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UDC

CRYSTAL STRUCTURES OF TWO ENANTIOMORPHOUS 2-ETHYLPIPERAZINEDIIUM HEXAAQUACOPPER SULFATES [(R OR S)-$C_5H_{14}N_2$][Cu(H_2O)$_6$](SO_4)$_2$

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Two new non-centrosymmetric copper sulfates are synthesized under slow evaporation conditions through the use of enantiomorphically pure sources of either (R)-2-methylpiperazine or (S)-2-methylpiperazine. Both crystallize in the non-centrosymmetric $P2_1$ space group, crystal data for [(R)-$C_5H_{14}N_2$][Cu(H_2O)$_6$](SO_4)$_2$ (**I**), a = 6.5276(2), b = 11.1955(3), c = 12.4559(4) Å, β = 101.196(2)°, Z = 2, V = 892.95(5) Å^3 and [(S)-$C_5H_{14}N_2$][Cu(H_2O)$_6$](SO_4)$_2$ (**II**), a = = 6.5188(2), b = 11.1786(2), c = 12.4365(3) Å, β = 101.205(1)°, Z = 2, V = 888.99(4) Å^3. The three-dimensional structure networks for these compounds consist of isolated $[Cu(H_2O)_6]^{2+}$ and $[(R)\text{-}C_5H_{14}N_2]^{2+}$ or $[(S)\text{-}C_5H_{14}N_2]^{2+}$ cations and SO_4^{2-} anions linked only by hydrogen bonds. The Cu atom is in a slightly distorted octahedral coordination environment. The crystal packings are influenced by cation-to-anion N—H…O and OW—H…O hydrogen bonds leading to an open framework structures.

Keywords: Non-centrosymmetric, three-dimensional structure, hydrogen bonds, open framework structures.

INTRODUCTION

In recent years, open-framework compounds have provoked significant interest owing to their enormous variety of intriguing structural topologies and fascinating physical properties (microporous, magnetic, catalytic, fluorescent, non-linear optical activity, and ferroelectricity) as well as great potential applications [1—7]. A large number of these materials are synthesized in the presence of organic amines as structure-directing agents [8—10].

Among the varieties of hybrid compounds explored, organically templated metal sulfates have been particularly investigated [11—17]. So far few double sulfates combining transition metal and chiral organic amines have been reported [18, 19].

In continuation of our search for non-centrosymmetric sulfate materials, both compounds [(R)-$C_5H_{14}N_2$][Cu(H_2O)$_6$](SO_4)$_2$ (**I**) and [(S)-$C_5H_{14}N_2$][Cu(H_2O)$_6$](SO_4)$_2$ (**II**) have been synthesized using enantiomerically pure sources of (R)-2-methylpiperazine or (S)-2-methylpiperazine respectively. In this paper, we wanted to observe the impact from the inclusion of chiral organic compounds into systems containing Jahn—Teller cations and comment upon this technique as an approach towards the synthesis of non-centrosymmetric complex architectures. The chemical preparations and the structure investigation of the title compounds are discussed.

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Table 1

Crystallographic data and Structure refinement Details for [(R)-$C_5H_{14}N_2$][Cu(H_2O)$_6$](SO_4)$_2$ (**I**) *and* [(S)-$C_5H_{14}N_2$][Cu(H_2O)$_6$](SO_4)$_2$ (**II**)

Empirical formula	$C_5H_{26}CuN_2O_{14}S_2$ (**I**)	$C_5H_{26}CuN_2O_{14}S_2$ (**II**)
Formula weight, g/mol	465.941	465.941
Temperature, K	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$
a, b, c, Å	6.5276(2), 11.1955(3), 12.4559(4)	6.5188(2), 11.1786(2), 12.4365(3)
β, deg.	101.196(2)	101.205 (1)
V, Å^3	892.95 (5)	888.99 (4)
Z	2	2
Calculated density, g/cm^3	1.681	1.718
Crystal size, mm	0.4×0.2×0.1	0.5×0.4×0.2
Habit-colour	Prism-blue	Prism-blue
λ (MoK_α), Å	0.71073	0.71073
Extinction coef	0.06 (1)	0.09 (6)
μ, mm^{-1}	1.523	1.532
Flack parameter	0.002(15)	–0.025(12)
θ Range for data collection, deg.	1.67—27.47	3.19—27.46
Index ranges	$-8 \le h \le 8, -14 \le k \le 14, -16 \le l \le 15$	$-8 \le h \le 8, -14 \le k \le 14, -16 \le l \le 16$
Unique data	4014	4032
Observed data [$I > 2\sigma(I)$]	3322	3819
F(000)	470	474
Refinement method	Full matrix least-squares on $\lvert F^2\rvert$	Full matrix least-squares on $\lvert F^2\rvert$
R_1	0.0342	0.0386
wR_2	0.0852	0.1232
GOOF	1.017	1.049
No. parameters	266	266
Transmission factors	0.6683 and 0.7354	0.4942 and 0.7603
Largest difference map peak and hole (eÅ^{-3})	–0.335 and 0.513	–0.721 and 0.710

EXPERIMENTAL

Synthesis. [(R)-$C_5H_{14}N_2$][Cu(H_2O)$_6$](SO_4)$_2$ (**I**) and [(S)-$C_5H_{14}N_2$][Cu(H_2O)$_6$](SO_4)$_2$ (**II**) compounds were prepared by slow evaporation through the reaction of 0.249 g (1.00×10^{-3} mol) of $CuSO_4.5H_2O$, 0.300 g (3.00×10^{-3} mol) of R-2-methylpiperazine or S-2-methylpiperazine, 0.098 g (1.00×10^{-3} mol) of H_2SO_4, and 10 ml of water. After a few days, transparent blue single crystals with prismatic shapes were isolated at room temperature. The yield was almost quantitative. Single crystals were found to be stable, non-hygroscopic and unaffected by the environment.

X-ray structure determination. A suitable single crystal of each compound was carefully selected under a polarizing microscope and glued to a glass fibre mounted on a four-circle Nonius Kappa CCD area-detector diffractometer. Intensity data sets were collected using MoKα radiation through the COLLECT program [20]. Corrections for the Lorentz polarisation effect, peak integration, and background determination were carried out with the DENZO program [21]. Frame scaling and unit cell parameters refinement were performed with the SCALEPACK program [21]. Analytical absorption corrections were performed by modelling the crystals faces [22]. The structure analyses were carried out with the monoclinic symmetry, $P2_1$ space group, according to the automated search for the space group available in WinGX [23]. Transition metal atoms (Cu (II)) and sulfur atoms were located using the direct methods with the SHELXS-97 program [24]. The oxygen atoms and the organic moieties were found from successive Fourier calculations using SHELXL-97 [24]. The drawings were made with Diamond [25]. The aqua H atoms were located in a difference map and refined with O—H distance restraints of 0.85(1) Å and H—H restraints of 1.39(1) Å so that the H—O—H angle fitted to the ideal value of a tetrahedra angle. H atoms bonded to C and N atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H and N—H bonds were fixed at 0.97 and 0.89 Å respectively.

The CIF files with complete information about the structures were deposited at CCDC (No. 789495 (**I**) and 789496 (**II**)), from which are available free of charge on request at www.ccdc.cam.ac.uk/data_request/cif. Crystallographic data and structural refinements are summarized in Table 1.

IR spectroscopy. Infrared measurements were obtained using a Perkin-Elmer FT-IR Spectrum. Samples were diluted with spectroscopic grade KBr and pressed into a pellet. A scan was run over the range of 400—4000 cm^{-1}.

RESULTS AND DISCUSSION

Description of the Structures. Both compounds (**I**) and (**II**) were found to crystallize in the non-centrosymmetric $P2_1$ space group, for which the only symmetry elements are a series of 2_1 screw axes. They consist of transition metal cations octahedrally coordinated by six water molecules $[Cu(H_2O)_6]^{2+}$, isolated sulfate anions SO_4^{2-}, and diprotonated single enantiomer $[(R)\text{-}C_5H_{14}N_2]^{2+}$ or $[(S)\text{-}C_5H_{14}N_2]^{2+}$. The cohesion is ensured by hydrogen bonds between the cationic groups and only the sulfate O atoms. The resulting H-bonding networks can be alternatively described by three-dimensional supramolecular frameworks belonging to the structures of (**I**) and (**II**), thus forming channels in which the 2-methylpiperazinediium cation plays a templating role (Fig. 1).

The possibility of pseudosymmetry with the inorganic components of (**I**) and (**II**) was investigated. The organic cations were removed from the crystallographic models, and PLATON [26] was used to probe for missing symmetry. The ADDSYM command suggests the possibility of a missing additional symmetry leading to the $P2_1/c$ space group. The use of ADDSYM EXTRA indicates that there is no obvious space group change needed. The flack parameters were refined to 0.002(15) and –0.025(12) for (**I**) and (**II**) respectively. This result confirms the occurrence of a non-centrosymmetric space group and agrees with the chemical pathway in which enantiomeric molecules have been used.

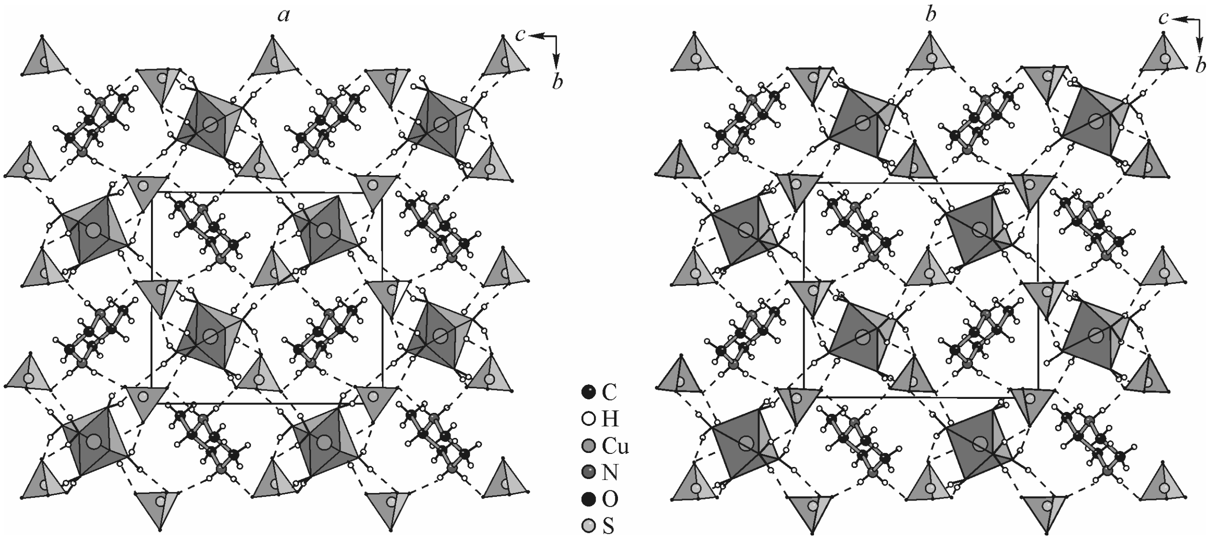

Fig. 1. Projection of the three-dimensional network of compound (**I**) (*a*) and compound (**II**) (*b*) on the (*bc*) plane. H bonds are shown as dashed lines

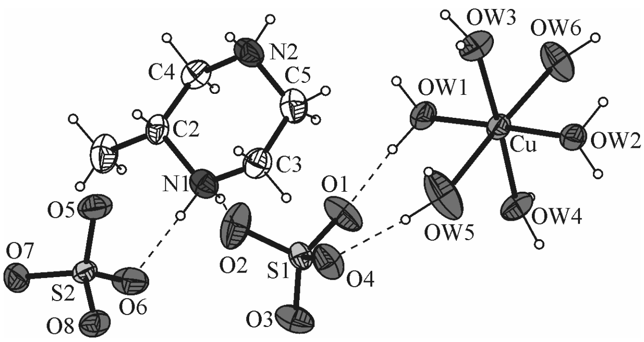

Fig. 2. A part of the crystal structure of [(R)-$C_5H_{14}N_2$][$Cu(H_2O)_6$]$(SO_4)_2$ showing the asymmetric unit and atom numbering. Displacement ellipsoids are drawn at the 50 % probability level. Hydrogen bonds are represented by dashed lines

In both structures, each asymmetric unit contains 24 non-hydrogen atoms, 17 of which belong to the inorganic framework, including one copper atom, two sulfate groups, and two unique cations, either two $[(R)\text{-}C_5H_{14}N_2]^{2+}$ or $[(S)\text{-}C_5H_{14}N_2]^{2+}$ (five carbon atoms and two nitrogen atoms), as shown in Figs. 2 and 3. In the structures of both compounds, the copper atom occupies a general position so that it is coordinated by six water oxygen atoms to form a slightly irregular octahedron, as seen in other isostructural templated metal sulfates [27—33]. The Cu ions display the so-called (4+2) type of coordination that has often been observed, which is consistent with a Jahn—Teller distortion. Indeed, metal-oxygen distances vary from 1.964(3) Å to 2.352(4) Å and from 1.964(1) Å to 2.346(1) Å for (**I**) and (**II**) respectively. Bond angles range between 84.97(2)° and 179.7(2)° for (**I**) and between 85.42(5)° and 179.66(9)° for (**II**), which are reasonable within the range of the Cu—O octahedron [34]. The mean Cu—OW distance value is 2.099(2) Å for (**I**) and 2.094(2) Å for (**II**). These values are in agreement with the values calculated from the bond valence program VALENCE [35] for a six-fold oxygen-coordinated copper atom; 2.105 Å and 2.102 Å in compounds (**I**) and (**II**) respectively. The metallic centres are isolated from one another with a shortest distance Cu—Cu = 6.528(2) Å for (**I**) and 6.519(1) Å for (**II**), which are shorter than those found in other sulfates templated by dabco [36] and piperazine [37] where Cu—Cu distances are 6.851(2) Å and 7.364(2) Å respectively. This result could probably be due to the size and shape of the amino groups involved in these structures.

The sulfate anions play a major role in the formation of the 3D supramolecular arrangement. All sulfur atoms are coordinated by four oxygen atoms to form a slightly distorted tetrahedron. In (**I**), the S—O bond distances are between 1.450(4) Å and 1.489(3) Å and the O—S—O bond angles are in the

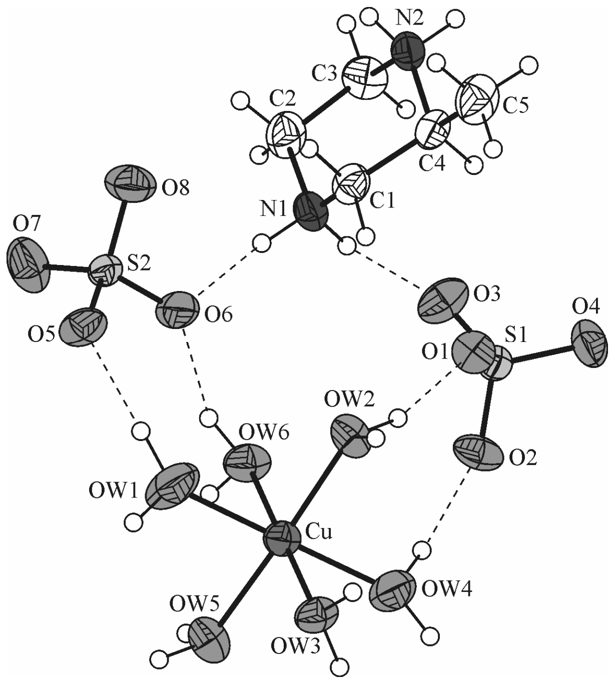

Fig. 3. Perspective view of the asymmetric unit of [(S)-$C_5H_{14}N_2$][$Cu(H_2O)_6$]$(SO_4)_2$ with the atom numbering scheme and thermal ellipsoids at 50 % of probability and arbitrary sphere for the H atoms

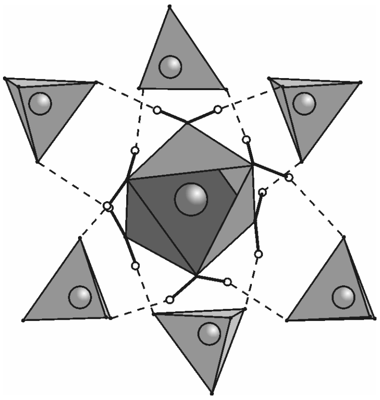

Fig. 4. Neighbouring sulfates in the environment of the Cu (II) octahedron for both compounds (**I**) and (**II**)

range 107.73(2)—112.5(2)°. Similarly, the S—O bonds in (**II**) range from 1.451(3) Å to 1.486(2) Å and the O—S—O bond angles vary from 108.01(2)° to 112.73(2)°, which is similar to other organically templated metal sulfates [28—33, 38]. These tetrahedra are stacked along the crystallographic *a* and *b* axes, so that anionic and mixed cationic layers alternate along the *c* axis and held together by N—H…O and OW—H…OW hydrogen bonds into an extensive three-dimensional infinite framework. Within the diprotonated chiral amine [(R)-$C_5H_{14}N_2$]$^{2+}$, the C—C and N—C distances range from 1.507(5) Å to 1.531(5) Å and from 1.474(5) Å to 1.518(5) Å respectively. In [(S)-$C_5H_{14}N_2$]$^{2+}$ cations, the C—C and N—C distances range respectively between 1.516(5) Å and 1.523(5) Å and between 1.475(4) Å and 1.502(4) Å. The characteristic bond distances and angles of the organic cations are in agreement with those reported in other compounds containing the same groups [33, 36, 37]. In the molecular structures of the title compounds, the role of a single enantiomer is 2-fold: first, they assume the well-established role of protonated amines, which includes acting as a source of charge balance for the anionic inorganic architectures. The second, which is less well established, involves the effects of cation chirality on the extended symmetry. The presence or absence of each enantiomer can be chemically controlled; if [(R)-$C_5H_{14}N_2$]$^{2+}$ cations alone are present in a structure, they can never be related to one another through centers of inversion because the required [(S)-$C_5H_{14}N_2$]$^{2+}$ cations are absent. Therefore, the formation of any inversion center is prohibited, and the space group of the material is constrained to be non-centrosymmetric. The chirality of [(R)-$C_5H_{14}N_2$]$^{2+}$ and [(S)-$C_5H_{14}N_2$]$^{2+}$ is reflected in the enantiomorphic and polar crystal class of these two compounds, **2** (*C2*).

For both compounds (**I**) and (**II**), each Cu octahedron is surrounded by six sulfate groups, H-bonded in a bidentate manner (Fig. 4). As shown in Fig. 5, organic cations in the form of either [(R)-$C_5H_{14}N_2$]$^{2+}$ or [(S)-$C_5H_{14}N_2$]$^{2+}$ engage their hydrogen atoms bonded to N atoms in N—H…O hydrogen bonds. So, they are connected to four neighbouring sulfate tetrahedra and contribute to the cohesion of the structures.

The two systems presented above display similarities and differences. The use of enantiomorphically pure sources of 2-methylpiperazine in each system precludes the formation of inversion centres and directs crystallization to non-centrosymmetric space groups. However, the differences between (**I**) and (**II**) are the presence of two complete [$C_5H_{14}N_2$]$^{2+}$ cations, either two [(R)-$C_5H_{14}N_2$]$^{2+}$ or two [(S)-$C_5H_{14}N_2$]$^{2+}$ respectively.

The intermolecular N—H…O bonds range from 2.683(4) Å to 2.805(5) Å and the OW—H…O bond lengths vary from 2.630(5) Å to 2.950(4) Å for both compounds. These values are not significantly different from those reported in other organically metal sulfates [14—17, 27, 29]. In addition, the structures of these materials remind of another type of similar compounds with the formula $M^{I}_2M^{II}(SO_4)_2 \cdot 6H_2O$, popularly referred to as Tutton's salts [[39—42] and references therein].

IR spectra. The presence of the template is confirmed by IR spectroscopy with C—H and N—H bands measured at 1432 cm^{-1} and 1611 cm^{-1} respectively. C—H and N—H stretches are observed at 2971 cm^{-1} and 2779 cm^{-1} respectively. S—O bands are observed at 986 cm^{-1} and 1106 cm^{-1}. These data are also in agreement with the double protonation of the organic moiety.

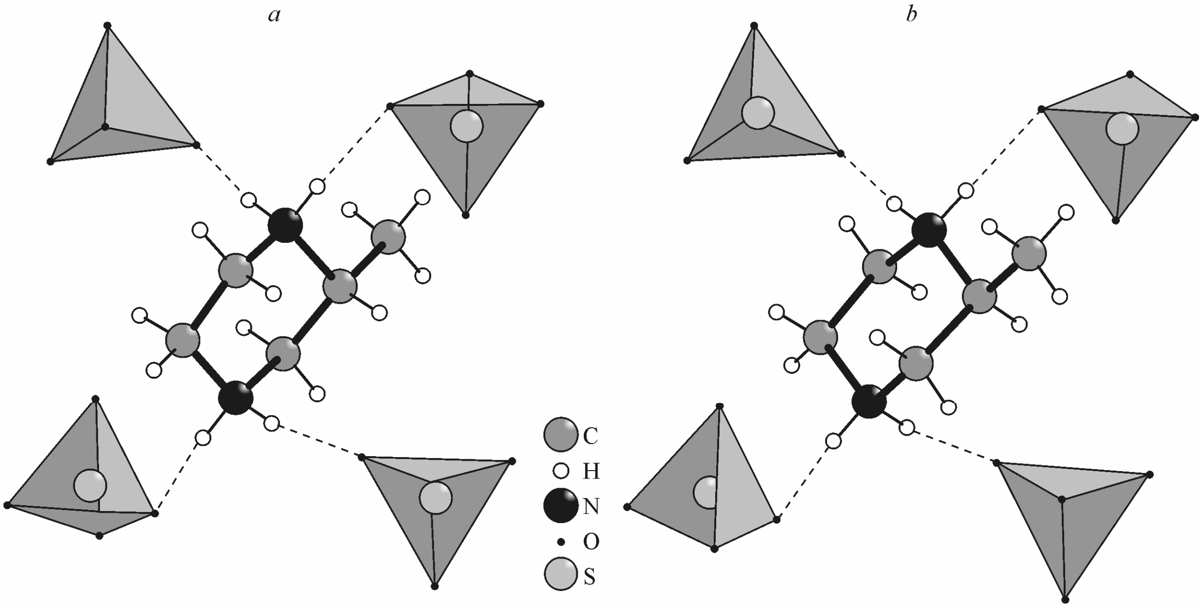

Fig. 5. H bonds established between $[C_5H_{14}N_2]^{2+}$ and sulfate tetrahedra in the structures of $[(R)\text{-}C_5H_{14}N_2][Cu(H_2O)_6](SO_4)_2$ and $[(S)\text{-}C_5H_{14}N_2][Cu(H_2O)_6](SO_4)_2$

CONCLUSIONS

In the present study, the use of chiral amine is an effective means for the preparation of a new non-centrosymmetric organic-inorganic hybrid material. Structural studies show that the title compounds $[(R)\text{-}C_5H_{14}N_2][Cu(H_2O)_6](SO_4)_2$ (**I**) or $[(S)\text{-}C_5H_{14}N_2][Cu(H_2O)_6](SO_4)_2$ (**II**) are built from isolated ions: $[Cu(H_2O)_6]^{2+}$, SO_4^{2-}, and a single enantiomer of $[C_5H_{14}N_2]^{2+}$ to generate a 0—D supramolecular fashion. The cohesion is ensured by intermolecular O—H…O and N—H…O hydrogen bonds. Further understanding of the role of enantiomorphically pure amines in determining the chiral structures will be helpful in the synthesis of new non-centrosymmetric function materials.

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