

A highly symmetric diamond-like assembly of cyclocatechylene-based tetrahedral cages

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Supporting Information

1. Crystallographic details
2. ESI mass spectra

S1. Crystallographic Details

A single crystal of $\text{Na}_8(\text{NC}_{16}\text{H}_{36})_6[\text{Cu}_6(\text{C}_{21}\text{H}_{12}\text{O}_6)]\text{I}_2$.solvate was transferred directly from the mother liquor to a protective oil without exposure to the atmosphere. The protective oil completely coated the crystal and did not allow the crystal to lose solvent molecules.

The crystal was then mounted on an Xcalibur CCD diffractometer (Oxford Diffraction) operating with Cu radiation. The crystal was placed in a stream of nitrogen at 130K.

Reflections measured as part of a pre-experiment analysis indicated that the crystals were face-centred cubic. Assuming $m-3$ Laue symmetry, a full set of data was collected. Despite the crystals being of a reasonable size the crystals were very weakly diffracting because of very large regions of highly disordered solvent and cations within the crystal. The diffraction data were consistent with $m-3m$ Laue symmetry.

Systematic absences are consistent with the space groups: $Fd-3$ ($m-3$ Laue symmetry) and $Fd-3m$ ($m-3m$ Laue symmetry). The structure was solved and refined in each of these space groups. The refinement in $Fd-3$ failed to reveal any structural features that were not apparent in the higher symmetry refinement. On this basis the space group, $Fd-3m$ was identified as the correct space group.

The non-hydrogen atoms of the $\text{Cu}_6\text{ctc}_4^{12-}$ anion were clearly defined in the structural solution and subsequent refinements. Disordered Na^+ ions and water molecules associated with the triangular windows of the tetrahedral cage were assigned with partial site occupations factors applied. A large peak of electron density was located at coordinates of 0.25, 0.25, 0.0. This peak was assigned as an iodide ion – the presence of iodide was indicated by elemental analysis and mass spectrometry. Anisotropic refinement of the iodide ion was consistent with the iodide ion being disordered over symmetry related sites that are within 0.6 Å of each other. The iodide ion was modeled accordingly.

As indicated in the main body of the paper a significant peak of electron density is apparent within each bowl-like cavity of the ctc ligand. On the basis of the separation between these peaks we believe it likely that these peaks correspond to the methyl carbon atoms of a highly disordered $\text{NMe}(\text{pent})_3^+$ cation however this assignment is only tentative.

The presence of extensive regions of disordered material between cages and at the centre of the cages prompted the use of the SQUEEZE routine within PLATON. The use of SQUEEZE led to the generation of a modified data set that was used for subsequent refinements.

Although the use of SQUEEZE has led to improved agreement values, the fact that almost 50% of the crystal volume is occupied by disordered material has meant that the final R1 value is high (12.8%). The large degree of disorder, the weakness of the data and the relatively high R1 value indicate that care should be exercised in any quantitative analysis of bond lengths and angles. Nevertheless the connectivity within the cages and the arrangement of the cages is unambiguous.

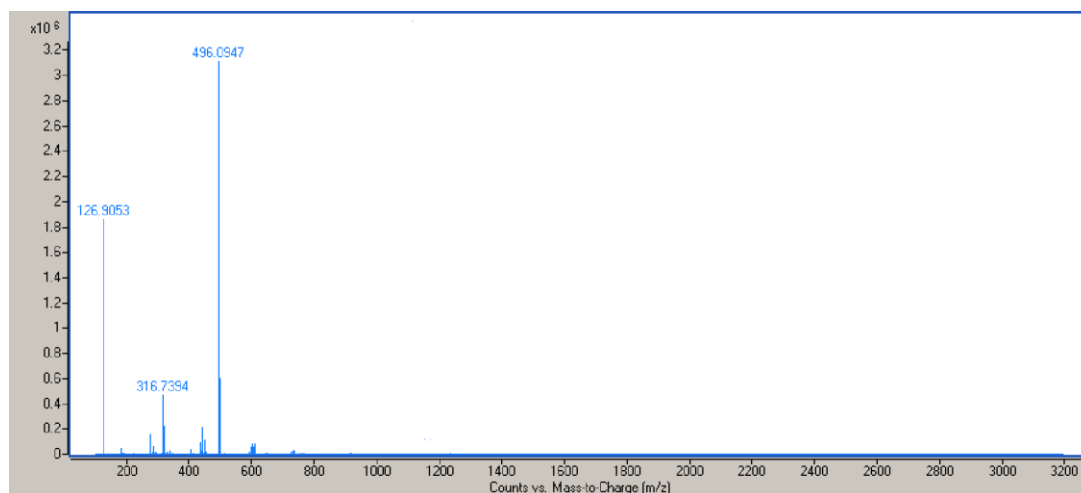


Fig S1. ESI mass spectrum in negative ion mode of $\text{Na}_8(\text{NC}_{16}\text{H}_{36})_6[\text{Cu}_6(\text{C}_{21}\text{H}_{12}\text{O}_6)]\text{I}_2 \cdot \text{solvate}$. Assignment: I^- 126.9053; CuI_2^- 316.7394; $[\text{I}_2(\text{NC}_{16}\text{H}_{36})]^-$ 496.0947.

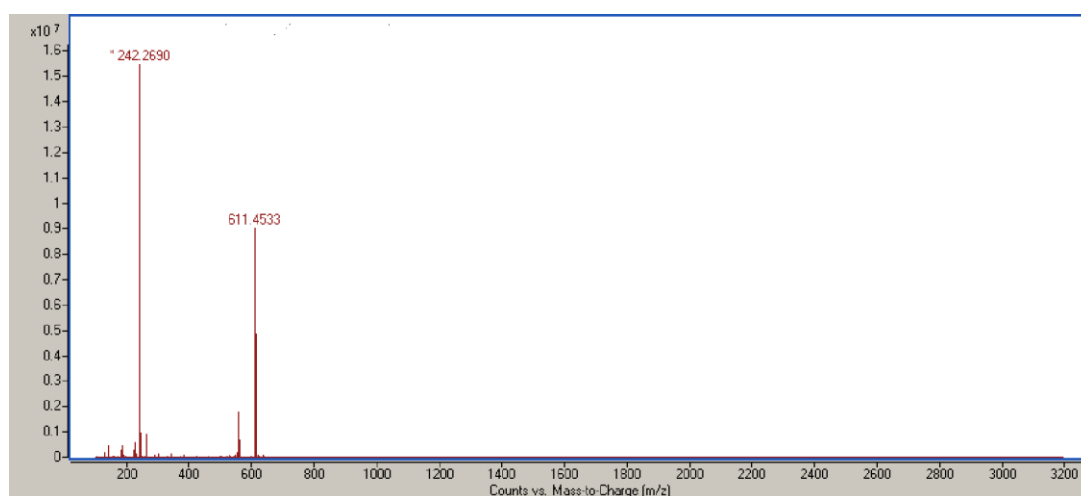


Fig S2. ESI mass spectrum in positive ion mode of $\text{Na}_8(\text{NC}_{16}\text{H}_{36})_6[\text{Cu}_6(\text{C}_{21}\text{H}_{12}\text{O}_6)]\text{I}_2 \cdot \text{solvate}$. Assignment: $\text{NC}_{16}\text{H}_{36}^+$ 242.2690; $[(\text{NC}_{16}\text{H}_{36})_2\text{I}]^+$ 611.4533.