



Fig. 1. (a) $\text{Pb}(\text{SCH}_2\text{CH}_2\text{NMe}_2)_2$ (**1**), $T = 100$ K;
 (b) $\text{E}^{14}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2$, $\text{E}^{14} = \text{Ge}$ (**2**), Sn (**3**), $T = 110$ K;
 (c) $\text{Pb}(\text{SCH}_2\text{CH}_2\text{NMe}_2)_2$ (**1**), $T = 290$ K

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

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Giant Bismuth Oxo-Core Diketonate Clusters. Evgeny V. Dikarev^a, Haitao Zhang^a. ^a *Department of Chemistry, University at Albany, SUNY, Albany, NY 12222, USA.*

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The first bismuth oxo-diketonate, $\text{Bi}_9\text{O}_7(\text{hfac})_{13}$ (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 $[\text{Bi}_6\text{O}_7]$ central oxo-core and three $\text{Bi}(\text{hfac})_3$ arms attached to its periphery. In coordinating solvents, this molecule irreversibly dissociates to give $\text{Bi}(\text{hfac})_3$ and very reactive coordinatively unsaturated species that aggregate into high-nuclearity bismuth oxo-diketonate clusters. One of such complexes, $\text{Bi}_{38}\text{O}_{45}(\text{hfac})_{24}$, that contains the largest known homometallic bismuth oxo-cluster, has been isolated in the form of single crystals. The crystal structure of this nanosized molecule revealed a giant $[\text{Bi}_{38}\text{O}_{45}]^{24+}$ core cluster with 24 β -diketonate ligands bound to its surface. Within the bismuth oxo-core, a central $[\text{Bi}_6]$ 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 μ_6 -O atom residing in the middle of octahedron, on an inversion center. Alternatively, the structure of the $[\text{Bi}_{38}\text{O}_{45}]^{24+}$ oxo-cluster can be described as assembled from 13 octahedral edge-sharing $[\text{Bi}_6]$ 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 Bi_2O_3 nanoparticles will be discussed.

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

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Bond Valence Analysis in Lanthanide Complexes with Planar Tridentate Ligand. Laure Guénee^a, Claude Piguet^a. ^a *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 $[\text{LnL}_3]^{3+}$, can be tuned by counter-anions and steric constrains. Since a reliable set of bond valence parameters R_{ij} 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.

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Keywords: bond valence method; complex compounds; lanthanides