Structural features in some layered hybrid copper chloride perovskites, ACuCl₄ or A₂CuCl₄

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Abstract
We present three new hybrid copper(II) chloride layered perovskites of generic composition ACuCl₄ or A₂CuCl₄, which exhibit three distinct structure types. (m-PdH₂)CuCl₄ (m-PdH₂²⁺ = protonated m-phenylenediamine) adopts a Dion–Jacobson (DJ-like) layered perovskite structure type and exhibits a very large axial thermal contraction effect upon heating, as revealed via variable-temperature synchrotron X-ray powder diffraction (SXRD). This can be attributed to the contraction of inter-layer block, via a slight repositioning of the m-PdH₂²⁺ moiety. (3-AbaH)₂CuCl₄ (3-AbaH⁺ = protonated 3-aminobenzoic acid) and (4-AbaH)₂CuCl₄ (4-AbaH⁺ = protonated 4-aminobenzoic acid) possess the same generic formula as Ruddlesden–Popper (RP) layered perovskites, A₂BX₄, but adopt different structures. (4-AbaH)₂CuCl₄ adopts a near-staggered structure type, whereas (3-AbaH)₂CuCl₄ adopts a near-eclipsed structure type, which resembles the DJ rather than the RP family. (3-AbaH)₂CuCl₄ also displays static disorder of the [CuCl₄]ₙ layers. The crystal structures of each are discussed in terms of the differing nature of the templating molecular species, and these are compared to related layered perovskites. Preliminary magnetic measurements are reported, suggesting dominant ferromagnetic interactions.

Introduction
In recent years organic-inorganic hybrid halide perovskites have attracted a great deal of attention, since they have already shown versatile chemical and physical properties.¹⁻³ Cu-based perovskites are particularly interesting because of their enhanced structural flexibility and magnetic properties; a consequence of the Jahn-Teller (J-T) distortion of the 3d⁹ ion
The Cu-based systems also offer the natural advantages of low toxicity, compared to Pb- or Cd-based perovskites, and greater stability to light and humidity, compared to Sn- or Bi-based perovskites. Among the well-known families of two-dimensional layered perovskites, the two generic families are conventionally referred to as Dion–Jacobson (DJ) and Ruddlestone–Popper (RP) phases, having stoichiometries ABX₃ and A₂BX₄, respectively for examples with single octahedral layers. These can be regarded as structural derivatives from the cubic perovskite ABX₃, obtained by ‘slicing’ through vertices of the BX₆ octahedra and inserting additional species between these layers. However, more detailed crystallographic analysis of the lead halide family of layered perovskites has recently shown that these idealised definitions, based on earlier work on inorganic-only perovskites, are no longer entirely suitable for hybrid layered perovskites as the shifts of adjacent perovskite-like layers are not fixed at ‘fully eclipsed’ (DJ-like) nor ‘fully staggered’ (RP-like) in these materials.

Two-dimensional layered copper (II) halide perovskites with the general formula (RNH₃)₂CuX₄ and (NH₃RNH₂)CuX₄ (X = Cl⁻ or Br⁻) contain layers of corner-shared CuX₆ octahedra, separated by the protonated (RNH₃)⁺ or (NH₃RNH₂)²⁺ cations. The J-T distortion produced by the Cu 3d⁹ electronic configuration causes the distortion of the CuX₆ octahedron, leading to an elongation of two Cu-X bonds within the plane of the inorganic sheets. The short in-plane Cu-X bond distance is relatively invariant within this family of compounds, whereas the elongated Cu-X bond distance is significantly flexible, varying from 2.8 Å to, in extremis, 4.6 Å. Such flexibility facilitates the incorporation of a wide variety of organic ammonium cations into these two-dimensional structures. These kinds of properties also make Cu-based halide perovskites sensitive to pressure and temperature. Pressure-induced changes in electronic, magnetic, and optical properties of Cu-based halide perovskites have been studied intensively, not only providing intriguing properties but also permitting insights into their structure-property relationships.

In this paper, we present three new hybrid layered copper(II) chloride perovskites (m-PdH₂)CuCl₄ (m-PdH₂²⁺ = protonated m-phenylenediamine), (3-AbaH)₂CuCl₄ (3-AbaH⁺ = protonated 3-aminobenzoic acid) and (4-AbaH)₂CuCl₄ (4-AbaH⁺ = protonated 4-aminobenzoic acid). Interestingly, (m-PdH₂)CuCl₄ exhibits a very large axial thermal contraction effect. (3-AbaH)₂CuCl₄ and (4-AbaH)₂CuCl₄ possess the same generic formula as RP phases, A₂BX₄, but adopt different structure types: (4-AbaH)₂CuCl₄ adopts a near-staggered structure type, whereas (3-AbaH)₂CuCl₄ adopts a near-eclipsed structure type, which resembles the DJ rather than the RP family. The crystal structures of each are discussed in terms of the differing nature...
of the templating molecular species. Preliminary magnetic measurements are carried out, and structural comparisons to related layered perovskites are made.

Experimental Section

Synthesis

Copper (II) chloride, anhydrous (CuCl₂, 98%), m-phenylenediamine (C₆H₈N₂, 98%), 3-aminobenzoic acid (C₇H₇NO₂, 98%), 4-aminobenzoic acid (C₇H₇NO₂, 99%) and hydrochloric acid (HCl, 36%, w/w aqueous solution) were purchased from Alfa Aesar, UK. Ethanol (CH₃CH₂OH, ≥99%) was purchased from Fisher Chemical, UK. All chemicals were directly used without further purification.

The title compounds, (m-PdH₂)CuCl₄, (3-AbaH)₂CuCl₄ and (4-AbaH)₂CuCl₄, were crystallized by a slow evaporation method. In each case, sample purity was confirmed by X-ray powder diffraction and elemental analysis.

(m-PdH₂)CuCl₄ (C₆H₁₀N₂CuCl₄), CuCl₂ (134.45 mg, 1 mmol) was dissolved in concentrated HCl (5 mL) with moderate heating until the solution turned clear bright green. Then m-phenylenediamine (108.14 mg, 1 mmol) and ethanol (5 mL) were added and stirred for 5 minutes. After cooling the solvent for a few hours, green, block-shaped crystals were obtained. Elemental analysis calculated (%) for (m-PdH₂)CuCl₄: C, 22.84; H, 3.19; N, 8.88. Found: C, 22.93; H, 3.08; N, 8.90.

(3-AbaH)₂CuCl₄ (C₁₄H₁₆N₂O₄CuCl₄), CuCl₂ (134.45 mg, 1 mmol) was dissolved in concentrated HCl (5 mL) with moderate heating until the solution turned clear bright green. Then 3-aminobenzoic acid (274.28 mg, 2 mmol) and ethanol (5 mL) were added and stirred for 5 minutes. After cooling the solvent for a few hours, yellow, plate-shaped crystals were obtained. Elemental analysis calculated (%) for (3-AbaH)₂CuCl₄: C, 34.91; H, 3.35; N, 5.82. Found: C, 35.01; H, 3.40; N, 5.86.

(4-AbaH)₂CuCl₄ (C₁₄H₁₆N₂O₄CuCl₄), CuCl₂ (134.45 mg, 1 mmol) was dissolved in concentrated HCl (10 mL) with moderate heating until the solution turned clear bright green. Then 4-aminobenzoic acid (274.28 mg, 2 mmol) and ethanol (10 mL) were added and stirred for 10 minutes. After cooling the solvent for a few hours, green, block-shaped crystals were obtained.
obtained. Elemental analysis calculated (%) for (4-AbaH)$_2$CuCl$_4$: C, 34.91; H, 3.35; N, 5.82. Found: C, 34.99; H, 3.42; N, 5.78).

Characterization

**Single crystal X-ray diffraction**

Single crystal X-ray diffraction data were collected on a Rigaku XtaLAB P200 diffractometer at 93 K and on a Rigaku SCX Mini diffractometer at 173 K and 298 K using Mo-Kα radiation. The data were processed by Rigaku CrystalClear software.$^{26}$ Structures were solved and refined by structure solution program SHELXT$^{27}$ incorporated in the WINGX program.$^{28}$ Absorption corrections were conducted empirically from equivalent reflections according to multi-scans by using CrystalClear.$^{26}$ All the hydrogen atoms were treated as riding atoms and all non-H atoms were refined anisotropically.

**Powder X-ray diffraction**

Preliminary X-ray diffraction data were collected on a PANalytical EMPYREAN diffractometer using Cu Kα1 ($\lambda = 1.5406$ Å) radiation in the range of 3 to 70°.

High-resolution synchrotron X-ray powder diffraction (SXRD) data of (m-PdH$_2$)CuCl$_4$ were collected at Beamline I11 Diamond Light Source, UK, using the Cryostream Plus (92 – 300 K). The X-ray wavelength was chosen as 1.0008(1) Å. All SXRD data were analyzed by the Rietveld method, using the GSAS/EXPGUI package.$^{29,30}$ Refinement strategies remained consistent at each temperature, with twelve background coefficients, four profile parameters, lattice parameters, atomic positional coordinates and isotropic atomic displacement parameters for all non-H atoms. Symmetry mode analysis, for both single crystal and powder crystallography, was carried out via the on-line tool ISODISTORT.$^{31}$

**Thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC)**

TGA data were collected on a STA-780 instrument at a heating rate of 10 K min$^{-1}$ under air flowing. A NETZSCH DSC 204 instrument was used to collect DSC data between 293 K and 93 K at a ramp rate of 5 K min$^{-1}$ under a N$_2$ flow.

**Magnetic measurements**

The magnetic measurements were made using a Quantum Design (MPMS XL) SQUID magnetometer. Data were collected by cooling a known mass of powdered material in an
applied magnetic field of 1000 Oe or 100 Oe between room temperature (~300 K) and 2 K. Measurements as a function of field were also performed at fixed temperatures of 200K and 2K in fields up to 20000 Oe.

**EPR measurements**

EPR (electron paramagnetic resonance spectra were collected on a Bruker EMX 10/12 continuous wave X-band (~9.5 GHz) EPR spectrometer. Low temperature measurements were performed at 120 K with the ER4141 VTM Nitrogen VT cryostat using N₂ as cooling agent.

All spectra were obtained using 0.2 mW microwave power, 0.3 mT modulation amplitude, 40.96 ms time constant, 41.67 ms conversion time, 100 kHz modulation frequency, and 130 mT field sweep centred at 315 mT with 1300 points resolution. Spectra were phase corrected to minimize the amplitude of the imaginary part and subsequently baseline corrected by a 1st order polynomial baseline.

**Results and Discussion**

**Crystal Structures**

The single crystal X-ray structures suggest no phase transitions in the regime 173 < T < 298 K, so the crystallographic details will be discussed based on the structures at 298 K. Details of the structures at 173 K are provided in ESI. Crystallographic parameters for all three compounds at 298 K are given in Table 1 and selected geometrical parameters in Table 2.

**Table 1.** Crystal and structure refinement data at 298 K.

<table>
<thead>
<tr>
<th></th>
<th>(m-PdH₂)CuCl₄</th>
<th>(3-AbaH)₂CuCl₄</th>
<th>(4-AbaH)₂CuCl₄</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>formula</strong></td>
<td>C₆H₁₀N₂CuCl₄</td>
<td>C₁₄H₁₆N₂O₄CuCl₄</td>
<td>C₁₄H₁₆N₂O₄CuCl₄</td>
</tr>
<tr>
<td><strong>formula weight</strong></td>
<td>315.52</td>
<td>481.63</td>
<td>481.63</td>
</tr>
<tr>
<td><strong>colour/habit</strong></td>
<td>Green/Block</td>
<td>Yellow/Plate</td>
<td>Green/Block</td>
</tr>
<tr>
<td><strong>crystal size (mm³)</strong></td>
<td>0.14 × 0.13 × 0.05</td>
<td>0.10 × 0.07 × 0.05</td>
<td>0.24 × 0.10 × 0.05</td>
</tr>
<tr>
<td><strong>crystal system</strong></td>
<td>orthorhombic</td>
<td>Triclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td><strong>space group</strong></td>
<td>Pnma</td>
<td>P-1</td>
<td>C2/c</td>
</tr>
<tr>
<td><strong>a (Å)</strong></td>
<td>6.8892(5)</td>
<td>5.2296(3)</td>
<td>37.6820(3)</td>
</tr>
<tr>
<td><strong>b (Å)</strong></td>
<td>18.8508(16)</td>
<td>5.2718(3)</td>
<td>8.0715(5)</td>
</tr>
<tr>
<td><strong>c (Å)</strong></td>
<td>8.4604(7)</td>
<td>16.7894(11)</td>
<td>6.8255(5)</td>
</tr>
<tr>
<td><strong>α (deg)</strong></td>
<td>90</td>
<td>83.5960(10)</td>
<td>90</td>
</tr>
<tr>
<td><strong>β (deg)</strong></td>
<td>90</td>
<td>83.2490(10)</td>
<td>92.3730(10)</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>80.848(5)</td>
<td>90</td>
</tr>
<tr>
<td>--------</td>
<td>-------</td>
<td>------------</td>
<td>-------</td>
</tr>
<tr>
<td>$\gamma$ (deg)</td>
<td>90</td>
<td>80.848(5)</td>
<td>90</td>
</tr>
<tr>
<td>$V$ ($\text{Å}^3$)</td>
<td>1098.73(15)</td>
<td>451.77(5)</td>
<td>2074.2(2)</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>$\rho_{\text{calc}}$ (g/cm$^3$)</td>
<td>1.907</td>
<td>1.770</td>
<td>1.542</td>
</tr>
<tr>
<td>$\mu$ (mm$^{-1}$)</td>
<td>2.915</td>
<td>1.822</td>
<td>1.588</td>
</tr>
<tr>
<td>$F(000)$</td>
<td>628</td>
<td>243</td>
<td>972</td>
</tr>
</tbody>
</table>

| No. of reflns collected | 7648 | 3298 | 7766 |
| independent reflns     | 995  | 1581 | 1828 |

| goodness of fit | $[R(\text{int}) = 0.0605]$ | $[R(\text{int}) = 0.0255]$ | $[R(\text{int}) = 0.0842]$ |
| final $R$ indices ($I > 2\sigma(I)$) | $R_1 = 0.0312$ | $R_1 = 0.0286$ | $R_1 = 0.0391$ |
| $wR_2 = 0.0684$ | $wR_2 = 0.0645$ | $wR_2 = 0.0728$ |

| largest diff. peak/hole (e Å$^{-3}$) | 0.354/-0.382 | 0.223/-0.239 | 0.329/-0.312 |

### Table 2. Cu-Cl bond lengths and Cu-Cl-Cu bond angles for the three structures at 298 K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(m-PdH$_2$)CuCl$_4$</th>
<th>(3-AbaH)$_2$CuCl$_4$</th>
<th>(4-AbaH)$_2$CuCl$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_S$ (Å)</td>
<td>2.274</td>
<td>2.288</td>
<td>2.282</td>
</tr>
<tr>
<td>$R_L$ (Å)</td>
<td>3.275</td>
<td>3.130</td>
<td>3.089</td>
</tr>
<tr>
<td>$R_Z$ (Å)</td>
<td>2.293</td>
<td>2.285</td>
<td>2.284</td>
</tr>
<tr>
<td>$\frac{2}{\sqrt{3}}[R_L-(R_S+R_Z)/2]$ (Å$^2$)</td>
<td>1.145</td>
<td>0.974</td>
<td>0.931</td>
</tr>
<tr>
<td>Cu-Cl-Cu (deg)</td>
<td>155.3</td>
<td>151.1</td>
<td>159.3</td>
</tr>
</tbody>
</table>

(m-PdH$_2$)CuCl$_4$

(m-PdH$_2$)CuCl$_4$ crystallizes in a DJ-like structure type (Figure 1), with expanded unit cell metrics, $a \sim \sqrt{2} a_P$, $b \sim 2 c_P$, $c \sim \sqrt{2} a_P$, relative to the parent DJ structure (tetragonal, $P4/mmm$, with unit cell metrics $a_P$, $c_P$). This structure is composed of two-dimensional perovskite-like [CuCl$_4$]$\propto$ layers of corner-shared CuCl$_6$ octahedra separated along the $b$-axis by the protonated m-PdH$_2^{2+}$ cation, with adjacent octahedral layers stacking in perfectly ‘eclipsed’ conformation. The CuCl$_6$ octahedra are distorted because of the J-T effect, with two short bridging in-plane Cu–Cl bonds (2.2743(10) Å), two short terminal out-of-plane Cu–Cl bonds (2.2926(10) Å) and two significantly elongated in-plane Cu–Cl bonds (3.2748(11) Å). Distortions of this type are typical of the wider family of layer copper (II) halide perovskites,$^{32-34}$ the J-T effect acts within the [CuCl$_4$]$\propto$ layers, with the shorter in-plane bond designated $R_S$, the longer one $R_L$ and the out-of-plane bond $R_Z$ (Table 2). A useful measure of the octahedral distortion is the ‘tetragonal normal coordinate’, defined in reference 23. The protonated m-PdH$_2^{2+}$ cation binds adjacent [CuCl$_4$]$\propto$ layers together through formation of N–H---Cl hydrogen bonds. The single-crystal
X-ray structures suggest no phase transitions in the regime $173 < T < 298$ K, with only slight expansion in the $a$ and $c$ parameters and an obvious contraction in the $b$ parameter between the two temperatures (unit cell at $173$ K; $a = 6.8183(5)$ Å, $b = 18.9376(14)$ Å, $c = 8.4294(5)$ Å). For the discussion of the variable temperature crystallographic data below, it is helpful to describe the key structural distortions in the language of symmetry mode analysis. There are three key distortion modes here, designated $M_2^+$ (a rigid rotation of octahedra around the $b$-axis), $A_5^+$ (an out-of-phase tilt of the octahedra out of the $ac$ plane, around the $a$-axis) and $M_3^+$ (the J-T distortion). Note that the designation of these modes depends on the choice of unit cell origin: here we set Cu at $(\frac{1}{2}, \frac{1}{2}, 0)$ in a $K_2NiF_4$-like parent unit cell, space group $I4/mmm$.

It is worth noting that the $A_5^+$ mode acts to tilt corresponding octahedra in adjacent layers in opposite senses, thus leading to a doubling of the $b$-axis relative to the ideal DJ parent structure. In terms of Glazer-like notation, the resulting tilt system can be described as $a'a'c/-(a'a')c$. This combination of octahedral tilts naturally gives rise to the observed unit cell metrics and space group, whilst also accommodating the option of a Jahn-Teller distortion; the same structure type has been seen in (Morph)$_2$CuCl$_4$, (NH$_3$C$_3$H$_6$NH$_3$)CuCl$_4$ and [(NH$_3$CH$_2$CH$_3$)$_2$NH$_2$Cl]CuCl$_4$. This structure can be compared with the already known structure $(p$-PdH$_2$)$_2$CuCl$_4$ ([p-PdH$_2$]$^{2+}$ = protonated p-phenylenediamine), containing an isomeric cation. The latter structure crystallizes in the monoclinic space group $P2_1/c$, and has unit cell metrics at $293$ K, $a = 10.007(2)$ Å, $b = 7.5094(15)$ Å, $c = 7.1365(14)$ Å, $\beta = 93.32(3)\degree$. It also consists of two-dimensional perovskite-like [CuCl$_4$]$_n$ layers of corner-shared CuCl$_6$ octahedra, but there are significant differences between the two structures. First, the elongated in-plane Cu-Cl bond distance, $R_1$, is $2.9310(6)$ Å, somewhat shorter than that in $(m$-PdH$_2$)$_2$CuCl$_4$. Moreover, it can be noted that the unit cell axis perpendicular to the layers is not doubled in this case. There are still ‘rotation’ and ‘tilt’ modes present, but the out-of-plane tilt mode in this case tilts octahedra in adjacent layers in the same (rather than opposite) senses (Figure 1(c)). The corresponding Glazer-like notation is $a'a'c$. Such a phenomenon has been previously observed in single-layered perovskites of the type $H_3N(CH_2)_nNH_3BCl_4$, where the $n = \text{odd parity}$ typically have a doubled $c$-axis and the $n = \text{even parity}$ examples do not, which was ascribed to the naturally distinct H-bonding opportunities for these types of diamines. A similar effect is observed here, if one regards the m-PdH$_2$ isomer as ‘odd’ and the p-PdH$_2$ isomer as ‘even’ based on the number of C atoms between the amine groups. As far as we are aware this is the first observation of such a parity-induced tilting effect in the case of cyclic diamines.
significant difference lies in the relative disposition of adjacent $[\text{CuCl}_4]^{\infty}$ layers which, in this case, show a slight offset (Figure 1(d)), described by the deviation of $\beta$ from 90°.

![Figure 1](image)

**Figure 1.** Crystal structure of (m-PdH$_2$)CuCl$_4$ at 298 K (a) parallel to the layer direction and (b) perpendicular to the layers; crystal structure of (p-PdH$_2$)CuCl$_4$ at 293 K (c) parallel to the layer direction and (d) plan view of the almost eclipsed adjacent layers.

The Rietveld refinement fits at 92 and 300 K are shown in Figure 2(a) and (b), which support the absence of a phase transition and similar quality of fit throughout this temperature regime. The refinement is based on a single phase fit to (m-PdH$_2$)CuCl$_4$, space group $Pnma$, with the starting model taken from the single crystal fits. Further details of the refinement outcomes are given in ESI.† Although there is no phase transition, we note that an unusual trend in unit cell parameters *versus* temperature is observed. Figure 2(c) and (d) show the thermal evolution of unit cell parameters $a$, $b$, $c$, and unit cell volume, $V$. Upon heating, the $a$ and $c$ parameters show a positive expansion, by about 0.13 and 0.04 Å, respectively (an increase of $\sim$1.85 and $\sim$0.45%). whereas, the $b$ parameter displays a contraction or negative thermal expansion (NTE), decreasing by about 0.11 Å ($\sim$0.58%). Meanwhile, the unit cell volume expands by about 18.64 Å$^3$ ($\sim$1.72%). The axial and volume expansivities can be approximated over linear regions:
\[ \Delta a/a \sim 88 \times 10^{-6} \text{ K}^{-1} \ (90-300 \text{ K}), \ \Delta b/b \sim -42 \times 10^{-6} \text{ K}^{-1} \ (90-200 \text{ K}), \ \Delta c/c \sim 18 \times 10^{-6} \text{ K}^{-1} \ (110-300 \text{ K}), \ \Delta V/V \sim 82 \times 10^{-6} \text{ K}^{-1} \ (90-300 \text{ K}). \] 

The thermal contraction of the \( b \)-axis is notably large compared to all-inorganic layered perovskites. For example, Ca\(_3\)Mn\(_2\)O\(_7\) has an axial NTE of \(-3.6 \times 10^{-6} \text{ K}^{-1}\) over the region 250-350 K.\(^9\) The NTE in such compounds relies on dynamical effects of soft phonon modes, and typically result in axial thermal contraction effects an order of magnitude smaller than observed here. However, the (110)-oriented layered perovskite LaTaO\(_4\) shows an axial value \(-40 \times 10^{-6} \text{ K}^{-1}\) (over the region 100-300 °C), which was ascribed to frozen-out changes in octahedral tilting.\(^10\)

**Figure 2.** (a) Rietveld refinement profiles for (m-PdH\(_2\))CuCl\(_4\) at 92 K, \( \chi^2 = 2.126 \) for 46 variables and (b) at 300 K, \( \chi^2 = 2.031 \) for 46 variables; (c) thermal evolution of the unit cell parameters \( a, b, \) and \( c \) and (d) volume, obtained from Rietveld refinement of SXRD data from 92 to 300 K.

In order to identify the structural characteristics leading to the anomalous expansivity behaviour here, we can define two parameters within the two neighbouring octahedral layers: the thickness of the \textit{inter}-layer block, \( d_1 \), the thickness of the single octahedral layer, \( d_2 \) (Figure 3(a)). From the geometry of these definitions it can be seen that

\[ b = 2(d_1 + d_2) \]
Thermal evolution of these two parameters is shown in Figure 3(b). As can be seen, the $d1$ parameter displays a significant change: contraction over the regime 92–240 K, followed by a slight increase. In contrast, $d2$ shows an insignificant variation in the temperature region studied. Hence, the behaviour of $d1$ appears to be largely responsible for the $b$-axis contraction.

*ISODISTORT* was used to derive mode amplitudes related to the inorganic layers from each Rietveld refinement: plots of the thermal evolution of the three significant modes are given in Figure 3(c). Both ‘tilt’ modes, $M_2^+$ and $A_5^-$ modes exhibit a decreasing trend on heating, which is fairly typical in perovskites. The J-T mode, $M_3^+$, increases slightly on heating. However, none of the trends in these three structural parameters related to the behaviour of the $[\text{CuCl}_4]_{\infty}$ framework can explain the anomalous behaviour of $d1$ and hence $b$. Therefore, it appears that the anomalous expansion of the inter-layer space, $d1$, on cooling must result from the behaviour of the inter-layer $[\text{m-PdH}_2]^2+$ moieties.

**Figure 3.** (a) View of adjacent octahedral layers with the definitions of the parameters, $d1$ and $d2$; thermal evolution of (b) the distortion parameters $d1$ and $d2$, (c) the three significant $[\text{CuCl}_4]_{\infty}$ layer modes, (d) the parameter $\Delta y$, describing the depth of penetration of the organic moiety into the inorganic layers; the red line is a least-squares fit, and (e) schematic representation of the re-positioning of the inter-layer species versus $T$. 
In Figure 3(d) we plot a measure of the degree of penetration of the organic moiety into the [CuCl₄]ₓ layer, taken as the distance along the b-axis between the apical Cl atom and the N atom of the m-PdH₂²⁺ cation: a positive value at lower T signifies lower penetration, and a change to negative values at higher T signifies the organic moiety penetrates further into the inter-layer space. We suggest that this is the parameter influencing the observed thermal expansion behaviour. This is shown schematically in Figure 3(e).

\[(3\text{-AbaH})_2\text{CuCl}_4\]

\((3\text{-AbaH})_2\text{CuCl}_4\) crystallizes in a partially-eclipsed layered perovskite structure type (Figure 4); i.e. closer to DJ than RP type, despite the stoichiometry. However, the [CuCl₄]ₓ layer exhibits disorder of each of the chloride ligands, which we model as ~50:50 disorder of both the apical and in-plane sites, leading to an otherwise ‘well-behaved’ structural model with low (triclinic) symmetry. The nature of the disorder is unchanged, even on cooling to 93 K, and we see no evidence of any further superlattice at any temperature. This situation is highly unusual, especially since the inter-layer organic moieties are perfectly ordered at each temperature studied. We have observed\(^{13}\) that disorder of organic moieties is quite common in layered hybrid lead halide perovskites at elevated temperatures, but this typically settles out to an ordered state at lower temperatures. It is not obvious to see why the present composition chooses to display this unusually disordered structure, nor why a more ordered ground state structure does not freeze out on cooling. It may relate to the large number of H-bonding opportunities seen in Figure 4(a) and Table S6. The unit cell metrics here are similar to those of the DJ parent phase, with no superlattice, and \(Z = 1\) formula unit per cell. This feature is also unusual in layered perovskites, which typically do display unit cell expansion due to octahedral tilting and other distortion modes.\(^{40}\) Nevertheless, from the nature of the disorder model, it is evident that localised distortions of both the octahedral tilting and J-T type are present (Figure 4(b)).
Figure 4. Crystal structure of (3-AbaH)$_2$CuCl$_4$ at 298 K, (a) showing the disordered inorganic layers and ordered organic layers, (b) plan view perpendicular to the layers, showing just one orientation of the [CuCl$_4$]$_{∞}$ layers and the partial eclipsing of neighbouring layers (for clarity the two layers are shown in different colours).

(4-AbaH)$_2$CuCl$_4$

(4-AbaH)$_2$CuCl$_4$ crystallizes in a near-staggered structure type (Figure 5); although the structure is quite close to the RP type, there is a small relative shift of neighbouring octahedral layers along the $c$-axis, described by the $β$ angle. Figure 5(a) shows that the octahedral tilt system to some extent resembles that in (m-PdH)$_2$CuCl$_4$, having an alternating sense of out-of-plane tilt in adjacent layers. Indeed, allowing for the slight shift of adjacent layers, the tilt system may be also described as $a^′a^′c/- (a^′a)c$. The $inter$-layer cohesion is performed by two hydrogen bond types N–H---Cl and O–H---O. In each of these aminobenzoic acid-templated structures, it is perhaps no surprise that the benzoic acid moieties form dimers via strong mutual H-bonds; this is a common motif in many pure carboxylic acid structures. These two compounds appear to be the first layered hybrid halides containing amino acids based on cyclic (aromatic) building blocks. However, there are several examples based on aliphatic, linear amino acids in lead halide systems$^{13}$ and in two examples in copper chloride systems. The present structure can therefore be usefully compared with the already known structures [NH$_3$(CH$_2$)$_2$COOH]$_2$CuCl$_4$, and [NH$_3$(CH$_2$)$_3$COOH]$_2$CuCl$_4$, containing two 3-aminopropanoic acid and 4-aminobutanoic acid cations, respectively.$^{41,42}$ These are shown in Figure 6. The 3-
aminopropanoic acid analogue is the most similar, structurally, also crystallizing in the monoclinic space group $C2/c$, with unit cell metrics at 293 K, $a = 25.1209(3) \, \text{Å}$, $b = 7.7432(2) \, \text{Å}$, $c = 7.4130(2) \, \text{Å}$, $\beta = 105.293(2)^\circ$. From these metrics it can be deduced that the octahedral tilt system is again $a'\bar{a}'c/-(a'\bar{a})c$. However, it can be noted that the relative disposition of adjacent $[\text{CuCl}_4]_6$ layers become almost eclipsed (DJ-like) in this case (Figure 6(b)). This is perhaps related to accommodation of the $[\text{NH}_3(\text{CH}_2)\text{COOH}]^+$ cations in a ‘twisted’ conformation (specifically, with a gauche conformation to the $\text{NH}_3^+$ group, Figure 6(a)). Both structures have a doubled $a$-axis perpendicular to the layers. However, $\text{(4-AbaH)}_2\text{CuCl}_4$ possesses a larger inter-layer Cu--Cu distance of 18.841 Å and is seen to exhibit larger octahedral and inter-octahedral distortions (i.e. Cu--Cl--Cu bond angles, Table S10). In contrast, $[\text{NH}_3(\text{CH}_2)\text{COOH}]_2\text{CuCl}_4$ exhibits a structure more similar to $(\text{p-PdH})_2\text{CuCl}_4$, with space group $P2_1/c$, and the simpler tilt system $a'\bar{a}'c$ (i.e. adjacent layers tilted ‘in-phase’ relative to each other leading to only a single layer per cell repeat, Figure 6(c)). The layers also stack in a near-DJ, almost eclipsed, style (Figure 6(d)), with the organic moiety having a ‘fully-stretched’ (i.e. all trans) conformation. Further examples would be required to establish whether there are any systematic and predictable trends in these similarities and differences amongst the templating effects of cyclic versus linear amino acids, and their isomers and homologues.

![Figure 5](image_url)

**Figure 5.** Crystal structure of $(4\text{-AbaH})_2\text{CuCl}_4$ at 298 K, (a) showing the alternately tilted $[\text{CuCl}_4]_6$ layers and the interactions with the inter-layer moieties, and (b) plan view of the near-staggered adjacent layers.
Figure 6. Crystal structure of $[\text{NH}_3(\text{CH}_2)_2\text{COOH}]_2\text{CuCl}_4$ at 298 K (a) parallel to the layer direction and (b) plan view of the almost eclipsed adjacent layers; crystal structure of $[\text{NH}_3(\text{CH}_2)_3\text{COOH}]_2\text{CuCl}_4$ at 298 K (c) parallel to the layer direction and (d) plan view of the almost eclipsed adjacent layers.

**Magnetic Properties**

The magnetic properties of all three compounds have been investigated in the range $2 \text{ K} < T < 300 \text{ K}$ with an applied d.c. field of 1000 Oe or 100 Oe. The susceptibility ($\chi$) is plotted as a function of $T$ during field cooling in Figure 7. The magnetic properties of all three compounds reveal features similar to previously reported 2D layered copper (II) perovskites, long-range ferromagnetic interactions within the $[\text{CuCl}_4]_{\infty}$ layers. The similar ferromagnetic behavior in related layered Cu$^{2+}$ perovskites, and also that of the related J-T active Mn$^{3+}$, have been quantified Aguado et al. In that work key structural parameters were associated with ferromagnetic behavior ($viz.$, interlayer and intralayer distances and octahedral tilt angles). The corresponding parameters of the present compounds fit neatly into this scheme, with ferromagnetic behavior being predicted in each case.

In each of the present compounds, there is a gradual rise with decreasing temperature of the $\chi T$ values at high temperature, followed by a rapid increase to the maximum value at around 5 K.
and then a decrease towards 2 K (Figure 7d-f). In all three compounds the sharp increase of $\chi$ below approximately 5 K implies the onset of ferromagnetic order. For (3-AbaH)$_2$CuCl$_4$ and (4-AbaH)$_2$CuCl$_4$, both having long inter-layer Cu-Cu distances of 16.789 and 18.841 Å, respectively, the magnetic data are extremely similar, reflecting the strong magnetic decoupling of the [CuCl$_4$]$\infty$ layers. For (m-PdH)$_2$CuCl$_4$, with a shorter inter-layer Cu-Cu distance, 9.425 Å, there is some indication of the onset of a peak in the value of $\chi$ itself, which may reflect the additional influence of weak antiferromagnetic coupling between layers in this structure.

The inverse susceptibility ($1/\chi$) plot shows a linear temperature dependence in the high temperature region, hence the inverse susceptibility was fitted with the Curie–Weiss law in the region 50–300 K. We obtained the Curie constant, $C = 0.46$, 0.31 and 0.30 cm$^3$ mol$^{-1}$ K, the Weiss constant $\theta = 20.5$, 34.1 and 34.6 K, the derived effective moment, $\mu_{\text{eff}} = 1.918$, 1.567 and 1.541 $\mu_B$ and Landé factor, $g = 2.215$, 1.810 and 1.781 for (m-PdH)$_2$CuCl$_4$, (3-AbaH)$_2$CuCl$_4$ and (4-AbaH)$_2$CuCl$_4$, respectively. Whilst the derived values for (m-PdH)$_2$CuCl$_4$ are within the expected range for one Cu$^{2+}$ ion with $S = 1/2^{46,47}$ it is clear that those for the latter two compounds are unusually low.

EPR data, however, reveal spectra representing rhombic symmetry for all three compounds both at 295 and 120 K. The hyperfine interaction with $^{63/65}$Cu nuclei ($I = 3/2$) is not resolved and this is attributed to the large copper content. The spectral features correspond to $g_x$, $g_y$, $g_z$ values of 2.169, 2.139 and 2.060 for (m-PdH)$_2$CuCl$_4$, 2.199, 2.120, and 2.051 for (3-AbaH)$_2$CuCl$_4$ and 2.249, 2.153 and 2.054 for (4-AbaH)$_2$CuCl$_4$, respectively. These values and the corresponding isotropic $g$ of 2.123 to 2.150 are in-line with expected values for Cu$^{2+}$ in this type of compound$^{20}$. 
Figure 7. Magnetic susceptibility ($\chi$) and its inverse $1/\chi$ with Curie–Weiss fit (red line) above 50 K for (a) (m-PdH$_2$)CuCl$_4$, (b) (3-AbaH)$_2$CuCl$_4$ and (c) (4-AbaH)$_2$CuCl$_4$, respectively. $\chi T$ versus $T$ for (d) (m-PdH$_2$)CuCl$_4$, (e) (3-AbaH)$_2$CuCl$_4$ and (f) (4-AbaH)$_2$CuCl$_4$, respectively.

The magnetization versus magnetic field for these three compounds at 2 K and 200 K are shown in Figure 8. All show a sharp increase at low fields, tending to saturate below 10000 Oe at 2 K, confirming the existence of predominantly ferromagnetic order below 5K. Furthermore, the hysteresis observed in all compounds is characteristic of a soft ferromagnet. The magnetization nearly saturates at a value of 1.04, 0.85, 0.81 $\mu_B$ (per formula unit) for (m-PdH$_2$)CuCl$_4$, (3-AbaH)$_2$CuCl$_4$ and (4-AbaH)$_2$CuCl$_4$, respectively. While compatible with the values obtained from the Curie-Weiss fits, the moment per atom of the latter two compounds are again unusually low for a $S = 1/2$ system under the assumption of purely ferromagnetic order. For comparison for each sample we also include the paramagnetic response measured at 200 K, well above the ordering temperature, supporting the idea of a transition to an ordered state below 5 K.
Figure 8. Magnetisation ($M$) versus magnetic field ($H$) at 2 K and 200 K for (a) (m-PdH$_2$)CuCl$_4$, (b) (3-AbaH)$_2$CuCl$_4$ and (c) (4-AbaH)$_2$CuCl$_4$, respectively. Inset: the low field region of the hysteresis loops.

Conclusions

In summary, we have prepared three new examples of hybrid copper(II) chloride layered perovskites, which exhibit some unique structural features. In (m-PdH$_2$)CuCl$_4$, we introduce a previously unseen parity-induced octahedral tilting effect in the case of cyclic diamines. Interestingly, this compound exhibits a very large axial thermal contraction effect upon heating, as revealed by variable-temperature SXRD. This can be ascribed to the contraction of the interlayer block, via a slight repositioning of the m-PdH$_2^{2+}$ moiety. The two new A$_2$BX$_4$ perovskites reported, (3-AbaH)$_2$CuCl$_4$ and (4-AbaH)$_2$CuCl$_4$, are the first examples of layered perovskites incorporating cyclic amino acid derivatives. (3-AbaH)$_2$CuCl$_4$ is unusual in displaying crystallographic disorder in the [CuCl$_4$]$_x$ layers, yet perfect order of the inter-layer species. These compounds are shown to display structural similarities and differences relative to (m-PdH$_2$)CuCl$_4$, and to other known amino acid-templated derivatives, apparently dictated by the structural flexibility of the amino-acid moieties. Preliminary magnetic measurements are presented which indicate long-range ferromagnetic interactions within the [CuCl$_4$]$_x$ layers of all three new materials. EPR spectra reveal rhombic symmetry with $g$-values in the typical
range for copper(II) compounds. In (m-PdH₂)CuCl₄, there is maximum in the χ observed at lower temperature, which may be attributable to weak antiferromagnetic coupling between layers. The various novel structural features and magnetic behavior exhibited in these materials highlights the need for greater exploration and study of hybrid layered copper perovskites toward potential functionalities.

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Supporting Information

Crystallographic data at 93 and 173 K, Rietveld refinements of powder X-ray diffraction data, asymmetric unit data, thermogravimetric analysis data, hydrogen-bonding details, Rietveld refinements of synchrotron X-ray powder diffraction data, EPR data.

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Synopsis

We present three new hybrid copper(II) chloride layered perovskites of generic composition $\text{ACuCl}_4$ or $\text{A}_2\text{CuCl}_4$, which exhibit three distinct structure types related to the Dion–Jacobson or Ruddlesden–Popper (RP) types. Interesting structural features are discussed, including an unusual mechanism of negative thermal expansivity.