Poster

Reactivity of the new caesium suboxometallate Cs_7MO_4 (M = In,Sc)

I. Zaytseva[1]**, C. Hoch**[1]

[1]Ludwig-Maximilians-Universität München, Department Chemie, Butenandtstrasse 5-13, D-81377 Munich, Germany
irina.zaytseva@cup.uni-muenchen.de

Suboxides of heavy alkali metals can be described as metal-rich oxides with a surplus of electrons. In their structures regions with ionic bonding as well as regions with metallic bonding can be discerned, and macroscopic metallic behaviour is observed. In this family of 'complex metals' or 'metals with holes' clusters of [A_6O] octahedra occur as discrete units, for example for caesium as three face-sharing octahedra $Cs_{11}O_3 = Cs^{+}_{11}O^{2-} \cdot 5e^-$. The 'surplus' e^- stabilise the clusters and provide bonding for additional metal atoms like in $Cs_7O = Cs_{10}[Cs_{11}O_3] = Cs^{+}_{10}Cs^{+}_{11}O^{2-}_{3} \cdot 15e^-$ [1].

Caesium suboxides are quite reactive. They react with refractory metals (e.g. Ta) at 300 °C forming caesium-rich oxometalates, like Cs_3TaO_4 [2] and dissolve oxides such as In_2O_3 at temperatures as low as 200 °C to form Cs_9InO_4 [3]. Like suboxides, the family of caesium suboxometallates Cs_9MO_4 (M = Al, Ga, In, Sc, Fe) consists of subvalent compounds, which can be summarised as $Cs_9^{+}(M^{III}O_4)^{5-} \cdot 3e^-$. The local ionic structure is now extended from monoatomic O^{2-} anions to $[MO_4]^{5-}$ tetrahedral anions. [Cs_8MO_4] columns of face sharing distorted Cs cuboctahedra surrounding [MO_4] together with purely metallically bound Cs atoms complete the structure as in Cs[Cs_8MO_4] [4].

When heated in vacuum, two equivalents of Cs are removed from Cs_9MO_4 (M = In, Sc, $In_{1-x}Sc_x$) in a equilibrium reaction. The resulting new caesium-poor suboxometallate Cs_7MO_4 (M = In, Sc, $In_{1-x}Sc_x$) crystallises in a new monoclinic structure type ($P2_1/c$, $Z = 4$, Cs_7InO_4: a = 13.0979(14) Å, b = 21.848(13) Å, c = 16.536(2) Å, β = 110.996(7)°, V = 4417.8(9) Å^3). Although caesium-'poor', Cs_7MO_4 is still subvalent, and can be described as $Cs^{+}_{7}(MO_4)^{5-} \cdot 2e^-$. Here, we present the reactivity of Cs_7MO_4 in first experiments: while heated under argon or in vacuum, as well as reactions with Cs, Rb and CsOH. New and reported oxometallates and suboxometallates can be synthesised starting from Cs_7MO_4, see figure 1 for examples. Crystallographic elucidation of the structures of all products is challenging due to poor crystal quality after thermolysis reaction and high air sensitivity. [5]

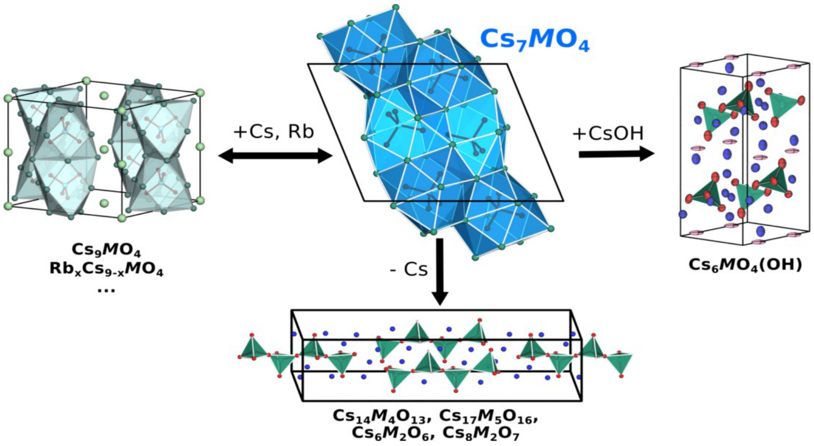

Figure 1. Reactions of Cs_7MO_4 (top, middle), and several new products: caesium tetracatena-scandate $Cs_{14}Sc_4O_{13}$ (bottom, middle), suboxometallate $Rb_3Cs_6InO_4$ (left) and caesium oxoindate hydroxide $Cs_6InO_4(OH)$ (right).

[1] Simon, A. (2017). *Suboxides and Other Low-Valent Species in Handbook of Solid State Chemistry*, edited by Dronskowski, R., Kikkawa, S.and Stein, A., pp. 139-160. Weinheim: Wiley-VCH.

[2] Zaytseva, I., Schulz, A., Hoch, C. (2024) *Inorg. Chem.* **63**, 3962.

[3] Hoch, C., Bender, J., Simon, A. (2009) *Angew. Chem. Int. Ed.* **48**, 2415.

[4] Hoch, C., Bender, J., Wohlfarth, A., Simon, A. (2009) *Z. Anorg. Allg. Chem.* **635**, 1777.

[5] Zaytseva, I., Waldmann, H., Linhart, M. P., Ispas Ungermann, S., Tambornino, F., Hoch, C. (2024), *J. Am. Chem. Soc.,* in print, DOI:10.1021/jacs.4c11286.

Authors acknowledge funding by DFG, project number 444769550.