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Dieuropium(III) trisulfate octahydrate: a redetermination at 120 K

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The title compound, $Eu_2(SO_4)_3{\cdot}8H_2O$, crystallizes in space group *C*2/*c*, with one of the anions lying on a twofold rotation axis and the other in a general position, and is best formulated as $[Eu(H_2O)_{4/1}(SO_4)_{3/3}(SO_4)_{1/2}]_2$, where one of the anions lies across a twofold axis. The coordination environment of Eu^{III} consists of four water molecules and four sulfate ions. All the water molecules and sulfate ions are involved in hydrogen-bonding interactions. The structure is similar to that previously determined at 293 K [Wei & Zheng (2003). *Z. Kristallogr. New Cryst. Struct.* **218**, 277–278], but the cell parameters and the interatomic distances are more precise in the present determination.

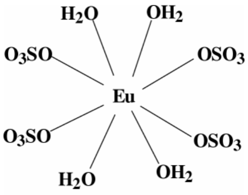
Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(S–O) = 0.002 Å
R factor = 0.019
wR factor = 0.054
Data-to-parameter ratio = 16.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Hydrated lanthanide(III) sulfates can adopt a number of different compositions, namely $M_2(SO_4)_3{\cdot}9H_2O$, $M_2(SO_4)_3{\cdot}8H_2O$, $M_2(SO_4)_3{\cdot}5H_2O$ and $M_2(SO_4)_3{\cdot}4H_2O$, and the octahydrated sulfates of lanthanides Ln^{III} exist as coordination polymers in which sulfate ions act as bridging bidentate and tridentate ligands; the presence of four coordinated water molecules leads to a coordination number of eight for the lanthanide ion (Wickleder, 2002). The unit-cell dimensions for hydrated europium(III) sulfate were reported many years ago (Geller, 1957), and the crystal structure, in space group *C*2/*c*, has recently been reported using data collected at 293 K (Wei & Zheng, 2003).



(I)

We report here the structure at 120 K. The similarity of the unit-cell dimensions and atomic coordinates at 293 and 120 K indicates that the same phase has been utilized in all of these studies. The aims of the present investigation are the determination of more precise metrical parameters and the determination of the extent of hydration. The structure (Table 1 and Fig. 1) indicates the presence of octacoordinate europium, with distorted square antiprismatic coordination by four water molecules, one O atom from a sulfate ion in the μ_2 bonding mode and three O atoms from three different anions in the μ_3 bonding mode. The triply bridging anions lie in general positions, while the doubly bridging anions lie on twofold rotation axes.

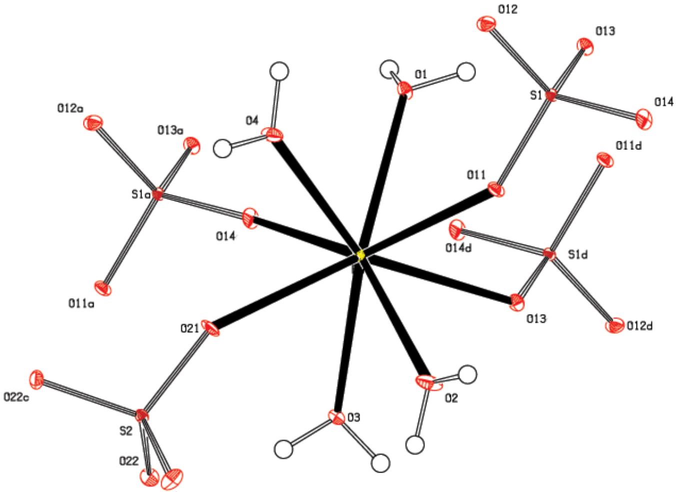


Figure 1
ORTEP diagram of (I), showing the coordination geometry around europium, with 50% probability ellipsoids. [Symmetry codes: (*a*) $-x, y, \frac{1}{2} - z$; (*b*) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (*c*) $\frac{1}{2} - x, \frac{3}{2} - y, 1 - z$.]

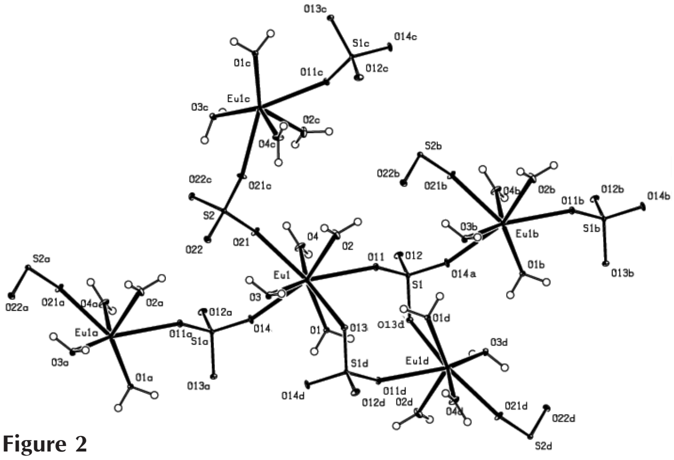


Figure 2
Crystal structure of (I), showing the sulfate coordination.

Compound (I) is, in fact, isostructural not only with yttrium(III) sulfate octahydrate (Held & Wickleder, 2003) but also with the analogous lanthanide sulfates $Ln_2(SO_4)_3{\cdot}8H_2O$, where Ln is Ce (Junk *et al.*, 1999), Pr (Ahmed Farag *et al.*, 1981), Nd (Bartl & Rodek, 1983), Sm (Podberezskaya & Borisov, 1976), Dy (Junk *et al.*, 1999), Er (Wickleder, 1999), Yb (Hiltunen & Niinistö, 1976) or Lu (Junk *et al.*, 1999). The coordination polymer in this structure is most readily envisaged as inversion-related pairs of chains comprising alternating cations and triply bridging anions, themselves generated by translation along the [010] direction, which are then linked into sheets by the doubly bridging anions. The coordination-polymer sheets are linked by hydrogen bonds (Table 2) into a continuous three-dimensional framework structure. As noted for the yttrium analogue (Held & Wickleder, 2003), one of the S—O bonds in the triply bridging anion is significantly longer than the others (Table 1).

Some of the lanthanides, such as europium, can also exhibit lower oxidation states in sulfate salts. Thus, for example, europium(II) sulfate has been shown to be anhydrous and to crystallize in space group *Pnma* (Mayer *et al.*, 1964).

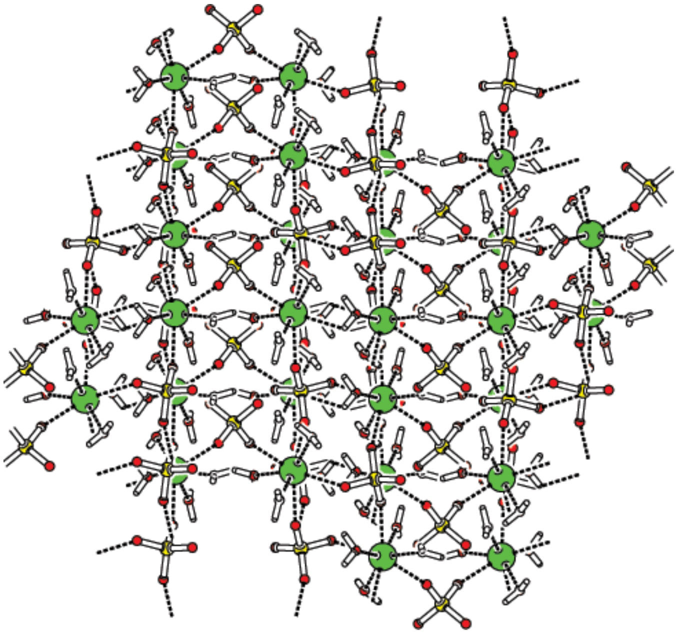


Figure 3
Packing diagram of (I), viewed along the *c* axis.

Accordingly, the oxidation state of europium in (I) was further confirmed by bond valence sum calculations (Brown, 1992, 2002). A total valence of 3.016 for europium was obtained using the observed Eu—O bond lengths (Table 1) and a bond valence parameter of 2.036 Å for europium (Trzesowska *et al.*, 2004).

Experimental

The title compound was obtained during the attempted preparation of a complex between 2,5-diketopiperazine and europium sulfate, in which 2,5-diketopiperazine (0.228 g, 2 mmol) was heated with europium sulfate (0.736 g, 1 mmol) in water (30 ml). The latter was obtained by the action of sulfuric acid on europium oxide. The crystallization of europium sulfate from solution is facilitated in the presence of other ligands (Held & Wickleder, 2003; Wei & Zheng, 2003).

Crystal data

$Eu_2(SO_4)_3{\cdot}8H_2O$
$M_r = 736.26$
Monoclinic, *C*2/*c*
$a = 13.5029$ (3) Å
$b = 6.7601$ (1) Å
$c = 18.2628$ (3) Å
$\beta = 102.2610$ (13)°
$V = 1629.02$ (5) Å^3
$Z = 4$

$D_x = 3.002$ Mg m^{-3}
Mo *K*α radiation
Cell parameters from 1869 reflections
$\theta = 3.1$–27.5°
$\mu = 8.12$ mm^{-1}
$T = 120$ (2) K
Block, colourless
$0.10 \times 0.08 \times 0.06$ mm

Data collection

Bruker–Nonius KappaCCD diffractometer with FR591 rotating anode
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.477$, $T_{max} = 0.616$
11 784 measured reflections

1869 independent reflections
1805 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$
$\theta_{max} = 27.5°$
$h = -17 \rightarrow 17$
$k = -8 \rightarrow 8$
$l = -22 \rightarrow 23$

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.054$
$S = 1.26$
1869 reflections
114 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0218P)^2 + 6.1179P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.71$ e Å^{-3}
$\Delta\rho_{\min} = -1.32$ e Å^{-3}

Table 1
Selected interatomic distances(Å).

Eu1—O1	2.450 (3)	Eu1—O21	2.339 (2)
Eu1—O2	2.390 (2)	S1—O11$^{\rm i}$	1.473 (2)
Eu1—O3	2.505 (2)	S1—O12	1.459 (3)
Eu1—O4	2.350 (3)	S1—O13	1.499 (2)
Eu1—O11	2.384 (2)	S1—O14$^{\rm ii}$	1.463 (2)
Eu1—O13	2.461 (2)	S2—O21	1.470 (2)
Eu1—O14	2.336 (2)	S2—O22	1.478 (2)

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H11···O3$^{\rm i}$	0.84	2.08	2.910 (3)	170
O1—H12···O13$^{\rm ii}$	0.84	2.06	2.771 (3)	143
O2—H21···O12$^{\rm iii}$	0.84	1.87	2.704 (4)	171
O2—H22···O22$^{\rm iv}$	0.84	1.99	2.814 (3)	169
O3—H31···O22	0.84	1.96	2.759 (3)	159
O3—H32···O13$^{\rm iii}$	0.84	2.16	2.994 (3)	170
O4—H41···O12$^{\rm v}$	0.84	1.93	2.748 (4)	163
O4—H42···O22$^{\rm vi}$	0.84	1.97	2.788 (4)	165

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

All H atoms were located in difference maps and then allowed to ride on their parent atoms, with O—H distances of 0.84 Å and with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm O})$.

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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