(Pyrazole)silver(I) and -gold(I) Complexes with Strong and Weak Hydrogen-Bonding Interactions as the Basis of One- or Two-Dimensional Structures

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Dedicated to Professor José Vicente on the occasion of his 60th birthday

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New Au^I/Ag^I complexes containing one or two substituted pyrazole ligands $[Au(Hpz^{bp2})(PPh_3)](p\text{-}CH_3C_6H_4SO_3)$ [Hpz^{bp2} = 3,5-bis(4-*n*-butoxyphenyl)pyrazole] (**1**) and $[M(Hpz^{R2})_2]_nX$ [Hpz^{R2} = Hpz^{bp2}, M = Au, *n* = 1, X = *p*-$CH_3C_6H_4SO_3$ (**2**), NO_3^- (**3**); *n* = 2, X = 1,5-naphthalenedisulfonate (1,5nds) (**4**); Hpz^{R2} = Hpz^{bp2}, M = Ag, *n* = 1, X = BF_4^- (**5**), $CF_3SO_3^-$ (**6**); Hpz^{R2} = Hpz^{NO2} (3,5-dimethyl-4-nitropyrazole), M = Ag, *n* = 1, X = BF_4^- (**7**), $CF_3SO_3^-$ (**8**)], have been prepared and characterized. Compounds **1**, **2**, **5** and **8** have been proved to be useful for supramolecular assembly from their single X-ray diffraction analysis. In all cases strong hydrogen bonds maintain the cationic units bonded to their corresponding counterions. The crystal packing arrangement of **1**, **2** and **5** is, however, determined by weak C–H···O/F hydrogen-bonding interactions involving the remaining O/F atoms of the counterion. By contrast, for **8** a two-dimensional layer-type polymeric network is formed by π···π (NO_2···NO_2) and coordinative Ag···O interactions in which the NO_2 substituent on the pyrazole is implicated.

Introduction

Supramolecular architectures derived from metallic complexes as building blocks are an attractive focus of current research. In this context coordinative interactions and/or hydrogen bonds have been extensively used to produce supramolecular one-, two- or three-dimensional polymeric structures.[1] However, although self-assembly has been well documented,[2] much work remains to extend the knowledge of relevant structures. The nature of the metal, counterions or ligands are factors that can be modulated to determine the molecular assembly.

The silver(I) ion is a favourable building block because of its various potential coordination modes such as linear,[3] trigonal[4] or tetrahedral,[5] and its affinity for hard donor atoms such as nitrogen or oxygen. In addition, some silver(I) derivatives have also been determined to present experimental evidence for an argentophilic attraction[6] and therefore with potential applications for self-assembled nets. In the same context, gold(I) complexes are promising for the construction of supramolecular structures based on the aurophilic nature of gold.[6b,7] Furthermore, experimental evidence from structures of Au/Ag-containing cationic complexes indicates the relevant role of the counterion in the molecular architecture.[2b,6c,8]

It has been postulated that the control and manipulation of weak interactions could be used as the key to tune the properties of the bulk materials. In addition to the classical O/N−H···X (X = O, N or F atoms) hydrogen-bonding interactions, other weaker C−H···X (X = O, N or F atoms) interactions have been shown to control the molecular packing in the solid.[1g,9]

In previous work from our lab we have made use of hydrogen-bonding interactions produced between cationic metal complexes containing pyrazole ligands and the corresponding counterions. Although the strong NH···X (X = O or F atoms from NO_3^- or BF_4^- counterions) hydrogen bonds are the predominant force driving the structure, other different intermolecular interactions, such as C−H···O/F, are also considered to be important for the molecular assembly.[10]

We have now extended these results to the use of new silver(I) and gold(I) pyrazole derivatives of the type $[M(Hpz^{R2})_2]^+$ [Hpz^{R2} = 3,5-bis(4-*n*-butoxyphenyl)pyrazole, Hpz^{bp2}; 3,5-dimethyl-4-nitropyrazole, Hpz^{NO2}) containing different counterions, as well as different substituents on the pyrazole rings. The related complex containing only one

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pyrazole ligand, [Au(Hpz^{bp2})(PPh$_3$)](*p*-CH$_3$C$_6$H$_4$SO$_3$), has also been prepared and studied (Scheme 1). We report herein how the presence of strong or weak N−H···O/F and C−H···O/F inter- and intramolecular hydrogen-bonding interactions, supported by the different counterions, are responsible for the molecular arrangement in the solid for complexes containing the Hpz^{bp2} ligand. In contrast, the molecular packing of those complexes with Hpz^{NO2} is dominated by interactions through the NO_2 substituents on the ligands.

Compound	Formula
1	[Au(Hpz^{bp2})(PPh$_3$)](*p*-CH$_3$C$_6$H$_4$SO$_3$)
2	[Au(Hpz^{bp2})$_2$](*p*-CH$_3$C$_6$H$_4$SO$_3$)
3	[Au(Hpz^{bp2})$_2$](NO$_3$)
4	[Au(Hpz^{bp2})$_2$]$_2$(1,5nds)[a]
5	[Ag(Hpz^{bp2})$_2$](BF$_4$)
6	[Ag(Hpz^{bp2})$_2$](CF$_3$SO$_3$)
7	[Ag(Hpz^{NO2})$_2$](BF$_4$)
8	[Ag(Hpz^{NO2})$_2$](CF$_3$SO$_3$)

Hpz^{bp2} = 3,5-bis(4-*n*-butoxyphenyl)pyrazole

Hpz^{NO2} = 3,5-dimethyl-4-nitropyrazole

[a] 1,5nds = 1,5-naphthalenedisulfonate ($O_3SC_{10}H_6SO_3$)

Scheme 1

Results and Discussion

Synthetic and Characterization Studies

Complex **1**, containing triphenylphosphane, was obtained from the reaction of [Au(*p*-CH$_3$C$_6$H$_4$SO$_3$)(PPh$_3$)] (prepared by a literature procedure)[8d] and one equivalent of Hpz^{bp2} in dry THF (Scheme 2). Compounds **2**−**4** were prepared by reaction of [AuCl(THT)] (THT = tetrahydrothiophene)[11] with two equivalents of Hpz^{bp2} and one equivalent of the corresponding silver salt in dry THF (Scheme 3). The related silver(I) derivatives **5**−**8** were synthesized by treatment of two equivalents of the corresponding pyrazole ligand with one equivalent of the silver salt in dry THF or acetonitrile (Scheme 4).

$$[Au(p\text{-}CH_3C_6H_4SO_3)(PPh_3)] + Hpz^{bp2} \longrightarrow$$

$$[Au(Hpz^{bp2})(PPh_3)](p\text{-}CH_3C_6H_4SO_3) \quad (\mathbf{1})$$

Scheme 2

$$[AuCl(THT)] + 2\ Hpz^{bp2} + AgX \longrightarrow [Au(Hpz^{bp2})_2]_nX \quad (\mathbf{2}\text{–}\mathbf{4})$$

Scheme 3

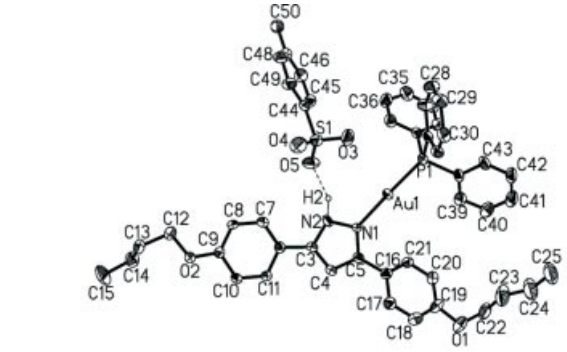
$$AgX + 2\ Hpz^{R2} \longrightarrow [Ag(Hpz^{R2})_2]X$$

$$Hpz^{R2} = Hpz^{bp2} \quad (\mathbf{5}\text{–}\mathbf{6})$$
$$Hpz^{R2} = Hpz^{NO2} \quad (\mathbf{7}\text{–}\mathbf{8})$$

Scheme 4

All compounds are air-stable white solids and they were characterized by elemental analysis and IR and ^{1}H NMR spectroscopy. In addition, ^{31}P NMR spectroscopy was also used for **1**. All data are listed in the Exp. Sect. The IR spectra show, amongst others, the characteristic bands of the pyrazole ligands, ν(C=N) + ν(C=C) at ca. 1600 cm^{-1} and ν(N−H) in the range 3112−3308 cm^{-1}, as well as those from the corresponding counterions.[8d,12]

The ^{1}H NMR spectra in $CDCl_3$ solution at room temperature show the expected signals of the ligands. It is interesting to note that the ^{1}H NMR spectra of **5**−**8** at room temperature are consistent with the presence of two equivalent coordinated pyrazole ligands, each of them having two equivalent substituents at the 3- and 5-positions. A related equivalence of the substituents has also been observed for **1**. Thus, it is possible to suggest a metallotropic equilibrium to explain the above behaviour similar to that previously found for related complexes.[13] Lowering the temperature slows down the dynamic process, resulting in the non-equivalence of the substituents, as observed for **5** and **6** at −40 °C by the well-defined signals for the aromatic and alkyl-



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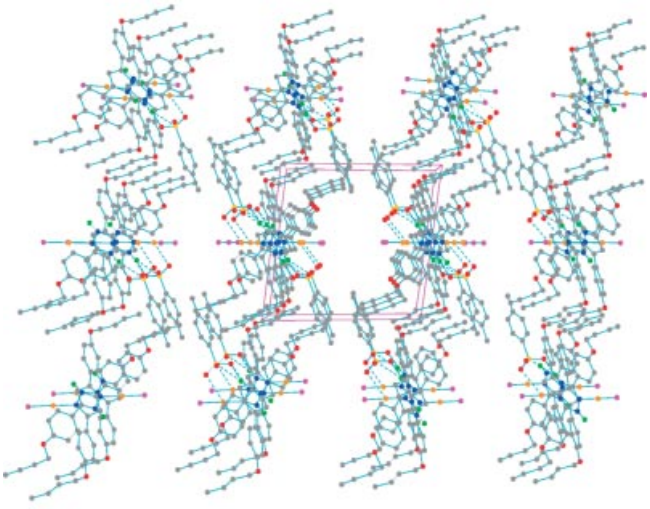

b

Figure 1. a) ORTEP plot of **1** at the 30% probability level; hydrogen atoms, except H2, and the labelling of some atoms have been omitted for clarity; b) view of the packing along the *a* axis (the phenyl groups of the phosphane ligands have been omitted)

Table 1. Bond lengths (Å) and angles (°) for **1**, **2**, **5** and **8**

[Au(Hpz^{bp2})(PPh$_3$)](*p*-CH$_3$C$_6$H$_4$SO$_3$) (**1**)				[Au(Hpz^{bp2})$_2$](*p*-CH$_3$C$_6$H$_4$SO$_3$) (**2**)			
Au1−N1	2.069(5)	N1−Au1−P1	177.1(2)	Au1−N1	2.019(7)	N1−Au1−N3	176.3(4)
Au1−P1	2.243(2)	O3−S1−O4	111.2(4)	Au1−N3	2.022(7)	O5−S1−O6	111.7(5)
N1−N2	1.396(7)	O3−S1−O5	113.5(4)	N1−N2	1.36(1)	O5−S1−O7	114.5(5)
S1−O3	1.449(5)	O4−S1−O5	113.6(4)	N3−N4	1.36(1)	O6−S1−O7	112.4(5)
S1−O4	1.451(6)	O3−S1−C44	107.1(3)	S1−O5	1.426(6)	O5−S1−C49	105.0(4)
S1−O5	1.433(6)	O4−S1−C44	104.7(3)	S1−O6	1.447(6)	O6−S1−C49	105.7(4)
S1−C44	1.775(7)	O5−S1−C44	106.0(3)	S1−O7	1.416(8)	O7−S1−C49	106.8(5)
				S1−C49	1.77(1)		
[Ag(Hpz^{bp2})$_2$]BF$_4$ (**5**)				[Ag(Hpz^{NO2})$_2$](CF$_3$SO$_3$) (**8**)			
Ag1−N1	2.129(3)	N1−Ag1−N3	170.1(1)	Ag1−N1	2.171(2)	N1−Ag1−N4	163.67(9)
Ag1−N3	2.118(3)	F1−B1−F2	108.5(3)	Ag1−N4	2.161(2)	O1−N3−O2	123.3(3)
N1−N2	1.355(4)	F1−B1−F3	108.9(3)	N1−N2	1.363(3)	O3−N6−O4	124.5(4)
N3−N4	1.359(4)	F1−B1−F4	109.7(3)	N4−N5	1.357(3)	O5−S1−O6	114.0(2)
B1−F1	1.378(4)	F2−B1−F3	111.5(3)	N3−O1	1.223(3)	O5−S1−O7	114.6(2)
B1−F2	1.360(4)	F2−B1−F4	108.8(3)	N3−O2	1.223(3)	O6−S1−O7	115.1(2)
B1−F3	1.354(3)	F3−B1−F4	109.5(3)	N6−O3	1.224(5)	O5−S1−C11	105.3(2)
B1−F4	1.375(4)			N6−O4	1.215(5)	O6−S1−C11	103.0(2)
				S1−O5	1.427(2)	O7−S1−C11	102.9(2)
				S1−O6	1.435(3)		
				S1−O7	1.443(3)		

chain protons of the butoxyphenyl substituents. A similar feature is also present in the gold derivatives **2**−**4**, which exhibit the non-equivalence of the butoxyphenyl substituents at room temperature. The protons at the 4-positions of the pyrazole rings of **2** and **3** show an unusual coupling with the NH proton, which was confirmed by homonuclear decoupling techniques. This situation has also been observed in some metal complexes containing related pyrazole ligands.[14] The ^{31}P NMR spectrum of **1** at room temperature in $CDCl_3$ shows a single resonance at $\delta = 31.06$ ppm in the characteristic region of gold-phosphane complexes.[15]

The photoluminescence study of **1**−**3** in the solid state shows that, under 325−330 nm UV irradiation, all of them emit luminescence in the 440−510 nm range. For **1** this emission occurs both at room temperature and 77 K, while for **2** and **3** this behaviour is only observed at low temperature. The maximum-emission wavelengths are red-shifted by ca. 100 nm relative to the free pyrazole ligands.

Crystal Structure of 1

The molecular structure of [Au(Hpz^{bp2})(PPh$_3$)](*p*-CH$_3$C$_6$H$_4$SO$_3$) (**1**) is depicted in Figure 1a, which also shows the numbering scheme. Selected bond lengths and angles and the hydrogen-bond parameters for all compounds crystallographically characterized in this work are collected in Table 1 and 2, respectively.

The structure of **1** consists of *p*-toluenesulfonate anions and cationic units where the gold(I) atom is two-coordinate. The coordinative environment (shape, Au−P and Au−N distances, and P−Au−N angles) are, as expected, similar to those of the complex [Au(Hpz^{bp2})(PPh$_3$)](NO$_3$) (**A**), previously reported by us,[10b] which contains the same cationic fragment and NO_3^- as counterion [Au1−P1, Au1−N1 and P1−Au1−N1 bond parameters are 2.243(2), 2.069(5) Å and 177.1(2)° in **1**, and 2.239(2), 2.077(5) Å and 178.1(2)° in **A**]. In addition, the cationic unit in both **1** and **A** is bonded to the corresponding counterion by a strong hydrogen bond, with N···O distances of 2.701(7) Å (Table 2) and 2.764(9) Å, respectively.

Table 2. Hydrogen bond geometries for **1**, **2**, **5** and **8** (lengths in Å and angles in degrees)

D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	∠(D−H···A)
[Au(Hpz^{bp2})(PPh$_3$)](*p*-CH$_3$C$_6$H$_4$SO$_3$) (**1**)				
N2−H2···O4	1.02	1.79	2.701(7)	147.2
C29−H29···O3[a]	0.93	2.55	3.39(1)	149.8
C31−H31···O2[b]	0.93	2.48	3.35(1)	156.2
C34−H34···O5[c]	0.93	2.84	3.43(1)	122.0
[Au(Hpz^{bp2})$_2$](*p*-CH$_3$C$_6$H$_4$SO$_3$) (**2**)				
N2−H2···O5	0.99(9)	1.72(9)	2.70(1)	174(8)
N4−H4···O6	0.9(1)	1.7(1)	2.71(1)	175(8)
C4−H4A···O7[d]	0.93	2.51	3.39(2)	158.4
C34−H34···O7[e]	0.93	2.61	3.42(2)	146.9
[Ag(Hpz^{bp2})$_2$]BF$_4$ (**5**)				
N2−H2···F1	0.97	1.88	2.776(4)	152.6
N4−H4···F4	0.95	1.85	2.779(4)	165.3
C7−H7···F3[f]	0.93	2.69	3.40(1)	134.2
[Ag(Hpz^{NO2})$_2$](CF$_3$SO$_3$) (**8**)				
N2−H2···O6	0.93	1.85	2.771(3)	176.0
N5−H5···O7	0.92	1.95	2.852(4)	165.9

[a] $-x, -y + 1, -z + 1$. [b] $-x, -y + 1, -z + 2$. [c] $x + 1, y, z$. [d] $-x + 2, -y + 1, -z + 1$. [e] $x - 1/2, -y + 1/2, z - 1/2$. [f] $-x, -y + 1, -z$.

However, when considering the packing arrangement in the solid several differences are observed. A two-dimensional structure was envisaged for **A** from weak intermolecular C−H···O interactions of 3.31−3.38 Å involving two of the oxygen atoms of the counterion, which were not implicated in the previous hydrogen bond.[10b] In contrast, in **1**

the *p*-toluenesulfonate counterion forms a weak C−H···O interaction at 3.39(1) Å (Table 2) to produce a columnar one-dimensional arrangement along the *a* axis (see b in Figure 1). These columns are also reinforced by the presence of a new C−H···O interaction between the O2 atom of the substituent on the pyrazole ligand and the C31 atom of the PPh_3 ligand of a neighbouring molecule (Table 2). Throughout this one-dimensional distribution the gold atoms are in a zig-zag disposition at a distance of 5.58(1) Å, which excludes the presence of intermetallic interactions.

The above differences in the supramolecular architectures are clearly dependent on the counterions. It can therefore be suggested that the driving force of the reorientation of cationic entities when the planar NO_3^- is substituted by the bulkier *p*-toluenesulfonate could be related to the pseudo-tetrahedral geometry of the SO_3 group; interactions through this group appear to preclude a layer-like distribution.

However, this result does not exclude the possibility of new contacts involving the remaining free oxygen atom of the SO_3 group (which was not used in the previous interactions). In fact, the columns in **1** are connected to each other by very weak C−H···O interactions at 3.43(1) Å (Table 2).

At this point, it is important to mention that similar weak C−H···O contacts observed in a large variety of compounds have been considered as support of the supramolecular network.[9,16] On these basis, we propose for **1** that the strong N−H···O hydrogen bonds as well as the weak C−H···O inter- and intramolecular contacts through the SO_3 group of the counterion stabilize the crystal structure in the solid state forming a two-dimensional network.

Crystal Structures of 2 and 5

The molecular structures of complexes **2** and **5** are represented in parts a of Figure 2 and 3, respectively. The structures of the mononuclear cations $[M(Hpz^{bp2})_2]^+$ [M = Au (**2**), Ag (**5**)] show similar features. In both cases an angular molecular shape is formed by the two 3,5-disubstituted pyrazole groups bonded through the pyridinic nitrogen to the metal centre. In addition, each cationic unit has both heterocycles in a *cis*-orientation and is bonded to its corresponding counterion by two strong hydrogen bonds using both NH groups and two of the oxygen or fluorine atoms of the counterion, forming an eight-membered metallacycle (O−N−N−Au−N−N−O−S and F−N−N−Ag−N−N−F−B in **2** and **5**, respectively). The molecules have a quasi-linear N−M−N atomic sequence [176.3(4) in **2** and 170.1(1)° in **5**] and the average Au−N (2.02 Å) and Ag−N (2.12 Å) lengths (Table 1) in **2** and **5**, respectively, are similar to those found for related complexes containing pyrazole-type ligands.[10b,15b,15d,17−19] The main difference in the molecular structure of **2** and **5** is related to the orientation of the two pyrazole rings; they are almost parallel in **2** [dihedral angle of 4.5(5)°] but slightly tilted in **5** [dihedral angle of 24.6(1)°]. Other dihedral angles are collected in Table 3.

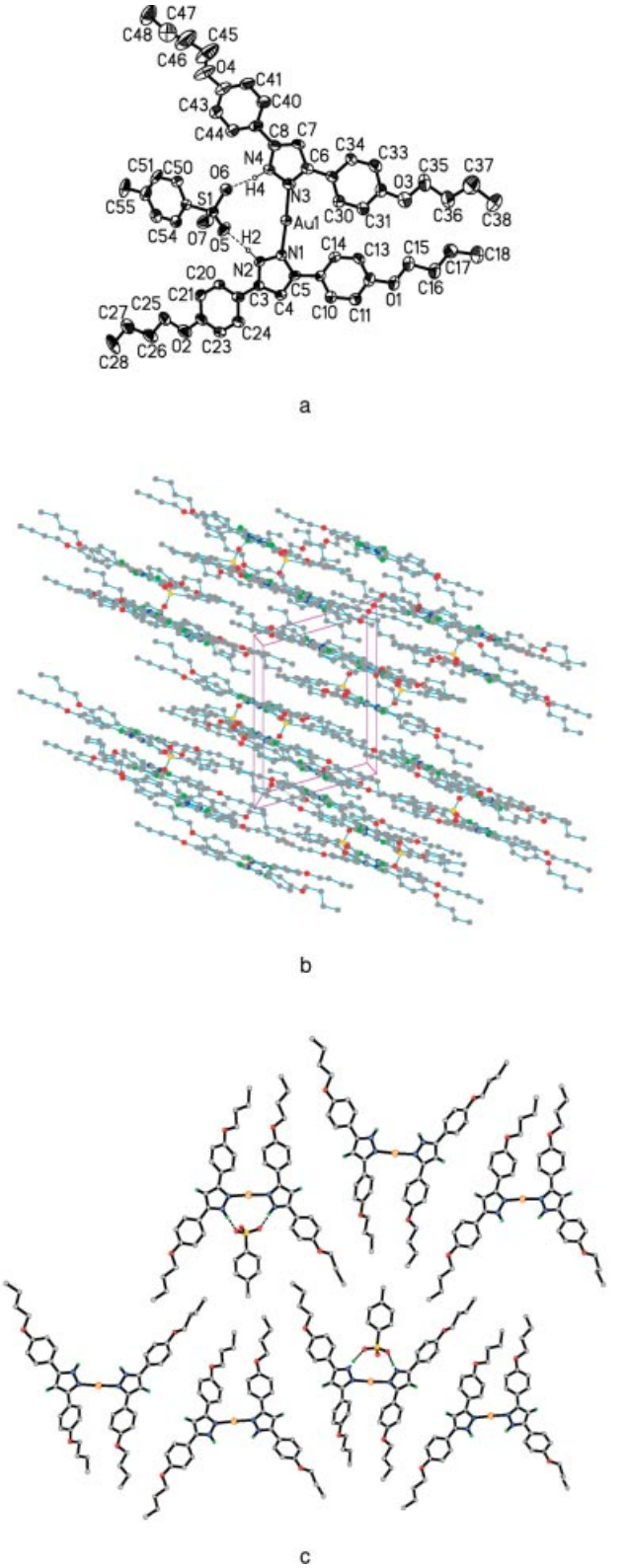

Figure 2. a) ORTEP plot of **2** at the 30% probability level; hydrogen atoms, except H2 and H4, and the labelling of some atoms have been omitted for clarity; b) view of the packing along the *b* axis showing the layer-like arrangement in the (1 0 $\bar{2}$) direction; c) view of the distribution in a layer

The crystal packing of **2** can be defined as layer-like (see b in Figure 2), with the sheet containing the cationic bis(pyrazole)gold units bonded to its corresponding counterion. The layers are situated in the (1 0 $\bar{2}$) direction. The cationic

Table 3. Dihedral angles (°) between selected planes[a] for **2** and **5**

	$[Au(Hpz^{bp2})_2](p\text{-}CH_3C_6H_4SO_3)$ (**2**)	$[Ag(Hpz^{bp2})_2]BF_4$ (**5**)
1−2	4.5(5)	24.6(2)
1−3	35.8(4)	39.9(2)
1−4	6.1(4)	21.8(2)
3−4	35.8(4)	61.5(2)
2−5	12.7(5)	27.1(2)
2−6	20.1(5)	3.6(2)
5−6	12.9(4)	29.1(2)

[a] Plane 1: N1−N2−C3−C4−C5; plane 2: N3−N4−C6−C7−C8; plane 3: C9−C10−C11−C12−C13−C14; plane 4: C19−C20−C21−C22−C23−C24; plane 5: C29−C30−C31−C32−C33−C34; plane 6: C39−C40−C41−C42−C43−C44.

entities in the layer adopt a head-to-tail alignment with no short contacts between them (see c in Figure 2). However, weak C−H···O interactions between the layers are observed which involve the free O7 atom of the counterion in a bifurcated form [C4···O7 ($-x + 2, -y + 1, -z + 1$) of 3.39(2) Å; C34···O7 ($x - 1/2, -y + 1/2, z - 1/2$) of 3.42(2) Å] (Table 2). These weak intermolecular contacts form a one-dimensional framework.

The crystal packing of **5** also presents similar characteristics, the layers being oriented in the (1 1 $\bar{4}$) direction (see b and c in Figure 3). Weak inter-layer interactions involving the BF_4^- counterion are also observed for this complex. These C−H···F interactions [C7···F3 ($-x, -y + 1, -z$) of 3.40(1) Å] (Table 2) also form a one-dimensional framework.

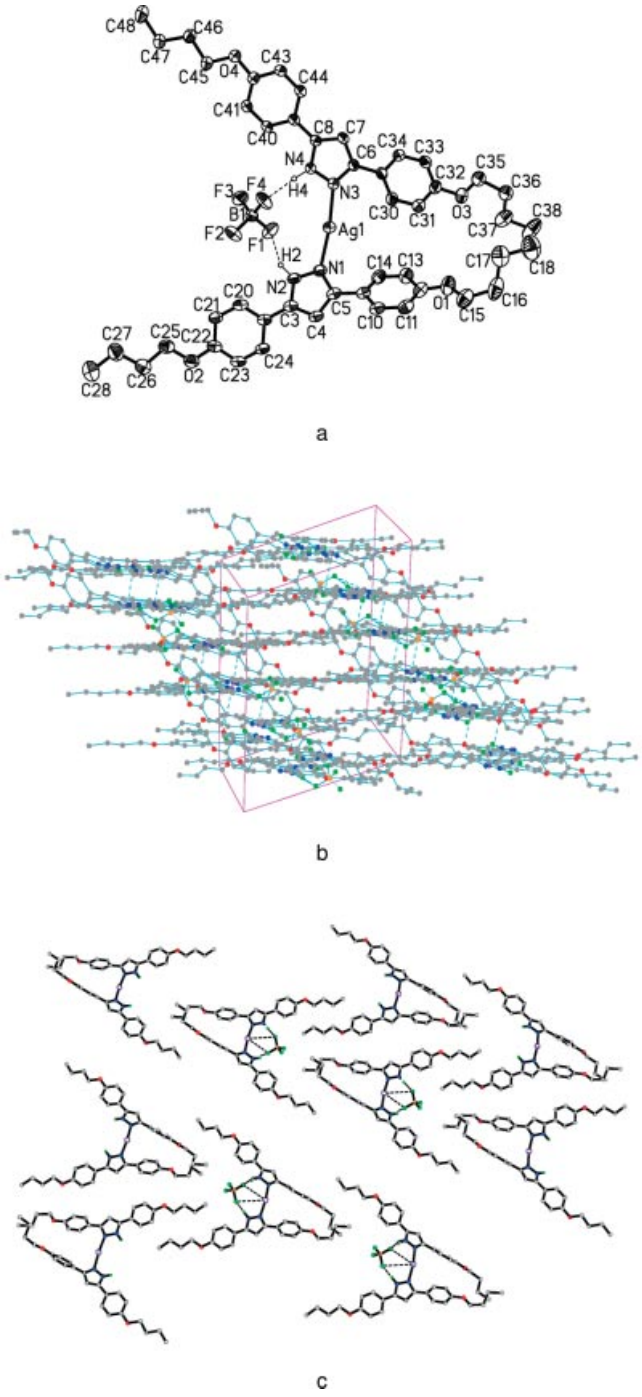

Figure 3. a) ORTEP plot of **5** at the 30% probability level; hydrogen atoms, except H2 and H4, and the labelling of some atoms have been omitted for clarity; b) view of the layer-like packing in the (1 1 $\bar{4}$) direction; c) view of the distribution in a layer

Crystal Structure of 8

The most relevant structure of complexes of the type $[M(Hpz^R)_2]X$ is that of complex **8**, where the pyrazole ligand is 3,5-dimethyl-4-nitropyrazole (Hpz^{NO2}) and X is $CF_3SO_3^-$. The structure of the cation $[Ag(Hpz^{NO2})_2]^+$ is shown in Figure 4 (see part a). The silver atom is coordinated to the two pyridinic nitrogen atoms of the heterocyclic ligands at ca. 2.17 Å (Table 1). The geometry around the metal is distorted lineal with an N1−Ag1−N4 angle of 163.67(9)°. Both pyrazole rings are almost parallel [angle of 4.8(1)°]. They show a *cis* orientation and are bonded through strong hydrogen bonds to the counterion [N2···O6: 2.771(3) Å; N5···O7: 2.852(4) Å] (Table 2). The nitro groups at the 4-position of the heterocyclic rings are almost coplanar with their own pyrazole planes [dihedral angles of 5.1(2) °and 6.3(4)°]; as a consequence the molecule shows a high planarity.

The structure built by the strongest interactions can be considered as that formed by dimers involving coordinative interactions Ag1···O5($-x + 1, -y + 1, -z + 1$) of 2.821(3) Å between the oxygen atom of the counterion (not implicated in the above hydrogen bond) and the silver centre of each molecule, giving rise to a closest distance of the metallic centres in the dimer of 3.7841(4) Å (b in Figure 4).

The next step in the packing is due to π···π contacts between dimers to form columns. The distances between atoms of the nitro groups from two neighbouring molecules, which are not implicated in the same dimer, are 3.268(4) Å [N6···N6($-x + 2, -y + 1, -z + 2$)] and 3.168(6) Å [O3···O3($-x + 2, -y + 1, -z + 2$)]. These are remarkably short distances and show the existence of a π···π interaction between those NO_2 groups,[16e−16g] which are situated in an alternating fashion. This mode of interaction

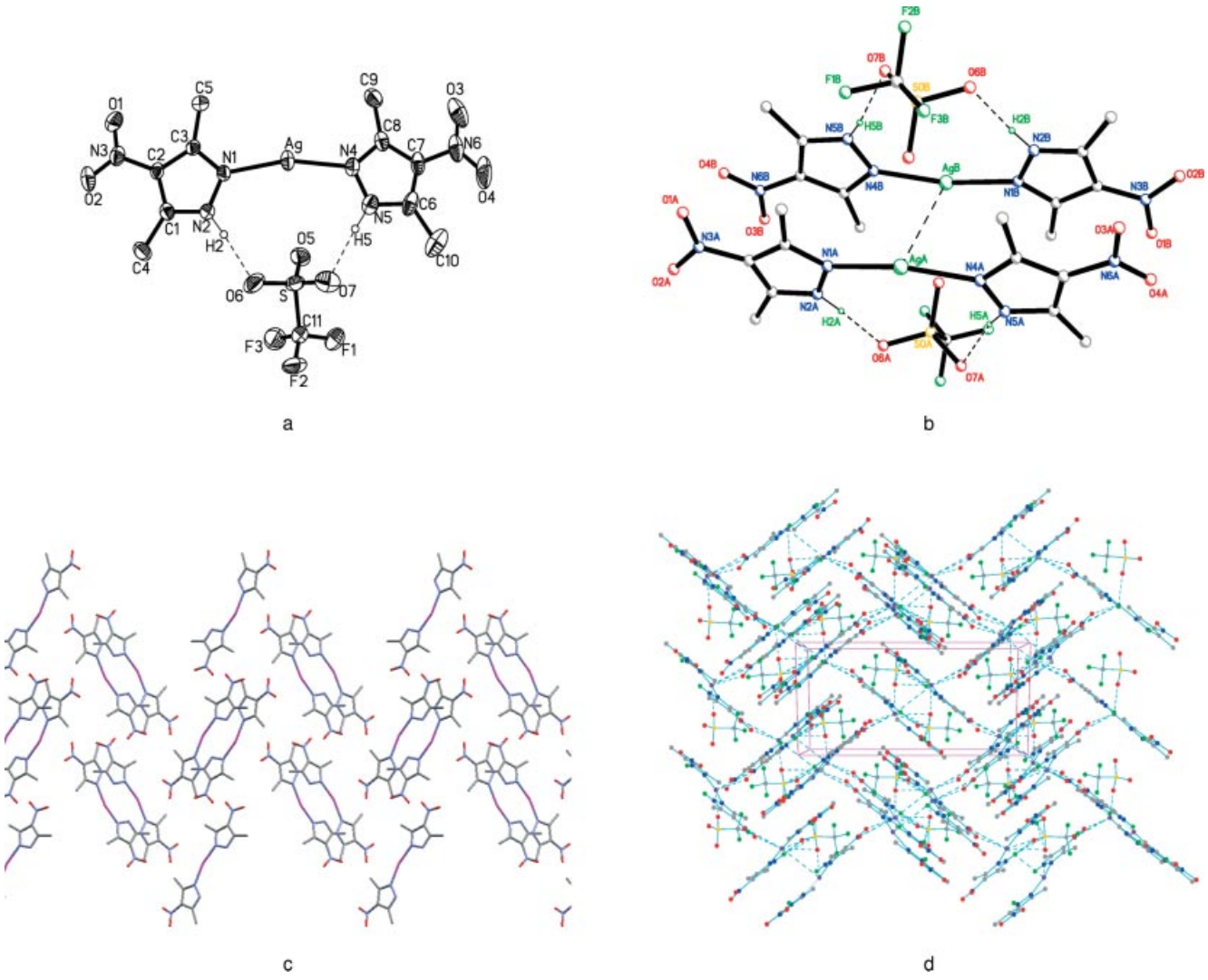

Figure 4. a) ORTEP plot of **8** at the 30% probability level; hydrogen atoms, except H2 and H4, and the labelling of some atoms have been omitted for clarity. b) View of the "dimeric unit" showing the close intermetallic approach. c) View of the two-dimensional network. d) View of the packing along the *c* axis showing the herringbone-type distribution

gives rise to the formation of columns along the (1 0 1) direction.

Finally, the columns are bonded each other to give a two-dimensional network which is extended parallel to the plane (1 0 $\bar{1}$) by long-range coordinative Ag1···O1(x + 1/2, $-y$ + 1/2, z + 1/2) interactions at 2.978(3) Å, produced between an oxygen atom of a NO_2 group, which is not implicated in the previously described π···π interactions, and the metal centre of neighbouring columns (c in Figure 4). This layer-like supramolecular structure can also be described as a herringbone-type arrangement of dimers connected through coordinative Ag···O interactions (d in Figure 4), the dimers being almost orthogonal to the layer as deduced by the angle defined between the C2−C7 line and the *a* axis of 77.01(3)°. No short interlayer distances are observed.

Concluding Remarks

The present work shows that Au/Ag complexes containing pyrazole-type ligands are efficient in constructing one- or two-dimensional networks. Complex **1** is formed by self-assembly of cationic $[Au(Hpz^{bp2})(PPh_3)]^+$ units and *p*-toluenesulfonate counterions, providing linear polymeric chains through N−H···O−S−O···H−C bridges containing both strong and weak hydrogen-bonding interactions. The geometry of the *p*-toluenesulfonate counterion appears to be responsible for the one-dimensional chain, which is different to the two-dimensional network produced by related interactions with the planar NO_3^- counterion. Therefore for cationic complexes containing one pyrazole ligand the one-dimensional supramolecular arrangement appears to be determined not only by the hydrogen-bonding interactions but also by the geometry of the counterion.

For complexes **2**, **5** and **8**, on the basis of the interactions between the counterion and the two NH-pyrazolic groups of each cationic unit, a polymeric chain was expected. However, the molecular conformation is responsible for a different assembly. In fact, in contrast to the observed *trans* disposition of the pyrazole groups found in the $[Ag(Hpz^{R2})_2]^+$

compounds (Hpz^{R2} = pyrazole, 3,5-dimethylpyrazole),[17] complexes **2**, **5** and **8** present a *cis* orientation, which gives rise to $[M(Hpz^{R2})_2]X$ unities containing the A−N−N−M−N−N−A−B metallacycle (A = donor atom of the counterion; B = central atom of the counterion). The molecular assembly in **2** and **5** is therefore determined by new, weak, intermolecular C−H···O/F contacts through the remaining O/F atoms of the counterion, its geometry being responsible for the polymeric one-dimensional network. Alternatively, an embracing effect of the cations around the anions could also be considered as driving force for encapsulation.

A special behaviour has been found for **8**. The presence of the nitro group on the pyrazoles plays the most relevant role in the formation of its polymeric architecture, which adopts a two-dimensional, herringbone-type structure involving both coordinative Ag···O and π···π interactions. The extensive hydrogen-bonds between the counterions and the cationic unities only determine the formation of dimers.

From the above results we can deduce that, in the absence of coordinative NO_2 groups as substituents on the pyrazole rings, which appear to be determinant for supramolecular interactions, the conformations of the complexes as well as intermolecular orientations between them and the counterions are responsible for the hydrogen-bonding contacts involved in the molecular assembly.

Experimental Section

Materials and Instrumentation: All commercial reagents were used as supplied. The ligands 3,5-bis(4-*n*-butoxyphenyl)pyrazole (Hpz^{bp2})[20] and 3,5-dimethyl-4-nitropyrazole (Hpz^{NO2})[21] as well as the starting gold(I) derivatives [AuCl(THT))][11] and [Au(*p*-$CH_3C_6H_4SO_3$)(PPh_3)][8d] were prepared by literature procedures. Commercial solvents were dried prior to use. Elemental analyses for carbon, hydrogen and nitrogen were carried out by the Microanalytical Service of the Complutense University. IR spectra were performed on a FTIR Nicolet Magna-550 spectrophotometer with samples as KBr pellets in the 4000−400 cm^{-1} region. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on Varian VXR-300 or Bruker DPX-300 spectrophotometers of the NMR Service of the Complutense University, from solutions in $CDCl_3$. Chemicals shifts δ(H) are given in ppm relative to $SiMe_4$, with the signal of the deuterated solvent as reference, and δ(P) in ppm relative to 85% H_3PO_4. Coupling constants (*J*) are in Hz. The ^1H and ^{31}P chemical shifts and coupling constants are accurate to ±0.01 ppm and ±0.3 Hz, respectively. Excitation and emission spectra of solid samples placed in capillary tubes were recorded on a Perkin−Elmer LS-55 luminescence spectrometer equipped with a R928 photomultiplier tube.

Synthesis of [Au(Hpz^{bp2})(PPh_3)](*p*-$CH_3C_6H_4SO_3$) (1): Hpz^{bp2} (18 mg, 0.05 mmol) was added to a solution of [Au(*p*-$CH_3C_6H_4SO_3$)(PPh_3)] (30 mg, 0.05 mmol) in freshly distilled THF (20 mL) and stirred for 24 h. The solvent was then removed in vacuo and the product was precipitated by addition of hexane/diethyl ether. Slow diffusion of diethyl ether into a dichloromethane/diethyl ether solution of this product gave colourless crystals suitable for crystallographic studies. $C_{48}H_{50}AuN_2O_5PS$ (994.90): calcd. C 57.95, H 5.02, N 2.82; found C 57.90, H 5.05, N 2.79. IR (KBr): $\tilde{\nu}$ = 3113 cm^{-1} ν(N−H), 1614 ν(C=N) + ν(C=C), 1174, 1162 and 1119 $\nu_d(SO_3)$, 1007 $\nu_s(SO_3)$. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.00 (t, 6 H, CH_3 Hpz^{bp2}), 1.48−1.56 (m, 4 H, CH_2 Hpz^{bp2}), 1.75−1.82 (m, 4 H, CH_2 Hpz^{bp2}), 2.27 (s, 3 H, *p*-$CH_3C_6H_4SO_3$), 3.97 (t, $^3J_{H,H}$ = 6.6 Hz, 4 H, OCH_2 Hpz^{bp2}) 6.71 (s, 1 H, H4 Hpz^{bp2}), 6.86 (d, $^3J_{H,H}$ = 8.5 Hz, 4 H, H_m Hpz^{bp2}), 6.95 (d, $^3J_{H,H}$ = 7.9 Hz, 2 H, *p*-$CH_3C_6H_4SO_3$), 7.60−7.48 (m, 15 H, PPh_3), 7.74 (d, $^3J_{H,H}$ = 7.9 Hz, 2 H, *p*-$CH_3C_6H_4SO_3$), 7.79 (d, $^3J_{H,H}$ = 8.5 Hz, 4 H, H_o Hpz^{bp2}) ppm. ^{31}P NMR (121.49 MHz, $CDCl_3$, 25 °C): δ = 31.06 (s) ppm.

Synthesis of [Au(Hpz^{bp2})$_2$](*p*-$CH_3C_6H_4SO_3$) (2): A THF solution (20 mL) of Hpz^{bp2} (116 mg, 0.32 mmol) was added to a solution of [AuCl(THT)] (50 mg, 0.16 mmol) in dry THF (15 mL), and finally a solution of silver(I) *p*-toluenesulfonate (44 mg, 0.16 mmol) in dry THF (15 mL) was also added. After 24 h of stirring, the resulting mixture was filtered through a plug of Celite and the obtained colourless clear filtrate was evaporated to dryness. The residue was dissolved in dichloromethane and precipitated with hexane. X-ray quality crystals were obtained by slow diffusion of hexane into a dichloromethane solution of the product. $C_{53}H_{63}AuN_4O_7S$ (1097.1): calcd. C 58.02, H 5.79, N 5.11; found C 58.00, H 5.68, N 5.03. IR (KBr): $\tilde{\nu}$ = 3112 cm^{-1} ν(N−H), 1613 ν(C=N) + ν(C=C), 1221, 1174 and 1124 $\nu_d(SO_3)$, 1037 $\nu_s(SO_3)$. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.01 (m, 12 H, CH_3 Hpz^{bp2}). 1.46−1.60 (m, 8 H, CH_2 Hpz^{bp2}), 1.75−1.86 (m, 8 H, CH_2 Hpz^{bp2}), 2.38 (s, 3 H, *p*-$CH_3C_6H_4SO_3$), 3.98 (t, $^3J_{H,H}$ = 6.5 Hz, 8 H, OCH_2 Hpz^{bp2}), 4.01 (t, $^3J_{H,H}$ = 6.5 Hz, 8 H, OCH_2 Hpz^{bp2}), 6.71 (d, $^4J_{H,H}$ = 2.0 Hz, 2 H, H4 Hpz^{bp2}), 6.79 (d, $^3J_{H,H}$ = 8.7 Hz, 4 H, H_m Hpz^{bp2}), 6.96 (d, $^3J_{H,H}$ = 8.7 Hz, 4 H, H_m Hpz^{bp2}), 7.21 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, *p*-$CH_3C_6H_4SO_3$), 7.76 (d, $^3J_{H,H}$ = 8.7 Hz, 4 H, H_o Hpz^{bp2}), 7.79 (d, $^3J_{H,H}$ = 8.7 Hz, 4 H, H_o Hpz^{bp2}), 7.96 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, *p*-$CH_3C_6H_4SO_3$), 14.54 (br. s, 2 H, NH Hpz^{bp2}) ppm.

Synthesis of [Au(Hpz^{bp2})$_2$](NO_3) (3): This compound was prepared by the same method previously described for **2**, from [AuCl(THT)] (50 mg, 0.16 mmol), $AgNO_3$ (27 mg, 0.16 mmol) and Hpz^{bp2} (116 mg, 0.32 mmol). $C_{46}H_{56}AuN_5O_7$ (987.96): calcd. C 55.92, H 5.71, N 7.09; found C 55.97, H 5.56, N 7.10. IR (KBr): $\tilde{\nu}$ = 3213 and 3141 cm^{-1} ν(N−H), 1614 ν(C=N) + ν(C=C), 1302 $\nu_{as}(NO_3)$. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.02 (m, 12 H, CH_3 Hpz^{bp2}), 1.46−1.60 (m, 8 H, CH_2 Hpz^{bp2}), 1.78−1.83 (m, 8 H, CH_2 Hpz^{bp2}), 3.99 (t, $^3J_{H,H}$ = 6.5 Hz, 4 H, OCH_2 Hpz^{bp2}), 4.03 (t, $^3J_{H,H}$ = 6.5 Hz, 4 H, OCH_2 Hpz^{bp2}), 6.75 (d, $^4J_{H,H}$ = 1.9 Hz, 2 H, H4 Hpz^{bp2}), 6.84 (d, $^3J_{H,H}$ = 8.9 Hz, 4 H, H_m Hpz^{bp2}), 7.02 (d, $^3J_{H,H}$ = 8.9 Hz, 4 H, H_m Hpz^{bp2}), 7.77 (d, $^3J_{H,H}$ = 8.9 Hz, 4 H, H_o Hpz^{bp2}), 7.80 (d, $^3J_{H,H}$ = 8.9 Hz, 4 H, H_o Hpz^{bp2}), 13.70 (br. s, 2 H, NH Hpz^{bp2}) ppm.

Synthesis of [Au(Hpz^{bp2})$_2$]$_2$(1,5nds) (1,5nds = 1,5-naphthalenedisulfonate) (4): Ag_2O (32 mg, 0.14 mmol) was added to an aqueous solution (25 mL) of 1,5-naphthalenedisulfonic acid (50 mg, 0.14 mmol) with constant stirring until all the solids had dissolved. Acetone was then added to this solution and the resulting white precipitate was filtered off, dried and identified as silver 1,5-naphthalenedisulfonate.

Compound **4** was obtained by the same procedure described for **2**, from [AuCl(THT)] (38 mg, 0.12 mmol), silver 1,5-naphthalenedisulfonate (60 mg, 0.12 mmol) and Hpz^{bp2} (87 mg, 0.24 mmol). $C_{102}H_{118}Au_2N_8O_{14}S_2$ (2138.2): calcd. C 57.30, H 5.56, N 5.24; found C 57.29, H 5.39, N 5.19. IR (KBr): $\tilde{\nu}$ = 3115 cm^{-1} ν(N−H), 1612 ν(C=N) + ν(C=C), 1178 $\nu_d(SO_3)$, 1031 $\nu_s(SO_3)$, 607 $\delta_s(SO_3)$. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.93 (t, $^3J_{H,H}$ = 7.3 Hz, 12 H, CH_3 Hpz^{bp2}), 1.02 (t, $^3J_{H,H}$ = 7.3 Hz, 12 H, CH_3 Hpz^{bp2}),

1.41−1.58 (m, 16 H, CH_2 Hpz^{bp2}), 1.69−1.84 (m, 16 H, CH_2 Hpz^{bp2}), 3.91 (t, $^3J_{H,H}$ = 6.5 Hz, 8 H, OCH_2 Hpz^{bp2}), 3.97 (t, $^3J_{H,H}$ = 6.5 Hz, 8 H, OCH_2 Hpz^{bp2}), 6.70 (s, 4 H, H4 Hpz^{bp2}), 6.79 (d, $^3J_{H,H}$ = 8.7 Hz, 8 H, H_m Hpz^{bp2}), 6.82 (d, $^3J_{H,H}$ = 8.7 Hz, 8 H, H_m Hpz^{bp2}), 7.47 (t, 2 H, 1,5nds), 7.72 (d, $^3J_{H,H}$ = 8.7 Hz, 8 H, H_o Hpz^{bp2}), 7.77 (d, $^3J_{H,H}$ = 8.7 Hz, 8 H, H_o Hpz^{bp2}), 8.44 (d, $^3J_{H,H}$ = 6.5 Hz, 2 H, 1,5nds), 9.30 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, 1,5nds), 14.53 (s, 4 H, NH Hpz^{bp2}) ppm.

Synthesis of $[Ag(Hpz^{bp2})_2](BF_4)$ (5): $AgBF_4$ (19 mg, 0.10 mmol) was added under nitrogen to a solution of Hpz^{bp2} (71 mg, 0.20 mmol) in dry THF (10 mL). After 24 h of stirring, the solvent was removed in vacuo, giving rise to an oil from which a white solid was isolated after addition of dichloromethane and pentane. This product was crystallized by diffusion of hexane into a dichloromethane solution. $C_{46}H_{56}AgBF_4N_4O_4$ (923.63): calcd. C 59.83, H 6.11, N 6.07; found C 59.64, H 6.10, N 5.94. IR (KBr): $\tilde{\nu}$ = 3308 cm^{-1} ν(N−H), 1614 ν(C=N) + ν(C=C), 1067 and 1037 ν(BF). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.00 (t, $^3J_{H,H}$ = 7.3 Hz, 12 H, CH_3 Hpz^{bp2}), 1.40−1.60 (m, 8 H, CH_2 Hpz^{bp2}), 1.70−1.90 (m, 8 H, CH_2 Hpz^{bp2}), 3.99 (t, $^3J_{H,H}$ = 6.6 Hz, 8 H, OCH_2 Hpz^{bp2}), 6.69 (s, 2 H, H4 Hpz^{bp2}), 6.70−7.00 (br. s, 8 H, H_m Hpz^{bp2}), 7.62 (d, $^3J_{H,H}$ = 8.8 Hz, 8 H, H_o Hpz^{bp2}), 11.95 (s, 2 H, NH Hpz^{bp2}) ppm. ^1H NMR (300 MHz, $CDCl_3$, −40 °C): δ = 0.95 ppm (t, $^3J_{H,H}$ = 7.2 Hz, 6 H, CH_3 Hpz^{bp2}), 0.96 (t, $^3J_{H,H}$ = 7.2 Hz, 6 H, CH_3 Hpz^{bp2}), 1.40−1.51 (m, 8 H, CH_2 Hpz^{bp2}), 1.68−1.80 (m, 8 H, CH_2 Hpz^{bp2}), 3.86 (t, $^3J_{H,H}$ = 6.6 Hz, 4 H, OCH_2 Hpz^{bp2}), 3.94 (t, $^3J_{H,H}$ = 6.6 Hz, 4 H, OCH_2 Hpz^{bp2}), 6.67 (s, 2 H, H4 Hpz^{bp2}), 6.72 (d, $^3J_{H,H}$ = 8.4 Hz, 4 H, H_m Hpz^{bp2}), 6.95 (d, $^3J_{H,H}$ = 8.7 Hz, 4 H, H_m Hpz^{bp2}), 7.53 (d, $^3J_{H,H}$ = 8.7 Hz, 4 H, H_o Hpz^{bp2}), 7.60 (d, $^3J_{H,H}$ = 8.4 Hz, 4 H, H_o Hpz^{bp2}), 11.86 (s, 2 H, NH Hpz^{bp2}) ppm.

Synthesis of $[Ag(Hpz^{bp2})_2](CF_3SO_3)$ (6): This compound was prepared in a similar way to **5**, from $AgCF_3SO_3$ (21 mg, 0.08 mmol) and Hpz^{bp2} (60 mg, 0.16 mmol). The resulting white solid was purified by washing with dichloromethane. $C_{47}H_{56}AgF_3N_4O_7S$ (985.92): calcd. C 57.26, H 5.73, N 5.68; found C 57.58, H 5.73, N 5.62. IR (KBr): $\tilde{\nu}$ = 3227 cm^{-1} ν(N−H), 1615 ν(C=N) + ν(C=C), 1226 $\nu_s(CF_3)$, 1028 $\nu_s(SO_3)$. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.00 (t, $^3J_{H,H}$ = 7.3 Hz, 12 H, CH_3 Hpz^{bp2}), 1.43−1.61 (m, 8 H, CH_2 Hpz^{bp2}), 1.73−1.87 (m, 8 H, CH_2 Hpz^{bp2}), 3.98 (br. s, 8 H, OCH_2 Hpz^{bp2}), 6.69 (s, 2 H, H4 Hpz^{bp2}), 6.70−7.00 (br. s, 8 H, H_m Hpz^{bp2}), 7.63 (d, $^3J_{H,H}$ = 8.0 Hz, 8 H, H_o Hpz^{bp2}), 12.66 (s, 2 H, NH Hpz^{bp2}) ppm. ^1H NMR (300 MHz, $CDCl_3$, −40 °C): δ = 0.95 (t, $^3J_{H,H}$ = 6.9 Hz, 12 H, CH_3 Hpz^{bp2}), 1.39−1.51 (m, 8 H, CH_2 Hpz^{bp2}), 1.69−1.80 (m, 8 H, CH_2 Hpz^{bp2}), 3.83 (t, $^3J_{H,H}$ = 5.1 Hz, 4 H, OCH_2 Hpz^{bp2}), 3.95 (t, $^3J_{H,H}$ = 5.4 Hz, 4 H, OCH_2 Hpz^{bp2}), 6.67 (s, 2 H, H4 Hpz^{bp2}), 6.69 (d, $^3J_{H,H}$ = 8.7 Hz, 4 H, H_m Hpz^{bp2}), 6.95 (d, $^3J_{H,H}$ = 8.7 Hz, 4 H, H_m Hpz^{bp2}), 7.53 (d, $^3J_{H,H}$ = 8.4 Hz, 4 H, H_o Hpz^{bp2}), 7.61 (d, $^3J_{H,H}$ = 8.4 Hz, 4 H, H_o Hpz^{bp2}), 12.54 (s, 2 H, NH Hpz^{bp2}) ppm.

Synthesis of $[Ag(Hpz^{NO2})_2](BF_4)$ (7): $AgBF_4$ (35 mg, 0.18 mmol) was added under nitrogen to a solution of Hpz^{NO2} (131 mg, 0.36 mmol) in dry acetonitrile (25 mL). After stirring for 24 h, the solvent was removed under vacuum to give an oil from which a white solid was isolated after addition of dichloromethane and pentane. $C_{10}H_{14}AgBF_4N_6O_4$ (476.93): calcd. C 25.18, H 2.96, N 17.62; found C 25.34, H 2.97, N 17.72. IR (KBr): $\tilde{\nu}$ = 3175 cm^{-1} ν(N−H), 1595 ν(C=N) + ν(C=C), 1506 $\nu_{as}(NO)$, 1363 $\nu_s(NO)$, 1034 ν(BF). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.71 (s, 12 H, CH_3 Hpz^{NO2}), 11.67 (s, 2 H, NH Hpz^{NO2}) ppm.

Table 4. Crystal and refinement data for **1**, **2**, **5** and **8**

	1	**2**	**5**	**8**
Formula	$C_{48}AuH_{50}N_2O_5PS$	$C_{53}H_{63}AuN_4O_7S$	$C_{46}H_{56}AgBF_4N_4O_4$	$C_{11}H_{14}AgF_3N_6O_7S$
Mol. mass	994.90	1097.10	923.63	539.21
Crystal system	triclinic	monoclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a (Å)	11.264(1)	11.518(1)	9.1023(6)	8.8207(6)
b (Å)	13.808(1)	28.170(2)	14.576(1)	18.165(1)
c (Å)	14.633(1)	16.315(1)	19.180(1)	12.3303(8)
α (°)	95.161(1)		111.201(1)	
β (°)	101.889(1)	106.830(2)	92.791(1)	106.143(1)
γ (°)	100.809(1)		105.387(1)	
V (Å^3)	2167.8(3)	5066.9(7)	2257.7(3)	1897.7(2)
Z	2	4	2	4
F(000)	1004	2240	960	1072
D_c (g cm^{-3})	1.524	1.438	1.359	1.887
T (K)	296(2)	296(2)	296(2)	296(2)
μ(Mo-K_α) (mm^{-1})	3.527	2.999	0.509	1.249
Crystal size (mm)	0.35 × 0.12 × 0.04	0.32 × 0.26 × 0.12	0.37 × 0.20 × 0.15	0.38 × 0.18 × 0.12
Scan technique	φ and ω	φ and ω	φ and ω	φ and ω
Data collected	(−14,−14,−19) to (14,18,19)	(−12,−33,−14) to (13,33,19)	(−10,−15,−22) to (10,17,17)	(−8,−22,−15) to (11,20,13)
θ (°)	1.44−28.72	1.45−25.00	1.15−25.00	2.05−26.37
Refls. collected	13974	26518	11769	10664
Refls. indep.	9846 (R_{int} = 0.072)	8933 (R_{int} = 0.084)	7845 (R_{int} = 0.030)	3870 (R_{int} = 0.037)
Data, restraints, parameters	9846/0/527	8933/13/601	7845/16/545	3870/0/216
Refls. observed [$(I) > 2\sigma(I)$]	5854	3716	4737	3068
GOF (F^2)	0.862	0.856	0.903	1.031
$R(F)$[a]	0.054	0.048	0.043	0.033
$wR(F^2)$ (all data)[b]	0.118	0.133	0.111	0.087
Largest residual peak (e·Å^{-3})	1.321	1.359	0.472	0.775

[a] $\Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Synthesis of $[Ag(Hpz^{NO2})_2](CF_3SO_3)$ (8): The synthetic procedure for **8** was analogous to that used for **5** from $AgCF_3SO_3$ (46 mg, 0.18 mmol) and Hpz^{NO2} (51 mg, 0.36 mmol). Crystals were obtained by the slow diffusion of hexane into a dichloromethane solution of the compound. $C_{11}H_{14}AgF_3N_6O_7S$ (539.21): calcd. C 24.50, H 2.62, N 15.59; found C 24.57, H 2.59, N 15.57. IR (KBr): $\tilde{\nu}$ = 3205 and 3128 cm^{-1} ν(N−H), 1600 ν(C=N) + ν(C=C), 1509 ν_{as}(NO), 1366 ν_s(NO), 1252 $\nu_d(SO_3)$, 1230 $\nu_s(CF_3)$, 1040 $\nu_s(SO_3)$. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.70 (s, 12 H, CH_3 Hpz^{NO2}), 12.50 (s, 2 H, NH Hpz^{NO2}) ppm.

X-Ray Structure Determinations: Crystals suitable for X-ray experiments were obtained from dichloromethane/diethyl ether for **1** or dichloromethane/hexane for **2**, **5** and **8**. Data collection was carried out at room temperature on a Bruker Smart CCD diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) operating at 50 kV and 20 mA. In all cases data were collected over a hemisphere of the reciprocal space by combination of three exposure sets. Each exposure covered 0.3 in ω. The cell parameters were determined and refined by least-squares fit of all reflections collected. The first 50 frames were recollected at the end of the data collection to monitor crystal decay; no appreciable decay was observed. A summary of the fundamental crystal and refinement data is given in Table 4.

The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2.[22] All non-hydrogen atoms were refined anisotropically, with some exceptions due to the thermal and non-resolvable positional disorder found for some atoms. For the C47 atom in **2**, only its coordinates were refined. The fluorine and oxygen atoms in **8** were refined anisotropically over two cycles and in the subsequent cycles their thermal parameters were kept constant. Additionally, for **2** and **5** some carbon atoms of the butoxy chain were refined with geometrical restraints and a variable common carbon−carbon distance. For **5** the BF_4^- group was also refined with geometrical restraints and a variable common boron−fluorine distance. Hydrogen atoms bonded to the nitrogen atoms were located in a Fourier synthesis, included and their coordinates fixed or refined. The remaining hydrogen atoms were included in calculated positions and refined as riding on their respective carbon atoms and the thermal parameters related to the bonded atoms. The largest residual peaks in the final difference map are located close to the metal atoms.

CCDC-226053−226056 (for compounds **1**, **2**, **5** and **8**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 (0)1223 336033; E-mail: deposit@ccdc.cam.ac.uk].

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