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# A New Class of Hybrid Materials via Salt Inclusion: Novel Copper(II) Arsenates $Na_5ACu_4(AsO_4)_4Cl_2$ (A = Rb, Cs) Composed of Alternating Covalent and Ionic Lattices

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Two novel salt-inclusion copper(II) arsenates $Na_5ACu_4(AsO_4)_4Cl_2$, where A = Rb (**1**) and Cs (**2**), were synthesized by conventional solid-state reactions. The new phases exhibit a composite structure of alternating magnetic and insulating slabs. The magnetic slab contains highly oriented oligomeric $\mu$-oxo $[Cu_4O_{12}]^{16-}$ tetrameric units with a *cyclo*-$S_8$-like $Cu_4O_4$ magnetic core that resembles the building block of layered cuprates.[1] The insulating slab consists of a novel ionic framework of mixed alkali metal chloride lattices and rarely seen $Na_6O_8$ clusters. **1** and **2** are magnetic insulators since the tetrameric units are isolated by closed-shell, nonmagnetic ions. Compounds of this type intuitively provide an electronically simplified system[2] for the experimental and theoretical studies of spin−spin and spin−lattice interactions in a confined oxide lattice.[3] We report here the synthesis, structure, and spectroscopy of $Na_5ACu_4(AsO_4)_4Cl_2$. Also briefly discussed is the formation of $NaCuAsO_4$, a new magnetic phase containing the revised cluster unit $[Cu_4O_{16}]$,$^{24-}$ via thermal decomposition of **1** and **2**.

Our ongoing research in salt-inclusion reactions has resulted in a fascinating class of hybrid materials of mixed covalent and ionic lattices.[4] Similar to organic−inorganic hybrid materials,[5] the two chemically dissimilar lattices reveal a host−guest relationship. The incorporated ionic lattice could be considered to support the covalent framework of nanostructured transition metal (TM) oxide. The novel salt-inclusion solids discovered thus far include the CU series where the nanostructured covalent framework can be viewed as templated by an extended lattice made of ionic salt.[4a,b] While the role of salt inclusion needs to be further determined, its utility in the formation of composite lattices has been evident in recent examples of $AHg_2O_2Cl_2$ (A = Sr, Ba)[6] and alkali halide incorporated cadmium oxalates.[7] The title compounds offer a new class of structures through which one could target the synthesis of confined magnetic clusters of different TM-oxide systems.

**1** and **2** can be synthesized by employing molten salt as a reactive flux. Single crystals of **2**, for example, were synthesized using $As_2O_5$, CuO, and $Na_2O$ to prepare a reaction mixture with the nominal composition $NaCu_4As_3O_{12.5}$. The NaCl/CsCl eutectic flux was employed, and the flux-to-charge ratio was 5:1 by weight. The reaction procedures were similar to those reported in ref 4. The typical yield was 70% based on CuO. Thermal decomposition of **1** and **2** led to the loss of two moles of chloride salt (NaCl and ACl) per formula unit at 900 °C and beyond and, in turn, the formation of $NaCuAsO_4$, according to the results of thermogravimetric analysis and powder X-ray diffraction studies.

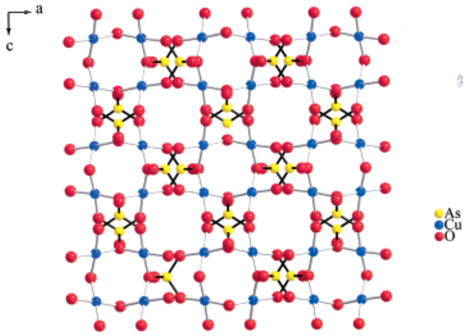

***Figure 1.*** Partial structure of the Cu−As−O slab showing the checkerboard patterns of tetrameric $[Cu_4O_{12}]^{16-}$ cluster units interlinked by the $As^{5+}$ cations.

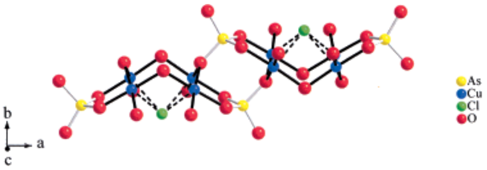

***Figure 2.*** Structural arrangements of two neighboring $Cu_4O_{12}$ cluster units, each being capped by a $Cl^-$ anion. Selected bond distances [Å] and angles [deg] of **1**: Cu−O 1.93−1.99, Cu−Cl(1) 2.78. ∠O−Cu−O 85.3−92.8, ∠Cu−O−Cu 108.7−110.9.

The title compounds exhibit a pseudo-2-D structure, in which the $[Cu_4O_{12}]^{16-}$ clusters are interlinked by the arsenic cations to form an extended Cu−As−O slab along the *ac* plane, as shown in Figure 1. The neighboring $[Cu_4O_{12}]^{16-}$ clusters are packed "back-to-back" in a parallel fashion along the slab and interconnected via sharing three of the four $AsO_4$ oxygen atoms, as shown in Figure 2. The Cu−As−O slabs are stacked along the *b* axis alternately with ionic slabs discussed below. Unlike the CU-2 phases where the salt can be removed by washing,[4a] the interaction at the interface of two chemically dissimilar lattices is rather strong; hence, no ion-exchange reaction was observed.

The $Cu_4O_{12}$ cluster is made of four square-planar $CuO_4$ units that share corner oxygen atoms, and it is capped by a $Cl^-$ anion (Figure 2). The Cu−Cl distances, 2.78 for **1** and 2.73 Å for **2**, are long relative to the sum of Shannon crystal radii, 2.46 Å, of a five-coordinated $Cu^{2+}$ cation (0.79 Å) and a six-coordinated $Cl^-$ (1.67 Å).[8] These tetrameric $Cu_4O_{12}$ clusters share one bridging ($O^b$) and

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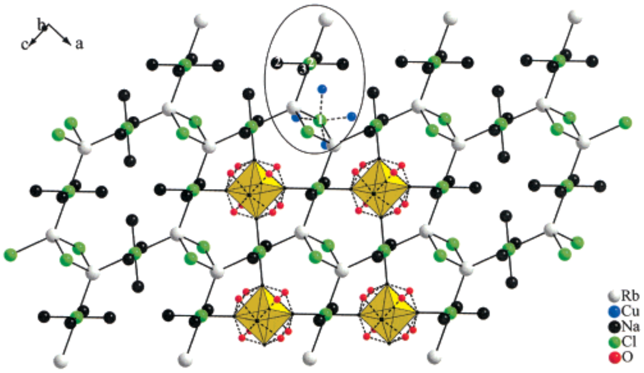

***Figure 3.*** Partial structure of salt lattice showing the six-coordination environment of chloride anions (circled region) and the $Na_6O_8$ clusters (polyhedral drawing). The capping chlorides, Cl1, coordinate to two rubidium (**1**), or cesium (**2**), cations (highlighted in one for clarity).

two terminal ($O^t$) oxygen atoms with $AsO_4$ tetrahedra extending the layer along the *ac* plane (Figures 1,2). The unshared oxygen atom of each $AsO_4$ unit points away from the network toward the $Na_6O_8$-containing slab (see discussion later). The intercluster distances, $d_{Cu\cdots Cu} = 4.26$ Å and 4.19 Å for **1** and similarly 4.26 Å and 4.17 Å for **2** (along *a* and *c* axes, respectively), are longer than the internuclear distances within the tetramer, 3.24 and 3.23 Å for **1** and 3.24 and 3.22 Å for **2**.

The $Cu_4O_{12}$ cluster forms a puckered *cyclo*-$S_8$-like $Cu_4O_4$ ring (Figure 2) due to the bond strain of the fused $AsO_4$ unit and the capping $Cl^-$ anion. Otherwise, the copper atoms lie in a plane between the layers of above-mentioned $O^b$ and $O^t$. The four Cu−O bond distances of the *Jahn−Teller* $Cu^{2+}$ cation are in a narrow range, 1.93−1.99 Å for both **1** and **2**, where the $O^t$ forms shorter Cu−O bonds than $O^b$. The sum of the four O−Cu−O angles is nearly 360°, for example, 359.6° for **1** and 359.7° for **2**, indicating that the $CuO_4$ unit adopts a nearly square-planar configuration. In addition, the intercluster $Cu{-}O^b\cdots O^b{-}Cu$ distance is 3.51 Å, which is responsible for the observed quasi-2-D magnetic coupling via the corresponding super-superexchange paths.[9−11]

The extended ionic slab exhibits a fascinating lattice of mixed alkali metal chloride and sodium oxide clusters that cooperatively facilitates the formation of highly oriented $Cu_4O_{12}$ tetramers. Figure 3 shows the partial structure of the ionic slab in which each chloride anion adopts octahedral coordination geometry. As shown in the circled area, each of the two crystallographically independent chloride anions coordinates to six cations. Cl1, the capping chloride, coordinates to two $Rb^+$ cations along with four $Cu^{2+}$ cations, while Cl2 coordinates to four $Na^+$ and two $Rb^+$ cations. The salt slab, in addition, consists of rarely seen face-capped $Na_6O_8$ (6-8)-type octahedral clusters. Figure 3 shows selected 6-8 clusters that are “embedded” in the alkali metal chloride lattice. These 6-8 clusters are interconnected by noncapping Cl2 anions. The salt lattices, in any event, stacked along the *b* axis in such a way allowing the $Cu_4O_{12}$ tetramers to reside in the “cage” formed by five 6−8 clusters. In our recent attempt to substitute $Na^+/Rb^+$ with $Cs^+$ cations to investigate its effect on the formation of magnetic clusters, we have instead isolated new noncentrosymmetric salt-inclusion solids showing metal-oxide frameworks wrapping around incorporated salt lattices.

The UV−vis spectra suggest that the new materials contain a “localized” $Cu^{2+}$ electronic state. The intense absorption above 3 eV (∼24 000 $cm^{-1}$), as shown in Figure 4, can be assigned to LMCT bands from the $\sigma$ lone pair of the anion to the $\sigma$ orbital of copper as similar designations have been made in $Cu^{II}(OH)_2$ and $Cu^{2+}$-containing complexes.[12] The ligand-field spectra show broad bands, with maxima at 1.43 and 1.77 eV (11 500 and 14 270 $cm^{-1}$), due to $d{-}d$ transitions. These are consistent with the confined nature of the copper-oxide units.

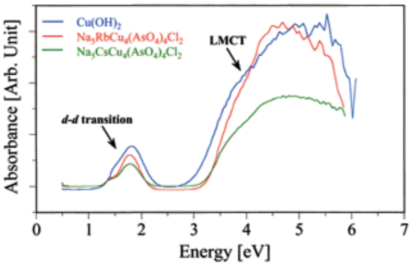

***Figure 4.*** UV-vis spectra of **1**, **2** and, for comparison, $Cu(OH)_2$.

In summary, we have had continued success in salt inclusion reactions using molten salt as a reactive flux. The resulting solids described in this report revealed a novel salt lattice that enables the formation of nanostructured copper oxide clusters. We anticipate that, by varying the size and stoichiometry of halide salt, more novel results are yet to come. The current discovery, in any case, provides a new insight in host−guest chemistry as an alternative means to the exploratory synthesis of hybrid materials.

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**Supporting Information Available:** Text describing the structure and thermal decomposition and figures of TGA and structures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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