

University of Parma Research Repository

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

This is the peer reviewd version of the followng article:

Original

Silver(I) and Thioether-bis(pyrazolyl)methane Ligands: The Correlation between Ligand Functionalization and Coordination Polymer Architecture / Bassanetti, Irene; Atzeri, Corrado; Tinonin, Dario Alberto; Marchio', Luciano. - In: CRYSTAL GROWTH & DESIGN. - ISSN 1528-7483. - 16:6(2016), pp. 3543-3552. [10.1021/acs.cgd.6b00506]

Availability: This version is available at: 11381/2807726 since: 2021-10-19T10:45:54Z

Publisher: American Chemical Society

Published DOI:10.1021/acs.cgd.6b00506

Terms of use:

Anyone can freely access the full text of works made available as "Open Access". Works made available

Publisher copyright

note finali coverpage

(Article begins on next page)



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

4 Irene Bassanetti,[†] Corrado Atzeri, Dario Alberto Tinonin, and Luciano Marchiò*

s Dipartimento di Chimica, Università degli studi di Parma, Parco Area delle Scienze 17/a, 43124 Parma, Italy

6 **Supporting Information**

7 ABSTRACT: This work examines the crystal structures of 15 Ag(I) complexes with thioether functionalized bis(pyrazolyl)-8 9 methane derivatives to rationalize the influence of the ligand on the formation of (a) coordination polymers (CPs), (b) 10 oligonuclear (hexameric and dinuclear) complexes, and (c) 11 mononuclear complexes. It was previously reported how this 12 ligand class could generate microporous architectures with 13 permanent porosity. Some ligand modifications could induce a 14 cavity size modulation while preserving the same overall 15 architecture. The bis(pyrazolyl)methane scaffold can be easily 16 functionalized with various structural fragments; hence the 17 structural outcomes were studied in this work using various 18 19



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 $L^{3,3'Me}$, $L^{5,3'Me}$, L^{CF3} , 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^{CF3} and L^{Br} offered the possibility to expand the type of interaction with respect to the ligands based on hydrocarbon substituents (CH₃, phenyl, naphthyl). The effect of the anions was explored using different Ag(I) precursors such as AgPF₆, AgBF₄, AgCF₃SO₃, or AgNO₃. 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 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

28 molecular chains.

20 21

22

23

24 25

26

27

29 INTRODUCTION

30 Over the last three decades, the design of metal-based 31 supramolecular assemblies has become one of the most intense $_{32}$ research areas in chemistry and material science¹⁻⁷ due to the 33 large number of potential applications of these materials, such 34 as catalysis,^{8,9} photochemistry,¹⁰ luminescence,¹¹ sensing,¹² 35 magnetism,^{13,14} gas storage,^{15–17} gas purification,^{18,19} and 36 medicine.²⁰ The ligand features and stereoelectronic character-37 istics of metal ions can control the arrangement of the 38 supramolecular assemblies. The majority of transition metal 39 ions usually exhibit a well-defined geometry (e.g., tetrahedral, 40 square planar, or octahedral). In contrast, the geometry of d¹⁰ 41 metal centers is typically dictated by steric factors, ensuring a 42 greater coordination flexibility. Additional control over the 43 resulting structural arrangement can be achieved by the use of 44 multitopic ligands, which can bridge different metal ions to 45 build flexible network structures. The mutual orientation of the 46 donor atoms defines the ligand geometry as well as the 47 coordinative directionality; the orientation has a profound 48 influence on the overall geometrical structure.¹ These concepts 49 are at play in the rational design in various architectures, such as 50 metal organic frameworks (MOFs), coordination polymers

(CPs), and supramolecular architectures, based upon extended 51 metal-ligand interactions such as polyoxometallates (POMs) 52 or networks based on supramolecular synthons.²¹⁻²⁴ Recent 53 reviews have covered the conceptual distinctions between 54 various types of metal based frameworks, in particular, between 55 MOFs and CPs.^{1,3,25,26} CPs commonly exhibit reversible 56 coordination bonds and can be considered as dynamic 57 synthons, which can assemble in various structural arrange- 58 ments. CP architectures can be influenced by numerous factors 59 including counterions, temperature, solvent systems, metal/ 60 ligand ratios, templates, and the coordination properties of the 61 ligand and metal types.^{27,28} CPs can also be prepared or 62 processed in various ways to obtain nanostructured materials 63 with potential applications in nanoelectronics^{29,30} or in hybrid 64 materials that can be incorporated into lipid membranes.³¹ As 65 far as the metal ion is concerned, the adaptable coordination 66 geometry of Ag(I) allows for the use of silver cationic 67 complexes as building blocks for the construction of 68

 Received:
 April 1, 2016

 Revised:
 May 3, 2016

f1

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 (BF₄⁻⁷, ⁷⁹ PF₆⁻⁷, NO₃⁻⁷, and CF₃SO₃⁻⁷).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



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 $[Ag(L)]_6(PF_6)_6$ complexes.

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





^{*a*}L^{3,5Me} 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^{SMe} 108 was prepared. L^{SMe} 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**

Materials and Methods. All reagents and solvents were 120 121 commercially available. 2-(Phenylthio)benzaldehyde and bis(3,5-122 dimethyl-1H-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 (ppm) referenced to residual solvent protons. Infrared spectra were 126 recorded from 4000 to 700 cm⁻¹ on a PerkinElmer FT-IR Nexus 127 spectrometer equipped with a Thermo-Nicolet microscope. Elemental 128 129 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 μ L) were injected 134 through direct infusion using a syringe pump at 10 μ L/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.

Single Crystal X-ray Structures. Single crystal data were 138 139 collected with a Bruker Smart APEXII area detector diffractometers 140 (Mo K α ; λ = 0.71073 Å). Cell parameters were refined from the observed setting angles and detector positions of selected strong 141 142 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 Selected geometric parameters are reported in Tables S1-S6 and 148 149 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

s2

Synthesis and Characterization. The synthesis of the liss ligands L^{Br} , L^{CF3} , $L^{3,3'Me}$, $L^{5,5'Me}$, $L^{5,3'Me}$, and L^{SMe} was lise 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

Scheme 2. Synthetic Route for the Preparation of the Ligands



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 f2



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).

also be obtained when using the pyrazole with the CF_3 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 $(AgPF_{6}, AgBF_{4}, 190)$ 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 f3

\$3

204 (Figure 1C). The complexes $[Ag(L^{Br})]_n(PF_6)_n$ acetone (1), 205 $[Ag(L^{Br})]_n(BF_4)_n$ acetone (2), and $[Ag(L^{Br})]_n(CF_3SO_3)_n$ 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 $L^{3,SMe}$ 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 N₂ 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



Figure 3. Molecular structure of $[Ag(L^{Br})]_n(PF_6)_n$. acetone (1) projected along the propagation direction of the molecular chain (A) and molecular chain side view (B).

215 asymmetric unit comprises a $[Ag(L^{Br})]_2(X)_2$ fragment (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 BF₄-, it lies out of 224 approximately 0.17-0.22 Å. With CF₃SO₃⁻, 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 bipyrazolyl 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





according to the fact that the structures are centrosymmetric. ²³⁵ The exterior of the chains is defined by alternate anions and ²³⁶ pyrazole rings, whereas those in the interior are located in the ²³⁷ peripheral aromatic moieties of the thioether fragments. ²³⁸ Contrary to the toroidal hexamers described in previous ²³⁹ works, ^{40,41} the crystal packing of **1**–**3** does not exhibit any ²⁴⁰ cavity with permanent porosity, even though acetone ²⁴¹ crystallization molecules are present. The steric profile of L^{Br} ²⁴² is slightly greater than that of L^{3,5Me}, according to the large size ²⁴³ of bromine and the long C–Br bond distance (approximately ²⁴⁴ 1.9 Å). This moderate increase of the steric hindrance on the 4- ²⁴⁵ pyrazole position may be the main reason that hinders the ²⁴⁶ formation of hexameric structures. In fact, by inspecting the ²⁴⁷ structures of the parent compounds $[Ag(L^{3,5Me})]_6(BF_4)_6$ and ²⁴⁸ $[Ag(L^{3,5Me})]_6(BF_4)_{60}$ it appears that the additional presence of ²⁴⁹ a bromine atom as in L^{Br} could provide some steric interference ²⁵⁰ between adjacent and symmetry related molecules. ²⁵¹

The molecular structure of $[Ag(L^{CF3})]_n(CF_3SO_3)_n$ (4) is 252 reported in Figure 4. The ligand L^{CF3} bridges between two 253 f4 metal centers with the N₂ 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 $[Ag(L^{CF3})]_n(CF_3SO_3)_n$ (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 ' = $3/2 - x_i y_i 1/2 + z$.

260 moieties as found with L^{Br}. This new conformation is likely a 261 consequence of the steric hindrance caused by the CF₃ 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 CH₃ 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 (2.62 Å) that is compensated for by a stronger interaction with 273 274 the triflate anions yielding a relatively short Ag-O bond (2.31 275 Å).

A different type of molecular chain is observed for the 276 277 complex $[Ag_2(L^{5,3'Me})]_n(CF_3SO_3)_{2n} \cdot 2CH_2Cl_2$ (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/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 consequence for the donor properties of this ligand. In fact, the 284 285 N(21) nitrogen atom is devoid of significant steric hindrance; therefore, it can interact with two silver atoms in a bridging 286 mode. Moreover, Ag(1) exhibits a distorted tetrahedral 287 2.88 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 Å). 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 additional Ag(2)-triflate fragment can easily interact with the 301 302 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) Å. 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.

Dinuclear Structures. When using the ligand $L^{5,5'Me}$, the structures of the silver complexes present a different arrangelike ment. In fact, the three complexes $[Ag(L^{5,5'Me})]_2(PF_6)_2$. Sis $2CH_2Cl_2$ (6), $[Ag(L^{5,5'Me})]_2(BF_4)_2$ ·CH₂Cl₂ (7), and $[Ag_{16} (L^{5,5'Me})]_2(CF_3SO_3)_2$ (8) crystallize in a dinuclear form, but stype of atoms involved in the metal coordination. In particular, sin 6 the ligand acts as a N₂ bidentate on a metal center, and it so interacts on a second silver atom with the thioether group. Within the dinuclear unit, there are two identical, very long secontacts between the silver atoms and the symmetrically related



Figure 5. Molecular structure of $[Ag_2(L^{5,3/Me})]_n(CF_3SO_3)_{2n}\cdot 2CH_2Cl_2$ (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) Å). As a consequence, the silver atoms 323 exhibit a distorted trigonal planar geometry (Figure 6) with the 324 66 metal that lies out of the trigonal plane of 0.22 Å and is directed 325 toward the N(22) nitrogen atom. The thioether is oriented on 326 the same side of the N₂ binding moiety. The resulting ligand 327 coordination mode is not typically observed for this ligand class 328 and forces the central phenyl ring to adopt a slightly less 329 favorable geometry than the remainder of the structures 330 presented here. In particular, the torsion angle τ is 19°, 331 which is significantly greater than the other structures reported. 332 As far as the crystal packing is concerned, the dinuclear units 333 assemble in supramolecular chains according to the presence of 334 sulfur- π (3.46 Å) and $\pi - \pi$ (3.46 Å) stacking between the 335 peripheral aromatic rings of adjacent molecules, illustrated in 336 Figure 6A.

The complexes 7 and 8 present a dinuclear structure with the 338 ligand that behaves as a bridging N_2 donor on two metal 339 centers. In these two complexes, the thioether does not 340 participate in the metal binding and is oriented as found in the 341 great majority of the structures with a τ_1 of $-4.6/1.7^{\circ}$ and 342



Figure 6. (A) Molecular structure of $[Ag(L^{5,5/Me})]_2(PF_6)_2 \cdot 2CH_2Cl_2$ (6) (left) together with the π stacking between the peripheral phenyl rings and portion of the supramolecular chain (right). (B) Molecular structure of $[Ag(L^{5,5/Me})]_2(BF_4)_2 \cdot CH_2Cl_2$ (7). (C) Molecular structure of $[Ag(L^{5,5/Me})]_2(CF_3SO_3)_2$ (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.

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 BF₄⁻ anion) or the oxygen atom (from a ³⁴⁶ monodentate CF₃SO₃⁻ 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 L^{5,5/Me} is conceptually derived by the parent

compound L^{3,5Me} (Scheme 1) by removing two methyl groups 353 adjacent to the nitrogen donor atoms. This modification 354 concurs to remove considerable steric hindrance on the donor 355 356 functions of the ligands, thus favoring the approach of two 357 ligand/metal systems and the formation of a dinuclear species. Molecular Structures with M:L 1:2 Stoichiometry. 358 359 Despite the use of a 1:1 M:L stoichiometry during the synthesis, some ligands yielded complexes with a M:L 1:2 360 stoichiometry, namely, $[Ag(L^{3,3/Me})_2](PF_6)$ ·2acetone (9), $[Ag(L^{5,3/Me})_2](PF_6)$ ·CH₂Cl₂ (10), $[Ag(L^{CF3})_2](PF_6)$ (11), and 361 362 $[Ag(L^{CF3})_2](BF_4) \cdot CH_2Cl_2$ (12), Figure 7. The structures are 363 364 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 $L^{3,3'Me}$ and $L^{5,3'Me}$ ligand exhibit a 369 distorted tetrahedral geometry with two bidentate N,N' ligand



Figure 7. (A) Molecular structures of $[Ag(L^{3,3/Me})_2](PF_6)$ -2acetone (9). (B) Molecular structure of $[Ag(L^{5,3/Me})_2](PF_6)$ -CH₂Cl₂ (10). (C) Molecular structure of $[Ag(L^{CF3})_2](PF_6)$ (11). (D) Molecular structure of $[Ag(L^{CF3})_2](BF_4)$ -CH₂Cl₂ (12) (D). 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.

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^{CF3} ligand, the longest 383 Ag-N bond distances are observed for the nitrogen atom close 384 to the CF₃. This observation can be readily explained by taking 385 into account the electron withdrawal effect exerted by the CF₃ 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 $_{393}$ CF₃ group and the peripheral phenyl ring, which exchanges a 394 $\pi - \pi$ interaction with the pyrazole moiety. The closest contact is between the N(22) and C(133) atoms (3.42 Å, see Figure 7). 395 396 In all structures, the thioether group is not involved in any interaction with the metal centers. 397

Molecular Structures with the L^{SMe} Ligand. The ligands 398 399 L^{3,3/Me}, L^{5,3/Me}, L^{5,5/Me}, L^{CF3}, 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.

Two polymeric complexes were isolated by the reaction of 414 415 AgNO3 and AgBF4 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 $[Ag_5(L^{SMe})_6]_n (BF_4)_{5n}$ 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 NO₃⁻ 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, analogously with the structure of 13, whereas the third Ag-S 433 434 interaction serves to link together two chains, thus forming a 435 molecular ribbon. An asymmetric unit comprising five silver cations, six ligands, and five BF₄⁻ anions characterizes this 436 437 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 $[Ag(L^{SMe})]_n$ - $(NO_3)_n$, nCH_2Cl_2 (13) (A), $[Ag_5(L^{SMe})_6]_n(BF_4)_{5n}$ (14) (B), and $[Ag_3(L^{CF3})_3(THF)]_n(BF_4)_{3n}$ (15) (C). Disordered anions, solvent molecules of crystallization, and hydrogen atoms were removed for clarity. Symmetry codes: ${}^{\$} = x$; *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 444 weak type of interaction with the metal ion. 445

Interestingly, the ligand L^{CF3} also gave a molecular chain in 446 the presence of AgBF₄ and after crystallization in the presence 447 of a weakly coordination solvent such as THF, namely 448 $[Ag_3(L^{CF3})_3(THF)]_n(BF_4)_{3n}$ (15). The structure is presented 449 here because it exhibits similarities with those of LSMe. 450 However, when crystallizing the crude product in CH2Cl2, 451 the complex $[Ag(L^{CF3})_2](BF_4) \cdot CH_2Cl_2 \ (12)$ described above $_{452}$ was isolated. The complex 15 (Figure 8) is characterized by the 453 presence of three types of silver atoms. Ag(1) exhibits a 454 distorted tetrahedral geometry achieved by two N,N bidentate 455 ligands, Ag(2) exhibits a distorted tetrahedral geometry and is 456 bound by two thioether groups and two fluorine atoms of BF_4^- 457 anions. Of the two Ag-F interactions, one is significantly 458 shorter than the other (Ag(2)-F(6b)/F(7b)) of approximately 459 2.4 Å and Ag(2)-F(4) of 2.64 Å). Finally, Ag(3) exhibits a 460 distorted tetrahedral geometry according to the chelation of an 461 N,N ligand, a bridging thioether, and the oxygen atom of the 462 THF molecule. At variance with the structures with the L^{SMe}_{463} ligand, and in line with the presence of a peripheral aromatic 464

⁴⁶⁵ ring in L^{CF3}, there is a $\pi - \pi$ interaction between the two phenyl ⁴⁶⁶ rings adjacent to the Ag(2) atom.

467 CONCLUSION

This paper reported the molecular structure of thioether-468 469 functionalized bis(pyrazolyl) methane complexes with Ag(I). 470 The purpose of this work was to investigate the role of the structural modification on the ligand scaffold and evaluate its 471 472 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.



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

The modification of the pyrazole substituents was inves-483 484 tigated to lead to a modulation of the cavity size. Another 485 interesting issue is related to the type of donor atoms surrounding the cavities, a fact that can have a strong impact 486 on the absorption properties of a microporous material. The 487 presence of F and Br atoms in L^{CF3} and L^{Br}, respectively, 488 489 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 N₂ 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... π 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 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 s22 considering the structures with the ligands $L^{3,3/Me}$, $L^{5,5/Me}$, s23 $L^{5,3/Me}$, L^{CF3} , and the parent ligand $L^{3,5Me}$. When the steric s24 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^{CF3} , it is more difficult to rationalize the 529 structural outcome. In fact, CPs having the shape of helicoidal 530 chains can be formed, as well as AgL₂ 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^{CF3}), 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 BF₄⁻ or PF₆⁻, however, the metal 550 tends to satisfy its electronic requirements by binding to two N2 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.

In conclusion, this work rationalizes the structural features of 660 Ag(I) complexes with thioether functionalized bis(pyrazolyl)-661 methane ligands. Various effects dictate the resulting 662 architectures, and the results based upon structural consid-663 erations can be valuable to direct future ligand modification to 664 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
- s70 ellipsoids plots of the asymmetric units of the Ag(I)
- 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, 578 Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

580 Corresponding Author

581 *E-mail: marchio@unipr.it.

582 Present Address

^{583 T}Dipartimento di Scienza dei Materiali, Università degli Studi di ⁵⁸⁴ Milano Bicocca, via Roberto Cozzi 55, 20125, Milano, Italy.

585 Notes

586 The authors declare no competing financial interest.

587 **ACKNOWLEDGMENTS**

588 This study was supported by the Università degli Studi di 589 Parma (Parma, Italy).

590 **REFERENCES**

(1) Cook, T. R.; Zheng, Y.; Stang, P. J. Chem. Rev. 2013, 113, 734–
 777.

- 593 (2) Cook, T. R.; Stang, P. J. Chem. Rev. 2015, 115, 7001-7045.
- (3) Biradha, K.; Ramanan, A.; Vittal, J. J. *Cryst. Growth Des.* **2009**, *9*, 595 2969–2970.
- 596 (4) Moulton, B.; Zaworotko, M. J. Chem. Rev. 2001, 101, 1629– 597 1658.
- 598 (5) Kitagawa, S.; Uemura, K. Chem. Soc. Rev. 2005, 34, 109–119.
- (6) Du, M.; Banerjee, R.; Shimizu, G. K. H. CrystEngComm 2013, 15, 600 9237–9238.
- (7) Robin, A. Y.; Fromm, K. M. Coord. Chem. Rev. 2006, 250, 2127–
 2157.
- 603 (8) Hasegawa, S.; Horike, S.; Matsuda, R.; Furukawa, S.; Mochizuki,
- 604 K.; Kinoshita, Y.; Kitagawa, S. J. Am. Chem. Soc. 2007, 129, 2607–605 2614.
- 606 (9) Kajiwara, T.; Fujii, M.; Tsujimoto, M.; Kobayashi, K.; Higuchi, 607 M.; Tanaka, K.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2016**, *55*, 2697– 608 2700.
- 609 (10) Flynn, D. C.; Ramakrishna, G.; Yang, H.; Northrop, B. H.;
- 610 Stang, P. J.; Goodson, T., III J. Am. Chem. Soc. 2010, 132, 1348-1358.
- 611 (11) Cui, Y.; Yue, Y.; Qian, G.; Chen, B. Chem. Rev. 2012, 112, 612 1126–1162.
- 613 (12) Xie, Z.; Ma, L.; de Krafft, K. E.; Jin, A.; Lin, W. J. Am. Chem. Soc. 614 **2010**, *132*, 922–923.
- 615 (13) Zhang, Q.; Li, B.; Chen, L. Inorg. Chem. 2013, 52, 9356-9362.
- 616 (14) Zhang, W.; Xiong, R. Chem. Rev. 2012, 112, 1163-1195.

- (15) Gygi, D.; Bloch, E. D.; Mason, J. A.; Hudson, M. R.; Gonzalez, 617
 M. I.; Siegelman, R. L.; Darwish, T. A.; Queen, W. L.; Brown, C. M.; 618
 Long, R. Chem. Mater. 2016, 28, 1128–1138.
- (16) Gándara, F.; Furukawa, H.; Lee, S.; Yaghi, O. M. J. Am. Chem. 620 Soc. 2014, 136, 5271–5274. 621
- (17) Ma, S.; Zhou, H. Chem. Commun. 2010, 46, 44-53.
- (18) Barea, E.; Montoro, C.; Navarro, J. A. R. *Chem. Soc. Rev.* **2014**, 623 43, 5419–5430. 624
- (19) Bloch, D. E.; Queen, W. L.; Krishna, R.; Zadrozny, J. M.; Brown, 625 C. M.; Long, J. R. Science **2012**, 335, 1606–1611. 626
- (20) Horcajada, P.; Gref, R.; Baati, T.; Allan, P. K.; Maurin, G.; 627 Couvreur, P.; et al. *Chem. Rev.* **2012**, *112*, 1232–1268. 628
- (21) Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. 629 Science **2013**, 341, 1230444. 630
- (22) Gao, W.; Chrzanowski, M.; Ma, S. *Chem. Soc. Rev.* **2014**, *43*, 631 5841–5866. 632
- (23) Miras, H. N.; Vilà-Nadal, L.; Cronin, L. Chem. Soc. Rev. 2014, 633 43, 5679–5699. 634
- (24) Atzeri, C.; Marchiò, L.; Chow, Y. C.; Kampf, J. W.; Pecoraro, V. 635 L.; Tegoni, M. *Chem. - Eur. J.* **2016**, *22*, 6482–6486. 636
- (25) Janiak, C.; Vieth, J. K. New J. Chem. 2010, 34, 2366–2388. 637
- (26) Batten, S. R.; Champness, N. R.; Chen, X.; Garcia-martinez, J.; 638 Kitagawa, S.; Ohrstrom, L.; et al. *CrystEngComm* **2012**, *14*, 3001–639 3004. 640
- (27) Janiak, C. Dalton Trans. 2003, 2781-2814.
- (28) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, 642 43, 2334–2375. 643
- (29) Puigmartí-luis, J.; Rubio-martínez, M.; Hartfelder, U.; Imaz, I.; 644 Maspoch, D.; Dittrich, P. S. J. Am. Chem. Soc. 2011, 133, 4216–4219. 645
- (30) Gómez-Herrero, J.; Zamora, F. Adv. Mater. 2011, 23, 5311–646 5317. 647
- (31) Ohtani, R.; Inukai, M.; Hijikata, Y.; Ogawa, T.; Takenaka, M.; 648 Ohba, M.; Kitagawa, S. Angew. Chem., Int. Ed. **2015**, 54, 1139–1143. 649
- (32) Khlobystov, A. N.; Blake, A. J.; Champness, N. R.; Lemenovskii, 650
- D. A.; Majouga, A. G.; Zyk, N. V.; Schröder, M. Coord. Chem. Rev. 651 2001, 222, 155–192. 652
- (33) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Rizzato, S. 653 CrystEngComm 2002, 4, 121–129. 654
- (34) Wu, H.; Dong, X.; Ma, J.; Liu, H.; Bai, H.; Yang, J. Dalton Trans. 655 2009, 3162–3174. 656
- (35) Caballero, A. B.; Maclaren, J. K.; Rodríguez-Diéguez, A.; Vidal, 657 I.; Dobado, J. a.; Salas, J. M.; Janiak, C. *Dalton Trans.* **2011**, 40, 658 11845–11855.
- (36) Lu, X.; Ye, J.; Sun, Y.; Bogale, R. F.; Zhao, L.; Tian, P.; Ning, G. 660 Dalton Trans. **2014**, 43, 10104–10113. 661
- (37) Serpe, A.; Artizzu, F.; Marchiò, L.; Mercuri, M. L.; Pilia, L.; 662 Deplano, P. Cryst. Growth Des. **2011**, *11*, 1278–1286. 663
- (38) Bassanetti, I.; Marchio, L. Inorg. Chem. 2011, 50, 10786-10797. 664
- (39) Gennari, M.; Bassanetti, I.; Marchio, L. Polyhedron **2010**, 29, 665 361–371. 666
- (40) Bassanetti, I.; Mezzadri, F.; Comotti, A.; Sozzani, P.; Gennari, 667 M.; Calestani, G.; Marchiò, L. J. Am. Chem. Soc. **2012**, 134, 9142–668 9145. 669
- (41) Bassanetti, I.; Comotti, A.; Sozzani, P.; Bracco, S.; Calestani, G.; 670 Mezzadri, F.; Marchio, L. J. Am. Chem. Soc. **2014**, *136*, 14883–14895. 671
- (42) Reger, D. L.; Watson, R. P.; Smith, M. D.; Pellechia, P. J.; 672 October, R. V. Organometallics **2006**, 25, 743–755. 673
- (43) Reger, D. L.; Foley, E. A.; Smith, M. D. Inorg. Chem. 2010, 49, 674 234–242. 675
- (44) Zhang, L.; Ren, Z.; Li, H.; Lang, J. *CrystEngComm* **2011**, *13*, 676 1400–1405. 677
- (45) Reger, D. L.; Watson, R. P.; Gardinier, J. R.; Smith, M. D. Inorg. 678 Chem. 2004, 43, 6609–6619. 679
- (46) Gardinier, J. R.; Tatlock, H. M.; Hewage, J. S.; Lindeman, S. V. 680 *Cryst. Growth Des.* **2013**, *13*, 3864–3877. 681
- (47) Reger, D. L.; Pascui, A. E.; Smith, M. D. Eur. J. Inorg. Chem. 682 2012, 2012, 4593-4604. 683
- (48) Morin, T. J.; Merkel, A.; Lindeman, S. V.; Gardinier, J. R. *Inorg.* 684 *Chem.* **2010**, *49*, 7992–8002. 685

622

641

- 686 (49) Santillan, G. A.; Carrano, C. J. Inorg. Chem. 2007, 46, 1751– 687 1759.
- 688 (50) Dura, G.; Manzano, B. R.; Carrión, M. C.; Jalón, F. A.; 689 Rodriguez, A. M. Cryst. Growth Des. 2014, 14, 3510–3529.
- 690 (51) Chandrasekhar, V.; Thilagar, P.; Senapati, T. *Eur. J. Inorg. Chem.*691 2007, 2007, 1004–1009.
- 692 (52) Reger, D. L.; Brown, K. J.; Gardinier, J. R.; Smith, M. D. 693 Organometallics **2003**, *22*, 4973–4983.
- 694 (53) Gardinier, J. R.; Hewage, J. S.; Lindeman, S. V. Inorg. Chem.
 695 2014, 53, 1975–1988.
- 696 (54) Gilday, L. C.; Robinson, S. W.; Barendt, T. A.; Langton, M. J.;
- 697 Mullaney, B. R.; Beer, P. D. Chem. Rev. 2015, 115, 7118-7195.
- 698 (55) SMART (control) and SAINT (integration) Software for CCD 699 Systems; Bruker AXS: Madison, WI, 1994.
- 700 (56) Area-Detector Absorption Correction; Siemens Industrial 701 Automation Inc.: Madison, WI, 1996.
- 702 (57) Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.;
- 703 Cascarano, G. L.; De Caro, L.; Giacovazzo, C.; Polidori, G.; Spagna, R. 704 *J. Appl. Crystallogr.* **2005**, *38*, 381–388.
- 705 (58) Sheldrick, G. M. Acta Crystallogr., Sect. A: Found. Crystallogr. 706 **2008**, 64, 112–122.
- 707 (59) Farrugia, L. J. J. Appl. Crystallogr. 1999, 32, 837–838.
- 708 (60) Macrae, C. F.; Edgington, P. R.; McCabe, P.; Pidcock, E.; 709 Shields, G. P.; Taylor, R.; Towler, M.; van de Streek, J. *J. Appl.* 710 *Crystallogr.* **2006**, *39*, 453–457.
- 711 (61) Ni, J.; Wei, K.-J.; Liu, Y.; Huang, X.-C.; Li, D. Cryst. Growth Des. 712 **2010**, *10*, 3964–3976.
- 713 (62) Yang, C.; Kaipa, U.; Mather, Q. Z.; Wang, X.; Nesterov, V.; 714 Venero, A. F.; Omary, M. A. J. Am. Chem. Soc. **2011**, 133, 18094– 715 18097.
- 716 (63) Hulvey, Z.; Sava, D. A.; Eckert, J.; Cheetham, A. K. *Inorg. Chem.* 717 **2011**, *50*, 403–405.
- 718 (64) Li, J.-R.; Kuppler, R. J.; Zhou, H. Chem. Soc. Rev. 2009, 38, 719 1477-1504.
- (65) Reger, D. L.; Pascui, A. E.; Foley, E. A.; Smith, M. D.; Jezierska,
 J.; Ozarowski, A. Inorg. Chem. 2014, 53, 1975–1988.
- 722 (66) Pilar Carranza, M.; Manzano, B. R.; Jalón, F. a.; Rodríguez, A. 723 M.; Santos, L.; Moreno, M. *New J. Chem.* **2013**, *37*, 3183–3194.
- 724 (67) Santillan, G. A.; Carrano, C. J. Inorg. Chem. 2008, 47, 930-939.
- 725 (68) Reger, D. L.; Pascui, A. E.; Smith, M. D.; Jezierska, J.;
- 726 Ozarowski, A. Inorg. Chem. 2012, 51, 11820–11836.
- 727 (69) Willis, C.; Messerle, B. A.; Ho, J. H. H.; Wagler, J. Dalton Trans. 728 **2011**, 40, 11031–11042.
- 729 (70) Reger, D. L.; Watson, R. P.; Smith, M. D. *Inorg. Chem.* **2006**, *45*, 730 10077–10087.
- 731 (71) Santillan, G. A.; Carrano, C. J. Dalton Trans. 2008, 3995-4005.
- 732 (72) Wang, S.; Zang, H.; Sun, C.; Xu, G.; Wang, X.; Shao, K.; Lan, Y.; 733 Su, Z. *CrystEngComm* **2010**, *12*, 3458–3462.
- 734 (73) Co, C. F.; So, C. F.; Jung, O.; Kim, Y. J.; Lee, Y.; Park, K.; Lee, 735 S. S. Inorg. Chem. **2003**, 42, 844–850.
- 736 (74) Lee, E.; Ju, H.; Kim, S.; Park, K.; Lee, S. S. *Cryst. Growth Des.* 737 **2015**, *15*, 5427–5436.
- 738 (75) Andreychuk, N. R.; Allard, S. R.; Parent, S. L. M.; Assoud, A.; 739 Mackinnon, C. D. *Cryst. Growth Des.* **2015**, *15*, 4377–4384.