Poster

The first oxides with mercury in the formal oxidation state 0? A_2HgO (A = Cs, Rb) and Cs(Cs$_{0.774(7)}$K$_{0.226(7)}$)HgO

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The chemistry of mercury-containing oxides shows an interesting variety regarding the role of mercury. Mercury can serve either as mono- or di-atomic cation in Hg(+II)- and Hg_2(+I)-oxometalates, as oxomercurate(+II) anion or, as recently reported by us, as mercuride cluster anion $[Hg_8]^{6-}$ with a formal oxidation state of "-6/8" in the mercuride oxide double salt $Cs_{18}Hg_8O_6$ [1]. Here, we report the new compounds A_2HgO (A=Cs, Rb) and Cs(Cs$_{0.774(7)}$K$_{0.226(7)}$)HgO and suggest a formal oxidation state of 0 for mercury.

Cs_2HgO ($C2/m$, a = 14.2923(14) Å, b = 4.3421(4) Å, c = 9.5830 Å, β = 108.508(5)°, V = 563.95(9) Å^3, Z = 4) and Rb_2HgO ($C2/m$, a = 13.6838(2) Å, b = 4.2136(5) Å c = 9.14560(11) Å, β = 108.526(5)°, V = 499.99(6) Å^3, Z = 4) were synthesised by reacting Cs or Rb with HgO, both crystallising isotypically in an own structure type. Analogously, by mixing Cs with small amounts of K, Cs(Cs$_{0.774(7)}$K$_{0.226(7)}$)HgO was obtained, which crystallises in its own new structure type ($Pnma$, a = 9.5932(4) Å, b = 4.3129(2) Å, c = 13.3517(6) Å, V = 552.42(4) Å^3, Z = 4). Both new structure types share the same basic motive, consisting of oxide centred [A_5HgO] octahedra, interconnected over common edges to bands of ${}^{1}_{\infty}[A_{3/3}A_{2/2}\mathrm{HgO}]$ with Hg as terminal, non-connecting corner. In Cs(Cs$_{0.774(7)}$K$_{0.226(7)}$)HgO, K only occupies the triple-connected corners of the octahedra, resulting in ${}^{1}_{\infty}[(\mathrm{Cs/K})_{3/3}\mathrm{Cs}_{2/2}\mathrm{HgO}]$ bands. While in both structure types these ${}^{1}_{\infty}[A_{3/3}A_{2/2}\mathrm{HgO}]$ bands run along the [010] direction, they differ in the arrangement in the respective ac planes. In A_2HgO (A=Cs, Rb) the bands form a layered structure, whereas in Cs(Cs$_{0.774(7)}$K$_{0.226(7)}$)HgO these bands are arranged in a herringbone-parquet-like fashion.

The Hg-O distances found in Cs_2HgO (d_{Hg-O} = 2.23 Å) and Rb_2HgO (d_{Hg-O} = 2.21 Å), as well as in Cs(Cs$_{0.774(7)}$K$_{0.226(7)}$)HgO (d_{Hg-O} = 2.24 Å) are significantly longer compared to known oxomercurates(+II) (e.g. Cs_2HgO_2: d_{Hg-O} = 1.97 Å [2], Rb_2HgO_2: d_{Hg-O} = 1.97 Å [3]) and mercury(+II)oxide (d_{Hg-O} = 2.02 Å [4]).

Assuming a formal oxidation number of +I for the alkali metals and -II for oxygen, the stoichiometry of these compounds A_2HgO dictates a formal oxidation number of 0 for mercury. The unusually long Hg-O distance in comparison to known Hg(+II) compounds, as well as the structural environment of Hg supports this suggested oxidation state. To further characterise this unusual compounds, the electronic structure has been calculated by DFT methods using VASP [5], showing a band gap of ca. 1.4 eV at E_F. Loewdin, Mulliken and Bader charge analysis gave a partially negative charge at Hg, whereas ELF calculations show electron density between Hg and O, hinting on an at least partially covalent bond [5,6]. Furthermore, COHP and COBI has been calculated using LOBSTER [6], suggesting bonding interactions with partially covalent character between Hg and O.

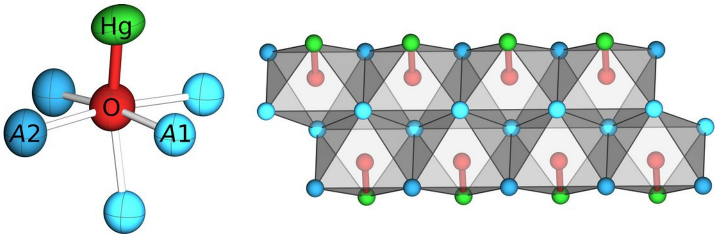

Figure 1. Main structural motives of the title compounds: [A_5HgO] octahedra (left) connected to ${}^{1}_{\infty}[A_{3/3}A_{2/2}\mathrm{HgO}]$ bands (right).

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The authors acknowledge support by DFG under grant number 513247541.