

Crystallized Pb(II)- and Sn(II)-ammine complexes as intermediates from the interaction of CH₃NH₂ with BX₂ and CH₃NH₃BX₃ (B = Pb, Sn; X = I, Br, Cl)

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The reaction of CH₃NH₂ with CH₃NH₃PbI₃ leads to the formation of a yellowish viscous liquid. Upon removal of the CH₃NH₂ gas via slow heating, pristine CH₃NH₃PbI₃ can be obtained again. [1] Through higher concentrations of CH₃NH₂, crystals begin to emerge out of the viscous liquid. Our group was able to identify these crystals as [Pb(CH₃NH₂)₆]I₂, the first homoleptic lead-ammine complex. By reducing the CH₃NH₂ concentration, [Pb(CH₃NH₂)₄]I could be isolated as an additional compound. [2] In continuation of this investigation, we herein report on the findings of the interactions of CH₃NH₂ with BX₂ and CH₃NH₃BX₃ (B = Pb, Sn; X = I, Br, Cl). [3] We were able to characterize cubic (*Fm* $\bar{3}$ *m*) [Pb(CH₃NH₂)₆]Br₂ (see figure 1) and [Sn(CH₃NH₂)₆]I₂, which crystallize isotypic to the analogous lead iodide compound and sport close similarities to the K₂PtCl₆-type.

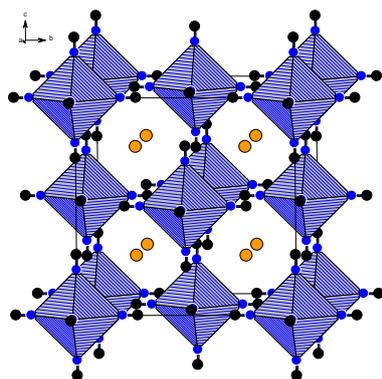


Fig 1: Unit cell of [Pb(CH₃NH₂)₆]Br₂; disorder of N-atoms not considered; H-positions not determined

Characteristic for all three compounds are partially disordered CH₃NH₂ ligands (see figure 2). Formal release of CH₃NH₂ in these cases yields [Sn(CH₃NH₂)₄]I and Pb(CH₃NH₂)₃Br₂. Here, Pb²⁺ is octahedrally coordinated by three CH₃NH₂ ligands and three Br⁻ as a *fac*-isomer. Charge neutrality is achieved by one terminal and two bridging Br⁻, forming edge-sharing dimers. [Sn(CH₃NH₂)₄]I is isotypic to its heavier lead analog, but exhibits significantly larger metal-halide distances. In the case of the lead chlorides, there is only a partial exchange of the halide ligands with CH₃NH₂. One compound obtained is Pb(CH₃NH₂)₂Cl₂, with a novel cubic (*Pa* $\bar{3}$) structure, showing two different octahedral coordination patterns for Pb²⁺: [PbCl₆] and [Pb(CH₃NH₂)₃Cl₃], which are corner shared connected via a chloride. The other is Pb(CH₃NH₂)₃Cl₂, where Pb²⁺ has a *fac*-coordination with one terminal and two bridging chlorides, forming chains in the direction of the *c*-axis. Since all chains possess the same orientation of the methylamine ligands, an acentric (*Cc*) structure results. Only [Sn(CH₃NH₂)₅]X₂ (X = Br, Cl) could be isolated in the case of the tin bromides and chlorides. The structures are isotypic and contain Sn²⁺ square-pyramidally coordinated by CH₃NH₂, boasting a strong stereo active lone-pair effect distorting the polyhedra. Furthermore, there is no direct interaction whatsoever between the tin(II) and the halide atoms, which are bound via hydrogen-bridges. All compounds are sensitive to heat and humidity readily reacting with moisture forming CH₃NH₃X and a metal hydroxide species like Pb(OH)X (X = I, Br, Cl) in the case of lead.

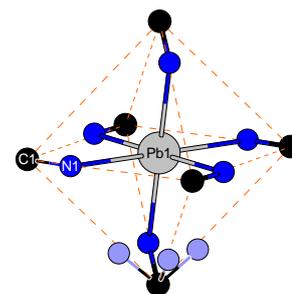


Fig 2: Coordination of Pb in [Pb(CH₃NH₂)₆]Br₂; disorder of N-atoms partially considered

[1] D. Bogachuk, L. Wagner, S. Mastroianni, M. Daub, H. Hillebrecht, A. Hinsch, *J. Mater. Chem. A* **2020**, *8*, 9788.

[2] M. Daub, H. Hillebrecht, *Eur. J. Inorg. Chem.* **2021**, 1490.

[3] M. Krummer, M. Daub, H. Hillebrecht, *Z. Anorg. Allg. Chem.* **2022**, *131*, 6050.