

Salt-Templated Open Frameworks (CU-2): Novel Phosphates and Arsenates Containing $M_3(X_2O_7)_2^{2-}$ (M = Mn, Cu; X = P, As) Micropores 5.3 Å and 12.7 Å in Diameter

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Abstract: We have recently isolated a novel family of salt-templated phosphates and arsenates, $A_2M_3(X_2O_7)_2 \cdot$ (salt) [where A = K, Rb, Cs; M = Mn, Cu; X = P, As]. The space-filling, charge-compensation alkali metal chloride salts can be removed conveniently without destroying the MXO framework. These materials (designated as CU-2-MXO) exhibit microporous structures (ca. 5.3 and 12.7 Å in diameter) in which the active transition metal sites are distributed in a spatially uniform manner throughout the bulk. The salt lattice functions as a structure-directing template. The single-crystal structure shows that the large pore contains a remarkable ACI/CsCl lattice that consists of two interpenetrating, square antiprismatic columns of ions. In contrast to organically templated microporous solids, these new materials were synthesized by conventional solid-state reactions at high temperatures. Consequently, the resulting compounds can endure extensive heating to ca. 650 °C. These materials, in fact, possess the highest thermal stability found thus far among zeolite and related materials. Along with the synthesis and structure of four CU-2-MXO compounds, we also report some preliminary results concerning studies of ion-exchange and topotactic deintercalation–intercalation reactions.

There is currently a great deal of research activity dealing with the use of organic as well as inorganic templates to direct the synthesis of micro- and mesoporous materials.^{1–4} This activity not only is due to fascination with their varied forms and novel structures, but also stems from their possible use as molecular sieves, sorbents, and catalysts and in chiral synthesis.^{3–12} Much of this recent research has concerned, in particular, the templated synthesis of phosphate and arsenate materials.^{1–3,8,9,11–22} These porous solids typically are prepared under low-temperature (~100–200 °C), hydrothermal conditions. The microporous framework is often subject to collapse upon the removal of the templating agent, diminishing the potential of these materials for applications.^{18,19,23–25} Several recent reports, therefore, have focused on the search for new microporous solids

that can demonstrate the removal of the space-filling, charge-compensation molecules without disrupting the framework.^{26–29} By using alkali metal chlorides as crystal growth media, we have isolated an unprecedented family of salt-templated, open-framework compounds. These materials were synthesized at high temperatures (500–800 °C), well above the temperature regime in which one typically finds open-framework structures. The title compounds exhibit a novel channel structure that contains water-soluble alkali metal chloride salt, giving a general formula $A_2M_3(X_2O_7)_2 \cdot$ (salt) (A = K, Rb, Cs; M = Mn, Cu; X = P, As). We anticipate certain redox chemistry because, upon removal of the salt, the transition-metal cation centers are

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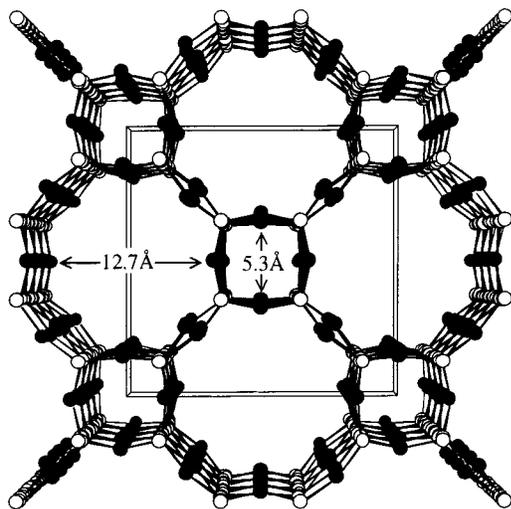


Figure 1. Projected view showing the microporous framework of the CU-2 materials.²⁶ The structure of the micropore is outlined by interconnecting transition metal (solid circles) and phosphorus (or arsenic) cations (open circles). The oxygen atoms, as well as ionic salts, are omitted for clarity.

exposed to the void space of the pores. Figure 1 presents a projected view of the microporous framework. It shows two fascinating channel structures, each of which consists of either eight (8-ring) or sixteen (16-ring) alternating cations of M and X. Table 1 lists four structurally characterized phases to demonstrate a possible range of salt inclusion and transition-metal cation incorporation. We also report here some preliminary results on ion-exchange and topotactic deintercalation–intercalation reactions for the CU-2-CuPO material.³⁰

The CU-2 materials can readily be synthesized by conventional solid-state methods, and the resulting solids are new additions to the relatively small family of *d-block*-metal-containing microporous solids. The single crystals of CU materials were grown at temperatures approximately 150–200 °C above the melting point of the eutectic salt mixture employed.³¹ The structure is adopted by di- and trivalent Mn/Cu-containing phases (Table 1). The valence state of the *d-block* cation may be manipulated by controlling the A/Cl ratio of the starting materials. The title compounds form sizable column crystals allowing for detailed structural analysis, through which the correlation between structure and catalytic properties can be studied.

The current discoveries suggest that open framework structures can be synthesized at relatively high temperatures by employing ionic salt as a templating agent. Conventionally, employing low temperatures avoids structural condensation, which

(30) CU-2 represents the second member of the salt-templated microporous solids discovered by the Clemson University (CU) team. The acronym “CuPO” is derived from the chemical formula of negatively charged framework, $\text{Cu}_3(\text{P}_2\text{O}_7)_2^{2-}$. The materials used for the ion-exchange and topotactic deintercalation–intercalation studies were synthesized via stoichiometric reactions.

(31) The single crystals of $\text{K}_{2.12}\text{Cs}_{2.76}\text{Mn}_{0.76}\text{Cu}_{2.24}(\text{P}_2\text{O}_7)_2\text{Cl}_{2.87}$ (Table 1), for example, were grown by employing CsCl flux. In a typical reaction, KMnO_4 (1.0 mmol), CuO (1.0 mmol), and P_2O_5 (1.0 mmol) were mixed and ground with CsCl flux (mp 645 °C) in a flux-to-charge ratio of 5: 1. The reaction was performed in a carbon-coated fused silica ampule. The mixture was heated to 650 °C over 48 h and held at that temperature for 24 h, heated to 800 °C over 12 h, and then soaked at that temperature for 3 days. The reaction was slowly cooled to 500 °C over 4 days, then furnace-cooled to room temperature. Light-orange crystals (ca. 45%) of the title compound, as well as some black crystals (ca. 15%) along with some light-green chunks (ca. 40%) of unidentified composition, were retrieved upon washing with deionized water and suction filtration. EDAX showed all the atoms found in the formula with a small amount of Mn. The crystal has a light-orange color, which is due to the Mn doping, and it is air stable.

in turn allows for the formation of open-framework structures. In this case, the micropore structure forms at high temperature as the result of “phase segregation” (for lack of a better term) between chemically dissimilar salt and covalent oxide lattices. As mentioned above, we have been employing halide salts as a flux to grow crystals of phosphates, arsenates, and silicates³² that otherwise only form polycrystalline phases. The inclusion of salt is, however, inevitable, and consequently we have synthesized several interesting low-dimensional lattices containing channel³³ and layered³⁴ frameworks. In a recent report, for example, we have shown the novel honeycomblike lattice of copper(II) phosphate, $[\text{BaCl}][\text{CuPO}_4]$, in which the spiral $[\text{CuPO}_4]_\infty$ framework is helical around the Ba–Cl–Ba chain.³³

The title compounds exhibit the same microporous structure consisting of two types of channels ca. 5.3 and 12.7 Å in diameter. In the structure of $\text{K}_{3.81}\text{Cs}_{1.44}\text{Cu}_3(\text{P}_2\text{O}_7)_2\text{Cl}_{3.25}$,³⁵ for example, the cross sections are made of eight (alternating polyhedra of four CuO_4 square planes and four PO_4 tetrahedra) and sixteen (alternating polyhedra of eight CuO_4 and eight PO_4) rings. In the skin layer of micropores, the square-planar CuO_4 units are evenly spaced, with each plane facing the center of the pores (Figure 2). The alternating CuO_4 and P_2O_7 units share vertex oxygen atoms giving rise to a negatively charged wall of $\text{Cu}_3(\text{P}_2\text{O}_7)_2^{2-}$. Both small and large channels are occupied by mixed KCl and CsCl salts. The chlorine atoms occupy the axial positions of the square-planar CuO_4 units. The X-ray studies show that the CU-2 materials (Table 1) crystallize in two different space groups ($I4/mcm$ and $P4/nbm$) due to the variation of the salt lattice. The small channel is centered by a linear “chain” of alternating A–Cl–A for $I4/mcm$ or A–□–A–Cl–A for $P4/nbm$ while the large channel is stuffed with mixed KCl/CsCl salt lattice (see next). It should be noted that, for an idealized formula of $\text{K}_2\text{Cs}_3\text{Cu}_3(\text{P}_2\text{O}_7)_2\text{Cl}_3$ (derived from the formula of the mixed Mn/Cu material stated in Table 1), 33% of the Cu^{2+} cations are statistically not coordinated by the chlorine anions.

A remarkable salt lattice resides in the large channel, functioning as a “template” directing the formation of inorganic framework. In the larger pore of the above $I4/mcm$ lattice, the extended salt structure (Figure 3) consists of two concentric columns of square antiprismatic (SAP) Cl^- anions and mixed K^+/Cs^+ cations centered by an array of Cs^+ cations. The cesium cations that reside in the center of the large channel are bonded to eight chlorine atoms which make up the inner-sphere SAP column. The outer-sphere SAP column is made of mixed K^+/Cs^+ cations, which give reasonable bond distances to the inner-sphere Cl^- anions. The chloride anions of the extended lattice are oriented such that the formation of Cu–P–O framework can be considered as “directed”, in which four chloride anions in each layer of the salt lattice are coordinated to a set of four corresponding copper cations (Figure 2). Judging from the relatively long Cu–Cl bond distances (2.70 and 2.85 Å for copper between two large channels, and 3.27 Å for copper at the interface between two different sized channels), as compared to 2.52 Å in CuCl_2 , the interaction between the salt template and CuPO framework should be weak. This is also true for the

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(35) Crystal data for $\text{K}_{3.81}\text{Cs}_{1.44}\text{Cu}_3(\text{P}_2\text{O}_7)_2\text{Cl}_{3.25}$: green, column crystal ($0.57 \times 0.17 \times 0.18 \text{ mm}^3$), $M_r = 993.8$, tetragonal $P4/nbm$ (No. 125) with $a = 17.741(2) \text{ \AA}$, $c = 13.337(2) \text{ \AA}$, $V = 4197.8(9) \text{ \AA}^3$, $Z = 8$, $\rho_{\text{calcd}} = 3.145 \text{ g cm}^{-3}$, $F_{000} = 3725.86$, $\mu = 70.03 \text{ cm}^{-1}$, $R/wR/\text{GOF} = 3.15\%/4.90\%/1.53$.

Table 1. Cell Constants of Some Salt-Templated Microporous Solids, $A_2M_3(X_2O_7)_2 \cdot (\text{salt})$ ($A = \text{K, Rb, Cs}$; $M = \text{Mn, Cu}$; $X = \text{P, As}$)

solids ^a	chemical formulas ^b	a , Å	c , Å	space group
CU-2-MnPO	$\text{K}_{1.23}\text{Cs}_{3.60}\text{Mn}_3(\text{P}_2\text{O}_7)_2\text{Cl}_{3.74}^c$	18.398(2)	14.048(3)	$I4/mcm$ (No. 140)
CU-2-MnCuPO	$\text{K}_{2.12}\text{Cs}_{2.76}\text{Mn}_{0.76}\text{Cu}_{2.24}(\text{P}_2\text{O}_7)_2\text{Cl}_{2.87}$	18.001(3)	13.530(4)	$I4/mcm$ (No. 140)
CU-2-CuPO	$\text{K}_{3.81}\text{Cs}_{1.44}\text{Cu}_3(\text{P}_2\text{O}_7)_2\text{Cl}_{3.25}$	17.741(2)	13.337(2)	$P4/nbm$ (No. 125)
CU-2-CuAsO	$\text{Rb}_{1.14}\text{Cs}_{4.15}\text{Cu}_3(\text{As}_2\text{O}_7)_2\text{Cl}_{3.19}$	17.928(3)	13.555(3)	$I4/mcm$ (No. 140)

^a CU: Clemson University. ^b Structural composition obtained from the single-crystal X-ray diffraction studies. ^c The compound contains mixed $\text{Mn}^{2+}/\text{Mn}^{3+}$ cations, and the formula can be written as $\text{CsMn}^{\text{II}}\text{Mn}^{\text{III}}(\text{P}_2\text{O}_7)_2 \cdot (\text{salt})$.

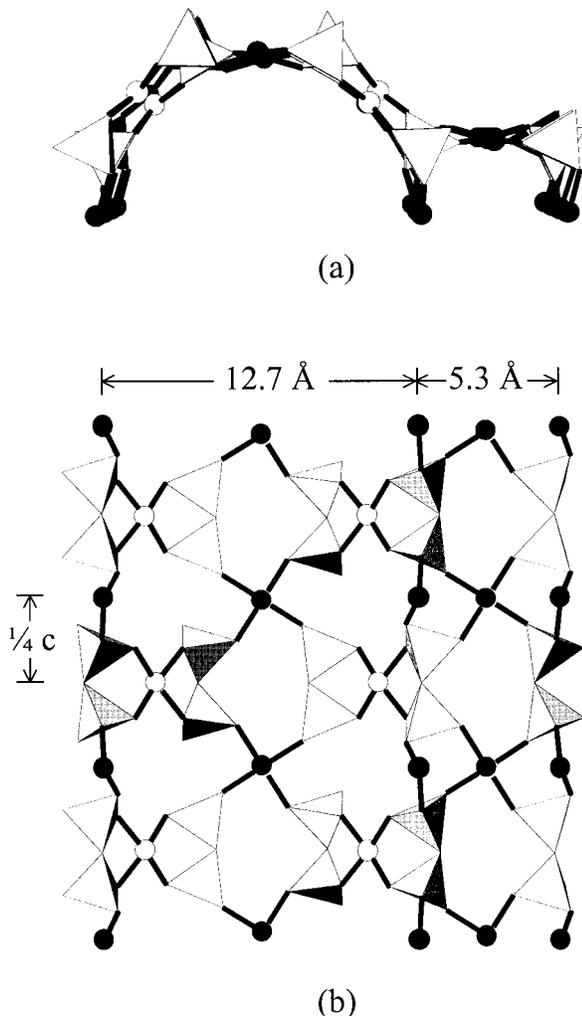


Figure 2. A partial structure of the half micropores viewed (a) along and (b) perpendicular to the direction of channel structures. The PO_4 units are drawn in tetrahedra and two independent Cu^{2+} cations are represented by solid (Cu(1)) and open (Cu(2)) circles.

salt residing in the small channel, where the $\text{Cu}-\text{Cl}$ bond adopts a long contact distance, 2.79 Å. The resulting long $\text{Cu}-\text{Cl}$ bonds can be in part attributed to the partially occupied chloride anion sites.³⁶

Our preliminary investigations have shown that the chemistry of this compound family is remarkably rich. At room temperature, the salt template can be conveniently removed by washing with water, and ion-exchanged, as well as re-intercalated with other salts, including nitrates. In a typical abstraction experiment, 100 mg of polycrystalline $\text{K}_2\text{Cs}_3\text{Cu}_3(\text{P}_2\text{O}_7)_2\text{Cl}_3$ is added to 15 mL of deionized water. The mixture is stirred for 10 h at room temperature to ensure the completion of the experiment. The solid changes color from light green to white in as little as 90 min, which indicates the loss of the $\text{Cu}-\text{Cl}$ bond due to chloride bleaching. The resulting solid forms a fine powder, and the

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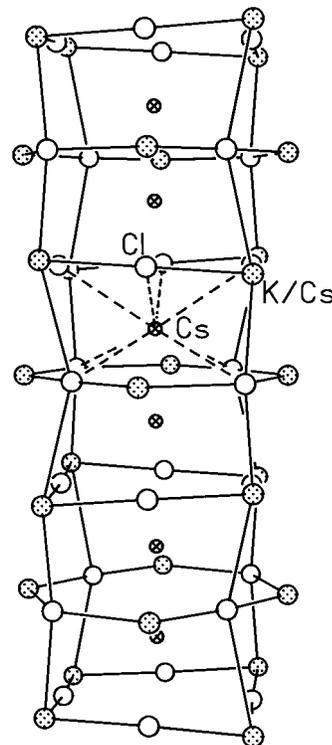
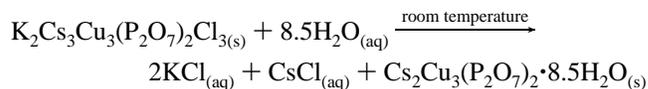


Figure 3. The ball-and-stick drawing of the structure of the salt template observed in $\text{K}_{2.12}\text{Cs}_{2.76}\text{Mn}_{0.76}\text{Cu}_{2.24}(\text{P}_2\text{O}_7)_2\text{Cl}_{2.87}$. The Cs to inner-sphere-Cl bonds are outlined in dashed lines from one of the cesium atoms, and the outer-sphere K/Cs to Cl bonds are drawn in filled lines. The small electron density between two Cs atoms, refined as partially occupied Cl, is omitted for clarity.

EDAX of this H_2O -treated product shows a small concentration of cesium with a trace amount of potassium. This suggests a replacement reaction of chloride salt by water as follows:



The “residual” cesium is believed to compensate for the amount of monovalent cations necessary to balance the negative charge of the $\text{Cu}-\text{P}-\text{O}$ framework. The chemical formula for the water-treated product, as well as the ion-exchanged and re-intercalated products, is derived from the TGA results shown below. The deintercalated product, $\text{Cs}_2\text{Cu}_3(\text{P}_2\text{O}_7)_2 \cdot 8.5\text{H}_2\text{O}$, can be re-intercalated with potassium chloride salt. It is interesting to note that the EDAX results of KCl re-intercalated product show no sign of the presence of Cs. This suggests that a possible reaction of combined ion-exchange and intercalation has occurred:

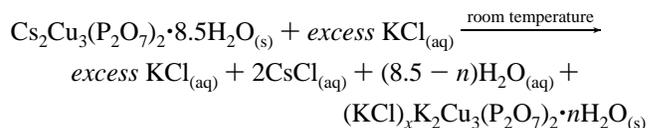


Table 2. Indexed Cell Constants^a for CU-2-CuPO, Water-Treated, and Intercalated Materials

sample	<i>a</i> (= <i>b</i> ; Å)	<i>c</i> (Å)	<i>V</i> (Å ³)	no. of peaks indexed
CU-2-CuPO ^b	17.878(4)	13.463(8)	4303(3)	20
CU-2-CuPO/H ₂ O ^c	14.637(4)	18.740(6)	4015(2)	16
CU-2-CuPO/KCl	17.596(9)	13.305(9)	4119(4)	11
CU-2-CuPO/KCl/CsCl	17.949(4)	13.460(5)	4336(2)	20

^a The cell constants are refined in the tetragonal crystal system. The pore size of the large channel is estimated according to $a/\sqrt{2}$, and the values are 12.6, 10.3, 12.4, and 12.7 Å, respectively. ^b K₂Cs₃Cu₃(P₂O₇)₂Cl₃, stoichiometric yield. ^c The PXRD pattern (see Supporting Information) is indexed by the TREOR program.

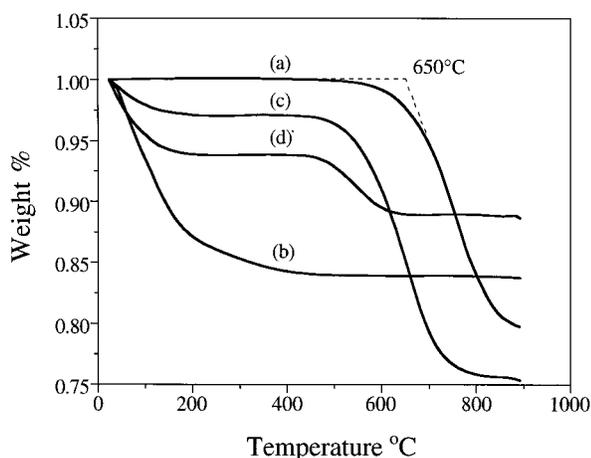
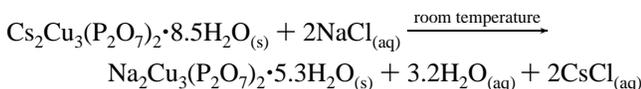


Figure 4. The TGA curves of (a) CU-2-CuPO, (b) H₂O-treated, (c) KCl/CsCl-intercalated, and (d) KCl-intercalated materials. In curve a, two tangent lines intersect at ca. 650 °C, where the onset point of decomposition is defined, see text.

(The *x* and *n* values are 0.47 and 2.51, respectively, assuming that the second weight loss observed in the following TGA study is corresponding to the 100% loss of the KCl salt.) For the NaCl reaction, however, a complete ion-exchange reaction takes place resulting in the Na₂Cu₃(P₂O₇)₂·5.3H₂O phase.



The powder X-ray diffraction (PXRD) experiments show that the H₂O-treated solid has a deflated unit cell (Table 2). Based on the *d*-spacing of the (110) diffraction peak, the large size channel shrinks from 12.6 Å to 10.3 Å. Re-intercalation in salt solutions yields new solids with almost totally recovered pores. For example, in an attempt to intercalate Cs₂Cu₃(P₂O₇)₂·8.5H₂O using a 4 M solution of mixed KCl/CsCl in water, we obtained a slightly expanded unit cell, compared to CU-2-CuPO (Table 2). This slight expansion is likely due to the co-intercalation of water. It should be noted also that the chloride-intercalated solid regains its green color, a characteristic of the Cu–Cl phase.

The CU-2-CuPO materials exhibit extended thermal stability compared to existing microporous solids. Figure 4 shows the TGA curves of CU-2 materials listed in Table 2. Polycrystalline solids were used for these studies under nitrogen atmosphere. The thermal decomposition curve of the original material, CU-2-CuPO, shows an onset temperature of ca. 650 °C (Figure 4a), roughly in the proximity of the melting point of the eutectic

salt (KCl/CsCl, 616 °C). It is also noted that, although the H₂O-treated solid loses its water molecules readily (Figure 4b), re-intercalated solids show a restored thermal stability (Figure 4c,d). The initial weight drop of these two curves is due to the loss of water molecules. The Cu–P–O framework is retained in the plateau area of the curve. Also, preliminary experiments show that the porous framework of CU-2-CuPO/H₂O remains intact after 10 h heating at 200 °C. The heat-treated solid can be re-intercalated to regain features similar to CU-2-CuPO, according to PXRD patterns.

In summary, we have developed an interesting class of transition-metal-containing phosphates and arsenates in which the negatively charged M₃(X₂O₇)₂²⁻ microporous structure is templated by water-soluble salt. The micropore exhibits uniformly distributed redox cation centers in the skin layer. We have shown that the framework of these CU-2 materials is robust, and that both 8- and 16-ring pores are chemically readily accessible. Through ion-exchange and topotactic deintercalation–intercalation reactions, one can conveniently modify the chemical as well as physical properties of the pores. The water-treated microporous material, Cs₂Cu₃(P₂O₇)₂·8.5H₂O, regains its thermal stability by re-intercalation with either single (KCl) or mixed (KCl/CsCl) salts. This is consistent with the earlier finding by Barrer et al., who demonstrated in their first synthesis of KFI-type zeolite solids^{37,38} that the inclusion of nonframework salt greatly increases the thermal stability of the microporous aluminosilicate materials. In addition, single-crystal structural studies have indicated that mixed transition metals of unique valence or different oxidation states as well as mixed A-site cations can be used for fine-tuning the properties of micropores. We are currently evaluating these materials for their catalytic properties in light of the fact that the coordination sites of transition-metal cations become unsaturated after the removal of salt.

The use of molten salt, as opposed to organic or organometallic templating agents, has allowed us to raise reaction temperatures to an under-investigated region for microporous solids. It is intriguing to recognize the formation of the ACL/CsCl salt lattice in the large pore. The highly ordered salt lattice seems to behave in a fashion similar to known organic and organometallic template molecules. Our continued studies suggest that more supportive results are forthcoming,³⁹ and that this approach surely deserves further investigation.

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Supporting Information Available: PXRD plots of materials listed in Table 2 and of calcined CU-2-CuPO at 650 °C and CU-2-CuPO/KCl/CsCl at 450 °C, tables of crystallographic data, atomic coordinates, selected bond lengths and angles, and anisotropic thermal parameters for K_{1.23}Cs_{3.60}Mn₃(P₂O₇)₂Cl_{3.74}, K_{2.12}Cs_{2.76}Mn_{0.76}Cu_{2.24}(P₂O₇)₂Cl_{2.87}, K_{3.81}Cs_{1.44}Cu₃(P₂O₇)₂Cl_{3.25}, and Rb_{1.14}Cs_{4.15}Cu₃(As₂O₇)₂Cl_{3.19} (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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