Electronic Supplementary Information for Dalton Transactions

Electronic Supplementary Information

Framework Materials Assembled from Magnesium Carboxylate Building Units

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Thermogravimetric Analyses

General Remarks:

All Thermal Gravimetric Analyses (TGA) were carried out using a Perkin Elmer Pyris 1 machine. TGA measurements were performed under a constant stream of dry nitrogen gas (flow rate 20 mL min^{-1}) over the temperature range of 30 to 700 °C at a heating rate of 10 °C min^{-1}, unless otherwise stated.

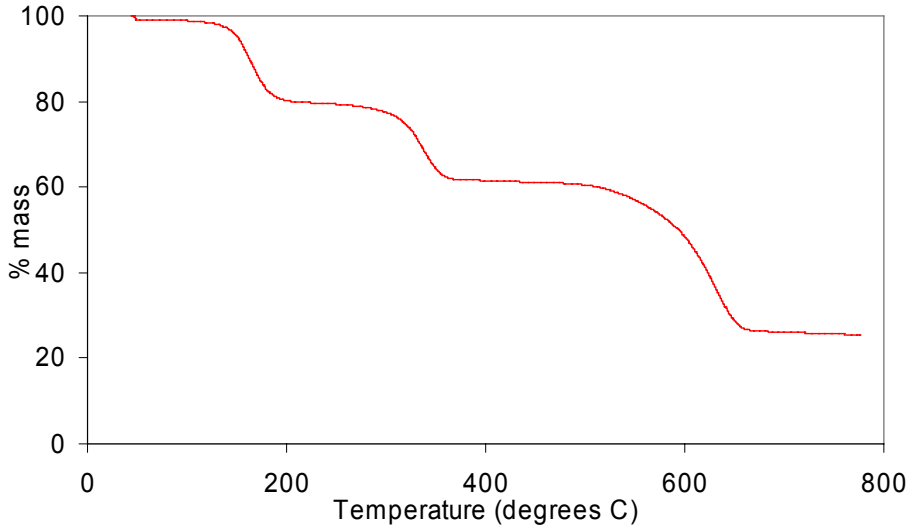

Figure S1 TGA trace of **1**

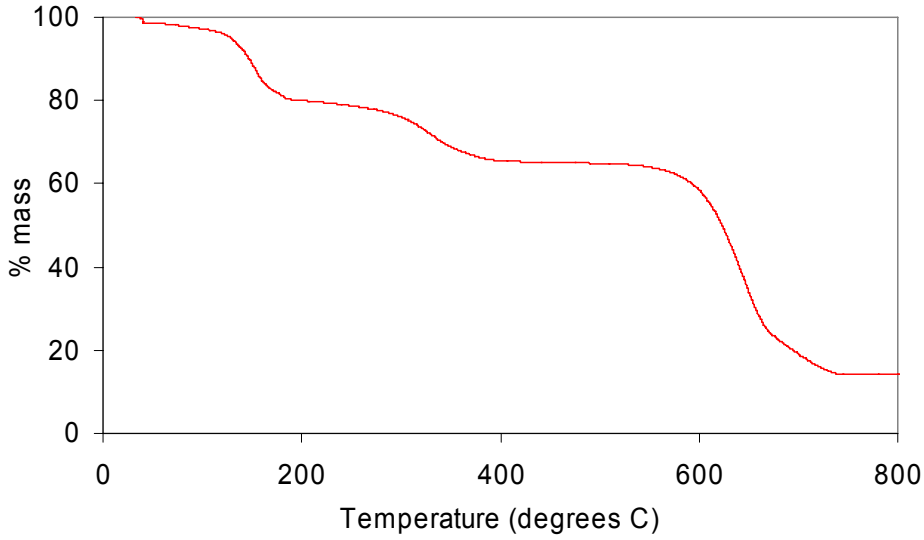

Figure S2 TGA trace of **1** after heating at 200 ˚C for 12 h and immediate soaking in DMA for 4 h

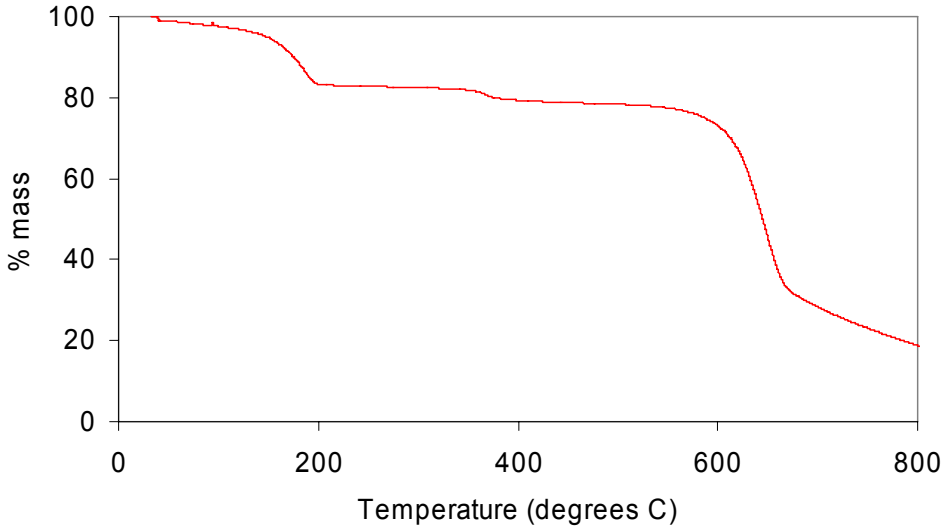

Figure S3 TGA trace of **1** after heating at 200 ˚C for 12 h and exposure to moist air for 4 h

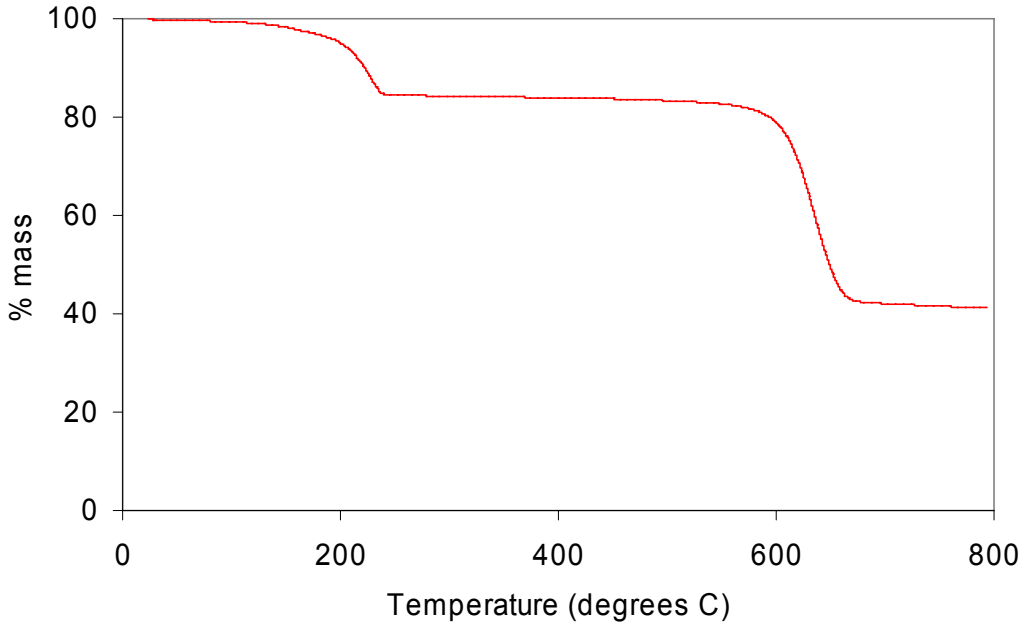

Figure S4 TGA trace of **2**

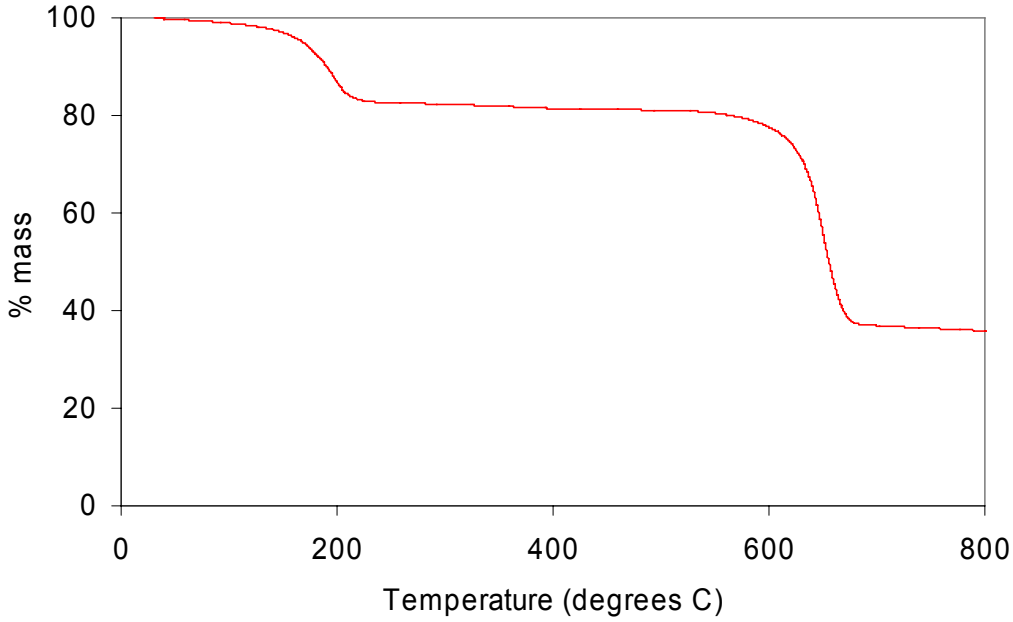

Figure S5 TGA trace of **2** after heating at 200 ˚C for 12 h and immediate soaking in EtOH for 4 h

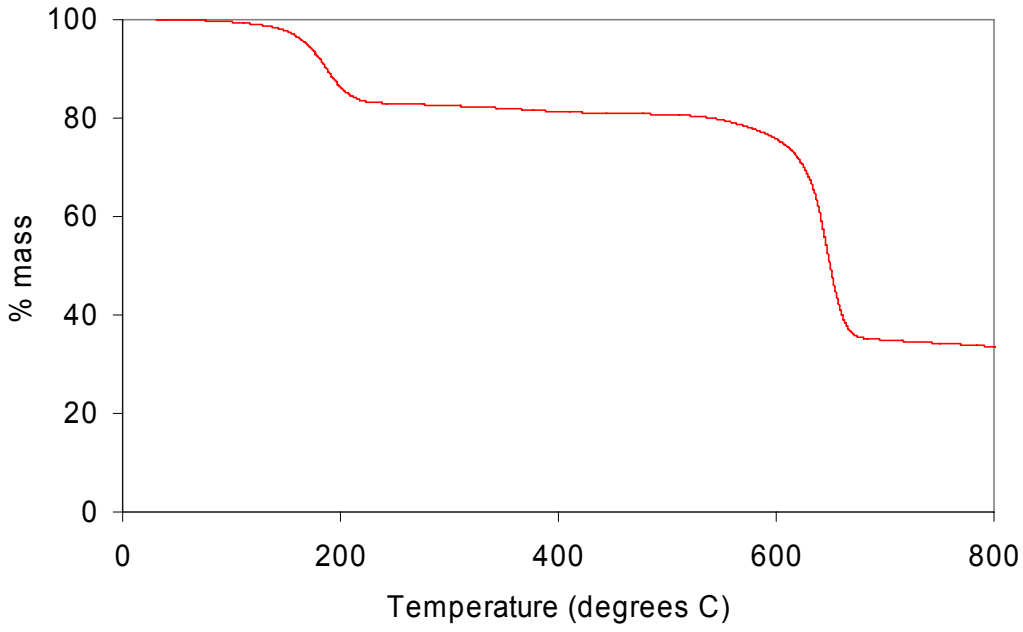

Figure S6 TGA trace of **2** after heating at 200 ˚C for 12 h and exposure to moist air for 4 h

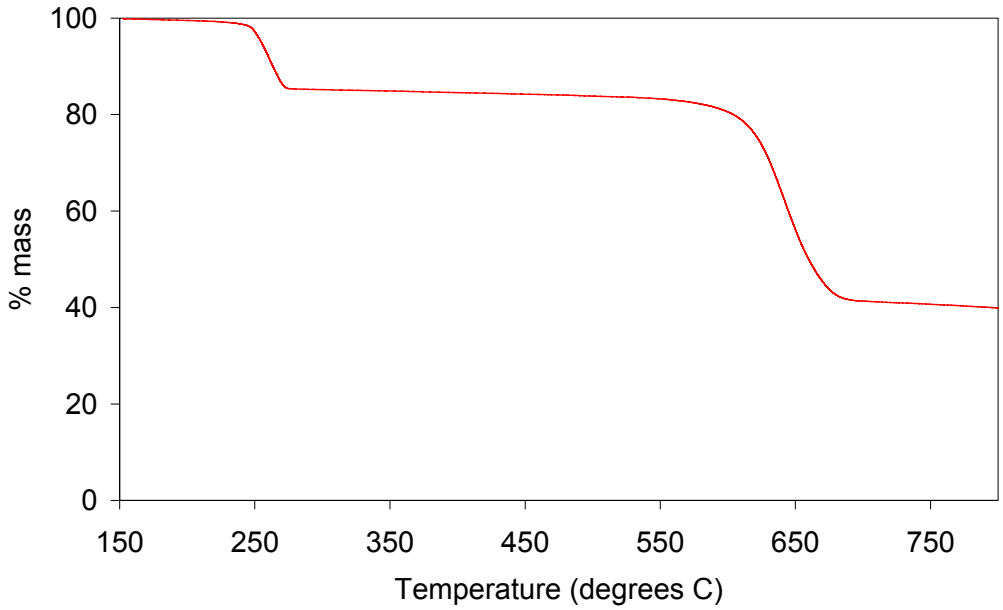

Figure S7 TGA trace of **2** after soaking in DMA for 72 h.

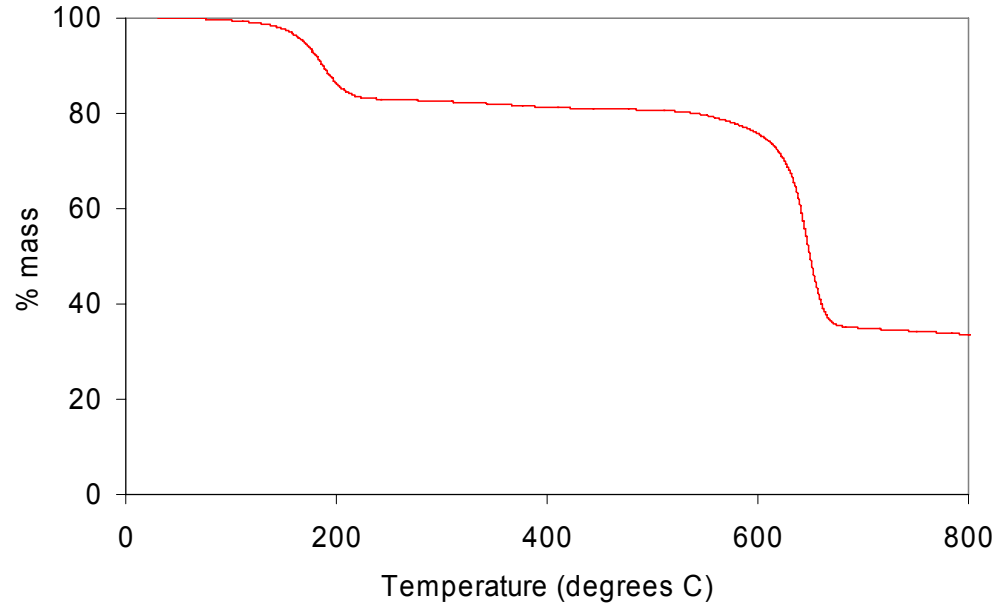

Figure S8 TGA trace of **3**

X-ray Crystallographic Supporting Information

Refinement of Structures 1-4

In the structures of both **1** and **2**, the coordinated solvent molecules were found to be disordered (the major occupancy orientations are depicted in Figs. S9 to S12). For **1**, four orientations were identified for the O(30) dimethylacetamide moiety, whilst two were located for the O(40) counterpart, contributing to the less than ideal thermal ellipsoids seen for the major occupancy orientations (Fig. S10). In **2**, two orientations were identified for the O(30) ethanol solvent molecule. In all these cases, however, the donor oxygen atom was not disordered, meaning that there was no disruption of the metal coordination sphere. Despite the disorder in the carbon atoms of the O(30) ethanol solvent molecule in the structure of **2**, a dominant position for the O–H proton was located from a ΔF map, and refined subject to an O–H distance constraint of 0.90 Å. The proton refined with a sensible isotropic thermal parameter, thus confirming the ethanol rather than ethoxide nature of this moiety. The somewhat high final *R*-factors for the structure of **2** are mainly a consequence of the poor crystal quality which led to a weak and diffuse diffraction pattern that indexed poorly. That the structure is as shown, however, seems beyond doubt.

The structure of compound **4** contains two different btc ligands (**I** and **II**). Ligand **I**, [based on O(1)] has D_3 symmetry and uses all six oxygens to link to magnesium centres, and as such is considered to be fully deprotonated (i.e. possessing a –3 charge). The O(2)-based btc ligand **II**, on the other hand, has C_3 symmetry and has three coordinated and three non-coordinated oxygen atoms. For charge balance reasons (*vide infra*) this is considered to have lost 1.5 protons and so have a –1.5 charge. In the asymmetric unit there is half a metal atom, one sixth of ligand **I**, and one third of ligand **II**. This gives an Mg : **I** : **II** ratio of 3 : 1 : 2. From an analysis of the packing, the O(3) atom is only 2.405(3) Å away from its counterpart in an adjacent ligand, and thus there must always be a proton between these two centres. The highest residual electron density peak was right in the middle of these two centres, on a two fold axis position. Attempts to refine a proton at this position did not work, so a 50% occupancy proton was added to the atom list in an idealised asymmetric position based on this [O(3)–H 0.90 Å] Thus, the exact position of this proton must be considered uncertain, though it is undoubtedly somewhere between

O(3) and its proximal symmetry related counterpart. The upshot of this is that each O(3) atom bears a 50% occupancy proton, and so the type **II** ligand overall has lost 1.5 protons, and so has a –1.5 charge. Thus, the three metals give an overall charge of (3 x +2) = +6, the sole type **I** btc ligand is fully deprotonated and so has a –3 charge, and the two type **II** ligands contribute another –3 between them (–1.5 each). The charges are therefore balanced, and thus the extra included material must be neutral, and so was assumed to be more, uncoordinated, dma solvent.

In Figs. S9 to S16 below, the atoms drawn as dashed circles and linked by dashed bonds are not part of the asymmetric unit, but have been generated from atoms within the asymmetric unit by the symmetry present in the structure, and have been included to show connectivity.

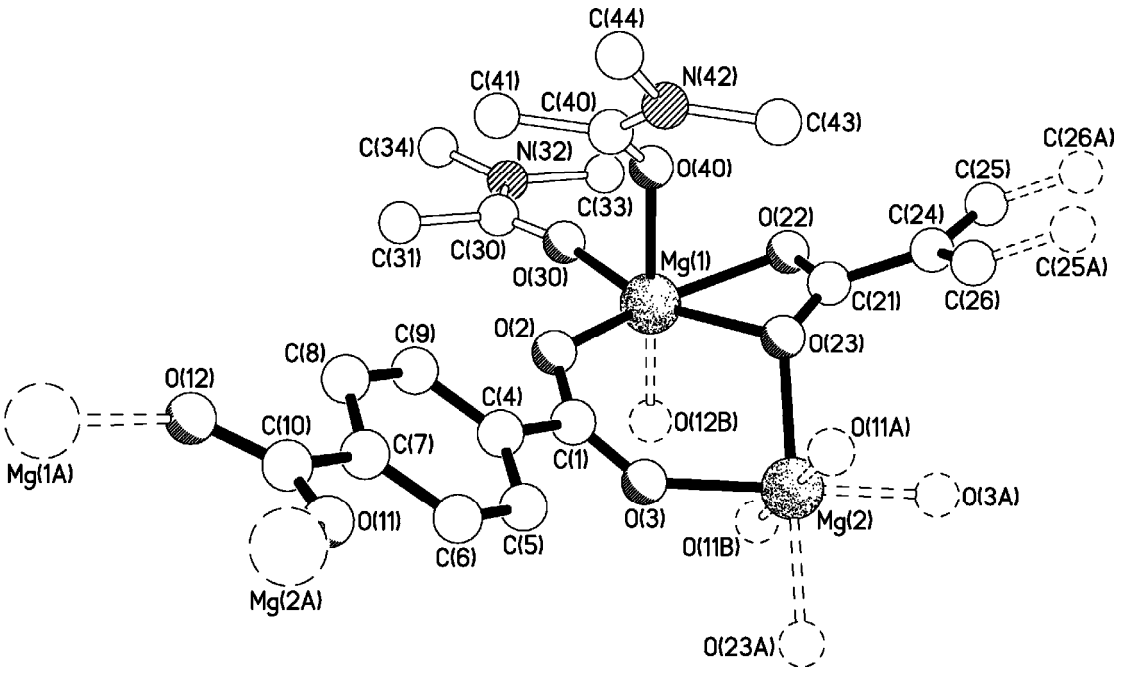

Figure S9 The asymmetric unit present in the structure of **1**.

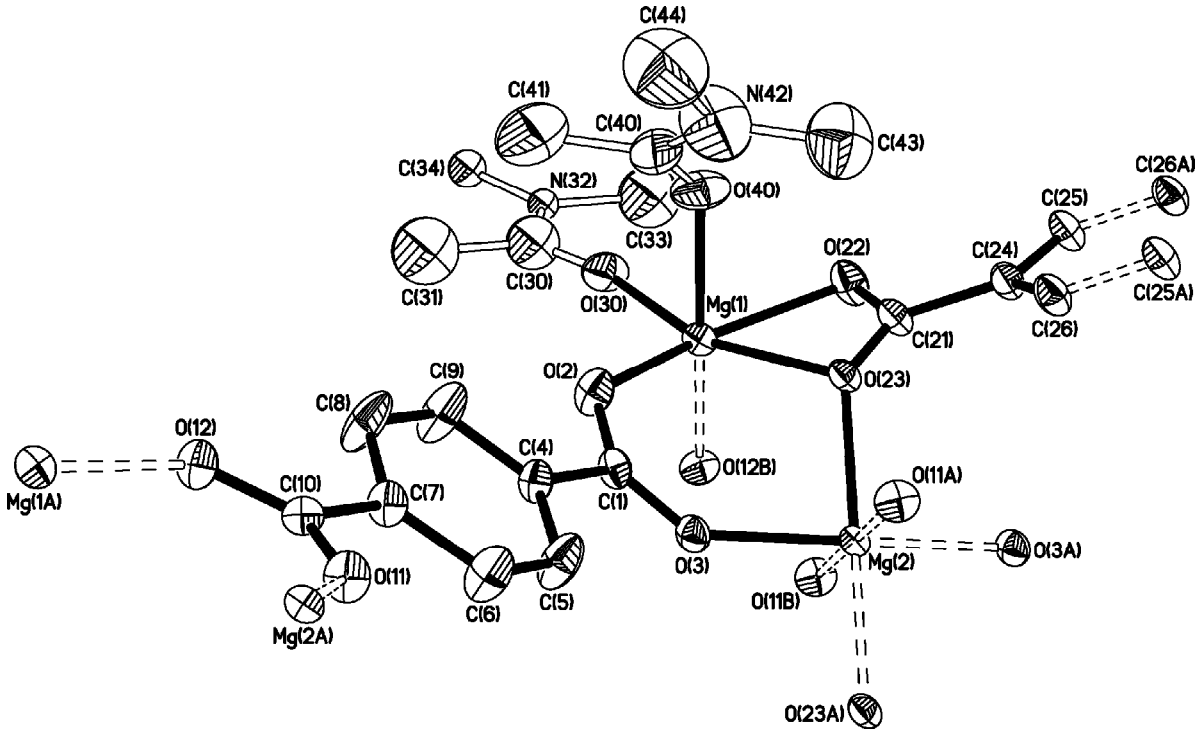

Figure S10 The asymmetric unit present in the structure of **1** (30% probability ellipsoids).

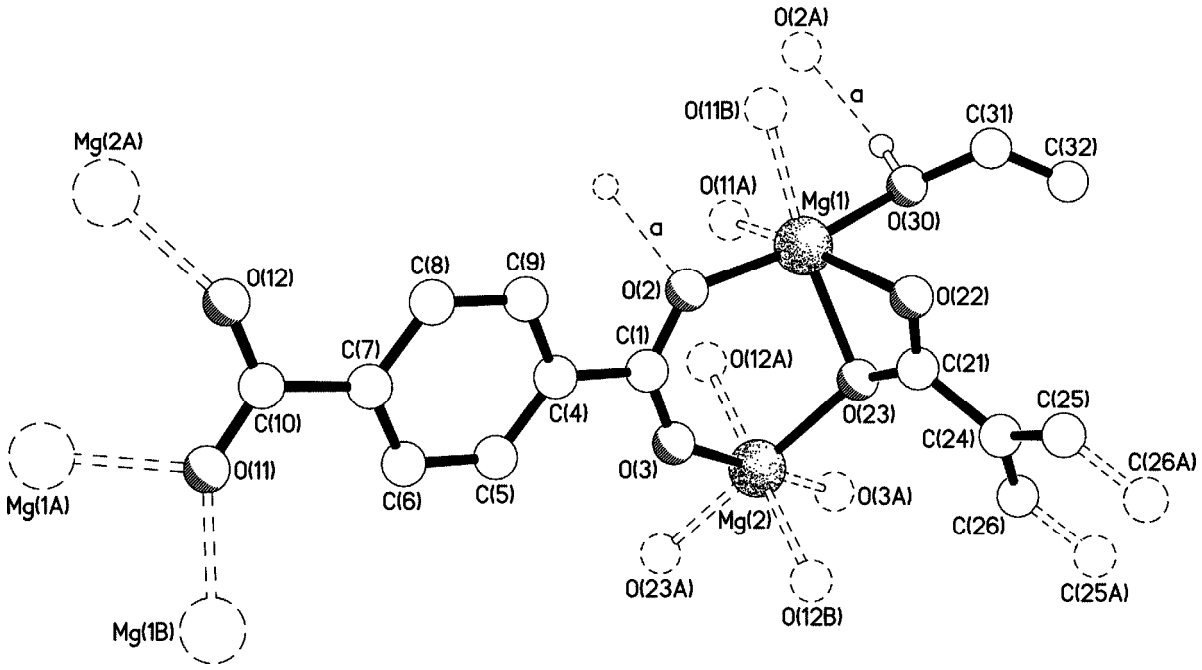

Figure S11 The asymmetric unit present in the structure of **2**.

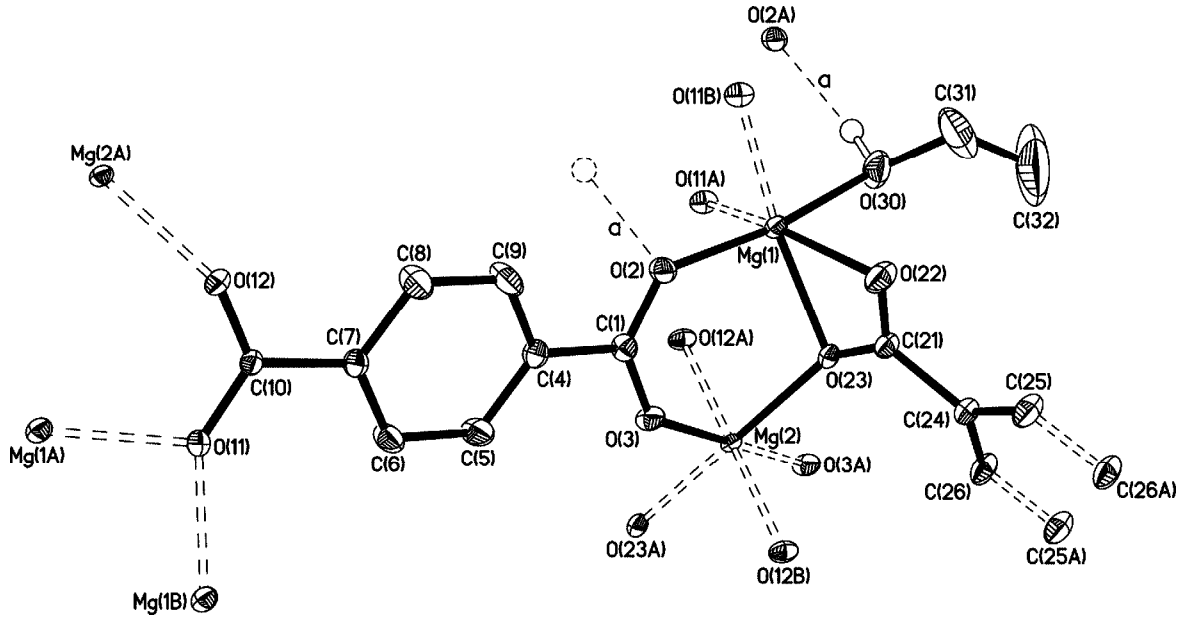

Figure S12 The asymmetric unit present in the structure of **2** (50% probability ellipsoids).

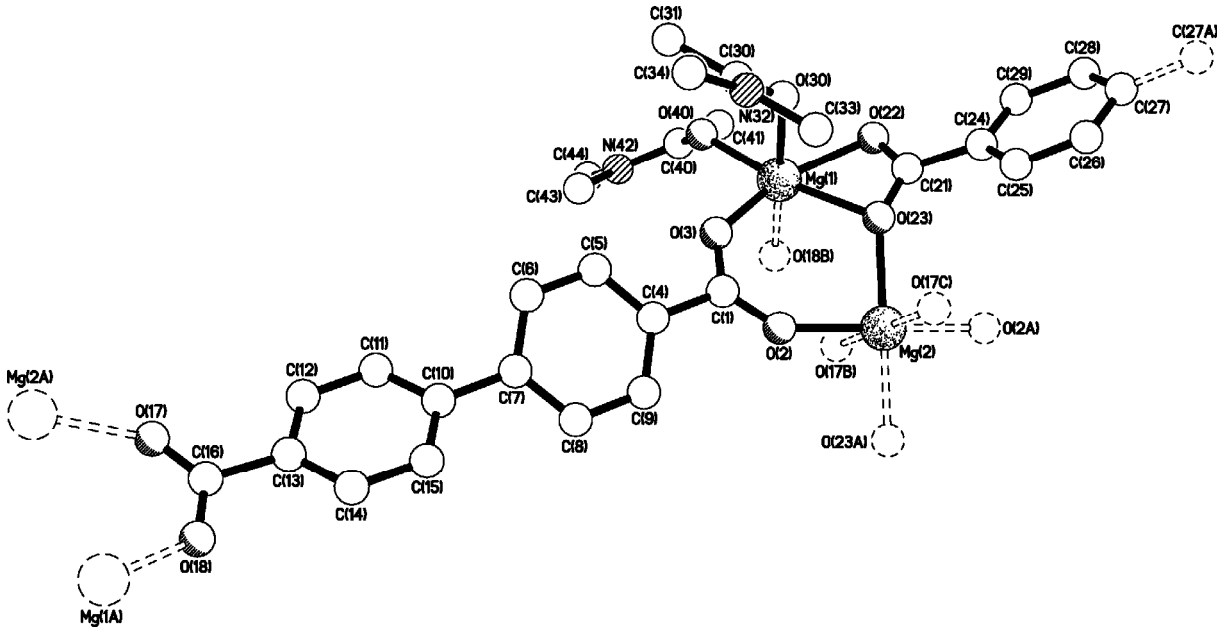

Figure S13 The asymmetric unit present in the structure of **3**.

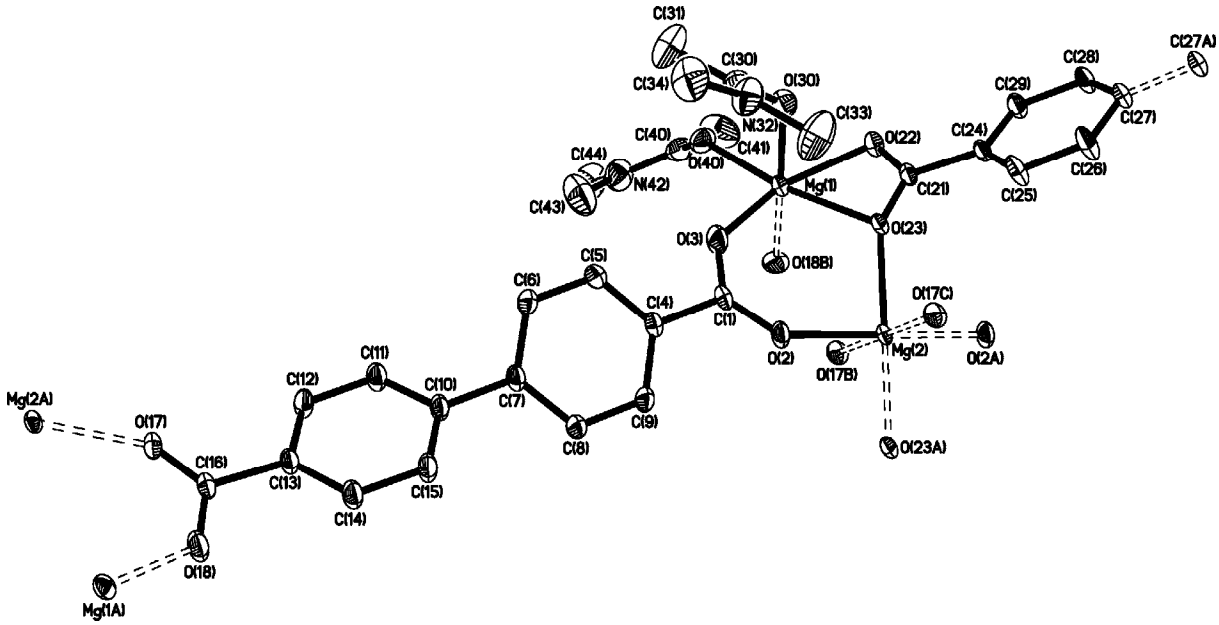

Figure S14 The asymmetric unit present in the structure of **3** (50% probability ellipsoids).

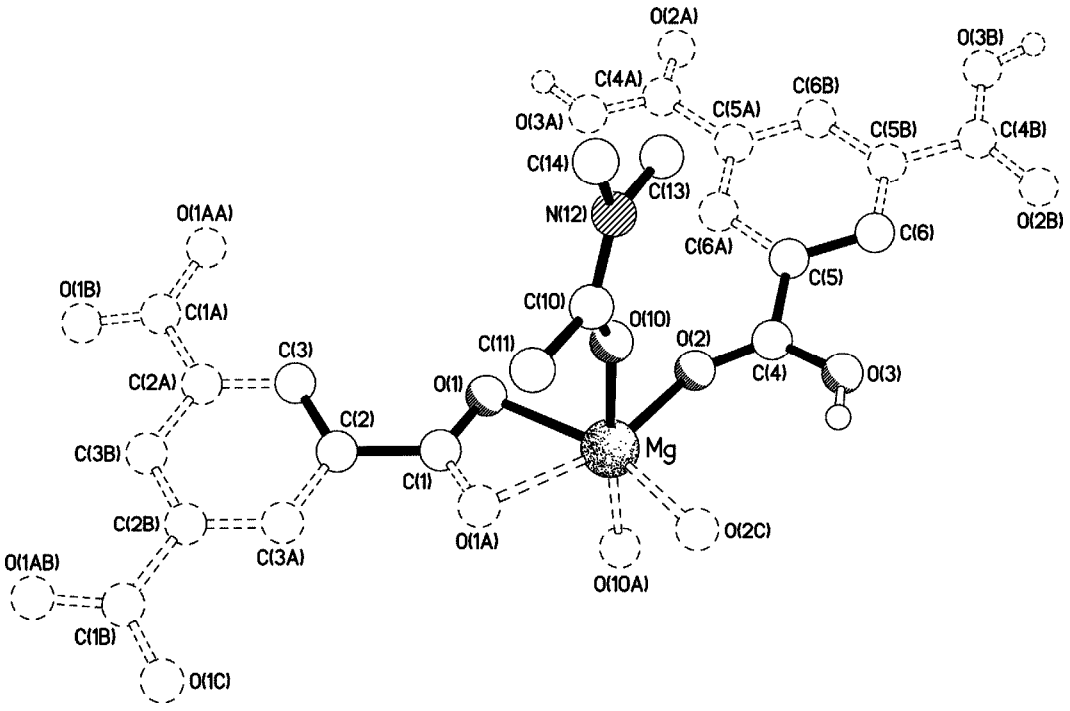

Figure S15 The asymmetric unit present in the structure of **4**.

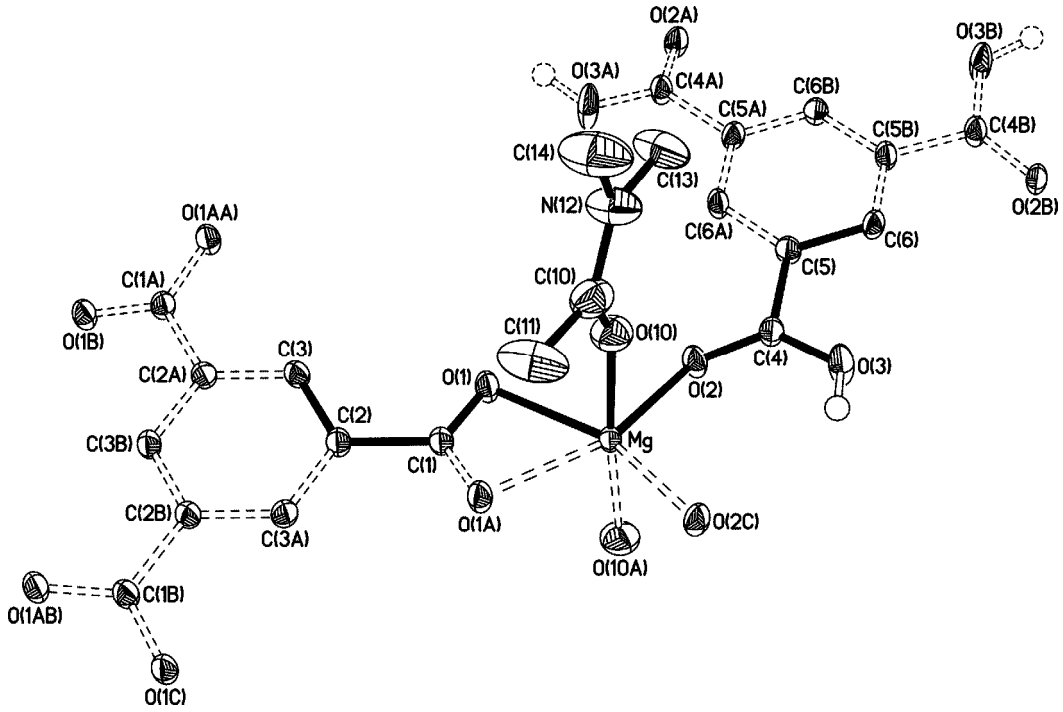

Figure S16 The asymmetric unit present in the structure of **4** (30% probability ellipsoids).