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## Coordination Polymers from Main Group Ring Compounds

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### GRAPHICAL ABSTRACT

**Abstract** *4,7-dicyano-2,1,3-benzothiadiazole, L1, and diethyl-4,7-dicarboxylato-2,1,3-benzothiadiazole, L2, form coordination polymers with silver(I) salts of weakly-coordinating anions. Synthesis was achieved by the slow diffusion of benzene solutions of the silver salts into dichloromethane solutions of L1 or L2. Slow growth of crystals occurred with partial evaporation of the solvent, leading to a number of different crystalline coordination polymers. For L1, both the nitrile and ring N atoms can coordinate with great variability of structural motifs, whereas for L2 a chelating geometry is always found in which each Ag<sup>+</sup> is coordinated by two N and two carbonyl O from different ligands. The resulting coordination polymers form layer structures that tend to fill with solvent benzene molecules in a stoichiometric fashion; the benzenes are found to  $\pi$ -coordinate to silver.*

**Keywords** 2,1,3-chalcogenadiazoles; silver(I) salts; network solids; solvent channels

## INTRODUCTION

Coordination polymers built from bridging organic ligands are well established in the literature and have been developed for numerous applications, including molecule-storage, luminescence, as sensors, in single-molecule magnets and for electrical conductivity.<sup>1-4</sup> Only rarely have the bridging ligands themselves been redox-active compounds.<sup>5</sup> Main group ring compounds provide a rich opportunity for the development of new redox active ligands.<sup>6-8</sup> Supramolecular architectures require *secondary bonding interactions* (SBI) to increase the density of intermolecular interactions for the stabilization of such coordination polymers. 2,1,3-chalcogenadiazoles are redox-active heterocycles with strong SBI.<sup>9,10</sup>

In general, coordination polymers can be used to build 3D-networks linking metal centers together into arrays, with the cavities filled with any necessary counterion, and intentional or adventitious guest molecules, including solvents. When these arrays are found to be sufficiently robust they are usually termed Metal Organic Frameworks (MOFs), Figure 1a, which are “engineered” porous solids. They may be overall neutral or cationic and thus the cavities in the framework may or may not need to accommodate counterions. A common application of this class is gas sorption with guest molecules filling the interstitial cavities.<sup>4</sup> A second class of MOF may be termed *functional* MOFs; for example, with paramagnetic transition metals (Figure 1b) to produce functional magnetic materials.<sup>4</sup> In such MOFs, the lattice serves to control the spin-interactions between metal centers. A third conceivable design (Figure 1c) adds redox-active frameworks where the ligands have variable and switchable oxidation states. Here we may expect: the “tuning” of magnetism, in- or out-migration of anions with applications e.g. to

sensors or energy storage, or activation/deactivation of luminescence. This report describes our initial efforts to build coordination polymers based on 4,7-disubstituted-2,1,3-benzothiadiazoles (BTD) which are capable of reduction to stable radical anions with a large redox-stability field and which possess strong luminescence in their neutral forms.<sup>9</sup>

## RESULTS AND DISCUSSION

The ligands investigated (Scheme 1) are 4,7-dicyano-2,1,3-benzothiadiazole, L1, and diethyl-4,7-dicarboxylato-2,1,3-benzothiadiazole, L2. The ligands were prepared according to published methods<sup>11,12</sup> and were fully characterized, including single-crystal X-ray structures.

The general procedure that we used for the preparation of coordination polymers was addition of a saturated benzene solution of the appropriate AgX salts (X = weakly-coordinating monoanion) to approximately equal volumes of L1 or L2 in dichloromethane. In most cases, the crystalline material obtained from solvent diffusion was analytically pure and suitable for X-ray diffraction studies. The structural motif of a representative coordination polymer is shown in Figure 2 which was found to have the stoichiometry  $[\text{Ag}(\text{L1})_2]\text{BF}_4$  and in which *only the nitrile N are coordinated to Ag<sup>+</sup>*. Here the  $\text{BF}_4^-$  ions occupy the only voids within the framework created by metal and ligand. However, under slightly different conditions the same constituents afford a polymer with the stoichiometry  $[\text{Ag}_4(\text{L1})_5](\text{BF}_4)_4$  wherein both nitrile N and *one* of the ring N are coordinated.

Similar reactions of  $\text{Ag}^+$  using larger anions disrupt the networks sufficiently to create additional cavities in the lattice and these were found to adsorb benzene from the solvent

mixture. In this way, coordination polymers with stoichiometry  $[\text{Ag}_2(\text{L1})](\text{SbF}_6)_2 \cdot 2\text{C}_6\text{H}_6$ ,  $[\text{Ag}(\text{L1})]\text{PF}_6 \cdot \text{C}_6\text{H}_6$  and  $[\text{Ag}_2(\text{L1})](\text{O}_3\text{SCF}_3)_2 \cdot \text{C}_6\text{H}_6$  were obtained.

A similar approach using L2 resulted in coordination polymers with a significant change in the local structure. As shown in the representative motif in Figure 3, a metal chelate geometry is favoured for the diester ligands, in which each  $\text{Ag}^+$  is coordinated by carbonyl oxygen and ring nitrogen atoms from two different ligands to afford approximately square-planar coordination around the metal. Variation between different counterions is observed in how the 5<sup>th</sup> and 6<sup>th</sup> coordination sites around  $\text{Ag}^+$  are arranged. In a structure with overall formula  $[\text{Ag}(\text{L2})]\text{ClO}_4$ , the anion supplies additional O donors to create local  $(\text{L2})_2(\text{O}-\text{ClO}_3)_2$  dimeric units with bridging perchlorates. For crystals grown from the mother liquors by slow evaporation, coordination polymers with formulae  $[\text{Ag}(\text{L2})]\text{X} \cdot \text{C}_6\text{H}_6$  ( $\text{X} = \text{ClO}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$  or  $\text{SbF}_6^-$ ) form layer-structures in which the counter ion and  $\pi$ -coordinated benzene fill the interstitial gaps and supply various donors for the two open coordination sites at the metal.

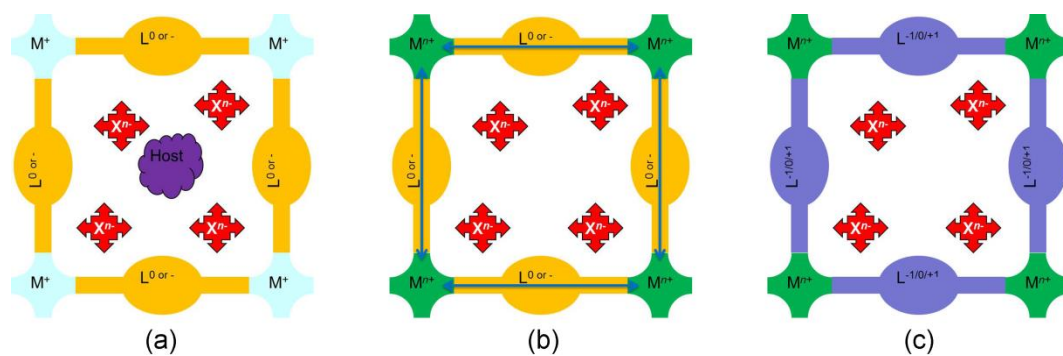
In summary, the chosen ligands L1 and L2 based on nitrile nitrogen and ester carbonyl oxygen donor groups, respectively, form a variety of interesting network structures with silver(I) in combination with a number of the more popular weakly-coordinating anions. The 3-D structures as determined by single-crystal X-ray diffraction show a variety of different structural motifs and are able to form structures with solvent channels that are readily occupied by benzene molecules.

## REFERENCES

1. Desiraju, G.R.; Vittal, J. J.; Ramanan A., *Crystal Engineering – A Textbook*; World Scientific: Singapore, 2011.
2. MacGillivray, L. R.; Lukehart, C. M., Eds., *Metal-Organic Framework Materials*, Wiley: Chichester, UK, 2014.
3. Medishetty, R.; Vittal, J. J., “Metal-organic frameworks for photochemical reactions”, in *Metal-organic frameworks for photonics applications* (Eds: Chen B.; Qian. G.), *Struct. & Bonding* **2014**, 157, 105-144.
4. Batten, S. R., *Coordination Polymers: Design, Analysis and Application*. RSC Publishing: Cambridge, 2008; pp. 297–307, 396–407.
5. Ghosh, S. K.; Kitagawa, S., “Surface pore engineering of porous coordination polymers”, in MacGillivray, L. R., Ed., *Metal-Organic Frameworks: Design and Applications*; Wiley: Chichester, 2010; pp 165-192.
6. Bashirov, D. A.; Sukhikh, T. S.; Kuratieva, N. V.; Naumov, D. Yu.; Konchenko, S. N.; Semenov, N. A.; Zibarev, A. V. *Polyhedron* **2012**, 42, 168-174.
7. Bashirov, D. A.; Sukhikh, T. S.; Kuratieva, N. V.; Chulanova, E. A.; Yushina, I. V.; Gritsan, N. P.; Konchenko, S. N.; Zibarev, A. V. *RSC Adv.* **2014**, 4, 28309-28316.
8. Sukhikh, T. S.; Bashirov, D. A.; Kuratieva, N. V.; Smolentsev, A. I.; Bogomyakov, A. S.; Burirov, V. A.; Mustafina, A. R.; Zibarev, A. V.; Konchenko, S. N. *Dalton Trans.* **2015**, 44, 5727-5734.
9. Boeré, R.T. and Roemmele, T.L. *Coord. Chem. Rev.* **2000**, 210, 369-445.
10. Cozzolino, A. F., Elder, P. J. W., Vargas-Baca, I. *Coord. Chem. Rev.* **2011**, 255, 1426–1438.

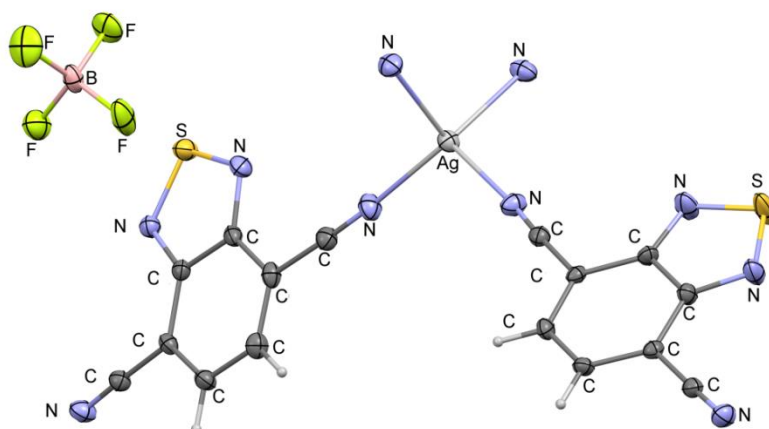
11. Pilgram, K.; Skiles, R. D. *J. Heterocycl. Chem.* **1974**, 11, 777-786.

12. Pilgram, K. *J. Heterocycl. Chem.* **1974**, 11, 835-837.

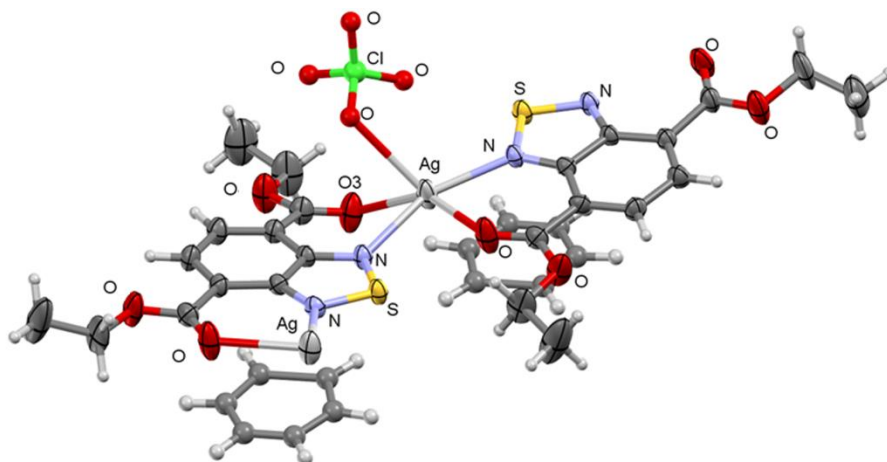


**Figure 1** Cartoon depictions of (a) a conventional MOF; (b) a functional MOF with paramagnetic metals; (c) a MOF where the spacer ligands have  $>1$  oxidation states in conjunction with diamagnetic or paramagnetic metals.

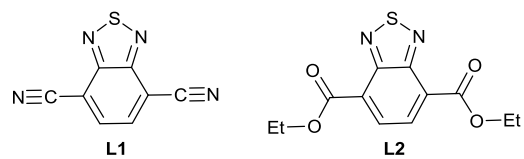




**Figure 2** Displacement ellipsoids plot of the coordination core in  $[Ag(L1)_2]BF_4$ .



**Figure 3** Displacement ellipsoids plot of the coordination core in [Ag(L2)][ClO<sub>4</sub>] $\cdot$ C<sub>6</sub>H<sub>6</sub>.



**Scheme 1** 4,7-X<sub>2</sub>-2,1,3-benzothiadiazole ligands.

