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Replacing the hydrogen in the intermolecular hydrogen bond of the cyanuric acid–bipyridyl adduct by Ag(I)

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Abstract. A complex between cyanuric acid (CA), 4,4′-bipyridyl (BP) and Ag(I), with the composition, $[Ag_2(C_3H_2N_3O_3\text{-}\kappa N)_2\ (C_{10}H_8N_2\text{-}\kappa N)]$ has been prepared. Crystal structure analysis shows that it has a chain structure in which the CA molecules are linked to the BP units through silver atoms by the formation of N–Ag–N bonds, wherein one of the hydrogens of CA is replaced by Ag(I), showing thereby the chains connected to one another by N–H...O hydrogen bonds formed between the CA molecules. This intermolecular chain structure resembles the chain structure of the CA.BP adduct where CA-BP-CA chains formed by N–H...N hydrogen bonds are linked to one another by N–H...O hydrogen bonds between the CA molecules.

Keywords. Cyanuric acid–Ag–4,4′-bipyridyl adduct; N–Ag–N chains; crystal structure analysis.

1. Introduction

Cyanuric acid (CA) forms interesting hydrogen-bonded structures with the aid of the three secondary *cis*-amide bonds [1]. It is known to form a variety of adducts when co-crystallized with heterocyclics and also with metal ions [2]. When co-crystallized with 4,4′-bipyridyl (BP), it forms different hydrogen-bonded assemblies depending on the solvent of crystallization, the structures bearing some resemblance to the hydrogen-bonded supramolecular assemblies of CA crystallized from the respective solvents [3]. CA also forms an adduct of the composition, Ag.CA with Ag(I) which has a layer structure comprising two-dimensional sheets of silver atoms which are pillared by chains of CA molecules [4]. In this complex, two of the hydrogens of CA are replaced by Ag. Recently, a mercury complex of CA of the composition, $Hg_3[CA\text{-}\kappa N]_2 3{\cdot}5H_2O$ wherein Hg replaces all the hydrogens of CA has been prepared.

Co-crystallization of CA and BP from water gives a 1:1 adduct. This adduct has a chain structure which is comparable to that of the $CA.H_2O$ complex, wherein water is replaced by BP molecules to form N–H...N hydrogen bonds. The hydrogen-bonded chains of CA and BP are held together by N–H...O hydrogen bonds between the CA

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Table 1. Crystallographic data of the complex, $[Ag_2(C_3H_2N_3O_3\text{-}\kappa N)_2(C_{10}H_8N_2\text{-}\kappa N)]$.

Formula	$[Ag_2(C_3H_2N_3O_3\text{-}\kappa N)_2(C_{10}H_8N_2\text{-}\kappa N)]$	μ (mm^{-1})	2·168
Mol. wt.	314·04	Crystal size (mm)	0·40 × 0·30 × 0·20
Crystal system	monoclinic	Diffractometer	Siemens, Smart CCD
Space group	$P2_1/n$	T (K)	293 (2)
a (Å)	13·089 (2)	X-radiation	Mo–K_α
b (Å)	4·586 (1)	θ range (deg)	1–24
c (Å)	15·996 (2)	h	–10 to 14
$\alpha°$	90	k	–5 to 5
$\beta°$	104·75 (1)	l	–17 to 17
$\gamma°$	90	Total reflections	3640
Cell volume ($Å^3$)	928·5 (3)	Non-zero reflections	1335
Z	4	σ-level	3
F(000)	612	R	0·0506
d_{calcd} ($g.cm^{-3}$)	2·246	R_w	0·1105
λ(Å)	0·71073	max. e ($Å^{-3}$)	1·162

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) of the complex, $[Ag_2(C_3H_2N_3O_3\text{-}\kappa N)_2(C_{10}H_8N_2\text{-}\kappa N)]$. $U_{(eq)}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	$U_{(eq)}$
Ag (I)	0·6404 (1)	0·2286 (2)	0·8551 (1)	0·036 (1)
N (3)	0·6671 (6)	0·0460 (2)	0·9803 (4)	0·025 (2)
O (3)	0·5473 (5)	–0·3005 (1)	0·9221 (4)	0·032 (2)
O (1)	0·7895 (5)	0·3815 (1)	1·0463 (4)	0·036 (2)
N (4)	0·6019 (6)	0·3713 (2)	0·7248 (4)	0·032 (2)
O (2)	0·6431 (5)	–0·2005 (1)	1·2135 (4)	0·044 (2)
C (1)	0·7300 (7)	0·1831 (2)	1·0505 (5)	0·026 (2)
C (3)	0·6019 (6)	–0·1732 (2)	0·9863 (5)	0·021 (2)
C (2)	0·6527 (7)	–0·1278 (2)	1·1428 (5)	0·026 (2)
N (2)	0·5967 (7)	–0·2577 (2)	1·0682 (4)	0·025 (2)
N (1)	0·7217 (6)	0·0825 (2)	1·1308 (4)	0·026 (2)
C (6)	0·5229 (7)	0·4745 (2)	0·5470 (5)	0·026 (2)
C (7)	0·4803 (8)	0·6161 (2)	0·6082 (5)	0·031 (2)
C (5)	0·6061 (8)	0·2888 (2)	0·5777 (5)	0·034 (2)
C (4)	0·5228 (9)	0·5521 (3)	0·6956 (6)	0·037 (3)
H (7)	0·430 (8)	0·768 (2)	0·588 (6)	0·030 (3)
H (8)	0·497 (6)	0·654 (2)	0·727 (5)	0·020 (2)
H (1)	0·757 (7)	0·184 (2)	1·180 (6)	0·040 (3)
H (5)	0·630 (7)	0·175 (2)	0·533 (6)	0·050 (3)
H (4)	0·693 (6)	0·107 (2)	0·676 (5)	0·023 (3)
H (2)	0·569 (7)	–0·380 (2)	1·073 (6)	0·030 (3)

molecules[3]. We wanted to investigate whether the hydrogen in the intermolecular N–H...N bonds in CA.BP can be replaced by Ag(I) and hence this structure. For this purpose, we have synthesized a Ag(I) complex containing CA and BP by the hydrothermal method and studied its structure by crystallography.

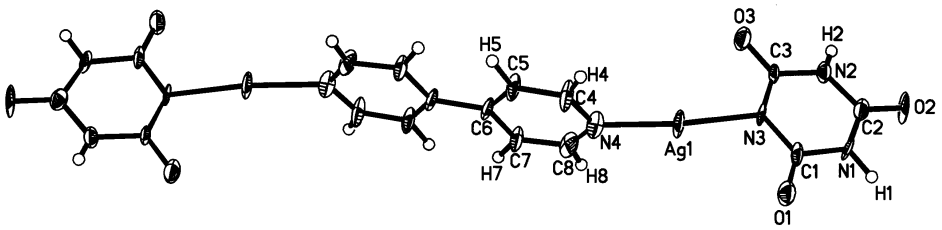

Figure 1. The asymmetric unit of **1**.

Table 3. Bond lengths [Å] and angles [°] in $[Ag_2(C_3H_2N_3O_3\text{-}\kappa N)_2(C_{10}H_8N_2\text{-}\kappa N)]$.

Ag (1)–N (3)	2·116 (6)	Ag (1)–N (4)	2·120 (7)
N (3)–C (3)	1·338 (10)	N (3)–C (1)	1·365 (11)
O (3)–C (3)	1·238 (10)	O (1)–C (1)	1·210 (10)
N (4)–C (8)	1·316 (12)	N (4)–C (4)	1·349 (12)
O (2)–C (2)	1·215 (10)	C (1)–N (1)	1·395 (10)
C (3)–N (2)	1·384 (11)	C (2)–N (2)	1·368 (11)
C (2)–N (1)	1·368 (11)	C (6)–C (5)	1·372 (12)
C (6)–C (7)	1·404 (12)	C (5)–C (4)	1·370 (12)
C (7)–C (8)	1·398 (13)		
N (3)–Ag (1)–N (4)	173·5 (3)	C (3)–N (3)–C (1)	123·3 (7)
C (3)–N (3)–Ag (1)	114·3 (5)	C (1)–N (3)–Ag (1)	121·0 (5)
C (8)–N (4)–C (4)	116·3 (8)	C (8)–N (4)–Ag (1)	120·8 (6)
C (4)–N (4)–Ag (1)	121·8 (7)	O (1)–C (1)–N (3)	124·3 (7)
O (1)–C (1)–N (1)	120·1 (8)	N (3)–C (2)–N (1)	115·6 (8)
O (3)–C (3)–N (3)	122·6 (7)	O (3)–C (3)–N (2)	119·7 (8)
N (3)–C (3)–N (2)	117·7 (8)	O (2)–C (3)–N (2)	122·2 (9)
O (2)–C (2)–N (1)	123·5 (8)	N (2)–C (2)–N (1)	114·2 (8)
C (2)–N (2)–C (3)	124·0 (9)	C (2)–N (1)–C (1)	124·9 (8)
C (5)–C (6)–C (7)	117·2 (8)	C (8)–C (7)–C (6)	118·3 (9)
C (4)–C (5)–C (6)	120·1 (8)	N (4)–C (4)–C (5)	123·7 (10)
N (4)–C (8)–C (7)	124.3 (9)		

The complex containing CA, BP and Ag(I), **1**, with the composition, $[Ag_2(C_3H_2N_3O_3\text{-}\kappa N)_2(C_{10}H_8N_2\text{-}\kappa N)]$ was prepared by the hydrothermal method as follows. In a typical preparation, 10 ml of a solution of CA, BP and $AgNO_3$ (1:1:1 molar ratio) taken in a teflon flask was placed in a steel bomb and kept in an oven maintained at 160°C for 36 h and then cooled to room temperature over a period of 6 h to obtain good quality single crystals of the complex. The crystals were colourless and had a needle-shaped geometry. This complex crystallizes in a $P2_1/n$ space group. The intensity data of the single crystals of the complex, $[Ag_2(C_3H_2N_3O_3\text{-}\kappa N)_2(C_{10}H_8N_2\text{-}\kappa N)]$ were collected on a Siemens diffractometer equipped with a CCD area detector [5] using Mo-K_α radiation in ω–2θ mode. Important crystal parameters related to data collection and the structures are given in table 1. The structure was determined and refined using the SHELXTL package [6]. 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 are listed in table 2. Selected bond lengths and angles are given in table 3. The hydrogen-bond lengths and angles were computed using PLATON [7] and the plots of arrangement of molecules were generated using XP package [6].

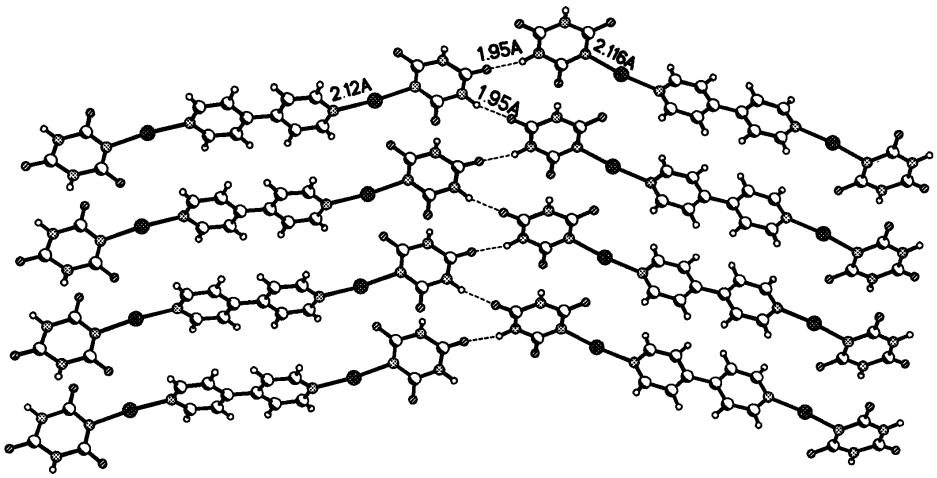

Figure 2. Two-dimensional structure of **1** showing the intermolecular CA-Ag-BP chains hydrogen-bonded to one another through CA molecules.

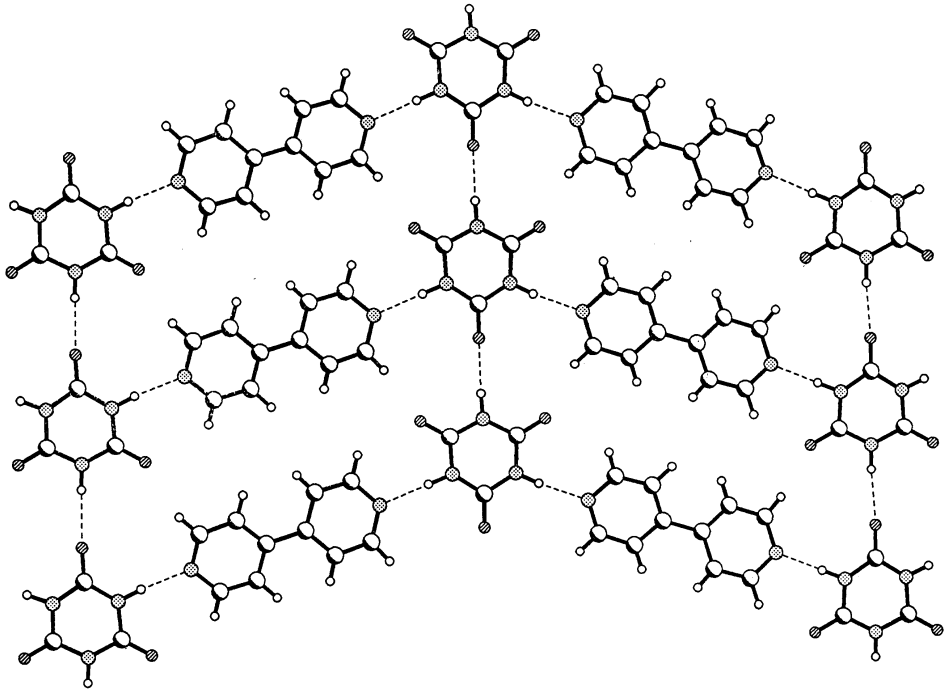

Figure 3. Structure of the CA.BP adduct showing hydrogen-bonded CA.BP chains, in turn hydrogen-bonded to one another through CA molecules.

We show the asymmetric unit of the complex **1** in figure 1. The asymmetric unit contains two CA molecules, one BP molecule and two Ag atoms. We show the detailed

structure of the complex in figure 2. The complex has a chain structure resembling the structure of the CA.BP adduct (figure 3). What is interesting is that Ag(I) replaces one of the hydrogens of CA to bond to the ring nitrogen of BP forming N–Ag–N bonds (N–Ag, 2.12 Å). Thus, the Ag(I) ion acts like a proton in forming the intermolecular chain. The CA–Ag–BP–Ag–CA chains are connected to one another by intermolecular N–H...O bonds (H...O, 1.95 Å), between the CA molecules of adjacent chains.

The N–Ag–N angle in the complex is 173·5°, unlike in the melamine-$AgNO_3$ complex where it is 127°. The Ag–N distance is 2·12 Å. In comparison to the melamine-4,4′-bipyridyl complex where the two pyridine rings of BP are not coplanar, the two pyridine rings in this complex, $[Ag_2(C_3H_2N_3O_3\text{-}\kappa N)_2(C_{10}H_8N_2\text{-}\kappa N)]$ are coplanar, the torsion angle being only 0.7°.

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