A New Class of Hybrid Materials *via* Salt Inclusion: Novel Copper(II) Arsenates $\text{Na}_5\text{ACu}_4(\text{AsO}_4)_4\text{Cl}_2$ (A = Rb, Cs) Composed of Alternating Covalent and Ionic Lattices

Shiou-Jyh Hwu,^{1,*} Mutlu Ulutagay-Kartin,¹ Jeffrey A. Clayhold,² Richard Mackay,¹ Tina A. Wardojo,³ Charles J. O'Connor⁴, Mariusz Krawiec¹

¹Department of Chemistry, Clemson University, Clemson, SC 29634-0973

²Department of Physics and Astronomy, Clemson University, Clemson, SC 29634-1911

³Department of Chemistry, Rice University, Houston, TX 77251

⁴Department of Chemistry, University of New Orleans, New Orleans, LA 70148-2820

Supporting Information:

Thermogravimetric Analysis

Figure 1s. Thermogravimetric analysis (TGA) curves showing the thermal decomposition results of $\text{Na}_5\text{RbCu}_4(\text{AsO}_4)_4\text{Cl}_2$

Figure 2s. The tetrameric units in **1** and **2** (left) and in NaCuAsO_4 (right). The color codes are the same as those in Fig. 1. The arrow indicates the structural conversion via thermal decomposition of **1** and **2**, see text.

Figure 3s. Unit cell structure of $\text{Na}_5\text{CsCu}_4(\text{AsO}_4)_4\text{Cl}$. Only one of the Na_6 octahedral units is outlined by dotted lines for clarity.

Figure 4s. Face-capped Na_6O_8 units interconnected by chlorine atoms along the *ac* plane. The Na_6 octahedron is outlined in thick dotted lines, Na-O bonds are drawn in thin dotted lines and the Na-Cl bonds are in solid lines.

Figure 5s. One Na_6O_8 cluster from $\text{Na}_5\text{RbCu}_4(\text{AsO}_4)_4\text{Cl}_2$ showing the coordination geometry around each Na in the Na_6 octahedron.

Thermogravimetric Analysis: TGA data was collected on an as-prepared polycrystalline sample in the nitrogen atmosphere. Based on both TGA (Figure 1s) and PXRD analyses, it was evident that the title compound is subject to a thermal decomposition as described by the following chemical equation:

The weight loss derived from TGA curve is 23.7 %. Based on the formula given above, however, the theoretical weight loss is 16.59 %. The excessive amount of weight loss compared to the theoretical value is probably attributed to the excess molten salt, RbCl and NaCl, present in the reaction product. This was supported by PXRD prior to the TGA experiment. In addition, the TGA product was also confirmed by PXRD to show the resulting solid was NaCuAsO₄.

Figure 1s. Thermogravimetric analysis (TGA) curves showing the thermal decomposition results of $\text{Na}_5\text{RbCu}_4(\text{AsO}_4)_4\text{Cl}_2$.

Figure 2s. The tetrameric units in **1** and **2** (left) and in NaCuAsO₄ (right) with copper drawn in blue circle and oxygen in red. The arrow indicates the structural conversion via thermal decomposition of **1** and **2**, see text.

Figure 3s. Unit cell structure of $\text{Na}_5\text{CsCu}_4(\text{AsO}_4)_4\text{Cl}$. Only one of the Na_6 octahedral units is outlined by dotted lines for clarity.

Figure 4s. Partial structure of ionic lattice between Cu-As-O slabs. Face-capped Na_6O_8 units interconnected by chlorine atoms along the ac plane. The Na_6 octahedron is outlined in dotted lines, Na-O and Na-Cl bonds are drawn in solid lines. As shown in the unit cell structure (Fig. 3s), the structure is made of Cu-As-O slabs with electropositive cations (Na^+ and A^+) as well as chloride anions Cl^- residing in the interspace. An unusual structure made of Cl-bridged Na_6O_8 clusters is also observed. In the octahedral Na_6O_8 cluster, the bridging oxygen atoms cap triangular faces of the Na_6 octahedron. The Na-Na distances are shorter than the interatomic distance in elemental Na (3.708 Å): $d(\text{Na}(1)\text{-Na}(2)) = 3.562(4)\text{Å}$, $d(\text{Na}(2)\text{-Na}(2)) = 3.331(7)\text{Å}$ and $3.497(7)\text{Å}$ for **1**, for instance.

Figure 5s. One Na_6O_8 cluster from $\text{Na}_5\text{RbCu}_4(\text{AsO}_4)_4\text{Cl}_2$ showing the coordination geometry around each Na in the Na_6 octahedron.