Alloying a single and a double perovskite: a Cu$^{+}/2+$ mixed-valence layered halide perovskite with strong optical absorption†

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Introducing heterovalent cations at the octahedral sites of halide perovskites can substantially change their optoelectronic properties. Yet, in most cases, only small amounts of such metals can be incorporated as impurities into the three-dimensional lattice. Here, we exploit the greater structural flexibility of the two-dimensional (2D) perovskite framework to place three distinct stoichiometric cations in the octahedral sites. The new layered perovskites $A_1[AuCu](CuIn)_{0.5}Cl_{8}$ (1, $A =$ organic cation) may be derived from a Cu$^+$–In$^{3+}$ double perovskite by replacing half of the octahedral metal sites with Cu$^{2+}$. Electron paramagnetic resonance and X-ray absorption spectroscopy confirm the presence of Cu$^{2+}$ in 1. Crystallographic studies demonstrate that 1 represents an averaging of the Cu$^+$–In$^{3+}$ double perovskite and Cu$^{2+}$ single perovskite structures. However, whereas the highly insulating Cu$^+$–In$^{3+}$ and Cu$^{2+}$ perovskites are colorless and yellow, respectively, 1 is black, with substantially higher electronic conductivity than that of either endmember. We trace these emergent properties in 1 to intervalence charge transfer between the mixed-valence Cu centers. We further propose a tiling model to describe how the Cu$^+$, Cu$^{2+}$, and In$^{3+}$ coordination spheres can pack most favorably into a 2D perovskite lattice, which explains the unusual 1 : 2 : 1 ratio of these cations found in 1. Magnetic susceptibility data of 1 further corroborate this packing model. The emergence of enhanced visible light absorption and electronic conductivity in 1 demonstrates the importance of devising strategies for increasing the compositional complexity of halide perovskites.

1. Introduction

The double perovskite lattice considerably increases the versatility of halide perovskites by enabling the incorporation of a much wider range of elements compared to single perovskites. Here, the divalent octahedral B-site cation of the three-dimensional (3D) $A^1B^4X_3$ ($X =$ halide) single perovskite structure is replaced with an ordered mixture of two different B-site occupants, yielding the general formula $A_1^1B^1B^2X_3$. Nevertheless, the double perovskite framework is still restrictive in that it requires exactly two distinct B-sites that satisfy charge balance requirements. Thus, double perovskites most commonly feature B-site combinations of 1+ and 3+ (e.g., Cs$_2$Ag$^+$/Bi$^{6+}$/Br$_6$) or 4+ and 0 (vacancy) (e.g., Cs$_2$Sn$^0$/Cl$_6$). Recent work has explored B-site alloying as a means of further expanding the compositional phase space of double perovskites. Isovalent alloying, in which the impurity cation carries the same charge as one of the two B-site cations, is a highly effective method for tuning the optical and electronic properties of these materials. Often, such alloys exist as solid solutions where the compositional and materials properties can be varied continuously between two pure endmember phases. However, compositional flexibility approaching that seen in isovalent alloys remains rare. Likely due to lattice mismatch, local charge imbalances, and formation of charge-compensating defects, most examples of aliovalent alloys exist only in a narrow composition window with low (ca. 1

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atom%) impurity concentrations. Nevertheless, complex perovskite compositions, which incorporate heterovalent cations in high concentrations, may exhibit unique optoelectronic properties and strategies for their syntheses are, therefore, highly desirable.

The close structural analogy between halide perovskites and their oxide analogues points to one exciting avenue for such work. Layered CuII-oxide perovskite derivatives feature \(S = 1/2\) spins in a square lattice. Famously, members of this family display a high-temperature superconducting transition induced by electron\(^{17}\) or hole\(^{18}\) doping. A similar electronic structure to that of electron-doped oxide cuprates may be accessible in the halide perovskites by incorporating both Cu\(^+\) and Cu\(^{2+}\) as B-site cations, which, to our knowledge, has not yet been accomplished. Here, we achieve this mixed-valence Cu state in an unusual layered perovskite containing three distinct metal cations disordered over the octahedral B sites with the formula: \(A_x[Bu^{	ext{III}}(Cu^{	ext{II}}In^{	ext{III}})_{0.5}Cl_8]\). Perovskite 1 may be derived from the layered Cu\(^+\)-In\(^{3+}\) double perovskite by replacing half of the octahedral metal sites with Cu\(^{2+}\), or equivalently from the layered Cu\(^{2+}\) perovskites by replacing half of the Cu\(^{2+}\) sites with an equal mixture of Cu\(^+\) and In\(^{3+}\). Importantly, spectroscopic characterization of 1 demonstrates that incorporation of three heterovalent B-site cations affords unique optical and electronic properties including enhanced optical absorption in the visible region (Fig. 1) and substantially increased electronic conductivity. We uncover the origins of the new optical, transport, and magnetic properties in the visible region (Fig. 1) and substantially unique optical and electronic properties including enhanced Cu\(^+/2+\) mixed valency.

2. Results and discussion

2.1. Perovskite structure

The 3D \(AB^\text{III}X_6\) single perovskite structure consists of a lattice of corner-sharing \(BX_6\) octahedra (\(B = \text{divalent cation, } X = \text{halide anion}\)) where small monovalent A-site cations fill the voids between octahedra. In the double perovskite structure, the B site is split into two different occupants that form an ordered arrangement yielding the general formula \(A_xB^\text{II}B^\text{III}X_6\). The B and B' sites can be vacant or filled by cations with charges of 1+

![Fig. 1](https://example.com/fig1.png)

Photographs of crystals of (A) the colorless double perovskite, \((\text{PEA})_4\text{CuInCl}_8\), (B) the yellow single perovskite, \((\text{PCA})_4\text{CuCl}_4\), and (C) the black perovskite, \((\text{BA})_4\text{Cu}_2\text{Cl}_{10}\text{Cl}_8\) (1\(_{\text{BA}}\)), featuring a 1 : 1 blend of the inorganic layers in A and B. The black color arises from Cu\(^{+}/2\) mixed valence. PEA = phenethylammonium, PCA = \(p\)-chloroanilinium, and BA = butylammonium.

2.2. Tracking the black phase in the synthesis of a Cu\(^+\)-In\(^{3+}\) layered double perovskite

The layered double perovskite \((\text{PEA})_4\text{CuInCl}_8\) (PEA = phenethylammonium; Fig. 2A),\(^{19,20}\) consists of sheets of corner-sharing \([\text{Cu}^\text{II}Cl_6]^{5-}\) and \([\text{In}^\text{III}Cl_6]^{3-}\) octahedra partitioned by bilayers of PEA cations. Crystals of \((\text{PEA})_4\text{CuInCl}_8\) grow as colorless plates under an inert N\(_2\) atmosphere (Fig. 1), but we observed the formation of thin, plate-like, black crystals (1\(_{\text{PEA}}\)) when droplets of the mother liquor in Paratone-N® oil were exposed to air for ca. 15 minutes. We hypothesized that formation of this black phase is related to the oxidation of Cu\(^+\) to Cu\(^{2+}\) and therefore attempted to prepare it directly. (A recent study on a layered Cu\(^+\)-In\(^{3+}\) perovskite also speculated that oxidation of Cu\(^+\) led to formation of black material, although this product was not characterized further.)\(^{21}\) Indeed, quickly cooling a 100 °C solution of CuCl, CuCl\(_2\), In\(_2\)O\(_3\), and phenethylenamine in HCl under N\(_2\) affords black plate-like crystals (ESI†). Unfortunately, these crystals diffracted poorly, yet slowing the cooling rate or allowing the black crystals to remain in the mother liquor afforded colorless crystals, hindering characterization and suggesting that the black phase was a kinetic product. Given the importance of the organoammonium A-site cation in dictating both the stability and crystallinity of perovskite phases,\(^{22,23,32,23}\) we sought to stabilize the black phase using different organic cations. In Sections 2.3 and 2.4, we prepare this black phase using two different organic cations. With butylammonium (BA) cations, we obtain a stable, phase-pure perovskite (1\(_{\text{BA}}\)) enabling accurate compositional characterization. However, we obtained higher-quality single-crystal X-ray diffraction (SCXRD) data using \(p\)-chloroanilinium (PCA) as the A-site cation, and thus, we used this analogue (1\(_{\text{PCA}}\)) to study structural details.

2.3. Composition of 1

2.3.1. SCXRD analysis of 1\(_{\text{BA}}\). Similar to the PEA system, colorless crystals form from a slowly cooled solution of CuCl, In\(_2\)O\(_3\), and butylamine in HCl under an N\(_2\) atmosphere. SCXRD
analysis of these colorless crystals reveals a dimen-
sionally reduced analog of the hypothetical \( A_2 CuIn^{III}Cl_6 \) 3D double
perovskite, \((BA)_2[Cu_{0.5}InCl_3][Cu_{0.5}Cl_2][BACl]\). This structure
consists of infinite 1D ribbons of corner-sharing [CuCl_6]^{2-}
and [InCl_6]^{3-} octahedra separated by CuCl_2^- monomers (see
Fig. S1 and ESI† note that this phase differs from the layered
\((BA)_2[CuIn^{III}]_{0.5}Cl_4\) perovskite obtained through a solid-state
synthesis). However, when this same precursor solution
is exposed to air, we observe the formation of black rectangular
plate-like crystals \( \text{1BA} \) (Fig. S2†). An air-free solution-state
approach where \( Cu^+, Cu^{2+}, \) and \( In^{3+} \) precursors are combined
in HCl with butylamine also affords black crystals (see ESI†).
Importantly, unlike \( 1\text{PEA} \), crystals of \( 1\text{BA} \) can be formed by slowly
cooling the mother liquor and do not convert to a colorless
phase over time.

Single-crystal structure determination of \( 1\text{BA} \) was complicat-
ed by weak diffraction, disorder, and a low-temperature
phase transition (see ESI†). Nevertheless, our data reveal that
\( 1\text{BA} \) has an \( n = 1 \) layered perovskite structure consisting of 2D
sheets of corner sharing metal-halide octahedra partitioned by
bilayers of BA cations (Fig. S3†). Interestingly, the structure is
best modeled when the B sites are treated as a disordered
mixture of Cu and In cations. Although too much emphasis
should not be placed on structural parameters extracted from
this solution due to the relatively low data quality, we were
nevertheless intrigued by the \( ca. 78 : 22 \) Cu : In site-occupancy
ratio found for the B sites (Table S1†). This ratio is very
different than the 50 : 50 ratio expected for a disordered \( n = 1 \)
perovskite with only \( Cu^+ \) and \( In^{3+} \) at the B sites. Because \( 1\text{BA} \)
forms only in the presence of \( Cu^{2+} \), we posited that \( Cu^{2+} \) cations
could replace equal amounts of \( In^{3+} \) and \( Cu^+ \) in the perovskite
lattice, thus altering the Cu : In occupancy ratio of the B site (see
Section 2.4 for an in-depth structural analysis of 1 performed
on a higher-quality SCXRD data set).

2.3.2. EPR and XAS analysis of \( 1\text{BA} \). The 77 K electron
paramagnetic resonance (EPR) spectrum of \( 1\text{BA} \) (Fig. 3A)
confirms incorporation of \( Cu^{2+} \) into this material, showing
a single feature with an axial spectral shape, where \( g_{\perp} \)= 2.06 and
\( g_{\parallel} \)= 2.16. These values are nearly identical to those extracted
from the spectrum of \((BA)_2Cu^{3+}Cl_4\), indicating the presence of
exchange-coupled \( Cu^{3+} \) centers\(^{14,32}\) in \( 1\text{BA} \). Note that the parallel
and perpendicular directions are defined with respect to the
unique axis of the perovskite structure (\( g_{\perp} \) refers to the plane of
the 2D perovskite sheets while \( g_{\parallel} \) refers to the direction
perpendicular to the sheets) rather than that of the Jahn–Teller
distorted \([Cu^{3+}Cl_6]^{4-}\) unit. By integrating the EPR spectrum of
\( 1\text{BA} \) and using the integrated spectrum of \((PCA)_2\)\\(Cu^{3+}Cl_4\) as
a standard, the weight% of \( Cu^{3+} \) in \( 1\text{BA} \) was calculated to be
7.79% (see Fig. S4 and the ESI†). This value agrees within
experimental error with the expected value of 8.67% for the
formula \((BA)_4[Cu^{III}(Cu^{III})_{0.5}Cl_8]\) which we calculate below
using inductively coupled plasma mass spectrometry (ICP-MS)
data (Section 2.3.3).

X-ray absorption spectroscopy (XAS) was also used to confirm
the presence of both \( Cu^+ \) and \( Cu^{2+} \) in \( 1\text{BA} \) and to estimate the
\( Cu^+ : Cu^{2+} \) ratio. Measurements were collected at the Cu K-edge
on finely ground powders of \( 1\text{BA} \) (EDBE)\\(Cu^{3+}Cl_4\) (EDBE = \( 2,2':\)
(ethylenedioxy)bis(ethylammonium)), and \((PEA)_4Cu^{III}Cl_8\),
and the latter two materials serving as \( Cu^{2+} \) and \( Cu^+ \) standards,
respectively (see ESI†). Here, we report data obtained using the
total electron yield (TEY) method; similar results were obtained
using the fluorescence method (Fig. S5 and Table S3†). We
found that samples of \( 1\text{BA} \), which were phase-pure by PXRD,
could be prepared using a range of precursor stoichiometries
(see ESI†), and we tested these for compositional variability
using XAS. Phase-pure samples of \( 1\text{BA} \) prepared using high
\( Cu^{3+} : Cu^+ \) \( 1 : 2 : 3 \) and low \( Cu^{2+} : Cu^+ \) \( 1 : 3 \) concentrations of \( Cu^{3+} \)
yield very similar XAS spectra (Fig. 3B). Both feature absorption onsets
intermediate between those of the \( Cu^+ \) and \( Cu^{2+} \) standards, indicating
the presence of both oxidation states in \( 1\text{BA} \). We fit these spectra
using a linear combination of the \( Cu^+ \) and \( Cu^{2+} \) standard
spectra (see ESI†), obtaining estimated \( Cu^+ : Cu^{2+} \) ratios of
\( 22 : 78 \) and \( 73 : 77 \) for high and low \( Cu^{2+} \) solution concentra-
tions, respectively (Fig. 3C and S6†). These ratios are only esti-
mates as they assume that the \( Cu^+ \) and \( Cu^{2+} \) environments in

Fig. 2 SCXRD structures of (A) \((PEA)_4CuInCl_8\); (B) \((PCA)_4[Cu^{III}(Cu^{III})_{0.5}Cl_8]\) (1\text{PCA}), and (C) \((PCA)_2CuCl_4\) (ref. 36) at 300 K with insets showing the
local coordination environments of the B sites in each structure and the antiferrodistortive arrangement of the elongated axes of the \( Cu^{2+} \)
octahedra in \((PCA)_2CuCl_4\) (C). Turquoise, red, yellow, green, gray, and blue spheres represent \( Cu^+, In^{3+}, Cu^{2+}, Cl, C, \) and \( N \) atoms, respectively.
Black spheres represent mixed \( Cu/In \) sites. H and disordered atoms are omitted for clarity.
1BA are identical to those in the Cu\(^+\) and Cu\(^{2+}\) standards. Notably, these results indicate relatively little flexibility in the Cu\(^+\) : Cu\(^{2+}\) ratio of 1BA despite the widely ranging precursor ratios employed in the different syntheses.

2.3.3. Elemental analysis of 1BA. To accurately measure the Cu : In ratio of 1BA, we used inductively coupled plasma mass spectrometry (ICP-MS). We measured the same samples made with high and low Cu\(^{2+}\) concentrations used for XAS, finding Cu : In weight % ratios of 1.73 and 1.59, respectively (Table S4†). Assuming that all Cu\(^+\) B-site cations are charge compensated by In\(^{3+}\) B-site cations, these ratios yield extremely similar formulas of (BA)\(_4\)(Cu\(^{II}\))\(_{1.04}\)(Cu\(^{III}\))\(_{0.48}\)Cl\(_8\) and (BA)\(_4\)(Cu\(^{II}\))\(_{1.09}\)(Cu\(^{III}\))\(_{0.51}\)Cl\(_8\), respectively (see ESI†). Formulas extracted from our SCXRD and XAS data (see ESI†) are consistent with these results, though the ICP-MS formulas are the most reliable given the greater accuracy of this method for such analyses.

Importantly, both our XAS and ICP-MS data indicate little variability in the B-site composition of 1BA and we propose the approximate formula of (BA)\(_4\)(Cu\(^{II}\))(Cu\(^{III}\))\(_{0.5}\)Cl\(_8\). In addition, EPR spin quantification (Section 2.3.2) and magnetic susceptibility measurements (Section 2.6.3) provide two independent estimates of the amount of Cu\(^{2+}\) in 1BA, both of which agree with this empirical formula. This validates our assumption that charge balance of the perovskite lattice is maintained by incorporating equal amounts of In\(^{3+}\) and Cu\(^+\) at the B sites. Furthermore, C, H, and N analyses of 1BA agree well with our proposed formula (see ESI†). Therefore, our analysis indicates that, in terms of composition, 1BA is a 50 : 50 mixture of a Cu\(^{II}\) single perovskite and a Cu\(^{2+}\)-In\(^{3+}\) double perovskite.

2.4. Structure of 1

2.4.1. SCXRD analysis of 1PCA. Crystallizing 1 with p-chloroanilinium (PCA) rather than BA also affords black plate-like crystals (1PCA), which provided much-higher-quality SCXRD data than 1BA (Table S2†). The structure of 1PCA is analogous to that of 1BA, with \(n = 1\) perovskite sheets partitioned by bilayers of PCA cations (Fig. 2B). At 300 K, the asymmetric unit contains only one unique B site, which is best modeled as a disordered mixture of Cu and In cations (17% In, 83% Cu) and shows two short axial B–Cl\(_{eq}\) bonds (2.2790(1) Å) and four long B–Cl\(_{ax}\) equatorial bonds (2.6600(1) Å, 2.6593(1) Å; Fig. 2B, inset). Upon cooling to 100 K, the material undergoes a phase transition from \(P2_1/c\) to \(Pcn2_1\), but the essential features of the structure remain unchanged: we find one unique B site (best modeled as 22% In, 78% Cu) with a similar coordination geometry (Fig. S7†).

Further characterization of 1PCA using the techniques employed above for 1BA was hindered by its instability in solution (similar to the case of 1PEA, see ESI†). Nevertheless, our structural data for 1PCA are fully consistent with the presence of both Cu and In cations at the B sites, and the Cu : In ratio of 78 : 22 (100 K structure) is in good agreement with our ICP-MS data for 1BA.

We can glean further insights into the black phase from the SCXRD structure of 1PCA. At both 300 and 100 K, the structure of 1PCA has only one unique B site, indicating that the Cu\(^{2+}\) cations disrupt the checkerboard-like ordering of Cu\(^+\) and In\(^{3+}\) cations found in the double-perovskite endmember. As seen in the SCXRD structures of the Cu\(^{II}\) and Cu\(^{2+}\)-In\(^{3+}\) endmember perovskites, these three B-site cations exhibit very different coordination environments. The Cu\(^+\) cations of (PEA)\(_4\)CuInCl\(_8\) adopt a linear [2 + 4] coordination, with two short axial bonds and four long equatorial bonds (Fig. 2A).\(^{38}\) Meanwhile, the elongated axis of the Jahn–Teller distorted Cu\(^{2+}\) cations of (PCA)\(_4\)CuCl\(_4\) (ref. 36) (and other Cu\(^{II}\) perovskites)\(^{39}\) lies in the plane of the 2D perovskite sheets with the long axes of adjacent [CuCl\(_4\)]\(^{2-}\) units positioned orthogonally to one another (an anti-ferrodistortive arrangement; Fig. 2C). In contrast, the In\(^{3+}\) cations of (PEA)\(_4\)CuInCl\(_8\) (ref. 30) (and other known \(n = 1\) perovskite structures)\(^{38,39}\) display relatively little deviation from octahedral coordination, with similar axial and equatorial bond lengths (Fig. 2A). Disordering of Cu\(^+\), Cu\(^{2+}\), and In\(^{3+}\) is expected
to yield a B-site coordination environment that is an average of the three very different coordination spheres of these cations, with two axial B–Cl\textsubscript{ax} bonds that are substantially shorter than the four equatorial B–Cl\textsubscript{eq} bonds. This is, in fact, what we observe in both the 300 and 100 K SCXRD structures of \textit{1}\textsubscript{PCA}. Also consistent with this picture, we find that the thermal ellipsoids of the equatorial Cl atoms are elongated along the directions of B–Cl–B connectivity (Fig. 2B, inset and Fig. S7\textsuperscript{†}) due to the presence of both very long (Cu\textsuperscript{II}–Cl\textsubscript{eq} = 2.9041(7) \text\AA for (PCA)$_2$CuCl\textsubscript{4} at 300 K, Cu\textsuperscript{I}–Cl\textsubscript{eq} = 3.0340(2) \text\AA for (PEA)$_4$CuInCl\textsubscript{8} at 300 K) and very short (Cu\textsuperscript{II}–Cl\textsubscript{eq} = 2.3067(6) \text\AA for (PCA)$_2$CuCl\textsubscript{4} at 300 K) B–Cl\textsubscript{eq} bond lengths. The thermal ellipsoids of the axial Cl atoms are less elongated, as expected based on the smaller variation in B–Cl\textsubscript{ax} bond lengths between the Cu\textsuperscript{+}, Cu\textsuperscript{2+}, and In\textsuperscript{3+} coordination spheres of the Cu\textsuperscript{I}–In\textsuperscript{III} and Cu\textsuperscript{II} end-member perovskites (Cu\textsuperscript{I}–Cl\textsubscript{ax} = 2.1779(1) \text\AA, Cu\textsuperscript{II}–Cl\textsubscript{ax} = 2.2674(7) \text\AA, In\textsuperscript{III}–Cl\textsubscript{ax} = 2.5483(1) \text\AA at 300 K). Although we performed this in-depth structural analysis for \textit{1}\textsubscript{PCA} rather than for \textit{1}\textsubscript{BA} due to the higher-quality SCXRD data obtained for the former, it is important to note that the structural parameters obtained from the SCXRD structure of \textit{1}\textsubscript{BA} are extremely similar (see ESI\textsuperscript{†}), and thus, the above analysis can be extended to the case of \textit{1}\textsubscript{BA}.

### 2.5. Impact of tiling three coordination spheres on the composition of 1

It is interesting to consider how the very differently shaped Cu\textsuperscript{+}, Cu\textsuperscript{2+}, and In\textsuperscript{3+} coordination spheres (Fig. 4A) can be arranged into an n perovskite lattice. The metal-halide octahedra pack efficiently in (PEA)$_4$CuInCl\textsubscript{8} and (PCA)$_2$CuCl\textsubscript{4}, with the large [Cu\textsuperscript{II}Cl\textsubscript{6}]\textsuperscript{3−} and small [In\textsuperscript{III}Cl\textsubscript{6}]\textsuperscript{3−} units adopting an alternating checkerboard pattern in the former and the elongated [Cu\textsuperscript{I}Cl\textsubscript{6}]\textsuperscript{4−} units forming an antiferrodistortive arrangement in the latter. However, mixing these three units in a single 2D lattice disturbs both of these well-defined arrangements. The elongated [Cu\textsuperscript{I}Cl\textsubscript{6}]\textsuperscript{4−} units do not fit the Cu\textsuperscript{I}–In\textsuperscript{III} perovskite lattice, introducing large packing mismatch (Fig. 4B). Likewise, [Cu\textsuperscript{II}Cl\textsubscript{6}]\textsuperscript{3−} and [In\textsuperscript{III}Cl\textsubscript{6}]\textsuperscript{3−} units disturb the arrangement of Jahn–Teller distorted [Cu\textsuperscript{II}Cl\textsubscript{6}]\textsuperscript{3+} octahedra (Fig. 4C). However, a new efficiently packed arrangement can be generated from the cell outlined in Fig. 4D that contains one [In\textsuperscript{III}Cl\textsubscript{6}]\textsuperscript{3−}, one [Cu\textsuperscript{II}Cl\textsubscript{6}]\textsuperscript{3−}, and two [Cu\textsuperscript{II}Cl\textsubscript{6}]\textsuperscript{4−} units. This cell can be tessellated in two dimensions to generate an n = 1 perovskite lattice with no significant packing mismatch. Notably, the resulting lattice has a 1 : 2 : 1 ratio of Cu\textsuperscript{+} : Cu\textsuperscript{2+} : In\textsuperscript{3+} cations, matching the results of our ICP-MS data for \textit{1}\textsubscript{BA} (Section 2.3.3). Thus, we propose that the problem of packing the differently shaped Cu\textsuperscript{+}, Cu\textsuperscript{2+}, and In\textsuperscript{3+} coordination spheres into an n = 1 perovskite lattice explains the robust composition adopted by \textit{1}\textsubscript{BA}; a composition in which 50% of the B sites of the Cu\textsuperscript{I}–In\textsuperscript{III} perovskite are replaced by Cu\textsuperscript{2+} cations represents a sweet spot that enables the most efficient packing arrangement of the different coordination spheres. Deviations from this composition will introduce packing mismatch (see ESI and Fig. S8\textsuperscript{†}), which may explain the lack of compositional flexibility observed for \textit{1}\textsubscript{BA}.

Slight variations on the tessellation pattern illustrated in Fig. 4D are also possible, generating 2D lattices with different packing arrangements (Fig. S9\textsuperscript{†}). Some of these packing arrangements are expected to be similarly favorable (Fig. S9B and C) which may explain the B-site disordering of \textit{1}. It is also important to point out that \textit{1}, (PCA)$_2$CuCl\textsubscript{4}, and (PEA)$_4$CuInCl\textsubscript{8} all exhibit similar degrees of octahedral tilting, making it unlikely that large packing mismatches are present in \textit{1} as they would likely need to be compensated by severe octahedral tilting.

### 2.6. Emergent properties in 1

Our characterization of \textit{1}\textsubscript{BA} and \textit{1}\textsubscript{PCA} has shown that the composition and structure of these materials are well-described as an average of the Cu\textsuperscript{II} and Cu\textsuperscript{I}–In\textsuperscript{III} endmember perovskites. However, \textit{1} displays new optical, electronic, and magnetic properties not seen in the endmembers.

#### 2.6.1. Optical absorption

The optical absorption of \textit{1} presents a dramatic contrast to that of (BA)$_2$CuCl\textsubscript{4} and...
(PEA)$_4$CuInCl$_6$ and cannot be described as a simple average. Whereas (BA)$_2$CuCl$_4$ and (PEA)$_4$CuInCl$_6$ are translucent yellow and colorless, respectively, 1$_{BA}$ and 1$_{PCA}$ are black (Fig. 1). We used diffuse reflectance spectroscopy and thin-film transmission measurements to understand the optical behavior of these black perovskites (see ESI† for experimental details). Consistent with its black color, the diffuse reflectance spectrum of 1$_{BA}$ exhibits strong absorption across the entire visible region, displaying features centered at 2.0 eV (with a shoulder at 1.5 eV) and 3.3 eV (Fig. 5A). Similar to prior reports on 2D Cu$^{II}$ perovskites, the diffuse reflectance spectrum of (BA)$_2$CuCl$_4$ exhibits features centered at ca. 1.5 eV and 3.3 eV (Fig. 5A) attributed to d–d and ligand-to-metal charge transfer (LMCT) transitions, respectively. Overlaying the spectra of 1$_{BA}$ and (BA)$_2$CuCl$_4$ points out their obvious similarities: the peak at 1.5 eV in (BA)$_2$CuCl$_4$ coincides with the low-energy shoulder of the peak at 2 eV in 1$_{BA}$, and both materials display matching features at ca. 3.3 eV. The only significant difference is the broad feature in 1$_{BA}$ centered at 2 eV (Fig. 5A). Unlike the weak Laporte forbidden d–d transitions of Cu$^{II}$ perovskites, this feature is also clearly apparent in the thin-film transmission spectrum of 1$_{BA}$ (though it is shifted to somewhat higher energy, Fig. S10†), indicating that it arises due to a strong absorption event.

Materials containing the same element in multiple valence states that are in electronic contact often exhibit intense colors because electron transfer between the different ions results in strong optical absorption in the visible region. Thus, we propose that the feature at 2 eV in 1$_{BA}$ arises due to the presence of both Cu$^+$ and Cu$^{2+}$ cations in 1$_{BA}$ and assign it as a Cu$^+$ → Cu$^{2+}$ intercalation charge transfer (IVCT) transition. Intriguingly, this IVCT transition endows crystals of 1$_{BA}$ with clear dichroic effects. Under linearly polarized light, thick plate-like single crystals of 1$_{BA}$ appear black when viewed face-on but translucent red-orange when viewed in the proper side-on orientation (Fig. 5A, inset). This indicates that the 2 eV transition can only be excited by light polarized in the plane of the perovskite sheet and thus corresponds to an IVCT transition between Cu ions in the same layer.

According to the Robin and Day classification, 1$_{BA}$ is best described as a class II mixed-valence material. The spectral features of the component ions (most notably the d–d and LMCT transitions of the [CuCl$_4$]$^{3–}$ unit) are preserved in the mixed-valence material, while a new IVCT absorption appears in the visible region at a location close to that observed for similar class II mixed-valent Cu$^{2+/3+}$ materials. Assignment of 1$_{BA}$ as a class II species is consistent with our structural characterization, which suggests that Cu$^+$ and Cu$^{2+}$ cations retain distinct coordination environments (excluding assignment as a class III material) but are both six-fold coordinated making structural rearrangement of the coordination spheres relatively easy (unlike in a class I material). Thus, 1$_{BA}$ joins the small number of class II mixed-valence halide perovskites, including lattices with Au$^{1+/2+}$ and Sb$^{3+/5+}$.

### 2.6.2. Electronic conductivity

Mixed valency is well known to significantly alter the electronic properties of a material relative to single-valent counterparts. We therefore used potentiostatic electrochemical impedance spectroscopy (PEIS) to measure the electronic conductivity of large single crystals of 1$_{BA}$, (PEA)$_4$CuInCl$_6$, and (PA)$_4$CuCl$_4$ (PA = propylammonium) painted with carbon contacts as nonreactive, ion-blocking electrodes (Fig. S11†). Single crystals of (PEA)$_4$CuInCl$_6$ and (PA)$_4$CuCl$_4$ are highly insulating, and even under 1 V bias, these materials exhibited immeasurably low electronic conductivity (Fig. S12†). This is consistent with a prior report of extremely low (ca. $10^{-12}$ S cm$^{-1}$) ionic conductivity for crystals of (NH$_4$)(CH$_2$)$_2$NH$_3$CuCl$_4$ with silver contacts. In contrast, for three different single crystals of 1$_{BA}$, we measure an average electronic conductivity of ca. $8 \times 10^{-9}$ S cm$^{-1}$ at ambient temperature (see ESI†). This conductivity increases with gentle heating (Fig. 5B, Table S6†) as expected for a semiconductor. Arrhenius plots for these three crystals yield an activation energy ($E_a$) of ca. 600 meV (Fig. 5C, see ESI†), similar to the value obtained for a related mixed valence chlorocuprate material. Notably, this $E_a$ is close to one-quarter of the energy required for optical excitation ($E_{op}$) of the Cu$^+$ → Cu$^{2+}$ transition extracted from thin-film measurements (2.28 eV, $E_a/E_{op} = 0.26$, see ESI† for peak analysis and further details).

![Fig. 5](image-url) (A) Diffuse reflectance spectra of 1$_{BA}$ (black) and (BA)$_2$CuCl$_4$ (red) with insets showing the dichroism of a plate-like crystal of 1$_{BA}$ in side-on and face-on orientations under linearly polarized light. (B) Nyquist plots for a single crystal of 1$_{BA}$ measured at a range of temperatures demonstrating the increase in conductivity with temperature ($Z =$ electrochemical impedance). (C) Arrhenius relationship for the data plotted in B showing an activation energy ($E_a$) for electronic conductivity ($\sigma$) of ca. 600 meV.
Previously, Hush developed a theory relating the energy required for thermal electron transfer (corresponding to $E_a$) to the energy of a vertical Frank–Condon transition (corresponding to $E_{op}$) for a given IVCT transition. For a symmetric one-electron transfer where the initial and final states have the same energy, $E_a/E_{op}$ is exactly 1/4. Redox asymmetry is expected to yield a larger ratio, and is likely at play in 1BA. Overall, our data are in good agreement with the work of Hush, providing strong evidence that the enhanced conductivity of 1BA arises due to charge hopping between Cu\(^{+}\) and Cu\(^{2+}\) centers within the same perovskite sheet.

2.6.3. Magnetism. Square 2D lattices of magnetic ions with $S = 1/2$ have long been studied due to their potential to host exotic physics, and as a result, the magnetic properties of Cu\(^{II}\) halide perovskites have been heavily investigated over the years.\(^47^-48\) Similar to other 2D Cu\(^{II}\) perovskites, (BA)\(_2\)CuCl\(_4\) displays ferromagnetic (FM) ordering (consistent with Goodenough–Kanamori rules)\(^49^-51\) below an ordering temperature $T_C = 7.3$ K as well as severe anisotropy between the plane of the inorganic sheets and the axis perpendicular to the sheets, as is expected for these layered materials.\(^7^-46,48\) This FM ordering is driven by the dominance of in-plane exchange interactions (over antiferromagnetic exchange interactions between adjacent perovskite layers) and arises from the fact that the unpaired electrons of adjacent Cu\(^{2+}\) centers occupy orthogonal orbitals.\(^48\)

Perovskite 1 allows us to test the impact of magnetically diluting this Cu\(^{2+}\) square lattice, with nonmagnetic Cu\(^{+}\) and In\(^{3+}\), on the long-range FM order. Further, 1BA presents an intriguing system for study since the magnetic occupancy of the metal square lattice (approximately 50% Cu\(^{2+}\) at the B sites) is close to the percolation threshold of a 2D simple square lattice with four nearest neighbors (59.2%).\(^51,52\) At and above this value, enough magnetic ions should exist to support long-range magnetic order. While the overall stoichiometry of 1BA is below this threshold, if some areas of the square lattice have a high enough concentration of Cu\(^{2+}\) ions, local puddles of long-range order may arise.

Our measurements reveal weak interactions between local Cu\(^{2+}\) moments with no long-range order down to $T = 2$ K, as shown by the lack of a peak in plots of the low-temperature zero-field AC susceptibility (Fig. 6A, insets) and low-field DC susceptibility (Fig. 6A). A spin glass ground state, which may also be expected for dilute magnetic ions, is ruled out by the lack of splitting between the zero-field cooled and field cooled susceptibility data at low temperature (Fig. 6A), the lack of a peak in the variable-temperature AC susceptibility ($\chi'$ and $\chi''$; Fig. 6A, insets), and the frequency-independence of the AC susceptibility (Fig. S17†). High-temperature DC susceptibility measured in an applied field of $\mu_0H = 5$ T ($\mu_0$ = permeability of free space, $H$ = magnetic field strength) is shown in Fig. 6B. After subtraction of a large temperature-independent diamagnetic contribution (likely from BA cations, $\chi_0 = -0.00108$ emu mol\(^{-1}\)) a Curie–Weiss fit of the inverse susceptibility data from $T = 100$–300 K yields a Curie constant $C = 0.362(4)$ K emu mol\(^{-1}\) and a Weiss temperature $\Theta = 10.9(2)$ K. Note that these calculations assume a formula weight given by the formula of 1BA determined above ([BA]\(_4\)[Cu\(^{II}\)(Cu\(^{I}\)In\(^{III}\))\(_0.5\)Cl\(_8\)]. The slightly positive value of $\Theta$ may indicate that the weak interactions between moments, or the interactions in somewhat more concentrated puddles, are FM. Our fit results are in line with those reported for (BA)\(_2\)CuCl\(_4\), which has a higher value of $\Theta$ (18.3(3) K), consistent with its long-range FM order at $T_C = 7.3$ K.\(^47,52\) The effective moment ($\mu_{\text{eff}}$) of 1BA is 1.702(1) $\mu_B$ ($\mu_B$ = Bohr magneton), consistent with magnetically isolated Cu\(^{2+}\) moments, and the Landé g-factor is 1.965(1), consistent with the g-factors extracted from EPR measurements (Section 2.3.2). The overall paramagnetic behavior and the absence of magnetic long-range order are consistent with our ICP-MS analysis, which yields a Cu\(^{2+}\) content below the site percolation threshold. In addition, as noted in Section 2.3.3, our magnetic susceptibility measurements allow us to estimate the amount of Cu\(^{2+}\) in 1BA as 0.97 mol Cu\(^{2+}\) per formula unit (see ESI†), in agreement with the values obtained from ICP-MS (Section 2.3.3) and EPR data (Section 2.3.2).

These findings present an interesting contrast with a report of an $n = 1$ Zn\(^{II}\) fluoride perovskite where 40% of the B sites are replaced with Cu\(^{2+}\). Here, the Cu\(^{2+}\) content is well below the site percolation threshold and also lower than that of 1BA yet EPR
data provide evidence for long-range magnetic order at 4.2 K.\textsuperscript{35} This suggests that Cu\textsuperscript{2+} cations may form clusters within the Zn\textsuperscript{2+} lattice, leading to the stronger magnetic interactions. The absence of long-range order in 1\textsubscript{BA} despite the higher Cu\textsuperscript{2+} content suggests that here, Cu\textsuperscript{2+} cluster formation may be disfavored. This further validates our proposed packing scheme discussed in Section 2.5 and the ESI,\textsuperscript{†} which shows that arrangements containing adjacent Cu\textsuperscript{2+} generally have larger packing mismatch (Fig. S9D and F†), potentially disfavoring formation of Cu\textsuperscript{2+} clusters.

3. Conclusion

We report the new layered perovskite (A)\textsubscript{4}[Cu\textsuperscript{II}(Cu\textsuperscript{I}In\textsuperscript{III})\textsubscript{0.5}Cl\textsubscript{8}] (1, A = BA, PCA, PEA), which contains a 1 : 2 : 1 mixture of Cu\textsuperscript{+}, Cu\textsuperscript{2+}, and In\textsuperscript{3+} cations at the B sites. The composition and structure of 1 are well-described as an average of a Cu\textsuperscript{II} single perovskite and a Cu\textsuperscript{II}–In\textsuperscript{III} double perovskite. Simple packing arguments suggest that this specific composition is enforced by the differently shaped Cu\textsuperscript{+}, Cu\textsuperscript{2+}, and In\textsuperscript{3+} coordination spheres that must pack efficiently into an n = 1 perovskite lattice. Magnetic studies of 1\textsubscript{BA} demonstrate the loss of long-range ferromagnetic order observed in the Cu\textsuperscript{II} perovskite, corroborating our proposed packing model, which disfavors segregated domains of Cu\textsuperscript{II} in the lattice of 1.

The presence of mixed-valent Cu in 1 affords new properties not seen in the endmember lattices. In particular, 1 is black, displaying strong optical absorption across the visible region, which is highly unusual for an n = 1 chloride perovskite. We further measure a large increase in conductivity between 1\textsubscript{BA} and its Cu\textsuperscript{II} and Cu\textsuperscript{II}–In\textsuperscript{III} endmembers. Thus, allowing two different 2D perovskites affords a new perovskite with properties not seen in either endmember.

The novel optoelectronic properties of 1 evidence the significant advantages of incorporating B-site cations with a range of valence states into the perovskite structure and set forth the tantalizing possibility of using this strategy to access exotic physical properties, similar to the discovery of high-temperature superconductivity in analogous electron-doped copper-oxide perovskites. We expect that the simple tiling arguments made here, based on using a mixture of long and short metal-halide bond lengths to construct the 2D footprint of the inorganic sheets, may be extended to other compositions to incorporate multiple metal ions in the perovskite lattice. Thus, increasing the complexity of the inorganic sheets, beyond the simple rock-salt ordering of most double perovskites,\textsuperscript{1} promises to enhance the optoelectronic diversity of halide perovskites with emergent properties arising from new electronic transitions.

Author contributions

B. A. C. performed all experimental work and analysis, except as noted below. J. L. synthesized materials for elemental analysis and EPR studies. B. A. C. and J. L. were advised by H. I. K. R. S. conducted the magnetic susceptibility measurements and data analysis, advised by Y. S. L. A. J. H. conducted EPR spin quantification studies. A. G.-P. conducted the XAS measurements and data analysis, advised by M. F. T. The project was conceived by B. A. C. with guidance from H. I. K.; they wrote the manuscript with contributions from all authors.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1. N. R. Wolf, B. A. Connor, A. H. Slavney and H. I. Karunadasa, Angew. Chem., Int. Ed., 2021, 60, 2–17.
2. A. H. Slavney, T. Hu, A. M. Lindenberg and H. I. Karunadasa, J. Am. Chem. Soc., 2016, 138, 2138–2141.
3. E. T. McClure, M. R. Ball, W. Windl and P. M. Woodward, Chem. Mater., 2016, 28, 1348–1354.
4. G. Engel, Naturwissenschaften, 1933, 21, 704.
5. A. H. Slavney, L. Leppert, D. Bartesaghi, A. Gold-Parker, M. F. Toney, T. J. Savenije, J. B. Neaton and H. I. Karunadasa, J. Am. Chem. Soc., 2017, 139, 5015–5018.
6. J. Luo, X. Wang, S. Li, J. Liu, Y. Guo, G. Niu, L. Yao, Y. Fu, L. Gao, Q. Dong, C. Zhao, M. Leng, F. Ma, W. Liang, L. Wang, S. Jin, J. Han, L. Zhang, J. Etheridge, J. Wang, Y. Yan, E. H. Sargent and J. Tang, Nature, 2018, 563, 541–545.
7. K. P. Lindquist, S. A. Mack, A. H. Slavney, L. Leppert, A. Gold-Parker, J. F. Stebbins, A. Salleo, M. F. Toney, J. B. Neaton and H. I. Karunadasa, Chem. Sci., 2019, 10, 10620–10628.
8. A. H. Slavney, L. Leppert, A. Saldivar Valdes, D. Bartesaghi, T. J. Savenije, J. B. Neaton and H. I. Karunadasa, Angew. Chem., Int. Ed., 2018, 57, 12765–12770.
9. A. E. Maughan, A. M. Ganose, M. M. Bordelon, E. M. Miller, D. O. Scanlon and J. R. Neilson, J. Am. Chem. Soc., 2016, 138, 8453–8464.
10. T. T. Tran, J. R. Panella, J. R. Chamorro, J. R. Morey and T. M. McQueen, Mater. Horiz., 2017, 4, 688–693.
