

Coordination Chemistry and Crystal Engineering of Picolyl-Substituted Cyclic Amines

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Introduction

Metal-Organic Frameworks (MOFs) are porous materials consisting of metal ion/cluster “nodes” and organic ligands or “linkers” such as those shown in Figure 1, which together form crystalline structures which have a variety of applications such as drug delivery, gas separation/storage and many more.¹ We aim to design MOFs for separation of CO₂ from flue gas and in direct air capture applications, needed to achieve meaningful emission reductions while scaling up renewable energy production. In order to rationally design materials for this function, the interactions governing their assembly require study.² In this work, subtle variations were made in the ligand backbones, and these were combined with cobalt(II) and silver(I) salts to examine the effect of these variants on the crystal structure of these compounds using X-Ray Diffraction and Hirshfeld Surface Analysis.

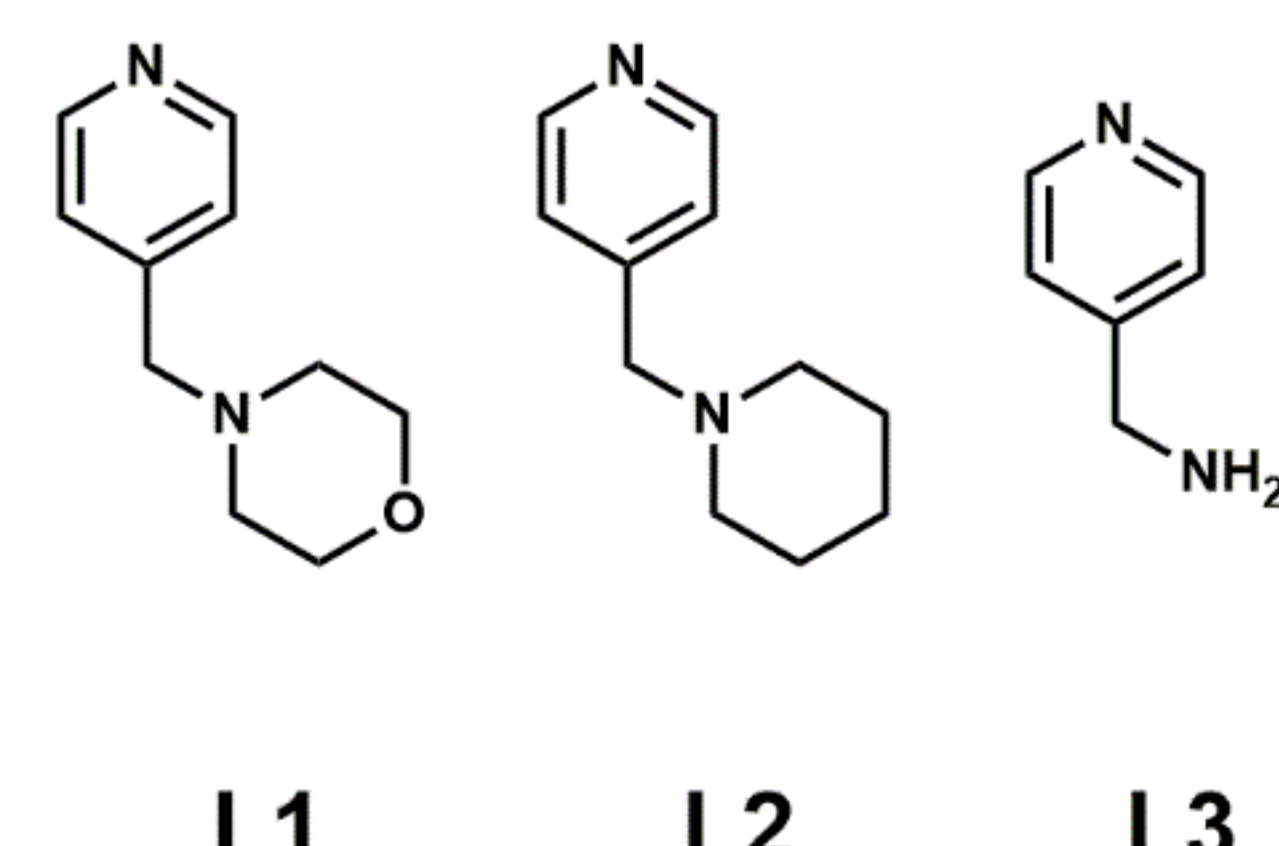


Figure 1. The ligands used in this study

Silver(I) Complexes

Complexes of AgSbF₆ and L1 and L2 allow for the comparison of the effect of the presence or absence of the oxygen atom on the crystal structure. The geometric flexibility of silver(I) results in it interacting with both nitrogen atoms in the ligand structures.

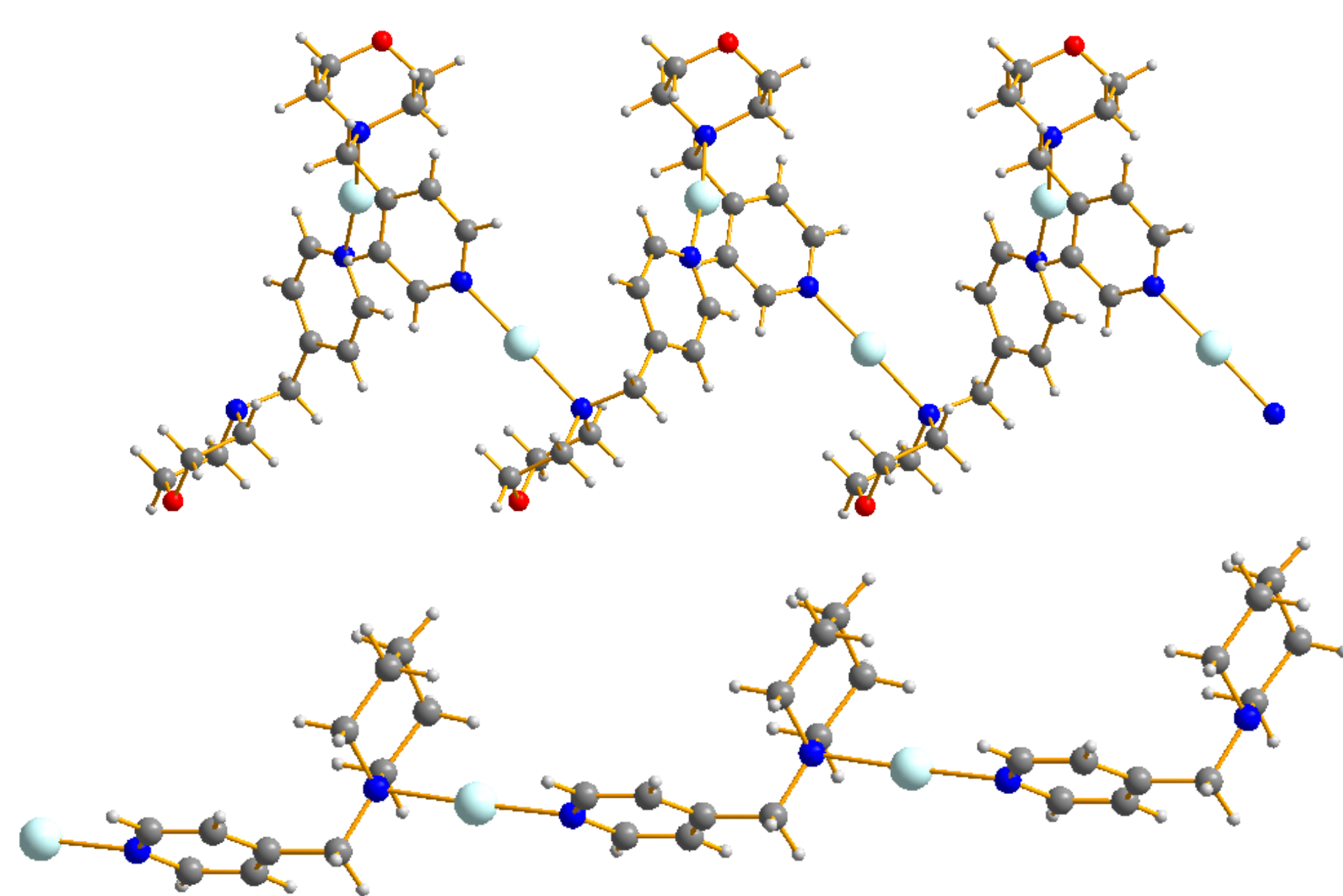


Figure 2. 1D polymer chains of AgSbF₆ with L1 (top) and L2 (bottom)

In both cases, the resulting structure is a 1D polymeric chain, shown in Figure 2, but the extended structures differ significantly. In L1 the chain extends in a linear fashion, with face-to-face π-π interactions between pyridine groups. In contrast, L2 gives a twisted chain with hydrogen bonding governing the interaction of neighbouring chains.

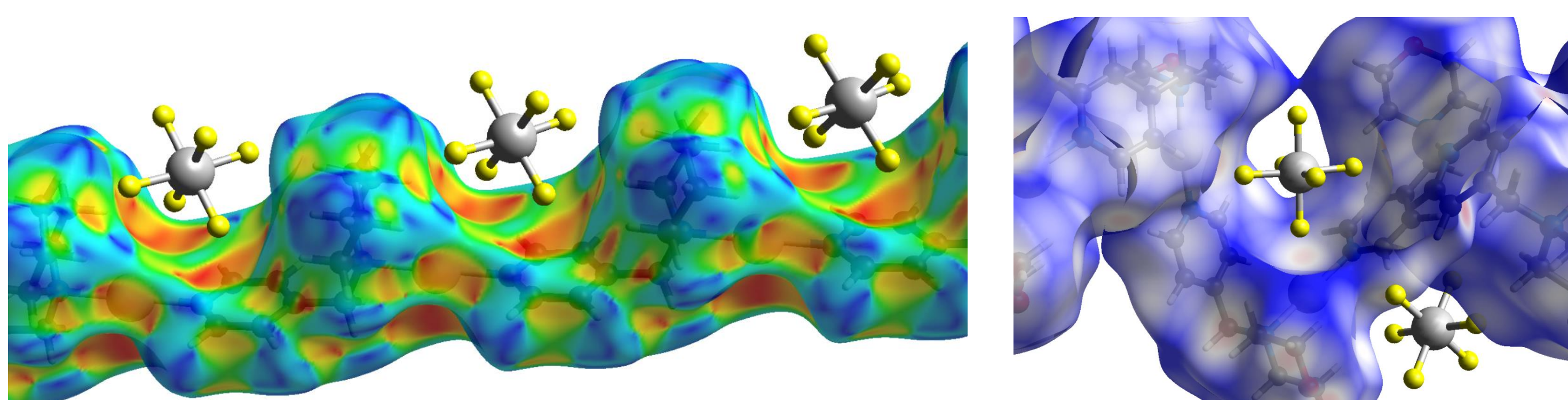


Figure 3. Hirshfeld surface diagrams of AgSbF₆ with L1 (left) and L2 (right)

Hirshfeld surface analysis diagrams seen in Figure 3 show the interactions between the hexafluoroantimonate anions and the polymeric chains of L1 and L2. In the case of the L1 complex, there are interactions present between the anion and the ligand as indicated by the yellow and orange/red areas of the Hirshfeld surface diagram. In contrast, the absence of these areas of the diagram of the complex of L2 indicates that there are no strong interactions between the chain and the counterion.

The analysis of crystal structures and Hirshfeld surface analysis has allowed for an insight into the effects of a slight variation in ligand structure on the interactions governing the assembly of these complexes.

Cobalt(II) Complexes

Combining CoCl₂·6H₂O with L1 and L2 gives discrete (non-polymeric) trichlorocobaltate structures seen in Figure 4. Cobalt(II) is less geometrically flexible than silver(I) and therefore only interacts with one of the nitrogen atoms in each ligand structure. The individual discrete complexes interact with each other through hydrogen bonding creating extended “zig-zag” structures, seen in Figure 5. For complexes of L1 and L2 this interaction varies slightly due to the difference in ligand structures, with a carbon atom replacing an oxygen atom in L2.

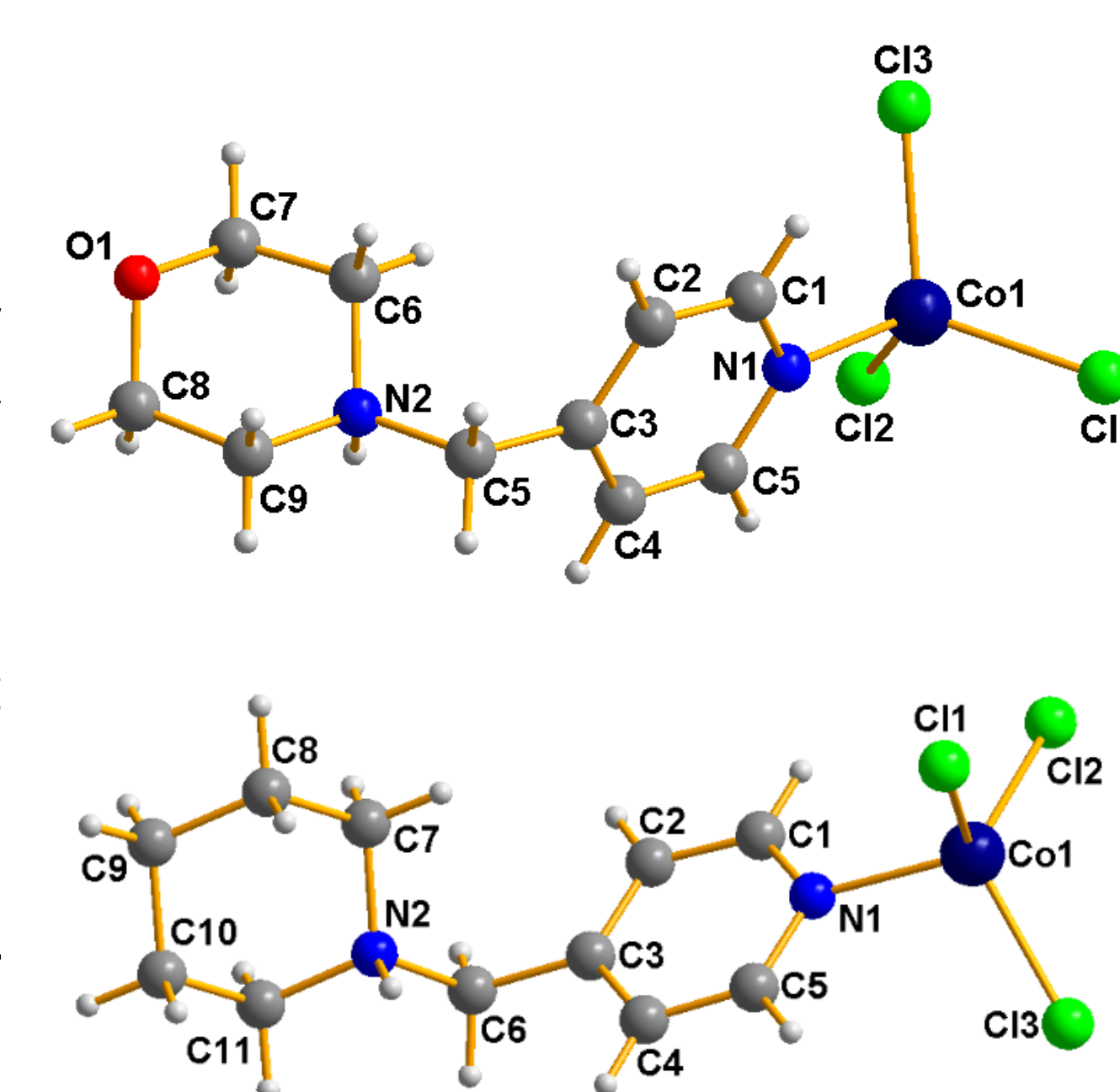


Figure 4. Discrete complexes of CoCl₂·6H₂O combined with L1 (top) and L2 (bottom)

This oxygen atom acts as an added hydrogen bond acceptor in L1, resulting in a larger angle between individual discrete complexes, due to the increased hydrogen bonding between neighbouring chains.

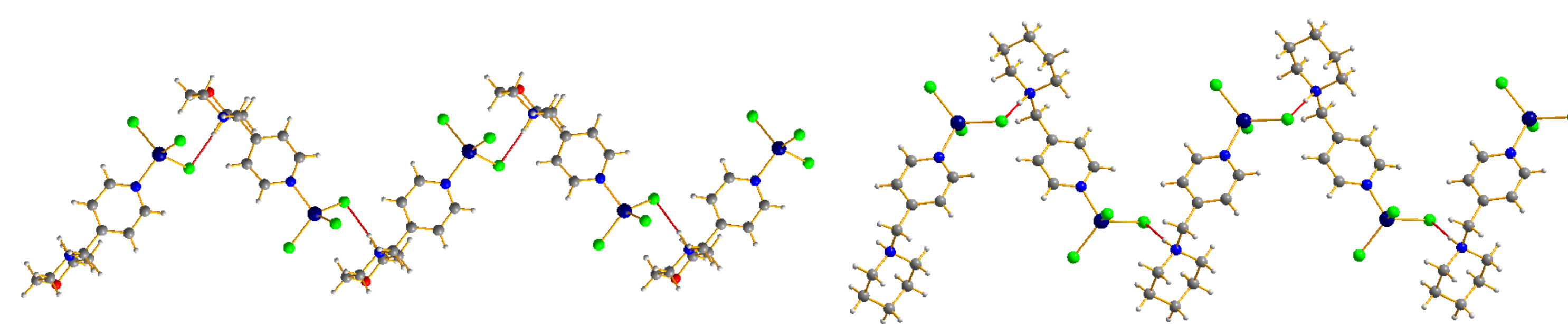


Figure 5. Extended “zig-zag” structures of CoCl₂·6H₂O combined with L1 (left) and L2 (right)

In contrast to L1 and L2, L3 has a less sterically hindered nitrogen atom, resulting in the cobalt(II) interacting with both of the nitrogen atoms in the ligand structure. In this case a 2D polymeric network is formed, shown in Figure 6. Neighbouring sheets interact with each other through hydrogen bonding, in a similar way to what is seen with L1 and L2.

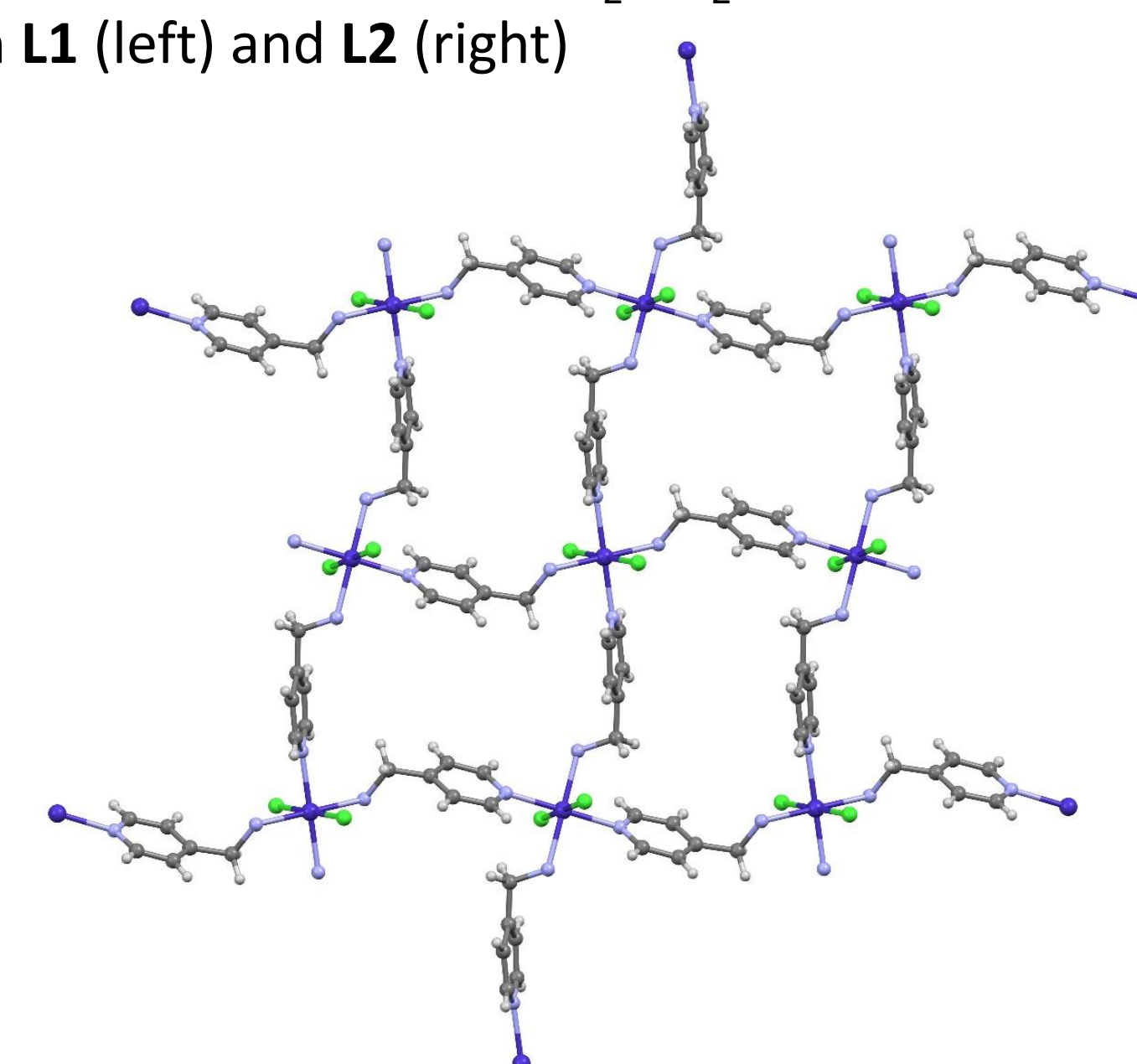


Figure 6. 2D polymeric chain of CoCl₂·6H₂O combined with L3

Conclusions & Current Work

The results above demonstrate the large-scale structural consequences of minor structural changes in flexible amine-derived ligands. In the design of functional coordination polymers and Metal-Organic Frameworks, control over such features becomes increasingly important as similar ligands with added complexity are explored for their interesting structural properties. Our current investigations concern semi-rigid fused hydrocarbon-based ligands and their structural chemistry, where non-classical hydrogen bonds and other weak intermolecular forces play key roles in dictating long-range structure in the absence of strong direction from π-π interactions.

References

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