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

Carsten Streb, De-Liang Long and Leroy Cronin*

WestCHEM, Department of Chemistry, The University of Glasgow, University Avenue, Glasgow G12 8QQ, UK. Fax: +44-141-330-4888; Tel:+44-141-330-6650; E-mail: L.Cronin@chem.gla.ac.uk

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 Na₂MoO₄ 2H₂O 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 H₃PO₄ (9%) and 1.00 g (5.70 mmol) of Na₂S₂O₄ 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 H₃PO₄ (9%). After stirring for 2 h, the mixture was filtered and a dark blue precipitate was separated 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: C₆₉H₁₁₃N₈O₆₈Na₁Mo₁₂P₈ (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 of the dried material shows three distinct weight losses over the temperature range from 150 °C to 600 °C. 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$_2$O$_5$. 