

## Crystallized Pb(II)- and Sn(II)-ammine complexes as intermediates from the interaction of CH<sub>3</sub>NH<sub>2</sub> with BX<sub>2</sub> and CH<sub>3</sub>NH<sub>3</sub>BX<sub>3</sub> (B = Pb, Sn; X = I, Br, Cl)

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

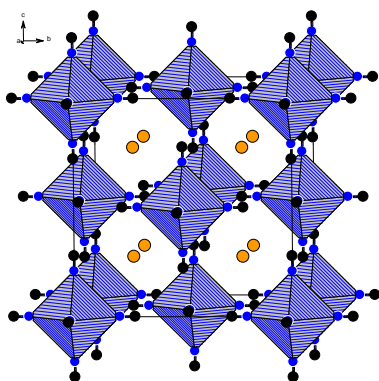


Fig 1: Unit cell of [Pb(CH<sub>3</sub>NH<sub>2</sub>)<sub>6</sub>]Br<sub>2</sub>; disorder of N-atoms not considered; H-positions not determined

Characteristic for all three compounds are partially disordered CH<sub>3</sub>NH<sub>2</sub> ligands (see figure 2). Formal release of CH<sub>3</sub>NH<sub>2</sub> in these cases yields [Sn(CH<sub>3</sub>NH<sub>2</sub>)<sub>4</sub>]I and Pb(CH<sub>3</sub>NH<sub>2</sub>)<sub>3</sub>Br<sub>2</sub>. Here, Pb<sup>2+</sup> is octahedrally coordinated by three CH<sub>3</sub>NH<sub>2</sub> ligands and three Br<sup>-</sup> as a *fac*-isomer. Charge neutrality is achieved by one terminal and two bridging Br<sup>-</sup>, forming edge-sharing dimers. [Sn(CH<sub>3</sub>NH<sub>2</sub>)<sub>4</sub>]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 CH<sub>3</sub>NH<sub>2</sub>. One compound obtained is Pb(CH<sub>3</sub>NH<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>, with a novel cubic (*Pa* $\bar{3}$ ) structure, showing two different octahedral coordination patterns for Pb<sup>2+</sup>: [PbCl<sub>6</sub>] and [Pb(CH<sub>3</sub>NH<sub>2</sub>)<sub>3</sub>Cl<sub>3</sub>], which are corner shared connected via a chloride. The other is Pb(CH<sub>3</sub>NH<sub>2</sub>)<sub>3</sub>Cl<sub>2</sub>, where Pb<sup>2+</sup> 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(CH<sub>3</sub>NH<sub>2</sub>)<sub>5</sub>]X<sub>2</sub> (X = Br, Cl) could be isolated in the case of the tin bromides and chlorides. The structures are isotypic and contain Sn<sup>2+</sup> square-pyramidally coordinated by CH<sub>3</sub>NH<sub>2</sub>, 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 CH<sub>3</sub>NH<sub>3</sub>X and a metal hydroxide species like Pb(OH)X (X = I, Br, Cl) in the case of lead.

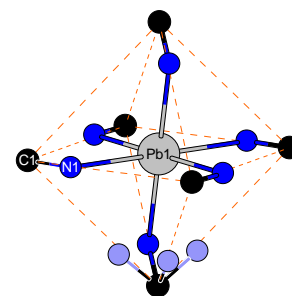


Fig 2: Coordination of Pb in [Pb(CH<sub>3</sub>NH<sub>2</sub>)<sub>6</sub>]Br<sub>2</sub>; disorder of N-atoms partially considered

[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.