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Anion controlled 2D assembly of a La–Cu cation array and its unusual magnetic properties

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A novel 2D La–Cu heteronuclear coordination polymer, formed by the synergetic effect of Cl^- and ClO_4^-, possesses an irregular triangular lattice of copper ions, and shows unusual magnetic relaxation properties.

Ladder-like 2D copper arrays have attracted much attention in the last fifteen years owing to the key role of Cu–O layers in high temperature superconductors.[1] Meanwhile, the structure and magnetic behavior of many square-planar molecular compounds have been studied extensively, especially for the A_2CuX_4 series.[2,3] On the other hand, geometrically frustrated two-dimensional systems with triangular or kagome lattices have attracted continued interest both theoretically and experimentally.[4] However, genuine 2D copper molecular materials containing such lattices are surprisingly scarce. $Cu_2(OH)_3X$ may be a unique example of a triangular lattice, which shows a coexistence of long range ordering and spin glass-like behavior.[5] In 1998, we reported the 2D 4f–3d coordination polymers $Ln_2M_3(EDTA)_3(H_2O)_{11}\cdot 12H_2O$ (M = Co, Mn), in which the connection of the M ions led to a kagome lattice.[6] In continuation of this work, nitrilotriacetic acid (H_3NTA) was used as a multidentate bridging ligand, and two types of inorganic anions were introduced, which led to a novel 2D La–Cu assembly formulated as $[LaCuCl(NTA)(H_2O)_6]ClO_4\cdot H_2O$ **1**, in which the copper connections afforded an irregular triangular lattice. From the view point of synthetic chemistry, the template effect of inorganic anions has been well documented in the formation of some cluster compounds, for example, Cl^- for $[Eu_{15}Cl(\mu_3\text{-Tyr})_{10}(\mu_3\text{-OH})_{20}(\mu_2\text{-}H_2O)_5(OH)_{12}(H_2O)_8](ClO_4)_2\cdot 56H_2O$, $\mu_{12}\text{-}ClO_4^-$ in $[Ln_6Cu_{12}(OH)_{24}(H_2O)_{18}(pyb)_{12}ClO_4](ClO_4)_{17}\cdot nH_2O$ (pyb = pyridine betaine) (Ln = Nd, Sm, Gd and Y) and O^{2-} in $[Ln_6O(OH)_8(H_2O)_{24}](ClO_4)_8\cdot 6H_2O$.[7] In contrast, as monodentate ligands and counter ions, both Cl^- and ClO_4^- play a crucial role in the formation of compound **1**.

A mixture of $Cu(OH)_2$ (3 mmol) and H_3NTA (3 mmol) was dissolved in 30 ml H_2O, then $La(ClO_4)_3$ (1.5 mmol) and $LaCl_3$ (1.5 mmol) were added under vigorous stirring. The pH of the solution was adjusted carefully to 5.0. After being filtered, the solution was concentrated to 15 ml and left at room temperature. Blue rectangular crystals of **1** were deposited in *ca*. 40% yield after two weeks.†

X-Ray crystallography‡ has established that complex **1** adopts a two-dimensional honeycomb-like layer with nine-coordinate lanthanum and five-coordinate copper ions located at the apexes of each hexagon. As shown in Fig. 1(a), the NTA ligand coordinates to Cu in a tetradentate manner through three oxygen atoms (O1, O3, O5) of three different carboxyl groups and a nitrogen atom (N), forming three five-membered rings. The fifth coordination site of Cu is occupied by a chloride ion (Cl1). The remaining three carboxyl oxygen atoms (O2, O4, O6) of the NTA coordinate to three different adjacent lanthanum ions forming three *anti–anti* carboxylic bridges between Cu and La ions. For La, three oxygen atoms from three different NTA ligands (O2, O4A, O6B) occupy three coordination sites of La with three similar angles (O2–La–O4A 76.0°, O2–La–O6B 81.6° and O4A–La–O6B 78.5°). The remaining six coordination sites of La are taken up by six water molecules (O7–O12). The complex can be regarded as a polymer in which CuCl(NTA) units are linked to each other by $La(H_2O)_6$ bridges from three different directions, forming a two-dimensional metal-apex honeycomb [Fig. 1(b)], very different from the honeycomb of $[Ln_2M_3]$ found in $Ln_2(ox)[Cu(pba)]_3[Cu(H_2O)_5]\cdot 20H_2O$ [Ln = La–Gd, pba = 1,3-propylenebis(ox-

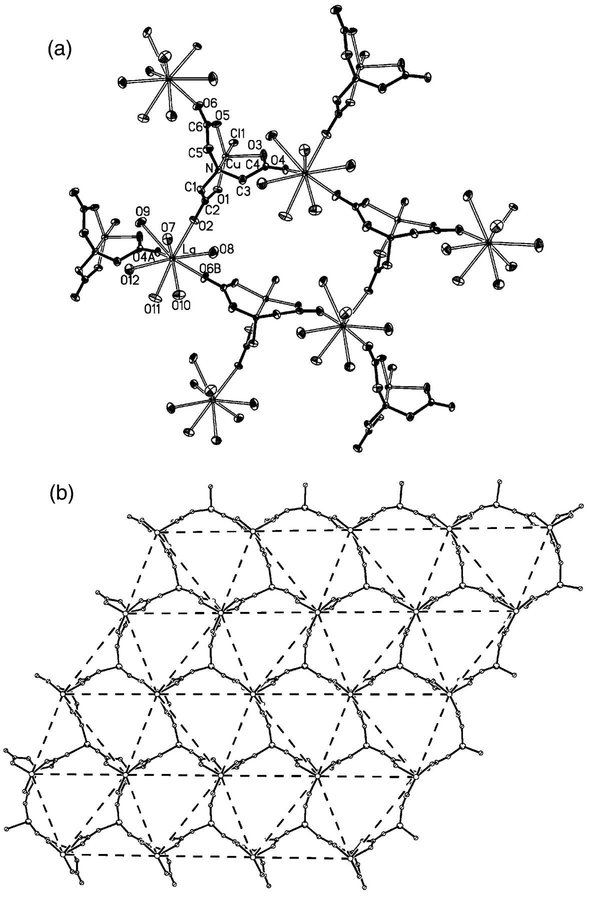

Fig. 1 (a) An ORTEP drawing of **1** showing the connections between La^{3+} and Cu^{2+}. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): La–O6 2.466(5), La–O4 2.501(5), La–O2 2.541(6), La–O7 2.545(6), La–O10 2.566(6), La–O11 2.568(6), La–O8 2.579(6), La–O12 2.604(7), La–O9 2.622(6), Cu–O1 1.969(4), Cu–O5 1.988(5), Cu–N 2.010(6), Cu–Cl1 2.218(2), Cu–O3 2.222(5); O4A–La–O6B 78.47(19), O2–La–O6B 81.6(2), O2–La–O4A 75.97(19), O1–Cu–O5 151.9(2), O1–Cu–N 84.3(2), O5–Cu–N 85.1(2), O1–Cu–Cl1 95.90(17), O5–Cu–Cl1 95.13(16), N–Cu–Cl1 178.97(18), O1–Cu–O3 110.0(2), O5–Cu–O3 93.9(2), N–Cu–O3 81.2(2). (b) Viewed along the *c* axis (*ab* plane) showing the honeycomb structure and the irregular triangular lattice formed by copper ions (dashed lines).

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amato)][8] and $Ln_2M_3(edta)_3(H_2O)_{11}\cdot 12H_2O$,[6] where M ions occupy the center position of edges of hexagons. The intralayer La···Cu distances (6.34, 6.35 and 6.43 Å) are nearly equal but the distortion of the hexagon leads to neighboring intralayer Cu···Cu distances of 8.57, 9.30 and 10.11 Å, respectively; accordingly the connection of closest neighboring copper ions affords an irregular triangular lattice. It is also noted that the closest interlayer Cu···Cu separations are 7.44, 8.56 and 9.16 Å, comparable with those in the layer. In this sense, **1** is not an ideal 2D compound.

Experiments using only $La(ClO_4)_3$ or $LaCl_3$ did not give rise to this La–Cu complex, suggesting that both Cl^- and ClO_4^- have a synergetic effect in forming this heteronuclear complex. Compared with the Ln_{15} cluster which contains a central Cl^- ion as a template and ClO_4^- ions as counter ions,[7a] the Cl^- in complex **1** does not act as a template, but directly coordinates to Cu, and formation of **1** was impossible without Cl^-. The role of ClO_4^- as a counter ion in complex **1** may lie in it occupying the holes of the honeycomb and stabilizing the lattice. Since the volume of Cl^- is much smaller than that of ClO_4^-, the lattice might be destabilized if the counter ion is changed from ClO_4^- to Cl^-. These facts suggest that the formation of **1** is controlled by both Cl^- and ClO_4^-. Presumably, Cl^- and ClO_4^- could be replaced by other anions similar to them. For example, Cl^- may be replaced by Br^-, I^-, CN^-, OCN^- or even SCN^- , and ClO_4^- may be replaced by PF_6^-, BF_4^-, NO_3^- *etc.* The use of larger organic anions to explore the possibility of obtaining well separated 2D triangular compounds as well as replacement of La^{3+} by other lanthanide ions to yield chain complexes, will be reported elsewhere.

Preliminary magnetic investigations were made for **1**. The temperature dependence of the magnetic susceptibility in the temperature range 2–200 K at an applied field of 10 kOe is shown in Fig. 2(a). The value of $\chi_M T$ is 0.4 $cm^3\ mol^{-1}$ K at 200 K and increases very slowly to a maximum of 0.47 $cm^3\ mol^{-1}$ K between 13 and 6 K, then decreases upon further cooling. The data could not be fitted well using the Lines' model for a quadratic layer Heisenberg antiferromagnet,[9] but fitting the data to the Curie–Weiss law gave $C = 0.398\ cm^3\ mol^{-1}$ K and $\theta = 2.6$ K, indicative of weak ferromagnetic behavior. This might be considered as the result of frustration in the 2D triangular array of copper ions. If so, spin glass behavior should be expected for the geometrically frustrated system as for $Cu_2(OH)_3X$.[5b] However, zero field ac measurements did not give any peaks for either real χ' or imaginary χ'' as shown in Fig. 2(b) probably owing to weak coupling between Cu ions in **1** at zero field as a result of the large Cu···Cu separations. When a dc field (10 kOe) was applied, the antiferromagnetic (AF) interactions among Cu ions (including inter-layer) will be enhanced, and accordingly the frustration due to the AF interaction of triangularly arranged Cu ions may result in the very unusual magnetic relaxation shown in Fig. 2(b).[10] Peaks for χ' and χ'' are observed in the dc field, and are strongly frequency dependent. If we calculate the value of relative variation of peak temperature (T_p) per decade of frequency, $\varphi = \Delta T_p/[T_p\Delta(\log f)] = 1.2$, which is rather large and distinctly different from the behavior of normal spin glasses ($\varphi < 0.1$).[11] Further investigation on the mechanism of the unusual magnetic relaxation is under way.

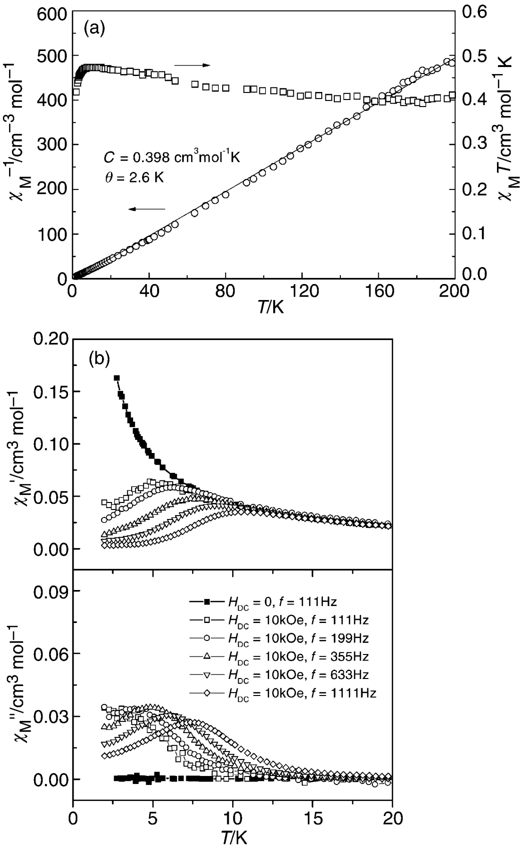

Fig. 2 (a) Temperature dependence of the dc susceptibility of **1** measured at a field of 10 kOe. (b) Temperature dependence of the ac susceptibility of **1** measured at zero dc bias field and at 10 kOe for different ac frequencies (top: real χ', bottom: imaginary χ'').

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Notes and references

† *Elemental analysis* for **1**: Calc. C, 11.06; H, 3.09; N, 2.15. Found: C, 11.18; H, 2.94; N, 1.95%.

‡ *Crystal data*: $C_6H_{20}Cl_2CuLaNO_{17}$, $M = 651.58$, orthorhombic, space group $Pca2_1$, $a = 15.975(2)$, $b = 9.2980(10)$, $c = 12.726(2)$ Å, $V = 1890.3(4)$ Å^3, $Z = 4$, $D_c = 2.290$ Mg m^{-3}, $\mu = 3.722$ mm^{-1}, $F(000) = 1276$, GOF = 1.040. The final R_1 and wR_2 are 0.0273 and 0.0698, respectively, for 275 parameters and 1948 relections [$I > 2\sigma(I)$]. CCDC 182/1730. See http://www.rsc.org/suppdata/cc/b0/b003293j/ for crystallographic files in .cif format.

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