

Accessory Publication

**Mg(II), Ca(II) and Co(II) Metal-Organic Framework Materials
with [Si(*p*-C₆H₄CO₂)₃(*p*-C₆H₄CO₂H)]³⁻ Struts**

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Single Crystal X-ray Crystallography Supporting Information p2

Powder X-ray Diffraction Plots p9

Single Crystal X-ray Crystallography Supporting Information

All of the crystal structures reported in this paper are polymeric, so the choice of formula (including solvent) and *Z* can be somewhat arbitrary, provided that the total contents of the unit cell equals the formula multiplied by *Z*. In each case here, the contents of the asymmetric unit was used as the formula.

The X-ray crystal structure of IMP-13Mg

Disorder was found for the C(31)-based benzoate unit in the structure of 4-Mg. Two partial occupancy orientations were identified of ca. 81 and 19% occupancy, their geometries were optimised, and the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (the others were refined isotropically). The O(80)- and O(85)-based coordinated ethanol molecules were found to be disordered. For the O(80) ethanol, three partial occupancy orientations of ca. 62, 22 and 16% occupancy were identified, their geometries optimised, and the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (the others were refined isotropically). For the O(85) ethanol, two partial occupancy orientations of ca. 73 and 27% occupancy were identified, their geometries optimised, and the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (the others were refined isotropically).

Six of the eight unique carboxylic acid groups were found to coordinate using both oxygen atoms. Of the remaining two, the C(31)-based group was found to be entirely non-coordinating, and so was presumed to be protonated (the hydrogen atom was not located). The C(71)-based group was found to coordinate using just one oxygen atom, and inspection of the C–O bond lengths [C(77)–O78 1.310(7) Å, C(77)–O79 1.227(7) Å] showed distinct C–O/C=O bond ordering with it being the C=O oxygen atom O(79) that coordinates. This suggests that O(78) is still protonated, though the O–H hydrogen atom was not located. As a consequence, the metal-ligand framework is neutral with the two –3 ligands balancing the three +2 metal atoms (two of the four unique metal sites are located at centres of symmetry and thus only contribute half of their charge to the asymmetric unit).

The included solvent was found to be highly disordered, and the best approach to handling this electron density was found to be the SQUEEZE routine of PLATON.^[1] This suggested a total of 225 electrons per unit cell, equivalent to approximately 113 electrons per asymmetric unit. The solvent used was ethanol (C₂H₆O, 26 electrons); 113 electrons equates to 4.5 ethanol molecules (117 electrons), and so this interpretation of the included solvent was used.

Subsequent to the use of SQUEEZE, an electron density peak not bound to the complex was located at approximately twice the electron density (0.87 eÅ⁻³) of the next largest peak. This was included as O(100), a 25% occupancy water molecule.

The O–H hydrogen atoms of the water and ethanol molecules, and of the non-coordinating C(37)- and C(77)-based carboxylic acid groups were not located. In conjunction with the disordered solvent removed by SQUEEZE, this makes the atom list for the asymmetric unit low by C₉H_{33.5}O_{4.5} (and the unit cell low by C₁₈H₆₇O₉) compared to what is actually presumed to be present.

The scattering of the crystal used for the determination of the structure of 4-Mg was particularly weak with a mean I/σ of just 4.3. As a consequence, the ratio of observed to unique reflections is low at ca. 29%.

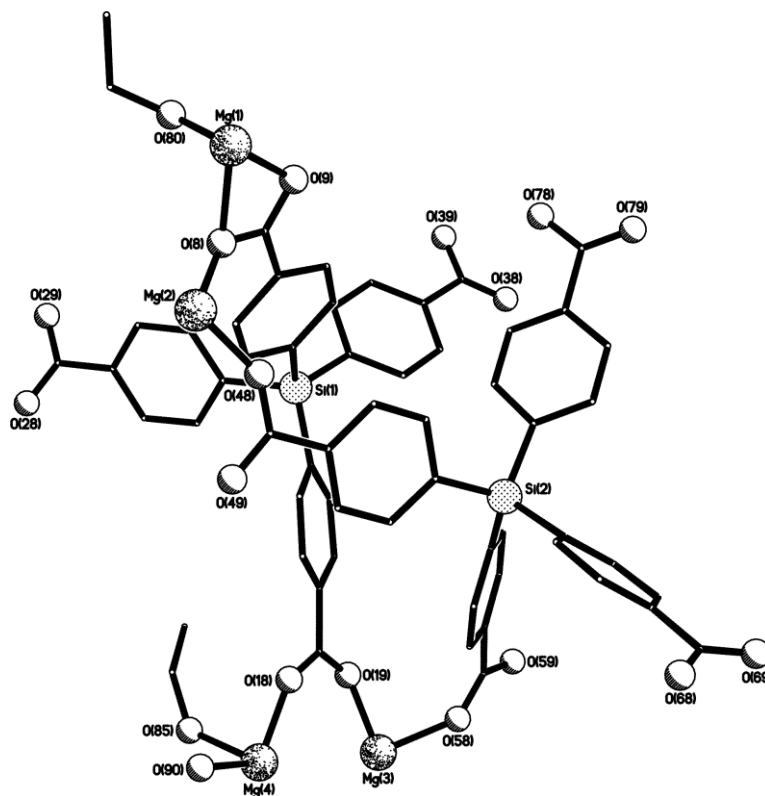


Figure S1 The molecular structure of the unique portion of the metal-organic framework present in the crystals of IMP-13Mg.

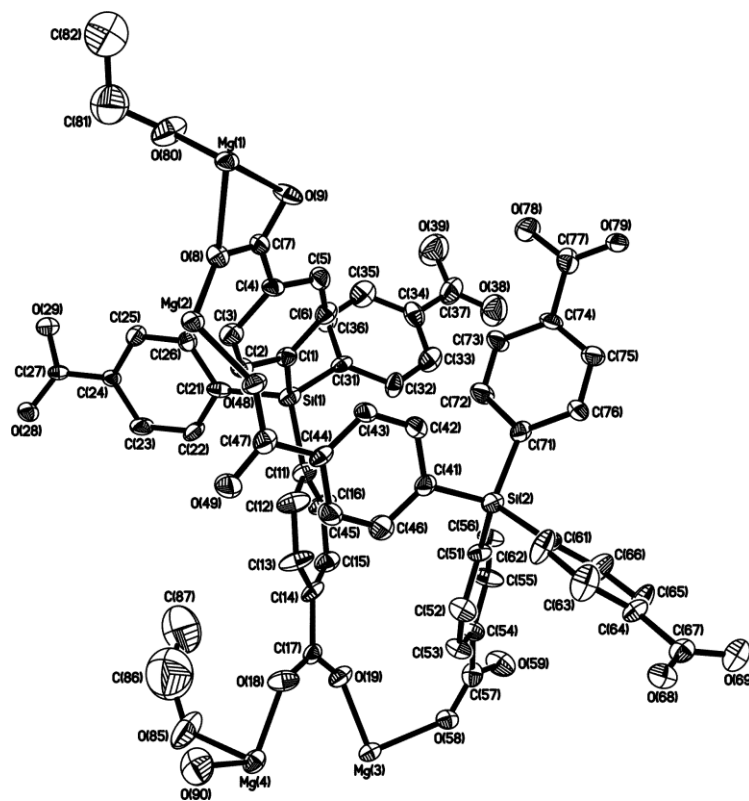


Figure S2 The molecular structure of the unique portion of the metal-organic framework present in the crystals of IMP-13Mg (30% probability ellipsoids).

The X-ray crystal structure of IMP-13Co

Disorder was found for the C(31)-based benzoate unit in the structure of 4-Co. Two partial occupancy orientations were identified of ca. 81 and 19% occupancy, their geometries were optimised, and the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (the others were refined isotropically). The O(80)- and O(85)-based coordinated ethanol molecules were found to be disordered. For the O(80) ethanol, three partial occupancy orientations of ca. 44, 32 and 24% occupancy were identified, their geometries optimised, and all of the atoms were refined isotropically. For the O(85) ethanol, two partial occupancy orientations of ca. 73 and 27% occupancy were identified, their geometries optimised, and the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (the others were refined isotropically).

Six of the eight unique carboxylic acid groups were found to coordinate using both oxygen atoms. Of the remaining two, the C(31)-based group was found to be entirely non-coordinating, and so was presumed to be protonated (the hydrogen atom was not located). The C(71)-based group was found to coordinate using just one oxygen atom, and inspection of the C–O bond lengths [C(77)–O78 1.304(3) Å, C(77)–O79 1.215(3) Å] showed distinct C–O/C=O bond ordering with it being the C=O oxygen atom O(79) that coordinates. This suggests that O(78) is still protonated, though the O–H hydrogen atom was not located. As a consequence, the metal-ligand framework is neutral with the two -3 ligands balancing the three $+2$ metal atoms (two of the four unique metal sites are located at centres of symmetry and thus only contribute half of their charge to the asymmetric unit).

The included solvent was found to be highly disordered, and the best approach to handling this electron density was found to be the SQUEEZE routine of PLATON.^[1] This suggested a total of 155 electrons per unit cell, equivalent to approximately 78 electrons per asymmetric unit. Before the use of SQUEEZE, refinements suggested that the included solvent was ethanol (C₂H₆O, 26 electrons); 78 electrons equates to 3 ethanol molecules (78 electrons), and so this interpretation of the included solvent was used.

The O–H hydrogen atoms of the coordinated water and ethanol molecules, and of the non-coordinating C(37)- and C(77)-based carboxylic acid groups were not located. In

conjunction with the disordered solvent removed by SQUEEZE, this makes the atom list for the asymmetric unit low by $C_6H_{24}O_3$ (and the unit cell low by $C_{12}H_{48}O_6$) compared to what is actually presumed to be present.

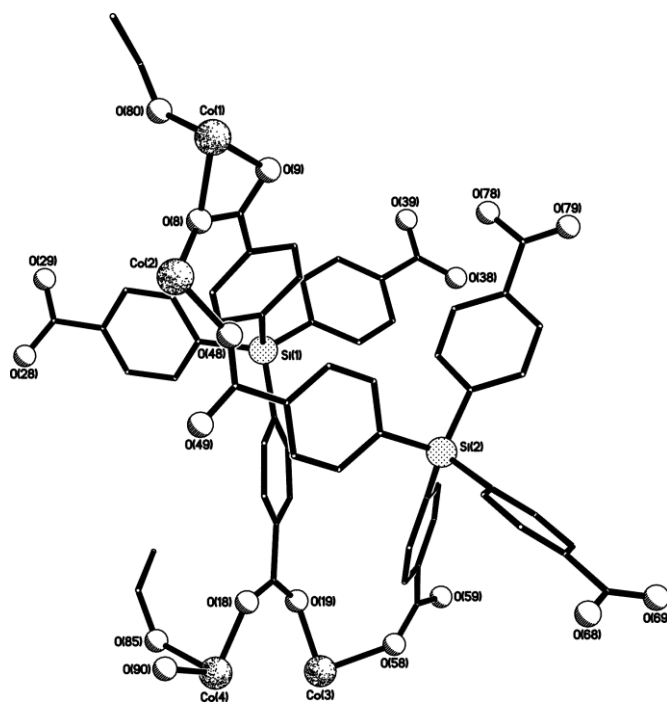


Figure S3 The molecular structure of the unique portion of the metal-organic framework present in the crystals of IMP-13Co.

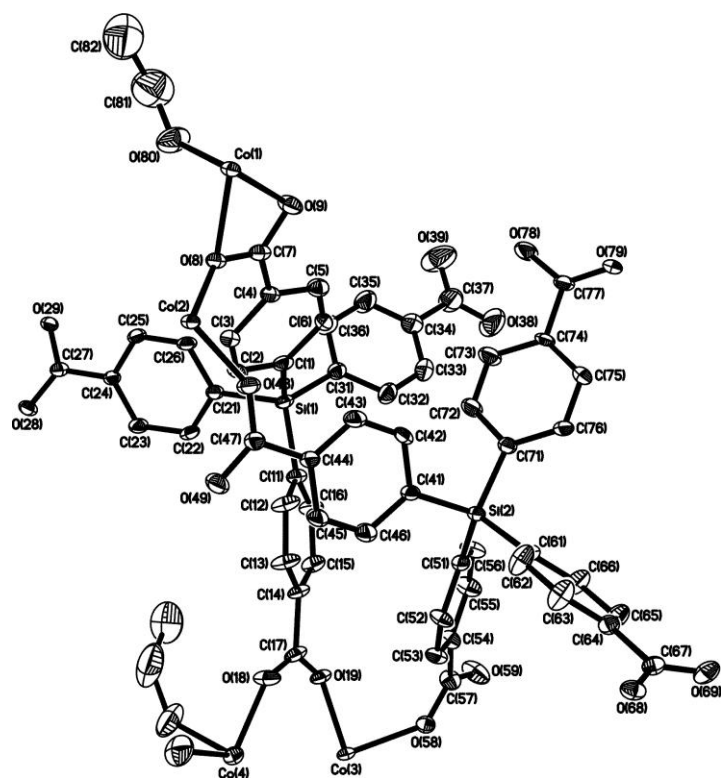


Figure S4 The molecular structure of the unique portion of the metal-organic framework present in the crystals of IMP-13Co (30% probability ellipsoids).

The X-ray crystal structure of IMP-14

The C(31)-based benzoic acid group in the structure of 3-Ca was found to be protonated—the O(39)–H hydrogen atom was located from a ΔF map. This hydrogen atom was refined freely subject to an O–H distance constraint of 0.90 Å. The silyl ligand is thus $[\text{Si}(\text{C}_6\text{H}_4\text{CO}_2)_3(\text{C}_6\text{H}_4\text{CO}_2\text{H})]^{3-}$, and bears a formal -3 charge. This is balanced by the 1.5Ca(II) atoms in the asymmetric unit, and thus the two coordinated and three included ethanol groups must be ethanol rather than ethoxide. Unfortunately, the O–H protons of these ethanol groups could not be reliably located. As a result the atom list is low by H_5 (and the unit cell low by H_{20}) compared to what is actually presumed to be present. The O(80) ethanol was found to be disordered. Three partial occupancy orientations were identified of ca. 40, 32 and 28% occupancy, their geometries were optimised, and all of the non-hydrogen atoms were refined isotropically.

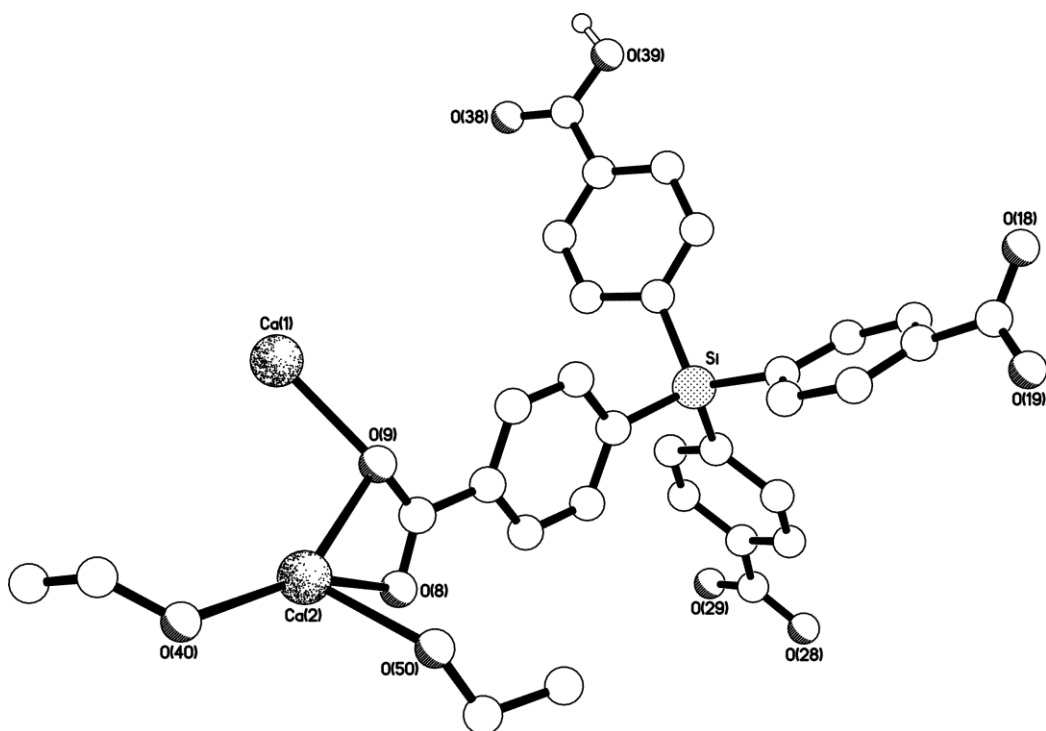


Figure S5 The molecular structure of the unique portion of the metal-organic framework present in the crystals of IMP-14.

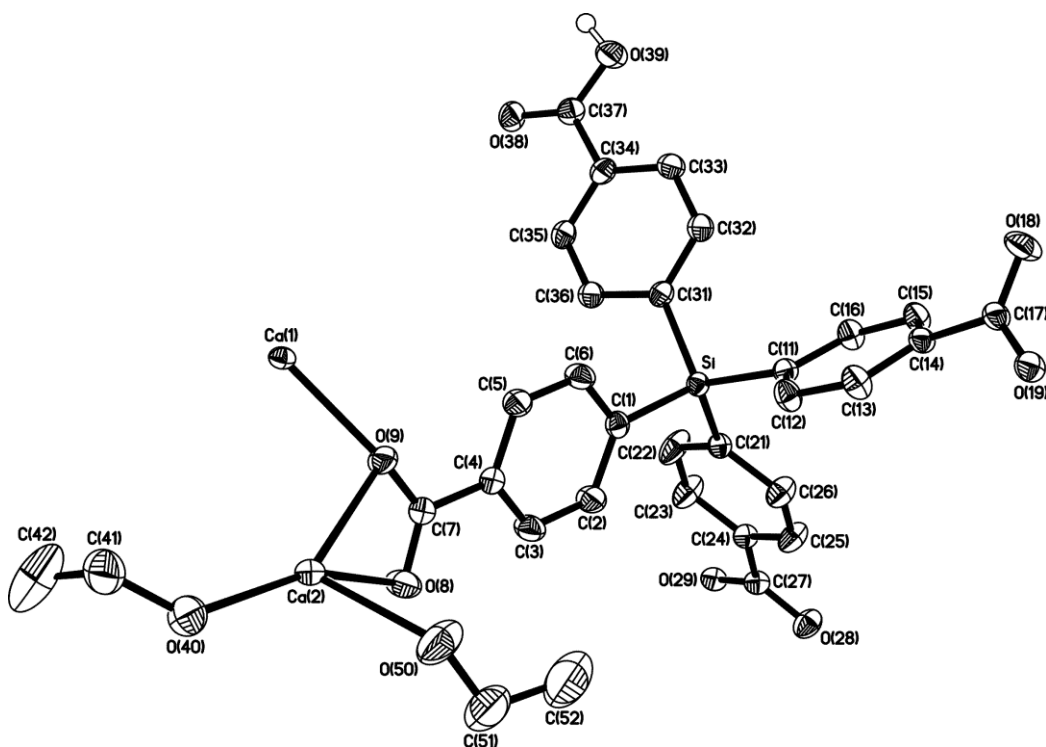


Figure S6 The molecular structure of the unique portion of the metal-organic framework present in the crystals of IMP-14 (50% probability ellipsoids).

- [1] A.L. Spek (2008) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands. See also A.L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7–13.

Powder X-ray Diffraction Studies

Phase purity of IMP-13Mg was confirmed using a Philips PW1700 series automated powder X-ray diffractometer with Cu-K α radiation and a graphite secondary crystal monochromator. The peaks are strongly affected by preferred orientation along the [0, *k*, 0] direction.

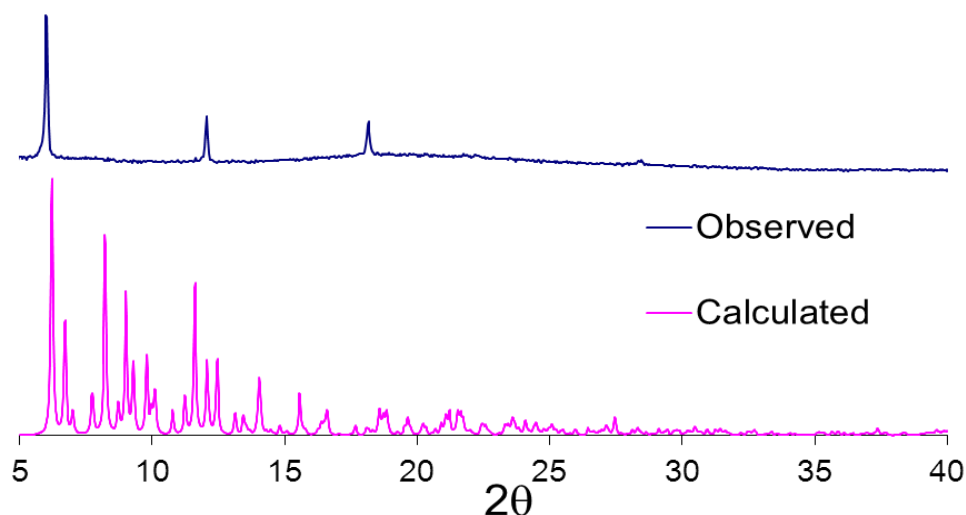


Figure S7. Powder X-ray diffraction (PXRD) patterns for IMP-13Mg calculated from the single crystal data and measured experimentally on a fresh bulk sample.

Table 1 Comparison of *d*-spacings for IMP-13

experimental <i>d</i> -spacing (Å)	simulated <i>d</i> -spacing (Å)	<i>hkl</i>
5.12	5.10	[0,1,0]
3.41	3.41	[0,2,0]
1.70	1.82	[0,3,0]