Metal-Organic Frameworks Containing Silicon-Based Ligands

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The synthesis and characterisation of metallo-organic frameworks based on a structural unit of tetrahedral, silicon-centred carboxylate ligands and their coordination to Zn\(^{2+}\), Mn\(^{2+}\), and Co\(^{2+}\) has been investigated.

The versatility of silicon based compounds for metal-organic-framework (MOF) formation is based on the ease of synthesis of novel ligands with up to four organic groups being introduced at a silicon centre via a single synthetic step:

\[
R_nSiCl_{4-n} + 4-n LiR' \rightarrow R_nSiR'_{4-n} + 4-n LiCl
\]

\( R = \text{Me, Bu}'\), \( \text{Ph etc.} \), \( R' = \text{substituted aryl} \)

This is significantly easier to achieve than for analogous organic compounds, and aryl bromide substituents can then easily be converted into useful carboxyl groups. Framework materials are formed on reaction of the multidentate carboxylic acids such as Si(C\(_{6}\)H\(_{4}\)CO\(_{2}\))\(_{4}\) with divalent transition metal nitrates under mild solvothermal conditions. These frameworks contain ligands extending in three dimensions forming porous networks by bridging between metal centres, as shown below.

View of the Si(C\(_{6}\)H\(_{4}\)CO\(_{2}\))^\(_{4}\) / Zn\(^{2+}\) complex down the a-axis.

The metallo-organic frameworks formed are characterised by single crystal X-ray crystallography and gas uptake measurements. Their potential as materials for the storage of hydrogen gas is assessed.