

Tetraberyllium- η^4 -oxo-hexa(arylcaboxylates)

Raphael J. F. Berger^a, Michael A. Schmidt^a, Jonas Jusélius^b, Dage Sundholm^b, Peter Sirsch^a, and Hubert Schmidbaur^a

^a Anorganisch-chemisches Institut, Technische Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany

^b Department of Chemistry, University of Helsinki, POB 55 (A. I. Virtasen aukio 1), FIN-00014 Helsinki, Finland

Reprint requests to Prof. Dr. H. Schmidbaur. E-mail: H.Schmidbaur@lrz.tum.de

Z. Naturforsch. **56 b**, 979–989 (2001); received June 26, 2001

Beryllium Chemistry, Beryllium Carboxylates, Quantum Chemical Calculations

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 $\text{Be}_4\text{O}(\text{OCOPh})_6(\text{C}_6\text{H}_6)_3$, and that of the mesitylcarboxylate from the phase $\text{Be}_4\text{O}(\text{OCOMes})_6(\text{CCl}_4)$. The two clusters have the μ^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 ^9Be 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 μ^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 $\text{OBe}_2\text{O}_2\text{C-Ar}$ 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 $\text{Be}_4\text{O}(\text{OCOR})_6$ clusters upon ionization in a mass spectrometer leads predominantly to cations $[\text{Be}_3\text{O}(\text{OCOR})_3]^+$ 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 $\text{Be}(\text{OH})_2$ with 4-HS- C_6H_4 -COOH and $\text{HS}(\text{CH}_2)_2\text{COOH}$ give the corresponding cluster compounds $\text{Be}_4\text{O}(\text{OCORSH})_6$, [R = C_6H_4 , $(\text{CH}_2)_2$] with six terminal mercapto functions.