Electronic Supporting Information

Revisiting the Formation of Giant Molybdenum Blue Clusters

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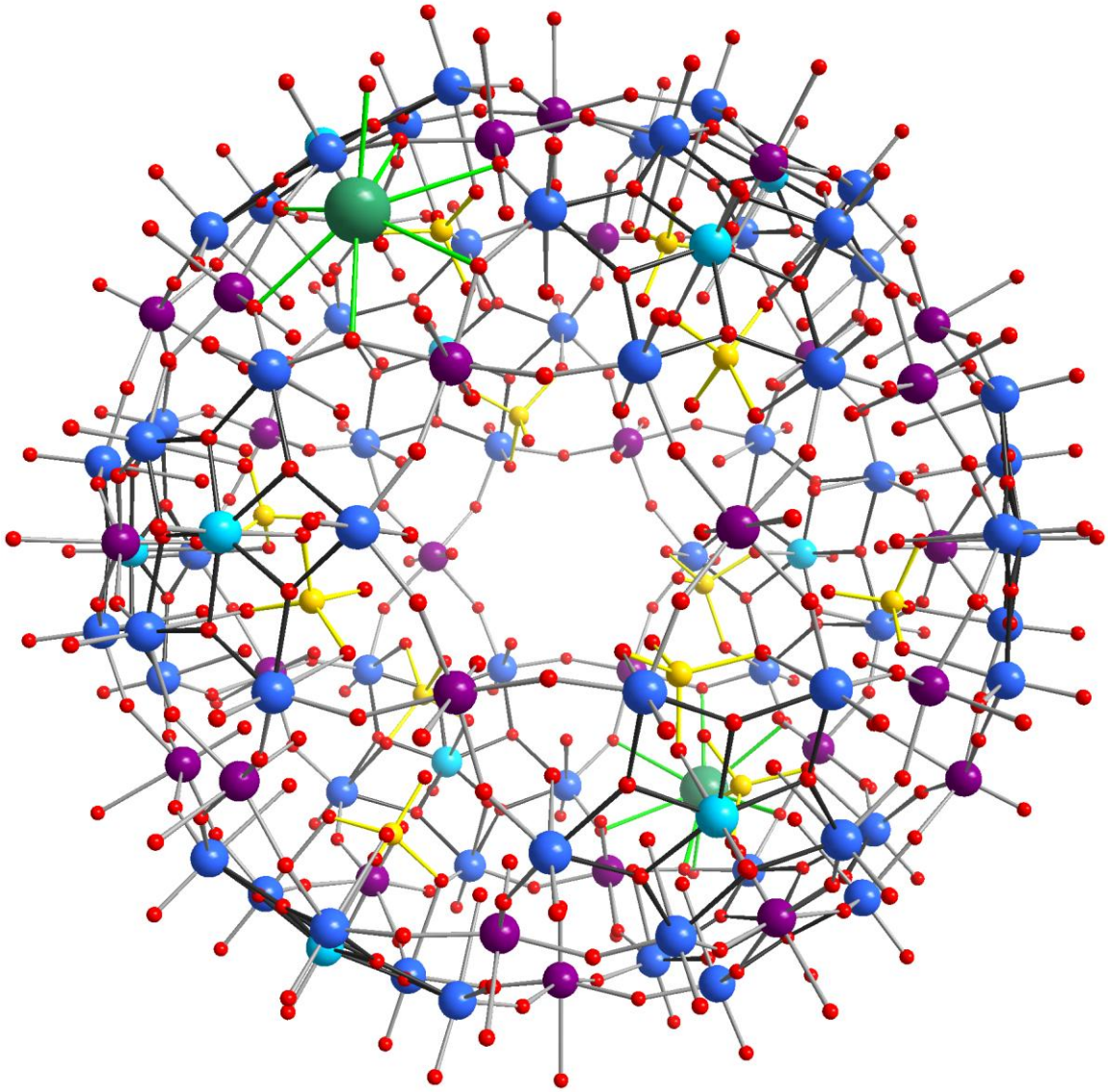

Figure S1. Ball-and-stick representation of the mixed-valent Keplerate-type polyoxomolybdate **3**, emphasizing the twelve slightly domed pentagonal {(Mo)Mo_5} building blocks (Mo in octahedral MoO_6 environments: dark blue spheres, Mo in pentagonal-bipyramidal MoO_7 environments: light blue spheres), where the Mo–(μ_3-O) bonds are shown as black lines, which are interlinked by thirty Mo(=O)(OH_2) groups (purple spheres). Also shown are two out of nine crystallographically located K^+ positions (large green spheres). Furthermore, sulfate groups coordinating to the {(Mo)Mo_5} building blocks from the interior of the cluster sphere are represented for an arbitrarily chosen configuration (one out of five evenly disordered S–O_{term} vectors per {(Mo)Mo_5} group; S: yellow, S–O bonds; yellow). O: small red spheres, hydrogen positions not shown for clarity.

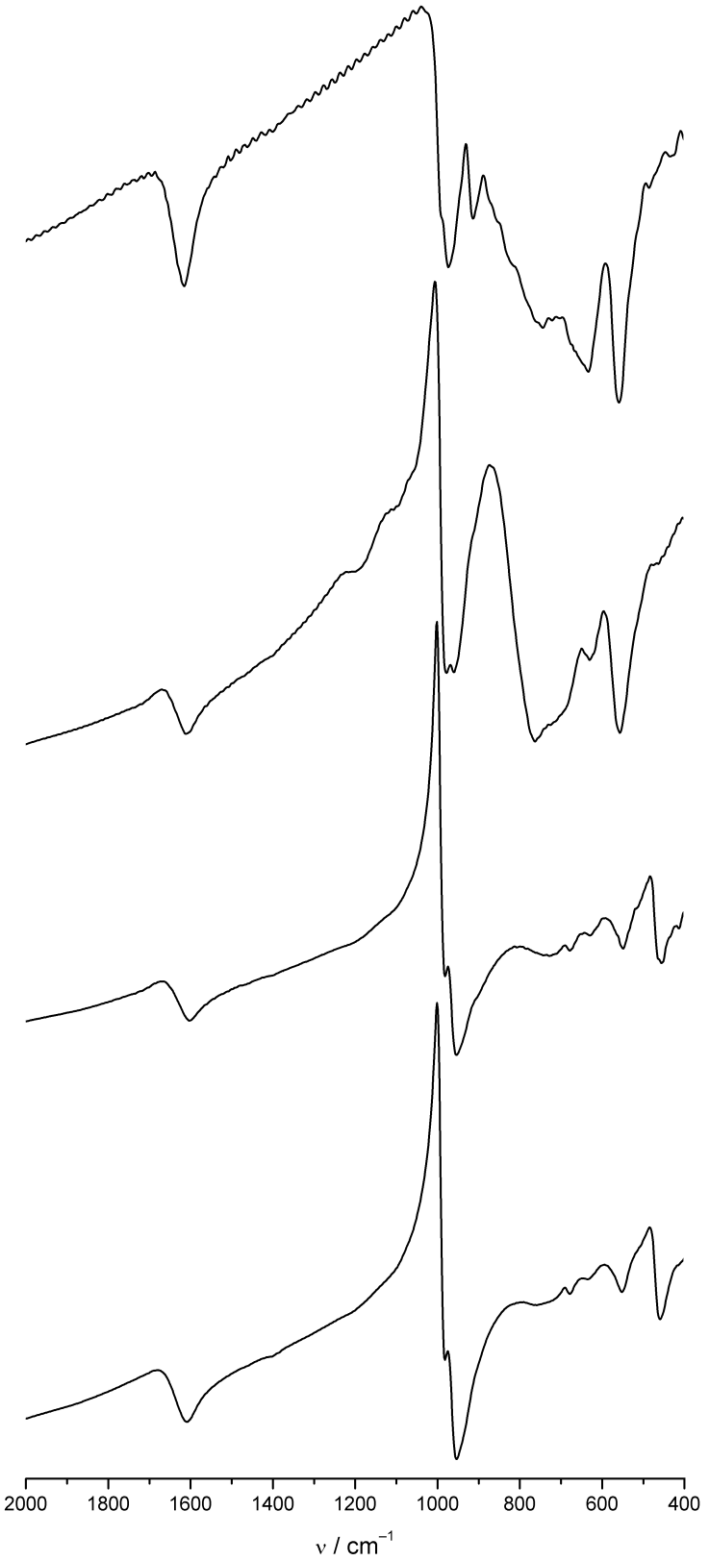

Figure S2. FT-IR spectra (KBr pellets) of molybdenum blue compounds: From bottom to top: (1) the spherical {Mo_{102}}-type Keplerate **3a**; (2) the Na^+ salt of **3**; (3) the Na^+ salt of the {Mo_{368}} cluster, **1a**; (4) the Na^+ salt of the {Mo_{154}} wheel-type polyanion, **2a**.

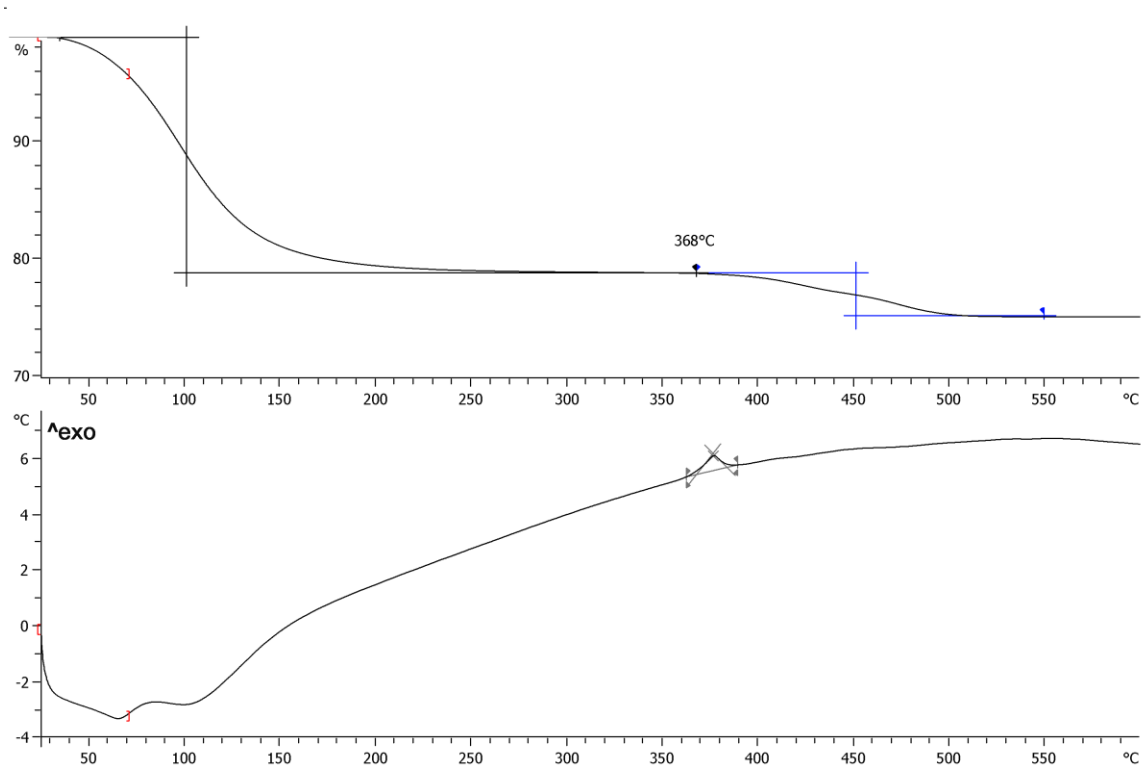

Figure S3. TGA (top) and DTA (bottom) data for **3a**. Crystalline samples were heated from 25 °C to 600 °C at a rate of 10 °C/min in an inert gas stream (N_2, 60 ml/min).