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A Novel Infinite 1-D Chain of Silver(I) Bridged by *trans*-Azobenzene

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Summary. The self-assembly of $Ag[BF_4]$ with *trans*-azobenzene in dichloromethane yields a new coordination polymer $([Ag(\mu\text{-}trans\text{-azobenzene})H_2O][BF_4])_n$ which was characterized by X-ray single crystal diffraction. The crystal consists of 1-D zigzag cationic chains made up from $[Ag(H_2O)]^+$ units linked by *trans*-azobenzene bridges and BF_4^- anions. Hydrogen bonding interactions between the chains and BF_4^- anions occur *via* intermolecular C–H···F and O–H···F contacts, and the crystal displays a 2-D supramolecular structure.

Keywords. Silver(I); Coordination polymer; *trans*-Azobenzene; Crystal structure.

Introduction

Metal-directed supramolecular self-assembly [1] is a subject of great current interest in the development of new solid-state polymeric materials with specific architectural and functional features [2]. In this context, the silver(I) ion has been used extensively for the formation of coordination networks [3]. In this work we report on the synthesis and structural characterization of a novel 1-D coordination polymer of silver(I) in which the metal centers are linked by *trans*-azobenzene bridges.

A large number of dinuclear metal transition complexes containing azobenzene bridges have been reported. In most of them the azobenzene bridge displays a *cis* conformation [4]. When the *trans* conformation is adopted, orthometalation reactions can occur as has been reported for a manganese dinuclear complex [5]. Alternatively, the *trans* azobenzene can link the two metal centres in a way that each nitrogen atom is coordinated only to one metal centre. Only one example has been found exhibiting this type of bridge: $[Cp_2^*Sm]_2N_2Ph_2$ [6], where two Cp_2^*Sm units are bridged by *trans*-azobenzene. In this case the ligand is not orthometalated, but agostic interactions between the metal centres and the *ortho* hydrogen atoms of the phenyl rings were found. To the best of our knowledge the complex described here represents the first example of a polymeric chain containing silver(I) centres bridged

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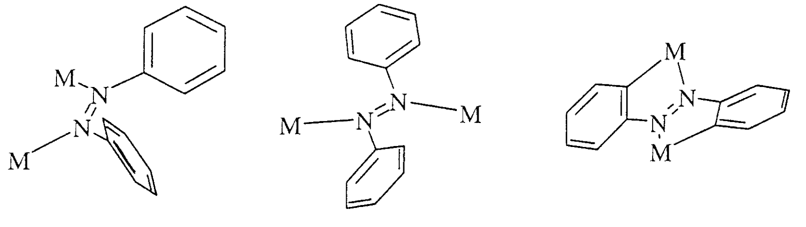


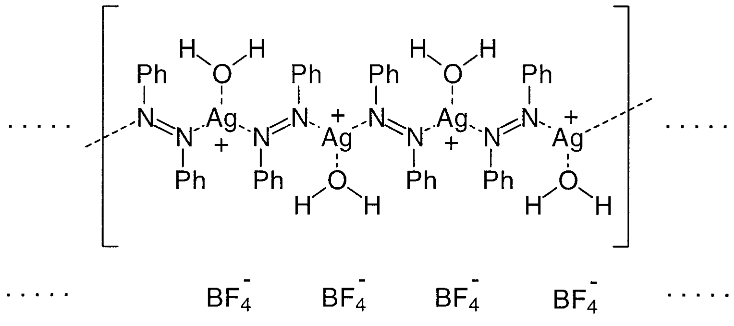
cis bridging *trans* bridging *trans-ortho*-metalated bridging

Scheme 1

by *trans*-azobenzene molecules. The coordination modes referred to above for azobenzene are illustrated in Scheme 1.

Results and Discussion

Addition of a dichloromethane solution of *trans*-azobenzene to a stoichiometric amount of $AgBF_4$ in dichloromethane resulted in an immediate colour change from the characteristic bright-orange of *trans*-azobenzene to pale yellow. A pale yellow precipitate of **1** was immediatly formed in essentially quantitative yield. The precipitate is slightly soluble in CH_2Cl_2 and can be recrystallized from hot CH_2Cl_2 to give pale-yellow needles suitable for single crystal X-ray analysis. The compound is fairly light-sensitive and should be stored in the dark. Solutions of the compound in solvents with coordinating ability such as *THF* or acetone give rise to orange solutions of free *trans*-azobenzene; for instance; the ^1H NMR spectrum of an acetone-d_6 solution of the compound is identical to that of *trans*-azobenzene. Solutions of compound **1** in CD_2Cl_2, do not show a colour change, and their ^1H and ^{13}C NMR spectra are very similar to those of free *trans*-azobenzene acquired under the same conditions.



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Crystal structure of ([Ag(μ-trans-azobenzene)H$_2$O][BF$_4$])$_n$

The polymeric nature of **1** was established by an X-ray single crystal diffraction study. The crystal structure is built up from an asymmetric unit composed from one

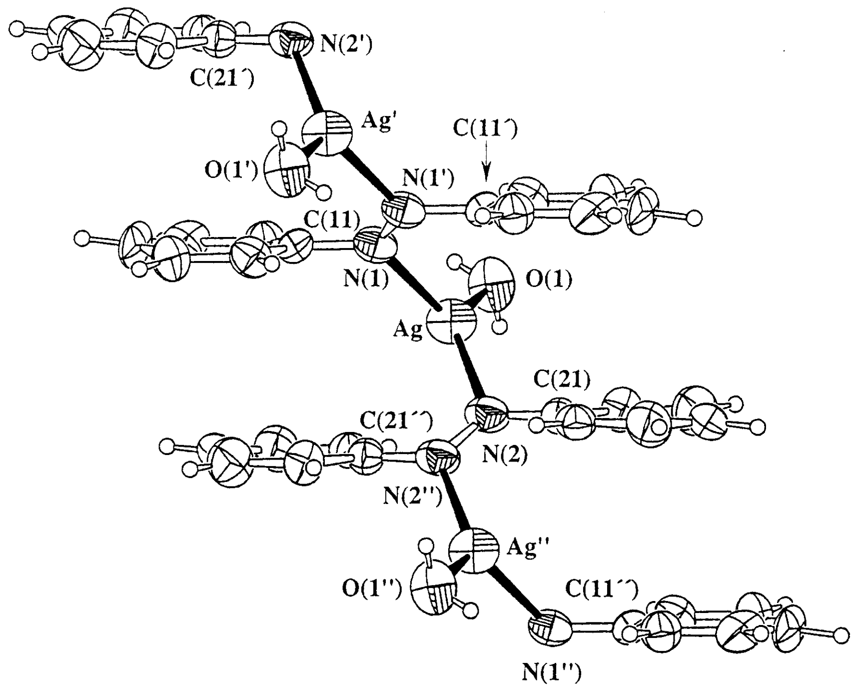

Fig. 1. An ORTEP diagram showing the structure of 1-D zigzag chain of the cationic entity (ellipsoids 40% of probability level); selected bond distances (Å) and angles (°): Ag-O(1), 2.25(1); Ag-N(1), 2.37(2); Ag-N(2) 2.36(2); O(1)-Ag-N(1), 123.7(6); O(1)-Ag-N(2), 135.8(6); N(2)-Ag-N(1), 98.7(8); $'$ and $''$ denote the symmetry operations $-x+2$, $-y+1$, $-z+1$ and $-x+1$, $-y+1$, $-z+1$ used to generate equivalent atoms

BF_4^- anion and one silver(I) cationic entity, containing additionally two half-molecules of *trans*-azobenzene and a water molecule. The centres of the N=N bonds of the *trans*-azobenzene molecules are localized at the crystallographic inversion centres, leading to 1-D infinite zigzag chains composed by units of [Ag(H_2O)]$^+$ linked by bridges of *trans*-azobenzene. Figure 1 shows an ORTEP view [7] of a zigzag cationic chain together with the labelling scheme. The silver is coordinated to one oxygen atom of a water molecule (Ag–O = 2.25(1) Å) and to two nitrogen atoms from two crystallographically independent molecules of *trans*-azobenzene (Ag–N = 2.36(2) and 2.37(2) Å). Selected distances and angles, listed also in Fig. 1, indicate that silver(I) displays a distorted trigonal coordination sphere. The two least-squares planes defined by the atoms Ag, Ag$'$, N(1), N(1$'$) and Ag, Ag$''$, N(2), N(2$''$) show maximum deviations of 0.044(17) and 0.062(9) Å, indicating that the Ag centres are almost coplanar with C–N=N–C moieties of two independent *trans*-azobenzene units. Phenyl rings of both units are tilted relative to these planes by 41.5(5) and 44.4(6)°, respectively. Furthermore, the two phenyl rings of each azobenzene molecule are parallel with distances of 0.83 and 0.77 Å. By contrast, the free *trans*-azobenzene is planar [8]. However, in the dinuclear samarium complex [6] one phenyl ring is almost coplanar with the plane defined by the metal centres and C–N=N–C moiety, and the other one is tilted relative to this plane by 34.1°. In the silver(I) complex the bridging *trans*-azobenzene units adopt a stacked arrangement with distances between the least squares planes defined by phenyl

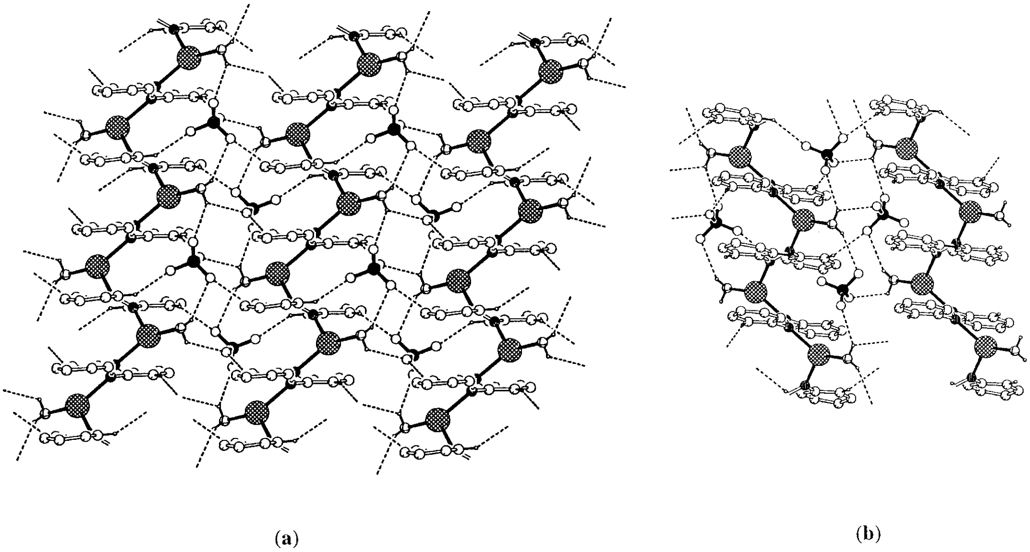

Fig. 2. Crystal packing diagram of the silver complex showing its solid state structure; a) view showing the hydrogen bonding interactions between 1-D∼*trans*-azobenzene-[Ag(H_2O)]-*trans*-azobenzene∼cationic chains and the BF_4^- anions; b) detailed view of the hydrogen bonds showing the formation of twelve- and eight-membered ring systems

rings of two adjacent units of 3.60 Å, which exceeds the sum of the *van der Waals* radii of two carbon atoms. The distances Ag–N and Ag–O fall in the ranges of 2.234–2.708 and 2.242–2.365 Å as also found for related three-coordinated complexes with an $AgON_2$ coordination sphere [9].

Figure 2 presents the crystal packing diagram and provides a complete picture of the solid state structure of **1**. The ∼*trans*-azobenzene-[Ag(H_2O)]-*trans*-azobenzene∼chains are intercalated by BF_4^- anions in the solid state. A detailed analysis of the intermolecular contacts reveals that in the crystal the chains are connected *via* OH···F and $C\text{–}H^{\delta+}\cdots F^{\delta-}$ hydrogen bonds. Two water molecules of two infinite chains are bridged by two fluorine atoms of two BF_4^- anions, thus leading to the formation of a twelve-membered centrosymmetric ring (four OH···F distances, twice 2.49 Å/139° and twice 2.50 Å/140°). Another centrosymmetric ring system (eight-membered) arises from two bifurcated OH···F hydrogen bonding interactions of two water molecules with two BF_4^- anions (four OH···F distances, 2.55 Å/112°) (see Fig. 2b). Furthermore, short charge-assisted $C\text{–}H^{\delta+}\cdots F^{\delta-}$ intermolecular contacts between fluorine atoms of BF_4^- anions and aromatic rings of *trans*-azobenzene ligands were found (2.46, 2.46, and 2.42 Å; 143, 135 and 155°). Therefore, the crystal exhibits a 2-D supramolecular structure based on the hydrogen bonding interactions between the 1-D∼*trans*-azobenzene-[Ag(H_2O)]-*trans*-azobenzene∼chains and BF_4^- anions.

Experimental

General

All manipulations were performed under an argon atmosphere using standard *Schlenk* techniques. *trans*-Azobenzene and $AgBF_4$ were purchased from Aldrich and used as received; CH_2Cl_2, purchased from Riedel-de Haën, was not previously dried. Infrared spectra were recorded as mulls on NaCl plates using an ATI Mattson Genesis FTIR spectrometer, NMR spectra on a Bruker ARX 400 instrument using *TMS* as internal reference. Elemental analyses (C, H, N) were performed at the microanalytical laboratory of the Universidade Técnica de Lisboa, Portugal, and agreed favourably with the calculated values.

([Ag(μ-trans-azobenzene)H_2O][BF_4])$_n$ ($C_{12}H_{12}AgBF_4N_2O$)$_n$

A solution of *trans*-azobenzene (0.55 g, 3.0 mmol) in CH_2Cl_2 (20 cm^3) was added to a suspension of Ag(BF_4) (0.58 g, 3.0 mmol) in CH_2Cl_2 (30 cm^3) at room temperature. A colour change was observed immediately from the orange colour of *trans*-azobenzene to pale-yellow. The mixture was left stirring for about 1 h, the solvent was removed by vacuum and the yellow residue washed with petroleum ether (3×20 cm^3) and extracted with hot CH_2Cl_2. Upon cooling, yellow needles formed which they were recovered by filtration, washed with petroleum ether, and dried in vacuum.

Yield: 1.16 g (98%); ^{1}H NMR (δ, CD_2Cl_2, 25°C): 7.80–7.78 (m, 4H, Ph), 7.57–7.55 (m, 6H, Ph), 1.8 (s, 2H, H_2O) ppm; $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 25°C): 153.28 (s, C–N), 131.96 (s, Ph), 129.75 (s, Ph), 121.96 (s, Ph); IR (nujol mull): $\nu = 3496$ (m, br, ν_{OH}), 1105–1020 (s, br, ν_{BF_4}) cm^{-1}.

X-Ray structure determination of ([Ag(μ-N,N′-trans-N_2Ph_2)H_2O][BF_4])$_n$

Suitable single crystals of ([Ag(μ-N, N′-*trans*-N_2Ph_2)H_2O][BF_4])$_n$ for X-ray diffraction studies were grown by cooling a CH_2Cl_2 solution of the complex.

Crystal data: $C_{12}H_{12}AgBF_4N_2O$; MW = 394.92; triclinic; space group $P\bar{1}$, $a = 7.771(8)$, $b = 9.860(12)$, $c = 10.548(12)$ Å, $\alpha = 71.68(1)$, $\beta = 68.48(1)$, $\delta = 87.41(1)°$; V = 711(7) Å^3 $Z = 2$; $D_c = 1.843\ \mathrm{g \cdot cm^{-3}}$; $\mu = 1.459\ \mathrm{mm^{-1}}$.

Data collection and processing: The X-ray data were collected with graphite monochromated Mo-K_α radiation (0.71073 Å) on a MAR-research image plate system at room temperature. The crystal was positioned at 75 mm from the plate. 95 frames were measured in intervals of 2° with a counting time suitable to the diffraction pattern revealed by the crystal under investigation. Data analysis was performed with the XDS program [10]. Intensities were not corrected for absorption effects.

Structure analysis and refinement: The structure was solved by a combination of direct methods and successive difference *Fourier* syntheses and refined by full matrix least-squares methods on F^2 using the SHELX-97 package [11]. All non-hydrogen atoms were refined with anisotropic thermal parameters. However, some thermal disorder was apparent from the temperature factors of the fluorine atoms. The positions of hydrogen atoms of the water molecule were discernible from difference *Fourier* maps and were introduced in the refinement with constraints on O–H and H$\cdots$H distances consistent with the expected tetrahedral geometry of a water molecule. The remaining hydrogen atoms were included in the refinement in geometric positions consistent with the hybridization of the parent carbon atom. The final refinement of 195 parameters converged to $R = 0.1894$ and $R' = 0.2091$ for all 1400 unique *hkl* reflections and to $R = 0.0787$ and $R' = 0.2091$ for observed reflections with $I > 2\sigma(I)$.

Molecular and crystal packing diagrams were drawn with PLATON software package; CCDC reference number: 143996.

Acknowledgements

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