MS15-1-13 The Hg-rich part of the binary system K-Hg revised: synthesis and crystal and electronic structure of the new mercurides KHg_4, KHg_5 and KHg_8
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Abstract
A thermoanalytical reinvestigation of the Hg-rich part of the binary phase diagram K-Hg (Fig. 1) revealed the three new incongruently melting compounds KHg_4, KHg_5 [1] and KHg_8, in addition to the known phases K_2Hg_7 [2], K_3Hg_{11} ([3], not reproduced), K_7Hg_{31} [3], KHg_6 [4] and KHg_{11} [5]. According to the revised phase diagram, KHg_4 and KHg_5 were obtained from melts of the elements using appropriate Hg-richer sample compositions.The Hg-rich compound KHg_8 was synthesized by slowly unfreezing a 31:7 mixture of Hg:K from -70 °C to r.t. The three title compounds all form new structure types, which were determined by means of single crystal X-ray data. In the structures of KHg_8 [triclinic, *P*-1, *a*=630.0(2), *b*=897.2(2) *c*=1263.7(3) pm, α=99.30(3), β=91.34(3), γ=98.36(3)°] and KHg_5 [monoclinic, $P2_1/c$, *a*=1148.3(1), *b*=1758.6(2), *c*=1031.5(1) pm, β=116.687(1)°], similar to KHg_6 [4] and related alkaline-earth compounds [6], the Hg atoms of all sites form nearly flat nets with 8/7-membered rings (yellow), regular pentagons (blue) and distorted pentagons, squares and triangles (red). The potassium cations are always centred in the 8/7-membered rings, which are completed by two nearly regular 5-membered rings (blue) of the shifted (cf. arrows in Fig. 2) adjacent nets to form overall 18/17 (5:8/7:5) cation coordination polyhedra (ccp). The space inbetween the columns of ccps, which increases with the Hg-content, consists of distorted trigonal prisms, octahedra and tetrahedra (red). These latter pure mercury polyhedra are formed by the smaller rings of the Hg nets. The orthorhombic structure of KHg_4 [*Cmcm*, *a*=937.4(3), *b*=873.5(3), *c*=645.6(2) pm] contains similar ccps and Hg_6 trigonal prisms, but an alternative structure description emphasizing flat square pyramids (green) relates this structure to those of other alkali and alkaline-earth mercurides in this composition range (e.g. K_3Hg_{11}, Rb_5Hg_{19} [7]). The calculated electronic structures show the expected metallic character of the compounds, but also a distinct electron transfer form K to Hg, which justifies to denote them 'mercurides'.

References
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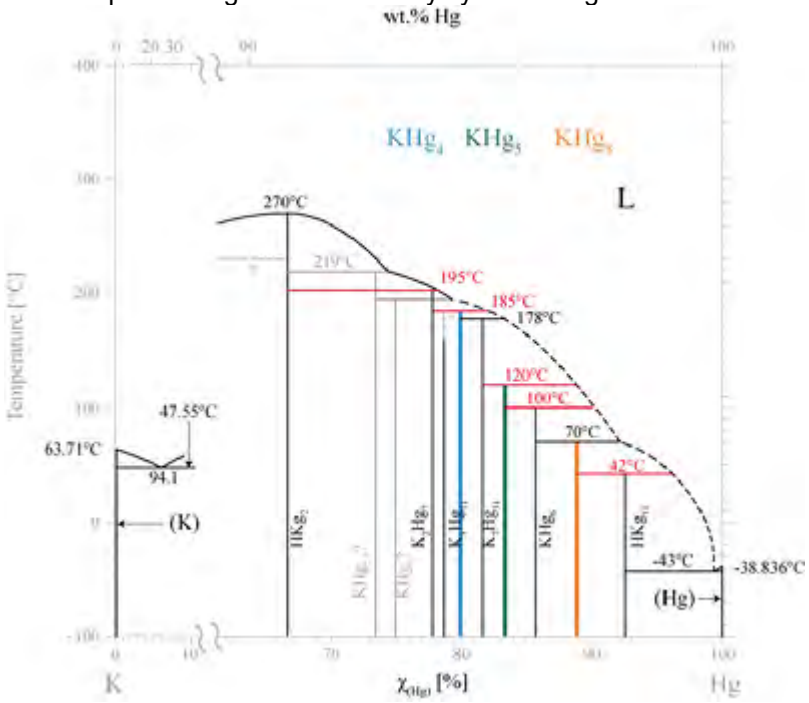
Revised phase diagram of the binary system K-Hg.



Comparison of the Hg nets in the crystal structure