Synthesis, crystal structure and Raman spectra of $AgBF_4 \cdot C_3O_3(NC_3H_5)_3 \cdot H_2O$, a silver(I) π-complex with 1,3,5-triallyl-1,3,5-triazine-2,4,6-trione

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ABSTRACT

$AgBF_4$, in aqueous solution, reacts with 1,3,5-triallyl-1,3,5-triazine-2,4,6 (1H,3H,5H)-trione (TTT) yielding $Ag[C_3O_3(NC_3H_5)_3]BF_4 \cdot H_2O$ (**I**). It crystallizes in the monoclinic space group $P2_1/n$, $a = 13.356(3)$ Å, $b = 9.4264(17)$ Å, $c = 13.360(3)$ Å, $\beta = 94.057(2)°$, $V = 1677.8(5)$ Å^3, and $Z = 4$. In the crystal structure **I**, Ag^+ is coordinated by two C=C groups from two TTT molecules, one O atom from a water molecule and one more distant O atom from the triazine ring, markedly shifted from the ideal apical position. The TTT molecule uses only two allyl groups for metal bonding. The bridging role of the Ag^+ cations and the TTT molecules results in the formation of infinite $\{Ag[C_3O_3(NC_3H_5)_3] \cdot H_2O\}_n$ chains. The Raman spectrum of **I** supports weak Ag–(C=C) bonding.

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1. Introduction

Ag^+ is a cation well known for its ability for η_2-coordination with a double carbon–carbon bond. Due its relatively large covalent radius it may bind to more than one C=C group, for example to two [1], three [2] or even four such [3]. The majority of known silver(I) compounds in which the metal atom is coordinated by two C=C bonds are Ag^+ adducts with aromatic rings. The various η_2-coordination abilities of triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TTT) are exemplified in $[Cu_4Br_4(TTT)_2]_n$ and $[Cu_6Br_6(TTT)_2]_n$ [4] in which this ligand is connected to two and three metal centers, respectively. The geometry of the TTT moiety promotes a bridging, but not a chelating, role in the metal complexes. In contrast to Cu^+ π-complexes with (poly)allyl derivatives, their analogues with larger Ag^+ have not been so widely studied. For that reason we decided to combine $AgBF_4$ (containing, easily accessible Ag^+ cation for the coordination due to the presence of weakly bonded BF_4^- anion) and potentially three-dentate TTT ligand in order to explore the peculiarities of the formation of 3D structure. The results are presented in this paper.

2. Materials and methods

2.1. Synthesis

$AgBF_4$ was prepared as described [5]. 1,3,5-Triallyl-1,3,5-triazine-2,4,6-trione was used as supplied. Its Raman spectrum was in agreement with that reported [6]. 100 mg of $AgBF_4$ was dissolved in water, and 250 mg of TTT (which is insoluble, or only slightly soluble, in water) was added. After 18 days of slow solvent evaporation, crystals of $Ag(TTT)BF_4 \cdot H_2O$ compound formed.

2.2. Crystallography

Single-crystal data were collected on a Rigaku AFC7 diffractometer equipped with a Mercury CCD area detector, using graphite monochromatized MoKα radiation. Data were treated using the Rigaku CrystalClear software suite package [7]. The structure was solved by direct methods using SIR-92 [8] program (teXan crystallographic software package of Molecular Structure Corporation [9]) and refined with SHELXL-97 [10] software implemented in program package WinGX [11]. The figure was prepared using DIAMOND 3.1 software [12].

2.3. Raman spectroscopy

Raman spectra were recorded on a Renishaw Raman Imaging Microscope System 1000, with the 632.8 nm exciting line of a He–Ne laser (50 mW) with a resolution of 2 cm^{-1}.

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Table 1
Details of experimental and crystallographic data for compound **I**.

Compound	**I**
Empirical formula	AgBF$_4$
	N$_3$O$_4$C$_{12}$H$_{17}$
Formula weight	461.97
Crystal size, mm	$0.1 \times 0.08 \times 0.07$
Temperature, K	150
Radiation	MoKα
Sp. gr.	$P2_1/n$
Unit cell dimensions	
a, Å	13.356(3)
b, Å	9.4264(17)
c, Å	13.360(3)
β, deg	94.057(2)
V, Å^3	1677.8(5)
Z	4
D_c g/cm^3	1.829
μ, mm^{-1}	1.266
$F(000)$	920
Scan range θ, °	4.48–58.1
Measured reflections	8352
Used ($I > 2\sigma(I)$)	3793
Parameters refined	226
$R(F)$	0.0571
$R(F)^2$	0.1503
Goodness-of-fit	1.122

CCDC 771650 (I) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail:deposit@ccdc.cam.ac.uk).

3. Results and discussion

3.1. Crystal structure

In the determined structure of **I** the ligand partially realizes its coordination abilities, being bound to two Ag atoms by two allyl groups (Table 1). The silver environment comprises two C=C groups, one from each of two ligand moieties, the oxygen atom from a water molecule and a more distant oxygen atom from the triazine ring (Fig. 1). Because of steric hindrances the O2 atom from the triazine core is markedly shifted from its ideal apical position

Table 2
Selected bond distances (Å) in the structure **I**.

Ag1−O4	2.266(4)	C11−C12	1.497(6)
Ag1−C13^i	2.331(5)	C12=C13	1.346(7)
Ag1−C12^i	2.382(4)	C21−C22	1.494(6)
Ag1−m1^i	2.259(5)	C22=C23	1.323(7)
Ag1−C23	2.394(5)	C31−C32	1.491(7)
Ag1−C22	2.417(4)	C32=C33	1.303(9)
Ag1−m2	2.308(5)	N1−C3	1.369(6)
Ag1−O2	2.659(3)	N1−C1	1.397(6)
F1−B1	1.367(9)	N1−C11	1.478(5)
F2−B1	1.351(8)	N2−C2	1.377(5)
F3−B1	1.348(8)	N2−C1	1.389(5)
F4−B1	1.425(9)	N2−C21	1.477(5)
O1=C1	1.208(5)	N3−C2	1.372(5)
O2=C2	1.228(5)	N3−C3	1.384(6)
O3=C3	1.219(6)	N3−C31	1.465(6)

Symmetry codes: (i) $x + 1/2$, $-y + 1/2$, $z − 1/2$.
m1 and m2 are the mid-points of C12=C13 and C22=C23 bonds respectively.

($\angle$ O2−Ag1−m2 80°, $\angle$ O2−Ag1−m1 102°, where m1 and m2 are the mid-points of the C12=C13 and C22=C23 bonds respectively). Despite the formal coordination number of 4, the Ag atom is located within the (m1, m2, O4) plane. Trigonal-pyramidal geometry, rather usual for Ag−(C=C) adducts, was observed, similar for example to that in a AgClO$_4$ complex with diallylamine (the silver environment consists of 2 C=C + N and O(ClO$_4^-$) at the apical position [13]). The Ag1−O2 bond, despite its weakness, exerts a marked influence on the Ag−(C=C) interaction. Because of mentioned steric obstructions, the C22=C23 group, which belongs to the same TTT moiety as coordinated to the Ag$^+$ cation O2 atom, is less elongated and slightly removed from the metal center than is the C12=C13 from another ligand moiety (Fig. 1, Table 2). The uncoordinated C32=C33 bond undergoes minor orientational disordering, which is seen in its apparent shortening and the slightly increased thermal parameters of both carbon atoms. A small elongation of the coordinated C=C bonds indicates the weakness of the Ag−(C=C) interaction.

Due to the bridging function of the Ag$^+$ cations and TTT molecules, infinite chains oriented along the 101 direction appear (Fig. 2). These chains, in turn, are associated into a three dimensional network by non-covalent interactions. BF$_4^-$ units
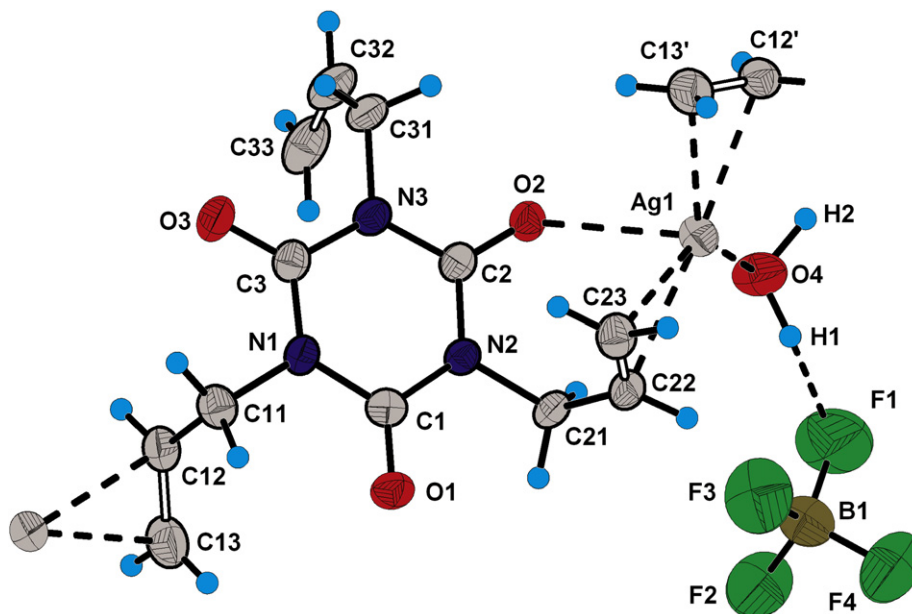
Fig. 1. Metal coordination and ligand surrounding in crystal structure of AgBF$_4$·C$_3$O$_3$(NC$_3$H$_5$)$_3$·H$_2$O.
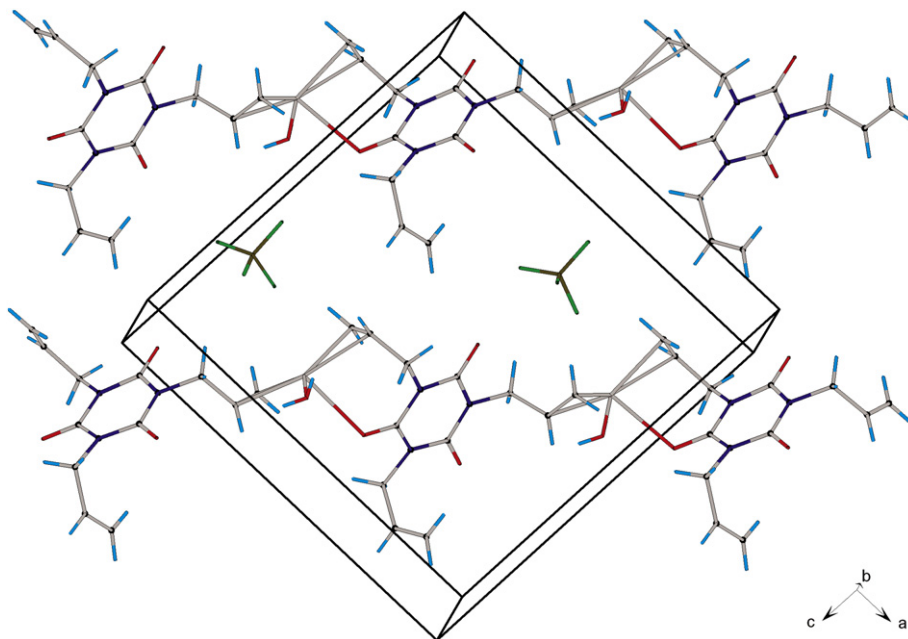
Fig. 2. Infinite {Ag[C$_3$O$_3$(NC$_3$H$_5$)$_3$]·H$_2$O}$_n$ chains in crystal structure **I**.

demonstrate the rather common tendency to be bonded with the 3d^{10} metal cations through water bridges. The O−H···F bonds around each anion are rather weak − the shortest F···H distance is 2.37(3) Å. The enlarged thermal parameters of all the F atoms indicate their libration.

Despite the dozens of silver compounds in which a metal is bound to two C=C groups, only one is known with a Ag$^+$ ion surrounded by C=C bonds from two different ligand moieties and an O (H$_2$O) [14]. Such a coordination is achieved as a result of the presence of weakly bonded BF$_4^-$ anions, the peculiarities of the TTT geometry and the absence of other active centers capable of coordinating with the metal centers.

3.2. Raman spectroscopy

Raman spectra of **I** and pure liquid 1,3,5-triallyl-1,3,5-triazone-2,4,6-trione (TTT) are shown in Fig. 3. Although the spectrum of **I** is quite complex, comparison with Raman spectrum of non-coordinated TTT leads to certain conclusions. The vibrational bands at 357, 765 and 1022 cm^{-1} are not present in the spectrum of pure TTT, and can therefore be assigned to the tetrahedral [BF$_4$]$^-$ anion. The vibrational band at 765 cm^{-1} results from symmetric stretching (v_1), and the lower wavelength band at 357 cm^{-1} to the bending mode (v_2) of the BF$_4$ group. In KBF$_4$, the corresponding bands are observed at 771 and 357 cm^{-1} [15].The vibrational band at 1022 cm^{-1} may be tentatively assigned to asymmetric stretching of the [BF$_4$]$^-$ anion (in KBF$_4$ at 1020 cm^{-1}) [15].

The vibrational band at 1594 cm^{-1} is attributed to the water bending motion (v_b(H$_2$O)). The wavelength of v_b(H$_2$O) is known to increase when water molecules are involved in hydrogen bonds. For example, in K$_2$AlF$_5$·H$_2$O, with O···F contacts (in O−H···F hydrogen bonds) of 2.73 Å, this value is shifted to 1680 cm^{-1} [16]. The much lower value observed in **I** is consistent with the long O···F contacts (Ag−OH$_2$···FBF$_3$, 2.961 Å) demonstrated in the crystal structure. The low value of v_b(H$_2$O) indicates very weak hydrogen bonding between the coordinated water on the silver atom and a fluorine atom belonging to the [BF$_4$]$^-$ anion. The vibrational bands

of O−H stretching modes (around 3000 cm^{-1}) in **I** overlap with those of the C−H vibrations of coordinated TTT ligands.

The rest of the vibrational bands can be assigned to TTT ligands, for which the most prominent vibrational bands were observed at 1759 and 1647 cm^{-1}. The former arises from the stretching mode of the C=O group of the triazine−trione ring and the latter from C=C vibrations on the allyl groups [17]. In pure TTT the C=C stretching mode is observed at 1645 cm^{-1} and, in the co-coordinated compound **I**, at 1647 cm^{-1}, the same within experimental error. Additional problem represents the possible coupling between the C=C double bonds interacting with Ag, and the C=C group not being coordinated. On the basis of the above results it can be concluded that the Ag−(C=C) interactions are rather weak.
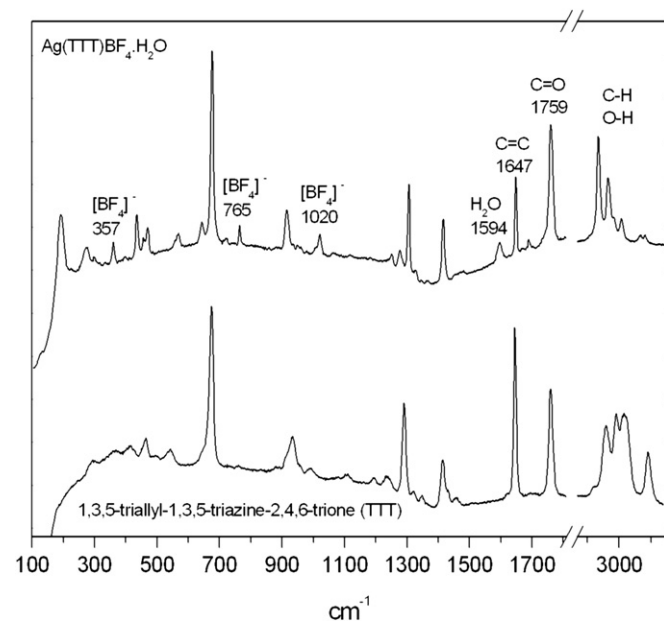

Fig. 3. Raman spectra of Ag[C$_3$O$_3$(NC$_3$H$_5$)$_3$]·H$_2$O (top) and 1,3,5-triallyl-1,3,5-triazine-2,4,6-trione ligand (bottom).

4. Conclusions

Combination of the rather large Ag^+ cation, capable of η_2-interaction with unsaturated carbon-carbon bonds, a weakly coordinated BF_4^- anion, and the potentially three-dentate TTT ligand has been shown to lead to the $Ag[C_3O_3(NC_3H_5)_3]BF_4 \cdot H_2O$ compound. The rare environment of the metal atom consists of the $C=C$ groups from two ligand molecules, the oxygen atom from a H_2O molecule and the weakly bonded O atom from a TTT moiety. The Raman spectrum of **I** supports the single-crystal data, where the weakness of the $Ag-(C=C)$ π-bonding and the $Ag-OH_2 \cdots FBF_3$ hydrogen bonding was observed.

Acknowledgements

Appendix A. Supplementary material

CCDC 771650 (**I**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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