

FA4-MS06-O1

Structure and Reactivity in Homogeneous Catalyst Model Systems. Stefanus Otto^a, Peter N. Bungu^a. ^a*Sasol Technology Research & Development, Sasolburg, South Africa.*
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X-ray crystallography was used extensively to obtain structural information on a series of bicyclic ligands of relevance in modified Co hydroformylation. [1] In addition the steric- and electronic nature of these ligands was further investigated through their respective phosphine selenides. [2, 3]

The oxidative addition of MeI to [Rh(bid)(CO)(L)] (bid = mono anionic bidentate ligand; L = phosphine ligand) is well known to be sensitive to the nature of the phosphine ligand. [4] Oxidative addition, to form the metal alkyl, is typically favored by an increase in electron density on the metal centre while steric hindrance would have a negative impact. The subsequent migratory insertion step, to form the metal acyl, is favored by both increased electron density and steric hindrance. These systems can be considered as convenient model systems to study both metal alkyl and acyl formation, as relevant in many catalytic processes, but at ambient temperature and pressure. Structure and reactivity relationships are presented based on X-ray crystallography, ³¹P NMR, IR and UV-vis measurements.

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Keywords: catalysis; structure; reactivity

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Metals and DNA: Crystallography as an Essential Tool in Bioinorganic Chemistry. Bernhard Spingler^a, Philipp M. Antoni^a, Alfredo Medina-Molner^a. ^a*Institute of Inorganic Chemistry, University of Zurich, Switzerland.*
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Our research group is interested in mono- and dinuclear metal complexes that interact with the rare left-handed Z-DNA. [1, 2] The temporary formation of Z-DNA during transcription could be exploited as a new target for rapidly replicating cells. This could lead to a completely novel strategy in the fight against cancer.

We are searching for metal complexes that can discriminate between the prevalent right-handed B-DNA and Z-DNA. The presentation will summarize our recent research efforts, mainly in the area of azamacrocyclic complexes. It will be shown for several cases that the ability to crystallize and study important intermediate and final products was essential for the progress of our research. [3]

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Keywords: DNA-metal interaction; mononuclear and dinuclear metal complexes; azamacrocyclic ligands

FA4-MS06-O3

A New Stable Monomeric Lead(II) Complex Pb(SCH₂CH₂NMe₂)₂: Structure and Dynamic Behaviour in Solid State. Victor N. Khurstalev^a, Rinat R. Aysin^a, Ivan V. Glukhov^a, Irina V. Borisova^b, Larissa A. Leites^a, Nikolai N. Zemlyansky^b. ^a*A.N.Nesmeyanov Institute of Organoelement Compounds of RAS, Moscow, Russia.* ^b*A.V.Topchiev Institute of Petrochemical Synthesis of RAS, Moscow, Russia.*
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In continuation of our investigations on the relative contributions of different factors to the stabilization of divalent Group 14 (E¹⁴) compounds, we report here the results of experimental and theoretical studies of a new stable lead(II) complex Pb(SCH₂CH₂NMe₂)₂ (**1**). The molecular structure of **1** was studied by single-crystal X-ray diffraction analysis at 100 and 290 K and variable-temperature (93-303 K) Raman spectroscopy in solid state. The electronic structure of **1** was elucidated by quantum-chemical calculations within the DFT approach.

The X-ray diffraction study has shown that **1** is a monomer stabilized by two intramolecular coordination N→Pb bonds with the formation of two five-membered rings, both having the usual *envelope* conformations. In the crystal of **1** at 100 K, the only asymmetrical conformer with the two five-membered rings differing in the positions of the cap-carbon atoms was observed (Fig. 1a). In contrast, at the same conditions the Ge(II) (**2**) and Sn(II) (**3**) analogs of **1** have symmetrical structures, in which the conformations of both five-membered rings are identical (Fig. 1b) [1]. However, the X-ray crystal structure analysis at 290 K has revealed that **1** exists both as the asymmetrical and symmetrical conformers in the 7:3 ratio, respectively; the minor symmetrical conformer has the same structure as those of **2** and **3** (Fig. 1c). It is interesting to note that only one of the two five-membered heterocycles in **1** (in the conformation unobserved in **2** and **3**) undergoes the transformation upon heating. The most striking feature of the Raman spectra of **1** is a doublet at 885/896 cm⁻¹, which is absent in the spectra of **2** and **3**. This doublet evidently reflects the presence of two different conformations of the five-membered rings and is explained by rotational isomerism about the ordinary C-C bond. The reasons of the phenomenon found for **1** are currently under investigation.

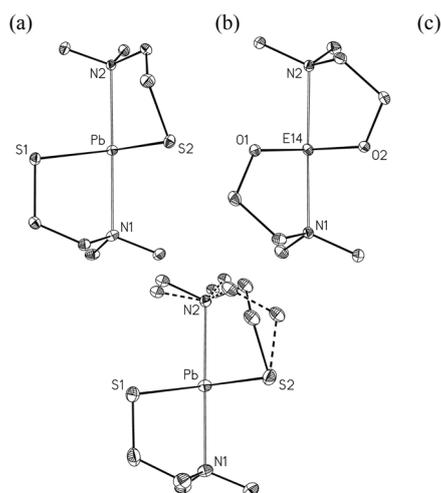


Fig. 1. (a) $\text{Pb}(\text{SCH}_2\text{CH}_2\text{NMe}_2)_2$ (**1**), $T = 100$ K;
 (b) $\text{E}^{14}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2$, $\text{E}^{14} = \text{Ge}$ (**2**), Sn (**3**), $T = 110$ K;
 (c) $\text{Pb}(\text{SCH}_2\text{CH}_2\text{NMe}_2)_2$ (**1**), $T = 290$ K

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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

FA4-MS06-O5

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 constraints. 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