

catena-Poly[[tetraaquacopper(II)]- μ -trithionato- κ^2 O:O']

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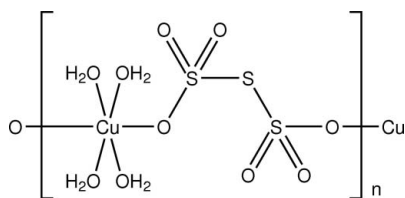
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{Cu}-\text{O}) = 0.004$ Å; R factor = 0.038; wR factor = 0.108; data-to-parameter ratio = 16.1.

The title supramolecular polymer, $[\text{Cu}(\text{S}_3\text{O}_6)(\text{H}_2\text{O})_4]_n$, features a tetragonally distorted octahedral Cu^{II} centre within an O_6 donor set with the longer $\text{Cu}-\text{O}$ bonds linking the dication and the trithionate dianion. Extensive $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bonding interactions connect the supramolecular chains into a three-dimensional network.

Related literature

For crystal structures containing the trithionate anion, see: Chun *et al.* (2000); Díaz de Vivar *et al.* (2005); Ferrari *et al.* (1977). For related copper(II) structures with bridging disulfonato ligands, see: Charbonnier *et al.* (1977*a,b*); Pasquale *et al.* (2007); Wang *et al.* (2005).



Experimental

Crystal data

$[\text{Cu}(\text{S}_3\text{O}_6)(\text{H}_2\text{O})_4]$
 $M_r = 327.78$
 Monoclinic, $P2_1/n$
 $a = 7.1816$ (1) Å
 $b = 21.4405$ (4) Å
 $c = 7.7286$ (1) Å
 $\beta = 116.092$ (1)°

$V = 1068.75$ (3) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 2.66$ mm⁻¹
 $T = 100$ K
 $0.30 \times 0.10 \times 0.05$ mm

Data collection

Bruker SMART APEXII
 diffractometer
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.911$, $T_{\text{max}} = 1$

9081 measured reflections
 2434 independent reflections
 2291 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.108$
 $S = 1.03$
 2434 reflections
 151 parameters

12 restraints
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 1.47$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.84$ e Å⁻³

Table 1

Selected bond lengths (Å).

Cu—O3	2.001 (3)	Cu—O4	2.047 (3)
Cu—O1	2.002 (3)	Cu—O5	2.524 (3)
Cu—O2	2.045 (3)	Cu—O8 ⁱ	2.564 (3)

Symmetry code: (i) $x + 1, y, z + 1$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
O1—H1o \cdots O9	0.84	2.29	3.080 (5)	157
O1—H2o \cdots O9 ⁱⁱ	0.84	2.25	3.071 (4)	166
O2—H3o \cdots O10 ⁱ	0.84	2.44	3.079 (5)	133
O2—H4o \cdots O6 ⁱⁱⁱ	0.84	2.21	3.026 (4)	165
O3—H5o \cdots O6 ⁱⁱⁱ	0.84	2.16	2.987 (4)	169
O3—H6o \cdots O10 ^{iv}	0.84	2.20	3.037 (5)	174
O4—H7o \cdots O9 ^{iv}	0.84	2.56	3.383 (5)	166
O4—H8o \cdots O8 ⁱⁱ	0.84	2.42	3.149 (4)	146

Symmetry codes: (i) $x + 1, y, z + 1$; (ii) $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (iii) $-x, -y + 2, -z + 1$; (iv) $x, y, z + 1$.

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS86 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg, 2006); software used to prepare material for publication: SHELXL97.

Dr Zhang Qichun, Nanyang Technological University, is gratefully thanked for the sample.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5217).

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supplementary materials

Acta Cryst. (2009). E65, i89 [doi:10.1107/S1600536809047096]

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E. R. T. Tiekink

Comment

The title compound, (I), was obtained from an hydrothermal synthesis (see Experimental) and characterized crystallographically. The asymmetric unit comprises a tetraqua copper(II) cation and a trithionato dianion, Fig. 1. In the crystal structure, the ions are connected as each trithionato dianion bridges two Cu^{II} centres thereby forming a supramolecular chain, Fig. 2. The Cu^{II} centre exists in a tetragonally distorted O₆ octahedron with the Cu—O_{aqua} bonds [2.047 (3) - 2.047 (3) Å] being significantly shorter than the Cu—O_{trithionato} bonds [2.524 (3) and 2.564 (3) Å]. The Cu atom lies 0.025 (2) out of the basal plane defined by the four aqua-O atoms (RMS = 0.080 Å) in the direction of the O8ⁱ atom, and the O5—Cu—O8ⁱ axial angle is 157.74 (10) ° for i: 1 + x, y, 1 + z. Within the trithionato dianion, the S1—S2 and S2—S3 bond distances are 2.1450 (11) and 2.1184 (12) Å, respectively, and the S1—S2—S3 angle is 101.68 (5) Å. In the crystal structure, there is a considerable number of hydrogen bonding interactions. These occur within the supramolecular chain as well as between chains to form a 2-D array in the *ac* plane, Fig. 3. Connections between layers lead to a 3-D network, Fig. 4.

Structures containing the trithionato dianion are comparatively rare, with only three such examples (Chun *et al.*, 2000; Díaz de Vivar *et al.*, 2005; Ferrari *et al.*, 1977). In the same way, structures having [Cu(OH₂)₄]²⁺ centres bridged by bi-functional sulfonato ligands are uncommon (Charbonnier *et al.*, 1977a, b; Pasquale *et al.*, 2007; Wang *et al.*, 2005).

Experimental

The blue crystal used in the present study was harvested from the hydrothermal reaction of stoichiometric amounts of CuCl, SeS₂, S, and N₂H₄·H₂O. The reagents were heated to 420 K for 3 d in a 25 ml Teflon-lined stainless-steel autoclave. After the reaction, the bomb was cooled to room temperature. The solution was filtered and layered with methanol. After four weeks, blue needles of (I) were collected and dried in air.

Refinement

The O-bound H-atoms were located in a difference Fourier map and were refined with O—H and H··H restraints of 0.840±0.001 Å and 1.39±0.01 Å, respectively, and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

Figures

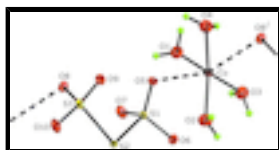


Fig. 1. The asymmetric unit in (I) extended to show the coordination geometry about the Cu atom, showing displacement ellipsoids at the 50% probability level. Symmetry code: (i) 1 + x, y, 1 + z.

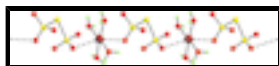


Fig. 2. Supramolecular chain formation in (I). Colour code: Cu, brown; S, yellow; O, red; and H, green.

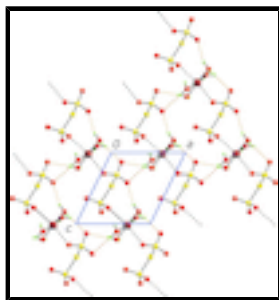


Fig. 3. Supramolecular layer formation in (I) viewed in projection down the *b* axis. Chains shown in Fig. 2 are linked *via* O–H···O (orange dashed lines) hydrogen bonds. Colour code as for Fig. 2.

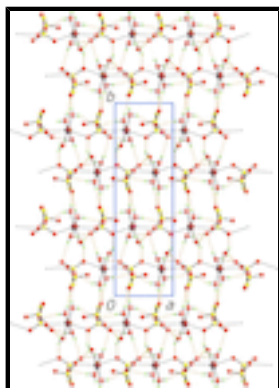


Fig. 4. Unit-cell contents for (I) highlighting the 3-D network. The O–H···O hydrogen bonds are shown as orange dashed lines. Colour code as for Fig. 2.

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Crystal data

[Cu(S₃O₆)(H₂O)₄]

M_r = 327.78

Monoclinic, *P*2₁/*n*

Hall symbol: -*P* 2yn

a = 7.1816 (1) Å

b = 21.4405 (4) Å

c = 7.7286 (1) Å

β = 116.092 (1)°

V = 1068.75 (3) Å³

Z = 4

F(000) = 660

D_x = 2.037 Mg m⁻³

Mo *K* α radiation, λ = 0.71073 Å

Cell parameters from 6028 reflections

θ = 3.1–27.6°

μ = 2.66 mm⁻¹

T = 100 K

Needle, blue

0.30 × 0.10 × 0.05 mm

Data collection

Bruker SMART APEXII
diffractometer

Radiation source: sealed tube
graphite

ϕ and ω scans

Absorption correction: multi-scan
(*SADABS*; Sheldrick, 1996)

2434 independent reflections

2291 reflections with *I* > 2 σ (*I*)

*R*_{int} = 0.020

θ_{\max} = 27.5°, θ_{\min} = 1.9°

h = -9→9

$T_{\min} = 0.911$, $T_{\max} = 1$
9081 measured reflections

$k = -27 \rightarrow 27$
 $l = -9 \rightarrow 10$

Refinement

Refinement on F^2

Primary atom site location: structure-invariant direct methods

Least-squares matrix: full

Secondary atom site location: difference Fourier map

$R[F^2 > 2\sigma(F^2)] = 0.038$

Hydrogen site location: inferred from neighbouring sites

$wR(F^2) = 0.108$

H-atom parameters constrained

$S = 1.03$

$w = 1/[\sigma^2(F_o^2) + (0.0493P)^2 + 7.019P]$

where $P = (F_o^2 + 2F_c^2)/3$

2434 reflections

$(\Delta/\sigma)_{\max} = 0.001$

151 parameters

$\Delta\rho_{\max} = 1.47 \text{ e } \text{\AA}^{-3}$

12 restraints

$\Delta\rho_{\min} = -0.84 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu	0.19601 (7)	0.85880 (2)	0.51918 (6)	0.01169 (14)
O1	0.2615 (5)	0.81059 (15)	0.3309 (5)	0.0268 (7)
H1O	0.1475	0.8079	0.2323	0.040*
H2O	0.3104	0.7753	0.3752	0.040*
O2	0.2609 (5)	0.93801 (15)	0.4087 (5)	0.0287 (7)
H3O	0.3791	0.9353	0.4120	0.043*
H4O	0.2480	0.9710	0.4611	0.043*
O3	0.1488 (5)	0.90825 (15)	0.7159 (5)	0.0264 (7)
H5O	0.1820	0.9459	0.7188	0.040*
H6O	0.0233	0.9046	0.6919	0.040*
O4	0.1007 (5)	0.77999 (16)	0.6068 (5)	0.0293 (7)
H7O	0.0526	0.7840	0.6876	0.044*
H8O	0.0311	0.7547	0.5190	0.044*
S1	-0.31167 (13)	0.90509 (4)	0.20735 (12)	0.01136 (19)
S2	-0.27573 (13)	0.94093 (4)	-0.03534 (11)	0.00925 (18)
S3	-0.28093 (13)	0.85804 (4)	-0.18661 (12)	0.0127 (2)

supplementary materials

O5	-0.1785 (4)	0.85083 (12)	0.2738 (4)	0.0145 (5)
O6	-0.2390 (5)	0.95873 (13)	0.3340 (4)	0.0194 (6)
O7	-0.5286 (4)	0.89104 (14)	0.1427 (4)	0.0185 (6)
O8	-0.4614 (4)	0.82243 (13)	-0.2060 (4)	0.0168 (5)
O9	-0.0873 (4)	0.82490 (13)	-0.0809 (4)	0.0169 (5)
O10	-0.2992 (4)	0.88484 (15)	-0.3653 (4)	0.0207 (6)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu	0.0123 (2)	0.0112 (2)	0.0125 (2)	-0.00021 (15)	0.00630 (17)	0.00000 (15)
O1	0.0282 (16)	0.0247 (15)	0.0250 (16)	0.0013 (13)	0.0094 (13)	-0.0021 (12)
O2	0.0325 (17)	0.0244 (16)	0.0334 (18)	0.0006 (13)	0.0183 (15)	0.0002 (13)
O3	0.0279 (16)	0.0248 (15)	0.0277 (16)	-0.0018 (12)	0.0133 (14)	-0.0020 (12)
O4	0.0320 (17)	0.0271 (16)	0.0283 (17)	-0.0018 (13)	0.0130 (14)	0.0019 (13)
S1	0.0125 (4)	0.0115 (4)	0.0101 (4)	0.0007 (3)	0.0050 (3)	0.0010 (3)
S2	0.0132 (4)	0.0077 (4)	0.0085 (4)	-0.0006 (3)	0.0063 (3)	0.0003 (3)
S3	0.0111 (4)	0.0163 (4)	0.0106 (4)	0.0000 (3)	0.0047 (3)	-0.0002 (3)
O5	0.0164 (13)	0.0124 (12)	0.0133 (12)	0.0027 (10)	0.0052 (10)	0.0026 (9)
O6	0.0286 (15)	0.0139 (13)	0.0148 (13)	-0.0004 (11)	0.0087 (11)	-0.0020 (10)
O7	0.0131 (13)	0.0269 (15)	0.0162 (13)	0.0011 (11)	0.0071 (11)	0.0044 (11)
O8	0.0140 (12)	0.0183 (13)	0.0173 (13)	-0.0026 (10)	0.0063 (10)	-0.0024 (10)
O9	0.0137 (12)	0.0189 (13)	0.0164 (13)	0.0031 (10)	0.0049 (10)	-0.0007 (10)
O10	0.0183 (13)	0.0321 (16)	0.0130 (13)	0.0008 (12)	0.0081 (11)	0.0034 (11)

Geometric parameters (\AA , $^\circ$)

Cu—O3	2.001 (3)	O3—H6O	0.8401
Cu—O1	2.002 (3)	O4—H7O	0.8401
Cu—O2	2.045 (3)	O4—H8O	0.8401
Cu—O4	2.047 (3)	S1—O7	1.443 (3)
Cu—O5	2.524 (3)	S1—O5	1.449 (3)
Cu—O8 ⁱ	2.564 (3)	S1—O6	1.450 (3)
O1—H1O	0.8401	S1—S2	2.1450 (11)
O1—H2O	0.8401	S2—S3	2.1184 (12)
O2—H3O	0.8401	S3—O10	1.448 (3)
O2—H4O	0.8401	S3—O9	1.452 (3)
O3—H5O	0.8401	S3—O8	1.454 (3)
O3—Cu—O1	176.54 (14)	Cu—O4—H8O	116.6
O3—Cu—O2	91.32 (13)	H7O—O4—H8O	111.9
O1—Cu—O2	87.46 (13)	O7—S1—O5	113.51 (17)
O3—Cu—O4	89.60 (14)	O7—S1—O6	114.36 (18)
O1—Cu—O4	91.95 (14)	O5—S1—O6	114.32 (16)
O2—Cu—O4	174.05 (14)	O7—S1—S2	107.39 (12)
Cu—O1—H1O	104.4	O5—S1—S2	106.44 (12)
Cu—O1—H2O	111.0	O6—S1—S2	99.21 (12)
H1O—O1—H2O	111.9	S3—S2—S1	101.68 (5)
Cu—O2—H3O	110.1	O10—S3—O9	113.18 (17)

Cu—O2—H4O	113.9	O10—S3—O8	114.04 (17)
H3O—O2—H4O	111.5	O9—S3—O8	113.01 (17)
Cu—O3—H5O	112.9	O10—S3—S2	99.54 (13)
Cu—O3—H6O	107.9	O9—S3—S2	108.67 (12)
H5O—O3—H6O	111.2	O8—S3—S2	107.22 (12)
Cu—O4—H7O	118.0		
O7—S1—S2—S3	-78.83 (14)	S1—S2—S3—O10	168.90 (12)
O5—S1—S2—S3	43.05 (12)	S1—S2—S3—O9	-72.54 (13)
O6—S1—S2—S3	161.92 (13)	S1—S2—S3—O8	49.91 (13)

Symmetry codes: (i) $x+1, y, z+1$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1o \cdots O9	0.84	2.29	3.080 (5)	157
O1—H2o \cdots O9 ⁱⁱ	0.84	2.25	3.071 (4)	166
O2—H3o \cdots O10 ⁱ	0.84	2.44	3.079 (5)	133
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Symmetry codes: (ii) $x+1/2, -y+3/2, z+1/2$; (i) $x+1, y, z+1$; (iii) $-x, -y+2, -z+1$; (iv) $x, y, z+1$.

Fig. 1

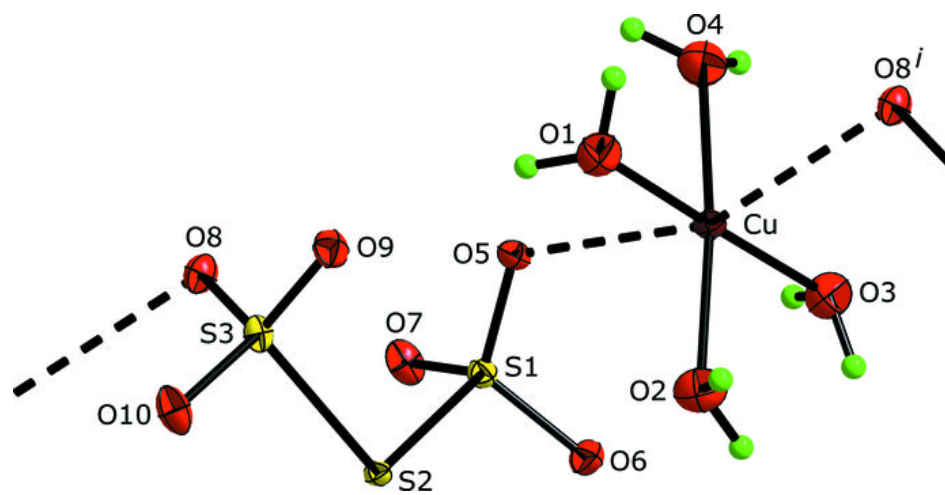


Fig. 2

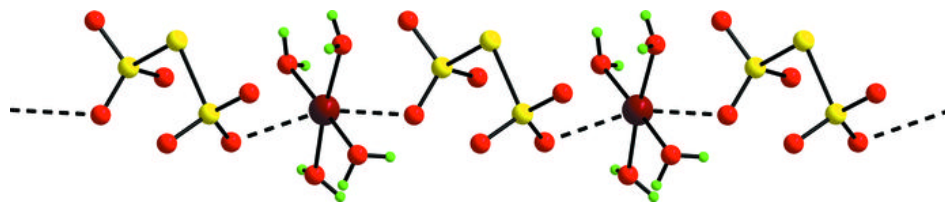


Fig. 3

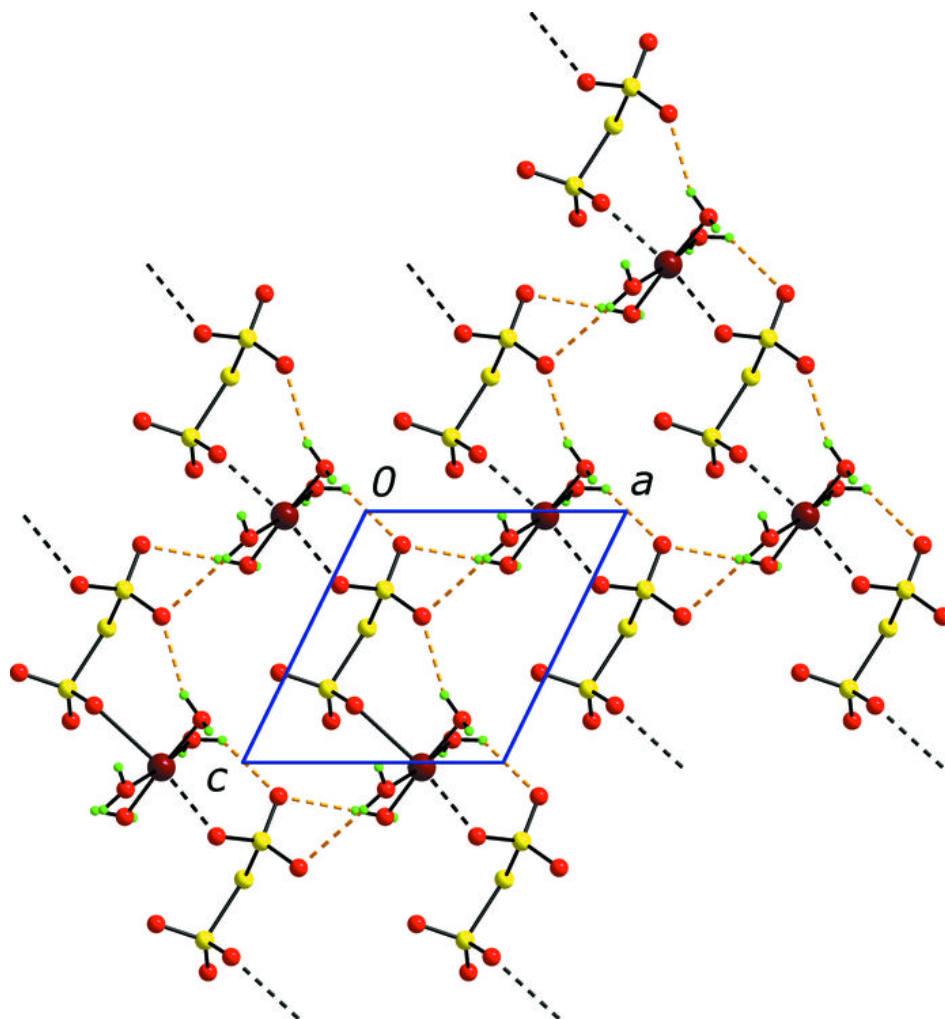


Fig. 4

