An azido–metal–isonicotinate complex showing long-range ordered ferromagnetic interaction: synthesis, structure and magnetic properties†

Yong-Fei Zeng,[a] Fu-Chen Liu,[a] Jiong-Peng Zhao,[a] Shuang Cai,[a] Xian-He Bu*[a] and Joan Ribas[b]

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A new 3D Cu^{II} complex [Cu$_{1.5}$(N$_3$)$_2$(isonicotinate)]$_n$ [1], which features two types of bridging modes for azide ($\mu_{1,1}$ and the rare asymmetric $\mu_{1,1,3}$) where the three bonds of the $\mu_{1,1,3}$-N$_3^-$ group to Cu exhibit three different distances, has been synthesized and characterized, and magnetic measurements indicate that [1] experiences long-range ferromagnetic ordering at approximately 6 K.

The investigation of molecule-based magnetic materials with novel topology has evoked researchers great interest in the field of coordination and material chemistry.[1] The design of systems exhibiting long range ferromagnetic ordering material is one of the main goals among them.[2] As a versatile bridging ligand, azide has attracted much attention for its inherent advantages to the construction of such materials.[3] The two typical coordination modes of bridging azide: end-to-end (EE) and end-on (EO) usually correspond to antiferromagnetic and ferromagnetic exchange interactions,[4] respectively. However, there is a common feature for most complexes with azide bridging ligand: their low-dimensionality.[5] Thus, a question arises: how to construct high-dimensional metal–azide materials? This is still an urgent problem confronted by researchers. A possible answer is to introduce a second bridging ligand into the azide-based system.[6] Up to now, most of the reported co-ligands are neutral.[7] Indeed, charged ligands as a second ligand together with azide, have been scarcely reported.[8,9]

Although hydrothermal reaction has been one of the powerful tools in synthesizing coordination architectures, as far as azide is concerned, few attempts have been made probably due to its explosive potential.[9] As a result of our continuing efforts in this study, we successfully isolated a new 3D azide Cu^{II} compound, [Cu$_{1.5}$(N$_3$)$_2$(isonicotinate)]$_n$ (**1**),‡ with isonicotinate as co-ligand, which is, to our knowledge, the first example of an azido–metal–isonicotinate complex exhibiting long-range ferromagnetic ordering, and demonstrating, thus, the potentiality of this 'two-ligands method'. In this new 3D azido–metal system, the azide ligand acts in the $\mu_{1,1}$ and the rare asymmetric $\mu_{1,1,3}$ modes.[10,11]

X-Ray analysis§ reveals that the unique crystallographic unit of **1** contains one and a half Cu^{II} ions, two azide anions and one isonicotinate anion. Cu(1) has a slightly distorted five-coordinated square-based pyramid (CuON4) and Cu(2) has a six-coordinated elongated octahedron (CuO$_2$N$_4$), resulting from the Jahn–Teller effect. The Cu(2) ion is located at the crystallographic inversion center (Fig. 1). The apical position of Cu(1) is occupied by a nitrogen atom N5 of the azide in $\mu_{1,1,3}$ mode [Cu(1)–N(5) 2.386(6) Å] and the equatorial plane is formed by an oxygen atom of carboxylato [Cu(1)–O(1) 1.939(3) Å] and two equivalent nitrogen atoms of two $\mu_{1,1}$ bridging azides [Cu(1)–N(5B) 2.027(5) Å], and one bridging pyridinecarboxylate [(Cu(1)–N(1B) 2.027(4) Å)], respectively. The apical positions of Cu(2) is occupied by two equivalent nitrogen atoms from two $\mu_{1,1,3}$ bridging azido ligands [Cu(2)–N(7D) 2.544 Å] and the equatorial plane formed by two equivalent oxygen atoms from two carboxylato ligands [Cu(2)–O(2) 1.939(3) Å] and two equivalent nitrogen atoms from two $\mu_{1,1}$ bridging azido ligands [Cu(2)–N(2) 1.992(5) Å]. The Cu(1)–N(2)–Cu(2) angle in the EO bridge is normal (106.7(2)°). One *syn-syn* carboxylato and one equatorial–equatorial (symmetric) $\mu_{1,1}$ (end-on) azido bridging group link two consecutive Cu^{II} ions to form a trinuclear Cu^{II} [Cu(1)–Cu(2)–Cu(1)] entity. These trinuclear entities form 2D sheets through equatorial (short)–apical (medium)–apical (long) $\mu_{1,1,3}$ azido briding groups (Fig. 2(a)). Finally, these sheets form a 3D structure *via* pyridinecarboxylate bridges (Fig. 2(b)).

The magnetic properties of complex **1** as a $\chi_M T$ *vs.* T plot (χ_M is the molar magnetic susceptibility for three Cu^{II} ions) are shown in Fig. 3 and Fig. S1 (ESI†). At low temperature $\chi_M T$ depends on the magnetic field. This feature is shown in a reduced scale in Fig. 3 (inset). The H values used in this experiment were 45, 200, 500, 1000, 5000 and 10000 G. For the smallest field (45 G) the maximum $\chi_M T$ reaches 250 cm^3 mol^{-1} K. These features indicate long-range magnetic order at approximately 6 K, which will be commented on below.

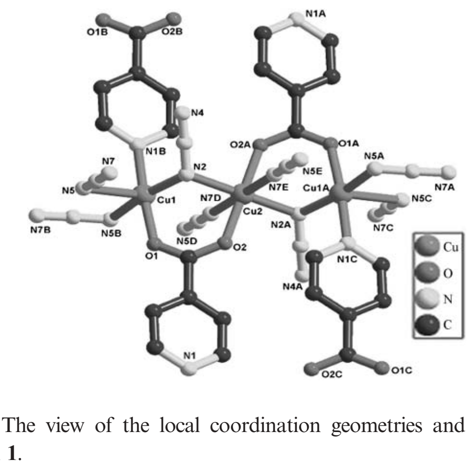

Fig. 1 The view of the local coordination geometries and linkage of complex **1**.

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[a] *Department of Chemistry, Nankai University, Tianjin, 300071, China. E-mail: buxh@nankai.edu.cn; Fax: +86-22-2350 2458; Tel: +86-22-2350 2809*
[b] *Departament de Química Inorgànica Universitat de Barcelona, Diagonal 6487, 08028-Barcelona, Spain*

† Electronic supplementary information (ESI) available: Synthetic procedures and cautionary measures. Fig. S1: The high-temperature $\chi_M T$ *vs.* T curve for complex **1** at 10000 G. See DOI: 10.1039/b601311b

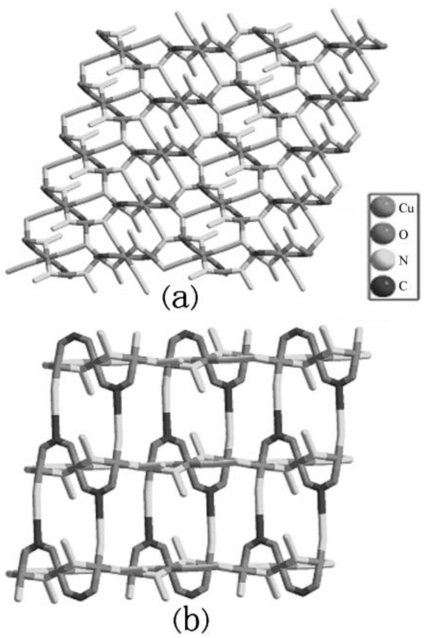

Fig. 2 (a) The 2D sheet constructed from azide and carboxylato in **1**. For clarity, the pyridine ring has been omitted; (b) The simplified 3D structure of **1** constructed from the 2D sheet through pyridinecarboxylate bridges.

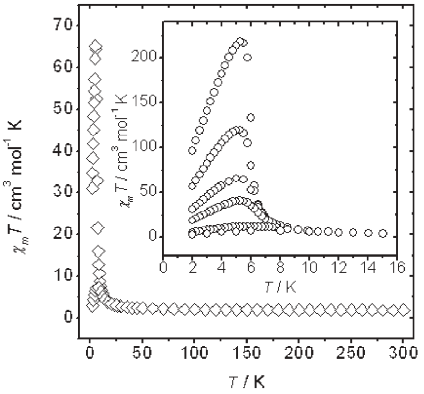

Fig. 3 Plot of $\chi_M T$ *vs.* T for complex **1**. Inset: plot of $\chi_M T$ *vs.* T depending on the magnetic field at low temperatures, the H values used in this experiment were 45, 200, 500, 1000, 5000 and 10000 G.

The high-temperature curve at 10000 G is shown in Fig. S1 (ESI†). The value of $\chi_M T$ at 300 K is 1.4 cm^3 mol^{-1} K, which is as expected for three magnetically quasi-isolated spin doublets ($g > 2.00$). Starting from room temperature, $\chi_M T$ values increase to 1.8 cm^3 mol^{-1} K at 60 K. Below this temperature there is the clear divergence with the field. Thus, for fitting the susceptibility data, we have eliminated the experimental data from 60 to 2 K .

Complex **1** is, actually, a complicated 3D network made by the trinuclear Cu^{II} [Cu1–Cu2–Cu1] entities with one *syn-syn* carboxylato and one equatorial–equatorial (symmetric) end-on ($\mu_{1,1}$) azido bridging group linking two consecutive Cu^{II} ions. These trinuclear entities form the 3D network through equatorial (short)–apical (medium)–apical (long) ($\mu_{1,1,3}$) azido bridging groups and pyridinecarboxylate bridges. This asymmetric coordination mode, as we will comment later, always gives weak magnetic coupling. Thus, the magnetic data at high temperature (Fig. S1, ESI†) can be fitted assuming quasi-isolated Cu^{II} trimers. The fit of the susceptibility data has been carried out using the Hamiltonian $H = -J(S_1S_2 + S_2S_3)$ and applying the formula given by Kahn.[12] The two parts of the trimer are identical (related by an inversion center at Cu2). Thus, only a single J value is necessary for the fit. The best-fit parameters obtained are $J = 80 \pm 5$ cm^{-1}, $g = 2.11 \pm 0.01$ and $R = 1.7 \times 10^{-5}$. The noticeable J value can be interpreted as a consequence of the existence of two different bridging ligands: (a) the isolated *syn-syn* carboxylato should give weak antiferromagnetic coupling. In the *syn-syn* coordination mode in the Cu^{II} complexes, there is a marked dependence of J on the number of carboxylate bridges (4 > 3 > 2 > 1). The two extreme cases ($n = 4$ or $n = 1$) are very different. For $n = 4$ the J parameter may have high antiferromagnetic values such as $J < -400$ cm^{-1}.[12] With only one carboxylate bridging group in *syn-syn* geometry very few complexes have been reported, an example is [{LCuX}$_2$(μ-benzoate)](ClO$_4$) (X = Cl, Br; L = 1,4,7-trimethyl-1,4,7- triazacyclononane).[13] The J values are very small: −2.4 and −4.6 cm^{-1} respectively;[14] (b) the other bridging ligand ($\mu_{1,1}$ (end-on) azido) is much more important from a magnetic point of view. Indeed, the studies carried out with $\mu_{1,1}$ azido bridges with different metal ions are very numerous and it has been clearly demonstrated that, with only a few exceptions, the coupling is always ferromagnetic.[15] Focusing on Cu^{II} (as in complex **1**) the magnitude of the J parameter depends on several factors, mainly the Cu–N–Cu angle, the Cu–N lengths and the torsion of the N$_3$ ligand with regard to the CuNCuN plane.[16] Values greater than 170 cm^{-1} have been reported for a Cu–N–Cu angle of 104.0°.[17] Thus the calculated J value of 80 cm^{-1} agrees with the standard values reported for such systems. It must be emphasized that in **1** the J value is not only the sum of the two separated components. Indeed, as reported by Kahn for similar, but not identical, systems,[12] and by Escuer and co-workers[8] for the same structural skeleton, the strong ferromagnetic coupling is due to the counter-complementarity of the superexchange pathways of the two ligands. For an angle of Cu–N–Cu of 111.9° Escuer *et al.* found a J value of +75 cm^{-1}, very similar to that calculated for complex **1** (Cu–N–Cu angle 106.7°). The MO calculations made by Escuer *et al.*, corroborate in a general manner the counter-complementarity of this geometry.[8]

The reduced molar magnetization ($M/N\beta$ value) per three Cu^{II} ions at 2 K (Fig. 4) tends to 3.0 $N\beta$ but the curve does not follow

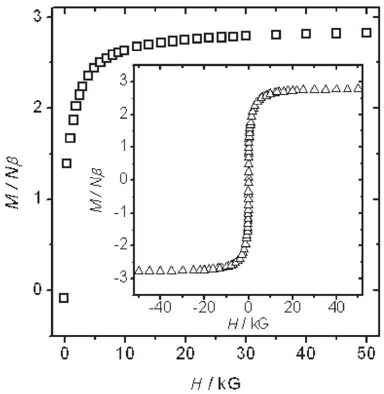

Fig. 4 The reduced molar magnetization ($M/N\beta$ value) per three copper ions at 2 K. Inset: plot of hysteresis loop for **1**.

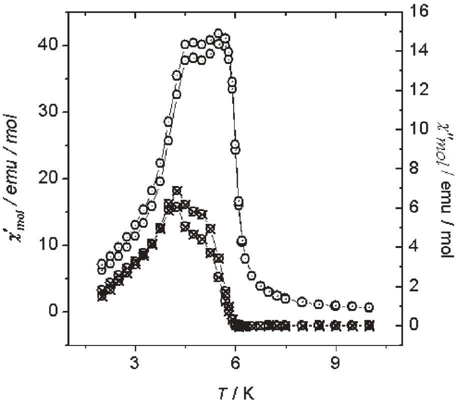

Fig. 5 Plot of χ' (○) and χ'' (●) *vs.* T for **1** (frequencies used; 1340 and 133 Hz).

the Brillouin law. Indeed, there is a rapid and abrupt increase of the $M/N\beta$ at low fields. This is the signature of long-range order, commented above when dealing with $\chi_M T$ values at low temperature. To corroborate this feature we carried out two new experiments: a hysteresis loop which indicates that there is no noticeable hysteresis (typical phenomenon in these soft magnets) and an ac susceptibility measurement (Fig. 5). Fig. 5 clearly corroborates the existence of long-range ferromagnetic order below 6 K. The presence of an out-of-phase (χ'') signal is the typical signature. This signal is frequency independent, indicating that the order is three-dimensional, as expected from the structure.

This 3D ordering may be explained by the existence of asymmetric azido bridges, that link (together to the pyridinecarboxylato units) the trinuclear entities to give the 3D net. The pyridinecarboxylato bridges do not likely have any importance in terms of the long-range order. However, the asymmetric azido bridges are very important. Indeed, Ruiz and co-workers[10] have recently demonstrated that these asymmetric azido bridges can give ferro- or antiferromagnetic coupling, following a general trend opposite to that reported for the symmetric cases: end-on bridges generally produce antiferromagnetic coupling while the end-to-end can present ferro- or antiferromagnetic coupling depending on the copper coordination sphere. Both types of asymmetric modes are present in the net of complex **1**, thus being responsible for the ferromagnetic ordering.

In conclusion, the first azido–metal–isonicotinate complex showing a long-range ordered ferromagnetic interaction, in which there are two types of bridging mode for azide, has been synthesized by hydrothermal reaction. We have, thus, opened a new perspective to generate molecule-based magnets starting from azido bridging ligands: to increase the dimensionality by adding a co-ligand that can be the versatile carboxylate anion.

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Notes and references

‡ Complex **1** was hydrothermally synthesized under autogenous pressure. A mixture of $Cu(NO_3)_2 \cdot 3H_2O$, NaN_3, Hnta and H_2O at a ratio of 2 : 2 : 1 : 3000 was sealed in a Teflon-lined autoclave and heated to 140 °C for 2 days and cooled to room temperature at 10 °C h^{-1}. The crystals were obtained in *ca.* 20% yield based on copper. The elemental analysis was satisfactory. **CAUTION!** Azide complexes are potentially explosive. The experiments were carried out in an isolated room and experimenters should be equipped with safeguards. Only a small amount of the materials should be prepared and handled with care. The detailed procedure for synthesis is presented in the ESI.†

§ *Crystal data* for **1**: monoclinic, space group $P2_1/c$, a = 9.0054(14), b = 6.1591(10), c = 17.402(3) Å, β = 100.392(2)°, V = 949.4(3) Å^3, Z = 2, λ(Mo-Kα) = 0.71073 Å, 4406 reflections collected, 1767 unique (R_{int} = 0.1087), $R1$ = 0.0461, $wR2$ = 0.1005 [$I > 2\sigma(I)$]. CCDC 272230. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b601311b

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