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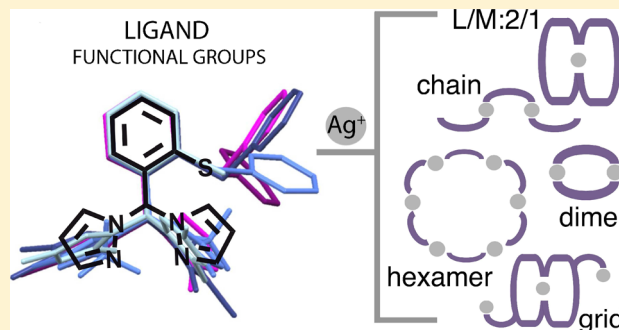
Silver(I) and Thioether-bis(pyrazolyl)methane Ligands: The Correlation between Ligand Functionalization and Coordination Polymer Architecture

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S Supporting Information

ABSTRACT: This work examines the crystal structures of 15 Ag(I) complexes with thioether functionalized bis(pyrazolyl)-methane derivatives to rationalize the influence of the ligand on the formation of (a) coordination polymers (CPs), (b) oligonuclear (hexameric and dinuclear) complexes, and (c) mononuclear complexes. It was previously reported how this ligand class could generate microporous architectures with permanent porosity. Some ligand modifications could induce a cavity size modulation while preserving the same overall architecture. The bis(pyrazolyl)methane scaffold can be easily functionalized with various structural fragments; hence the structural outcomes were studied in this work using various ligand modifications and Ag(I) salts. In particular, six new ligand classes were prepared with the following features: (1) The steric hindrance on the pyrazole rings $L^{3,3'/Me}$, $L^{5,5'/Me}$, $L^{5,3'/Me}$, L^{CF_3} , and L^{Br} was modified. (2) The steric hindrance was reduced on the peripheral thioether group: L^{SMe} . (3) Finally, the presence of fluorine and bromine atoms in L^{CF_3} and L^{Br} offered the possibility to expand the type of interaction with respect to the ligands based on hydrocarbon substituents (CH_3 , phenyl, naphthyl). The effect of the anions was explored using different Ag(I) precursors such as $AgPF_6$, $AgBF_4$, $AgCF_3SO_3$, or $AgNO_3$. A comparison of the crystal structures allowed for the tentative identification of the type of substituents able to induce the formation of CPs having permanent porosity to include a symmetric and moderate steric hindrance on the pyrazolyl moieties (four CH_3) and an aromatic and preorganized thioether moiety. An asymmetric steric hindrance on the pyrazole groups led to the formation of more varied structural types. Overall, the most frequently reported structural motifs are the porous hexameric systems and the molecular chains.



INTRODUCTION

Over the last three decades, the design of metal-based supramolecular assemblies has become one of the most intense research areas in chemistry and material science^{1–7} due to the large number of potential applications of these materials, such as catalysis,^{8,9} photochemistry,¹⁰ luminescence,¹¹ sensing,¹² magnetism,^{13,14} gas storage,^{15–17} gas purification,^{18,19} and medicine.²⁰ The ligand features and stereoelectronic characteristics of metal ions can control the arrangement of the supramolecular assemblies. The majority of transition metal ions usually exhibit a well-defined geometry (e.g., tetrahedral, square planar, or octahedral). In contrast, the geometry of d¹⁰ metal centers is typically dictated by steric factors, ensuring a greater coordination flexibility. Additional control over the resulting structural arrangement can be achieved by the use of multitopic ligands, which can bridge different metal ions to build flexible network structures. The mutual orientation of the donor atoms defines the ligand geometry as well as the coordinative directionality; the orientation has a profound influence on the overall geometrical structure.¹ These concepts are at play in the rational design in various architectures, such as metal organic frameworks (MOFs), coordination polymers

(CPs), and supramolecular architectures, based upon extended metal–ligand interactions such as polyoxometallates (POMs) or networks based on supramolecular synthons.^{21–24} Recent reviews have covered the conceptual distinctions between various types of metal based frameworks, in particular, between MOFs and CPs.^{1,3,25,26} CPs commonly exhibit reversible coordination bonds and can be considered as dynamic synthons, which can assemble in various structural arrangements. CP architectures can be influenced by numerous factors including counterions, temperature, solvent systems, metal/ligand ratios, templates, and the coordination properties of the ligand and metal types.^{27,28} CPs can also be prepared or processed in various ways to obtain nanostructured materials with potential applications in nanoelectronics^{29,30} or in hybrid materials that can be incorporated into lipid membranes.³¹ As far as the metal ion is concerned, the adaptable coordination geometry of Ag(I) allows for the use of silver cationic complexes as building blocks for the construction of

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69 coordination polymers.^{32–37} Previous works investigated the
 70 coordination properties of thioether functionalized bis-
 71 (pyrazolyl)methane ligand systems (N₂S donors), which were
 72 able to generate CPs with metal ions such as Cu(I) and
 73 Ag(I).^{38,39} Interestingly, it was found that in the presence of a
 74 specifically preorganized thioether-bis(pyrazolyl)methane li-
 75 gand, Ag(I) could give hexameric and toroidal supramolecules
 76 (panels A and C in Figure 1) that self-assembled into diverse
 77 three-dimensional (3D) porous supramolecular architectures
 78 and microporous cavities as a function of the anion used (BF₄⁻,
 79 PF₆⁻, NO₃⁻, and CF₃SO₃⁻).⁴⁰ The employed type of ligand
 80 offered the possibility to functionalize the thioether moiety to
 81 modulate the porous properties of the resulting assemblies. In

particular, ligands with bulky substituents led to a reduction in 82
 the size of some of the structural cavities. In one case, the 83
 interior of the cavities could be decorated with heteroatoms 84
 such as fluorine. Gas absorption measurements proved that the 85
 ligand bulkiness is directly correlated with the absorption 86
 properties of the resulting systems.⁴¹ A large number of 87
 molecular structures based on the bis(pyrazolyl)methane 88
 scaffold were reported, in which bis(pyrazolyl)methane 89
 functionalization provided additional donor moieties (O, S, 90
 P) to the N₂ system or added specific linkers capable of 91
 generating extended multitopic ligands.^{42–53} The scope of this 92
 work was to investigate the role of the bis(pyrazole)methane 93
 moiety on the structural arrangement of previously reported 94
 silver complexes (see panels A and C in Figure 1); thus various 95
 bis(pyrazolyl)methane scaffolds were prepared with different 96
 groups on the pyrazole rings, as shown in Scheme 1. 97 s1

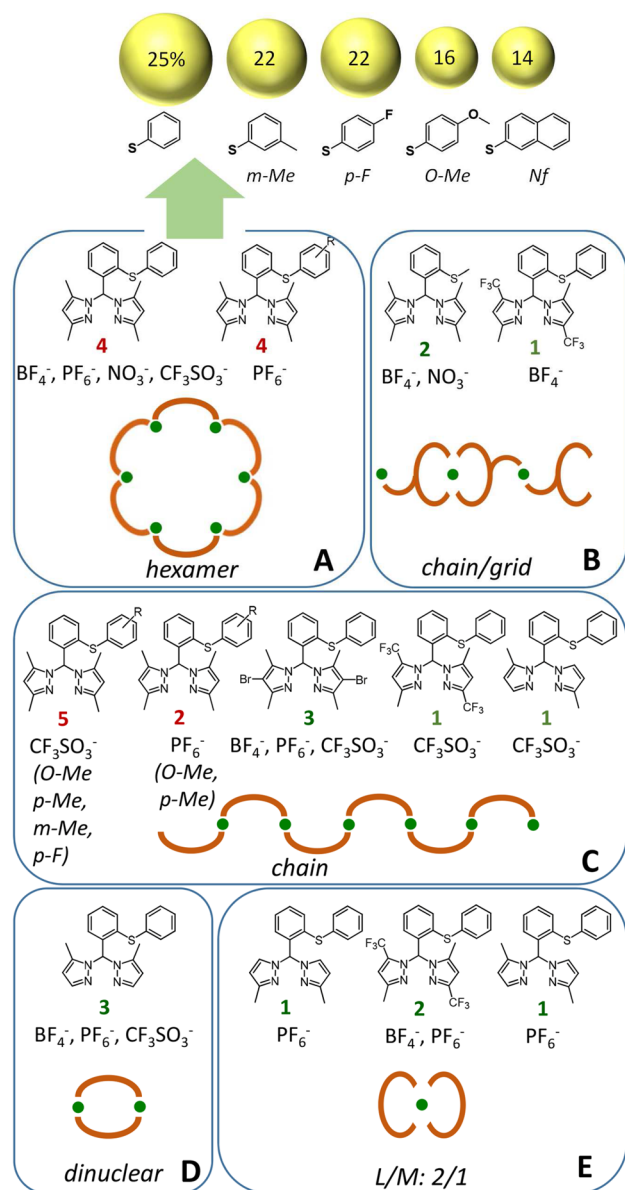
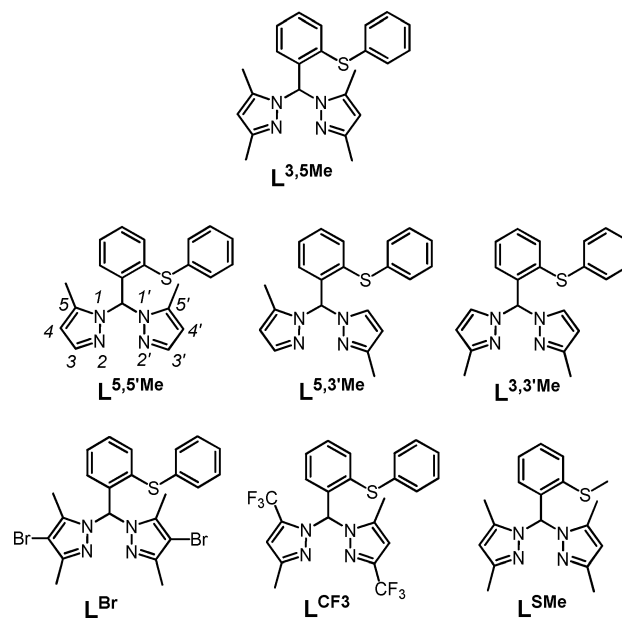


Figure 1. (A–E) Depiction of the structural variability of the thioether functionalized bispyrazolylmethane ligands with Ag(I) and different counteranions. The red number indicates previously reported structures, and green numbers indicate the structures reported in this work. The upper part of the picture shows the cavity dimensions (intra- and intercapsular) as a percentage of the unit cell volume for the [Ag(L)]₆(PF₆)₆ complexes.

Scheme 1. Molecular Structures of the Six Ligand Classes Described This Work^a



^aL_{3,5}Me was the parent ligand previously described.

In particular, the three isomers L_{3,3'/Me}, L_{5,5'/Me}, and L_{5,3'/Me} 98
 offered the possibility to investigate the steric hindrance role 99
 close to both the pyrazole nitrogen atoms. The L^{CF₃} ligand was 100
 used to increase slightly the steric hindrance close to the N₂ 101
 system and to modify the electronic nature of the cavity surface 102
 in putative porous architectures. L^{Br} was chosen as a system 103
 exhibiting a moderate bulkiness on the pyrazole rings. When 104
 examining an expansion of the interactions occurring in these 105
 architectures, the bromine atoms of L^{Br} could also act as a 106
 halogen bond donor.⁵⁴ Moreover, with the aim of increasing 107
 the cavity size of potential porous architectures, the ligand L^{SMc} 108
 was prepared. L^{SMc} exhibits a limited steric hindrance of the 109
 ligand periphery, and it could provide hexameric building 110
 blocks with augmented porosity (see Figure 1). The molecular 111
 structures of the six classes of ligands with Ag(I) are used as a 112
 continuation of a previous study on the structural properties of 113
 Ag(I)-based CPs. The role of the counterion on coordination 114
 geometry, topology, and crystal packing was taken into 115
 consideration by using PF₆⁻, BF₄⁻, CF₃SO₃⁻, and NO₃⁻. A 116

117 comprehensive view of the structural variability obtained with
118 these ligand classes, Ag(I) and anions is provided in Figure 1.

119 ■ EXPERIMENTAL SECTION

120 **Materials and Methods.** All reagents and solvents were
121 commercially available. 2-(Phenylthio)benzaldehyde and bis(3,5-
122 dimethyl-1*H*-pyrazol-1-yl)methanone were prepared as reported
123 elsewhere.⁴⁰ ¹H-NMR and ¹³C-NMR spectra were recorded on a
124 Bruker Advance 300 and 400 spectrometer using standard Bruker
125 pulse sequences. Chemical shifts are reported in parts per million
126 (ppm) referenced to residual solvent protons. Infrared spectra were
127 recorded from 4000 to 700 cm⁻¹ on a PerkinElmer FT-IR Nexus
128 spectrometer equipped with a Thermo-Nicolet microscope. Elemental
129 analyses (C, H, and N) were performed with a Carlo Erba EA 1108
130 automated analyzer. Electrospray ionization mass spectra (ESI-MS)
131 were collected on a Micromass LCZ TOF electrospray ionization mass
132 spectrometer. A capillary voltage of 3.0 V and a positive cone voltage
133 of 50 V (ESI+ ion mode) were used. Samples (40 μL) were injected
134 through direct infusion using a syringe pump at 10 μL/min, and the
135 spectra were recorded in full scan analysis mode. The synthesis of the
136 ligands and of the silver(I) complexes is reported in the Supporting
137 Information.

138 **Single Crystal X-ray Structures.** Single crystal data were
139 collected with a Bruker Smart APEXII area detector diffractometers
140 (Mo Kα; λ = 0.71073 Å). Cell parameters were refined from the
141 observed setting angles and detector positions of selected strong
142 reflections. Data collection was performed with a 0.3° scan and with
143 several series of exposure frames covering at least a hemisphere of the
144 reciprocal space.⁵⁵ A multiscan absorption correction was applied to
145 the data using the program SADABS.⁵⁶ The structures were solved by
146 direct methods (SIR programs)⁵⁷ and refined with full-matrix least-
147 squares (SHELXL-2014)⁵⁸ using the Wingx software package.⁵⁹
148 Selected geometric parameters are reported in Tables S1–S6 and
149 Tables S7–S10 report the crystallographic data. Graphical material was
150 prepared with the Mercury⁶⁰ 3.0 program. Thermal ellipsoids plots of
151 the asymmetric units for all of the molecular structures are reported in
152 the Supporting Information Figures S3–S7.

153 ■ RESULTS AND DISCUSSION

154 **Synthesis and Characterization.** The synthesis of the
155 ligands L^{Br}, L^{CF₃}, L^{3,3′Me}, L^{5,5′Me}, L^{5,3′Me}, and L^{5Me} was
156 performed as described in Scheme 2.

157 The N₂S donor set of the ligand described here is generated
158 by treating substituted bis(pyrazolyl)ketones with function-
159 alized (phenylthio)acetaldehyde using CoCl₂ hydrate as the

catalyst and heating at 90 °C for 2 h and without solvent. 160
Different pyrazoles were employed as the starting reagents. In 161
particular, the pyrazole used comprised (i) bromine in position 162
4 together with methyl groups in positions 3 and 5, (ii) CF₃ 163
and methyl groups in the 3, 5 positions, and (iii) a single 164
methyl group. When using the pyrazole with a single methyl 165
group and the pyrazole functionalized with a CF₃ group, 166
different isomers were obtained. In particular, with a single 167
methyl group, the synthesis led to the formation of three 168
isomers, namely, L^{3,3′Me}, L^{5,3′Me}, and L^{5,5′Me}. Different 169
purification steps via a chromatographic column were 170
performed to isolate the three ligands from the reaction 171
mixture. Different experimental conditions were attempted by 172
changing the eluent mixture, the stationary phase (silica or 173
alumina), or the column diameter. The best condition was 174
identified with silica as stationary phase and hexane/ethyl 175
acetate 8/2 as the eluent (see Figure S1). Nevertheless, the 176
products L^{5,3′Me} and L^{5,5′Me} proved to be difficult to separate 177
because they exhibited a very similar chromatographic behavior. 178
After several chromatographic cycles it was possible to 179
quantitatively purify L^{3,3′Me} and isolate two pure fractions of 180
L^{5,3′Me} and L^{5,5′Me}, which were then used for the complexation 181
studies. The purity of the three ligands was confirmed by ¹H 182
NMR, as shown in Figure 2. Furthermore, different isomers can 183

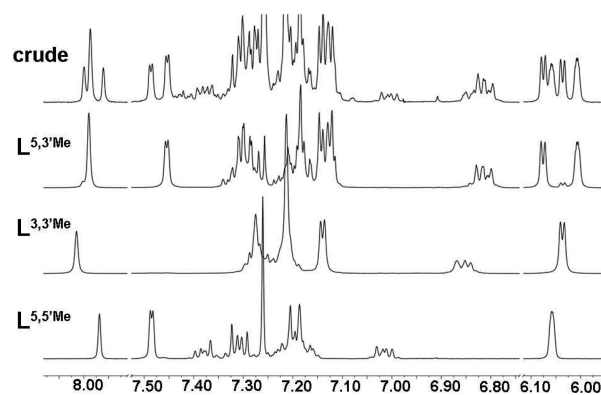
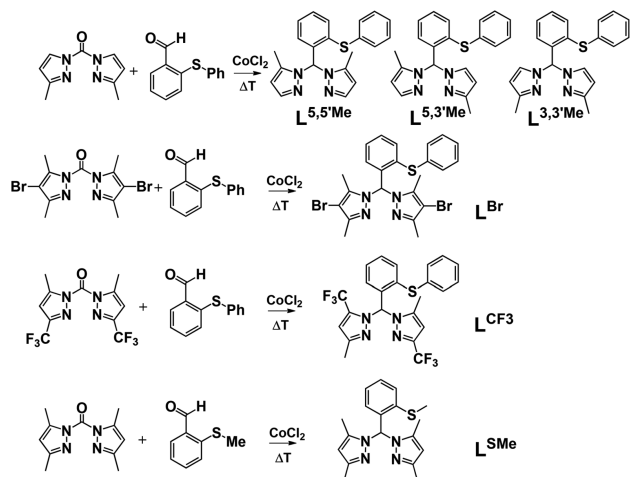


Figure 2. Stack between the aromatic region ¹H NMR spectra of the raw product and of the three purified ligands. In the raw product, the main impurity is represented by the aldehyde (reagent).

Scheme 2. Synthetic Route for the Preparation of the Ligands



also be obtained when using the pyrazole with the CF₃ group. 184
This is confirmed by the ¹H NMR spectrum of the crude 185
product (Figure S3). Nevertheless, the isomer with the CF₃ 186
groups in 3 and 5′ position (L^{CF₃}) always showed a greater 187
abundance over the other ones, which we did not attempt to 188
purify. The complexes were prepared mixing equimolar 189
amounts of the ligands with Ag(I) salts (AgPF₆, AgBF₄, 190
AgCF₃SO₃, or AgNO₃) in acetone and in the air at room 191
temperature. The purified products were investigated by means 192
of ¹H NMR, which usually showed the presence of a single set 193
of signals. Furthermore, the ESI-mass spectra showed the 194
occurrence of [Ag(L)]⁺ and in some cases also of the [Ag(L)₂]⁺ 195
species. This evidence points to the presence of potential 196
dynamic equilibria in solution, which then resulted in the 197
crystallization of different mononuclear, oligonuclear, and 198
polynuclear structures as described below. 199

Crystals Structures of the Silver Complexes. Molecular 200
Chains. Four ligand classes (L^{Br}, L^{3,5Me}, L^{CF₃}, L^{5,3′Me}) exhibit 201
the chain-like structural motif, which is the most represented 202
among the silver complexes and comprise 12 overall structures 203

204 (Figure 1C). The complexes $[\text{Ag}(\text{L}^{\text{Br}})]_n(\text{PF}_6)_n \cdot \text{acetone}$ (1),
 205 $[\text{Ag}(\text{L}^{\text{Br}})]_n(\text{BF}_4)_n \cdot \text{acetone}$ (2), and $[\text{Ag}(\text{L}^{\text{Br}})]_n(\text{CF}_3\text{SO}_3)_n \cdot \text{ace}$ -
 206 tone (3) crystallize in the form of very similar molecular chains
 207 in the orthorhombic space group *Pbca*. This type of structure
 208 was previously found for ligand types ideally derived by $\text{L}^{3,5\text{Me}}$
 209 and whose differences were represented by various function-
 210 alization of the peripheral thioether moiety (Figure 1).⁴¹ For all
 211 of these compounds, the ligand acts as N_2 bidentate on a metal
 212 and bridges on another silver atom with the thioether group
 213 and with the central phenyl ring in a rigid geometry, as
 214 presented in Figure 3 and Figure S5. In these complexes, the

Scheme 3. Torsion Angle Used to Describe the Conformational Rigidity of the Ligands

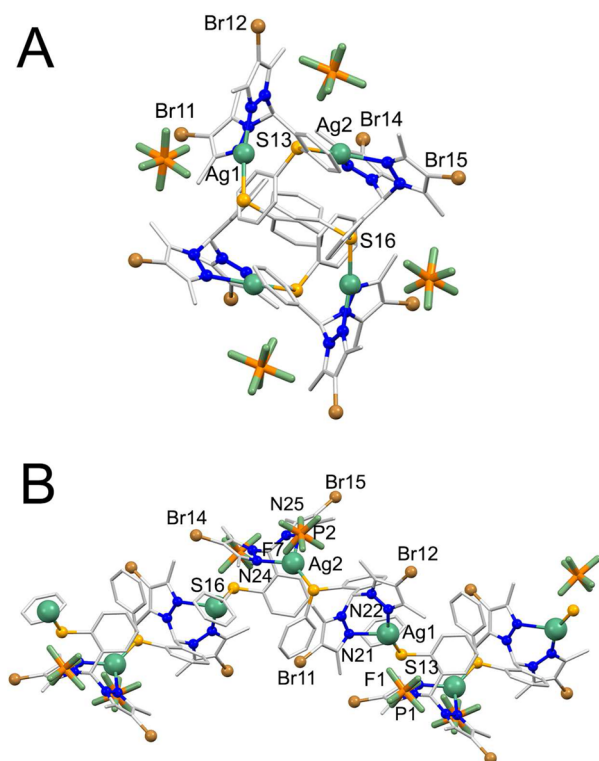
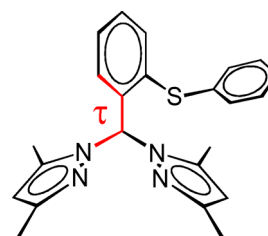


Figure 3. Molecular structure of $[\text{Ag}(\text{L}^{\text{Br}})]_n(\text{PF}_6)_n \cdot \text{acetone}$ (1) projected along the propagation direction of the molecular chain (A) and molecular chain side view (B).

215 asymmetric unit comprises a $[\text{Ag}(\text{L}^{\text{Br}})]_2(\text{X})_2$ fragment ($\text{X} =$
 216 anion), as shown in Table S1. The metal is in a trigonal planar
 217 environment, which is slightly distorted toward the tetrahedral
 218 according to the presence of long contact with the fluorine
 219 atoms of BF_4^- or PF_6^- or the oxygen atoms of CF_3SO_3^- . In all
 220 structures, the metal is out of the trigonal plane to an extent
 221 that depends on the interaction degree with the anions. With
 222 PF_6^- , the metal lies out of the coordination plane of
 223 approximately 0.16–0.17 Å, whereas with BF_4^- , it lies out of
 224 approximately 0.17–0.22 Å. With CF_3SO_3^- , the metal lies out
 225 of 0.23–0.24 Å in agreement with the presence of a moderately
 226 short Ag–O contact (2.52 and 2.57 Å). The torsion angles
 227 (described as the angle between the bipyrzoyl scaffold and the
 228 phenyl linker) τ in Scheme 3 varies in the 0.0/–3.9° range,
 229 confirming a conserved ligand conformational rigidity among
 230 the three complexes. The structures present a π stacking
 231 between the pyrazole ring and the peripheral phenyl ring with
 232 distances that vary in the 3.3–3.5 Å range. These molecular
 233 chains exhibit a helical arrangement; both the left-handed and
 234 the right-handed directions are present in the crystal packing

235 according to the fact that the structures are centrosymmetric. 236
 The exterior of the chains is defined by alternate anions and 237
 pyrazole rings, whereas those in the interior are located in the 238
 peripheral aromatic moieties of the thioether fragments. 239
 Contrary to the toroidal hexamers described in previous 240
 works,^{40,41} the crystal packing of 1–3 does not exhibit any 241
 cavity with permanent porosity, even though acetone 242
 crystallization molecules are present. The steric profile of L^{Br} 243
 is slightly greater than that of $\text{L}^{3,5\text{Me}}$, according to the large size 244
 of bromine and the long C–Br bond distance (approximately 245
 1.9 Å). This moderate increase of the steric hindrance on the 4- 246
 pyrazole position may be the main reason that hinders the 247
 formation of hexameric structures. In fact, by inspecting the 248
 structures of the parent compounds $[\text{Ag}(\text{L}^{3,5\text{Me}})]_6(\text{BF}_4)_6$ and 249
 $[\text{Ag}(\text{L}^{3,5\text{Me}})]_6(\text{BF}_4)_6$,⁴⁰ it appears that the additional presence of a 250
 bromine atom as in L^{Br} could provide some steric interference 251

The molecular structure of $[\text{Ag}(\text{L}^{\text{CF}_3})]_n(\text{CF}_3\text{SO}_3)_n$ (4) is 252
 reported in Figure 4. The ligand L^{CF_3} bridges between two 253
 metal centers with the N_2 system on one side and the thioether 254
 group on the opposite side. The oxygen atom of a triflate anion 255
 completes the tetrahedral coordination of the metal center. The 256
 most notable difference with the previously described structures 257
 exhibiting the L^{Br} ligand is in the arrangement of the peripheral 258
 phenyl ring, which in 4 is not stacked above one of the pyrazole 259

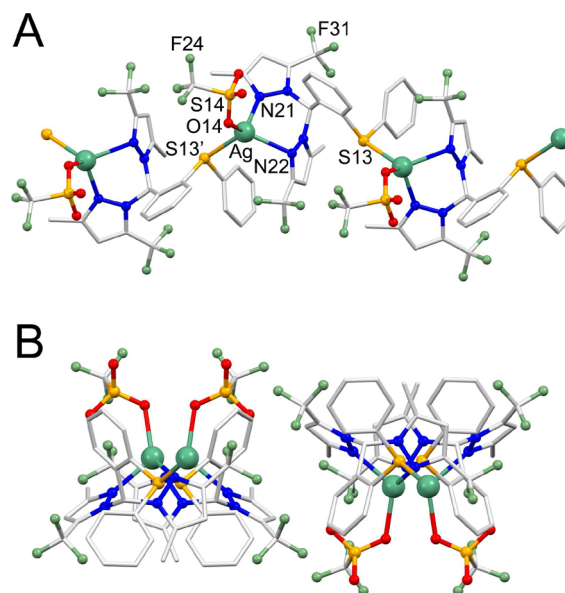


Figure 4. Molecular structure of $[\text{Ag}(\text{L}^{\text{CF}_3})]_n(\text{CF}_3\text{SO}_3)_n$ (4) (A). Portion of the crystal packing as viewed along the *c* axis; two molecular chain are depicted (B). Hydrogen atoms were removed for clarity. Symmetry code ' = 3/2 - *x*; *y*; 1/2 + *z*.

260 moieties as found with L^{Br} . This new conformation is likely a
 261 consequence of the steric hindrance caused by the CF_3 residues
 262 on the pyrazole rings belonging to the same ligand. To
 263 minimize the steric repulsion, the phenyl moiety is positioned
 264 above one of the CH_3 groups. The rigidity of the central phenyl
 265 ring is nevertheless preserved, as the τ angle is 2.9° (Scheme 3).
 266 The ligand conformation implies a different orientation of the
 267 lone pairs of sulfur; consequently, a different chain-like
 268 structure is formed. Interestingly, the peripheral phenyl
 269 interacts with the pyrazole ring of a symmetry related ligand,
 270 conserving the energetically favorable π stacking as found for
 271 the structure with L^{Br} . A possible consequence of the thioether
 272 organization is a significant lengthening of the Ag–S bond
 273 (2.62 \AA) that is compensated for by a stronger interaction with
 274 the triflate anions yielding a relatively short Ag–O bond (2.31
 275 \AA).

276 A different type of molecular chain is observed for the
 277 complex $[\text{Ag}_2(\text{L}^{5,3/\text{Me}})]_n(\text{CF}_3\text{SO}_3)_{2n} \cdot 2\text{CH}_2\text{Cl}_2$ (**5**) where the
 278 metal ligand ratio is 2:1 even though the synthesis was
 279 performed with a 1:1 stoichiometry, as presented in Figure 5. In
 280 this complex, the ligand $L^{5,3/\text{Me}}$ adopts a conformation similar
 281 to that observed for the L^{Br} system, having the peripheral
 282 aromatic ring stacked above the 5-Me functionalized pyrazole
 283 ring. The absence of the 3'-Me group has an important
 284 consequence for the donor properties of this ligand. In fact, the
 285 N(21) nitrogen atom is devoid of significant steric hindrance;
 286 therefore, it can interact with two silver atoms in a bridging
 287 mode. Moreover, Ag(1) exhibits a distorted tetrahedral
 288 coordination achieved by two nitrogen atoms, a bridging sulfur
 289 atom of a symmetry related ligand, and an oxygen atom of a
 290 triflate anion O(15). The Ag(2) metal also exhibits a distorted
 291 tetrahedral geometry achieved by three oxygen atoms from
 292 three different triflate anions (two of them centrosymmetrically
 293 related). Ag(2) also interacts with the central aromatic ring of
 294 the ligand, giving rise to a metal- π interaction with the shortest
 295 distance observed between Ag(2) and C(33) (3.11 \AA). Because
 296 of this latter interaction, there is a slight rotation of the central
 297 phenyl ring with respect to the bis(pyrazole) scaffold, and the τ
 298 angle is approximately 16.6° . From a different perspective, the
 299 structural arrangement of **5** can be viewed as a molecular chain
 300 that involves the ligand, the Ag(1), and a triflate anion. An
 301 additional Ag(2)-triflate fragment can easily interact with the
 302 N(21) bridging nitrogen according to the limited steric
 303 hindrance on this donor atom. Additionally, Ag(1) and Ag(2)
 304 give rise to an argentophilic interaction with a metal–metal
 305 distance of $3.173(1) \text{ \AA}$. The Ag(2)-triflate fragment links
 306 together two molecular chains with this second triflate anion
 307 that bridges on the Ag(1) via the O(35) oxygen atom,
 308 producing an overall supramolecular grid, which is parallel to
 309 the bc crystallographic plane, as shown in Figure 5. Dichloro-
 310 methane molecules of crystallization are allocated in the
 311 interstices of these layers.

312 **Dinuclear Structures.** When using the ligand $L^{5,5/\text{Me}}$, the
 313 structures of the silver complexes present a different arrange-
 314 ment. In fact, the three complexes $[\text{Ag}(\text{L}^{5,5/\text{Me}})]_2(\text{PF}_6)_2 \cdot$
 315 $2\text{CH}_2\text{Cl}_2$ (**6**), $[\text{Ag}(\text{L}^{5,5/\text{Me}})]_2(\text{BF}_4)_2 \cdot \text{CH}_2\text{Cl}_2$ (**7**), and $[\text{Ag}$ -
 316 $(\text{L}^{5,5/\text{Me}})]_2(\text{CF}_3\text{SO}_3)_2$ (**8**) crystallize in a dinuclear form, but
 317 they can be grouped in two classes according to the different
 318 type of atoms involved in the metal coordination. In particular,
 319 in **6** the ligand acts as a N_2 bidentate on a metal center, and it
 320 interacts on a second silver atom with the thioether group.
 321 Within the dinuclear unit, there are two identical, very long
 322 contacts between the silver atoms and the symmetrically related

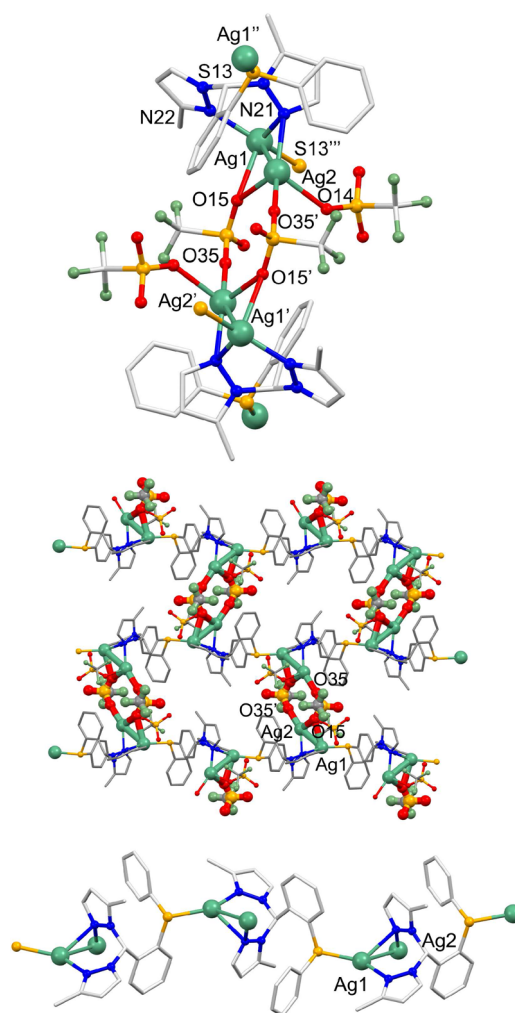


Figure 5. Molecular structure of $[\text{Ag}_2(\text{L}^{5,3/\text{Me}})]_n(\text{CF}_3\text{SO}_3)_{2n} \cdot 2\text{CH}_2\text{Cl}_2$ (**5**) highlighting the bridging triflate anions (top). Depiction of the supramolecular layers generated by the triflate bridges (middle) and of the molecular chain (bottom). Hydrogen atoms and solvent molecules of crystallization were removed for clarity. Symmetry codes: ' = $1/2 - x; 1/2 - y; 1 - z$, '' = $1/2 - x; 1/2 + y; 1/2 - z$, ''' = $1/2 - x; y - 1/2; 1/2 - z$.

N(22) atoms ($2.993(3) \text{ \AA}$). As a consequence, the silver atoms
 exhibit a distorted trigonal planar geometry with the metal that
 lies out of the trigonal plane of 0.22 \AA and is directed toward
 the N(22) nitrogen atom. The thioether is oriented on the same
 side of the N_2 binding moiety. The resulting ligand coordination
 mode is not typically observed for this ligand class and forces
 the central phenyl ring to adopt a slightly less favorable
 geometry than the remainder of the structures presented here.
 In particular, the torsion angle τ is 19° , which is significantly
 greater than the other structures reported. As far as the crystal
 packing is concerned, the dinuclear units assemble in
 supramolecular chains according to the presence of sulfur- π (3.46 \AA)
 and π - π (3.46 \AA) stacking between the peripheral aromatic
 rings of adjacent molecules, illustrated in Figure 6A.

The complexes **7** and **8** present a dinuclear structure with the
 ligand that behaves as a bridging N_2 donor on two metal centers.
 In these two complexes, the thioether does not participate in the
 metal binding and is oriented as found in the great majority of
 the structures with a τ_1 of $-4.6/1.7^\circ$ and

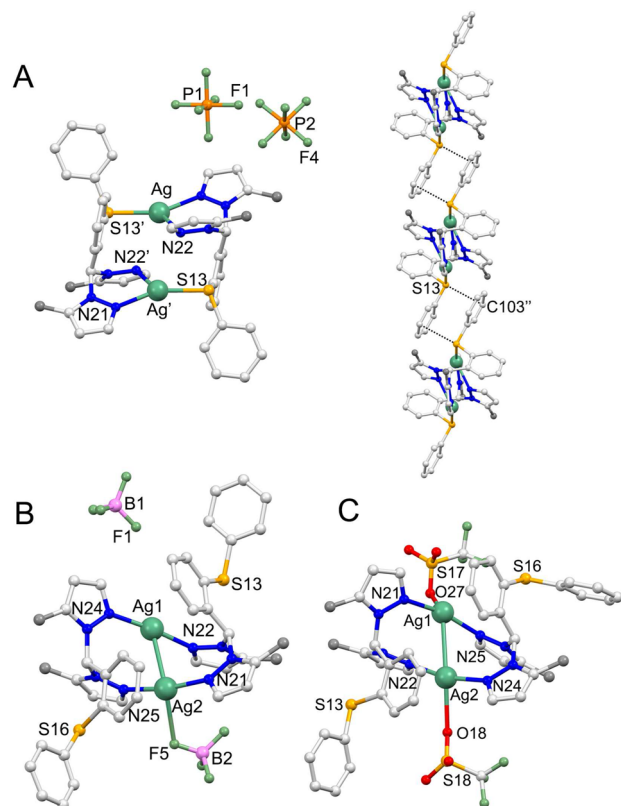


Figure 6. (A) Molecular structure of $[\text{Ag}(\text{L}^{5,5/\text{Me}})]_2(\text{PF}_6)_2 \cdot 2\text{CH}_2\text{Cl}_2$ (**6**) (left) together with the π stacking between the peripheral phenyl rings and portion of the supramolecular chain (right). (B) Molecular structure of $[\text{Ag}(\text{L}^{5,5/\text{Me}})]_2(\text{BF}_4)_2 \cdot \text{CH}_2\text{Cl}_2$ (**7**). (C) Molecular structure of $[\text{Ag}(\text{L}^{5,5/\text{Me}})]_2(\text{CF}_3\text{SO}_3)_2$ (**8**). The hydrogen atoms and the solvent of crystallization were omitted for clarity. Symmetry codes: ' = $-x$; $1 - y$; $-z$, '' = $-1/2 - x$; $3/2 - y$; $-z$.

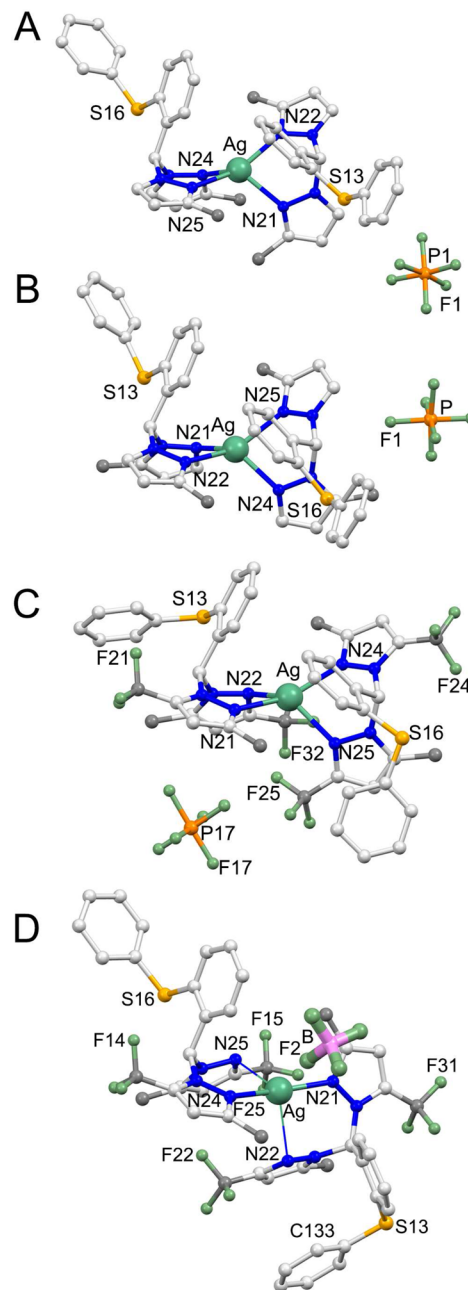


Figure 7. (A) Molecular structures of $[\text{Ag}(\text{L}^{3,3/\text{Me}})](\text{PF}_6)_2 \cdot 2\text{acetone}$ (**9**). (B) Molecular structure of $[\text{Ag}(\text{L}^{3,3/\text{Me}})]_2(\text{PF}_6) \cdot \text{CH}_2\text{Cl}_2$ (**10**). (C) Molecular structure of $[\text{Ag}(\text{L}^{\text{CF}_3})_2](\text{PF}_6)$ (**11**). (D) Molecular structure of $[\text{Ag}(\text{L}^{\text{CF}_3})_2](\text{BF}_4) \cdot \text{CH}_2\text{Cl}_2$ (**12**). Disordered anions, solvent molecules of crystallizations, and hydrogen atoms were removed for clarity. The carbon atoms of the functional groups of the pyrazole rings are highlighted in dark-gray.

343 $-7.5/11.2^\circ$. The silver atom has a linear geometry, which is
 344 distorted by the interactions with the fluorine atom (from a
 345 disordered BF_4^- anion) or the oxygen atom (from a
 346 monodentate CF_3SO_3^- anion), **Figure 6**. Another notable
 347 difference with the structures of **6** is the occurrence of an
 348 argentophilic interaction between the two silver atoms. This is
 349 supported by the presence of short contacts between the metal
 350 atoms of 2.94 Å in **7** and 3.11 Å in **8** and is significantly shorter
 351 than the vdW radii sum (3.44 Å).

352 The ligand $\text{L}^{5,5/\text{Me}}$ is conceptually derived by the parent
 353 compound $\text{L}^{3,3/\text{Me}}$ (**Scheme 1**) by removing two methyl groups
 354 adjacent to the nitrogen donor atoms. This modification
 355 concurs to remove considerable steric hindrance on the donor
 356 functions of the ligands, thus favoring the approach of two
 357 ligand/metal systems and the formation of a dinuclear species.

358 Molecular Structures with M:L 1:2 Stoichiometry.

359 Despite the use of a 1:1 M:L stoichiometry during the
 360 synthesis, some ligands yielded complexes with a M:L 1:2
 361 stoichiometry, namely, $[\text{Ag}(\text{L}^{3,3/\text{Me}})]_2(\text{PF}_6)_2 \cdot 2\text{acetone}$ (**9**), $[\text{Ag}-$
 362 $(\text{L}^{5,3/\text{Me}})]_2(\text{PF}_6)_2 \cdot \text{CH}_2\text{Cl}_2$ (**10**), $[\text{Ag}(\text{L}^{\text{CF}_3})_2](\text{PF}_6)$ (**11**), and
 363 $[\text{Ag}(\text{L}^{\text{CF}_3})_2](\text{BF}_4) \cdot \text{CH}_2\text{Cl}_2$ (**12**), **Figure 7**. The structures are
 364 presented and the reasons rationalized here that underlie this
 365 occurrence. By inspecting the coordination environment of the
 366 four complexes, there is a modulation of the geometry that
 367 varies between the distorted tetrahedral and the linear one. The
 368 complexes having the $\text{L}^{3,3/\text{Me}}$ and $\text{L}^{5,3/\text{Me}}$ ligand exhibit a
 369 distorted tetrahedral geometry with two bidentate N,N' ligand

and four nearly equivalent Ag–N distances (range 2.31–2.35 Å, **370**
Table S4, Figure 7A,B). Oppositely, **12** shows a relatively linear **371**
 geometry because Ag–N(21) and Ag–N(24) are markedly **372**
 shorter (2.18 and 2.19 Å) than the other two Ag–N distances **373**
 (2.61 and 2.68 Å) and the angle N(21)–Ag–N(24) approaches **374**
 180°. An intermediate type of geometry, between the linear and **375**
 the tetrahedral, is more evident in the complex **11**. In fact, the **376**
 Ag–N(21) and Ag–N(24) distances are significantly shorter **377**
 (2.32 and 2.34 Å) than the Ag–N(22) and Ag–N(25) (2.42 **378**
 and 2.43 Å), but the difference is not as pronounced as in **12**. **379**
 Additionally, in this case, the N(21)–Ag–N(24) angle (156°) **380**

381 points to a distortion toward the linearity of the complex.
 382 Interestingly, in the complexes with the L^{CF_3} ligand, the longest
 383 Ag–N bond distances are observed for the nitrogen atom close
 384 to the CF_3 . This observation can be readily explained by taking
 385 into account the electron withdrawal effect exerted by the CF_3
 386 residue on the nitrogen atom, thus reducing the donor
 387 capability of its lone pair. The τ angle of the central phenyl
 388 ring is $-12.7/5.5$ for **11**, $-3.6/5.7$ in **9**, and $-1.7/7.6$ in **10**. In
 389 **12**, one of the ligand exhibits a τ angle of -11.9° ; however, for
 390 the second ligand, τ is of -31.5° , which is considerably greater
 391 than all of the structures presented in this work. This large
 392 deviation is a consequence of the steric hindrance between the
 393 CF_3 group and the peripheral phenyl ring, which exchanges a
 394 π – π interaction with the pyrazole moiety. The closest contact
 395 is between the N(22) and C(133) atoms (3.42 Å, see Figure 7).
 396 In all structures, the thioether group is not involved in any
 397 interaction with the metal centers.

398 **Molecular Structures with the L^{SMe} Ligand.** The ligands
 399 $L^{3,3/Me}$, $L^{5,3/Me}$, $L^{5,5/Me}$, L^{CF_3} , L^{Br} were prepared to evaluate the
 400 influence of the functional groups of the pyrazole rings on the
 401 structural properties of the resulting coordination polymers. It
 402 was previously investigated how the modification of the
 403 peripheral thioether aromatic moiety would alter the structure
 404 and gas absorption capacity of hexameric assemblies (see Figure
 405 1). By combining the results of these studies, it can be inferred
 406 that to obtain porous hexameric architecture, the sufficient
 407 condition is the presence of methyl groups in 3 and 5 positions
 408 on both the pyrazole rings. The nature of the peripheral group
 409 on the thioether moiety remained to be investigated because in
 410 all previous cases it was an aromatic system. The ligand L^{SMe}
 411 was therefore prepared to evaluate the effect of reducing the
 412 steric hindrance of the ligand with the purpose of increasing the
 413 porous capacity of putative hexameric species.

414 Two polymeric complexes were isolated by the reaction of
 415 $AgNO_3$ and $AgBF_4$ with L^{SMe} , and they both exhibit silver
 416 atoms in a distorted tetrahedral geometry achieved by two
 417 bidentate bispyrazolyl moieties. The thioether group then binds
 418 to an additional metal ion extending the polymeric structure
 419 demonstrated in Figure 8. The main difference between
 420 $[Ag(L^{SMe})_n](NO_3)_n \cdot nCH_2Cl_2$ (**13**) and $[Ag_5(L^{SMe})_6](BF_4)_5$
 421 (**14**) is in the overall framework generated, which depends on
 422 the number of metal–sulfur bonds present in the structures. In
 423 particular, in **13**, one of the two independent silver atoms
 424 interacts with two thioether groups and with two NO_3^- anion
 425 in a distorted tetrahedral environment. One of the nitrate
 426 anions, as well as the interacting silver cation, is statically
 427 disordered, and the geometry exhibited by this metal site is
 428 intermediate between the trigonal planar and tetrahedral. The
 429 resulting overall arrangement is in the form of a polymeric
 430 chain. On the other hand, in **14**, one of the metals is in a
 431 trigonal planar geometry deriving from three thioether groups.
 432 Two of the thioethers extend the assembly along one direction,
 433 analogously with the structure of **13**, whereas the third Ag–S
 434 interaction serves to link together two chains, thus forming a
 435 molecular ribbon. An asymmetric unit comprising five silver
 436 cations, six ligands, and five BF_4^- anions characterizes this
 437 complex. Three metals adopt a distorted tetrahedral geometry
 438 bound by two bidentate N,N ligands, whereas two metals adopt
 439 a trigonal planar geometry bound by three thioether groups.
 440 The quality of the data collection was not satisfactory for this
 441 structure, and the position and refinement of some of the
 442 anions are affected by some uncertainty. Nevertheless, above
 443 and below the trigonal plane of the S-bound silver atom are

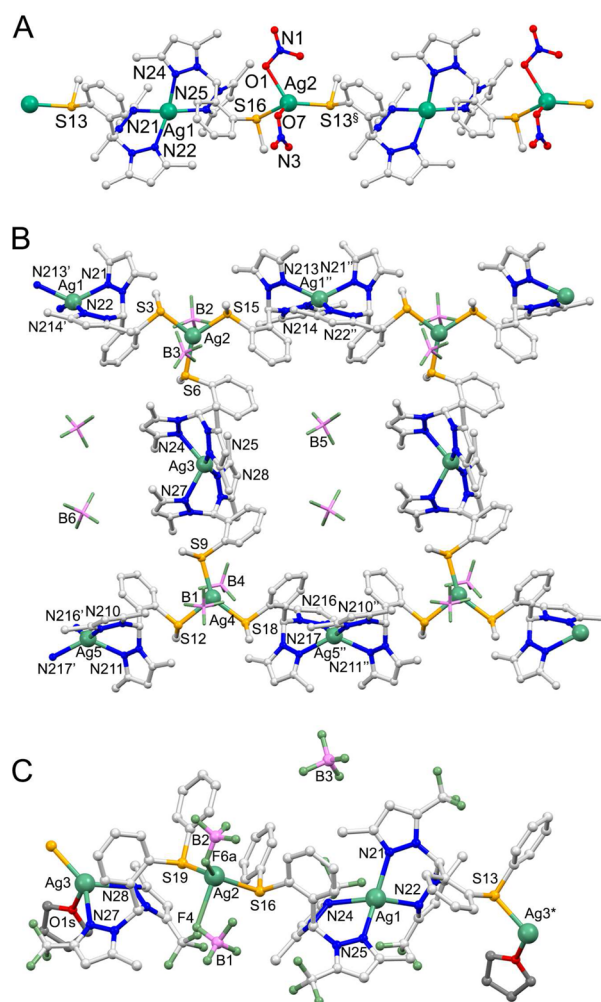


Figure 8. Molecular structures of the complexes for $[Ag(L^{SMe})_n](NO_3)_n \cdot nCH_2Cl_2$ (**13**) (A), $[Ag_5(L^{SMe})_6](BF_4)_5$ (**14**) (B), and $[Ag_3(L^{CF_3})_3](THF)_n(BF_4)_{3n}$ (**15**) (C). Disordered anions, solvent molecules of crystallization, and hydrogen atoms were removed for clarity. Symmetry codes: $\S = x; y; 1 + z$, $' = 1 + x; y; z$, $'' = x - 1; y; z$, $* = x; y; 2 + z$.

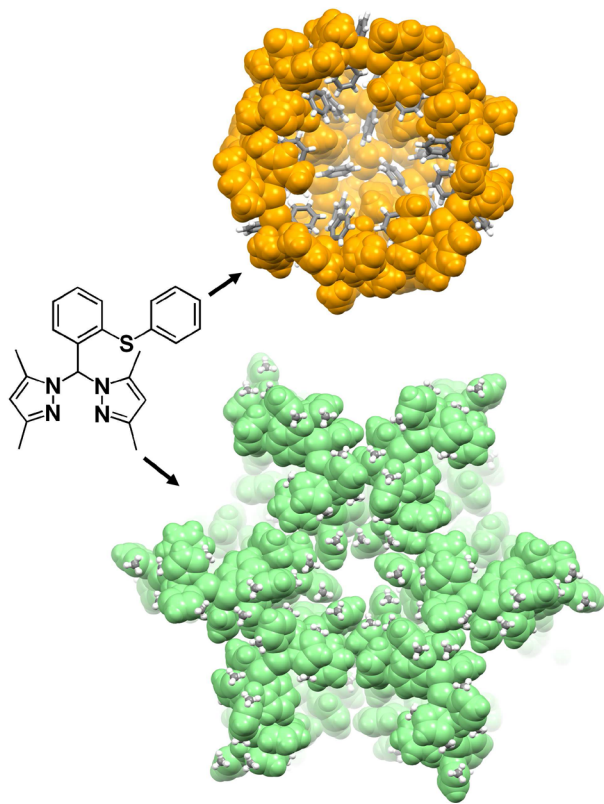
located two BF_4^- anions, suggestive of the occurrence of a very
 weak type of interaction with the metal ion.

Interestingly, the ligand L^{CF_3} also gave a molecular chain in
 the presence of $AgBF_4$ and after crystallization in the presence
 of a weakly coordination solvent such as THF, namely
 $[Ag_3(L^{CF_3})_3](THF)_n(BF_4)_{3n}$ (**15**). The structure is presented
 here because it exhibits similarities with those of L^{SMe} .
 However, when crystallizing the crude product in CH_2Cl_2 ,
 the complex $[Ag(L^{CF_3})_2](BF_4) \cdot CH_2Cl_2$ (**12**) described above
 was isolated. The complex **15** (Figure 8) is characterized by
 presence of three types of silver atoms. Ag(1) exhibits a
 distorted tetrahedral geometry achieved by two N,N bidentate
 ligands, Ag(2) exhibits a distorted tetrahedral geometry and is
 bound by two thioether groups and two fluorine atoms of BF_4^-
 anions. Of the two Ag–F interactions, one is significantly
 shorter than the other (Ag(2)–F(6b)/F(7b) of approximately
 2.4 Å and Ag(2)–F(4) of 2.64 Å). Finally, Ag(3) exhibits a
 distorted tetrahedral geometry according to the chelation of an
 N,N ligand, a bridging thioether, and the oxygen atom of the
 THF molecule. At variance with the structures with the L^{SMe}
 ligand, and in line with the presence of a peripheral aromatic

465 ring in L^{CF_3} , there is a π - π interaction between the two phenyl
466 rings adjacent to the Ag(2) atom.

467 ■ CONCLUSION

468 This paper reported the molecular structure of thioether-
469 functionalized bis(pyrazolyl)methane complexes with Ag(I).
470 The purpose of this work was to investigate the role of the
471 structural modification on the ligand scaffold and evaluate its
472 influence on the overall complex geometry. The work was
473 inspired by recent findings that the change in the peripheral
474 substituents could lead to cavity size modulation in micro-
475 porous frameworks based on the same ligand class and with
476 Ag(I).⁴¹ Inspection of the crystal packing of these previously
477 reported complexes clearly shows that two types of micro-
478 porous structures were present and were surrounded by two
479 ligand components. In particular, the larger cavity was lined
480 with pyrazole methyl groups, whereas the smaller cavity was
481 lined with the peripheral phenyl ring of the thioether moiety
482 shown in Figure 9.



483 **Figure 9.** Depiction of the internal surface of the intracapsular (above)
484 and intercapsular cavities of the $[Ag_6(L^{3,5})_6](BF_4)_6$ complex.^{40,41}

483 The modification of the pyrazole substituents was inves-
484 tigated to lead to a modulation of the cavity size. Another
485 interesting issue is related to the type of donor atoms
486 surrounding the cavities, a fact that can have a strong impact
487 on the absorption properties of a microporous material. The
488 presence of F and Br atoms in L^{CF_3} and L^{Br} , respectively,
489 compared to the other ligands certainly modifies the selectivity
490 index toward gaseous guests when a microporous material is
491 obtained.^{61–64} Nevertheless, in none of the reported com-
492 pounds did the crystal packing exhibit a permanent porous
493 structure. Fifteen structures are coordination polymers
494 (molecular chains or grids, panels B and C in Figure 1), and

seven structures are nonpolymeric (panels D and E in Figure
495 1). Some general observations can be drawn by inspecting the
496 30 structures of this ligand class with Ag(I) (see Figure 1). In
497 particular, (1) the central phenyl ring provides a certain degree
498 of ligand preorganization that favors a conformation in which
499 the N_2 system and the thioether sulfur atom point in opposite
500 directions, usually favoring a bridging ligand mode. This
501 conclusion is supported by the occurrence of this ligand
502 behavior in 23 out of 30 structures (compare panels A–C with
503 D and E in Figure 1). This observation is also supported by the
504 structures of similar bis(pyrazolyl)methane systems function-
505 alized with a central aromatic moiety.^{38,39,42,46,49,65–72} (2) The
506 peripheral phenyl ring plays an important role as a source of
507 various supramolecular interactions. In most of the cases it is
508 involved in π -stacking, as in the case of the porous hexamers
509 and the molecular chains, or it participates into $CH\cdots\pi$
510 interactions. The presence of the π -stacking with one of the
511 pyrazole rings contributes to an additional ligand preorganiza-
512 tion that may be relevant to the formation of isostructural
513 hexameric species. A depiction of the various ligands arrange-
514 ments is summarized in Figure S10. The substitution of the
515 phenyl group with a methyl one in L^{SMe} limits either the
516 supramolecular interactions that can be exchanged by the ligand
517 and it decreases significantly the steric hindrance. As an
518 example, the absence of the aromatic ring in L^{SMe} allowed for
519 the approach of three thioether groups toward a metal center in
520 $[Ag_5(L^{SMe})_6]_n(BF_4)_{5n}$ (14, see Figure 8). (3) The effect of the
521 methyl groups on the pyrazole rings can be appreciated by
522 considering the structures with the ligands $L^{3,3/Me}$, $L^{5,5/Me}$,
523 $L^{5,3/Me}$, L^{CF_3} , and the parent ligand $L^{3,5Me}$. When the steric
524 hindrance is removed from the N_2 donor system as in $L^{5,5/Me}$,
525 dinuclear complexes can be formed because two AgL fragments
526 can easily approach each other (see panel D in Figure 1).
527 Furthermore, when a less symmetric steric hindrance occurs, as
528 with $L^{5,3/Me}$, and L^{CF_3} , it is more difficult to rationalize
529 structural outcome. In fact, CPs having the shape of helicoidal
530 chains can be formed, as well as AgL_2 complexes, even though
531 the synthesis was performed in the 1:1 M:L ratio (panel E of
532 Figure 1). However, the four methyl groups in the parent ligand
533 $L^{3,5Me}$ can provide a moderate steric hindrance stabilizing a
534 specific ligand conformation in analogy the effect exerted by the
535 central phenyl ring, thus resulting in the preferred formation of
536 oligonuclear structures (porous hexamers). (4) The anion
537 appears to have a significant influence on the resulting
538 structural arrangement. In particular, the less symmetric but
539 more coordinating triflate anion induces the formation of high
540 nuclearity systems. In fact, out of the 10 reported structures
541 with this anion, eight comprise an helicoidal molecular chain
542 (irrespective of the pyrazole substituents: $L^{3,5Me}$, L^{Br} , $L^{5,3/Me}$,
543 L^{CF_3}), one is dinuclear and one is hexameric. The reason for
544 this structural influence can be found in the coordination
545 geometry of Ag(I) imposed by the triflate when compared to
546 the less coordinated BF_4^- or PF_6^- . The presence of a N_2S
547 donor ligand and the oxygen atom of the triflate anion tend to
548 satisfy the requirement of Ag(I). In the presence of weakly
549 coordinating anions such as BF_4^- or PF_6^- , however, the metal
550 tends to satisfy its electronic requirements by binding to two N_2
551 systems and providing more varied molecular geometry, whose
552 structural arrangements are driven by the aforementioned steric
553 effect described in points (1)–(3). The combined effects of the
554 anion properties and of the supramolecular interactions were
555 investigated for other types of Ag(I) complexes, pointing to the
556

557 strength of the metal-anion interaction^{73,74} or anion size⁷⁵ as
558 key factors governing the overall architectures.

559 In conclusion, this work rationalizes the structural features of
560 Ag(I) complexes with thioether functionalized bis(pyrazolyl)-
561 methane ligands. Various effects dictate the resulting
562 architectures, and the results based upon structural consid-
563 erations can be valuable to direct future ligand modification to
564 obtain a desired (porous) crystalline structure.

565 ■ ASSOCIATED CONTENT

566 ● Supporting Information

567 The Supporting Information is available free of charge on the
568 ACS Publications website at DOI: 10.1021/acs.cgd.6b00506.

569 Synthesis of the ligands and complexes, thermal
570 ellipsoids plots of the asymmetric units of the Ag(I)
571 coordination polymers, crystallographic tables (PDF)

572 Accession Codes

573 CCDC 1457814–1457828 contains the supplementary crys-
574 tallographic data for this paper. These data can be obtained free
575 of charge via www.ccdc.cam.ac.uk/data_request/cif, or by
576 emailing data_request@ccdc.cam.ac.uk, or by contacting The
577 Cambridge Crystallographic Data Centre, 12 Union Road,
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585 Notes

586 The authors declare no competing financial interest.

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