Acta Crystallographica Section E
**Structure Reports**
**Online**

ISSN 1600-5368

# Cadmium sulfite hexahydrate revisited

**Sergio Baggio,[a] Andrés Ibáñez[b] and Ricardo Baggio[c]***

[a]Universidad Nacional de la Patagonia, Sede Puerto Madryn, and, CenPat, CONICET, 9120 Puerto Madryn, Chubut, Argentina, [b]Departamento de Física, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile and CIMAT, Casilla 487-3, Santiago de Chile, Chile, and [c]Departamento de Física, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina
Correspondence e-mail: unbaggio@cenpat.edu.ar

Received 8 March 2008; accepted 21 April 2008

Key indicators: single-crystal X-ray study; $T$ = 150 K; mean $\sigma$(S–O) = 0.002 Å; $R$ factor = 0.018; $wR$ factor = 0.040; data-to-parameter ratio = 13.9.

The present structural revision of the title compound, tetracadmium tetrasulfite hexahydrate, $[Cd_4(SO_3)_4(H_2O)_5]\cdot H_2O$, is a low-temperature upgrade ($T$ = 100 K and $R$ = 0.017) of the original room-temperature structure reported by Kiers & Vos [*Cryst. Struct. Commun.* (1978). **7**, 399–403; $T$ = 293 K and $R$ = 0.080). The compound is a three-dimensional polymer with four independent cadmium centres, four sulfite anions and six water molecules, five of them coordinated to two cadmium centres and the remaining one an unbound solvent molecule which completes the asymmetric unit. There are two types of cadmium environment: $CdO_8$ (through four chelating sulfite ligands) and $CdO_6$ (by way of six monocoordinated ligands). The former groups form planar arrays [parallel to (001) and separated by half a unit cell translation along $c$], made up of chains running along [110] and [$\overline{1}$10], respectively. These chains are, in turn, interconnected both in an intraplanar as well as in an interplanar fashion by the latter $CdO_6$ polyhedra into a tight three-dimensional framework. There is, in addition, an extensive network of hydrogen bonds, in which all 12 water H atoms act as donors and eight O atoms from all four sulfite groups and two water molecules act as acceptors.

## Related literature

For related literature, see: Agre *et al.* (1981); Brown & Altermatt (1985); Elder *et al.* (1978); Harvey *et al.* (2006); Kiers & Vos (1978); Larsson & Kierkegaard (1969).

## Experimental

### Crystal data

$[Cd_4(SO_3)_4(H_2O)_5]\cdot H_2O$
$M_r$ = 877.94
Monoclinic, $P2_1/c$
$a$ = 12.1406 (3) Å
$b$ = 10.5485 (3) Å
$c$ = 13.9329 (4) Å
$\beta$ = 103.93 (1)°
$V$ = 1731.82 (11) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 5.41 mm$^{-1}$
$T$ = 150 (2) K
0.24 × 0.12 × 0.08 mm

### Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{min}$ = 0.40, $T_{max}$ = 0.64
31336 measured reflections
3959 independent reflections
3922 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.021

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.017
$wR(F^2)$ = 0.040
$S$ = 1.26
3959 reflections
284 parameters
18 restraints
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.70 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.56 e Å$^{-3}$

**Table 1**
Selected bond lengths (Å).

| | | | |
|---|---|---|---|
| Cd1—O13 | 2.2452 (18) | Cd2—O14 | 2.6091 (18) |
| Cd1—O32$^{i}$ | 2.2839 (18) | Cd2—O21 | 2.8126 (18) |
| Cd1—O22 | 2.3065 (18) | Cd3—O2*W* | 2.215 (2) |
| Cd1—O21 | 2.4078 (17) | Cd3—O1*W* | 2.2272 (19) |
| Cd1—O12 | 2.4542 (18) | Cd3—O3*W* | 2.278 (2) |
| Cd1—O31 | 2.4752 (18) | Cd3—O31 | 2.3201 (17) |
| Cd1—O23 | 2.6544 (18) | Cd3—O12 | 2.3482 (18) |
| Cd1—O12$^{i}$ | 2.7665 (19) | Cd3—O11$^{iii}$ | 2.3518 (18) |
| Cd2—O34 | 2.3311 (18) | Cd4—O34 | 2.2412 (18) |
| Cd2—O14$^{ii}$ | 2.3365 (18) | Cd4—O4*W* | 2.2599 (18) |
| Cd2—O33 | 2.3440 (18) | Cd4—O5*W* | 2.2601 (19) |
| Cd2—O11 | 2.3545 (18) | Cd4—O32$^{iv}$ | 2.2816 (18) |
| Cd2—O24$^{ii}$ | 2.4074 (18) | Cd4—O23$^{v}$ | 2.3203 (17) |
| Cd2—O23 | 2.4446 (18) | Cd4—O21 | 2.3571 (17) |

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

**Table 2**
Hydrogen-bond geometry (Å, °).

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| O1*W*—H1*WA*$\cdots$O13$^{i}$ | 0.82 (3) | 1.88 (2) | 2.693 (3) | 170 (4) |
| O1*W*—H1*WB*$\cdots$O14$^{vi}$ | 0.82 (3) | 1.93 (2) | 2.679 (3) | 151 (3) |
| O2*W*—H2*WA*$\cdots$O4*W*$^{iv}$ | 0.82 (3) | 1.93 (2) | 2.719 (3) | 162 (4) |
| O2*W*—H2*WB*$\cdots$O6*W* | 0.82 (3) | 1.95 (2) | 2.681 (3) | 149 (4) |
| O3*W*—H3*WA*$\cdots$O6*W*$^{vii}$ | 0.82 (3) | 2.02 (2) | 2.833 (3) | 172 (4) |
| O3*W*—H3*WB*$\cdots$O22$^{i}$ | 0.82 (3) | 2.29 (2) | 3.092 (3) | 168 (4) |
| O4*W*—H4*WA*$\cdots$O22 | 0.82 (3) | 1.87 (2) | 2.651 (3) | 159 (3) |
| O4*W*—H4*WB*$\cdots$O31$^{v}$ | 0.82 (3) | 1.98 (2) | 2.780 (3) | 167 (3) |
| O5*W*—H5*WA*$\cdots$O33 | 0.82 (3) | 2.05 (2) | 2.848 (3) | 167 (4) |
| O5*W*—H5*WB*$\cdots$O24$^{viii}$ | 0.82 (3) | 1.92 (2) | 2.708 (3) | 162 (4) |
| O6*W*—H6*WA*$\cdots$O24$^{ix}$ | 0.82 (3) | 2.16 (2) | 2.876 (3) | 146 (4) |
| O6*W*—H6*WB*$\cdots$O33$^{x}$ | 0.82 (3) | 2.18 (2) | 2.948 (3) | 157 (4) |

Symmetry codes: (i) $-x+1, -y, -z+1$; (iv) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (v) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (vi) $x+1, y, z$; (vii) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (viii) $-x, y-\frac{1}{2}, -z+\frac{3}{2}$; (ix) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (x) $x+1, -y+\frac{1}{2}, z+\frac{1}{2}$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

We acknowledge the Spanish Research Council (CSIC) for providing us with a free-of-charge licence for the CSD system (Allen, 2002).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2070).

## References

Agre, V. M., Kozlova, N. P., TrunovV, K. & Ershova, S. D. (1981). *Zh. Strukt. Khim.* **22**, 138–146.

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.

Bruker (2001). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Elder, R. C., Heeg, M. J., Payne, M. D., Trkula, M. & Deutsch, E. (1978). *Inorg. Chem.* **17**, 431–440.

Harvey, M. A., Baggio, S. & Baggio, R. (2006). *Acta Cryst.* B**62**, 1038–1042.

Kiers, C. Th. & Vos, A. (1978). *Cryst. Struct. Commun.* **7**, 399-403.

Larsson, L. O. & Kierkegaard, P. (1969). *Acta Chem. Scand.* **23**, 2253–2260.

Sheldrick, G. M. (2001). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

**i44** Baggio *et al.* • $[Cd_4(SO_3)_4(H_2O)_5]\cdot H_2O$ *Acta Cryst.* (2008). E**64**, i43–i44

# supplementary materials

*Acta Cryst.* (2008). E**64**, i43-i44 [ **doi:10.1107/S1600536808011409** ]

# Cadmium sulfite hexahydrate revisited

**S. Baggio, A. Ibáñez and R. Baggio**

## Comment

The sulfite $SO_3^{-2}$ ion is a most versatile inorganic ligand: the four atoms in the group can act as coordination donors and thus the molecule displays an enormous collection of different binding modes, from the very simple μ-S, as in pentaamminesulfite cobalt(III) chloride hydrate (Elder *et al.*, 1978), or μ-O, as in trisodium ethylenediamine-tetra-acetato-sulfite-indium(iii) tetrahydrate (Agre *et al.*, 1981), to an impressive $\mu_{10}$-S:*O*:*O*:*O*:*O*':*O*':*O*':*O*'':*O*'':*O*'' in anhydrous disodium sulfite (Larsson & Kierkegaard, 1969).

In combination with transition metals the anion can generate interesting structures, many of them reported in pioneering structural works. Some of these, however, even if proficiently worked out to the state of the art at the time of publication, appear nowadays below acceptable (and desirable) standards. This was the case for cadmium sulfite hydrate [$Cd_4(SO_3)_4(H_2O)_5.(H_2O)$], originally reported by Kiers & Vos, 1978, in a R.T.,low resolution structure determination (T: 293 K, *R*:0.080) and for which we present herein an upgrade, by way of a low temperature data refinement (T: 100 K, *R*: 0.017).

The structure (shown in Fig. 1) is a three-dimensional polymer with four independent cadmium centres, four sulfite anions and six water molecules, five of them coordinated to two cadmium centres and the remaining one, an unbound solvate which completes the asymmetric unit.

The cadmium environments in the structure split naturally into two types, *viz*.: two $CdO_8$, centred at Cd1 and Cd2 and achieved through four chelating sulfite bites each, and two $CdO_6$, centred at Cd3 and Cd4 and where no chelating bites whatsoever take part, the donor O atoms being either bridging (sulfite) or monocoordinated (aqua) (Table 1).

The two octacoordinated cadmium centres are comparable, but due to multiple chelation the corresponding $CdO_8$ polyhedra are difficult to describe by any regular model. However, both centres present a similar "tetrahedral" environment of ligands, the one around Cd1 being more flattened and describable as something midway a tetrahedral and a square planar arrangement. The one around Cd2, instead, is much more biased towards a tetrahedral shape.

In this regard the groups are adequate for a Vector Bond Valence treatment (hereafter VBV, Harvey *et al.*, 2006), a novel approach tending to a simpler description of multidentate binding, in which the action of each ligand is replaced by a single interaction vector, the Vector Bond Valence (or VBV), derived from the individual bond valences (Brown & Altermatt, 1985) of the coordinating atoms.

Even though for the four-ligand coordination geometry the VBV model would not predict a definite geometry for the four VBV vectors, the requirement of a bond valence of ~2 for both cations and a nil resultant of their vectorial sum would still be in force.

These requirements are satisfactorily fulfilled in both cases, with a scalar Bond Valence of 2.017 and 1.949, and a resultant VBV of 0.047 and 0.084 valence units for Cd1 and Cd2, respectively. Also the geometries of the (distorted) tetrahedra are correctly described by the VBV vectors, with the flattened Cd1 polyhedron presenting two large angles between *trans* VBV (126.8 (1) and 130.8 (1)°), and a much tighter span for the rest (Range: 94.9 (1)–111.7 (1)°) while the tetrahedron centred at Cd2 presents a close angle distribution throughout (Range: 100.9 (1)–115.9 (1)°).

The remaining cadmium centres Cd3 and Cd4, lacking any chelating ligand in their polyhedra, present rather regular octahedral arrangements (Table 1).

The anions coordinate through all their three donor O atoms, though not through sulfur, in $\mu_3$, $\mu_4$ and $\mu_5$ modes (Fig. 2). The internal geometry of the anions is quite regular and similar, as judged by the S—O (Å), O—S—O (°) mean values: S1, 1.543 (7), 103.2 (21); S2, 1.536 (6), 102.5 (12); S3, 1.540 (19), 103.3 (24); S4, 1.539 (18), 102.8 (17).

In addition to the diversity in cation environments, there is a more profound difference setting apart these two types of polyhedra, and it consists in their quite diverse structural function.

On one side, both $CdO_8$ groups join to each other forming two sets of straight chains (See Fig. 3 for details) at $z = 0$, running along $[\bar{1}10]$, and $z = 1/2$, running along [110], (A and B in Fig. 5; see below) both orientations subtending and angle of 98.0 (1)° to each other. Inspection of Fig. 3 reveals that the chains embed the crystallographic symmetry centres at sites $X$ (at 1/2,0,1/2) and Y (at 0,1/2,1/2). There is, however, an extra, nearly perfect (though non crystallographic) pseudo centre midway the former two at site $Z$ = 0.255,0.263, 1/2, relating Cd1 with Cd2, and $SO_3(1)$ with $SO_3(3)$. The degree of local pseudo symmetry involved can be assessed by the least squares fit of the Cd1, Cd2, $SO_3(1)$ and $SO_3(3)$ group (built up around the pseudo centre) and its inverted image, which gives a mean deviation of 0.11 (1)Å and a maximum of 0.14 (1)Å for the O31—O33 pair (Fig. 4). Fig. 5 shows the way in which these one-dimensional structures interact with each other: the chains containing Cd1—Cd2 (in bold) appear at nearly right angles to each other, either coming out the plane of the paper (type A) or lying on the plane of the paper (type B). The remaining polyhedra, in weak lining, interconnect them in such a way that while $Cd3O_6$ groups link parallel chains (A—A, B—B) along [110] and $[\bar{1}10]$, $Cd4O_6$ ones link perpendicular chains (A—B), along [001], with the final result of a very tight three-dimensional framework building up.

All six water molecules in the structure are involved in H-bonding through their twelve H atoms as donors (Table 2). The acceptor role is covered by eight O atoms coming from the four sulfite groups and two water molecules. The sulfite anions participate in a rather uneven way, *e.g.*: sulfite(1) through only one H-bond involving O31, sulfite(2), through two bonds, both involving O22, sulfite(3) and sulfite(4) through three bonds each, *via* O13 and O33 (twice) for the former, and by way of O14 and O24 (twice) for the latter. Among the water molecules, only one aqua participates as an acceptor (O4W, bound to Cd4), the remaining one being the crystal water O6W, which receives two bonds, and thus completes the scheme.

Contrasting with what is found in other sulfite structures, strong involvement in H-bonding of sulfite O atoms does not seem to weaken their S—O interactions; thus, the three O's which receive two H-bonds each and could thus be suspected of being affected by a strong electron-withdrawal effect, irrespective of this fact present either similar or significantly shorter S—O distances in their $SO_3$ groups. This can be assesed in the following data, where the S—O under consideration, its bond length, and the mean value of the remaining two S—O's in the group (mean-rest) are shown. Thus, in sulfite(2), S2—O22: 1.5302 (19), mean-rest: 1.541 (2) Å; in sulfite(3), S3—O33: 1.5269 (18), mean-rest: 1.547 (15) Å; in sulfite(4), S4—O24: 1.5189 (19), mean-rest: 1.549 (6) Å.

The complexity of this H-bonding scheme turns almost impossible any meaningful representation of the network to which it gives rise, for which a detailed packing figure including them has been spared, for the sake of clarity.

## Experimental

The compound was obtained by slow inter diffusion of $Na_2SO_3$ and $Cd(CH_3CO_2)_2$ aqueous solutions in (1:1) molar ratio. The connecting path between the two vessels was filled with an aqueous solution of $NaCH_3CO_2$, in order to minimize concentration gradients. After several weeks of unperturbed diffusion a crop of colourless, prismatic crystals of the title compound was obtained.

## Refinement

Hydrogen atoms (all of them pertaining to water molecules) were found in the difference- Fourier synthesis and refined with restrained O—H:0.82 (3) Å, H···H:1.35 (3) Å and free isotropic displacement parameters.

## Figures

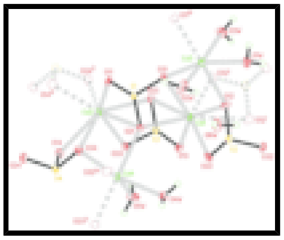


Fig. 1. a view of the structure with the independent atoms drawn in full 50% displacement ellipsoids. The symmetry related part, in dashed ellipsoids and bonds. Hydrogen interactions not shown, for clarity. Symmetry codes: (i) $-x + 1, -y, -z + 1$; (ii) $-x, -y + 1, -z + 1$; (iii) $-x + 1, -y + 1, -z + 1$; (iv) $-x + 1, y + 1/2, -z + 3/2$; (v) $x, -y + 1/2, z + 1/2$.

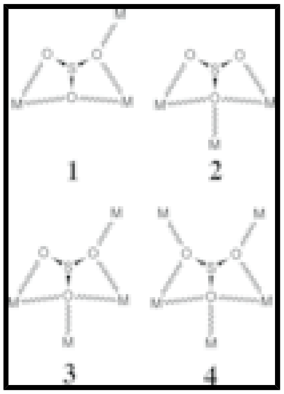


Fig. 2. The the coordination of the anions anions through all their three donor O atoms in $\mu_3$, $\mu_4$ and $\mu_5$ modes.

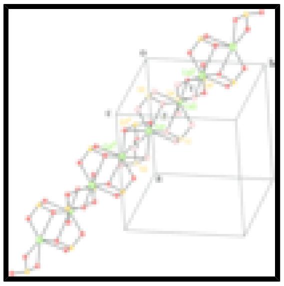


Fig. 3. A detailed view of one of the two Cd1—Cd2 chains (the one evolving along [110] and embedding symmetry centers at [1/2,0, 1/2] (*X*) and [0, 1/2, 1/2] (Y). Note the local pseudo symmetry centre *Z*.

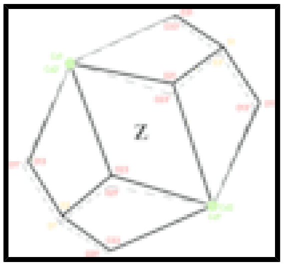


Fig. 4. Least-squares overlap of the Cd1—Cd2 nucleus with its inverted image thorugh a ($X$=0.255, Y=0.263, $Z$=0.500, site $Z$) inversion.

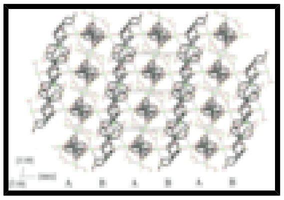


Fig. 5. Schematic representation of the structure packing. See text for details.

## cadmium sulfite hexahydrate

### *Crystal data*

$[Cd_4(SO_3)_4(H_2O)_5]\cdot H_2O$

$M_r$ = 877.94

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a$ = 12.1406 (3) Å

$b$ = 10.5485 (3) Å

$c$ = 13.9329 (4) Å

β = 103.93 (1)º

$V$ = 1731.82 (11) $Å^3$

$Z$ = 4

$F_{000}$ = 1648

$D_x$ = 3.367 Mg $m^{-3}$

Mo $K\alpha$ radiation
λ = 0.71073 Å

Cell parameters from 9999 reflections

θ = 1.9–27.2º

μ = 5.41 $mm^{-1}$

$T$ = 150 (2) K

Prisms, colourless

0.24 × 0.12 × 0.08 mm

### *Data collection*

Bruker CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T$ = 150(2) K

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 2001)

$T_{min}$ = 0.40, $T_{max}$ = 0.64

31336 measured reflections

3959 independent reflections

3922 reflections with $I > 2\sigma(I)$

$R_{int}$ = 0.021

$\theta_{max}$ = 27.8º

$\theta_{min}$ = 1.7º

$h = -15\rightarrow15$

$k = -13\rightarrow13$

$l = -18\rightarrow18$

### *Refinement*

Refinement on $F^2$

Least-squares matrix: full

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.017$

$wR(F^2) = 0.040$

$S = 1.26$

3959 reflections

284 parameters

18 restraints

Primary atom site location: structure-invariant direct methods

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0143P)^2 + 2.6649P]$
where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.70$ e Å$^{-3}$

$\Delta\rho_{min} = -0.56$ e Å$^{-3}$

Extinction correction: SHELXL97 (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.00228 (6)

*Special details*

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

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Cd1 | 0.374818 (15) | 0.126886 (17) | 0.512881 (12) | 0.01034 (5) |
| Cd2 | 0.126635 (15) | 0.392254 (17) | 0.488405 (12) | 0.00985 (5) |
| Cd3 | 0.651371 (15) | 0.304514 (17) | 0.535886 (13) | 0.01196 (5) |
| Cd4 | 0.251030 (14) | 0.282648 (17) | 0.748125 (12) | 0.00938 (5) |
| S1 | 0.39723 (5) | 0.40991 (6) | 0.57849 (4) | 0.00932 (11) |
| O11 | 0.30501 (15) | 0.49090 (17) | 0.51101 (13) | 0.0124 (4) |
| O21 | 0.33019 (15) | 0.29972 (16) | 0.60990 (13) | 0.0126 (4) |
| O31 | 0.45766 (15) | 0.34041 (17) | 0.50750 (13) | 0.0126 (3) |
| S2 | 0.58417 (5) | 0.04129 (6) | 0.66523 (4) | 0.01119 (12) |
| O12 | 0.58184 (16) | 0.10397 (17) | 0.56483 (13) | 0.0151 (4) |
| O22 | 0.45763 (15) | 0.03386 (19) | 0.66270 (13) | 0.0167 (4) |
| O32 | 0.61638 (16) | −0.09653 (17) | 0.64740 (13) | 0.0139 (4) |
| S3 | 0.11611 (5) | 0.11583 (6) | 0.42209 (4) | 0.01077 (12) |
| O13 | 0.20348 (15) | 0.03728 (17) | 0.49607 (13) | 0.0142 (4) |
| O23 | 0.19010 (15) | 0.22405 (17) | 0.39362 (13) | 0.0131 (4) |
| O33 | 0.04828 (15) | 0.18855 (17) | 0.48327 (13) | 0.0146 (4) |
| S4 | 0.01096 (5) | 0.43144 (6) | 0.66480 (4) | 0.01148 (12) |
| O14 | −0.05477 (15) | 0.40529 (17) | 0.55726 (13) | 0.0144 (4) |
| O24 | −0.01213 (16) | 0.57150 (18) | 0.67606 (13) | 0.0166 (4) |
| O34 | 0.13592 (15) | 0.42562 (18) | 0.65556 (13) | 0.0137 (4) |
| O1W | 0.81699 (17) | 0.20277 (19) | 0.57164 (16) | 0.0197 (4) |
| H1WA | 0.814 (3) | 0.1330 (18) | 0.546 (3) | 0.045 (12)* |
| H1WB | 0.868 (2) | 0.246 (3) | 0.559 (3) | 0.030 (10)* |
| O2W | 0.7011 (2) | 0.3753 (2) | 0.68995 (16) | 0.0286 (5) |
| H2WA | 0.693 (3) | 0.4504 (13) | 0.700 (3) | 0.045 (12)* |
| H2WB | 0.760 (2) | 0.347 (3) | 0.725 (2) | 0.037 (11)* |

| | | | | |
|---|---|---|---|---|
| O3W | 0.61491 (18) | 0.2464 (2) | 0.37382 (15) | 0.0203 (4) |
| H3WA | 0.6757 (19) | 0.249 (4) | 0.358 (3) | 0.046 (12)* |
| H3WB | 0.586 (3) | 0.1767 (18) | 0.359 (3) | 0.034 (11)* |
| O4W | 0.36903 (15) | 0.11969 (18) | 0.80645 (13) | 0.0133 (4) |
| H4WA | 0.411 (2) | 0.101 (4) | 0.7709 (19) | 0.032 (11)* |
| H4WB | 0.405 (2) | 0.133 (4) | 0.8633 (11) | 0.034 (11)* |
| O5W | 0.12980 (17) | 0.1237 (2) | 0.68645 (14) | 0.0186 (4) |
| H5WA | 0.100 (3) | 0.132 (4) | 0.6275 (9) | 0.033 (10)* |
| H5WB | 0.082 (2) | 0.113 (4) | 0.718 (2) | 0.047 (13)* |
| O6W | 0.83535 (18) | 0.2464 (2) | 0.83907 (16) | 0.0233 (4) |
| H6WA | 0.861 (3) | 0.180 (2) | 0.822 (3) | 0.058 (15)* |
| H6WB | 0.885 (3) | 0.284 (3) | 0.879 (3) | 0.052 (14)* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cd1 | 0.00977 (9) | 0.01060 (9) | 0.01059 (9) | 0.00073 (6) | 0.00235 (7) | 0.00000 (6) |
| Cd2 | 0.00950 (9) | 0.00952 (9) | 0.01055 (9) | 0.00085 (6) | 0.00243 (6) | 0.00000 (6) |
| Cd3 | 0.01045 (9) | 0.01000 (9) | 0.01560 (9) | 0.00038 (6) | 0.00346 (7) | 0.00120 (6) |
| Cd4 | 0.00934 (9) | 0.00987 (9) | 0.00873 (9) | 0.00011 (6) | 0.00176 (7) | 0.00026 (6) |
| S1 | 0.0086 (3) | 0.0090 (3) | 0.0101 (3) | 0.0010 (2) | 0.0019 (2) | 0.0000 (2) |
| O11 | 0.0097 (8) | 0.0102 (8) | 0.0169 (9) | 0.0021 (7) | 0.0027 (7) | 0.0033 (7) |
| O21 | 0.0167 (9) | 0.0100 (8) | 0.0131 (8) | 0.0000 (7) | 0.0071 (7) | 0.0011 (6) |
| O31 | 0.0110 (8) | 0.0147 (9) | 0.0130 (8) | 0.0020 (7) | 0.0047 (7) | 0.0004 (7) |
| S2 | 0.0119 (3) | 0.0101 (3) | 0.0110 (3) | 0.0023 (2) | 0.0015 (2) | −0.0009 (2) |
| O12 | 0.0159 (9) | 0.0134 (9) | 0.0150 (9) | −0.0016 (7) | 0.0019 (7) | 0.0036 (7) |
| O22 | 0.0130 (9) | 0.0238 (10) | 0.0145 (9) | 0.0067 (8) | 0.0054 (7) | 0.0030 (7) |
| O32 | 0.0172 (9) | 0.0101 (8) | 0.0136 (8) | 0.0053 (7) | 0.0022 (7) | 0.0003 (7) |
| S3 | 0.0099 (3) | 0.0109 (3) | 0.0115 (3) | 0.0002 (2) | 0.0025 (2) | −0.0015 (2) |
| O13 | 0.0128 (9) | 0.0107 (9) | 0.0186 (9) | 0.0004 (7) | 0.0029 (7) | 0.0019 (7) |
| O23 | 0.0143 (9) | 0.0129 (9) | 0.0135 (8) | 0.0006 (7) | 0.0060 (7) | 0.0003 (7) |
| O33 | 0.0134 (9) | 0.0148 (9) | 0.0179 (9) | 0.0012 (7) | 0.0082 (7) | −0.0013 (7) |
| S4 | 0.0106 (3) | 0.0121 (3) | 0.0123 (3) | 0.0021 (2) | 0.0038 (2) | 0.0015 (2) |
| O14 | 0.0138 (9) | 0.0145 (9) | 0.0139 (8) | −0.0008 (7) | 0.0010 (7) | −0.0009 (7) |
| O24 | 0.0201 (10) | 0.0140 (9) | 0.0164 (9) | 0.0065 (8) | 0.0057 (7) | −0.0001 (7) |
| O34 | 0.0096 (8) | 0.0172 (9) | 0.0144 (8) | 0.0029 (7) | 0.0033 (7) | 0.0025 (7) |
| O1W | 0.0131 (10) | 0.0123 (9) | 0.0336 (11) | −0.0006 (8) | 0.0052 (8) | −0.0019 (8) |
| O2W | 0.0419 (14) | 0.0186 (11) | 0.0201 (10) | 0.0122 (10) | −0.0027 (9) | −0.0021 (8) |
| O3W | 0.0221 (11) | 0.0204 (10) | 0.0206 (10) | −0.0038 (8) | 0.0094 (8) | −0.0028 (8) |
| O4W | 0.0134 (9) | 0.0144 (9) | 0.0119 (8) | 0.0023 (7) | 0.0028 (7) | −0.0005 (7) |
| O5W | 0.0201 (10) | 0.0231 (10) | 0.0129 (9) | −0.0100 (8) | 0.0046 (8) | −0.0013 (8) |
| O6W | 0.0177 (10) | 0.0271 (12) | 0.0230 (10) | 0.0056 (9) | 0.0006 (8) | −0.0002 (9) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Cd1—O13 | 2.2452 (18) | Cd3—O12 | 2.3482 (18) |
| Cd1—O32$^{\text{i}}$ | 2.2839 (18) | Cd3—O11$^{\text{iii}}$ | 2.3518 (18) |
| Cd1—O22 | 2.3065 (18) | Cd4—O34 | 2.2412 (18) |

| | | | |
|---|---|---|---|
| Cd1—O21 | 2.4078 (17) | Cd4—O4W | 2.2599 (18) |
| Cd1—O12 | 2.4542 (18) | Cd4—O5W | 2.2601 (19) |
| Cd1—O31 | 2.4752 (18) | Cd4—O32$^{iv}$ | 2.2816 (18) |
| Cd1—O23 | 2.6544 (18) | Cd4—O23$^{v}$ | 2.3203 (17) |
| Cd1—O12$^{i}$ | 2.7665 (19) | Cd4—O21 | 2.3571 (17) |
| Cd2—O34 | 2.3311 (18) | S1—O11 | 1.5364 (18) |
| Cd2—O14$^{ii}$ | 2.3365 (18) | S1—O21 | 1.5416 (18) |
| Cd2—O33 | 2.3440 (18) | S1—O31 | 1.5504 (18) |
| Cd2—O11 | 2.3545 (18) | S2—O22 | 1.5302 (19) |
| Cd2—O24$^{ii}$ | 2.4074 (18) | S2—O32 | 1.5410 (18) |
| Cd2—O23 | 2.4446 (18) | S2—O12 | 1.5413 (18) |
| Cd2—O14 | 2.6091 (18) | S3—O33 | 1.5269 (18) |
| Cd2—O21 | 2.8126 (18) | S3—O13 | 1.5323 (18) |
| Cd3—O2W | 2.215 (2) | S3—O23 | 1.5618 (18) |
| Cd3—O1W | 2.2272 (19) | S4—O24 | 1.5189 (19) |
| Cd3—O3W | 2.278 (2) | S4—O14 | 1.5435 (18) |
| Cd3—O31 | 2.3201 (17) | S4—O34 | 1.5544 (18) |

| | | | |
|---|---|---|---|
| O13—Cd1—O32$^{i}$ | 95.70 (7) | O34—Cd2—O21 | 68.10 (6) |
| O13—Cd1—O22 | 96.10 (7) | O14$^{ii}$—Cd2—O21 | 134.22 (6) |
| O32$^{i}$—Cd1—O22 | 135.43 (6) | O33—Cd2—O21 | 89.52 (6) |
| O13—Cd1—O21 | 92.82 (6) | O11—Cd2—O21 | 54.99 (5) |
| O32$^{i}$—Cd1—O21 | 136.46 (6) | O24$^{ii}$—Cd2—O21 | 148.24 (6) |
| O22—Cd1—O21 | 85.53 (6) | O23—Cd2—O21 | 74.20 (6) |
| O13—Cd1—O12 | 147.85 (6) | O14—Cd2—O21 | 119.61 (5) |
| O32$^{i}$—Cd1—O12 | 89.36 (6) | O2W—Cd3—O1W | 85.69 (8) |
| O22—Cd1—O12 | 59.93 (6) | O2W—Cd3—O3W | 173.70 (9) |
| O21—Cd1—O12 | 105.18 (6) | O1W—Cd3—O3W | 92.38 (8) |
| O13—Cd1—O31 | 138.85 (6) | O2W—Cd3—O31 | 97.98 (8) |
| O32$^{i}$—Cd1—O31 | 89.02 (6) | O1W—Cd3—O31 | 160.09 (7) |
| O22—Cd1—O31 | 108.83 (7) | O3W—Cd3—O31 | 85.86 (7) |
| O21—Cd1—O31 | 58.40 (6) | O2W—Cd3—O12 | 99.36 (8) |
| O12—Cd1—O31 | 72.77 (6) | O1W—Cd3—O12 | 82.53 (7) |
| O13—Cd1—O23 | 58.36 (6) | O3W—Cd3—O12 | 86.31 (7) |
| O32$^{i}$—Cd1—O23 | 70.94 (6) | O31—Cd3—O12 | 77.57 (6) |
| O22—Cd1—O23 | 148.13 (6) | O2W—Cd3—O11$^{iii}$ | 86.15 (8) |
| O21—Cd1—O23 | 77.80 (6) | O1W—Cd3—O11$^{iii}$ | 104.64 (7) |
| O12—Cd1—O23 | 150.86 (6) | O3W—Cd3—O11$^{iii}$ | 88.54 (7) |
| O31—Cd1—O23 | 85.29 (6) | O31—Cd3—O11$^{iii}$ | 95.15 (6) |
| O13—Cd1—O12$^{i}$ | 81.22 (6) | O12—Cd3—O11$^{iii}$ | 171.36 (6) |
| O32$^{i}$—Cd1—O12$^{i}$ | 55.66 (6) | O34—Cd4—O4W | 166.47 (7) |
| O22—Cd1—O12$^{i}$ | 84.10 (6) | O34—Cd4—O5W | 91.25 (7) |
| O21—Cd1—O12$^{i}$ | 167.41 (6) | O4W—Cd4—O5W | 82.57 (8) |
| O12—Cd1—O12$^{i}$ | 75.58 (6) | O34—Cd4—O32$^{iv}$ | 103.74 (7) |
| O31—Cd1—O12$^{i}$ | 132.23 (5) | O4W—Cd4—O32$^{iv}$ | 84.65 (7) |

| | | | |
|---|---|---|---|
| O23—Cd1—O12$^{i}$ | 107.85 (5) | O5W—Cd4—O32$^{iv}$ | 162.15 (7) |
| O34—Cd2—O14$^{ii}$ | 93.39 (6) | O34—Cd4—O23$^{v}$ | 103.74 (6) |
| O34—Cd2—O33 | 95.19 (6) | O4W—Cd4—O23$^{v}$ | 88.31 (6) |
| O14$^{ii}$—Cd2—O33 | 135.02 (6) | O5W—Cd4—O23$^{v}$ | 89.67 (7) |
| O34—Cd2—O11 | 88.74 (6) | O32$^{iv}$—Cd4—O23$^{v}$ | 77.53 (6) |
| O14$^{ii}$—Cd2—O11 | 84.47 (6) | O34—Cd4—O21 | 78.39 (6) |
| O33—Cd2—O11 | 139.70 (6) | O4W—Cd4—O21 | 90.23 (6) |
| O34—Cd2—O24$^{ii}$ | 143.60 (6) | O5W—Cd4—O21 | 95.87 (7) |
| O14$^{ii}$—Cd2—O24$^{ii}$ | 60.23 (6) | O32$^{iv}$—Cd4—O21 | 96.59 (6) |
| O33—Cd2—O24$^{ii}$ | 88.82 (7) | O23$^{v}$—Cd4—O21 | 174.04 (6) |
| O11—Cd2—O24$^{ii}$ | 111.03 (6) | O11—S1—O21 | 103.67 (10) |
| O34—Cd2—O23 | 134.72 (6) | O11—S1—O31 | 105.04 (10) |
| O14$^{ii}$—Cd2—O23 | 131.44 (6) | O21—S1—O31 | 100.83 (10) |
| O33—Cd2—O23 | 59.77 (6) | O22—S2—O32 | 103.91 (11) |
| O11—Cd2—O23 | 89.63 (6) | O22—S2—O12 | 101.66 (10) |
| O24$^{ii}$—Cd2—O23 | 77.64 (6) | O32—S2—O12 | 102.03 (10) |
| O34—Cd2—O14 | 57.77 (6) | O33—S3—O13 | 105.97 (10) |
| O14$^{ii}$—Cd2—O14 | 76.06 (7) | O33—S3—O23 | 101.25 (10) |
| O33—Cd2—O14 | 71.77 (6) | O13—S3—O23 | 102.63 (10) |
| O11—Cd2—O14 | 139.30 (6) | O24—S4—O14 | 102.06 (10) |
| O24$^{ii}$—Cd2—O14 | 89.80 (6) | O24—S4—O34 | 104.78 (11) |
| O23—Cd2—O14 | 129.84 (6) | O14—S4—O34 | 101.50 (10) |

Symmetry codes: (i) −*x*+1, −*y*, −*z*+1; (ii) −*x*, −*y*+1, −*z*+1; (iii) −*x*+1, −*y*+1, −*z*+1; (iv) −*x*+1, *y*+1/2, −*z*+3/2; (v) *x*, −*y*+1/2, *z*+1/2.

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1W—H1WA···O13$^{i}$ | 0.82 (3) | 1.88 (2) | 2.693 (3) | 170 (4) |
| O1W—H1WB···O14$^{vi}$ | 0.82 (3) | 1.93 (2) | 2.679 (3) | 151 (3) |
| O2W—H2WA···O4W$^{iv}$ | 0.82 (3) | 1.93 (2) | 2.719 (3) | 162 (4) |
| O2W—H2WB···O6W | 0.82 (3) | 1.95 (2) | 2.681 (3) | 149 (4) |
| O3W—H3WA···O6W$^{vii}$ | 0.82 (3) | 2.02 (2) | 2.833 (3) | 172 (4) |
| O3W—H3WB···O22$^{i}$ | 0.82 (3) | 2.29 (2) | 3.092 (3) | 168 (4) |
| O4W—H4WA···O22 | 0.82 (3) | 1.87 (2) | 2.651 (3) | 159 (3) |
| O4W—H4WB···O31$^{v}$ | 0.82 (3) | 1.98 (2) | 2.780 (3) | 167 (3) |
| O5W—H5WA···O33 | 0.82 (3) | 2.05 (2) | 2.848 (3) | 167 (4) |
| O5W—H5WB···O24$^{viii}$ | 0.82 (3) | 1.92 (2) | 2.708 (3) | 162 (4) |
| O6W—H6WA···O24$^{ix}$ | 0.82 (3) | 2.16 (2) | 2.876 (3) | 146 (4) |
| O6W—H6WB···O33$^{x}$ | 0.82 (3) | 2.18 (2) | 2.948 (3) | 157 (4) |

Symmetry codes: (i) −*x*+1, −*y*, −*z*+1; (vi) *x*+1, *y*, *z*; (iv) −*x*+1, *y*+1/2, −*z*+3/2; (vii) *x*, −*y*+1/2, *z*−1/2; (v) *x*, −*y*+1/2, *z*+1/2; (viii) −*x*, *y*−1/2, −*z*+3/2; (ix) −*x*+1, *y*−1/2, −*z*+3/2; (x) *x*+1, −*y*+1/2, *z*+1/2.

**Fig. 1**

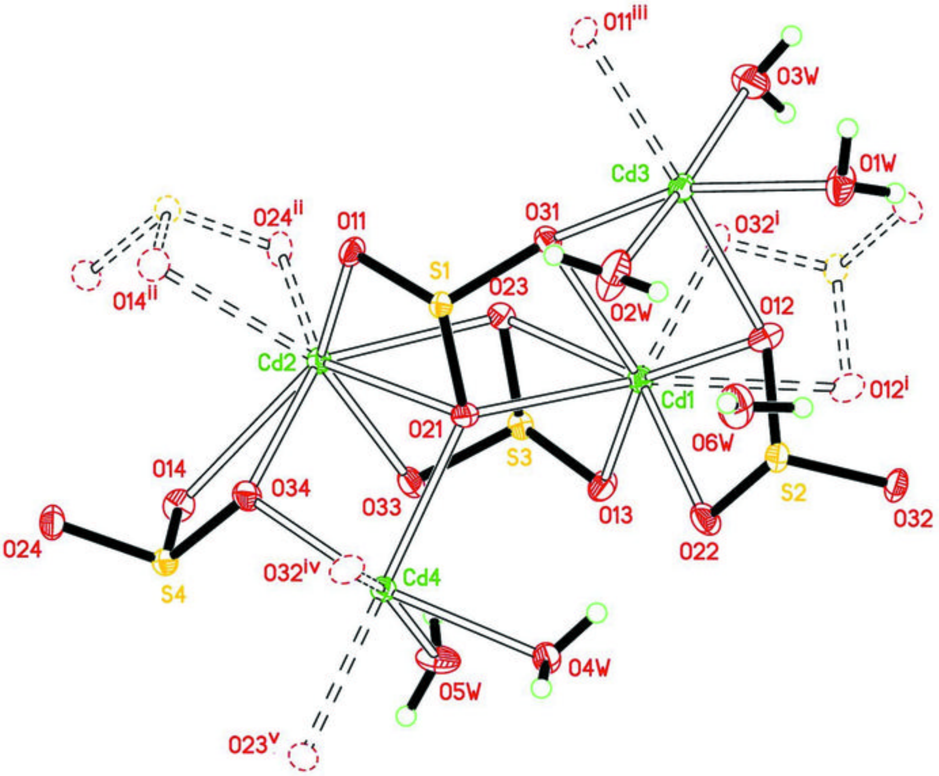
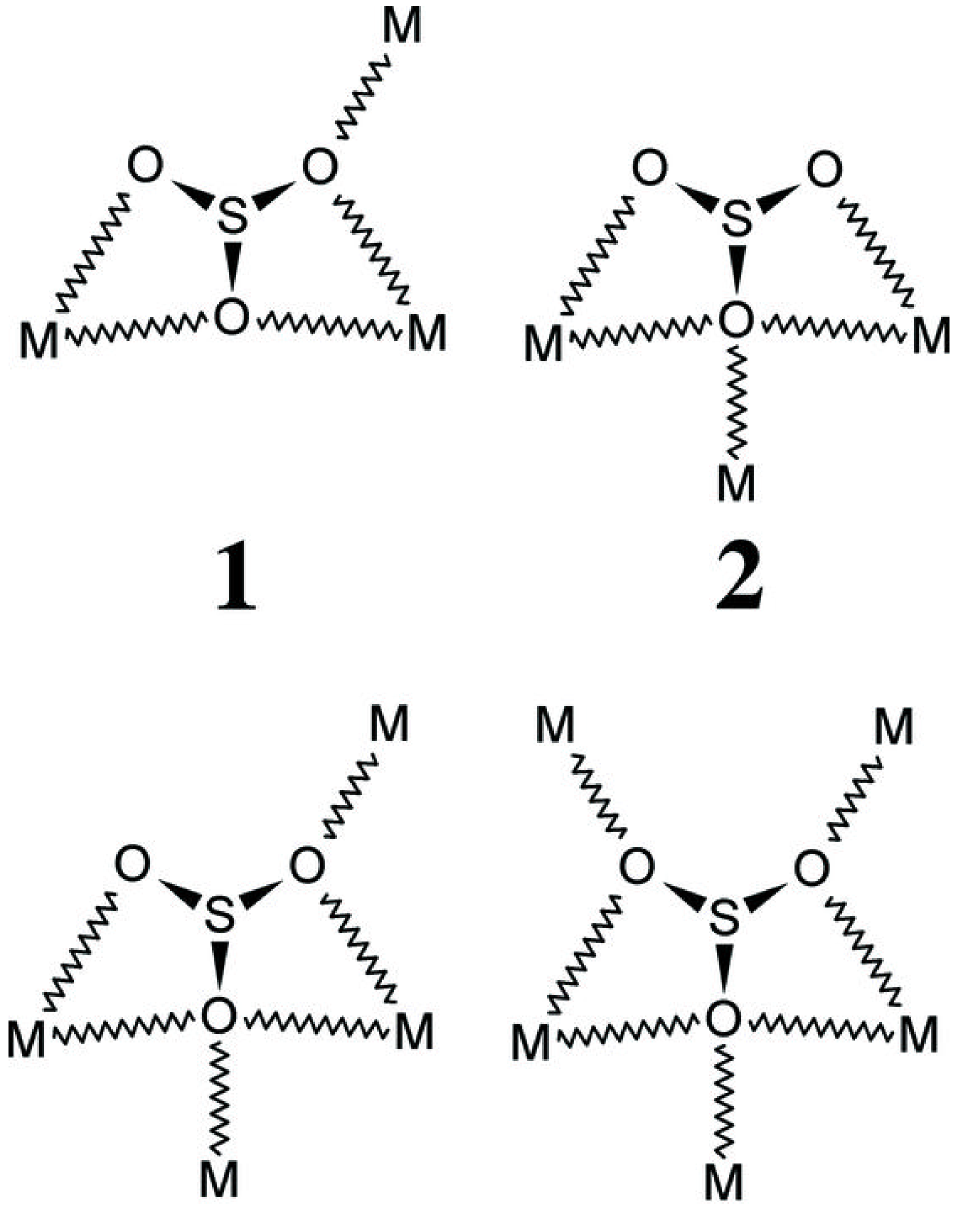

O11$^{iii}$
O3W
O1W
Cd3
O24$^{ii}$
O11
O31
O32$^{i}$
S1
O23
O2W
O14$^{ii}$
Cd2
O12
Cd1
O12$^{i}$
O21
O6W
S3
O14
O34
S2
O33
O13
O32
O24
O22
O32$^{iv}$
Cd4
S4
O4W
O5W
O23$^{v}$

Fig. 2



**1** **2**

**3** **4**

Fig. 3

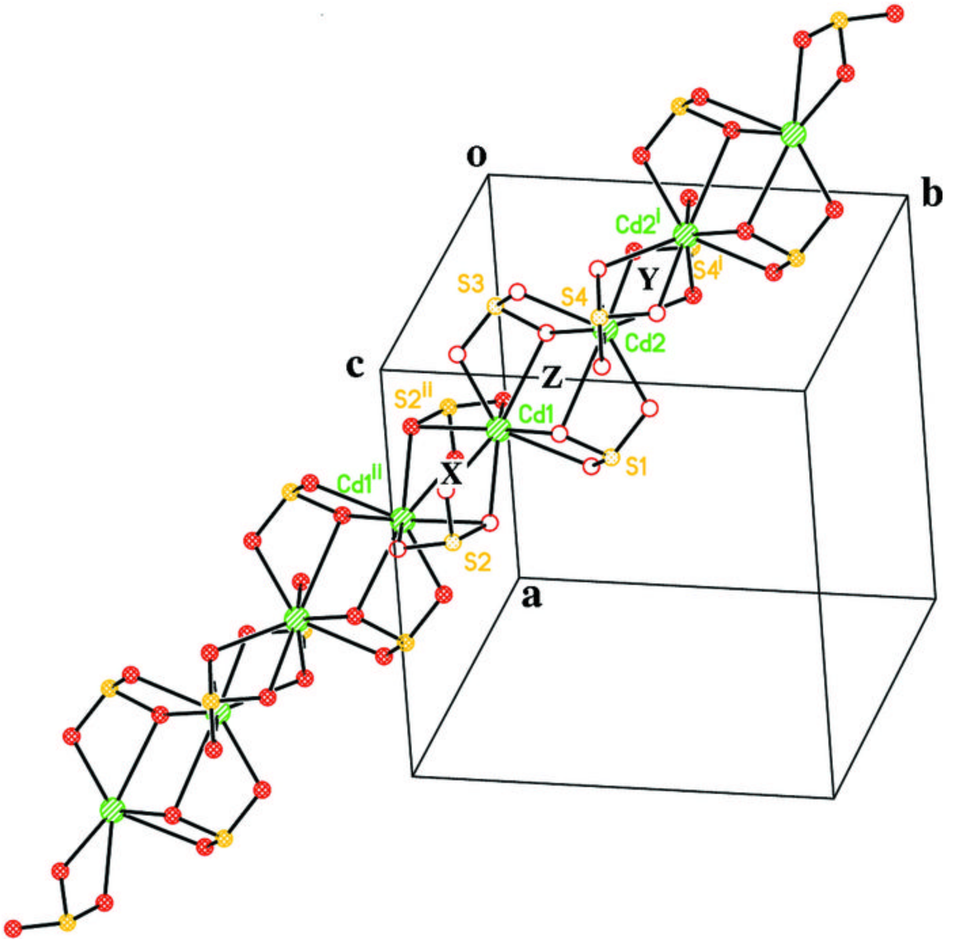


**Fig. 4**

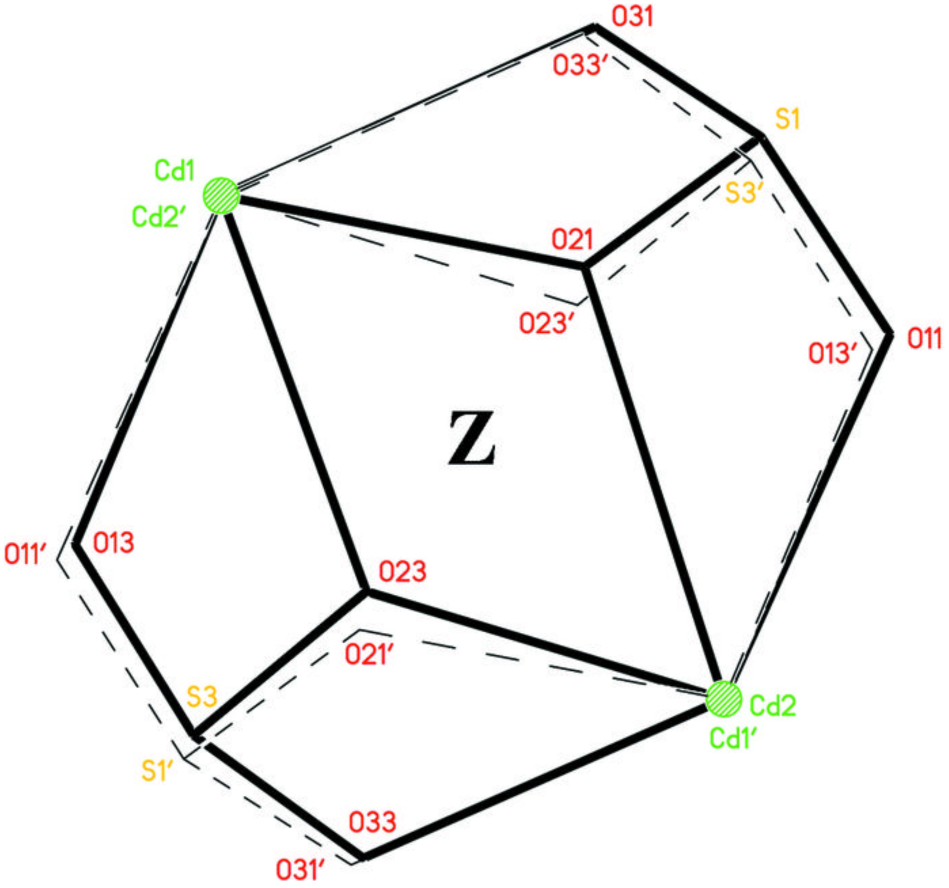

O31
O33′
S1
S3′
Cd1
Cd2′
O21
O23′
O13′
O11
Z
O11′
O13
O23
O21′
Cd2
Cd1′
S3
S1′
O33
O31′

**Fig. 5**