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Substituent Effects on the Supramolecular Aggregation of Ag^I-Pyrazolato Trimers

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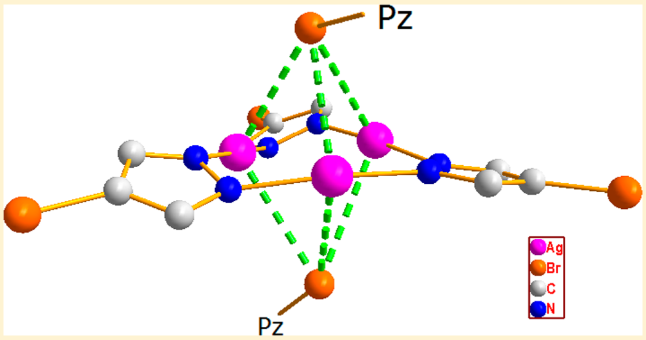
Supporting Information

ABSTRACT: The interplay of argentophilic and dipolar (π-acid···base) interactions, on one hand, and the presence or absence of interstitial solvent molecules, on the other, determines the supramolecular organization of trinuclear silver-pyrazolato complexes in the solid state. The crystal structures of one gold and six silver metallacyclic complexes of the type $[M^I(\mu\text{-pz}^*)]_3$, where pz* are the substituted pyrazolato anions 3,5-Ph_2-pz, 3-Me-5-Ph-pz, 4-Br-3,5-Ph_2-pz, 4-Br-3-^{t}Bu-pz and 3-(*o*-Cl-C_6H_4)-pz and M = Ag and Au, are discussed in the context of their supramolecular organization. Two silver complexes, for which the π-acid character of their Ag_3-faces is maximized by their peripheral electron-withdrawing substituents, show crystal packing dominated by short Ag_3···Br contacts, the first structural manifestation of supramolecular structure via dipolar interactions involving the tunable π-acidity of the Ag_3-face.



■ INTRODUCTION

Supramolecular structures depend on the interplay of a host of weak intermolecular interactions.[1] In a biological context and in aqueous media in general, H-bonds of 4−10 kcal/mol are typically the dominant structure determining factor. In the absence of H-bonds, however, weaker dipolar and van der Waals interactions in the range of 2−5 kcal/mol manifest themselves in the three-dimensional assemblies, and metallophilic interactions of comparable strength can be competitive with the latter.[2] Because of the weak forces involved in such assemblies, more than one structure is often possible with the same components (polymorphs), as molecules tumble from one supramolecular arrangement to another, each one representing a kinetically trapped local energy minimum.[3]

Trinuclear group-11 metal pyrazolato complexes have been a convenient platform to study the interplay of weak intermolecular forces in crystalline compounds.[4] The crystal packing of sterically unhindered gold pyrazolates is dictated by aurophilic interactions.[5] However, when long aliphatic substituents were introduced to the pyrazoles, columnar gold pyrazolate structures resulted.[6] Wider structural variety is known in silver pyrazolates, in which the argentophilic interactions, weaker than the aurophilic ones, can be easier to overcome by the sum of weak dipolar interactions.[7,8] So, supramolecular arrangements in which silver−silver contacts are maximized are known, just as are ones containing a combination of silver−silver and dipolar interactions, as well as arrangements based solely on dipolar and van der Waals contacts.[9−12] Two independent studies have suggested that silver pyrazolato complex aggregates can persist even in solution.[13,14] A detailed computational study of triangular group-11 metal complexes (including pyrazolates) has shown that the π-acidity/basicity of their M_3-faces — and consequently, their supramolecular structures — depends on both the nature of the metal and the peripheral substituents of the bridging ligands. Silver was found, in that study, to be the most acidic of the three metals, whose acidities increase for bridges with electron-withdrawing substituents and decrease for electron-releasing ones.[15] This has been clearly demonstrated experimentally in the cases of silver pyrazolates with trifluoromethyl substituents.[16,17] On the other hand, several cyclic trinuclear gold(I) imidazolates and carbeniates display π-basicity, forming stacks with π-acids.[18−23] As supramolecular architectures are intimately associated with the physicochemical and biological properties of materials, such as luminescence and bioavailability,[24,25] the exploration of the possible aggregation modes of a given motif, with a long-term view of gaining predictive capacity over it, is a worthwhile endeavor.

We report here the synthesis and crystallographic characterization of five new silver pyrazolato trimers with the general formula $[Ag(\mu\text{-pz}^*)]_3$ (Scheme 1), where pz* = peripherally substituted pyrazolato anion: pz* = 3,5-Ph_2-pz (**1**), 3-Me-5-Ph-pz (**2**), 4-Br-3,5-Ph_2-pz (**3**), 4-Br-3-^{t}Bu-pz (**4**) and 3-(*o*-Cl-C_6H_4)-pz (**5**). We also report the methanol solvate of **2** (**2**·MeOH) and the gold analogue of **3** (**3-Au**).

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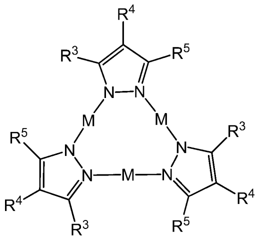
Scheme 1.



1: R^3 = Ph, R^4 = H, R^5 = Ph, M = Ag
2: R^3 = Me, R^4 = H, R^5 = Ph, M = Ag
3: R^3 = Ph, R^4 = Br, R^5 = Ph, M = Ag
3-Au: R^3 = Ph, R^4 = Br, R^5 = Ph, M = Au
4: R^3 = ^{t}Bu, R^4 = Br, R^5 = H, M = Ag
5: R^3 = *o*-Cl-C_6H_4, R^4 = R^5 = H, M = Ag

EXPERIMENTAL SECTION

3,5-Diphenylpyrazole and 3(5)-methyl-5(3)-phenylpyrazole, obtained from commercial sources, were used as received, while 4-bromo-3,5-diphenylpyrazole,[26] 3(5)-*tert*-butylpyrazole, and 3(5)-*ortho*-chlorophenylpyrazole were prepared by literature methods.[27] All solvents were distilled and stored over molecular sieves prior to use. The ^{1}H-NMR spectra were recorded with a Bruker AVANCE DPX-300 spectrometer.

Synthesis of 4-Bromo-3(5)-*tert*-butyl-1*H*-pyrazole (4-Br-5-^{t}Bu-pzH). 3(5)-*tert*-Butylpyrazole (0.71 g, 5.8 mmol) was dissolved in 50 mL of CH_2Cl_2. Bromine (0.92 g, 5.8 mmol) was added dropwise under stirring until the yellow color of bromine persisted in solution. The resulting solution was refluxed for 30 min and cooled to ambient temperature. Concentrated aqueous NaOH solution was added to the reaction solution until it was slightly basic, resulting in precipitation of an off-white solid. The mixture was filtered under suction, and the residue was washed with cold water and air-dried. To the dry residue was added a small amount of diethyl ether, and the suspension was filtered under suction to remove insoluble NaBr. Removal of ether from the filtrate left a pale yellow powder of 4-bromo-3-*tert*-butylpyrazole in 75% yield. mp 122−123 °C (recrystallized from petroleum ether).

Calcd. for $C_7H_{11}N_2Br$: C, 41.40; H, 5.46; N, 13.79%. Found: C, 40.67; H, 5.60; N, 13.61%. ^{1}H-NMR: ($CDCl_3$, ppm) δ = 1.40 (s, 9H, ^{t}Bu), 7.49 (s, 1H, 5-pz), 11.16 (s, br, 1H, N−H).

[Ag(μ-3,5-Ph$_2$-pz)]$_3$·1/4C$_6$H$_{14}$ (1·1/4C$_6$H$_{14}$). A CH_2Cl_2/hexane solution of [Ag(μ-3,5-Ph$_2$-pz)]$_3$[7,8] was allowed to slowly evaporate at −5 °C for several weeks, yielding colorless large blocks of **1**·1/4C_6H_{14}.

Synthesis of [Ag(μ-3-Me-5-Ph-pz)]$_3$ (2). 3-Me-5-Ph-pzH (47 mg, 0.3 mmol) and AgPhCOO (69 mg, 0.3 mmol) were mixed together in 10 mL of dry THF. The mixture was stirred for several hours at room temperature to give a turbid solution. The resulting solution was filtered under suction, and the white residue was washed with ether. The white solid was taken up in CH_2Cl_2, and a small amount of PPh$_3$ (33 mg, 0.13 mmol) was added to facilitate the crystallization process. Slow diethylether diffusion in a vial containing the above solution yielded colorless needles in 37% yield after several days.

Calcd. for $C_{30}H_{27}Ag_3N_6$: C, 45.46; H, 3.44; N, 10.61%. Found: C, 45.54; H, 3.52; N, 10.49%.

Single crystals of **2**·MeOH were obtained by carefully layering methanol over the surface of a CH_2Cl_2 solution of **2**.

Synthesis of [Ag(μ-4-Br-3,5-Ph$_2$-pz)]$_3$ (3). To a THF solution (10 mL) of Ag(OCOPh) (415 mg, 1.83 mmol) was added 4-Br-3,5-Ph$_2$-pzH (545 mg, 1.83 mmol). The clear reaction mixture was stirred for 18 h, the solvent was reduced to approximately 1/5 of its volume, and the product was crushed out as a white powder by addition of Et$_2$O. The supernatant was removed and the product was washed with EtOH and Et$_2$O. Yield: 70%. Single crystals of **3**·1/2CH_2Cl_2 suitable

Table 1. Crystallographic Data

	1·1/4C_6H_{14}	2	2·CH_3OH	3·1/2CH_2Cl_2	3-Au·CH_2Cl_2	4	5
formula	$C_{45}H_{33}Ag_3N_6$·1/4C_6H_{14}	$C_{60}H_{54}Ag_6N_{12}$	$C_{30}H_{27}Ag_3N_6$·CH_4O	$C_{45}H_{30}Ag_3Br_3N_6$·1/2CH_2Cl_2	$C_{45}H_{30}Au_3Br_3N_6$·CH_2Cl_2	$C_{21}H_{30}Ag_3Br_3N_6$	$C_{27}H_{18}Ag_3Cl_3N_6$
mol. wt.	1024.47	1590.37	827.23	1260.56	1570.31	929.85	865.43
crystal system	triclinic	triclinic	triclinic	monoclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1$	$C2/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.806(7)	14.082(4)	7.617(6)	10.289(2)	30.132(4)	11.144(18)	7.624(6)
b (Å)	13.182(8)	15.035(4)	14.224(11)	27.383(6)	17.197(2)	11.983(9)	14.456(12)
c (Å)	14.862(9)	16.149(5)	15.311(12)	15.356(3)	17.427(2)	13.076(10)	14.713(12)
α (deg)	100.076(7)	115.984(6)	108.204(9)			113.598(10)	114.799(8)
β (deg)	101.519(7)	100.687(5)	102.225(10)	91.952(4)	98.396(2)	100.645(13)	91.273(2)
γ (deg)	107.103(7)	100.292(6)	90.820(10)			101.305(13)	94.630(10)
V (Å^3)	2098(2)	2886.4(14)	1534(2)	4324.0(16)	8933.2(19)	1500(3)	1464(2)
Z	2	2	2	4	8	2	2
T (K)	298	298	298	298	298	298	298
$\rho_{calcd.}$ (Mg/m^3)	1.582	1.830	1.791	1.936	2.335	2.058	1.942
μ(mm^{-1})	1.425	2.045	1.930	4.220	12.674	5.953	2.288
reflns collected	12369	12875	8723	19280	19438	9676	8756
reflns unique	8687 (R_{int} = 0.0266)	8271 (R_{int} = 0.0604)	6420 (R_{int} = 0.0307)	12379 (R_{int} = 0.0730)	6427 (R_{int} = 0.0371)	6167 (R_{int} = 0.0267)	6079 (R_{int} = 0.0200)
reflns obs/param	7153/514	4158/637	4597/375	6309/844	5233/542	3733/307	3765/353
final R indices	R_1 = 0.0349	R_1 = 0.0529	R_1 = 0.0440	R_1 = 0.0595	R_1 = 0.0254	R_1 = 0.0526	R_1 = 0.0577
[$I > 2\sigma(I)$]	wR_2 = 0.1155	wR_2 = 0.1136	wR_2 = 0.1178	wR_2 = 0.0991	wR_2 = 0.0540	wR_2 = 0.1324	wR_2 = 0.1628
Flack param				0.040(15)			
S	1.055	0.908	0.977	0.874	1.048	1.107	1.030
$\Delta\rho_{max}$ (e Å^{-3})	1.000	0.805	0.653	0.760	1.308	0.839	1.522

for X-ray work were obtained by slow diffusion of Et_2O into a CH_2Cl_2 solution of **3**.

Calcd. for $C_{45}H_{30}Ag_3Br_3N_6$: C, 44.56; H, 2.50; N, 6.93%. Found: C, 44.05; H, 2.55; N, 6.68%. ^{1}H-NMR: (CD_2Cl_2, ppm) $\delta = 7.20$ (t, 2H, *m*-Ph), 7.32 (t, 1H, *p*-Ph), 7.55 (d, 2H, *o*-Ph).

Synthesis of [Au(μ-4-Br-3,5-Ph_2-pz)]$_3$ (3-Au). To a clear THF solution (5 mL) of AuClTHT (0.1 mmol, 32 mg) and 4-Br-3,5-Ph_2pzH (0.1 mmol, 30 mg) was added an equivalent amount of Et_3N. The reaction mixture was stirred for 12 h, the solvent was reduced to approximately 1/5 of its volume, and the product was crushed out as a white powder by addition of hexane. The supernatant was removed, and the residue was dissolved in CH_2Cl_2. After filtration, Et_2O was allowed to slowly diffuse into the filtrate, affording colorless prisms of the product. Yield: 60%.

Calcd. for $C_{45}H_{30}Au_3Br_3N_6$: C, 36.36; H, 2.00; N, 5.66%. Found: C, 35.91; H, 2.09; N, 5.48%.

Synthesis of [Ag(μ-4-Br-3-^{t}Bu-pz)]$_3$ (4). 4-Br-3-^{t}Bu-pzH (0.5 mmol, 102 mg) and $AgNO_3$ (0.5 mmol, 85 mg) were mixed in 10 mL of MeCN. After stirring for 10 min, a methanol solution (5 mL) of equivalent Et_3N was added dropwise. Soon afterward, white precipitate appeared. The mixture was stirred for another 2 h at room temperature and then filtered with suction. The white powder obtained was washed by MeOH and then Et_2O. Yield: 65%. Single crystals of **4** suitable for X-ray work were obtained by slow diffusion of Et_2O into a CH_2Cl_2 solution of **4**.

Calcd. for $C_{21}H_{30}Ag_3Br_3N_6$: C, 27.13; H, 3.25; N, 9.04%. Found: C, 26.92; H, 3.30; N, 8.94%. ^{1}H-NMR: ($CDCl_3$, ppm) $\delta = 1.57$ (s, 27H, ^{t}Bu), 7.40 (s, 3H, 5-pz).

Synthesis of [Ag(μ-3-(*o*-Cl-C_6H_4)-pz)]$_3$ (5). This compound was prepared as **3**. Yield: 81%.

Calcd. for $C_{27}H_{18}Ag_3Cl_3N_6$: C, 38.04; H, 2.13; N, 9.86%. Found: C, 37.91; H, 2.22; N, 9.90%. ^{1}H-NMR: (CD_2Cl_2, ppm) $\delta = 6.65$ (d, 3H, 4-pz), 7.28–7.42 (m, 9H), 7.45–7.60 (m, 6H).

X-ray Crystallography. Diffraction intensities were collected on a Bruker Smart CCD 1K diffractometer with graphite-monochromated Mo-Kα radiation (0.71073 Å). Absorption corrections were applied using the multiscan program. The structures were solved by direct methods and refined by least-squares techniques using the SHELXS-97 and SHELXL-97 programs.[28] All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were generated geometrically. The phenyl groups of **2** have been refined as rigid hexagons. Crystallographic data are summarized in Table 1.

■ RESULTS AND DISCUSSION

Synthesis. All the silver trimers were prepared by either reaction of silver benzoate with pyrazole or reaction of silver nitrate with pyrazoles in the presence of triethylamine. Benzoate here acts in the same way as Et_3N, namely, a base required to deprotonate pyrazole.

General Description of the Structures of the Trimer. All six silver-pyrazolato structures feature nine-membered [Ag–N–N]$_3$ metallacycles with Ag–N bond lengths being 2.049(15)–2.132(14) Å. All Ag-atoms are two-coordinate in approximately linear geometry, as indicated by N–Ag–N angles in the 169.31(9)–179.8(2)° range. The [Ag–N–N]$_3$ metallacycles are approximately planar with smaller deviations from ideal geometry for **2**, **2**·MeOH and **5** and larger ones for **1**, **3** and **4**: The mean deviations from the planes defined by three Ag-atom and six pyrazole N-atoms are 0.2457 Å for **1**; 0.0530 Å and 0.0523 Å for **2**; 0.0259 Å for **2**·MeOH; 0.1304 Å and 0.1460 Å for **3**; 0.1090 Å for **4**; 0.0623 Å for **5**, respectively. For the gold-pyrazolato complex **3-Au**, the corresponding value is 0.0344 Å. Complete tables of bond lengths and angles for all seven complexes are in the Supporting Information section (Tables S1 and S2). For structures **2**, **2**·MeOH, **4** and **5**, involving unsymmetrically substituted pyrazoles, there are two possible geometrical isomers of each: a 3-fold symmetric and an unsymmetrical one with approximate C_{3h} and C_s point group symmetries, respectively. For all four complexes, only the C_{3h} isomer was found in the solid state.

Crystal Packing Patterns. Compound **1**, [Ag(3,5-Ph_2-pz)]$_3$·1/4C_6H_{14}, is a new solvate of silver 3,5-diphenylpyrazolate. Two other crystalline forms for this complex, [Ag(3,5-Ph_2-pz)]$_3$·2THF and {[Ag(3,5-Ph_2-pz)]$_3$}$_2$, have been reported by Fackler et al.[7,8] Interestingly, **1** is isomorphous to [Cu(3,5-Ph_2-pz)]$_3$·1/2C_6H_{14}.[29] In the crystal structure of **1** (Figure 1), [Ag(3,5-Ph_2-pz)]$_3$ exists as a single trimer; however, it is by no means isolated in the lattice. A careful inspection reveals extensive intermolecular and intramolecular π–π and C–H···π interactions among the 3,5-phenyl substituents, while additional C–H···π interactions involve pyrazole rings. In addition, one of the phenyl rings is capping one side of an Ag_3 plane of an adjacent trimer with approximately parallel face-to-face distance and dihedral angle being 3.55 Å and 6.9° (Figure 1). This is indicative of a π-acid–base stack, providing structural evidence for the π-acidity displayed by the trimeric silver pyrazolate.[15] The absence of intermolecular Ag···Ag contacts in **1** confirms the earlier observation that while quite short Ag···Ag contacts of 2.971(1) Å are sterically allowed in the dimer-of-trimers structure {[Ag(3,5-Ph_2-pz)]$_3$}$_2$,[8] those interactions are disrupted in the presence of either weakly coordinating solvents, as in [Ag(3,5-Ph_2-pz)]$_3$·2THF,[7] or interstitial solvents enabling the manifestation of π–π and C–H···π interactions, exemplified by **1**. The conclusion drawn here is that the packing patterns of [Ag(μ-3,5-Ph_2-pz)]$_3$-units in the solid state are the results of a compromise between the above interactions.

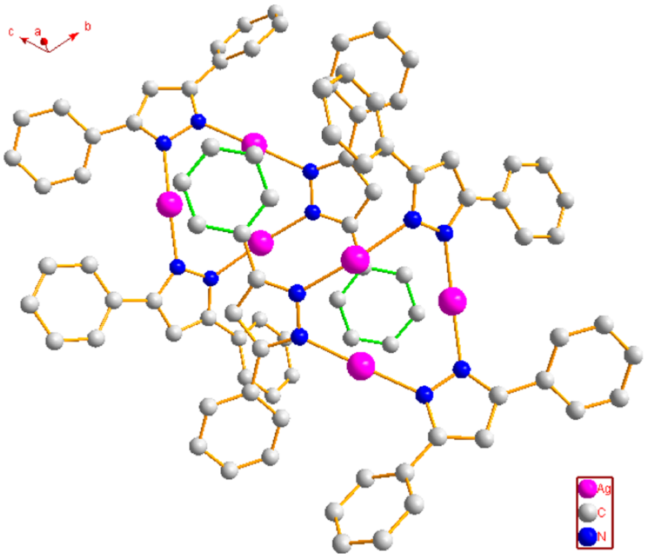


Figure 1. A ball-and-stick diagram of [Ag(μ-3,5-Ph_2-pz)]$_3$ (**1**), highlighting phenyl groups (green-colored) capping Ag_3 faces.

The asymmetric unit of **2** consists of two crystallographically independent trimers, both in the C_{3h} isomer topology (Figure 2). After an inversion operation is applied, two structurally similar but still different "dimers-of-trimers" can be generated via Ag···Ag contacts, in which the six Ag-atoms defining a chair geometry (Figure 2). Close inspection reveals that these two dimers in **2** are different not only in their inter-trimer Ag···Ag distances but also the π–π interaction patterns. The inter-trimer Ag···Ag distances are 3.203(2) and 3.321(2) Å for two dimers of trimers, respectively. On the other hand, [Ag(μ-3-

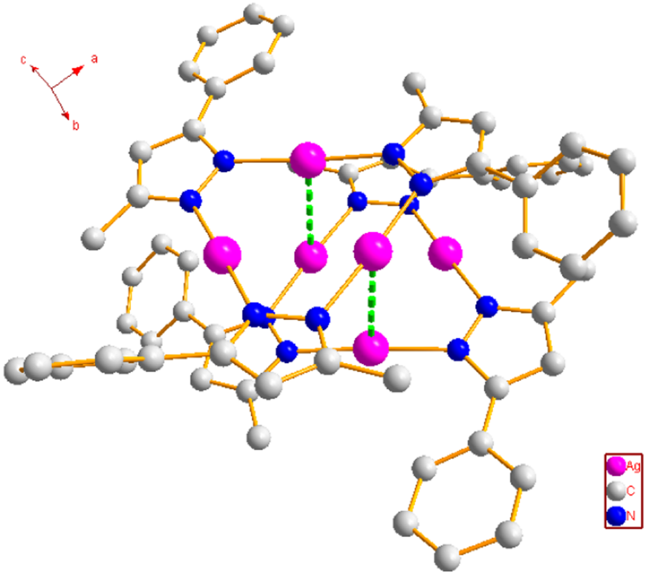


Figure 2. A ball-and-stick diagram of the dimer of trimers of [Ag(μ-3-Me-5-Ph-pz)]$_3$ (**2**), formed via argentophilic contacts (dashed green lines).

Me-5-Ph-pz)]$_3$ exists as a single trimer in the crystal structure of its methanol solvate, **2**·MeOH. The closest inter-trimer Ag···Ag distance in **2**·MeOH is only 3.419(2) Å, which is still shorter than the sum of Bondi's van der Waals radii for Ag atoms (2 × 1.72 = 3.44 Å). Comparison of the intermolecular Ag···Ag distances in **2** and **2**·MeOH shows an increase from 3.203 Å and 3.321 Å to 3.419 Å, reflecting the disruption of argentophilic interactions by the inclusion of an interstitial solvent molecule in the lattice.

Complex **3** contains two crystallographically independent [Ag(μ-4-Br-3,5-Ph$_2$-pz)]$_3$ molecules in its asymmetric unit and shows extensive intra-trimer π-interactions including $\pi-\pi$ stacking and C—H···π interaction, as seen in the structures of **1**,[7,8] but no inter-trimer Ag···Ag contacts (Figure 3a,b). Interestingly, three of the six Br atoms point to the centers of neighboring trimers (Figure 3a). A close inspection reveals that eight of the nine Ag···(μ_3-Br) distances (3.208−3.722 Å) are shorter than the sum of Bondi's van der Waals radii of Ag and Br atoms (1.72 + 1.85 = 3.57 Å), indicative of dipolar Ag···Br interactions promoted by the π-acidity of **3** (Table S2). The network of Ag···Br interactions generate two-dimensional wavy chiral sheets stacked along the crystallographic *b*-axis (Figure 3b), which are responsible for the polar space group $P2_1$ of **3**.

The crystal structure of the Au^{I}-complex **3-Au** shows isolated planar [Au(μ-4-Br-3,5-Ph$_2$-pz)]$_3$ molecules arranged parallel to each other and to the crystallographic C-face (Figure 3c). The closest intermolecular Au···Au and Au···Br distances are 4.442(1) Å and 4.970(1) Å, respectively.

The asymmetric unit of **4** consists of only one [Ag(μ-4-Br-3-^{t}Bu-pz)]$_3$ molecule, related by an inversion center to its closest neighbor. The two parallel Ag$_3$-units are held together by two argentophilic Ag···Ag contacts of 3.142(3) Å forming a dimer-of-trimers (Figure 4). One of the Br atom of each trimer points to the center of a neighboring Ag$_3$ triangle, in a similar fashion to that observed in **3**; however, the Ag···Br distances, 3.567, 3.766, and 3.968 Å, are longer than the corresponding values in **3**, indicative of a weaker Ag···Br interaction in **4**.

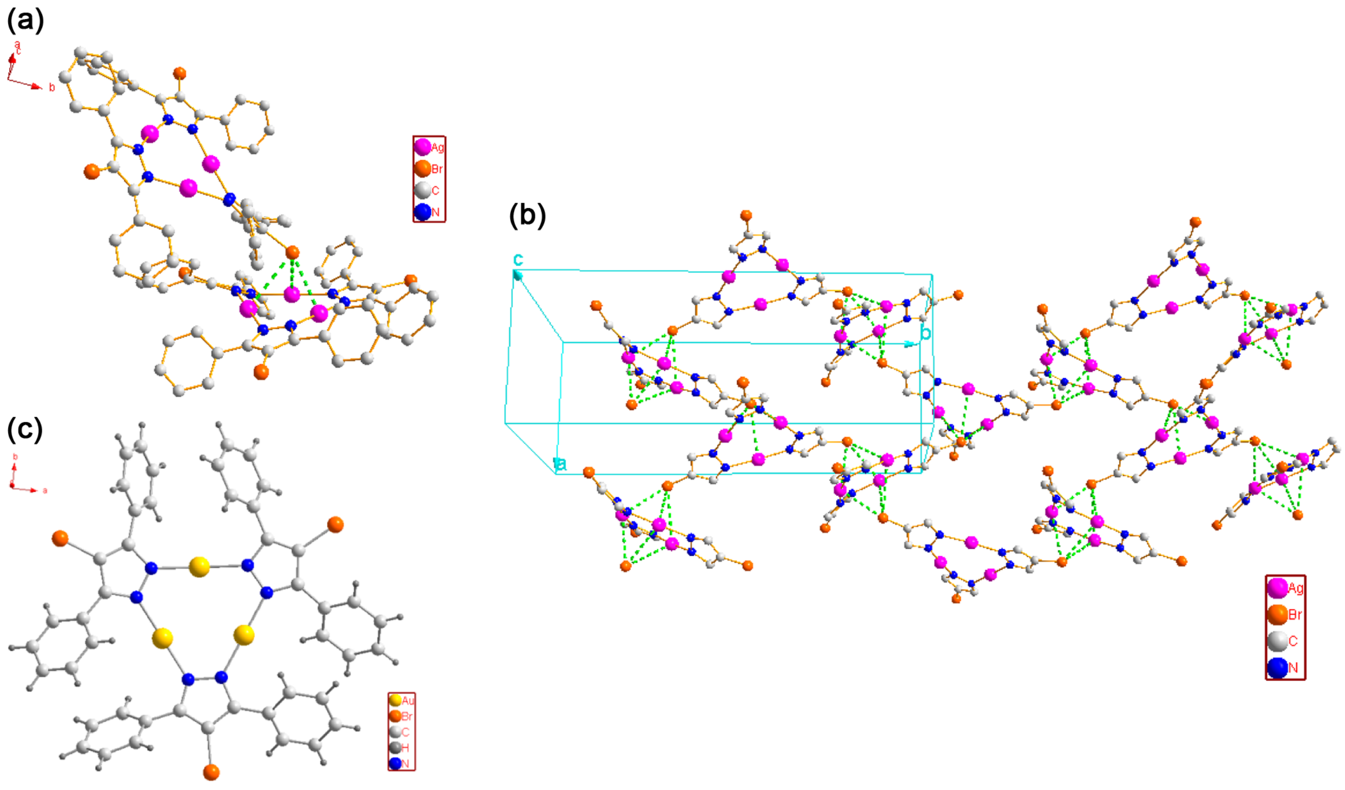


Figure 3. (a) A ball-and-stick diagram of [Ag(μ-4-Br-3,5-Ph$_2$-pz)]$_3$ (**3**), showing the Ag$_3$···Br weak interactions (dashed green lines). (b) A 2D net of [Ag(μ-4-Br-3,5-Ph$_2$-pz)]$_3$ via Ag$_3$···Br weak interactions (dashed green lines). The phenyl groups have been omitted for clarity. (c) A ball-and-stick diagram of [Au(μ-4-Br-3,5-Ph$_2$-pz)]$_3$ (**3-Au**).

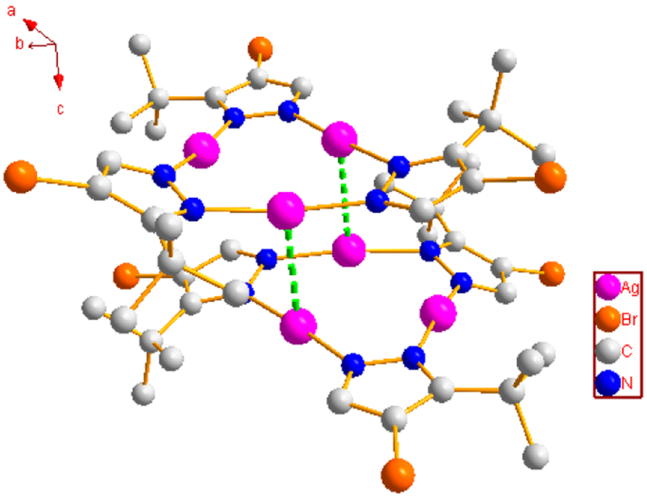


Figure 4. A ball-and-stick diagram of the dimer-of-trimers of $[Ag(\mu\text{-4-Br-3-}^tBu\text{-pz})]_3$ (**4**), formed via argentophilic contacts (dashed green lines).

The unit cell of complex **5** contains two parallel, inversion-related $[Ag(\mu\text{-3-}(o\text{-Cl-}C_6H_4)\text{-pz})]_3$ molecules, rotated by approximately 60° with respect to each other, forming a "head-to-tail" assembly of S_6 symmetry with inter-trimer Ag···Ag distance of 3.524(1)–4.281(1) Å, longer than the sum of Bondi's van der Waals radii for Ag atoms (Figure 5).

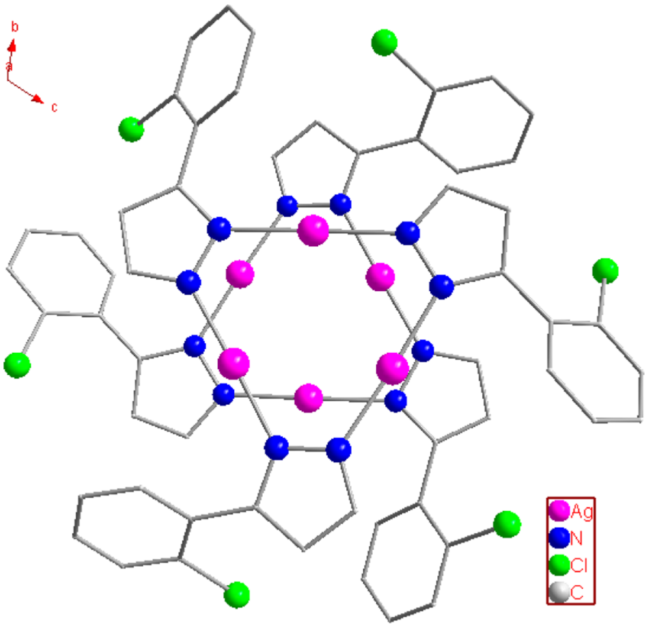


Figure 5. Ball-and-stick diagram of a pair of $[Ag(\mu\text{-3-}(o\text{-Cl-}C_6H_4)\text{-pz})]_3$ (**5**) molecules.

The six phenyl groups are rotated as to position their six Cl-atoms in the space between the two parallel Ag_3 planes, with the inter-trimer Ag···Cl distances ranging from 4.350(2) to 5.330(2) Å. Evidently, the S_6 assembly is held together only by crystal packing forces. Similar intermolecular Ag···Ag distance of 3.516(1) Å are also found between Ag_3 units in consecutive unit cells along the crystallographic *a*-axis.

The π-acidity/basicity of the Ag_3-faces of $[Ag(\mu\text{-pz*})]_3$ complexes, which is tuned by the peripheral 3-, 4- and 5-pyrazole substituents, results in variation of the pattern of supramolecular interactions among the trinuclear units in the solid state. The bulky 3,5-Ph_2-pz ligands do not prevent the close argentophilic interaction of 2.971(1) Å in the nonsolvated complex **1**.[8] However, the presence of interstitial solvent molecules, like hexane in the structure of $\mathbf{1}\cdot 1/4C_6H_{12}$ here, or weakly coordinating THF, as in **1**·2THF,[7] are sufficient to disrupt that argentophilic contact. Similar to **1**, the nonsolvated complex **2**, containing the less bulky 3-Me-5-Ph-pz ligands, forms dimer-of-trimer assemblies via weak argentophilic contacts, which are disrupted in the structure of its methanol solvate, **2**·MeOH, the latter containing only isolated trinuclear complexes in its crystal structure.

The situation changes when 4-Br substituents are introduced. The electron withdrawing bromine atoms increase the π-acidity of the Ag_3-faces of the complexes and also constitute an electron-rich donor polar terminus. Consequently, in the structures of **3** and **4**, containing the 4-Br-3,5-Ph_2-pz and 4-Br-3-^{t}Bu-pz ligands, respectively, show intermolecular interactions between the Ag_3-faces of the complexes and the Br-atoms and are acid–base in character. The Ag_3···Br are shorter in **3** than in **4**, consistent with the stronger π-acidity of **3**, caused by its electron-withdrawing Ph-groups, compared to the opposite effect caused by the electron-releasing ^{t}Bu-groups of **4**. The Ag_3···Br are also the only intermolecular contacts in **3**, while **4** contains argentophilic contacts in addition to π-acid···base ones. It is interesting to compare the crystal structures of **3** and **4** with that of $[Ag(4\text{-Br-3,5-}^iPr_2pz)]_3$:[10] The latter exists as a dimer-of-trimers via Ag···Ag contacts, but also contains several inter-trimer Ag···Br links of 3.513, 3.889, and 4.898 Å for one Br atoms to its nearest Ag_3 trimer, longer than those in **3**, but comparable to those in **4**. Consistent with the predicted relative π-acidity, Ag > Cu > Au, by DFT calculations,[15] the crystal structure of **3-Au**, the Au-analogue of **3**, contains no Au_3···Br contacts; gold is less π-acidic than silver. Halide···π acid (Cu_3) interactions have also been observed in a series of polymeric structures constructed from copper halides and 3,5-diethyl-4-(4-pyridyl)-pyrazolate, containing $[Cu(\mu\text{-pz*})]_3$-units.[30] Short Ag^I···X-aryl (X = Br, I) interactions have been reported by Mak et al., with notable Ag···Br distances of 2.584 and 2.599 Å,[31] even shorter than those found in crystal structure of AgBr (2.88 Å). The introduction of Cl-atoms at a site remote from the Ag-centers in **5** does not increase the π-acidity of its Ag_3-face and the presence of basic halogen atoms in this complex is mute.

■ CONCLUSION

Although the molecular structures of monovalent group-11 pyrazolates are largely dictated by the strength and direction of M-N dative bonds, the noncoordinative groups in 3,4,5-positions of pyrazole rings are by no means spectators. Besides their straightforward steric requirements, they also exert electronic effects manifested in the varying strength of dipolar and/or metallophilic interactions. The conclusion drawn from the study of structures **1**, **2** and **2**·MeOH is that Ag···Ag contacts and π–π interactions are comparable in strength. Elegant computational and experimental studies have demonstrated how the π-acid/base properties of such complexes are tuned by the electron withdrawing or releasing properties of the substituents.[15−23] Our present work demonstrates examples in which the increased π-acid character of complexes **3** and **4** together with the presence of basic Br-atoms bring about dominant Ag_3···Br acid–base interactions that compete with argentophilicity to determine their supramolecular organization. Clearly, for Ag_3···halogen interactions to dominate, the other substituents need to induce sufficient π-acidity to the Ag_3-core. When this is not the case, as in complex **5**, no acid−base interactions are observed.

Germane to this is the observation that in a thallium-trispyrazolylborate system, the substitution at the pyrazole 3-position influences the length of intermolecular Tl−Tl, closed shell contacts.[32] A detailed study of the effect of pyrazole peripheral substitution on the strength of metallophilic interactions is still lacking.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

ORTEP diagrams, tables of interatomic distances and angles for **1**−**5** and packing diagrams for **3-Au** and **5**. This information is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Lehn, J.-M. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4763−4768. (b) Turro, N. J. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 10766−10770. (c) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629−1658.

(2) (a) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597−636. (b) Schmidbaur, H. *Gold Bull.* **2000**, *33*, 3−10. (c) Jahnke, A. C.; Pröpper, K.; Bronner, C.; Teichgräber, J.; Dechert, S.; John, M.; Wenger, O. S.; Meyer, F. *J. Am. Chem. Soc.* **2012**, *134*, 2938−2941.

(3) Henkelis, J. J.; Kilner, C. A.; Halcrow, M. A. *Chem. Commun.* **2011**, *47*, 5187−5189.

(4) (a) Mohamed, A. A. *Coord. Chem. Rev.* **2010**, *254*, 1918−1947. (b) Burini, A.; Mohamed, A. A.; Fackler, J. P. *Comments Inorg. Chem.* **2003**, *24*, 253−280. (c) Gao, G.-F.; Li, M.; Zhan, S.-Z.; Lv, Z.; Chen, G.; Li, D. *Chem.—Eur. J.* **2011**, *17*, 4113−4117. (d) Halcrow, M. A. *Dalton Trans.* **2009**, 2059−2073.

(5) Yang, G.; Raptis, R. G. *Inorg. Chem.* **2003**, *42*, 261−263.

(6) (a) Kim, S. J.; Kang, S. H.; Park, K.-M.; Kim, H.; Zin, W.-C.; Choi, M.-G.; Kim., K. *Chem. Mater.* **1998**, *10*, 1889−1893. (b) Torralba, M. C.; Ovejero, P.; Mayoral, M. J.; Cano, M.; Campo, J. A.; Heras, J. V.; Pinilla, E.; Torres, M. R. *Helv. Chim. Acta* **2004**, *87*, 250−263. (c) Lintang, H. O.; Kinbara, K.; Yamashita, T.; Aida, T. *Chem. Asian J.* **2012**, *7*, 2068−2072.

(7) Murray, H. H.; Raptis, R. G.; Fackler, J. P., Jr. *Inorg. Chem.* **1988**, *27*, 26−33.

(8) Mohamed, A. A.; Pérez, L. M.; Fackler, J. P., Jr. *Inorg. Chim. Acta* **2005**, *358*, 1657−1662.

(9) Masciocchi, N.; Moret, M.; Cairati, P.; Sironi, A.; Ardizzoia, G. A.; La Monica, G. *J. Am. Chem. Soc.* **1994**, *116*, 7668−7676.

(10) Dias, H. V. R.; Diyabalanage, H. V. K. *Polyhedron* **2006**, *25*, 1665−1661.

(11) Dias, H. V. R.; Gamage, C. S. P.; Keltner, J.; Diyabalanage, H. V. K.; Omari, I.; Eyobo, Y.; Dias, N. R.; Roehr, N.; McKinney, L.; Poth, T. *Inorg. Chem.* **2007**, *46*, 2979−2987.

(12) Fujisawa, K.; Ishikawa, Y.; Miyashita, Y.; Okamoto, K. *Inorg. Chim. Acta* **2010**, *363*, 2977−2989.

(13) Meyer, F.; Jacobi, A.; Zsolnai, L. *Chem. Ber.* **1997**, *130*, 1441−1447.

(14) Krishantha, D. M. M.; Gamage, C. S. P.; Schelly, Z. A.; Dias, H. V. R. *Inorg. Chem.* **2008**, *47*, 7065−7067.

(15) Tekarli, S. M.; Cundari, T. R.; Omary, M. A. *J. Am. Chem. Soc.* **2008**, *130*, 1669−1675.

(16) Dias, H. V. R.; Gamage, C. S. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 2192−2194.

(17) Tsupreva, V. N.; Titov, A. A.; Filippov, O. A.; Bilyachenko, A. N.; Smol'yakov, A. F.; Dolgushin, F. M.; Agapkin, D. V.; Godovikov, I. A.; Epstein, L. M.; Shubina, E. S. *Inorg. Chem.* **2011**, *50*, 3325−3331.

(18) Mohamed, A. A.; Rawashdeh-Omary, M. A.; Omary, M. A.; Fackler, J. P., Jr. *Dalton Trans.* **2005**, 2597−2602.

(19) Burini, A.; Bravi, R.; Fackler, J. P., Jr.; Galassi, R.; Grant, T. A.; Omary, M. A.; Pietroni, B. R.; Staples, R. J. *Inorg. Chem.* **2000**, *39*, 3158−3156.

(20) Burini, A.; Fackler, J. P., Jr.; Galassi, R.; Grant, T. A.; Omary, M. A.; Rawashdeh-Omary, M. A.; Pietroni, B. R.; Staples, R. J. *J. Am. Chem. Soc.* **2000**, *122*, 11264−11265.

(21) Rawashdeh-Omary, M. A.; Omary, M. A.; Fackler, J. P., Jr.; Galassi, R.; Pietroni, B. R.; Burini, A. *J. Am. Chem. Soc.* **2001**, *123*, 9689−9691.

(22) Burini, A.; Fackler, J. P.; Galassi, R.; Macchioni, A.; Omary, M. A.; Rawashdeh-Omary, M. A.; Pietroni, B. R.; Sabatini, S.; Zuccaccia, C. *J. Am. Chem. Soc.* **2002**, *124*, 4570−4571.

(23) Olmstead, M. M.; Jiang, F.; Attar, S.; Balch, A. L. *J. Am. Chem. Soc.* **2001**, *123*, 3260−3267.

(24) Badjić, J. D.; Nelson, A.; Cantrill, S. J.; Turnbull, W. B.; Stoddart, J. F. *Acc. Chem. Res.* **2005**, *38*, 723−732.

(25) Metrangolo, P.; Neukirch, H.; Pilati, T.; Resnati. *Acc. Chem. Res.* **2005**, *38*, 386−395.

(26) Zueva, E. M.; Petrova, M. M.; Herchel, R.; Trávníček, Z.; Raptis, R. G.; Mathivathanan, L.; McGrady, J. E. *Dalton Trans.* **2009**, 5924−5932.

(27) Trofimenko, S.; Calabrese, J. C.; Thompson, J. S. *Inorg. Chem.* **1987**, *26*, 1507−1514.

(28) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112−122.

(29) Raptis, R. G.; Fackler, J. P., Jr. *Inorg. Chem.* **1988**, *27*, 4179−4182.

(30) Hou, L.; Shi, W.-J.; Wang, Y.-Y.; Wang, H.-H.; Cui, L.; Chen, P.-X.; Shi, Q.-Z. *Inorg. Chem.* **2011**, *50*, 261−270.

(31) Zang, S.-Q.; Cheng, P.-S.; Mak, T. C. W. *CrystEngComm* **2009**, *11*, 1061−1067.

(32) Gosh, P.; Rheingold, A. L.; Parkin, G. *Inorg. Chem.* **1999**, *38*, 5464−5467.