Supplementary Material (ESI) for Chemical Communications

Supplementary data

Chiral Channels within a Heteropolyoxometalate-Based Framework: The Templating Effect of Benzenetricarboxylic Acid

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Full synthetic procedure for compound 1:

A saturated solution of 1,3,5-benzenetricarboxylic acid (BTC) in water was prepared by refluxing 15 g BTC in 150 ml water for 2 h, cooling to room temperature and removing the excess BTC by filtration.
1.33 g (5.49 mmol) of Na_2MoO_4 $2H_2O$ were then dissolved in 100 ml of the saturated aqueous BTC solution. H3PO4 (9%) was added to the colourless reaction mixture to raise the pH from 4.7 to 4.9. During this process, the solution colour changed to yellow, indicating the formation of a HPM precursor. This formation also explains the unexpected raise of the pH value upon addition of a mineral acid. 1.25 g (2.96 mmol) of (-)-sparteine sulfate pentahydrate were added, resulting in immediate precipitation of a white material. The precipitate was redissolved by adjusting the pH to ca. 8 using a concentrated aqueous NaOH solution The pH was then lowered to 4.0 using H_3PO_4 (9%) and 1.00 g (5.70 mmol) of $Na_2S_2O_4$ were added. The colour of the mixture changed instantly to dark blue. After ca. 5 min. of stirring, the pH of the mixture was lowered from 4.6 to 3.5 with H_3PO_4 (9 %). After stirring for 2 h, the mixture was filtered and a dark blue precipitate was seperated from a clear brown solution. After storage for three days, red-brown crystals of **1** were isolated.

Yield: 344.0 mg (0.094 mmol, 20.6 % based on Mo).

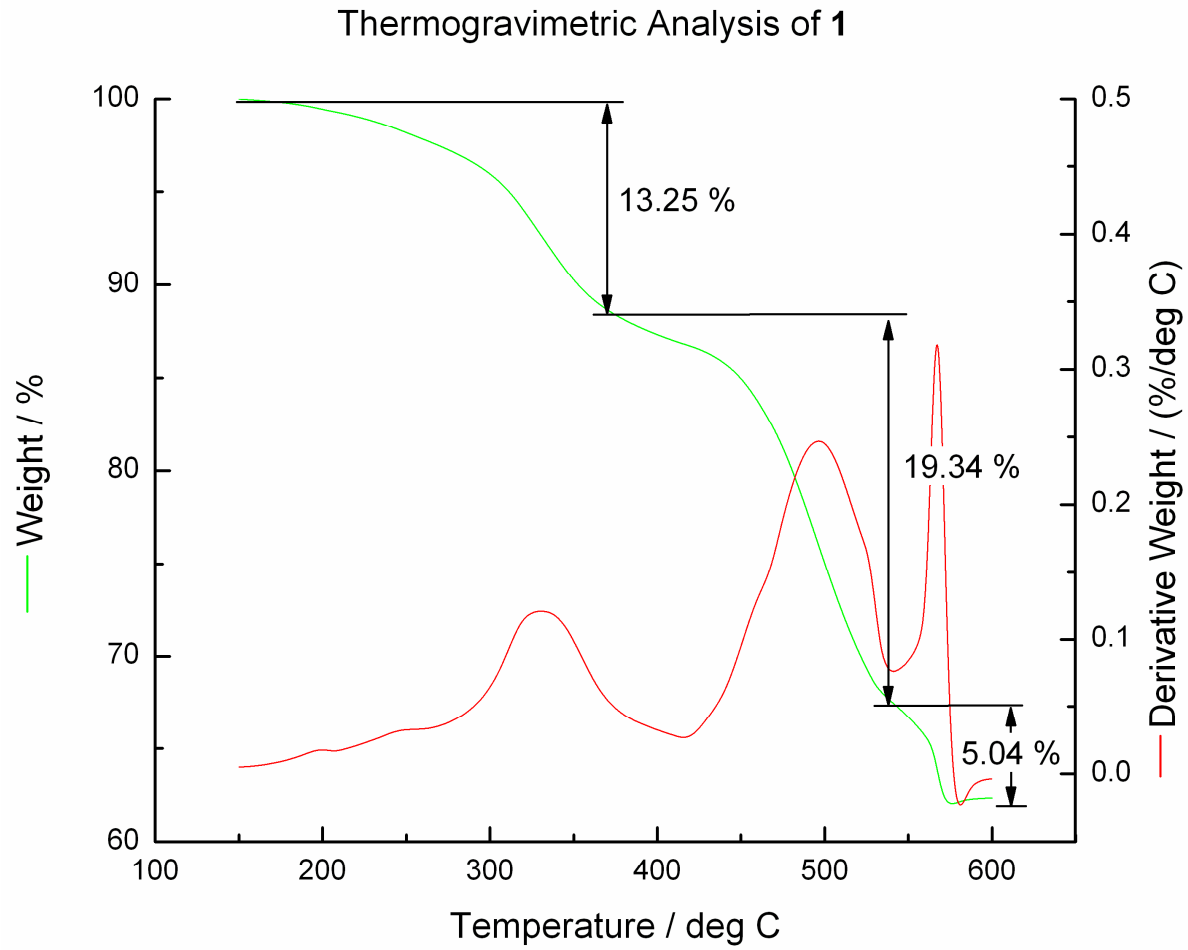
Characteristic IR-bands: 3435.56 (m, b), 2947.66 (m), 1715.37 (m), 1635.34 (m), 3468.53 (m) 1263.15 (m), 1065.48 (s), 966.16 (s), 743.42 (m).

Due to the water sorption capabilities of the material, the elemental analysis of **1** had to be performed on the completely dehydrated material in order to obtain consistent results: $C_{69}H_{113}N_8O_{68}Na_1Mo_{12}P_8$ (in percent, calculated values in brackets): C: 23.44 (23.12), H: 3.91 (3.74), N: 2.96 (3.13).

Flame Atomic Absorption for Na analysis:

Na content: experimental: 0.58 ppm, calculated: 0.54 ppm

Thermogravimetric analysis



Thermogravimetric analysis of the dried material shows three distinct weight losses over the temperature range from 150 ºC to 600 ºC. The first two weight losses correspond to 13.25% and 19.34 % respectively and add up to 32.59 % which correlates to the calculated loss for all BTC and (-)-sparteine moieties (calc: 32.24 %). The third weight loss of 5.04 % can most likely be assigned to a partial decomposition of the cluster with the loss of the phosphate moieties as volatile P_2O_5.