Isolation of a new two-dimensional honeycomb carbonato-bridged copper(II) complex exhibiting long-range ferromagnetic ordering†

Arpi Majumder,[a] Chirantan Roy Choudhury,[a] Samiran Mitra,*[a] Georgina M. Rosair,[b] M. Salah El Fallah*[c] and Joan Ribas[c]

Received (in Cambridge, UK) 9th November 2004, Accepted 21st February 2005
First published as an Advance Article on the web 7th March 2005
DOI: 10.1039/b417019a

Atmospheric CO_2 fixation by an aqueous solution containing $Cu(ClO_4)_2 \cdot 6H_2O$ and 4-aminopyridine (4-apy) yields a novel example of a two-dimensional μ_3-CO_3 bridged copper(II) complex $\{[Cu(4\text{-}apy)_2]_3(\mu_3\text{-}CO_3)_2(ClO_4)_2 \cdot \frac{1}{2}CH_3OH\}_n$ 1 that has been characterized by IR, UV and X-ray crystallography; preliminary magnetic measurements show that complex 1 exhibits long-range ordered ferromagnetic coupling.

The carbonate anion can act as an extremely versatile bridging ligand, with its flexibility in coordination modes, leading to a wide variety of magnetic behaviour from strong to moderate or weak coupling which is either antiferromagnetic or ferromagnetic.[1] Focusing our interest on copper(II) complexes, the carbonato bridging ligand is able to generate complexes with varying nuclearity ranging from dimers,[1a] trimers[1b–1i] and tetramers,[1j] as well as one-dimensional,[2a,b] two-dimensional[2c,d] and three-dimensional[2e] extended systems. Natural chalconatronite, $Na_2Cu(CO_3)_2 \cdot 3H_2O$ is one-dimensional,[2b] its artificial anhydrous form is two-dimensional[2d] and the minerals malachite and azurite $[Cu_3(OH)_2(CO_3)]$ are three-dimensional systems. Among all these systems, the triangular μ_3-CO_3 coordination mode is the most frequent,[1b–1i] with the added interest that this geometry might offer the possibility to study frustrated spin systems.[3]

Metal-carbonato complexes are structurally characterised in relation to bio-inorganic models, environmental fields[4a] as well as catalytic studies.[4b] On the other hand, the nucleophilic fixation of atmospheric CO_2 by metal complexes to afford the metal-hydrogenocarbonate or carbonate species is relevant to some metalloenzymes such as carbonic anhydrase, D-ribulose, non-heme iron in the photosynthetic system-II or copper complexes of the cyclic peptide ascidiacyclamide.[5] The isolation of carbonato-bridged complexes from the reaction between a solution of an appropriate aminate ligand as a blocking agent with copper(II) precursor salts by the nucleophilic fixation of atmospheric CO_2 was first suggested by Curtis *et al.*[6a] and structurally confirmed by Einstein and Willis.[6b]

In recent years, new methods of making new magnetic molecular materials have been devised.[7] Molecular-based magnets have been obtained using organic radicals, extended metal-complexes or hybrids of metal-complexes and organic radicals.[8] The origin of this long-range order can be the ferromagnetic

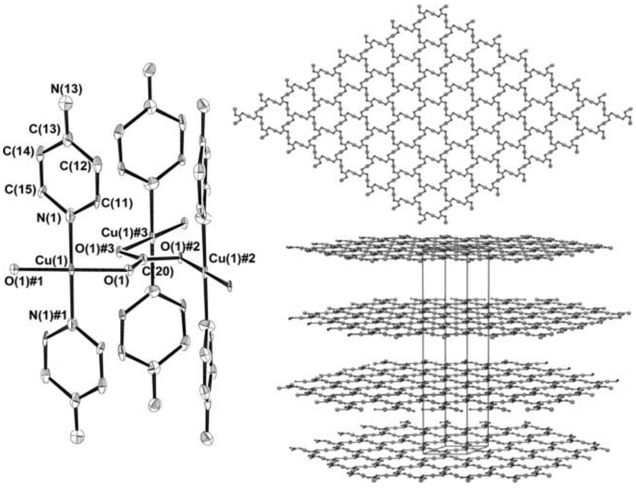

Fig. 1 Left: crystal structure of **1** (without H, ClO_4 and CH_3OH for clarity). Selected bonds lengths [Å] and angles [°]: Cu(1)–O(1) 1.951(7), Cu(1)–O(1)#1 1.951(7), Cu(1)–N(1) 1.998(9), Cu(1)–N(1)#1 1.997(9), C(20)–O(1) 1.288(7), C(20)–O(1)#2 1.288(7), C(20)–O(1)#3 1.288(7), O(1)–Cu(1)–O(1)#1 180.0(4), O(1)#1–Cu(1)–N(1), 89.9(3), O(1)–Cu(1)–N(1), 90.1(3), N(1)#1–Cu(1)–N(1), 180.0(1), C(20)–O(1)–Cu(1), 107.6(4), O(1)–C(20)–O(1)#2, 119.97(7), O(1)–C(20)–O(1)#3, 119.97(7). Right: schematic diagram showing a honeycomb-like motif based upon 24-membered tessellated rings in which only Cu and μ_3-CO_3 are shown for clarity.

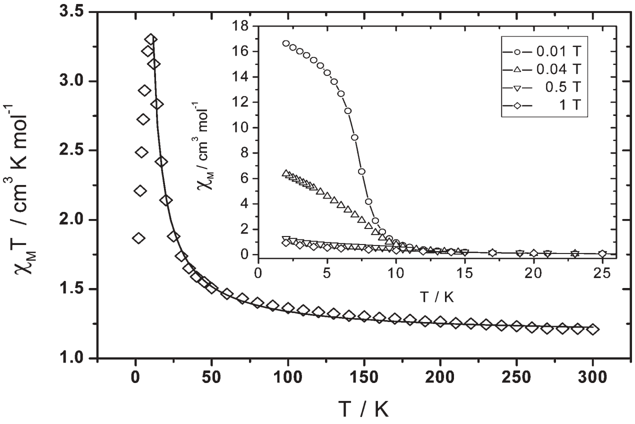

Fig. 2 Plot of $\chi_M T$ *vs.* T for a polycrystalline sample of **1**. Solid line corresponds to the best fit (see text). The χ_M *vs.* T curves below 25 K for **1** at an applied field of 1, 0.5, 0.04 and 0.01 T are shown in the inset.

---

† Electronic supplementary information (ESI) available: $\chi_M T$ *vs.* T curves below 25 K for **1** measured at different fields. See http://www.rsc.org/suppdata/cc/b4/b417019a/

*smitra_2002@yahoo.com (Samiran Mitra)
salah.elfallah@qi.ub.es (M. Salah El Fallah)

Table 1 X-Ray structural parameters and magnetism for Cu(II) trinuclear μ_3-CO_3 complexes

Complex[a]	Cu–O$_{av.}$/Å	Cu–O–C$_{av.}$/°	J/cm^{-1}	Ref.
$[Cu_3(pip)_3(H_2O)_3(\mu_3\text{-}CO_3)](NO_3)_4$	1.956[b]	109.2[b]	9.64	1*f*
$[Cu_3(pip)_3(H_2O)_3(\mu_3\text{-}CO_3)](ClO_4)_4$	1.956[b]	109.2[b]	8.94	1*f*
$[Cu_3(dmbpy)_6(\mu_3\text{-}CO_3)](BF_4)_4(H_2O)(C_2H_5OH)$	1.981	114.2	9.3	1*b*
$[Cu_3(L_2)_3(\mu_3\text{-}CO_3)](ClO_4)_4\cdot 2H_2O$	2.001[b]	112.2[b]	17.2	1*h*
$[Cu_3(bpy)_6(\mu_3\text{-}CO_3)](BF_4)_4(H_2O)_2(C_2H_6O)$	2.023	112.3	10.6	1*c*
$[Cu_3(tpa)_3(\mu_3\text{-}CO_3)](ClO_4)_4$	1.954	124.9	−1.19	1*d*
$[Cu_3(L)_3(\mu_3\text{-}CO_3)](ClO_4)_4$	1.933[b]	123.9	8.2	1*g*
$[Cu_3(Medpt)_3(\mu_3\text{-}CO_3)](ClO_4)_4$	1.972	118.5	12.6	1*e*
Complex **1**	1.952[b]	107.6[b]	6.4	Present paper

[a] Abbreviations: pip = 2-[2-(2-pyridyl)ethyliminomethyl]pyridine; dmbpy = 4,4'-dimethyl-2,2'-bipyridine; L_2 = 1,4,7,10-tetraazabicyclo[5.5.3]pentadecane; bpy = 2,2-bipyridine; tpa = tris(pyridylmethyl)amine; L = macrocycle [15]aneN_3O_2; Medpt = bis(3-aminopropyl)methylamine. [b] Equilateral.

interactions extended in the lattice or canted antiferromagnetic interactions, extended also in the 3D lattice. In the following, we will study a new complex that can be added to this family of molecular-based magnets, complex **1**,‡ being the first μ_3-CO_3 bridged copper(II) system exhibiting significant long-range ferromagnetic order.

An ORTEP drawing of **1** is shown in Fig. 1. The crystal structure§ is best described as a two-dimensional polymeric cationic network of $\{[Cu(4\text{-}apy)_2]_3(\mu_3\text{-}CO_3)_2\}_3^{2+}$ in which each copper atom has a practically square-planar environment coordinated by the two symmetry-related tridentate bridging carbonate groups and two nitrogens from two 4-aminopyridines arranged in *trans*-fashion. The Cu–O (1.951(7) Å) and the Cu–N (1.997(9) Å) lengths are equal and comparable to those found in literature.[1] Each oxygen atom of the bridging carbonato ligands are bonded to different copper centres by the 3-fold rotation of the C-atom of carbonato ligand showing the rare μ_3-CO_3 bridging. This infinite two dimensional network in the 001 plane has a tessellated 24-membered honeycomb-like motif subunit (24, 3) with a cavity dimension of *ca.* 8.2 × 8.6 Å. The nets are not interpenetrating and the cavities are filled by the 4-aminopyridine ligands and perchlorate ions which lie on a 3-fold axis in between the bridging carbonates. The Cu···Cu closest distance between all the copper centres is 4.5778(10)Å.

The magnetic behaviour§ of this compound is shown in Fig. 2 as a plot of the $\chi_M T$ *vs.* T measured in a field of 1 T and the χ_M *vs.* T plots measured at different fields (inset). The $\chi_M T$ value at 300 K is 1.21 cm^3 K mol^{-1} (close to the value expected for three uncoupled copper atoms: 1.25 cm^3 K mol^{-1} when g = 2.0). $\chi_M T$ increases smoothly as T is lowered, to a maximum value of 3.30 cm^3 K mol^{-1} at 10 K, indicating ferromagnetic coupling. Below this temperature, $\chi_M T$ rapidly drops down. This decrease must be interpreted carefully taking into account the plots of χ_M *vs.* T (Fig. 2 inset). Experimental data above the maximum have been fitted to the high-temperature series expansion eqn. (1), for a S = ½ Heisenberg model in a hexagonal 2D lattice[9] in which $a_1 = 1.5$, $a_2 = 0.75$, $a_3 = -0.125$, $a_4 = 0.3125$, $a_5 = 0.66875$, $a_6 = -0.5927$, $a_7 = -0.74$, $a_8 = 1.4848$ and $K = J/kT$. The J value has been obtained by minimizing the function $R = \Sigma(\chi_M T^{calc} - \chi_M T^{obs})^2/\Sigma(\chi_M T^{obs})^2$ (36 data points). The best fitting parameters obtained are J = 6.23 cm^{-1}, g = 2.05 and $R = 1.14 \times 10^{-4}$. In Table 1, we report the main X-ray structural parameters and J values for all similar isolated Cu^{II} trinuclear μ_3-CO_3 compounds together with those of **1**. This last one fits nicely into the list: for a Cu–C–O angle of 107.6° a J value between 5 and 10 cm^{-1} can be expected.

$$\chi = \frac{Ng^2\mu_B^2}{3kT}S(S+1)\left(1+\sum_{n=1}^{n=8}a_nK^n\right) \qquad (1)$$

However, the most important feature of **1**, is the behaviour of the χ_M *vs.* T values. Indeed, these values are field dependent at temperatures lower than 12 K: as the field is lowered (inset in Fig. 2) a strong increase in the χ_M values is observed. For H = 100 G there is a clear tendency to saturation. This feature is the typical signature for long-range ferromagnetic ordering.[10] The corresponding $\chi_M T$ curves show a maximum which is only due to the product of χ_M (tending to saturation) multiplied by decreasing T values.†

In conclusion, we present in this work the first two-dimensional copper(II) system bridged by μ_3-CO_3 showing long-range ferromagnetic ordering. Obviously, from a magnetic point of view, this long-range ordering must be three-dimensional. In our case the three-dimensionality may be attributed to the packing among the layers through the pyridine rings of the aminopyridine terminal ligand. Only one semi-analogous compound has been reported so far: $Na_2Cu(CO_3)_2$,[2c] whose structure is also two-dimensional but quadratic instead of honeycomb-like such as in **1**. Furthermore, $Na_2Cu(CO_3)_2$ shows intra-layer ferromagnetic coupling but the coupling between the layers is antiferromagnetic, just the opposite found in **1**.

This work was supported by the grants from UGC (New Delhi, India). M. S. El Fallah thanks the Ministerio de Educación y Ciencia (Programa Ramón y Cajal) for the financial support.

Arpi Majumder,[a] Chirantan Roy Choudhury,[a] Samiran Mitra,*[a] Georgina M. Rosair,[b] M. Salah El Fallah*[c] and Joan Ribas[c]
[a]*Department of Chemistry, Jadavpur University, Kolkata-700 032, India. E-mail: smitra_2002@yahoo.com*
[b]*Department of Chemistry, Heriot-Watt University, Edinburgh, UK EH14 4AS*
[c]*Department de Quimica Inorganica, Universitat de Barcelona, Marti I Franques, 1-11, 08028-Barcelona, Spain. E-mail: salah.elfallah@qi.ub.es*

Notes and references

‡ *Experimental*: In a typical experiment when a CO_2 free aqueous solution (5 ml) of $Cu(ClO_4)_2\cdot 6H_2O$ (0.370 g, 1.0 mmol) was mixed with 5 ml methanolic solution of 4-apy (0.094 g, 1 mmol) and exposed to air at pH 9.5 (adjusted by addition of NaOH), CO_2 is rapidly absorbed, forming small violet hexagonal crystals of **1** in a yield of 65% (0.72 g). Anal. calc. for $C_{33}H_{40}Cl_2Cu_3N_{12}O_{15}$: C, 35.79; H, 3.64; N, 15.18; found: C, 35.65; H, 3.56;

N, 15.02%. We are able to reproduce the same complex with very high purity and confirmed by C, H, N percentage as well as the spectral studies (UV-vis, IR) in all cases. The infrared (KBr pellet, cm^{-1}) spectrum of **1** shows bands at 3455m for ν(O–H), 3360s, 3210s for ν(N–H), 1660m for ν_{as}(C=N), 1630vs for ν_{as}(C=C), 1520m, 1475s, 1460m for ν_{as}(CO), 1395s, 1370m, 1345m for ν_{as}(CO$_2$), 1210s for δ(C–H), 1055w, 1025m for ν_s(CO), 835s for δ(CO$_2$). The complex displays two strong absorption bands in the regions of 205 and 262 nm. These are clearly charge transfer in origin. The UV absorption band observed at 382 nm can be assigned to the charge transfer transition from the ligands to the Cu(II) ion. As usual, the spectrum shows a very weak low-intensity absorption band associated with d–d transitions at 640 nm.

§ *Crystal data* for **1**: $C_{33}H_{40}Cl_2Cu_3N_{12}O_{15}$, $M = 1106.28$, rhombohedral, space group *R*-3, $a = 9.156(2)$, $b = 9.156(2)$, $c = 44.51(3)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 120°$, $V = 3231(2)$ Å^3, $Z = 3$, $D_c = 1.705$ Mg m^{-3}, $\mu = 1.673$ mm^{-1}, $F(000) = 1689$. A total of 1389 reflections were measured, 1254 reflections were unique ($R_{int} = 0.0944$). $T = 100(2)$ K, $2.61° < \theta < 24.98°$, $0 \leqslant h \leqslant 10$, $-10 \leqslant k \leqslant 0$, $0 \leqslant l \leqslant 52$, $R_1 = 0.1037$, $wR_2 = 0.2539$ ($I > 2\sigma(I)$), $R_1 = 0.1664$, $wR_2 = 0.3044$ (all data). X-Ray data were collected on a Bruker AXS P4 diffractometer with MoKα radiation ($\lambda = 0.7107$ Å) at 100 K with an Oxford Cryosystems Cryostream. The structures were solved by direct and different Fourier methods and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters and other atoms were constrained to idealised geometries and refined with riding isotropic displacement parameters (1.2 times that of the bound C atom). The methanol solvent was partially modelled as one carbon atom of ⅓ partial occupancy. Crystallographic computing was performed using SHELXTL programs. CCDC 238039. See http://www.rsc.org/suppdata/cc/b4/b417019a/ for crystallographic data in .cif or other electronic format. Magnetic measurements were made on 38 mg of powdered polycrystalline sample by the use of a Quantum Design MPMS SQUID magnetometer (from 300 K to 2 K). Diamagnetic corrections were estimated from Pascal Tables and a TIP of 180×10^{-6} cm^3 mol^{-1} (3 Cu^{II} ions) was applied to the χ_M data.

1 (*a*) A. Escuer, F. A. Mautner, E. Peñalba and R. Vicente, *Inorg. Chem.*, 1998, **37**, 4190; (*b*) G. A. van Albada, I. Mutikainen, O. S. Roubeau, U. Turpeinen and J. Reedijk, *Inorg. Chim. Acta*, 2002, **331**, 208; (*c*) G. A. van Albada, I. Mutikainen, O. S. Roubeau, U. Turpeinen and J. Reedijk, *Eur. J. Inorg. Chem.*, 2000, 2179; (*d*) J. Cui, X. Liu, P. Cheng, D. Liao, Z. Jiang, G. Wang, H. Wang and X. Yao, *Sci. China, Ser. B*, 1999, 535; (*e*) A. Escuer, R. Vicente, E. Peñalba, X. Solans and M. Font-Bardía, *Inorg. Chem.*, 1996, **35**, 248; (*f*) G. Kolks, S. J. Lippard and J. V. Waszczak, *J. Am. Chem. Soc.*, 1980, **102**, 4833; (*g*) C. Bazzicalupi, A. Bencini, A. Bencini, A. Bianchi, F. Corana, V. Fusi, C. Giorgi, P. Paoli, P. Paoletti, B. Valtanconi and C. Zanchini, *Inorg, Chem.*, 1996, **35**, 5540; (*h*) J. Springbord, J. Glerup and I. Sotofte, *Acta Chem. Scand.*, 1997, **51**, 832; (*i*) Z.-W. Mao, G. Liehr and R. van Eldink, *J. Chem. Soc., Dalton Trans.*, 2001, 1593; (*j*) A. Escuer, E. Peñalba, R. Vicente, S. Solans and M. Font-Bardía, *J. Chem. Soc., Dalton Trans.*, 1997, 2315.

2 (*a*) J. Sertucho, A. Luque, O. Castillo, P. Roman, F. Lloret and M. Julve, *Inorg. Chem. Commun.*, 1999, **2**, 14; (*b*) P. D. Brotherton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1973, 2338; (*c*) A. K. Gregson and P. C. Healy, *Inorg. Chem.*, 1978, **17**, 2969; (*d*) P. C. Healy and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1972, 1913; (*e*) B. F. Abrahams, M. G. Haywood, R. Robson and D. A. Slizys, *Angew. Chem., Int. Ed.*, 2003, **42**, 1112.

3 A. S. Wills, R. Ballou and C. Lacroix, *Phys. Rev. B*, 2002, **66**, 144407.

4 (*a*) M. Rodríguez, A. Llobet, M. Corbella, P. Muller, M. A. Usón, A. E. Martell and J. Reibenspies, *J. Chem. Soc., Dalton Trans.*, 2000, 2900; (*b*) A. L. van den Brenk, K. A. Byriel, D. P. Fairlie, L. R. Gahan, G. R. Hanson, C. J. Hawkins, A. Jones, C. H. L. Kennard, B. Moubaraki and K. S. Murray, *Inorg. Chem.*, 1994, **33**, 3549.

5 N. Kitajama, S. Hikichi, M. Tanaka and Y. Moro-oka, *J. Am. Chem. Soc.*, 1993, **115**, 5496.

6 (*a*) N. F. Curtis, R. W. Hay and Y. M. Curtis, *J. Chem. Soc. A*, 1968, 182; (*b*) F. W. B. Einstein and A. C. Willis, *Inorg. Chem.*, 1981, **20**, 609.

7 (*a*) *Magnetic Molecular Materials*, eds. D. Gatteschi, O. Kahn, J. S. Miller and F. Palacio, Kluwer Academic Publishers, Dordrecht, 1991; (*b*) M. Verdaguer, *Science*, 1996, **272**, 698.

8 (*a*) J. S. Miller, A. J. Epstein and W. M. Reiff, *Chem. Rev.*, 1988, **88**, 201; (*b*) A. Caneschi, D. Gatteschi, R. Sessoli and P. Rey, *Acc. Chem. Res.*, 1989, **22**, 392; (*c*) J. S. Miller, *Inorg. Chem.*, 2000, **39**, 4392.

9 G. S. Rushbrooke, G. A. Baker and P. J. Woods, in *Phase Transitions and Critical Phenomena*, ed. C. Domb and M. S. Green, Academic Press, New York, 1974, vol. III, ch. 5.

10 (*a*) E. Coronado, J. R. Galán-Mascarós, C. J. Gómez-García and J. M. Martínez-Agudo, *Inorg. Chem.*, 2001, **40**, 103; (*b*) D. Armentano, G. de Munno, F. Lloret, A. V. Palii and M. Julve, *Inorg. Chem.*, 2002, **41**, 2007.