Supramolecular Arrays of Cationic Complexes Containing Pyrazole Ligands and Tetrafluoroborate, Trifluoromethanesulfonate, or Nitrate as Counterions. Crystal Structure of Bis(3,5-dimethyl-4-nitro-1*H*-pyrazole-κN^2)silver(1+) Nitrate ([Ag(Hpz^{NO2})$_2$](NO$_3$))

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The structures of [Pd(η^3-C$_3$H$_5$)(Hpz^{R2})$_2$](BF$_4$) (Hpz^{R2} = Hpz^{bp2} = 3,5-bis(4-butoxyphenyl)-1*H*-pyrazole, **1**; Hpz^{R2} = Hpz^{NO2} = 3,5-dimethyl-4-nitro-1*H*-pyrazole = Hdmnpz, **2**) and [Ag(Hpz^{R2})$_2$](A) (Hpz^{R2} = Hpz^{bp2}, A = BF$_4^-$, **3**; Hpz^{R2} = Hpz^{NO2}, A = CF$_3$SO$_3^-$, **4**) were comparatively analyzed to determine the factors responsible for polymeric assemblies. In all cases, the H-bonding interactions between the pyrazole moieties and the appropriate counterion and, in particular, the orientation of the NH groups of the pyrazole ligands are determinant of one-dimensional polymeric arrays. In this context, the new compound [Ag(Hpz^{NO2})$_2$](NO$_3$) (**5**) was synthesized and its structure analyzed by X-ray diffraction (*Fig. 4*). The Hpz^{NO2} serves as N-monodentate ligand, which coordinates to the Ag^I center through its pyrazole N-atom giving rise to an almost linear N–Ag–N geometry. The planar NO$_3^-$ counterion bridges two adjacent Ag^I centers to form a one-dimensional zigzag-shaped chain which is also supported by the presence of N–H$\cdots$O bonds between the pyrazole NH group of adjacent cationic entities and the remaining O-atom of the bridging NO$_3^-$ (*Fig. 5*). The chains are further extended to a two-dimensional layer-like structure through additional Ag$\cdots$O interactions involving the NO$_2$ substituents at the pyrazole ligands (*Fig. 6*).

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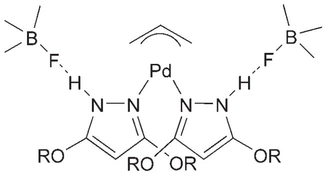
1. Introduction. – Technological materials useful to fabricate functional supramolecular devices are one of the reasons of the increasing research of supramolecular architectures [1][2].

In the last years, a large number of supramolecular one-, two-, or three-dimensional (1D, 2D, or 3D) networks based on the self-assembly of metallorganic compounds have been described [1][3]. H-Bonds, covalent bonds, $\pi\cdots\pi$ interactions as well as nonconventional interactions were used as support of those molecular assemblies. Therefore, systematic studies to establish guidelines to design networks are interesting.

In previous works, we have explored the ability of cationic complexes of the type [M(Hpz^{bp2})$_n$]$^+$ (Hpz^{bp2} = 3,5-bis(4-butoxyphenyl)-1*H*-pyrazole; $n = 1$, M = Au(PPh$_3$); $n = 2$, M = Pd(η^3-C$_3$H$_5$), Au, Ag), isolated as salts of different counteranions A (A = BF$_4^-$, NO$_3^-$, CF$_3$SO$_3^-$, *etc.*) to generate supramolecular structures [4][5]. In all cases, N–H$\cdots$A bonding interactions which depended on the metal fragment and the counterion were determinant for the supramolecular arrays. In this context, we now analyze our previous results on the Ag- and Pd-complexes **1**–**4** and extend this study to related derivatives.

2. Results and Discussion. – 2.1. *Analysis of Known Supramolecular Structures.* In general, in Pd-complexes of the type $[Pd(\eta^3\text{-}C_3H_5)(Hpz^R)_2]^+$ (Hpz^R = substituted 1*H*-pyrazole), the two *cis*-coordinated pyrazole ligands can have different NH orientations, which should allow variations on the supramolecular arrays. These NH orientations are now evaluated by measuring the torsion angle τ defined by the four N-atoms of the two pyrazole ligands. In particular, for the complex $[Pd(\eta^3\text{-}C_3H_5)(Hpz^{bp2})_2](BF_4)$ (**1**), the angle τ had a mean value of 175.3°, thus generating an orientation of both NH groups that allowed their interaction with two different BF_4^- counteranions (*Fig. 1*) [4]. These N–H ··· F interactions were expanded along the *c* axis giving rise to a 1D polymeric assembly [4].



R = 4-BuO–C_6H_4

Fig. 1. *Schematic representation of the structure of* $[Pd(\eta^3\text{-}C_3H_5)(Hpz^{bp2})_2](BF_4)$ (**1**) [4]

However, for complexes of the type $[Ag(Hpz^R)_2]^+$ exhibiting a linear N–Ag–N coordination, either a '*cis*' or '*trans*' orientation of the two pyrazole ligands to each other, and hence of their NH groups, are possible (*Fig. 2*). Thus, the molecular structure of $[Ag(Hpz^{bp2})_2](BF_4)$ (**3**) showed the '*cis*' orientation, which was also supported by an angle τ of 7.3° [5]. Hence, as expected, both pyrazole ligands were H-bonded to the same counterion BF_4^- and, thus, the two strong N–H ··· F bonds gave rise to a closed structure in which the –F–HNN–Ag–NNH–F–B– metallocycle could be defined (*Fig. 3*). From these cyclic entities, new weak intermolecular C–H ··· F contacts involving the free F-atoms of the BF_4^- counterion were responsible for a one-dimensional framework [5]. By contrast, the previously described complexes $[Ag(Hpz^{R2})_2](NO_3)$ ($Hpz^{R2} = Hpz^{Me2}$ = 3,5-dimethyl-1*H*-pyrazole [6]; Hpz^{R2} = Hpz = 1*H*-pyrazole [7]) showed the '*trans*' orientation of the pyrazole ligands, and the cationic units were linked by bridging nitrate groups in a polymeric structure.

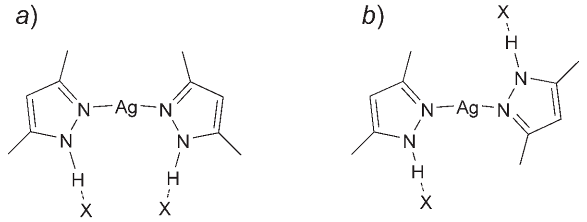


Fig. 2. *Complexes* $[Ag(Hpz^{R2})_2]^+$ *with* a) 'cis' *and* b) 'trans' *orientation*

Following these precedents, we were encouraged in assessing the influence of the spatial disposition of the pyrazole ligands in the molecular assembly of Ag- and Pd-complexes related to the above described.

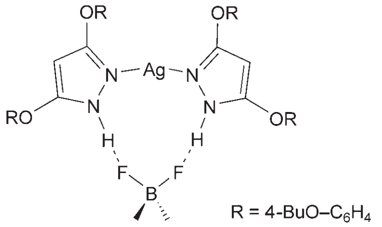


Fig. 3. *Schematic representation of the structure of* $[Ag(Hpz^{bp2})_2](BF_4)$ (**3**) [5]

We thought that by including an NO_2 substituent at the 4 position of the pyrazole ligand, like in Hpz^{NO2} (=3,5-dimethyl-4-nitro-1*H*-pyrazole = Hdmnpz), new coordinative elements such as the O-atoms of the NO_2 substituent should allow to extend the dimensionality of the framework. This was the case for the Pd-derivative $[Pd(\eta^3\text{-}C_3H_5)(Hpz^{NO2})_2](BF_4)$ (**2**) whose X-ray structure was solved [8]. The molecular structure of **2** established the *cis*-coordinated pyrazole ligands, with an angle τ of 179.9°, analogously to that found in **1** [4]. On a supramolecular level, the structure again consisted of the expected polymeric chain, propagated by strong N–H···F bonds between the two NH groups of each cationic unit and the neighboring counterions which acted as bridging groups [8]. In addition, the same BF_4^- counterions linked adjacent chains through bifurcated H-bonds to construct a 2D network which was extended to a 3D one through new intermolecular interactions involving the NO_2 substituents. The complex $[Ag(Hpz^{NO2})_2]^+$ corresponding to **2** should also be a potential building block of 2D or 3D architectures. Unfortunately, we were unable to isolate adequate crystals of $[Ag(Hpz^{NO2})_2](BF_4)$ [5], and therefore, the X-ray structure of the related complex $[Ag(Hpz^{NO2})_2](CF_3SO_3)$ (**4**) containing trifluoromethanesulfonate ($CF_3SO_3^-$) as counterion was determined [5]. The molecular structure of **4** revealed a '*cis*' orientation of the two ligands with the corresponding angle τ of 2.0°, this fact avoiding the potential polymeric-structure characteristic of the '*trans*' arrangement. In contrast to **2**, the $CF_3SO_3^-$ counterion of **4** was situated between the two pyrazole ligands within each $[Ag(Hpz^{NO2})_2]^+$ unit and interacted *via* two strong N–H···O H-bonds to produce a –O–HNN–Ag–NNH–O–S– metallocycle structure, analogously to that observed in **3** [5]. The crystal packing of **4** showed that the above pyrazole-silver units were linked by additional strong coordinative Ag···O interactions from the free O-atom of the counterion giving rise to dimers [5]. These dimers were arranged in columns due to $\pi\cdots\pi$ ($NO_2\cdots NO_2$) interactions, analogous to those described in previous works [9]. New intermolecular coordinative Ag···O interactions through the free O-atoms of the NO_2 groups were responsible for a 2D layer-like framework.

By considering all these results, we can summarize that factors such as the adequate orientation of the pyrazole ligands, the presence of coordinative atoms from the counterion, and the $NO_2\cdots NO_2$ interactions due to the substituents at the pyrazole ligands are responsible for the different supramolecular networks.

2.2. *Structure of* $[Ag(Hpz^{NO2})_2](NO_3)$ (**5**). To extend the above studies and in support of the deduced conclusions, the related complex $[Ag(Hpz^{NO2})_2](NO_3)$ (**5**) was now prepared and characterized (see *Exper. Part*) and its X-ray structure determined.

The X-ray crystal structure of **5** is depicted in *Fig. 4*, and selected distances and angles are listed in *Table 1*. The compound crystallizes in the monoclinic system, space group $P2_1/c$. The asymmetric unit shows two $[Ag(Hpz^{NO2})_2]^+$ entities held together by two NO_3^- counterions. Both units are chemically equivalent but crystallographically different, with slight differences in some structural parameters (see *Tables 1–3*). The N–Ag–N angle in both cationic entities is *ca.* 175°, consistent with a linear coordination around the Ag-center (*Table 1*). The Ag–N distances (2.12 to 2.14 Å) are similar to those found in related compounds containing heterocyclic ligands [5–7][10]. The NO_2 planes are almost parallel to the planes of the pyrazole units to which they are attached, indicating the planarity of the whole ligand (*Table 2*).

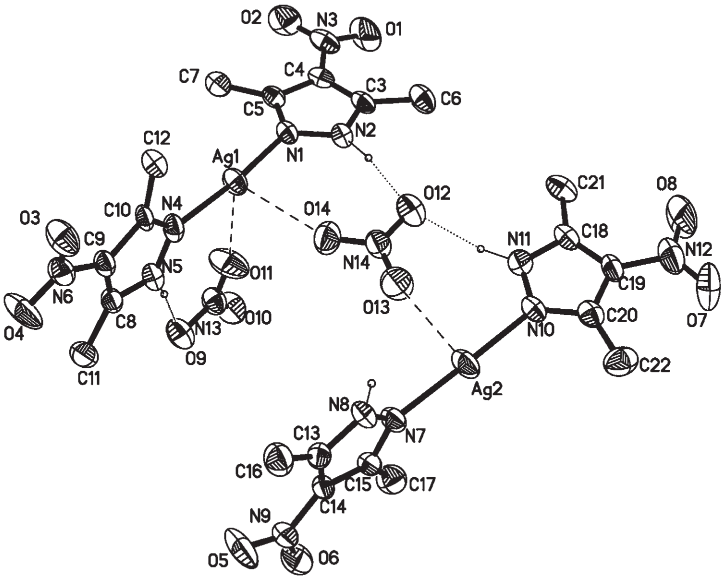


Fig. 4. *Perspective ORTEP plot of* $[Ag(Hpz^{NO2})_2](NO_3)$ (**5**). H-Atoms, except H(2), H(5), H(8), and H(11) are omitted for clarity. The thermal ellipsoids are at 40% probability level. Arbitrary atom numbering.

Table 1. *Selected Distances* [Å] *and Angles* [°] *of* **5**

Ag(1)–N(1)	2.142(4)	Ag(1)···O(14)	2.673(4)
Ag(1)–N(4)	2.126(4)	Ag(2)···O(13)	2.727(5)
Ag(2)–N(7)	2.144(4)	Ag(2)···O(10) [a])	2.732(4)
Ag(2)–N(10)	2.149(4)	Ag(1)···O(5)[b])	3.322(5)
Ag(1)···O(11)	2.728(4)	Ag(2)···O(1)[c])	3.347(5)
N(1)–Ag(1)–N(4)	174.1(1)	N(7)–Ag(2)–N(10)	176.8(2)

[a]) $x+1, y, z$. [b]) $x, -y+½, z-½$. [c]) $x+1, -y+½, z+½$.

It is remarkable to note that in this complex, the pyrazole planes are almost orthogonal. This fact generates a particular orientation of the NH groups of the two pyrazole ligands in each cationic unit (the angle τ has a mean value of 92.6°), intermediate between the '*cis*' or '*trans*' orientation in related compounds as described

Table 2. *Dihedral Angles* [°] *between Selected Planes for* **5**

Plane No.	Plane-defining atoms	Plane No.	Plane-defining atoms
1	N(1)N(2)C(3)C(4)C(5)	*6*	O(3)–N(6)–O(4)
2	N(4)N(5)C(8)C(9)C(10)	*7*	O(5)–N(9)–O(6)
3	N(7)N(8)C(13)C(14)C(15)	*8*	O(7)–N(12)–O(8)
4	N(10)N(11)C(18)C(19)C(20)	*9*	O(9)O(10)O(11)N(13)
5	O(1)–N(3)–O(2)	*10*	O(12)O(13)O(14)N(14)
Selected planes	Dihedral angle [°]	Selected planes	Dihedral angle [°]
1–2	89.2(1)	*1–5*	9.1(4)
1–3	89.3(2)	*2–6*	9.4(3)
1–4	8.5(2)	*3–7*	6.3(4)
2–3	7.9(2)	*4–8*	0.5(5)
2–4	89.9(2)	*9–10*	86.9(2)
3–4	89.8(2)		

Table 3. *H-Bond Geometries for* **5**

D–H···A	*d*(D–H) [Å]	*d*(H···A) [Å]	*d*(D···A) [Å]	∢(D–H···A) [°]
N(2)–H(2)···O(12)	1.20	1.74	2.871(5)	154.7
N(5)–H(5)···O(9)	1.16	1.84	2.985(6)	168.0
N(11)–H(11)···O(12)	1.00	2.03	3.016(6)	165.8
N(8)–H(8)···O(9) [a])	1.11	1.80	2.905(5)	172.7

[a]) *x* + 1, *y*, *z*.

in *Sect. 2.1*. This intermediate orientation is supported by the coordinative and H-bonding interactions produced by the planar NO_3^- group (*Fig. 4*).

The NO_3^- counterions are located between the cationic $[Ag(Hpz^{NO2})_2]^+$ units, generating a polymeric structure. The cation–anion interaction is produced by bifurcated N–H···O bonds between one O-atom of the NO_3^- and two NH groups of neighboring cationic units (*Table 3*), resulting in a zigzag distribution which expands along the *a* axis (*Fig. 5*). This 1D arrangement is additionally supported by bridging coordinative Ag···O interactions (*Table 1*), in which the two remaining O-atoms of the NO_3^- groups are connecting the two adjacent cationic units. The Ag···O distances are characteristic of strong coordinative interactions, therefore a four-coordination around each Ag-center (by two N- and two O-atoms) could be considered.

The zigzag chains are further extended to a 2D network by new, but weaker coordinative Ag···O interactions with the O-atoms of the NO_2 substituents (*Table 1*), which generates to a layer-like arrangement in the *ac* plane (*Fig. 6*).

3. Conclusions. – Complexes of the type $[M(Hpz^{R2})_2](A)$ ($M = Pd(\eta^3\text{-}C_3H_5)$, $Hpz^{R2} = Hpz^{bp2}$ or Hpz^{NO2}, $A = BF_4$; $M = Ag$, $Hpz^{R2} = Hpz^{bp2}$, $A = BF_4$; $M = Ag$, $Hpz^{R2} = Hpz^{NO2}$, $A = CF_3SO_3$ or NO_3) were shown to be building bocks of supramolecular networks. The orientation of the NH groups of the coordinated pyrazole ligands, defined by the torsion angle τ, was found to be responsible for the formation of 1D polymeric structures involving strong H-bonds with the counterions. The

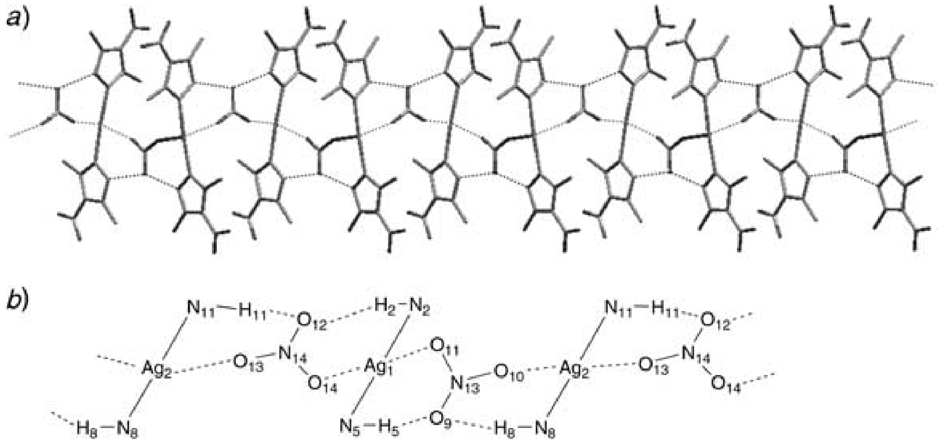


Fig. 5. a) *View of the polymeric zigzag distribution along the* a *axis for* **5**. b) *Schematic representation of the zigzag chain*.

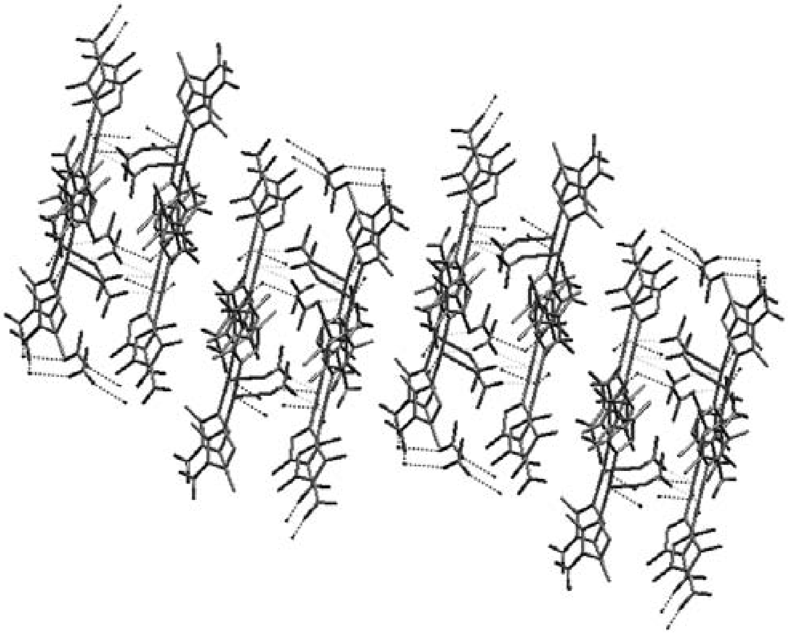


Fig. 6. *View of the two-dimensional network in the* ac *plane for* **5**

coordinative ability of the counterion contributed to this type of polymeric assemblies. In particular, when Hpz^{NO2} was used as ligand, the NO_2 substituents also participated in the build-up of extended supramolecular structures.

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Experimental Part

General. The ligand 3,5-dimethyl-4-nitro-1*H*-pyrazole (Hpz^{NO2}) was prepared according to [11]. All commercial reagents were used as supplied. IR Spectra: *Nicolet IR200* spectrophotometer; KBr discs; 4000–350 cm^{-1} region; in cm^{-1}. ^{1}H-NMR Spectra: *Bruker AC-200* (200.13 MHz) spectrophotometer of the NMR Service of the Complutense University; CDCl$_3$ soln., r.t.; chemical shifts δ in ppm ($\pm$0.01 ppm) rel. to SiMe$_4$, with the signal of the deuterated solvent as reference. Elemental analyses (C, H, N) were carried out by the Center for Elemental Microanalysis of the Complutense University.

*Bis(3,5-dimethyl-4-nitro-1*H*-pyrazole-κ*N^2*)silver(1+) Nitrate ([Ag(Hpz^{NO2})$_2$](NO$_3$)*; **5**). AgNO$_3$ (34 mg, 0.20 mmol) was added under N$_2$ to a soln. of Hpz^{NO2} (57 mg, 0.40 mmol) in dry THF (10 ml). After 24 h of stirring, evaporation gave an oil from which a white solid was isolated by addition of CH$_2$Cl$_2$ and pentane. The product was crystallized from acetone solns. by diffusion of hexane/Et$_2$O: 43 mg (48%) of **5**. IR: 3202 and 3140 ($\tilde{\nu}$(N–H)), 1587 ($\tilde{\nu}$(C=N)), 1506 ($\tilde{\nu}_{as}$(NO$_2$)), 1382 ($\tilde{\nu}_d$(NO$_3$)), 1363 ($\tilde{\nu}_s$(NO$_2$)). ^{1}H-NMR: 2.63 (*s*, Me). Anal. calc. for $C_{10}H_{14}AgN_7O_7$ (452.14): C 26.57, H 3.12, N 21.69; found: C 26.50, H 3.35, N 21.84.

X-Ray Structure Determination of [Ag(Hpz^{NO2})$_2$](NO$_3$) (**5**): Colorless single crystals ($0.07 \times 0.12 \times 0.46$ mm) were grown by slow diffusion of hexane/Et$_2$O to acetone solns. of **5**. Crystal data: $C_{20}H_{28}N_{14}O_{14}Ag_2$; M_r 904.30; T 293(2) K; λ 0.71073 Å; *Bruker-Smart-CCD* diffractometer (operating at 50 kV and 20 mA); monoclinic, space group $P2_1/c$; $a = 9.6507(9)$, $b = 22.742(2)$, $c = 14.579(2)$ Å, $\beta = 90.339(2)°$, $V = 3199.5(5)$ Å^3, $Z = 4$; $D_c = 1.877$ g cm^{-3}; μ (mm^{-1}) = 1.312. The data were collected over a hemisphere of the reciprocal space by combination of three exposure sets. The cell parameters were determined and refined by least-squares fit of all reflections collected (θ range, 1.66–28.64°; index range, (−12, −30, −19) to (12, 23, 19)). Each exposure of 20 s covered 0.3° in ω. The first 50 frames were recollected at the end of the data collection to monitor crystal decay. No appreciable decay in the intensities of standard reflections was observed. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 [12]. Anisotropic thermal parameters were used in the last cycles of refinement for all non-H-atoms. H-Atoms were included in calculated positions, except H(2), H(5), H(8), and H(11), which were located in a *Fourier* synthesis and refined as riding on their respective N-atoms with the thermal parameters related to their bonded atoms. The final R indices with $I > 2\sigma(I)$ was 0.044 for 3271 observed reflections, while wR_2 for all data (7646 independent reflections, $R_{int} = 0.0623$) was 0.114. The g.o.f. (F^2) was 0.841, and the largest residual peak and hole in the final difference map were 0.622 and −0.622 e Å^{-3}, respectively.

CCDC-265087 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Center via* www.ccdc.cam.ac.uk/data_request/cif.

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