear, but this is not the case here. The N-Ag-N bond in **2** is bent, the angle being  $127^\circ$  leading to the formation of a helical conformation rather than a linear chain. We show the helical nature in Fig. 6 by means of the space-filling structure, the twist resulting from hydrogen bonding between the adjacent chains. As we see from Fig. 5, the helices are held together in a two-dimensional arrangement by N-H...N hydrogen bond couplings between the melamine molecules. The H...N distance in these hydrogen bonds is 2.16 Å (Fig. 5). In each melamine molecule of **2**, two of the ring nitrogens are coordinated to Ag atoms, the third ring nitrogen being involved in N-H...N hydrogen bonding with another melamine molecule. Of the

Table 4  
Bond lengths (Å) and angles (°) for complexes **1** and **2**

<b>1</b>			
N(13)–C(11)	1.338(3)	N(13)–C(12)	1.351(4)
N(11)–C(11)	1.352(6)	N(14)–C(12)	1.348(3)
C(3)–C(4)	1.394(4)	C(12)–N(12)	1.336(4)
N(2)–C(9)	1.331(5)	C(3)–C(2)	1.387(5)
C(6)–C(10)	1.383(4)	C(3)–C(6)	1.478(4)
C(2)–C(1)	1.366(5)	N(2)–C(8)	1.338(5)
N(1)–C(1)	1.334(5)	C(6)–C(7)	1.383(4)
C(10)–C(9)	1.375(5)	N(1)–C(5)	1.328(5)
C(7)–C(8)	1.376(5)	C(4)–C(5)	1.374(5)
C(11)–N(13)–C(12)	113.3(3)	N(12)–C(12)–N(13)	116.5(3)
N(12)–C(12)–N(14)	117.2(3)	N(13)–C(11)–N(11)	116.3(2)
N(14)–C(12)–N(13)	126.3(3)	C(2)–C(3)–C(6)	122.4(3)
C(2)–C(3)–C(4)	116.5(3)	C(9)–N(2)–C(8)	115.8(3)
C(4)–C(3)–C(6)	121.1(3)	C(10)–C(6)–C(3)	121.5(3)
C(10)–C(6)–C(7)	116.8(3)	C(1)–C(2)–C(3)	120.0(4)
C(7)–C(6)–C(3)	121.7(3)	C(5)–C(4)–C(3)	118.9(4)
C(5)–N(1)–C(1)	115.8(3)	C(8)–C(7)–C(6)	119.6(4)
C(9)–C(10)–C(6)	119.7(4)	N(1)–C(5)–C(4)	124.8(4)
N(2)–C(9)–C(10)	124.1(4)	N(2)–C(8)–C(7)	123.8(4)
N(1)–C(1)–C(2)	124.0(4)		
<b>2</b>			
Ag(1)–O(1)	2.569(2)	Ag(1)–N(1)	2.289(2)
N(1)–C(1)	1.351(3)	N(1)–C(3)	1.350(3)
N(7)–O(3)	1.238(3)	N(7)–O(2)	1.226(3)
C(3)–N(6)	1.330(4)	N(7)–O(1)	1.258(4)
C(1)–N(2)	1.331(4)	C(3)–N(3)	1.347(4)
N(5)–C(2)	1.325(4)	C(1)–N(4)	1.346(4)
C(2)–N(3)	1.366(4)	C(2)–N(2)	1.340(4)
N(1)–Ag(1)–O(1)	101.69(7)	C(3)–N(1)–C(1)	114.6(2)
C(3)–N(1)–Ag(1)	120.3(2)	C(1)–N(1)–Ag(1)	120.4(2)
O(2)–N(7)–O(3)	120.9(3)	O(2)–N(7)–O(1)	119.4(2)
O(3)–N(7)–O(1)	119.7(3)	N(6)–C(3)–N(1)	118.0(3)
N(6)–C(3)–N(3)	117.5(3)	N(1)–C(3)–N(3)	124.5(2)
N(2)–C(1)–N(4)	117.1(3)	N(2)–C(1)–N(1)	125.7(2)
N(2)–C(1)–N(1)	117.2(3)	N(7)–O(1)–Ag(1)	101.6(2)
N(5)–C(2)–N(3)	118.2(3)	N(5)–C(2)–N(2)	117.3(3)
C(1)–N(2)–C(2)	115.0(2)	C(3)–N(3)–C(2)	114.9(2)
N(2)–C(2)–N(3)	124.5(2)	N(5)–Ag(1)–N(6)	127.2(2)

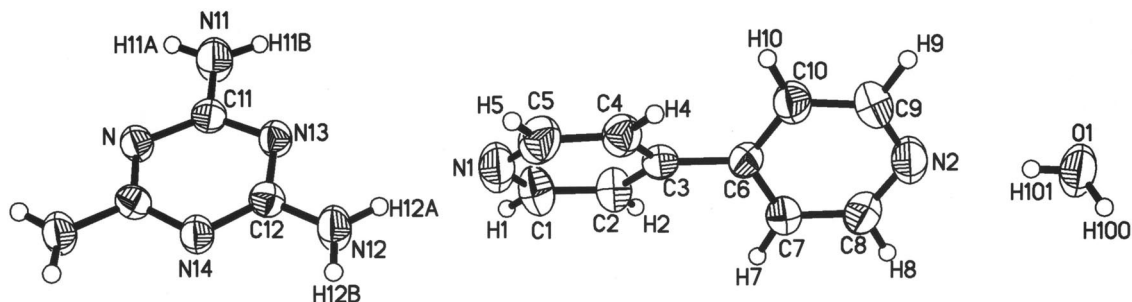


Fig. 1. The asymmetric unit of  $C_{10}H_8N_2:0.5(C_3H_6N_6):H_2O$ , **1** showing melamine, **M** and 4,4'-bipyridyl (**BP**) containing water of crystallization.

Table 5  
Hydrogen bond distances (Å) and angles (°) in complexes **1** and **2**

	D–H	H···A	D···A	D–H···A
<b>1</b>				
N(11)–H(11B)···O(1)	0.871	2.175	2.982	154.0
N(12)–H(12A)···N(1)	0.873	2.126	2.982	166.4
N(12)–H(12B)···O(1)	0.900	2.162	3.033	163.0
O(1)–H(100)···N(13)	0.880	2.088	2.915	156.1
O(1)–H(101)···N(2)	0.790	2.056	2.840	172.0
<b>2</b>				
N(4)–H(4B)···N(1)	0.962	2.159	3.077	159.0
N(4)–H(4B)···O(1)	0.785	2.404	3.177	168.6
N(5)–H(5B)···O(3)	0.780	2.381	2.912	126.4
N(6)–H(6B)···O(3)	0.642	2.556	3.198	177.5

three amino groups of melamine, two groups interact with two  $\text{NO}_3^-$  ions each, forming N–H···O hydrogen bonds. The third amino group is involved in intermolecular N–H···O (by interaction with one  $\text{NO}_3^-$  ion) and N–H···N hydrogen bonding with a neighboring melamine molecule. A similar helical structure has been found in a polymeric Ag(I) complex,  $[\text{Ag}_4(\text{bpsb})_2(\text{NO}_3)_4]_n$  where bpsb stands for 1,2-bis[(2-pyrimidinyl)-sulfanylmethyl]benzene. In this complex, the array of ligands linked by Ag atoms forms a single stranded helix. And each silver atom is tetracoordinated [18].

The structure of  $\text{M}\cdot\text{AgNO}_3$  is somewhat comparable to the parent structure of melamine [1,2]. In the structure of melamine (Fig. 3a), adjacent molecules are held together by N–H···N hydrogen bonds to yield molecular tapes, producing a hexagonal network. In **2**, the hydrogen bonds are replaced by N–Ag–N bonds. There is one N–Ag–N bond, instead of two hydrogen bonds, because of the helical nature of **2**. However, the interaction between the adjacent tapes in melamine or the chains in **2** is similar, being governed by N–H···N hydrogen bonds.

#### 4. Conclusions

In the present study, it has been possible to prepare a complex of melamine with 4,4'-bipyridyl which forms rectangular hydrogen-bonded structures, involving hydrogen-bonded molecular tapes formed by **M** and water molecules. The tapes themselves are connected by hydrogen bonds with the bipyridyl molecule. This rectangular structure is quite distinct from the other tape structures commonly found in the complexes of melamine with other heterocyclic compounds. The complex of **M** with  $\text{AgNO}_3$  is unique in the sense **M** forms chains involving

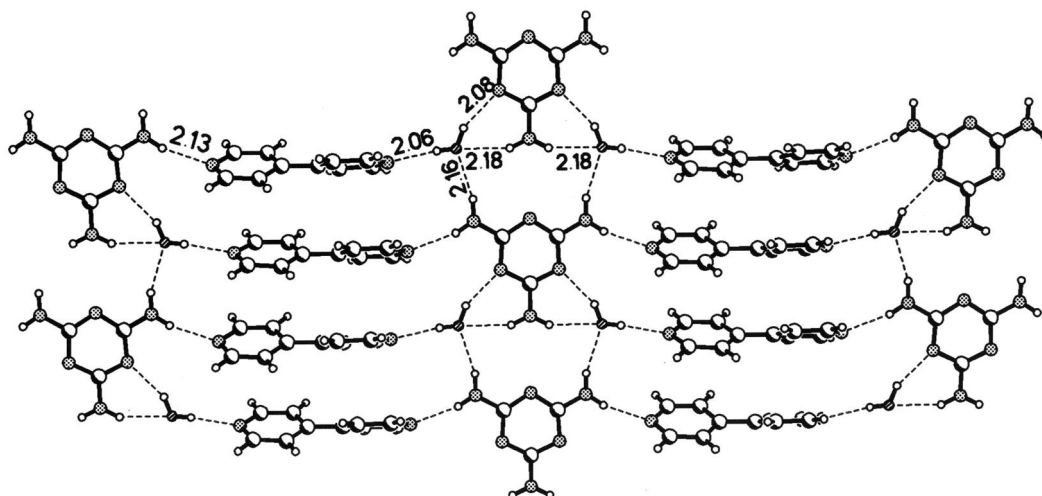


Fig. 2. Two-dimensional packing arrangement of **M**, **BP** and water molecules in **1**.

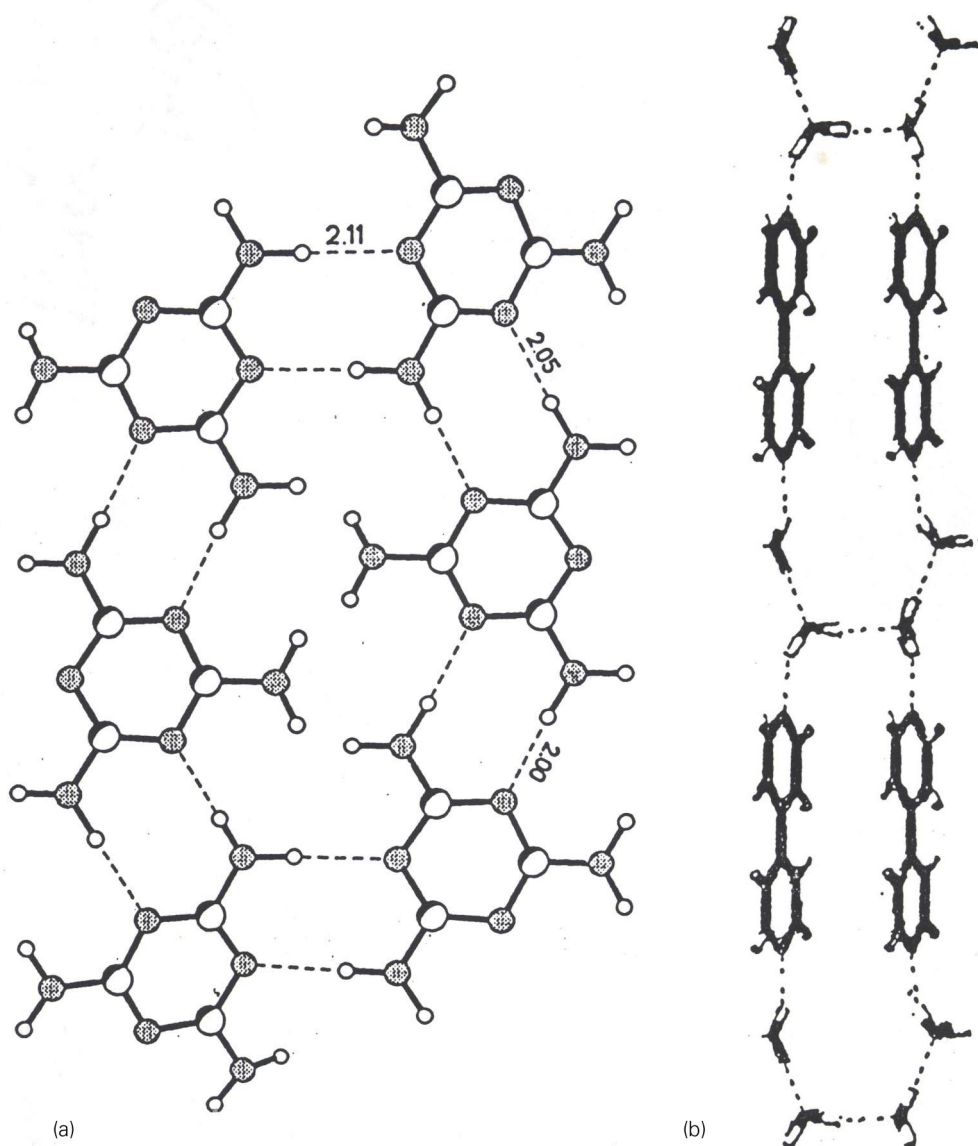
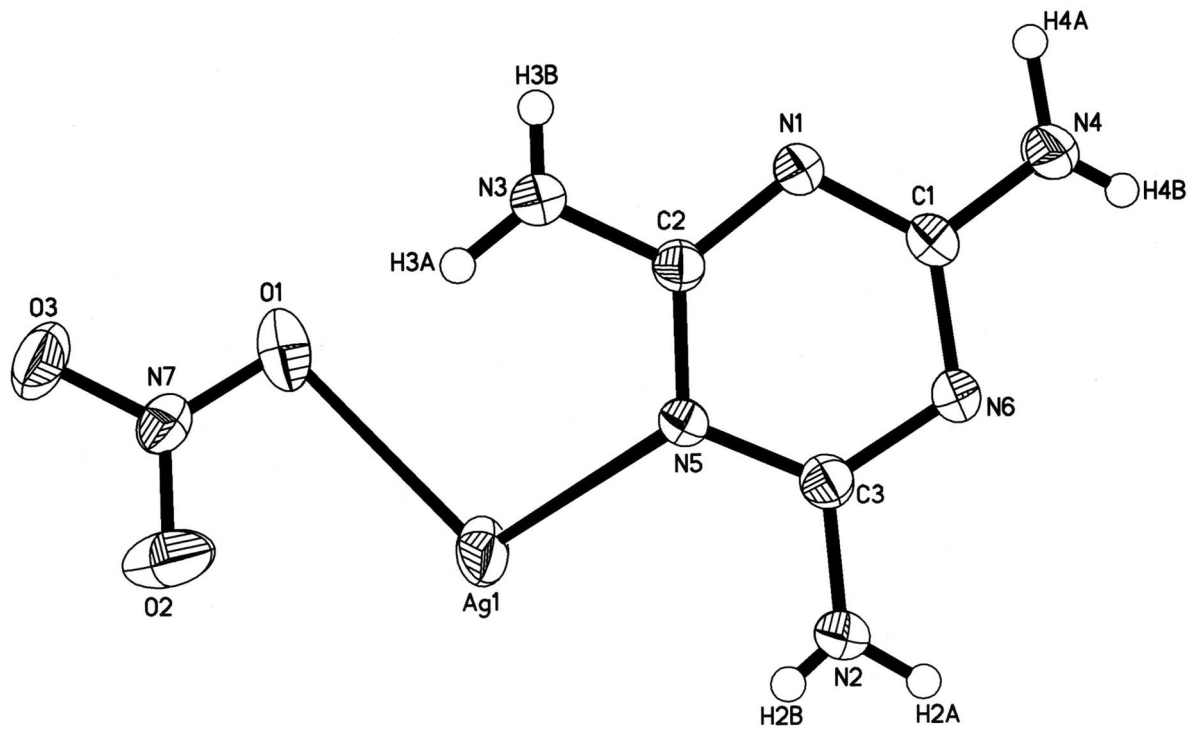
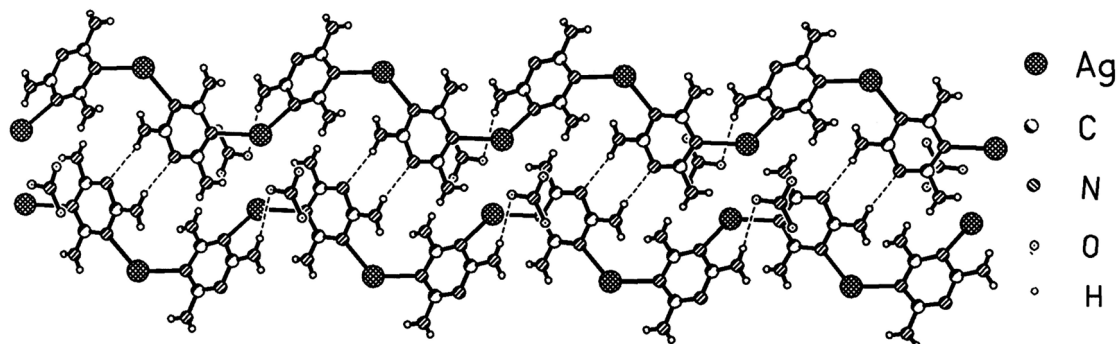


Fig. 3. (a) Hydrogen-bonded tapes of **M** molecules in **1**. (b) A two-dimensional packing diagram showing **BP** molecules connected through water molecules by hydrogen bonds.

N–Ag–N bonds. The chains are held together by intermolecular hydrogen bonds between the melamine molecules. The N–Ag–N bond in this complex is somewhat different from that present in other silver complexes where Ag actu-

ally replaces the hydrogen atom involved in hydrogen bonding. The hydrogen bonds in both **1** and **2** are of moderate strength as can be summarized from the bond lengths given in Table 5.

Fig. 4. The asymmetric unit of  $M-AgNO_3 \cdot 2$ .Fig. 5. A two-dimensional packing arrangement depicting the chains of  $M-AgNO_3$ . The chains are hydrogen bonded to each other.

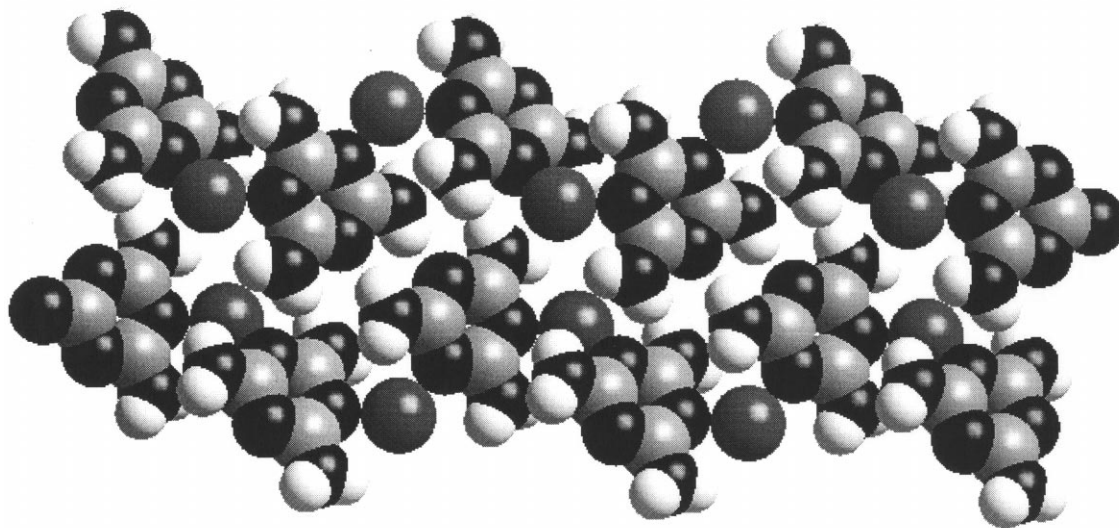


Fig. 6. The helical nature of the  $M-AgNO_3$  chains.

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