

The 3,5-dimethyl-4-nitropyrazole ligand in the construction of supramolecular networks of silver(I) complexes

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Abstract

Three new ionic silver complexes based on the 3,5-dimethyl-4-nitropyrazole ligand (Hpz^{NO₂}) and 1:2 or 1:3 (Ag : Hpz^{NO₂}) stoichiometries, [Ag(Hpz^{NO₂})₂][BF₄], [Ag(Hpz^{NO₂})₃][SbF₆] and [Ag(Hpz^{NO₂})₃][PO₂F₂] · Hpz^{NO₂} have been prepared and structurally characterised. The linear or trigonal metallic coordination environment, the NO₂ groups on the pyrazole ligand as well as the presence of counteranions of the type AX_n⁻ as BF₄⁻, SbF₆⁻ or PF₆⁻ (the latter one evolving to PO₂F₂⁻) were strategically selected to produce molecular assemblies established on the basis of hydrogen-bonds (N–H···X) and π···π or coordinative interactions involving the NO₂ group. The complex [Ag(Hpz^{NO₂})₂][BF₄] exhibited polymeric N–H···F hydrogen-bonded chains which were assembled in a 3D network by weaker coordinative Ag···O(NO₂) and π(NO₂)···π(NO₂) interactions. In the complex [Ag(Hpz^{NO₂})₃][SbF₆], consistent with the three-coordinated molecular environment, the interactions were extended to give rise to an open 3D cationic sub-network in which the counteranions SbF₆⁻ were encapsulated. By contrast, in the related complex [Ag(Hpz^{NO₂})₃][PO₂F₂] · Hpz^{NO₂} the presence of a fourth non-coordinated pyrazole Hpz^{NO₂} avoided the formation of a 3D network giving rise to a double-chained 1D structure.

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1. Introduction

The design of new materials with predictable structures and properties, main goal of crystal engineering, is an increasing area of current research due its multidisciplinary incidence in different areas as materials chemistry, supramolecular chemistry or biology. In this context, the knowledge of the molecular arrangement in the crystal network as responsible for the properties of the material is of capital importance, the intermolecular interactions being the main tool to achieve the required packing for selected properties.

Among the intermolecular interactions, strong hydrogen-bonds and coordinative bonds have been mainly devel-

oped for a wide variety of supramolecular 1D, 2D and 3D architectures based on 0D coordination compounds [1,2], or for multifunctional compounds [3].

However, in order to complete the crystal engineering studies the presence of other weaker interactions as π···π interactions or non-conventional hydrogen-bonds are more and more recognised in building new interesting supramolecular architectures [4].

Previous works in our lab have been dealt with the study of the molecular assembly of several ionic metal complexes based on substituted pyrazole ligands, in which the hydrogen-bonds between the counteranion and the NH-pyrazole groups were the main tool for the molecular assembly [5–8], although some other factors as variations of the counteranion and substituents on the pyrazole ligands also drove the supramolecular arrangement.

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In this work, we extend the potentiality of new ionic silver complexes based on the 3,5-dimethyl-4-nitropyrazole (Hpz^{NO₂}) ligand for a rational design of extended hydrogen-bonding polymers or supramolecular arrays established on coordinative, $\pi \cdots \pi$ and/or non-conventional hydrogen-bond interactions. The influence of a *cis* or *trans* molecular geometry, the nature of the counteranion (geometry and coordinative ability), the presence of the NO₂ group on the pyrazole ligands and the molecular stereochemistry are the factors examined on the final 1D, 2D or 3D architectures.

2. Results and discussion

2.1. Structural comparative study of ionic silver complexes based on pyrazole-type ligands

In order to analyse the main factors which can control the molecular assembly of ionic silver(I) pyrazole-based complexes, a comparative study of the previous structural results of those of the type [Ag(Hpz*)₂][AX_n] (Hpz* = substituted pyrazole ligand; AX_n = counteranion) is considered here as potential support for predictable structures of new derivatives. Following the literature data and our own research results [6,8–10], we have found in all cases a linear N–Ag–N coordination with a *cis*, *trans* or interme-

diate *cis*–*trans* orientation of the two NH groups from the two pyrazole ligands (deduced from the torsion angle τ defined by the four nitrogens of the two pyrazoles [8]), which is determinant of the supramolecular assembly. In particular, in the complex *cis*-[Ag(Hpz^{bp2})₂][BF₄] (**1**) (Hpz^{bp2} = 3,5-di(*p*-butoxyphenyl)pyrazole) both pyrazole ligands are hydrogen-bonded to the same counteranion BF₄[−] giving rise to closed molecular unities, which are bonded through additional weaker intermolecular C–H \cdots F contacts in a 1D framework (Fig. 1a) [6,8]. By contrast, in the related complex *trans*-[Ag(Hpz^{Me2})₂][NO₃] (**2**) (Hpz^{Me2} = 3,5-dimethylpyrazole) the cationic units are linked by bridging NO₃[−] groups in a zig-zag polymeric 1D chain involving strong N–H \cdots O hydrogen-bonds (Fig. 1b) [10]. Those structural results suggest that bulky substituents on the pyrazole group appear to prevent the formation of polymeric hydrogen-bonded chains based on the *trans*-oriented pyrazole groups. However, it was not at all true.

So, the complex [Ag(Hpz^{NO₂})₂][CF₃SO₃] (**3**) where Hpz^{NO₂} is 3,5-dimethyl-4-nitropyrazole (this ligand having the same CH₃ substituents at the 3 and 5 positions of the ring as they are in **2**) surprisingly exhibits a *cis* orientation ($\tau = 2.0^\circ$), from which cyclic unities with the corresponding counteranion are formed (Fig. 1c) [6,8]. The cyclic molecular entities are linked in dimers (by strong coordinative

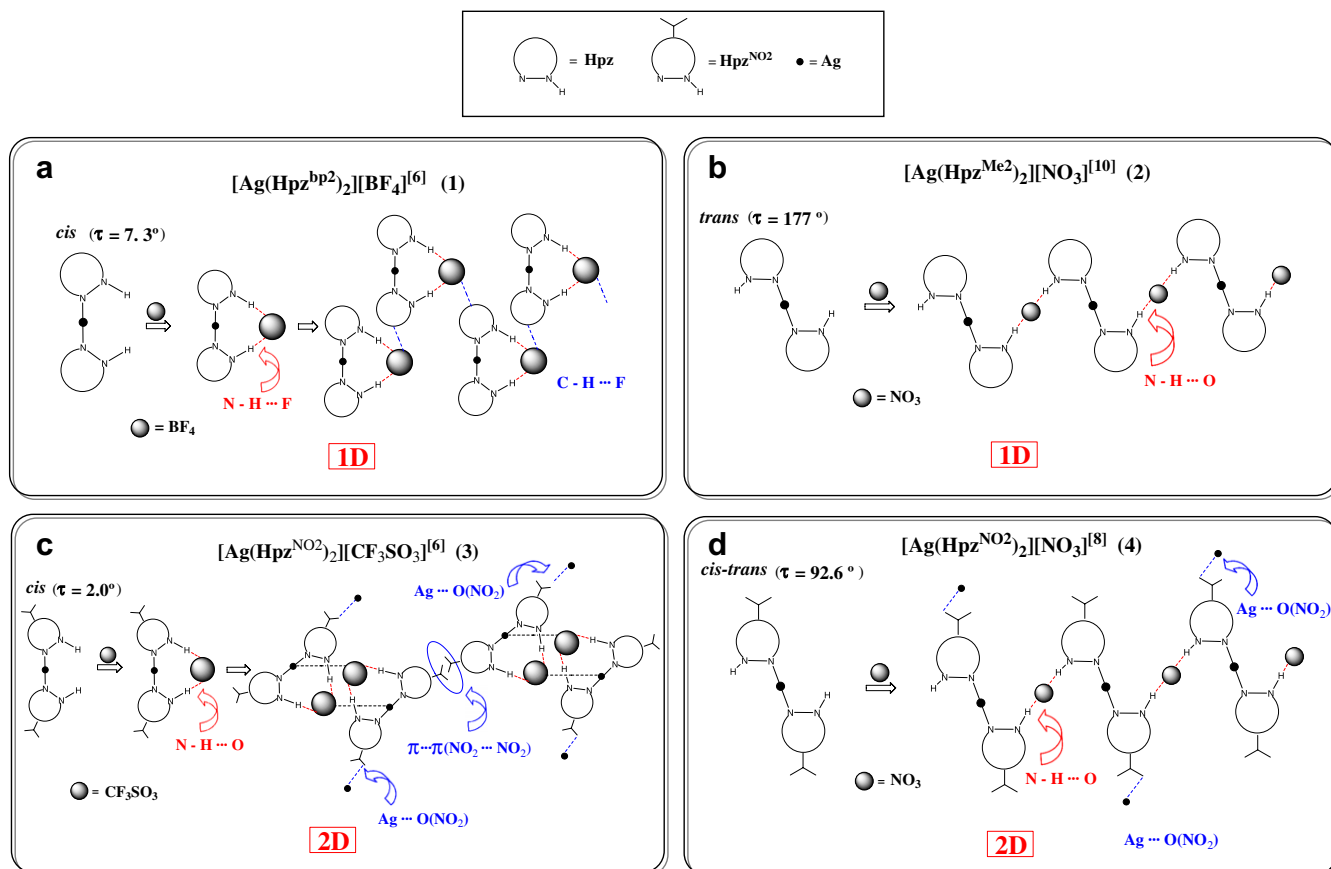


Fig. 1. Schematic representation of the molecular assemblies of complexes **1–4** ((a)–(d), respectively).

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