Tetraberyllium-$\eta^4$-oxo-hexa(arylcarboxylates)

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Tetraberyllium-oxo-hexabenzoate and -hexa(mesitylcarboxylate) were prepared from benzoic / mesitylcarboxylic acid and freshly precipitated beryllium hydroxide in a tetrahydrofuran / water two-phase system. The crystal structure of the benzoate was determined from Be$_4$O(OCOPh)$_6$(C$_6$H$_6$)$_3$, and that of the mesitylcarboxylate from the phase Be$_4$O(OCOMes)$_6$(CCl$_4$). The two clusters have the $\eta^4$-oxo cage structure also detected for the acetate and nitrate complexes, and for the related hexacarbonato hexaanion. The high symmetry of the cluster allows the observation of $^9$Be and $^{17}$O signals in the solution NMR spectra.

The terminal atoms of the rigid carboxylate groups may be expected to lie at the vertices of large octahedra enclosing the cluster molecules. The axes of the six aryl groups would thus coincide with the axes of the cartesian coordinates with the $\mu^4$ oxygen atom at the origin. This disposition suggests a connectivity suitable for cubic lattices if $p$-difunctional arene-dicarboxylate anions are employed instead of aryl-monocarboxylate anions. However, the new results show that significant deviations of the OBe$_2$O$_2$C-Ar six-membered rings from planarity cause major deviations from octahedral symmetry and therefore no connectivity in cubic symmetry is to be expected.

Fragmentation of the Be$_4$O(OCOR)$_6$ clusters upon ionization in a mass spectrometer leads predominantly to cations [Be$_3$O(OCOR)$_3$]$^+$ which can be assigned a planar, highly symmetrical tricyclic core structure of D$_{3h}$ symmetry. Quantum chemical calculations confirm discrete energy minima for these cations and show that their stability is largely due to the favourable arrangement of alternating charges of neighbouring core atoms. The high polarity of Be-O bonds rules out any significant contributions from aromaticity. The reactions of Be(OH)$_2$ with 4-HS-C$_6$H$_4$-COOH and HS(CH$_2$)$_2$COOH give the corresponding cluster compounds Be$_4$O(OCORSH)$_6$, [R = C$_6$H$_4$, (CH$_2$)$_2$] with six terminal mercapto functions.