

MS15-2-11 Caesium oxide mercurides – a new class of double salts
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L. Nusser¹, C. Hoch¹¹Ludwig-Maximilians-Universität - München (Germany)**Abstract**

While its neighbouring elements Pt, Au and Tl reportedly form anions in combination with electropositive metals in compounds such as Cs₂Pt [1], CsAu [2] and NaTl [3], Hg does not form anions that easily. When reacted with electropositive metals, mercury tends to form amalgams, which feature negatively polarised Hg atoms or atom groups [Hg_n]⁻, but no ‘true’ mercuride anions, therefore resulting in the *bad metal* behaviour of these amalgams. This may be due to its closed shell configuration 4f¹⁴5d¹⁰6s²6p⁰, illustrated by the fact that mercury does not form a stable atomic anion in the gas phase [4].

By ternary combinations of Cs, Hg and O a series of double salts with the first mercuride anions now has been made accessible. We present Cs₁₈Hg₈O₆ (*I*23, *a* = 13.3920(10) Å, *V* = 2401.8(5) Å³, *Z* = 2) featuring the mercuride anion [Hg₈]⁶⁻ next to isolated oxide anions [5]. [Hg₈]⁶⁻ has a slightly distorted cubic shape and is coordinated by caesium atoms, capping faces and edges (Fig. 1, left. Caesium atoms in blue, Hg atoms in green. All atoms are shown with their thermal displacement ellipsoids at 99% probability). The ionic character of the double salt is confirmed by DFT calculations of the electronic structure. Due to very close structural relations, Cs₁₈Hg₈O₆ can be described as homeotypic to the thallide oxide Cs₁₈Tl₈O₆ [6].

Cs₈Hg₈O is dimorphic: α-Cs₈Hg₈O (*R*3, *a* = 10.0844(11) Å, *c* = 46.475(6) Å, *V* = 4093.1(8) Å³, *Z* = 6) transforms at ~220 °C into the β modification (*R*3, *a* = 10.080(6) Å, *c* = 116.71(7) Å, *V* = 10270(11) Å³, *Z* = 12). Both Cs₈Hg₈O modifications represent a new structure type, again containing cubic [Hg₈]⁶⁻ anions and oxide anions, coordinated by caesium cations.

The structure of ‘Cs₅₈[Hg₈]₆O₁₂’ (*P*1, *a* = 16.360(2) Å, *b* = 18.888(2) Å, *c* = 19.120(2) Å, α = 61.779(4)°, β = 69.705(4)°, γ = 68.431(4)°, *V* = 4749.5(7) Å³, *Z* = 1) shows a still unresolved twinning problem, resulting in the formal charge of ‘5⅔⁻’ for the [Hg₈]⁶⁻ anion.

Cs₁₄Hg₁₂O₄ (*P*2₁/*c*, *a* = 10.734(3) Å, *b* = 15.688(3) Å, *c* = 17.378(3) Å, β = 128.146(10)°, *V* = 2301.4(9) Å³, *Z* = 4) contains the cluster anion [Hg₁₂]⁶⁻, which can be described as stack of two face-sharing [Hg₈] cubes. Analogous to the [Hg₈]⁶⁻ anion, the edges and faces of the [Hg₁₂]⁶⁻ anion are capped by caesium cations (Fig. 1, right. Caesium atoms in blue, Hg atoms in green. All atoms are shown with their thermal displacement ellipsoids at 99% probability), while the oxide anions are octahedrally coordinated.

References

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