A novel microporous copper silicate: $Na_2Cu_2Si_4O_{11}\cdot 2H_2O$†

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The synthesis and structural characterisation of a thermally stable novel three-dimensional microporous copper silicate open-framework are described; the material is capable of undergoing reversible zeolitic water removal without destruction of the framework.

Molecular sieves containing metal cations with the ability to exhibit a range of coordination geometries have been extensively studied due to their novel topologies and interesting chemical properties when compared to those of classical zeolites. We have been interested in the synthesis and structural characterisation of novel open-frameworks containing Si and metal cations (such as Ti, V, Cr, Nb, Zr and Sn) in tetrahedral and (more commonly) octahedral coordination environments, respectively.[1] Lanthanide silicates exhibiting interesting photoluminescence properties have also been prepared.[2,3] Searching for microporous functional materials displaying magnetic properties, Jacobson and co-workers have recently reported the first example of a copper silicate CuSH-1A (where A = Na, K, Rb or Cs) containing a one-dimensional 12-ring channel system filled with channel-blocking AOH.[4] Here, we wish to report the synthesis and structural characterisation of a novel microporous copper silicate, $Na_2(Cu_2Si_4O_{11})\cdot 2H_2O$, named AV-23 (Aveiro microporous solid number 23).

AV-23 was isolated as large spherical aggregates of long green needles (Fig. 1) using a typical hydrothermal approach.‡ Single crystals suitable for single-crystal X-ray diffraction analysis were isolated by sonication and formulated as $Na_2(Cu_2Si_4O_{11})\cdot 2H_2O$.§ The single Cu^{2+} metal centre appears six-coordinated and exhibiting a strong Jahn–Teller distortion. It is coordinated to five SiO_4 tetrahedra and one crystallisation water molecule, in a geometry resembling a highly distorted octahedron in which the equatorial plane is composed of four distinct SiO_4 tetrahedra [Si–O bond lengths found within the 1.924(2)–1.979(2) Å range], and the apical positions are occupied by the crystallisation water molecule [$Si–O_{water}$ of 2.892(2) Å] and by a SiO_4 tetrahedron [Si–O of 2.505(2) Å] (Fig. 2). Adjacent SiO_4 tetrahedra are linked along the *a* direction by corner-sharing which leads to the formation of zigzag metallic anionic chains, $[(Cu_2Si_4O_{11})\cdot 2H_2O]_n^{2n-}$, in which the metal-to-metal distances are of $Cu\cdots Cu^{i}$ 3.011(7) Å (*via* bridging SiO_4 tetrahedra) and $Cu\cdots Cu^{ii}$ 3.141(7) Å (*via* the SiO_4 tetrahedron in the apical position) [symmetry codes: (i) $3-x, 2-y, -z$; (ii) $2-x, 2-y, -z$] (Fig. 2). $[(Cu_2Si_4O_{11})\cdot 2H_2O]_n^{2n-}$ chains are interconnected along the *b* direction (Fig. 3, *right*) to form layers which grow in the (1 1 0) direction (Fig. 3, *left*). Similarly, adjacent layers are connected *via* corner-sharing SiO_4 tetrahedra leading to a three-dimensional microporous framework with the major channels running along the *a* direction, formed by eight-membered rings and having an effective cross-section of *ca.* 4.2 × 2.5 Å (Fig. 4). Interestingly, the Na^+ cations are remarkably close to the previously described layers, and have a coordination environment resembling a distorted capped square pyramid [$Na\cdots O$ contacts found within the 2.329(2)–2.378(2) Å range with the capping $Na\cdots O(4)$ contact being 2.607(2) Å]. This distribution of the cations leads, on the one hand, to remarkably small $Cu\cdots Na$ distances [3.0559(14), 3.2109(13) and 3.3538(14) Å] and, on the other, to the ability to reversibly remove the crystallisation water molecules. In fact, these molecules are pointing towards the interior of the channels (Fig. 4), further facilitating their removal, as observed in thermogravimetric measurements.

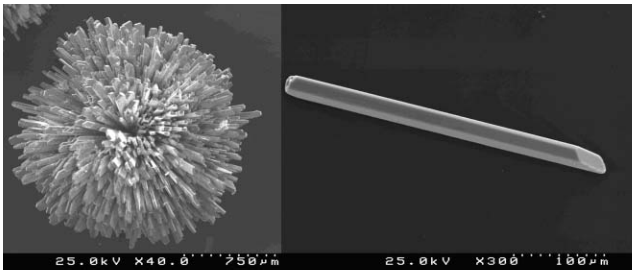

Fig. 1 Scanning Electron Microscopy (SEM) images of AV-23.

TGA (see Supporting Information) shows only one weight loss (*ca.* 7%) in the 100–250 °C temperature range, corresponding to the removal of 1.8 H_2O molecules *per* formula unit, which is in good agreement with the two molecules determined from the X-ray crystal analysis. The thermal treatment of AV-23 in air at 300 °C for six hours leads to the removal of these crystallisation water molecules without destruction of the framework, as confirmed by TGA and powder X-ray diffraction measurements (see Supporting Information). This removal of the guest solvent molecules was also found to be completely reversible, confirming the zeolitic behaviour of AV-23.

Preliminary magnetic measurements show that this material behaves as an S = 1/2 antiferromagnetic linear chain, with coupling energy of *ca.* 100 K. A Curie–Weiss fit of the data in the paramagnetic regime revealed about 2.13 μ_B/Cu, in good agreement with the expected values for Cu^{2+}.

We are currently investigating the possibility of exchanging the Na^+ for smaller cations to create less steric hindrance within the channels and, therefore, increase the porosity of the structure. We are also interested in investigating further the magnetic properties, and potential applications, of this new family of microporous structures.

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† Electronic supplementary information (ESI) available: experimental section. See http://www.rsc.org/suppdata/cc/b4/b410731d/

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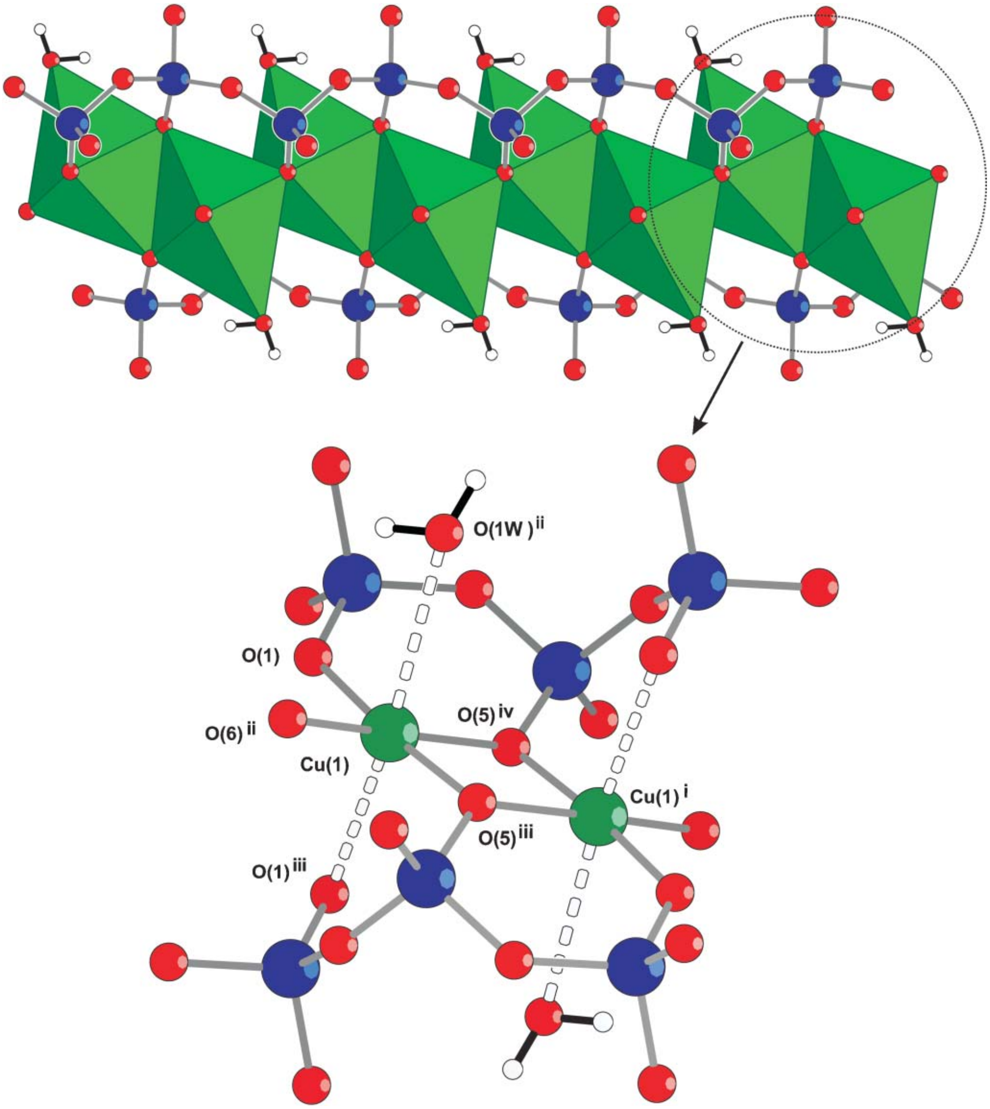

Fig. 2 (*Top*) Mixed ball-and-stick and polyhedral representation of the zigzag metallic chain $[(Cu_2Si_4O_{11})\cdot 2H_2O]_n^{2n-}$ running along the *a* direction, and (*Bottom*) a magnification showing the coordination environment of the Cu^{2+} cations. Selected bond lengths (in Å): Cu(1)–O(1) 1.942(2); Cu(1)–O(6)^{ii} 1.924(2); Cu(1)–O(5)^{iii} 1.967(2); Cu(1)–O(5)^{iv} 1.979(2); Cu(1)–O(1)^{iii} 2.505(2); Cu(1)–O(1W)^{ii} 2.892(2). Symmetry codes used to generate equivalent atoms: (i) $3 - x, 2 - y, -z$; (ii) $1 + x, 1 + y, z$; (iii) $2 - x, 2 - y, -z$; (iv) $1 + x, y, z$.

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Notes and references

‡ *Synthesis*: AV-23 was synthesised in Teflon-lined autoclaves under static hydrothermal conditions. Chemicals were purchased from commercial sources and used without further purification. Typically, an alkaline solution was prepared by mixing 13.86 g of a sodium silicate solution (Na_2O 8 wt%, SiO_2 27 wt%, Merck), 16.13 g H_2O and 4.11 g NaOH (Merck). A second solution was prepared by mixing 17.87 g H_2O with 7.60 g of $Cu(SO_4)\cdot 15H_2O$ (Merck). These two solutions were combined and stirred thoroughly. The resulting gel, with a molar composition of CuO : $3.1SiO_2$: $1.4Na_2O$: $94.5H_2O$, was autoclaved for 10 days at 230 °C.

§ X-ray single-crystal diffraction data were collected at ambient temperature (at the *Unidade de Raios-X*, RIAIDT, *University of Santiago de Compostela*, Spain) on a Bruker SMART 1000 charge coupled device (CCD) area-detector diffractometer (Mo K_α graphite-monochromated radiation, $\lambda = 0.7107$ Å), controlled by the SMART software package.[5] Images were processed using the SAINTPlus software package,[6] and data were corrected for absorption by using the semi-empirical method of SADABS.[7] The structure was solved by the direct methods of SHELXS-97,[8] and refined by full-matrix least squares on F^2 using SHELXL-97.[9] Atoms were directly located from difference Fourier maps and refined with anisotropic displacement parameters. H-atoms associated with the crystallisation water molecule were also found from successive difference Fourier maps syntheses and refined with an isotropic displacement parameter fixed at 1.5 times U_{eq} of the parent atom. The O–H and H···H distances were restrained to 0.84(1) and 1.37 Å, respectively, to ensure a chemically reasonable geometry for the water molecule. *Crystal data*: $Cu_2H_4Na_2O_{13}Si_4$, $M = 497.45$, triclinic, space group $P\bar{1}$, $Z = 1$, $a = 5.2228(7)$ Å, $b = 6.4109(9)$ Å, $c = 8.5169(12)$ Å, $\alpha = 101.107(2)°$,

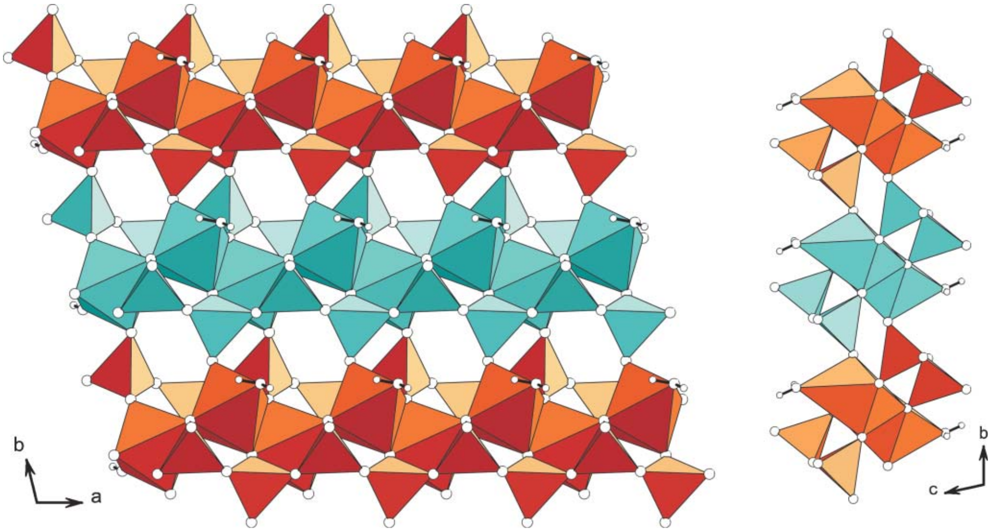

Fig. 3 Schematic representation of the construction of the anionic layers placed in the *ab* plane *via* parallel linking of adjacent $[(Cu_2Si_4O_{11})\cdot 2H_2O]_n^{2n-}$ chains.

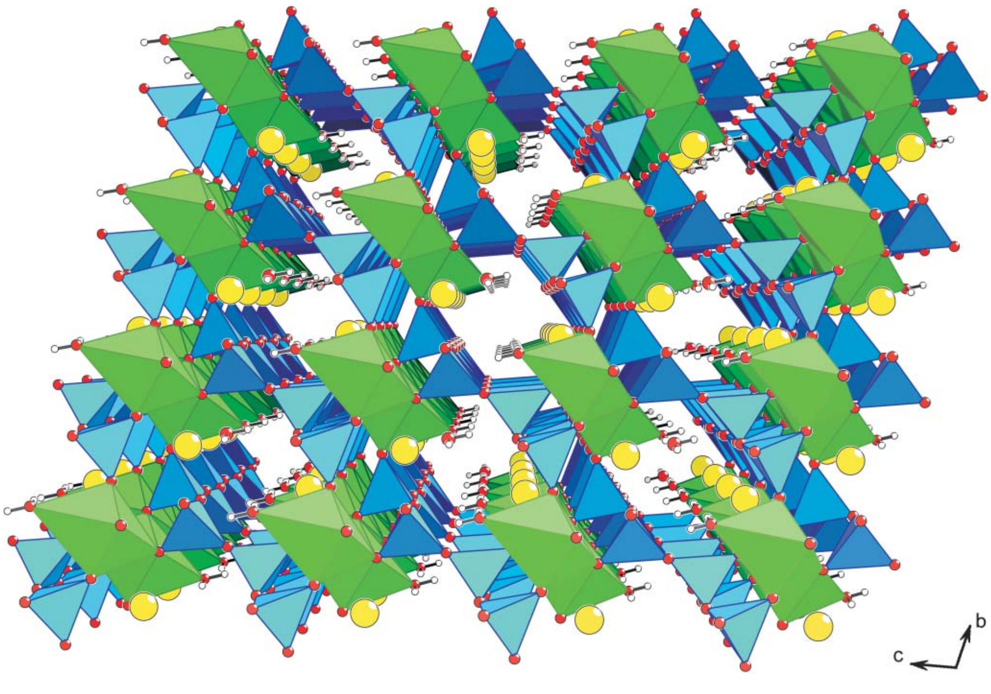

Fig. 4 Polyhedral representation of the crystal packing viewed along the *a* direction. Na^+ cations are represented as yellow-filled spheres.

β = 94.340(2)°, γ = 102.480(2)°, V = 271.16(7) Å^3, μ(Mo-Kα) = 4.520 mm^{-1}, D_c = 3.046 g cm^{-3}. Of a total of 3412 reflections collected, 1099 were independent (R_{int} = 0.0233). Final $R1$ = 0.0233 [$I > 2\sigma(I)$] and $wR2$ = 0.0610 (all data). Data completeness to theta = 26.37°, 99.5%. Further crystallographic information (excluding structure factors) can be obtained free of charge from Fachinformationszentrum Karlsruhe, 76344, Eggenstein-Leopoldshafen, Germany (e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-414048. CCDC 245207. See http://www.rsc.org/suppdata/cc/b4/b410731d/ for crystallographic data in .cif or other electronic format.

1 J. Rocha and M. W. Anderson, *Eur. J. Inorg. Chem.*, 2000, 801.
2 A. Ferreira, D. Ananias, L. D. Carlos, C. M. Morais and J. Rocha, *J. Am. Chem. Soc.*, 2003, **125**, 14573.
3 D. Ananias, A. Ferreira, J. Rocha, P. Ferreira, J. P. Rainho, C. Morais and L. D. Carlos, *J. Am. Chem. Soc.*, 2001, **123**, 5735.
4 X. Q. Wang, L. M. Liu and A. J. Jacobson, *Angew. Chem., Int. Ed.*, 2003, **42**, 2044.
5 *SMART, Bruker Molecular Analysis Research Tool V5.054*®, 1997–1998, Bruker AXS, Madison, Wisconsin, USA.
6 *SAINTPlus, Data Reduction and Correction Program v. 6.01*®, 1997–1998, Bruker AXS, Madison, Wisconsin, USA.
7 G. M. Sheldrick, *SADABS v. 2.01, Bruker/Siemens Area Detector Absorption Correction Program*, 1998, Bruker AXS, Madison, Wisconsin, USA.
8 G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution*, University of Göttingen, 1997.
9 G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, 1997.