

# Oral Contributions

## [MS19–02] Influence of ‘lone-pair’ cations (Pb<sup>2+</sup>, Tl<sup>+</sup>) on geometry and dimensionality of oxysalt inorganic compounds.

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Minerals and inorganic compounds with lone electron pair cations are of great interest because of their unusual structural and electronic properties. The outstanding feature of Tl(I) and Pb(II) is the presence of a lone electron pair that might, or might not, be stereochemically active. In the inactive state, the cation coordination is symmetrical with more or less equal bonds to the anions. A stereochemically active ‘lone pair’ plays the role of an additional ligand and occupies a volume approximately equal to that of an O<sup>2-</sup>-anion. Some recently discovered structures demonstrate also considerably different degree of distortion for symmetrically inequivalent Pb<sup>2+</sup> or Tl<sup>+</sup> atoms. There is some obvious correlation observed for the degree of distortion of the Pb<sup>2+</sup> or Tl<sup>+</sup> coordination polyhedra and presence of strong Lewis bases in the structures of inorganic oxysalts [1]. It has been demonstrated that the lone electron pair of Tl<sup>+</sup> cations is active when the Lewis base strength exceeds 0.22 valence units (v.u.). A similar limit is for Pb<sup>2+</sup> cations. An interesting feature of the structures with cations having stereoactive lone electron pairs is the association of those pairs into so-called lone electron pair micelles, or the formation of certain areas in the structure where the lone electron pairs are located in 1D channels or tubes. The partial delocalization of these electrons may cause interesting physical properties. Several recently discovered unusual structural architectures will be demonstrated and discussed. For instance ‘lone pair’ cavity inside of {Pb<sub>6</sub>[Si<sub>7</sub>O<sub>22</sub>]<sub>2</sub>}<sup>20-</sup> unit is rather large with dimensions that can be estimated as ~0.6×1.1 nm in the structure of

novel Pb<sub>21</sub>[Si<sub>7</sub>O<sub>22</sub>]<sub>2</sub>[Si<sub>4</sub>O<sub>13</sub>]. The similar units with approximately the same dimensions were previously observed in hyttsjöite. But the cavity inside of {Pb<sub>6</sub>[Si<sub>7</sub>O<sub>22</sub>]<sub>2</sub>}<sup>20-</sup> is filled by Cl<sup>-</sup> anions in the last case. Thus the replacement of large Cl anion in ClPb<sub>6</sub> octahedron by electrons may occur without considerable distortion of the structural moiety. The similar phenomenon was observed also previously in Tl<sup>3+</sup>, Tl<sup>+</sup> tellurates. These and other observations reveal the prominent role of ‘lone pair’ in some Pb<sup>2+</sup> and Tl<sup>+</sup> oxysalts as an important structural stabilizing agent. In this sense the stereochemical activity of ‘lone pair’ can be considered as an element of design for obtaining novel structural architectures with unusual properties.

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[1] S.V. Krivovichev, O. Mentré, O.I. Siidra, M. Colmont, S.K. Filatov, Chem. Rev. (2013) 113, dx.doi.org/10.1021/cr3004696.

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