

An organic–inorganic hybrid perovskite containing copper paddle-wheel clusters linking perovskite layers : $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4^\ddagger$

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The incorporation of $\text{Cu}_2(\text{CO}_2)_4$ clusters, built up from amino carboxylic acid zwitterionic molecules, led both to the stabilization of a layered hybrid perovskite, and to the formation of a covalent bond pathway between adjacent perovskite layers.

The achievement of structural arrangements with a deliberately designed architecture remains a difficult challenge for solid state chemists. Nevertheless, the supramolecular approach, developed for instance in the field of Metal–Organic Framework compounds (MOFs), by using clusters as building blocks, leads to the finding of predictable topologies.¹ Also, in the field of organic–inorganic perovskites, a layered structure can be predicted if suitable organic cations are incorporated. Thus, starting from such cations, with an ammonium moiety and a well-defined shape,² many hybrids consisting of perovskite layers alternating with organic sheets, with the general formulas $(\text{RNH}_3)_2\text{M}^{\text{II}}\text{X}_4$ or $(\text{NH}_3\text{RNH}_3)\text{M}^{\text{II}}\text{X}_4$ (in most cases, M = Pb, Sn, Cu; X : I, Br, Cl; R = alkyl, phenyl or thiophene derivative),^{2,3} have been synthesized in the past decade.

Extensive work has been recently devoted to semiconductive hybrid perovskites based on iodostannate perovskite layers, used as semiconducting channels in thin-film field-effect transistor (TFTs).^{4,5} A high charge carrier mobility was evidenced ($0.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) in $(\text{C}_6\text{H}_5\text{C}_2\text{H}_5\text{NH}_3)_2\text{SnI}_4$ ⁵ which nevertheless remains two orders of magnitude smaller than that observed in the $\text{CH}_3\text{NH}_3\text{SnI}_4$ metallic 3D perovskite.⁶ In order to improve this charge carrier mobility or other semiconductive properties, several strategies have been considered, including a melt-processing technique⁷ rather than a solution one, and the design of hybrids with enhanced dimensionality, either multilayer perovskite materials^{3c,8} or compounds with short interlayer iodine–iodine contacts.⁹

In the search for new multifunctional hybrid perovskite compounds, the use of zwitterionic amino-based molecules has not been considered up to now, possibly due to the conditions for the synthesis of hybrids which is often carried out in concentrated acid aqueous solutions. Even so, such bifunctional organic entities would be able to anchor the perovskite layer *via* the cationic ammonium part in one hand, and able to complex a metal *via* the anionic part on the other hand.

Herein, we report the preparation and the X-ray structural characterization of the first organic–inorganic hybrid perovskite incorporating zwitterionic molecules, and displaying a cluster covalently linking adjacent perovskite sheets. The title compound **1** combines dimeric units of copper atoms held on by four carboxylate bridges belonging to $-\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3^+$ zwitterionic molecules, with lead bromide perovskite layers, the axial positions of the dimeric units being coordinated by apical bromines of PbBr_4 sheets.

Most crystals of ammonium based hybrids are synthesized from concentrated acid aqueous solutions, especially to improve the solubility of the halide salt.² Thus, to keep the $-\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3^+$ zwitterionic state of 4-aminobutyric acid, only one drop of concentrated HBr (about 20 μL) was added to an aqueous solution (10 mL) containing a mixture of 4-aminobutyric acid (0.655 mmol) and copper(II) bromide (0.327 mmol) in stoichiometric quantities.

A small quantity of PbBr_2 (0.031 mmol) was then added, leading to its complete solubilization due to a large excess of bromide ions. A slow evaporation of the clear blue solution, over a period of two days at room temperature, gave rise to **1** before the complete evaporation of water. The air-stable blue-green crystals, whose sizes are up to $(2 \times 2 \times 0.2) \text{ mm}^3$ for the biggest ones, were then collected by filtration, and washed with acetonitrile.

The layered crystal structure of **1** can be first described as perovskite layers of lead(II) bromide octahedra, separated by organic sheets, these last also enclosing copper(II) ions (Fig. 1).[‡] In fact, the zwitterionic molecules of 4-aminobutyric acid point their ammonium parts towards the perovskite layers, whereas the carboxylate parts act as ligands to complex copper atoms. Dimeric units of copper atoms held on by four carboxylate bridges are so defined between the perovskite layers. This well-known robust $\text{Cu}_2(\text{CO}_2)_4$ paddle-wheel cluster, encountered for instance in hydrated copper acetate, has been extensively studied in copper carboxylate complexes, especially for the metal–metal interactions.¹⁰ More recently, an extensive work by Yaghi has been devoted to the use of such carboxylate clusters as secondary building units (SBUs) for the design of porous metal–organic frameworks (MOFs).¹ Polytopic rigid carboxylate linkers ensure the connection of SBUs in the structure, leading to the formation of such open frameworks in MOFs. Here, the flexible carboxylate ligands, also possessing ammonium units, lead to both the formation of paddle-wheel clusters and the achievement of the perovskite layers. A main interesting structural feature is that the terminal ligands of the $\text{Cu}_2(\text{CO}_2)_4$ units are coordinated by apical bromines of PbBr_4 sheets, finally implying a Br–Cu–Cu–Br covalent link between consecutive perovskite layers, and consequently an increase of the dimensionality.

A view of the copper cluster together with linked lead octahedra are shown in Fig. 2a. Geometric characteristics of both copper and lead coordination polyhedra are close to those quoted in the

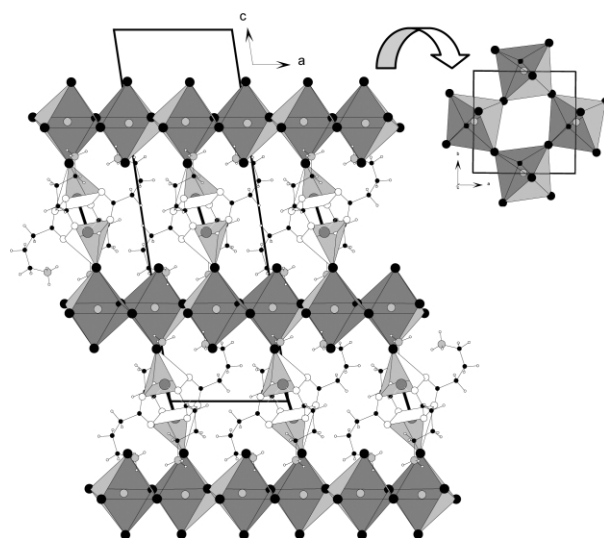


Fig. 1 View of the layered structure of **1**, showing perovskite layers (one is displayed as viewed along *c*) connected by dimeric units of copper atoms held on by four carboxylate bridges.

[‡] Electronic supplementary information (ESI) available: powder X-ray pattern of blue-green sample of $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)]\text{PbBr}_4$. See <http://www.rsc.org/suppdata/cc/b3/b316847f/>

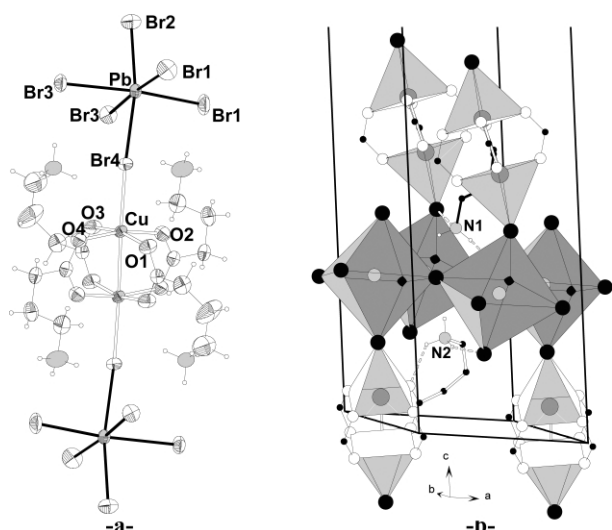


Fig. 2 a) ORTEP plot of a part of the structure of **1** showing the copper cluster connected to two lead octahedra *via* apical bromine atoms of the PbBr_4 sheets. Selected bond lengths [\AA] and angles [$^\circ$]: Cu–Cu 2.649(2); Cu–O1 1.969(5); Cu–O2 1.957(5); Cu–O3 1.9983(5); Cu–O4 1.961(5); Cu–Br4 2.643(1); Pb–Br4 3.103(1); Pb–Br2 2.871(1); Pb–Br_{equatorial} 3.031 (average value); Cu–Cu–Br4 169.81(6); Cu–Br4–Pb 152.09(4); Br4–Pb–Br2 169.03(3). b) Perspective view of a part of the structure of **1** showing the connection of copper clusters to four adjacent lead octahedra, together with the hydrogen bonding at the organic–inorganic interface (dashed lines). Except for two $-\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3^+$ molecules, the propylammonium units have been removed for clarity.

literature. Copper atoms are slightly out of the square plane of oxygen atoms, directed towards the terminal bromine atoms. Cu–O and Cu–Cu bond distance values (Fig. 2a) can be compared to those found in $[\text{Cu}_2(\text{H}_2\text{O})_2(\text{CH}_3\text{CO}_2)_4]\cdot\text{CH}_3\text{CO}_2\text{H}$ (1.975 \AA and 2.617 \AA respectively),¹¹ or in $[\text{Cu}_2\text{Br}_2(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_4]\text{Br}_2$ (1.973 \AA and 2.653 \AA respectively),¹² while Cu–Br4 distance ($d = 2.643(1)$ \AA) indicates a strong interaction between both atoms. For comparison, Cu–Br_{terminal} bond distance evidenced in the last quoted salt is 2.597(1) \AA , and in $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{CuBr}_4$,¹³ based on copper(II) octahedra displaying a [4+2] Jahn–Teller effect, $d(\text{Cu}–\text{Br})$ are found to be 2.435 \AA and 3.057 \AA for the equatorial and axial bonds respectively (average values). The lead atom is surrounded by a slightly distorted octahedral coordination of bromide. The Pb–Br2 bond distance, Br2 being the free apical bromine atom, appears shorter than the five other Pb–Br bond distances (Fig. 2a). The PbBr_6 octahedra define a well-ordered perovskite layer which appears distorted owing both to hydrogen bonding between the NH_3^+ part of the molecules and bromide, and to the structural constraint imposed by robust clusters. Nevertheless, distortions are not so important, as illustrated by the Pb–Br_{equatorial}–Pb bond angles of 163.56(3) $^\circ$ and 153.55(4) $^\circ$.

The four copper cluster connected to four adjacent lead octahedra of PbBr_4 sheets can be considered roughly related by a pseudo -4 symmetry axis parallel to the c axis (Fig. 2b). The hydrogen bonding provides two different situations. As encountered in organic–inorganic perovskites, only $\text{N}–\text{H}\cdots\text{X}$ (here, $\text{X} = \text{Br}$) are found for $\text{N} = \text{N1}$ ($\text{N1}–\text{H}\cdots\text{Br1}$: 2.58 \AA ; $\text{N1}–\text{H}\cdots\text{Br4}$: 2.47 \AA). For $\text{N} = \text{N2}$, one oxygen atom belonging to a carboxylate group also participates in the hydrogen bond network ($\text{N2}–\text{H}\cdots\text{O3}$: 2.09 \AA ; $\text{N2}–\text{H}\cdots\text{Br2}$: 2.55 \AA). Finally, it must be noted that the replacement of the four carbon chain of butyric acid molecules by shorter or longer chain molecules in hybrids, would certainly modulate the distortions of perovskite layers, if formed, the hydrogen bond network, or the tilt angle of copper clusters related to the perovskite sheets.

In conclusion, we have prepared and structurally characterized an organic–inorganic perovskite based on 4-aminobutyric acid zwitterionic molecules, displaying $\text{Cu}_2(\text{CO}_2)_4$ paddle-wheel clusters which connect adjacent PbBr_4 perovskite sheets. This molecular approach opens interesting perspectives to achieve new SnI_4 based materials with enhanced mobility properties, by selecting suitable entities able to be covalently linked to perovskite layers or able to covalently link adjacent perovskite layers. On the other hand, the incorporation of zwitterionic molecules opens the way to a new class of perovskite based multifunctional materials, and many compounds may be imagined, for instance displaying a bidimensional inorganic subnetwork templating by the anionic parts. Work in these directions is in progress.

Notes and references

‡ Crystal data for **1**: $\text{C}_8\text{H}_{18}\text{N}_2\text{O}_4\text{Br}_4\text{CuPb}$, $M = 796.60$, monoclinic, $a = 8.4581(5)$ \AA , $b = 8.3703(4)$ \AA , $c = 26.907(2)$ \AA , $\beta = 98.62(1)^\circ$, $V = 1883.4(2)$ \AA^3 , space group $P2_1/n$, $Z = 4$, calculated density 2.809, crystal dimensions (mm^3): $0.35 \times 0.12 \times 0.04$, $T = 293$ K, STOE-IPDS diffractometer, graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ \AA), $\mu = 18.55$ mm^{-1} , $2\theta_{\text{max}} = 51.5^\circ$, 14122 measured reflections of which 3572 were unique ($R_{\text{int}} = 0.054$) and 2554 had $I/\sigma(I) > 2$. The intensities were corrected for Lorentz-polarization effects, as well as for absorption effect (Gauss method). The structure was solved by direct methods, and refined by full-matrix least-squares routines against F^2 using the SHELXL97 package. The hydrogen atoms were treated with a riding model. The refinements of positions and anisotropic thermal motion parameters of the non-H atoms, converge to $R(F) = 0.0303$ (2554 reflections, 181 parameters), $wR2(F^2) = 0.0685$ (all data), GOF on F^2 0.892, $\Delta\rho_{\text{max}} = 2.37$ $e \text{ \AA}^{-3}$. CCDC 215378. See <http://www.rsc.org/suppdata/cc/b3/b316847f/> for crystallographic files in .cif format.

- See for instance: (a) J. Kim, B. Chen, T. M. Reineke, H. Li, M. Eddaoudi, D. B. Moler, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2001, **123**, 8239; (b) M. Eddaoudi, J. Kim, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2002, **124**, 376; (c) M. Eddaoudi, J. Kim, D. T. Vodak, A. Sudik, J. Watcher, M. O'Keeffe and O. M. Yaghi, *Proc. Natl. Acad. Sci. USA*, 2002, **99**, 4900.
- D. B. Mitzi, *Progr. Inorg. Chem.*, 1999, **48**, 1–121.
- For instance, for $\text{R} = \text{alkyl}$: (a) D. B. Mitzi, *Chem. Mater.*, 1996, **8**, 791; (b) for $\text{R} = \text{phenylethyl}$: G. C. Papavassiliou, I. B. Koutselas, A. Terzis and M. H. Whano, *Solid State Commun.*, 1994, **91**, 965; (c) for $\text{R} = \alpha$ -methylthiophene: X. H. Zhu, N. Mercier, A. Riou, P. Blanchard and P. Frère, *Chem. Commun.*, 2002, **8**, 2160.
- D. B. Mitzi, K. Chondroudis and C. R. Kagan, *IBM J. Res. Dev.*, 2001, **vol. 45**, n^o 1.
- C. R. Kagan, D. B. Mitzi and K. Chondroudis, *Sciences*, 1999, **286**, 945.
- D. B. Mitzi, C. A. Field, Z. Schlesinger and R. B. Laibowitz, *J. Solid State Chem.*, 1995, **114**, 159.
- D. B. Mitzi, C. D. Dimitrakopoulos, J. Rosner, D. R. Medeiros, Z. Xu and C. Noyan, *Adv. Mater.*, 2002, **14**(n^o 23), 1772.
- (a) D. B. Mitzi, C. A. Feild, W. T. Harrison and A. M. Guloy, *Nature*, 1994, **369**, 467; (b) J. Calabrese, N. L. Jones, R. L. Harlow, N. Herron, D. L. Thorn and Y. Wang, *J. Am. Chem. Soc.*, 1991, **113**, 2328.
- Z. Xu, D. B. Mitzi and D. R. Medeiros, *Inorg. Chem.*, 2003, **42**, 1400.
- R. J. Doedens, *Prog. Inorg. Chem.*, 1976, **21**, 209.
- V. K. Trunov, N. O. Endeladze and A. D. Chaubinidze, *Russ. J. Struct. Chem.*, 1988, **29**, 153.
- Green crystals of $[\text{Cu}_2\text{Br}_2(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_4]\text{Br}_2$ were obtained after a complete evaporation of an aqueous solution containing CuBr_2 and $\text{HO}_2\text{C}-(\text{CH}_2)_3-\text{NH}_2$ in $\frac{1}{2}$ ratio. Crystal data: triclinic, $a = 8.577(5)$ \AA , $b = 8.972(6)$ \AA , $c = 10.503(3)$ \AA , $\alpha = 100.60(4)^\circ$, $\beta = 105.73(3)^\circ$, $\gamma = 111.38(4)^\circ$, $V = 687.4(6)$ \AA^3 , $P1$, $Z = 1$, $\mu = 7.40$ mm^{-1} , 1664 unique reflections, 1366 reflections with $I/\sigma(I) > 2$, $R(F) = 0.032$ (156 parameters), $wR2(F^2) = 0.081$, GOF on F^2 1.097. The structure is built up from cationic clusters of dimeric units of copper atoms $[\text{Cu}_2\text{Br}_2(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_4]^{2+}$ and bromide ions.
- R. D. Willet, *Acta Crystallogr., Sect. C*, 1990, **46**, 565.