# Synthesis and Characterization of Cu-containing Chiral Metal Halides and Role of Halogenation of the Organic Ligand

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#### ABSTRACT

We report herein novel chiral copper metal chlorides, namely  $(R/S-CIMBA)_2CuCl_4$  (CIMBA = 4-(chloromethyl)benzylammonium), together with the corresponding racemic compound. The two chiral samples are composed of isolated CuCl<sub>4</sub> tetrahedra and crystallize in the noncentrosymmetric C2 space group and present a significant absorption in the visible region of the spectrum with band gap around 2.50 eV. The racemic compound, on the other hand, gives origin to a different structural topology characterized by the presence of a quite unusual five coordination for Cu(II), with  $Cu_2Cl_6^-$  dimers forming infinite chains along the b axis and presents, in addition, a strong reduction of band gap (around 1.76 eV). The two chiral samples display a circular dichroism response with anisotropy factors values around 0.02. The actual novel samples are investigated in comparison to the MBA-based (MBA=methylbenzylammonium) system in order to unveil the role of benzene ring halogenation on the structural and chiroptical properties indicating that the presence of chlorine leads to a doubling of the anisotropy factor.

### TOC



# Introduction

Chiral metal halides are triggering a huge interest for their potential use in different applicative areas such as chiroptoelectronics and spintronics due to their peculiar nonlinear optical and spin-dependent properties.<sup>1-3</sup> In addition, their intrinsic noncentrosymmetric structure may be exploited in ferroelectric and piezoelectric devices.<sup>4</sup> Lead represents the most common metal employed in the synthesis of chiral metal halides with R/S-MBA<sub>2</sub>PbI<sub>4</sub> (MBA=methylbenzylammonium), reported by Billing in 2006 and deeply investigated for its chiroptical response in 2017, representing a sort of archetypal composition in this field.<sup>5,6</sup> The need of getting rid of toxic lead has prompted the search of alternative metals, and several lead-free chiral metal halides including Sn, Mn, Ge, Co, Bi and Cu, have been prepared in the last years showing intriguing properties induced by the nature of central metal.<sup>7–12</sup> Among the listed elements, copperbased systems have attracted considerable interest, with (R-/S-MBA)<sub>2</sub>CuCl<sub>4</sub> being object of extensive investigation. These chiral metal halides have been first reported in 2016 and investigated for their biological activity by Salah and co-workers.<sup>13</sup> The crystal structure shows a 0D structural motif made of a layered lamellar structure with a layer of disconnected CuCl<sub>4</sub> tetrahedra and a bilayer of organic MBA cations.<sup>13</sup> However, their chiroptical properties have been only investigated in 2020 by Hao.<sup>14</sup> Through circular dichroism (CD) measurements they showed that the chirality transfer from the organic ligand to the inorganic framework led to one of the highest values of the absorption anisotropy factor ( $g_{CD}$ ) to date of the order of 0.06.<sup>14</sup> The chiral (MBA)<sub>2</sub>CuCl<sub>4</sub> has been used as an absorbing layer to prepare a circularly polarized light (CPL) detector by creating a heterojunction with a semiconducting single-walled carbon nanotube transport channel, providing a high photoresponsivity of 452 A/W, a current response of the order of microamperes, and low working voltage down to 0.01 V.14 Further investigation on the same material in 2021 confirmed previous results and added the

evidence of second-order non-linear optical (NLO) coefficients for the chiral (R-/S-MBA)<sub>2</sub>CuCl<sub>4</sub> films which are about 50 times larger than that of the Y-cut quartz reference at 800 nm.<sup>15</sup> Copper-based chiral metal halides have been also studied for their thermochromic and ferroelectric responses.  $(R-/S-CTA)_2CuCl_4$  (CTA = 3-chloro-2hydroxypropyltrimethylammonium) materials, still composed of isolated CuCl<sub>4</sub> tetrahedra, showed switchable properties in dielectricity, conductivity, second harmonic generation (SHG), piezoelectricity, ferroelasticity, chiral, and thermochromic properties.<sup>16</sup> Very recently, Das and co-workers were able to use the bromide halide for the preparation of the chiral pairs (*R*-/S-MBA)<sub>2</sub>CuBr<sub>4</sub>.<sup>17</sup> While still composed of isolated tetrahedra, the very short (Cu–Br···Br–Cu) lengths compared to the chloride analogue, indicates the formation of a "quasi-2D" network of CuBr<sub>4</sub> units. Interestingly, these chiral copper metal halides present the highest values of g<sub>CD</sub> in the orange-red part of the visible spectrum among all hybrid materials reported so far.<sup>17</sup> The presence of bromide brings a reduction of the band gap of about 0.8 eV with respect to (R-/S-MBA)<sub>2</sub>CuCl<sub>4</sub>, thus extending the chiroptical properties to longer wavelengths together with a peculiar broadband CD response.<sup>17</sup>

As can be seen, the data collected so far on chiral copper-based metal halides are limited to few ligands. However, it is well known that the nature of the chiral protonated amine has a strong impact on the structural topology and chiroptical properties.<sup>2,4</sup> For example, in the similar lead-analogue, namely  $(R-/S-MBA)_2PbI_4$ , it has been shown that the halogenation of the benzene ring can modulate the optical response due to the variation of the strength of the halogen-halogen interaction in the system, leading to a variation of circular dichroism intensity of the in order (CIMBA)<sub>2</sub>PbI<sub>4</sub>>(BrMBA)<sub>2</sub>PbI<sub>4</sub>>(IMBA)<sub>2</sub>PbI<sub>4</sub>>(MBA)<sub>2</sub>PbI<sub>4</sub>>(FMBA)<sub>2</sub>PbI<sub>4</sub>.<sup>18</sup>

Moreover, the rational study of homologous series of chiral metal halides where the organic ligand, or the central metal, or the halide is varied, can contribute to the understanding of role of chemical degrees of freedom in impacting the structural and optical properties. For these reasons, in this paper we report the preparation of the novel  $(R-/S-CIMBA)_2CuCl_4$  system (CIMBA = 4-(chloromethyl)benzylammonium), including also the racemic composition, and provide a characterization of the structural and chiroptical properties together with the analogous study on the  $(R-/S-MBA)_2CuCl_4$  chiral metal halides where the chiral cation is not halogenated. The reported data, not only enlarge the plethora of copper-based chiral metal halides, but also confirm the positive role of the presence of a halide (Cl) on the benzene ring of the organic ligand in improving the CD response.

### **Results and Discussion**

Single crystals of the (rac/R/S-CIMBA)<sub>2</sub>CuCl<sub>4</sub> compounds have been grown by solution method as described in the Experimental Section. We also grew the (R/S-MBA)<sub>2</sub>CuCl<sub>4</sub> compositions which, even though already known, were herein prepared and characterized under the same conditions as the CIMBA samples for a consistent comparison of the physical properties investigation.

Table 1 reports the main crystallographic data of the five compounds considered. (*rac*-MBA)<sub>2</sub>CuCl<sub>4</sub> was the only single crystal that we did not grow but just synthesized a powdered sample for optical characterization.

	(R-ClMBA) <sub>2</sub> CuCl <sub>4</sub>	(S-CIMBA) <sub>2</sub> CuCl <sub>4</sub>	(rac-CIMBA)CuCl <sub>3</sub>	( <i>R</i> -MBA) <sub>2</sub> CuCl <sub>4</sub>	(S-MBA) <sub>2</sub> CuCl <sub>4</sub>
Formula weight	518.61	518.61	326.53	449.72	449.72
Temperature (K)	298	298	298	298	298
Wavelength (Å)	0.7107	0.7107	0.7107	0.7107	0.7107
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C</i> 2	<i>C</i> 2	$P2_{1}/c$	C2	<i>C</i> 2
Lattice parameters (Å)	<i>a</i> = 10.2416(8)	<i>a</i> = 10.2216(7)	<i>a</i> = 13.5245(6)	<i>a</i> = 10.5424(6)	<i>a</i> = 10.5384(6)
	<i>b</i> = 7.2883(5)	<i>b</i> = 7.2771(5)	<i>b</i> = 5.9914(2)	<i>b</i> = 7.2403(4)	<i>b</i> = 7.2407(3)
	<i>c</i> = 15.6161(11)	<i>c</i> = 15.5886(13)	<i>c</i> = 15.6879(6)	c = 13.9021(7)	<i>c</i> = 13.8923(7)
	<i>β</i> = 91.352(7)	$\beta = 90.999(8)$	$\beta = 103.657(4)$	$\beta = 95.892(5)$	$\beta = 95.935(5)$
Lattice Volume (Å <sup>3</sup> )	1165.32(15)	1159.36(15)	1235.26(9)	1055.54(10)	1054.38(9)
Z	2	2	4	2	2
CCDC code	2320448	2320449	2320447	2324108	2324109

The two novel  $(R/S-CIMBA)_2CuCl_4$  chiral compounds crystallize in the noncentrosymmetric C2 space group in analogy with  $(R/S-MBA)_2CuCl_4$ . Note that the crystallographic data reported for the last two samples are herein collected under the same conditions (*i.e.*, wavelengths and temperature) as the present novel CIMBAcontaining compounds and have therefore redeposited in the database for consistency.<sup>13</sup>

Figure 1 reports a sketch of the crystal structure for  $(R/S-CIMBA)_2CuCl_4$  along different projections, while a picture of the aspect of the green crystals is reported in Figure 1e. The analogous plots for  $(R/S-CIMBA)_2CuCl_4$  are shown in the Supporting Information (Figure S1).



**Figure 1** a) and b) represent sketches of the crystal structure of (*R*-ClMBA)<sub>2</sub>CuCl<sub>4</sub> while c) and d) of (*S*-ClMBA)<sub>2</sub>CuCl<sub>4</sub>, respectively, along different axis; e) photo of single crystals of (*R*-ClMBA)<sub>2</sub>CuCl<sub>4</sub>.

The structural arrangement of  $(R/S-CIMBA)_2CuCl_4$  resembles that of the MBA analogue, with a lamellar structure of isolated CuCl<sub>4</sub> tetrahedra and a bilayer of organic ligands. The Cl of the benzene ring points inside such bilayer while the protonated amino group is directed towards the chloride of the tetrahedron. There is a clear expansion of

the unit cell along the *c*-axis when moving from MBA to ClMBA cation, namely from about 13.89 Å to about 15.60 Å (see Table 1). The four Cl-Cu-Cl bond angles for (*R/S*-ClMBA)<sub>2</sub>CuCl<sub>4</sub> varies from ~91.7 to ~97.3° for both enantiomers, showing a significant distortion with respect to the ideal tetrahedron angle (109.5°), while the two Cu-Cl bond lengths are in the range ~2.23 Å and ~2.26 Å. The full list of bond angles and bond lengths for (*R/S*-ClMBA)<sub>2</sub>CuCl<sub>4</sub> and (*R/S*-MBA)<sub>2</sub>CuCl<sub>4</sub> are reported in the SI (Table S1) showing that the nature of the chiral cation has a modest impact on the Cu-Cl bond lengths while seems to affect more the bond angles of the CuCl<sub>4</sub> tetrahedra. The distortion index, *D*, defined by Baur and calculated as<sup>19</sup>

$$D = \frac{1}{n} \sum_{i=1}^{n} \frac{|l_i - l_{av}|}{l_{av}}$$

where  $l_i$  is the distance from the central atom to the *i*th coordinating atom, and  $l_{av}$  is the average bond length, turned to be around 0.00645 for MBA containing samples and 0.0080 for CIMBA copper halides.

The crystal structure of the racemic copper chloride including CIMBA has been as well determined and the main crystallographic data are reported in Table 1. Even after repeating the synthesis several times and with different methodology, in all the cases we could observe that the racemic material crystallizes in the centrosymmetric  $P2_1/c$  space group with a different stoichiometry with respect to the enantiopure samples, namely (CIMBA)CuCl<sub>3</sub>. This is not an isolated case and in a recent report about hybrid organic inorganic germanium halides the racemic compound, differently from the enantiopure ones, led to a (*rac*-NEA)GeI<sub>3</sub> (NEA= 1-naphthalen-1-ylethanammonium) stoichiometry.<sup>8</sup> In (CIMBA)CuCl<sub>3</sub> the crystal structure is composed of Cu<sub>2</sub>Cl<sub>6</sub><sup>-</sup> dimers with five-coordinated Cu(II) ions tied together into infinite chains along the *b* axis, as

depicted in Figures 2a and 2b. The appearance of the crystals is also different compared to the R/S samples (Figure 1e) and presents a dark brown colour shown in Figure 2c.



**Figure 2** a) and b) represent sketches of the crystal structure of (*rac*-ClMBA)CuCl<sub>3</sub> while c) is a photo of single crystals of (*rac*-ClMBA)CuCl<sub>3</sub>.

It is interesting to note that the five coordination for Cu(II) in hybrid organic inorganic copper halides, as found here for (*rac*-ClMBA)CuCl<sub>3</sub>, is quite unusual and rarely observed before. Specifically, the other example has been reported in 1965 by Willet for the (CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>CuCl<sub>3</sub> material crystallizing in the monoclinic *I*2/*a* space group and presenting the dimers running along the *a* axis.<sup>20</sup> The five Cu-Cl bond distances are found to range from 2.2540(13) Å to 2.3200(12) Å, while the bond angles are in the range from about 84.5° to 92.7°, indicating a significant level of distortion of the inorganic framework, significantly higher with respect to the (*R/S*-ClMBA)<sub>2</sub>CuCl<sub>4</sub> samples. The analogous racemic sample including MBA leads, on the opposite, to the same crystal motif found for *R/S* samples crystallizing, however, in the achiral orthorhombic space group *Aea*2.<sup>14</sup> This last was the only crystal structure that we have not determined relying on a previous literature report.<sup>14</sup>

The stability of all the six samples has been checked by differential scanning calorimetry (DSC) in the temperature range -80-130°C (DSC) both during cooling and

heating runs. DSC measurements (Figure S2) rule out the presence of structural phase transitions in the considered temperature range. For  $(R-CIMBA)_2CuCl_4$  a broad peak around 60°C, found only in the heating run, has been observed which can be related to solvent evaporation.

Optical properties of (*R/S*-MBA)<sub>2</sub>CuCl<sub>4</sub> and (*rac/R/S*-ClMBA)<sub>2</sub>CuCl<sub>4</sub> have been measured by UV-Vis (on powdered single crystals) and CD spectroscopy (on spin-coated polycrystalline thin films of about 300 nm thickness). Details about thin films preparation are reported in the SI. Room temperature steady-state photoluminescence measurements were attempted but not clear emission was observed for all the samples. This is in agreement with previous reports on other copper-based metal halides.<sup>14,17</sup>

The linear absorption spectra of  $(R/S-MBA)_2CuCl_4$  (see Figure S2) are superimposable and show quite sharp edge around 450 nm followed by a broader absorption at higher wavelength: the first can be associated to the ligand-to-metal charge transfer (LMCT) transition while the second to the Cu d–d transitions.<sup>21</sup> A possible contribution from the MBA cation may be observed around 250 nm. The Tauc plots are reported in Figure 3a leading to a direct band gap of about 2.41 eV for *R* and 2.45 eV for *S* sample. The spectra for the (*R/S*-ClMBA)<sub>2</sub>CuCl<sub>4</sub> and (*rac*-ClMBA)CuCl<sub>3</sub> samples are reported in Figure S4 while the corresponding Tauc plot in Figure 3b. When replacing ClMBA for MBA in the *R* and *S* samples, the UV-Vis spectra are, in general, similar with a slightly less sharp absorption edge. The band gap values, as well, are quite close and equal to 2.48 eV for (*R*-ClMBA)<sub>2</sub>CuCl<sub>4</sub> and 2.46 eV for (*S*-ClMBA)<sub>2</sub>CuCl<sub>4</sub>. A different behaviour is observed for (*rac*-ClMBA)CuCl<sub>3</sub>, in agreement with the different crystal structure and colour observed (see above). In this last case the main absorption from the inorganic network is significantly red-shifted resulting in a band gap value around 1.76 eV.



Figure 3 Tauc plots for a) (R/S-MBA)<sub>2</sub>CuCl<sub>4</sub> and b) (R/S-ClMBA)<sub>2</sub>CuCl<sub>4</sub> and (rac-ClMBA)CuCl<sub>3</sub>.

The CD spectra have been collected on thin films prepared by spin coating as reported in the Experimental. In all the cases, the diffraction patterns of the films resulted to be significantly oriented along the (00*l*) direction, as can be seen from Figure 4a displaying, as a selected example, the XRD pattern of a 300 nm thick (*S*-ClMBA)<sub>2</sub>CuCl<sub>4</sub> film.





**Figure 4** a) X-ray diffraction of a (*S*-ClMBA)<sub>2</sub>CuCl<sub>4</sub> thin film; CD spectra for b) (*rac/R/S*-MBA)<sub>2</sub>CuCl<sub>4</sub> and c) (*R/S*-ClMBA)<sub>2</sub>CuCl<sub>4</sub> and (*rac*-ClMBA)CuCl<sub>3</sub>.

The CD spectra of (*R/S*-MBA)<sub>2</sub>CuCl<sub>4</sub> films show three mirrored distinct peaks from 310 to 470 nm, with this last well corresponding to the position of the absorption edge (see Figure S3), as a result of the Cotton effect.<sup>22</sup> The presence of opposite signs in the CD peaks for the two samples confirms the chirality transfer from the chiral ligand MBA to the inorganic framework. As a matter of fact, the two chiral amines have CD spectra with a peak cantered around 245 nm (see Figure S5). On the other hand, the racemic compound does not present any CD signal, as expected. The chiral anisotropy factor,  $g_{CD}$ , has been calculated from the CD measurements and resulted to be around  $1.13 \times 10^{-2}$  for the *R* sample, and  $-1.67 \times 10^{-2}$  for the *S* sample, in fairly good agreement with previous data on these samples where, however, the CD spectra appears different and with an absorption close to the UV region of the spectrum, with the highest wavelength peak centred around 378 nm which seems to contradict the optical response and colour of the samples.<sup>15</sup> An analogous result also holds for the (*R/S*-CIMBA)<sub>2</sub>CuCl<sub>4</sub> films showing, however, a narrow signal around 350 nm and a broader one extending up to

about 430 nm. Also in this case the two CD spectra are similar but with peaks with opposite sign and, again, the racemic compound has no CD response. For (R/S-ClMBA)<sub>2</sub>CuCl<sub>4</sub> the g<sub>CD</sub> increases with respect to the MBA samples, giving values two times higher and corresponding to  $2.51 \times 10^{-2}$  and  $-2.01 \times 10^{-2}$  for the *R* and *S* samples, respectively. Such observation of a doubling of the CD response by moving from MBA to CIMBA has reported, to date, only for the 2D lead iodide systems including halogenated organic ligands with different halogens in para position of the benzene ring.<sup>18</sup> In that case the main role was associated to the reduction of the distance between perovskite layers as a function of the chiral ligand and to the presence of a halogen. However, such dependence could not hold here and, as a matter of fact, the presence of isolated polyhedral rule out the role of connectivity in the CD response. The origin of the increased asymmetry factor by moving from MBA to ClMBA could have various possible origins. On one hand, as reported above, the distortion index of the polyhedra increases when the halogenated cation is present, and this correlation between inorganic framework distortion and chiroptical properties has been established in chiral 2D lead perovskites.<sup>23,24</sup> While the available data on chiral hybrid organic-inorganic copper halides is still scarce, some evidence on this direction start to accumulate, and this work adds further indications to corroborate this scenario. On the other hand, there is another evidence that it starts to become evident now that more and more chiral metal halides are synthesized and characterized, *i.e.* the impact of the CD response of the chiral ligand. The CD spectra of the MBA and ClMBA are different, and the dichroism of the latter is in general greater than that of MBA.<sup>18</sup> Since the chirality is transferred from the organic ligand to the inorganic framework, it may be possible that the intrinsic extent of the CD response of the chiral amine impacts the overall chiroptical properties of the metal halide. It is clear, however, that more data are needed to reach a definite conclusion about

the parameters affecting the chiral properties of organic-inorganic metal halides, and this work represents a further piece of useful information about copper-based systems.

# Conclusions

In this paper we reported three novel chiral organic-inorganic copper halides, namely (R/S-CIMBA)<sub>2</sub>CuCl<sub>4</sub> and (rac-CIMBA)CuCl<sub>3</sub>. The crystal structure of the three samples has been determined by SC-XRD showing that the chiral compounds crystallize in a noncentrosymmetric space group and are composed of isolated CuCl<sub>4</sub> tetrahedra and a bilayer of organic ligands. On the other hand, the racemic compound crystallizes in the centrosymmetric  $P2_1/c$  space group and shows a quite unusual five coordination for Cu(II), with Cu<sub>2</sub>Cl<sub>6</sub> dimers forming infinite chains along the *b* axis. Chiral samples have strong absorption in the visible range (crystals are green in color) with direct band gap around 2.4 eV. The CD spectra show as well extended features in the same range of the absorption measurements with anisotropy factors around 0.02. The comparison of the structural and chiroptical properties of the analogous system with MBA chiral cation allowed to observe a doubling of the gCD when the benzene ring is chlorinated in the para position. The origin of this enhanced CD response may be related to an increase of structural distortion when CIMBA is introduced into the structure and, possibly, to the set up of halogen-halogen interactions in analogy with lead-based 2D perovskites. Present results indicate also the need of further expanding the family of chiral metal halides, specifically of Pb-free systems, in order to provide stronger structure-property correlation required for the engineering of novel and optimized phases.

# **Declaration of interests**

The authors declare no competing interests.

# **Supplemental Information**

Supporting Information Available: Experimental section, additional data.

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