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Keywords: lead compounds; intramolecular interactions; X-ray crystallography

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Giant Bismuth Oxo-Core Diketonate Clusters.
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The first bismuth oxo-diketonate, Bi38O45(hfac)13 (hfac = hexafluoroacetylacetonate), has been obtained and characterized to reveal a nonanuclear core molecule. The structure features metal atoms in two distinctively different coordination environments: the [Bi6O13] central oxo-core and three Bi(hfac)4 arms attached to its periphery. In coordinating solvents, this molecule irreversibly dissociates to give Bi(hfac), and very reactive coordinatively unsaturated species that aggregate into high-nuclearity bismuth oxo-diketonate clusters. One of such complexes, Bi9O6(hfac)6, that contains the largest known homometalic bismuth oxo-cluster, has been isolated in the form of single crystals. The crystal structure of this nanosized molecule revealed a giant [Bi9O6]6+ core cluster with 24 β-diketonate ligands bound to its surface. Within the bismuth oxo-core, a central [Bi9] unit can be identified whose metal atoms are connected only to oxo-groups. All other 32 bismuth “surface” atoms are coordinated to both oxo- and diketonate ligands. The “internal” unit consists of an octahedron of bismuth atoms, each face of which is centered by an oxo-group. In addition, there is a unique μ6-O atom residing in the middle of octahedron, on an inversion center. Alternatively, the structure of the [Bi6O13]+ oxo-cluster can be described as assembled from 13 octahedral edge-sharing [Bi6] units. The arrangement of bismuth atoms is close to an fcc structure, in which all of the tetrahedral and some of the octahedral voids are occupied by oxygen atoms. The applications of bismuth oxo-diketonates as models for studying the chemistry of Bi2O3 nanoparticles will be discussed.

Keywords: bismuth compounds; oxo-clusters; β-diketonate complexes

FA4-MS06-O5
Bond Valence Analysis in Lanthanide Complexes with Planar Trideterminate Ligand. Laure Guénée1, Claude Piguet2. “Department of inorganic chemistry, University of Geneva, Switzerland.
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The use of bond valence sum analysis in solid state structure of metal-organic complexes is illustrated here through the study of the complexation of trivalent lanthanide ions with tridentate aromatic ligand based on 2,6-bis(benzimidazol-2-yl)pyridine (L) [1].

The stability and structures of lanthanide coordination complexes formed by the successive fixation of ligands, eventually leading to the triple-helical complexes [LnL3]3+, can be tuned by counter-anions and steric constrains. Since a reliable set of bond valence parameters Rij for Ln-O [2] and Ln-N [3] bonds involved in metal-organic complexes has been recently computed, we have performed bond valence sum analysis on single crystals structures of a series of complexes possessing different compositions (variable stoichiometries and counter-anions).

The bond valence method appears to be an efficient tool for comparing metal-ligand affinities and ligand distortion in the solid state, which corroborate the stability trend of complex formation found in solution.


Keywords: bond valence method; complex compounds; lanthanides