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# THE STRUCTURE OF COPPER(II) DODECYLSULPHATE TETRAHYDRATE

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**Abstract**—Crystals of the title compound $Cu(OSO_3C_{12}H_{25})_2 \cdot 4H_2O$ were obtained from an aqueous solution and characterized by X-ray crystallography. The $Cu^{II}$ ion is six-coordinated in a tetragonally elongated octahedral geometry with the four O atoms of water equatorial and the two O atoms of the dodecylsulphate groups axial. The Cu—O(dodecylsulphate) bonds are much longer at 2.456(4) Å than the Cu—O (water) bonds at 1.860(4) and 1.870(4) Å. The Cu—O—S angle is 173.9(3)°. The extended alkyl chains are tilted between the planes of copper atoms but there is no interdigitating between the alkyl chains from two adjacent layers.

There is much current interest in the interaction between surfactants and inorganic compounds. For example, surfactants are used in the thermal preparation of mesoporous materials such as transition metal oxides[1] or silicas.[2] From an environmental point of view, there is increasing interest in the removal of surfactants by ion exchangers such as layered double hydroxides (LDH)[3] or hydroxy double salts (HDS).[4] There is also concern with respect to the presence of stable complexes formed between surfactants and metal salts in natural effluents.[5] However, there have only been a few crystal structure determinations of these compounds. In this paper, the crystal structure of a copper complex obtained from an aqueous mixture of copper nitrate and sodium dodecylsulphate has been studied.

Among the structures that contain a copper atom coordinated to the oxygen atom of an alkyl sulphate group is copper ethylsulphate tetrahydrate.[6] The $Cu^{II}$ ion is in a centrosymmetric slightly distorted octahedral environment with bond lengths to water molecules of 1.98 and 1.96 Å. Two other oxygens belonging to the sulphate groups are at 2.39 Å from the metal atom. The Cu—O—S angle is 148.9°. The structure consists of chains of $Cu(C_2H_5SO_4)_2 \cdot 4H_2O$ parallel to the *c*-axis. Adjacent chains are held together by hydrogen bonds involving one water oxygen of one chain to ethylsulphate oxygens of adjacent chains. Another comparable structure is $Cu(CH_3SO_3)_2 \cdot 4H_2O$.[7] The Cu—O bond length to the sulphonato group is 2.387(2) Å long, the Cu—O(water) bond lengths are 1.969(2) Å and 1.947(2) Å, the Cu—O—S angle is 145.7(1)°. Of more relevance to the title compound, the crystal structure of a complex of copper(II) with two dodecylsulphates and two ethylenediamines has also been established.[8] The Cu atom lies on a centre of symmetry in a tetragonally distorted coordination. There is planar four-coordination of the copper atom by the N atoms of two ethylenediamine ligands at a mean distance of 2.007 Å. Two oxygen atoms of the dodecylsulphato ligands occupy axial positions, 2.517 Å from the Cu atom. There are two intramolecular and two intermolecular hydrogen bonds. Each $NH_2$ group of the ethylenediamine ligand forms one of each kind of hydrogen bond. The intramolecular hydrogen bonds involve the oxygen atom linked to the alkyl chain for one $NH_2$ group and the nearest free oxygen atom of the sulphate for the adjacent $NH_2$ group. The intermolecular hydrogen bonds involve the oxygen atom linked to the copper atom and the nearest hydrogen atom of each $NH_2$ group of one ethylenediamine ligand. The hydrogen bonds in this structure are weak. The dodecyl chains are extended

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and form a highly ordered interdigitating structure. The structure consists of alternating polar layers of $Cu(H_2NCH_2CH_2NH_2)_2(OSO_3)_2$ units in the *xy* plane, interlinked by hydrogen bonds and non-polar layers of perfectly aligned $C_{12}H_{25}$ chains. However, there have not been any previous crystal structures reported regarding the copper(II) dodecylsulphate tetrahydrate. There is particular interest in the nature of the interactions of the hydrocarbon chains and the role of hydrogen bonding in this structure and whether mono or bilayers are formed.

## EXPERIMENTAL

Copper nitrate hemipentahydrate and dodecylsulphate sodium salt were Aldrich compounds and used without further purification. The crystals were grown from a mixture obtained from 5 $cm^3$ of a solution of $Cu(NO_3)_2$ (1.25 mol $l^{-1}$) and 75 $cm^3$ of a solution of dodecylsulphate sodium salt (0.10 mol $l^{-1}$). After 3 h, a few crystals appeared but the mixture was left at room temperature during one further day. The solid was separated from the mother solution by filtration, washed with doubly deionized water and then dried in air at room temperature. The crystals obtained were blue with a lamellar shape. Found: Cu, 9.3; C, 43.4; H, 8.8. Calc. for $[Cu(OSO_3C_{12}H_{25})_2 \cdot 4H_2O]$: Cu, 9.5; C, 43.2; H, 8.7%.

Carbon, hydrogen and nitrogen analyses were carried out by Medac Ltd, Brunel University. Thermal analysis was carried out using a Stanton Redcroft STA 1000 TG-DTA Simultaneous Thermal Analyser referenced against recalcined alumina. The thermal analysis of the compound was run in air at a ramp-rate of 10°C $min^{-1}$. The FTIR spectrum was measured on a Perkin–Elmer 1720-X FTIR with an IRDM data management system. For the surface analysis, the method of nitrogen adsorption at 77 K on a Gemini 2375 (Micromeritics) was used. The surface area was calculated using the BET model.[9] With a complete isotherm involving adsorption and desorption, the size distribution of the pores was evaluated using the BJH method.[10] Before the analysis each sample was

Table 1. Crystal data and structure refinement for $Cu(OSO_3C_{12}H_{25})_2 \cdot 4H_2O$, **1**

| | |
|---|---|
| Empirical formula | $C_{24}H_{58}CuO_{12}S_2$ |
| Formula weight | 666.36 |
| Temperature | 293(2) K |
| Wavelength | 0.71072 Å |
| Crystal system | triclinic |
| Space group | $P1$ |
| Unit cell dimensions | $a = 5.988(6)$ Å |
| | $b = 6.009(6)$ Å |
| | $c = 25.069(6)$ Å |
| | $\alpha = 87.714(10)°$ |
| | $\beta = 90.272(10)°$ |
| | $\gamma = 75.252(10)°$ |
| Volume | 871.5(13) $Å^3$ |
| $Z$ | 1 |
| Density (calculated) | 1.270 Mg $m^{-3}$ |
| Absorption coefficient | 0.797 $mm^{-1}$ |
| $F(000)$ | 359 |
| Crystal size | 0.2 × 0.2 × 0.04 mm |
| Theta range for data collection | 3.25–25.58 |
| Index ranges | $0 \leqslant h \leqslant 7$, $-6 \leqslant k \leqslant 6$, $-29 \leqslant l \leqslant 29$ |
| Independent reflections collected | 2423 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/parameters | 2419/271 |
| Goodness-of-fit on $F^2$ | 1.025 |
| Final $R$ indices $[I > 2\sigma(I)]$ | $R1 = 0.0559$, $wR2 = 0.1285$ |
| $R$ indices (all data) | $R1 = 0.0646$, $wR2 = 0.1336$ |
| Extinction coefficient | 0.025(3) |
| Largest diff. peak and hole | 0.489 and $-0.622$ e $A^{-3}$ |

Table 2. Dimensions in the metal coordination sphere

| | Distances (Å), Angles (°) |
|---|---|
| Cu(1)—O(1W) | 1.860(4) |
| Cu(1)—O(2W) | 1.870(4) |
| Cu(1)—O(4) | 2.456(4) |
| O(1W)—Cu(1)—O(2W) | 91.5(2) |
| O(1W)—Cu(1)—O(4) | 93.1(2) |
| O(2W)—Cu(1)—O(4) | 93.9(2) |

heated at 100°C for 2 h under a flow of nitrogen gas.

*Crystallography*

Crystal data are given in Table 1, together with refinement details. Data were collected with Mo-$K_\alpha$ radiation using the MARresearch Image Plate System. The crystal was positioned at 75 mm from the Image Plate; 95 frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.[11] The structure was solved using direct methods with the SHELX86 program.[12] The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms on the carbon chain were included in calculated positions. The methyl group hydrogen atoms were included as a rigid group. The structure was then refined using SHELXL.[13] All calculations were carried out on a Silicon Graphics R4000 Workstation. The dimensions in the coordination sphere are given in Table 2. Supplementary material includes atomic coordinates, anisotropic thermal parameters, hydrogen positions, remaining dimensions and structure factor tables.

## RESULTS AND DISCUSSION

The structure is shown in Fig. 1 with the atomic numbering scheme. The copper atom occupies a crystallographic centre of symmetry and has a regular six-coordinate octahedral environment. However the Cu—O(4) bond to the sulphate ligand is very much longer at 2.456(4) Å than the Cu—O(1W), Cu—O(2W) bonds to the water molecules [1.860(4), 1.870(4) Å]. The conformation of the undecane chain is as expected with all torsion angles around C—C bonds within 5° of 180°. The crystal consists of alternating polar layers of $Cu(H_2O)_4(OSO_3)_2$ molecules interlinked by hydrogen bonds and non-polar layers of perfectly aligned $C_{12}H_{25}$ chains as shown in Fig. 2. The Cu—O(4)—S angle is 173.9(3)°. This is much larger than the equivalent angle in the tetraaquacopper(II) ethylsulphate structure[6] and in the tetraaquacopper(II) methylsulphonate structure[7] (Table 3). These also have a centre of symmetry, however, the Cu—O—S angles are only 148.9° and 145.7° respectively. Concomitant with this variation in angle is a difference in bond lengths as Cu—O(water) are longer and Cu—O(sulphate) shorter than the equivalent bond lengths in **1**. The bis(ethylenediamine)-bis(do-

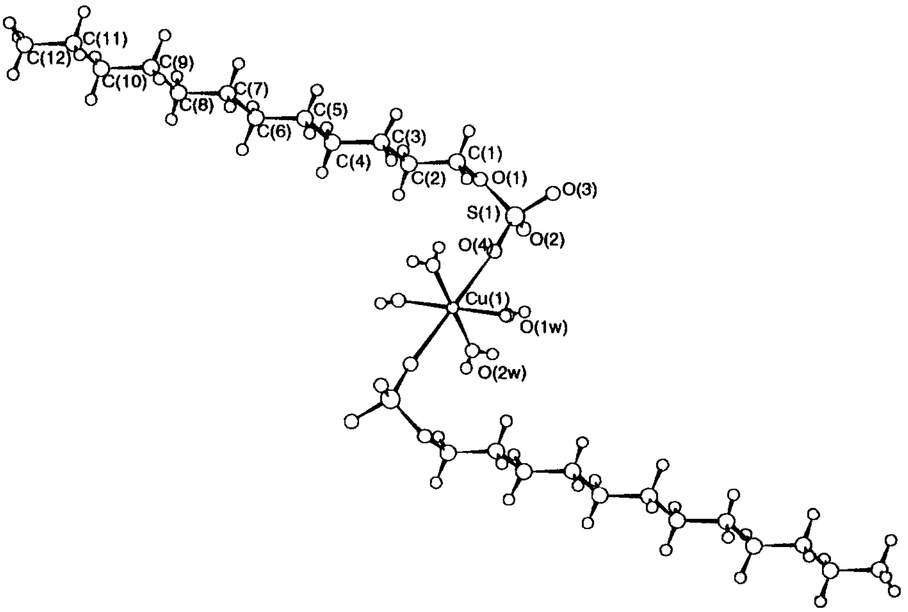

Fig. 1. The $Cu(OSO_3C_{12}H_{25})_2 \cdot 4H_2O$ molecule, **1**, showing the atomic numbering scheme.

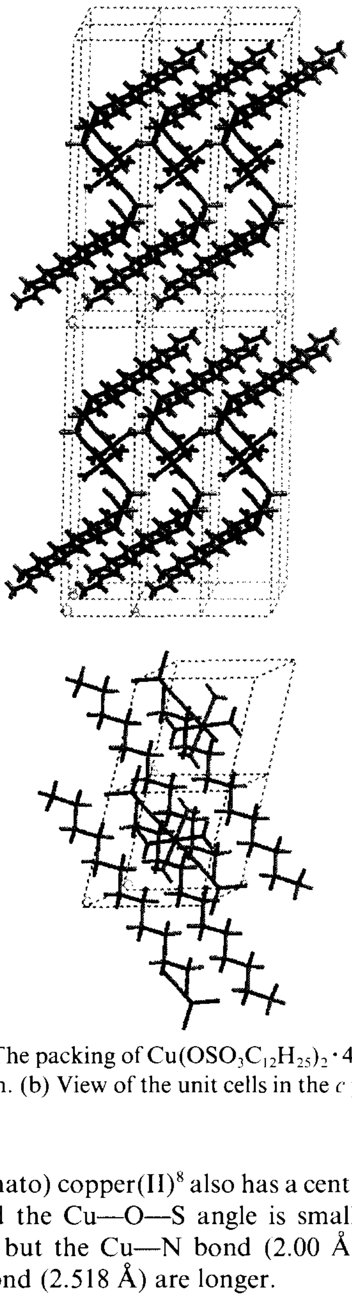

Fig. 2. (a) The packing of $Cu(OSO_3C_{12}H_{25})_2 \cdot 4H_2O$ in the *b* projection. (b) View of the unit cells in the *c* projection.

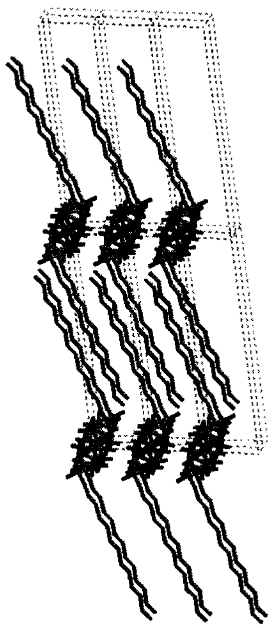

Fig. 3. The packing of $Cu(OSO_3C_{12}H_{25})_2(en)_2$ in the *b* projection, which is to be compared with the same projection of $Cu(OSO_3C_{12}H_{25})_2 \cdot 4H_2O$ in Fig. 2(a).

decylsulphato) copper(II)[8] also has a centre of symmetry and the Cu—O—S angle is smaller 123.4° than in **1** but the Cu—N bond (2.00 Å) and the Cu—O bond (2.518 Å) are longer.

In this structure (Fig. 3) the dodecyl chains are extended but form a highly ordered interdigitating structure which differs from **1** where the alkyl chains of two different layers are parallel but completely separated (Fig. 2). The same double layer structure has been deduced from powder diffraction patterns of heavy metal soaps.[5] In the copper(II) dodecylsulphate tetrahydrate, the area occupied by the alkyl chains belonging to the same layer when viewed along their axis is 27 Å$^2$. On the other hand, in the bis(ethylenediamine)-bis(dodecylsulphato) copper(II) that area is much bigger with 45 Å$^2$, which allows the formation of the interdigitating structure, similar to the one found in triacetylsphingosine.[14] The area around the alkyl chain is reduced to about 20 Å$^2$ which is close to 21 Å$^2$, the limiting area calculated at high pressure for single saturated alkyl chains at a water–air interface.[15] The angle formed by the alkyl chain axis and the plane of the layer is around 72°. This value is much smaller for **1** with 34° which can be related to the value of 29° suggested for the layered dodecylsulphate basic copper zinc salt, (Zn,Cu) $(OH)_3(C_{12}H_{25}OSO_3)$ by Lagaly and co-workers.[4a]

Table 3. Geometrical data of the moiety Cu—O—S in different complexes

| Compound | Cu—lig.equat. (Å) | Cu—O(sulph) (Å) | Cu—O—S (°) | Reference |
|---|---|---|---|---|
| $Cu(CH_3SO_3)_2 \cdot 4H_2O$ | 1.969(2), 1.947(2) | 2.387(2) | 145.7(1) | 7 |
| $Cu(C_2H_5SO_4)_2 \cdot 4H_2O$ | 1.981, 1.960 | 2.386 | 148.9 | 6 |
| $Cu(C_{12}H_{25}SO_4)_2(en)_2 \cdot 4H_2O$ | 2.008(2), 2.006(2) | 2.517(2) | 123.3(1) | 8 |
| $Cu(C_{12}H_{25}SO_4)_2 \cdot 4H_2O$ | 1.857(3), 1.865(3) | 2.456(4) | 173.9(3) | This work |

In the *xy* plane the crystal **1** is held by a network of intermolecular bonds between the free O atoms of the sulphate group and the nearest H atoms of the water molecules as shown in Fig. 4. All four O···O distances (given in Table 4) represent strong hydrogen bonds, being between 2.63 and 2.70 Å. This is different from the hydrogen bonding system of the bis(ethylenediamine)-bis(dodecylsulphato) copper(II), which is discontinuous along the *x* axis, as shown in Fig. 5.

### Thermal analysis

The thermal analysis of the title compound is shown in Fig. 6 and the results are summarized in Table 5. Since porous materials may be made, for

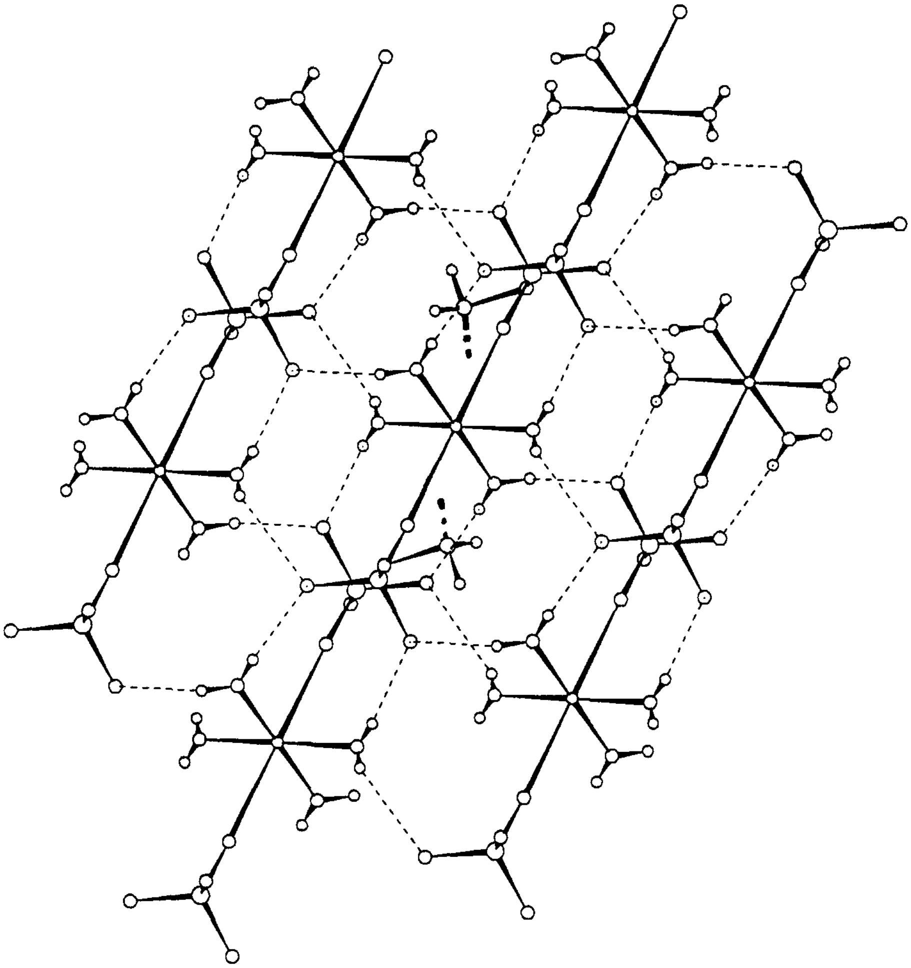

Fig. 4. The hydrogen bond pattern in $Cu(OSO_3C_{12}H_{25})_2 \cdot 4H_2O$ in the *c* projection. Hydrogen bonds are shown as dotted lines. For clarity the alkane chains are omitted.

Table 4. Hydrogen bonds in **1**, distance in Å, angles in degrees. Symmetry positions \$1 $1+x, y-1, z$ : \$2 $x+1, y, z$ : \$3 $x, y-1, z$

| | O···O | O—H···O | H···O |
|---|---|---|---|
| O(1W)—H(1WB)···O(2)\$1 | 2.631 | 161.4 | 1.858 |
| O(1W)—H(1WA)···O(3)\$2 | 2.701 | 162.8 | 1.905 |
| O(2W)—H(2WA)···O(2)\$3 | 2.689 | 135.8 | 2.085 |
| O(2W)—H(2WB)···O(3)\$1 | 2.657 | 172.3 | 1.852 |

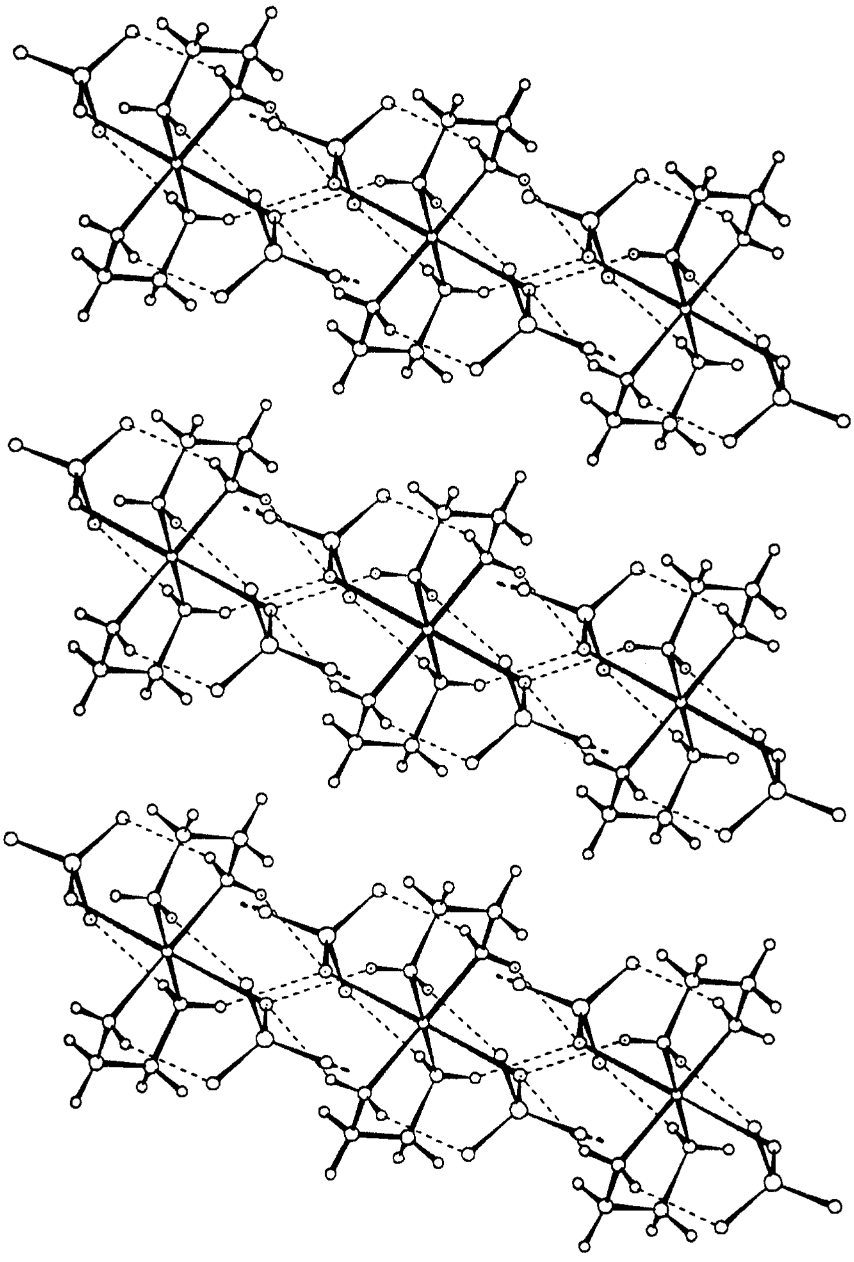

Fig. 5. The hydrogen bond pattern in Cu(OSO$_3$C$_{12}$H$_{25}$)$_2$(en)$_2$ in the *c* projection. Hydrogen bonds are shown as dotted lines. For clarity the alkane chains are omitted.

example, by heating silica/surfactant complexes to 450°C,[2] two thermal treatments were applied to the crystal to verify whether or not the formation of well-defined porosity can occur. Both thermal treatments consisted of a heating of 1°C min$^{-1}$ in air at maximum temperatures of 250°C (compound CUDS250) and of 500°C (compound CUDS500).

### *Surface analysis*

The surface area of the title compound is rather low at 2 m$^2$ g$^{-1}$. The surface area of the compound CUDS250 is much larger with 103 m$^2$ g$^{-1}$. Both exhibit type-IV isotherms (Fig. 7) with a type-H3 desorption hysteresis according to the IUPAC classification.[17] The amount of mesopores is negligible in **1** but is slightly larger for CUDS250 at 0.32 ml g$^{-1}$. This quantity is smaller than, for example, mesoporous kanemite (0.77 ml g$^{-1}$).[18] After heating at 500°C, the surface area decreases to 4 m$^2$ g$^{-1}$.

### *Infrared analysis*

The FT-IR spectrum of the title compound in Fig. 8 shows two broad absorption bands in the

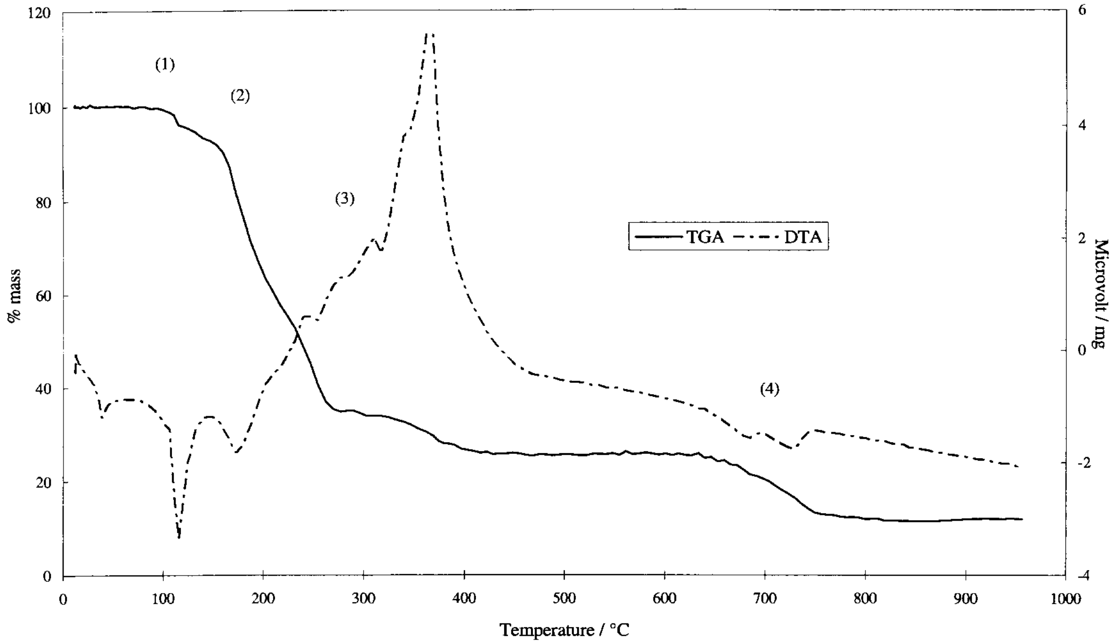

Fig. 6. Thermal analysis of $Cu(OSO_3C_{12}H_{25})_2 \cdot 4H_2O$.

Table 5. TG/DTA analysis of the title compound (10°C min$^{-1}$ in air)

| Initial compound | Products | Temperature (°C) | % Mass exp. | % Mass calc. | |
|---|---|---|---|---|---|
| $2Cu(OSO_3C_{12}H_{25})_2 \cdot 4H_2O$ | $2Cu(OSO_3C_{12}H_{25})_2 \cdot H_2O$<br>$6H_2O$ | 114,<br>endothermic | 100 | 100 | **1** |
| $2Cu(OSO_3C_{12}H_{25})_2 \cdot H_2O$ | $CuOSO_3 \cdot Cu(OSO_3C_{12}H_{25})_2$<br>$C_{12}H_{25}OSO_3H$<br>$C_{12}H_{25}OH$ | 172,<br>endothermic | 91.1 | 89.20 | **2** |
| $CuOSO_3 \cdot Cu(OSO_3C_{12}H_{25})_2$ | $2CuOSO_3$<br>$24CO_2$<br>$25H_2O$ | 243–366<br>exothermic | 25.1 | 23.95 | **3** |
| $2CuOSO_3$ | $2CuO$<br>$2SO_3$ | 685, 730<br>endothermic[16] | 10.7 | 11.94 | **4** |

range 3600–3200 cm$^{-1}$ which are assigned to the antisymmetric and symmetric OH stretching modes of hydrogen-bonded water molecules. The corresponding HOH bending mode is found to be around 1650 cm$^{-1}$. There are two medium intensity bands at 2955 and 2871 cm$^{-1}$ and two strong intensity bands at 2919 and 2850 cm$^{-1}$ associated with $\nu_{as}(CH_3)$, $\nu_s(CH_3)$, $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$, respectively. The bending modes of $(CH_3)$ are observed around 1470 cm$^{-1}$. Intense bands are observed in the range 1300–1150 cm$^{-1}$ which are assigned to the vibration modes of the sulphato moiety. The weak band at 404 cm$^{-1}$ is assigned to the Cu—O stretching vibration.[19]

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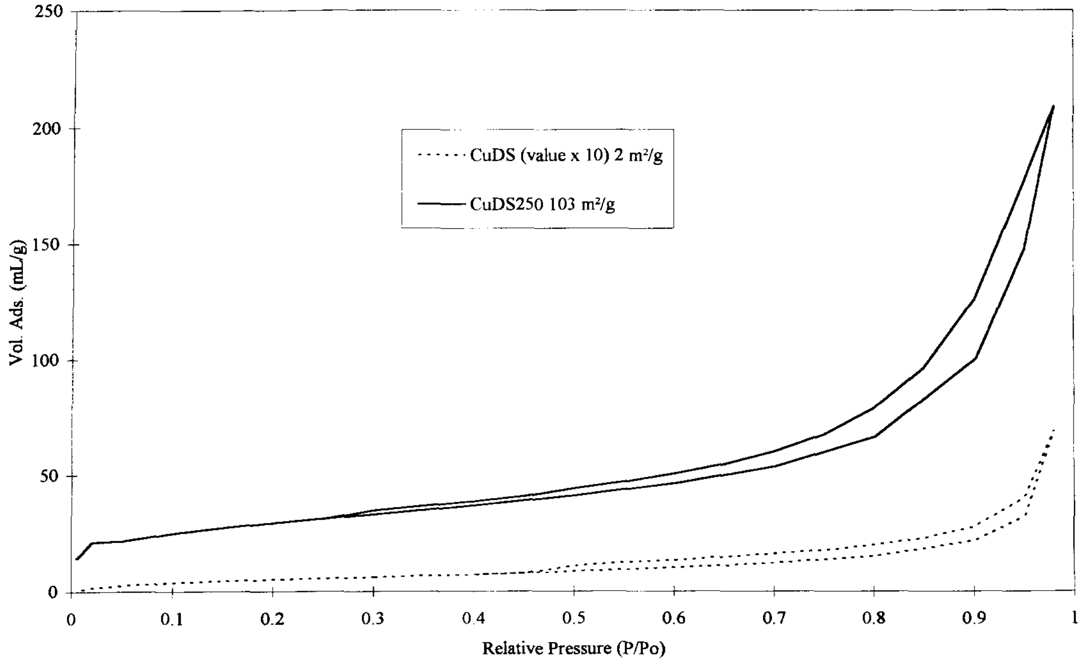

Fig. 7. Nitrogen adsorption isotherm at 77 K of $Cu(OSO_3C_{12}H_{25})_2 \cdot 4H_2O$ and of the same compound after heating at 250°C.

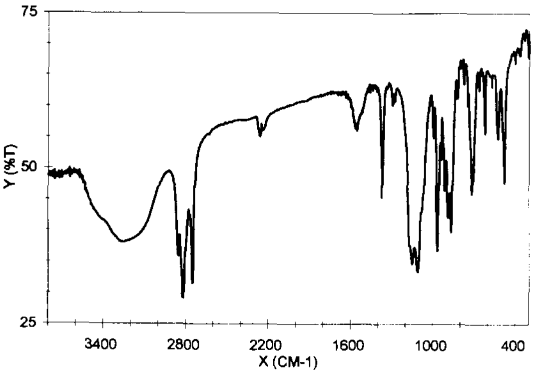

Fig. 8. FT-IR spectrum of $Cu(OSO_3C_{12}H_{25})_2 \cdot 4H_2O$.

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