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Lead Halide Layers Linked by *trans*-Cu(Gly)$_2$ (Gly = $^-O_2C–CH_2–NH_2$) Pillars in Heterometallic Glycinate Based Organic–Inorganic Hybrids

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The novel hybrid compounds $Pb_2Cu(O_2C–CH_2–NH_2)_2X_4$ (X = Br, Cl) were prepared and characterized by single-crystal X-ray diffraction. TA analysis and DSC measurements show that the compounds are stable up to 200 °C. As in hybrid perovskites, their layered structures are based on metal(II) halide 2D frameworks, which are here covalently linked by *trans*-Cu(Gly)$_2$ flat SBUs. These rigid pillars are able to accommodate some of the void that exists in between the PbX_2 layers. However, the results from hydrogen absorption experiments that were conducted at 77 K indicate that the hybrids are not good candidates for absorption materials.

Introduction

During the past decade, organic–inorganic compounds have received considerable attention because of the opportunity that exists to combine useful properties of both components. For example, in hybrid perovskites, whose typical formula is $(R\text{-}NH_3)_2M^{II}X_4$, the organic component allows the solution to be processed as thin films by room temperature techniques such as spin-coating, whereas the inorganic component may possess semiconducting properties.[1] Extensive work has been notably devoted to the study of materials that are based on iodostannate perovskite layers that can be used as semiconducting channels in thin-film field-effect transistors (TFTs)[2] with the potential of relatively high electrical mobility. For instance, a mobility of $0.6\ cm^2 V^{-1} s^{-1}$ is attained in $(C_6H_5C_2H_5NH_3)_2SnI_4$.[2a] Nevertheless, this value remains two orders of magnitude smaller than that evidenced in $CH_3NH_3SnI_3$, which is a 3D perovskite with metallic conductivity.[3] Several strategies have been considered in order to improve the charge carrier mobility of such semiconducting thin film materials. This includes the search of new, possibly nonperovskite, halogenometallate-based salts.[4] Another way is to tune the bandgap that is associated to a given perovskite network. This is made possible because of the incorporation of selected cations that are able to impact the bonding features of the inorganic framework.[5] Hybrids with enhanced structural dimensionality have also been considered.[6,7] In particular, we recently showed that in $[Cu\{O_2C\text{-}(CH_2)_3\text{-}NH_3\}_2]PbBr_4$ the amino carboxylic acid zwitterionic molecules led both to the stabilization of a layered hybrid perovskite and to the formation of a Br–Cu–Cu–Br covalent bond pathway between adjacent perovskite layers.[7] In relation to amino acids, several coordination compounds have been prepared from molecules that adopt their zwitterionic form.[7–9] However, amino acids, which are ubiquitous in biology, are often used in material chemistry (e.g. coordination polymers, open-framework compounds) in their basic form, as they can coordinate to metal ions through both its carboxylate group and its amino group. With a focus on glycine, metal(II) glycinate salts that are based on robust $M^{II}(Gly)_2$ entities are often cluster-type[10] or pseudo 1D compounds;[11] only a few 2D coordination polymers of heterometallic glycinates have been reported.[12]

In this communication, we report the preparation and the X-ray structural characterization of two 3D heterometallic glycinate hybrids $Pb_2Cu(O_2C–CH_2–NH_2)_2X_4$ [X = Br (**1**), Cl (**2**)]. In the structure of both complexes, the adjacent lead halide layers are linked by *trans*-Cu(Gly)$_2$ (Gly = $^-O_2C–CH_2–NH_2$) to form 3D frameworks. These layered structures can be conceptually considered as a result of the intercalation of neutral *trans*-Cu(Gly)$_2$ entities in the PbX_2 layered network. The rigid pillars do not accommodate much of the void in between the PbX_2 layers and the structures are not porous[13] because of the small size of the glycinate ligand.

Results and Discussion

Reactions of glycine, copper halide, and lead halide (halide = Br, Cl) give rise to two hybrid compounds:

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Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

$Pb_2Cu(O_2C–CH_2–NH_2)_2X_4$ [X = Br (**1**), Cl (**2**)]. A broad band in the 500–800 nm range with a maximum at about 620 nm, is observed in their UV/Vis absorption spectra, which is correlated to the blue color of the crystals and is assigned to a 3*d*–3*d* electronic transition of cupric ions (ESI). The form of the amino acids (HO_2C-R-NH_2) in the solution varies according to the pH value of the solution. The amino acids will be in the cationic, zwitterionic, or basic form in acidic, neutral, or basic solutions, respectively. In the field of hybrid perovskites, bifunctional molecules such as HO_2C-R-NH_3^+ have already been used by us and we demonstrated the role of 1D carboxylic acid supramolecular synthons in the formation of a noncentrosymmetrical hybrid perovskite structure.[14] Recently, we have also shown that $^{-}O_2C$-$(CH_2)_3$-NH_3^+ zwitterionic molecules form a paddle-wheel-type of cluster with copper, which connects the perovskite layers that are stabilized by ammonium counterions.[7] Here, we show that a mixture of glycine, copper, and lead halide, under neutral conditions, affords nice blue crystals of $Pb_2Cu(O_2C–CH_2–NH_2)_2X_4$ (X = Br, Cl) containing $^{-}O_2C–CH_2–NH_2$ anions. The compound crystallizes in the $P2_1/c$ space group, and the crystal structure can be described as layers of lead(II) halide that are linked together by *trans*-Cu(Gly)$_2$ pillars (Figure 1). Copper ions are at the center of a symmetrical unit that consists of two glycinato ligands, and all non-hydrogen atoms approximately lie in a plane that contains the *c* axis (Figures 1 and 2). Two more weakly bonded bromine atoms complete the [4+2] copper(II) coordination sphere as a result of the Jahn–Teller effect (Figure 1). All bond lengths [**1**: $d_{N–Cu}$ = 1.972(5) Å, $d_{O–Cu}$ = 1.967(4) Å, $d_{Br–Cu}$ = 3.167(4) Å; **2**: $d_{N–Cu}$ = 1.959(4) Å, $d_{O–Cu}$ = 1.976(3) Å, $d_{Cl–Cu}$ = 2.995(4) Å] are in good accordance with those reported in the literature for Cu(Gly)$_2$ entities[10,11] or Cu–Br in [4+2] copper polyhedra.[15]

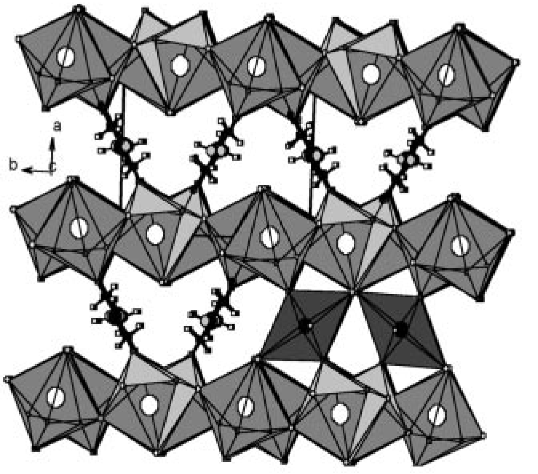

Figure 1. Structure of $Pb_2Cu(O_2C–CH_2–NH_2)_2Br_4$ viewed along the *c* axis that shows layers of lead polyhedra linked by pillars formed by *trans*-Cu(Gly)$_2$ entities. Two copper [4+2] coordination polyhedra, with the weakly bonded bromide atoms taken into account, are shown in deep grey.

Figure 2 shows *trans*-Cu(Gly)$_2$ entities and lead polyhedra that are connected to each other by the carboxylate groups of the organic ligands. The coordination mode of glycinato ligands is [3.2_{12} 2_{23} 1_3] according to the Harris notation,[16] which means that the whole ligand is bound to three metals and that the donor atoms O1, O2 and N chelate to two Pb^{2+} outer ions, one Pb^{2+} and one inner Cu^{2+} ion, and one inner Cu^{2+} ion, respectively. Each lead atom is surrounded by three oxygen atoms and five bromine atoms to build a distorted polyhedron that can be described as an O_2Br_4 trigonal prism capped by two other Br1 and O1 atoms. The last rectangular face that is defined by O1–Br1–Br2–Br2 is open and certainly reveals the stereo effect of the $6s^2$ lone pair of electrons of lead(II) (Figure 2). Pb–O bond lengths are in the range 2.6–2.8 Å [1: O1 2.599(4) Å and 2.720(4) Å, O2 2.820(4) Å; 2: O1 2.585(3) Å and 2.682(3) Å, O2 2.777(7) Å], whereas the distance of the Pb–X bonds are in the range 2.928(1)–3.237(1) Å and 2.796(1) Å–3.120(1) Å for **1** and **2**, respectively. The ability of the soft Pb^{2+} cation to be surrounded by more than six donor atoms together with the weak chelating effect of the bromine atoms allow for the formation of this layered compound which can be conceptually described to result from the intercalation of neutral *trans*-Cu(Gly)$_2$ entities into the PbX_2 layered structure. This intercalation would be associated with a concerted electronic effect between both components: copper(II) is stabilized by part of the electronic density that comes from the halide atoms in the lead halide layers, whereas all the lead atoms accept electronic density from the carboxylate moieties of the glycinato ligands (Figure 3).

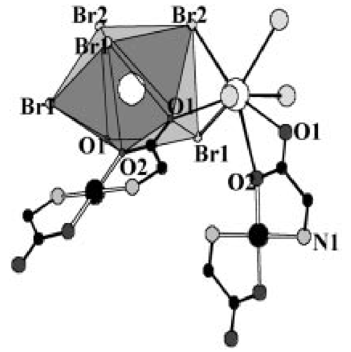

Figure 2. The coordination environment of Pb^{II} and Cu^{II} ions in **1** that shows the *trans*-Cu(Gly)$_2$ entities and the polyhedra of Pb linked together by the carboxylate groups of the organic ligands. The coordination mode of the glycinato ligands is [2.2_{12} 2_{23} 1_3] according to the Harris notation[16] (All of the hydrogen atoms are omitted for clarity).

The representation of the structure by lead polyhedra and *trans*-Cu(Gly)$_2$ pillars (Figure 1) shows infinite channels that run along the *c* axis. However, the drawing of the [4+2] copper polyhedra in Figure 1, or a space filling representation (see Supporting Information) only show small windows, which reveals that both complexes are not porous structures with infinite channels. Nevertheless, consecutive *trans*-Cu(Gly)$_2$ pillars (or [4+2] copper polyhedra) along the *b* axis are shifted from each other by a distance of *c*/2; there are some discrete lattice voids between the lead halide layers and their spherical volume is defined by a radius of 1.6 Å.

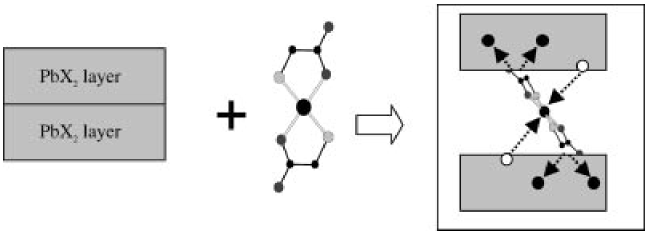

Figure 3. Schematic representation of an hypothetical intercalation of *trans*-Cu(Gly)$_2$ into the PbX$_2$ layered structure, which affords $Pb_2Cu(O_2C–CH_2–NH_2)_2X_4$. Arrows indicate the electron donor effect of the halide and the oxygen atom towards copper(II) and lead(II) ions, respectively.

H_2 absorption measurements were then carried out at 77 K under a pressure of up to 25 bars to give a maximum capacity at high pressure of 0.28% weight for the $Pb_2Cu(O_2C–CH_2–NH_2)_2Br_4$ sample (see Supporting Information), which is far from the values that were obtained in MOFs chemistry (1–8% range).[17]

In conclusion, we have described the synthesis and the structural characterization of 3D heterometallic glycinate salts $Pb_2Cu(O_2C–CH_2–NH_2)_2X_4$ (X = Br, Cl). As in hybrid perovskites, their layered structure is based on a metal(II) halide 2D framework, which is here covalently linked by *trans*-Cu(Gly)$_2$ units by the carboxylate groups of glycinato ligands. We now plan to use others such linkers with non-oxidative metals in order to achieve lead(II) or tin(II) iodide based materials that possess semiconducting properties. With regard to the field of coordination polymers, we have shown that the association of the glycinato ligands with both Cu^{2+} and soft Pb^{2+} cations and halide anions leads to an unprecedented 3D architecture. Suitable microporous coordination polymers, especially those that possess small pores or compounds that are based on ligands with incorporated open metal sites,[18] are increasingly sought, and *trans*-M^{II}(Gly)$_2$ could be considered as a building block for the design of such compounds.

Experimental Section

Synthesis and Thermal Analysis: $CuBr_2$ (0.2241 g, 1 mmol, 99%) was dissolved in distilled water (60 mL). The solution was stirred and glycine (0.7539 g, 10 mmol, 99.7%) was then added. After 2 h, $PbBr_2$ (0.7345 g, 2 mmol, 98%) was added to the solution, and the solution was then heated at 60 °C and stirred for another 4 h before it was placed into an aerator. Diamond-like blue crystals were obtained several hours later in a yield of 68.3% (0.646 g, based on $CuBr_2$). The synthesis of **2** was almost the same as **1**, but blue crystals were obtained after one day in a yield of 53.6% (0.411 g, based on $CuCl_2·2H_2O$). For both compounds, X-ray powder diffraction indicated single-phase samples (ESI).

Thermogravimetric analysis measurements and differential scanning calorimetry were performed in the range of 20–900 °C and 20–450 °C, respectively. The first endothermic peak that was observed at about 200 °C was assigned to the melting of the compounds (DSC), and it occurs just before the first weight loss of 10.6% (for **1**) or 13.4% (for **2**) observed in TGA. The second weight loss of 81.3% (for **1**) or 69.8% (for **2**) can be assigned to the departure of PbX_2 (theoretical: **1** 77.6%, **2** 72.0%). The first weight loss probably corresponds to the departure of a part of the ligands [$H_2N–CH_2–COOH$: 150 g/mol, observed 99.3 g/mol (for **1**) or 102.9 g/mol (for **2**)], the remaining compound was CuO at higher temperature.

Crystal Data for 1: $C_4H_8Br_4CuN_2O_4Pb_2$, M = 945.68, monoclinic, a = 8.556(1) Å, b = 10.971(2) Å, c = 8.376(1) Å, β = 108.68(3), V = 744.8(3) Å^3, space group $P2_1/c$, Z = 2, calculated density 4.217, crystal dimensions (mm^3): 0.12 × 0.10 × 0.08, T = 293 K, Bruker Nonius Kappa CCD diffractometer, graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å), μ = 34.69 mm^{-1}, $2\theta_{max}$ = 60.04°, 11337 measured reflections of which 2173 were unique (R_{int} = 0.057) and 1744 had $I/\sigma(I) > 2$. The intensities were corrected for Lorentz-polarization effects, as well as for absorption effect (SADABS). The structure was solved by direct methods, and refined by full-matrix least-squares routines against F^2 with the use of the SHELXL97 package. Hydrogen atoms were placed in idealized positions in riding mode. The refinements of positions and anisotropic thermal motion parameters of the non-H atoms, converge to $R_{(F)}$ = 0.0274 (1744 reflections, 80 parameters), $wR_{2(F2)}$ = 0.0605 (all data), GOF on F^2 = 1.124, $\Delta\rho_{max}$ = 1.224 eÅ^{-3}.

Crystal Data for 2: $C_4H_8Cl_4CuN_2O_4Pb_2$, M = 767.84, monoclinic, a = 8.424(1) Å, b = 10.404(2) Å, c = 8.237(1) Å, β = 109.02(3), V = 682.5(3) Å^3, space group $P2_1/c$, Z = 2, calculated density 3.736, crystal dimensions (mm^3): 0.15 × 0.10 × 0.10, T = 293 K, Bruker Nonius Kappa CCD diffractometer, graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å), μ = 26.93 mm^{-1}, $2\theta_{max}$ = 60.04°, 8282 measured reflections of which 1987 were unique (R_{int} = 0.039) and 1553 had $I/\sigma(I) > 2$. The intensities were corrected for Lorentz-polarization effects. The structure was solved by direct methods, and refined by full-matrix least-squares routines against F^2 with the use of the SHELXL97 package. Hydrogen atoms were placed in idealized positions in riding mode. The refinements of positions and anisotropic thermal motion parameters of the non-H atoms, converge to R_F = 0.0276 (1553 reflections, 79 parameters), $wR_{2(F2)}$ = 0.0445 (all data), GOF on F^2 = 1.028, $\Delta\rho_{max}$ = 0.835 eÅ^{-3}.

CCDC-613293 and -613294 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Hydrogen Storage Measurements: Hydrogen storage measurements were made with a volumetric device (Sievert's method) equipped with calibrated and thermalized volumes and pressure gauges. In order to remove water and all species that can lie within the pores and channels, the samples were outgassed while heated at 150 °C over a 16 h period under primary vacuum. All weight capacities refer here to outgassed samples. For measurements at 77 K, the sample holder was immersed in liquid nitrogen and the pressure variations due to both gas cooling and hydrogen adsorption were measured with the use of high-purity hydrogen (Alphagaz H22). Under these thermodynamic conditions, the ideal gas law is no longer valid and different equations of state were used depending of the temperature ranges.[19]

Supporting Information (see footnote on the first page of this article): UV/Vis absorption and XRPD pattern of crystals **1** and **2**, TGA and DSC graphs of both compounds, absorption analysis and additional figures for structural illustration of **1**.

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