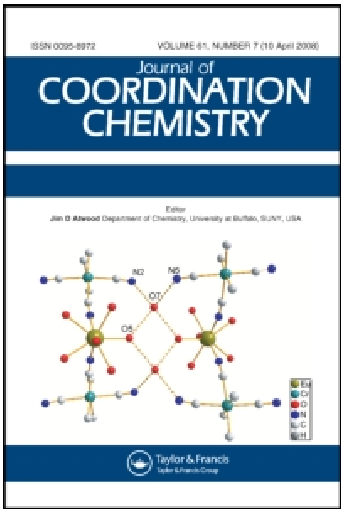

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A totally unexpected synthesis of single crystals of the mineral Chalconatronite, $Na_2[Cu(Co_3)_2]\cdot 3h_2o$, from a solution of a Copper coordination compound and Atmospheric Co_2, at room temperature

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A TOTALLY UNEXPECTED SYNTHESIS OF SINGLE CRYSTALS OF THE MINERAL CHALCONATRONITE, $Na_2[Cu(CO_3)_2] \cdot 3H_2O$, FROM A SOLUTION OF A COPPER COORDINATION COMPOUND AND ATMOSPHERIC CO_2, AT ROOM TEMPERATURE

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In an effort to produce additional polymorphs of $[Cu(HL)]_2)(ClO_4)_2 \cdot 2H_2O$ (**V**) by dissolving that compound in slightly basic, deionized water, we obtained a beautiful set of crystals, obviously containing Cu(II), which turned out to have the composition $Na_2[Cu(CO_3)_2] \cdot 3H_2O$. The fact that a chemical reaction occurred while waiting for crystals of the parent compound to form was unknown to us until we solved the crystal structure of the royal-blue crystals. This substance has the interesting property of being a naturally occurring mineral and has also been prepared in the laboratory but by an appropriate mixing of the substance's components, in basic solution.

Each copper contains a bidentate carbonato ligand with one oxygen bridging an adjacent copper. The oxygen that is not bound to the first copper is bonded to two adjacent sodium ions, thus making Na–O–C–O–Cu bridges. Copper occurs in infinite strings formed by carbonato oxygens that bridge the Cu(II) cations. There are also Cu–H_2O–Na and Na–H_2O–Na bridges in the lattice. The copper and sodium ions are far from ideal octahedral coordination, with large deviations of the bond lengths and angles from those of that geometry.

A rational synthesis of the compound was carried out to obtain a significant amount of this compound for physical measurements, such as magnetic susceptibility. **VI** behaves *almost* as a simple paramagnet throughout the 35–300 K temperature range and the data points can be fitted to the Curie–Weiss law with $\theta = 2.05^\circ$K. In that temperature range, the compound is slightly antiferromagnetically coupled (typical $\mu = 1.58$ BM at 200 K). However, below *ca.* 35 K the unpaired electrons of the Cu(II) cation couple ferromagnetically, and at 2 K the magnetic moment is 2.27 BM.

Keywords: X-ray crystallography; Chalconatronite; Copper; CO_2

INTRODUCTION

Recently structures, magnetic behavior and polymorphism were studied in compounds of general composition $[Cu(HL)]_2Cl_2 \cdot 4H_2O$ (**I**), $[Cu(HL)]_2Cl_2 \cdot 2H_2O$ (**II**),

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$[Cu(HL)]_2)(NO_3)_2 \cdot 4H_2O$ (**III**), $[Cu(HL)]_2)(NO_3)_2 \cdot 2H_2O$ (**IV**) and $[Cu(HL)]_2)(ClO_4)_2 \cdot 2H_2O$ (**V**) (HL = [(3-aminopropyl)-di-(2-hydroxopropyl)]-amine anion [1]. In an effort to obtain different polymorphs of the perchlorate, recrystallization from slightly basic, deionized water was attempted since **V** was grown from methanol : water (1 : 1). Changes in the methanol : water ratio had given rise to the pairs (**I** and **II** and **III** and **IV**) and the solutions were also basic (pH *ca.* 8.0).

The solubility of the perchlorate in slightly basic water is very high and the length of time needed to obtain crystalline material was very long. Eventually, royal-blue crystals were obtained whose composition turned out to be $Na_2[Cu(CO_3)_2] \cdot 3H_2O$ (**VI**), a known compound synthesized under much more drastic conditions from the obvious components and under some very vaguely described conditions [2]. As a mineral, it was discovered in 1955 [3]. Its single crystal structure was determined in 1973 [4] using space group $P2_1/n$ and in 1975 using the $P2_1/c$ setting [5]. The former study was done with film data, the latter used a diffractometer.

From the above, it is clear, in hindsight, that long standing and exposure to atmospheric CO_2, at room temperature, accidentally yielded excellent crystals of chalconatronite from a solution of a copper coordination compound under some very mild, and unexpected, conditions.

EXPERIMENTAL

Accidental Preparation of the Crystals

This compound was synthesized during attempts to obtain different polymorphs of the compound of composition $[Cu(HL)]_2(ClO_4)_2 \cdot 2H_2O$ [1]. The parent polymorph was dissolved in pure water and the pH was adjusted to ~8.0 by adding NaOH. The solution was kept in air for a long time (approx. 15 days) and unexpected royal-blue crystals obtained were suitable for single-crystal X-ray diffraction studies.

Rational Preparation of the Crystals

Since we only had a small number of tiny crystals of $Na_2[Cu(CO_3)_2] \cdot 3H_2O$ we decided to prepare a gram-quantity sample using the literature synthesis [2]. The original report is very vague, especially for the amount of copper acetate needed to obtain pure product. Therefore, we recorded the exact conditions we used in preparing our sample: to a solution of Na_2CO_3 (10 g in 100 cm^3 deionized water) was added 4 g $NaHCO_3$ with stirring and the temperature was adjusted to 50°C. A concentrated solution of copper acetate (5 g in 50 cm^3 deionized water) was added dropwise with constant stirring. A clear, deep-blue solution, free of any suspended particles of basic copper carbonate, was obtained. The addition of copper acetate was stopped at the first hint of insoluble, basic copper carbonate formation. The solution was filtered and kept overnight at room temperature in a covered beaker. Well-formed blue crystals were deposited at the bottom of the vessel, which were filtered, rinsed with alcohol, dried in a desiccator, and used in the measurements of the magnetic susceptibility.

A single crystal taken from this sample was examined by X-ray diffraction; the space group and cell constants obtained were identical with the data reported below.

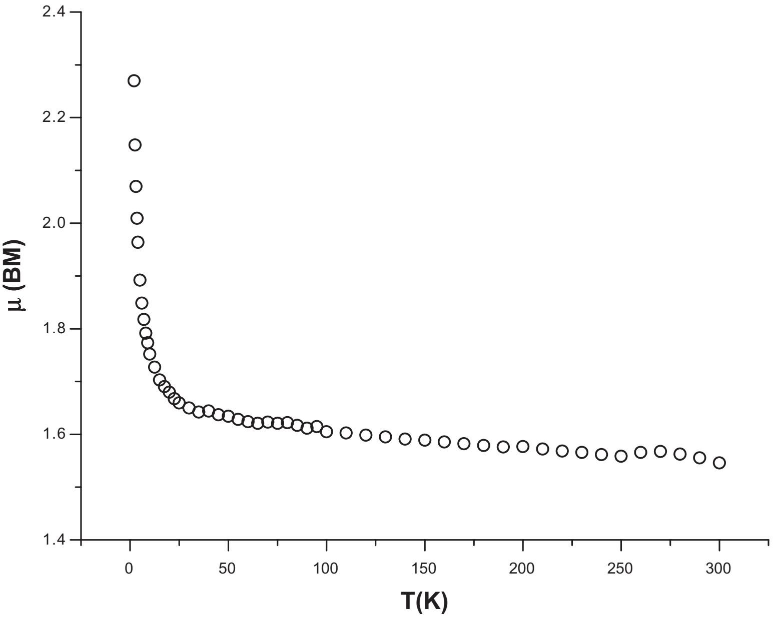

FIGURE 1 The susceptibility curve recorded from 300 to 2 K. Note that if the entire range is plotted, the temperature dependence (from 300–35 K) is nearly that for a Curie–Weiss paramagnet, were it not for the value of the nearly constant magnetic moment, which is indicative of a weak antiferromagnetic coupling (see text). Below 35 K, the magnetic moment rapidly increases to a maximum value of 2.27 BM, at 2 K.

Magnetic Measurements

Magnetic measurements were made using a SQUID over the temperature range of 2-297 K and a magnetic field of 0.1 Tesla. The results are shown in graphical form in Fig. 1. These data can be readily fitted to the Curie–Weiss equation with $\Theta = 2.05°K$. **VI** is weakly antiferrromagnetically coupled in the range 300–35 K (typically $\mu = 1.58$ at 200 K); at lower temperatures it becomes ferromagnetically coupled and achieves a value of μ of 2.27 BM at 2 K.

Crystallography

Data were collected with an Enraf-Nonius CAD-4 diffractometer, using monochromatized Mo Kα radiation. Data were collected over the range $4° \leq 2\Theta \leq 52°$ and corrected for absorption. Data were processed using the data reduction package of WinGX [6] which determined the space group to be $P2_1/n$ [4]. Details of data collection and refinement parameters are listed in Table I. Bond lengths are listed in Table II. Other stereochemical parameters are available from the CIF document. We wish to emphasize the totally unprecedented means by which this substance was prepared, and not the details of the crystal structure since the description by Harlow and Simonsen [5] is in good agreement with our results. However, the packing diagram (drawn by hand) is not adequate by today's standards, so we provide Figs. 2–5. Harlow and Simonsen [5] did not publish a packing diagram, or packing information, and defer on this issue to reference [4]. Figures 2–4 show the coordination sphere about Cu, Na(1) and

TABLE I Data collection and refinement parameters

Empirical formula	$C_2H_6N_4O_9Na_2Cu$
Formula weight	339.6
Crystal color	Blue
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	9.6933(3)
b (Å)	6.0926(2)
c (Å)	13.7863(4)
β (°)	91.908(2)
V (Å^3)	813.73
Z	4
T (K)	293
D_{calc} (g cm^{-3})	2.31
μ(Mo Kα cm^{-1})	28.17
No. observations ($I > 2.00\sigma$)	2366
R^a	0.0373
R_w	0.095
Goodness of fit	1.053

TABLE II Bond lengths (Å)

Cu(1)–O(4)	1.9446(19)	Na(1)–O(5)	2.420(2)
Cu(1)–O(6)	1.9521(19) 2_645	Na(1)–Ow(1)	2.460(3)
Cu(1)–O(2)	1.9872(18)	Na(1)–O(2)	2.902(2) 2
Cu(1)–O(1)	2.0088(19)	Na(1)–C(1)	3.013(3) 2
Cu(1)–Ow(1)	2.361(2)	Na(1)–Na(2)	3.1065(17) 2
Cu(1)–C(1)	2.399(2)	Na(1)–Na(1)	3.6966(15) 2_545
Cu(1)–Na(1)	3.2519(13)	O(6)–C(2)	1.306(3)
Na(2)–Ow(2)	2.345(2)	O(6)–Cu(1)	1.9521(19) 2_655
Na(2)–Ow(3)	2.361(3)	Ow(3)–Na(1)	2.384(2) 2_545
Na(2)–O(5)	2.366(2)	O(1)–C(1)	1.308(3)
Na(2)–O(3)	2.413(2) 2	O(3)–C(1)	1.247(3)
Na(2)–O(2)	2.423(2)	O(3)–Na(1)	2.346(2) 1_545
Na(2)–Ow(2)	2.460(3) 3_655	O(3)–Na(2)	2.413(2) 2_545
Na(2)–C(2)	3.096(3)	O(3)–Na(1)	2.419(2) 2_545
Na(2)–Na(1)	3.1065(17) 2_545	O(5)–C(2)	1.259(3)
Na(2)–Na(1)	3.1961(16)	O(4)–C(2)	1.293(3)
Na(2)–Na(2)	3.468(2) 3_655	O(2)–C(1)	1.307(3)
Na(1)–O(3)	2.346(2) 1_565	O(2)–Na(1)	2.902(2) 2_545
Na(1)–O(2)	2.363(2)	C(1)–Na(1)	3.013(3) 2_545
Na(1)–Ow(3)	2.384(2) 2	Ow(2)–Na(2)	2.460(3) 3_655
Na(1)–O(3)	2.419(2) 2		

For bond angles, torsional angles and hydrogen bonds, see CIF as well as the Supplementary Information for details to download the file.

Na(2) and also the strings formed by these cations as a result of bridges formed by either carbonato oxygens or by water.

RESULTS AND DISCUSSION

Chalconitronite was obtained by the absorption of atmospheric CO_2 causing the parent complex to hydrolyze in solution, which stood open to air for about 15 days prior to crystal formation. The crystals we obtained were of a color not compatible with the color of the original compound. However, until the structure was solved we had no

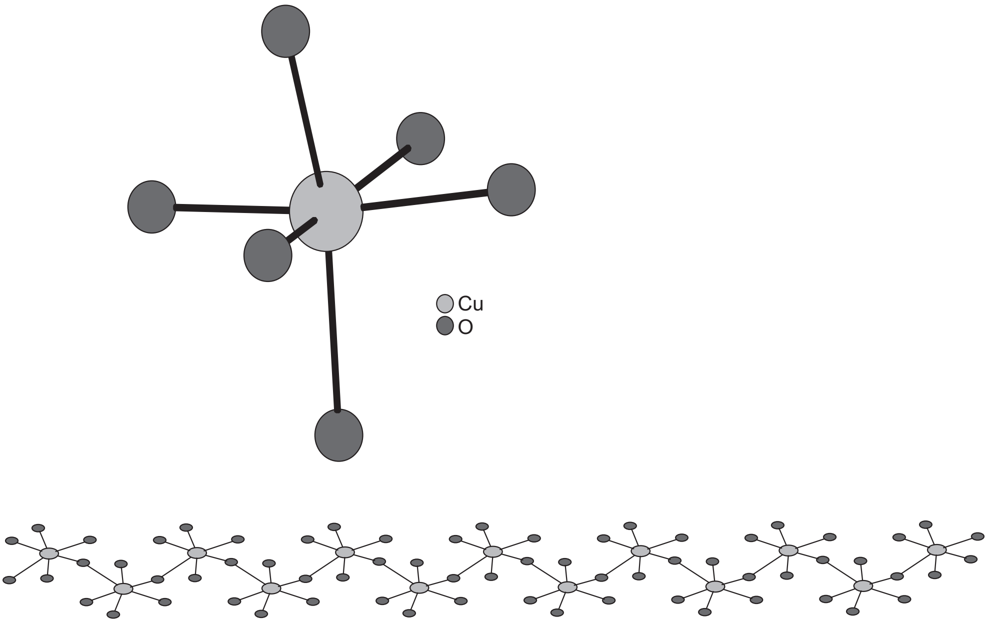

FIGURE 2 Top, the coordination sphere around the Cu(II) cations. Note that there are six ligands arranged in a highly distorted manner. Bottom, the Cu(II) strings are strung together by oxygens of the bidentate carbonato ligands.

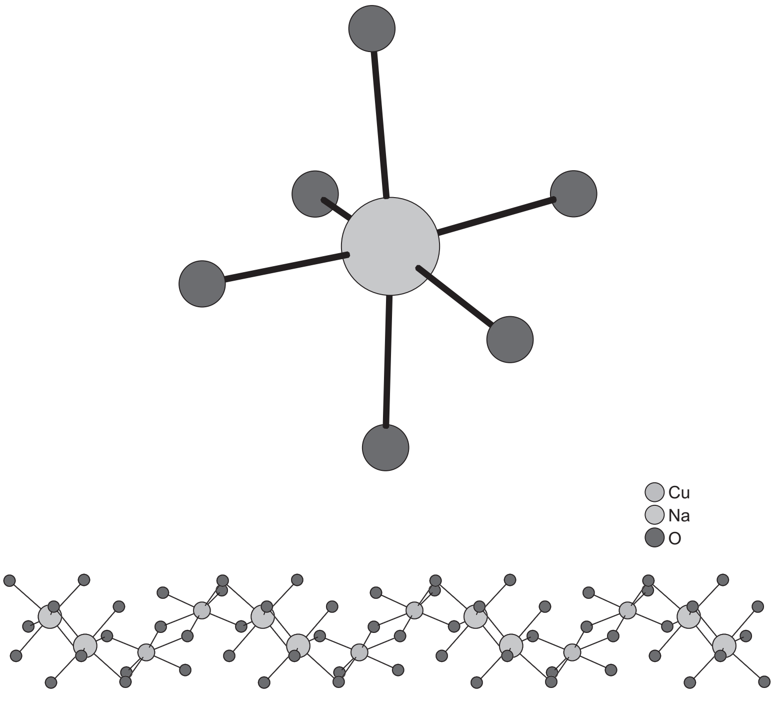

FIGURE 3 Top, the coordination sphere around Na(1). Like Cu(II) it is also six-coordinate and highly distorted from ideal octahedral geometry. Bottom, Na(1) cations form strings of their own which are kept separate by the intercalation of copper strings.

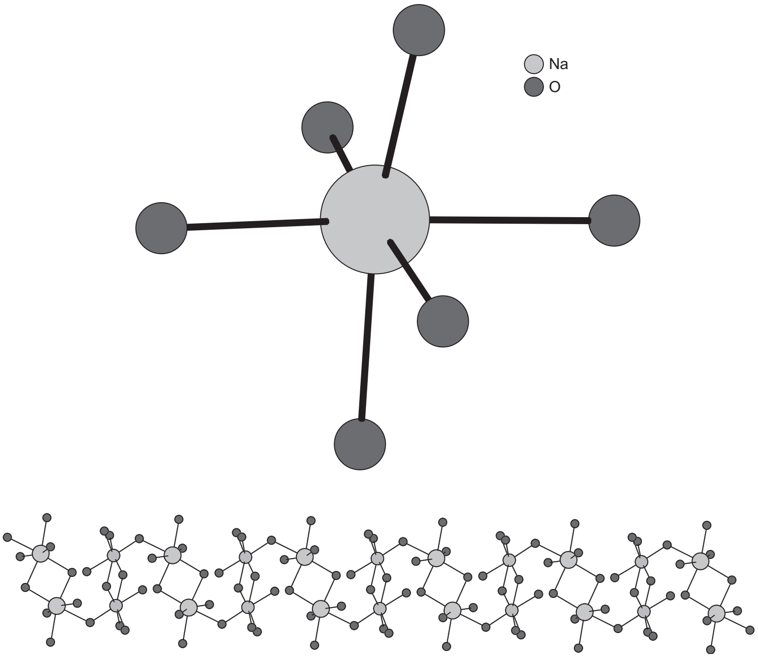

FIGURE 4 Top, coordination sphere around Na(2). Bottom, the strings formed by these cations are strung together by lattice water molecules. As in Fig. 3, the Na(2) strings are kept apart by copper strings.

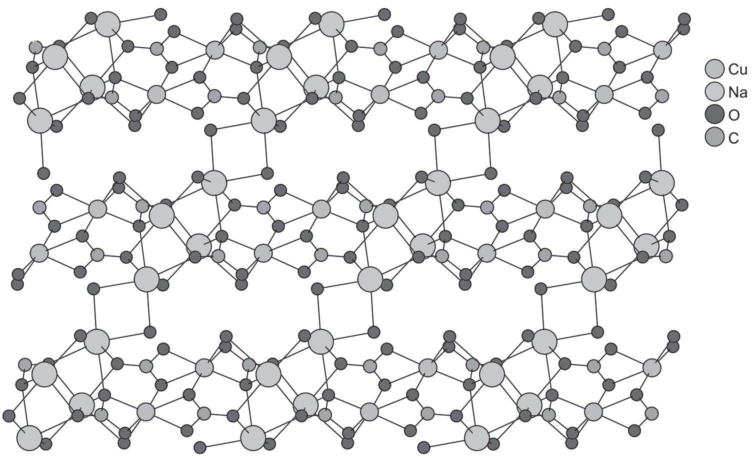

FIGURE 5 Packing diagram of the compound with hydrogen atoms omitted for clarity. This is an *a*–*c* projection which is the clearest line of sight for this complex lattice. Note the strings formed by the cations and the fact they intercalate into one another. The Na(2) cations link the strings; Na(1) cations are within the strings of the Cu(II) cations.

idea what had changed, why or how. Moreover, the displacement of the [(3-aminopropyl)-di-(2-hydroxopropyl)]-amine anion by carbonate is unprecedented.

The geometry of Cu in compound **VI** is shown in Fig. 1, which also shows one of the bridged copper strings. From the figures it is clear the Cu(II) complexes are anionic given the fact that each one is associated with two carbonato ligands, one of which forms the strings. The carbonato ligands oxygens belong to three categories: one is bidentate to one Cu(II), with one oxygen binding solely to that copper, and the carbonate also forms two hydrogen bonds with water molecules. The second oxygen spans over to another copper, as shown at the bottom of Fig. 2 and also forms a hydrogen bond. The third oxygen binds two adjacent sodium cations (see Figs. 3 and 4). In a highly symmetric manner, a second copper contains the identical binding pattern, and thereby forms a symmetrical, dinuclear copper fragment, sitting at inversion centers with a unique Cu–O–Cu angle of 150.9°. Each copper ion is also linked to sodium cations by three water molecules, as shown clearly in Fig. 5. Thus, each copper is bound to six ligands, which form a rather distorted coordination sphere around the central Cu(II). Values of the angle O–Cu–O (see CIF) range from 66.01(7)° in the case of O(1)–Cu–O(2) to 199.29(7)° for O(6)–Cu–Ow(1). Bond lengths also span a large range, from Cu–O(4) = 1.945(2) Å to Cu–Ow(1) = 2.361(2) Å. Therefore, no classical, or nearly classical, coordination sphere can be assigned to the Cu(II) cations.

As far as packing is concerned, Fig. 5 (an *a*–*c* projection, with *a* as the horizontal) shows that the constituents of the crystals are infinite strings extending along the *a*-axis. These strings consist of copper ions linked to one another by carbonato oxygens and separated by sodium–water strings shown in Figs. 3 and 4. The infinite copper strings must provide a magnetic interaction between the copper cations; however, given that the strings are isolated from one another, no inter-string magnetic interactions are expected.

There is a report in the literature [7] that the magnetic behavior of this substance is of a simple Curie–Weiss type. However, it was studied only from 297–80 K and the structure of the compound was unknown then. Therefore, knowing that the structure of the compound contains infinite string units of bridged copper cations, we assumed that any ordering transition (ferro- or antiferromagnetic) had to lie below 80 K; we therefore explored the susceptibility curve down to *ca.* 2 K. The magnetic and structural results are now self-consistent.

The unique Cu–O–Cu angle is 150.9°, which is not typical of oxygen-bridged Cu(II) dimers since the most common ones contain Cu–OR–Cu bridges with R = H, aryl or alkyl fragments. Details of the angular dependence of the coupling constants in bridged Cu(II) compounds have been reported [8]. In our case the bridges between Cu(II) cations are formed by carbonato oxygens as shown in Figs. 2–5. The large value of the Cu–O–Cu angle is atypical of most of those discussed previously [8]. Therefore it is not surprising that the substance is nearly a simple paramagnet in the range 300–35 K, with a very small Weiss constant of 2.05°.

CONCLUSIONS

(1) We found it quite surprising that this carbonato complex, which is a known mineral, could be formed from atmospheric CO_2. We are unaware of additional examples of atmospheric CO_2 attacking coordination compounds and displacing their ligands (especially a quadridentate one) in basic water solutions, at room temperature and atmospheric partial pressure of CO_2. (2) It is also unusual that CO_2 can displace a quadridentate ligand since carbonate is weakly bidentate. (3) The magnetic behavior

of the compound was studied previously by Hatfield [7] who described it as a "Curie–Weiss paramagnet". Given the fact that he did not know the structure of this solid, and the fact that his data were collected from 297 to 80 K using a Gouy balance, it was conceivable that coupling (ferro- or antiferromagnetic) occurs at a temperature below 80 K. Our results indicate Hatfield was not quite correct, even if the magnetic moment measured for three temperatures between 297 and 80 K changed little. The important issue is that in that range, our SQUID data show a μ value of *ca.* 1.6 BM between 300 and 35 K. Thus, in that range there is a weak antiferromagnetic coupling which remains more or less constant for that range. However, as shown in Fig. 1, thereafter **VI** rapidly changes to a ferromagnet that achieves a μ value of 2.27 BM at 2 K. These results produce a picture consistent with the observations on the structural data. The presence of bridging carbonato links creates infinite strings of –Cu–O–Cu– units expected to produce coupling, even if at low temperature. The temperature at which the onset of ferromagnetism is observed is 30 K, not particularly low.

Acknowledgments

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Supporting Information

An X-ray crystallographic file in CIF format has been deposited with a CSD-number 413232. The material can be obtained, free of charge, on application to ICSD-Team, Fachinformationzentrum Karlsruhe, Abt. IDNT/ Faktendatenbank, Herrmann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany. E-mail: CrysDATA⟨CRYSDATA@FIZ-Karlsruhe.DE⟩.

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