

Dy₂(SO₃)₂(SO₄)(H₂O)₂: the first lanthanide mixed sulfate–sulfite inorganic compound

Zai-Chao Zhang,^{a,b*} Jia-Hong Wang^a and Pu-Su Zhao^a

^aJiangsu Key Laboratory for the Chemistry of Low-dimensional Materials, School of Chemistry and Chemical Engineering, Huaiyin Normal University, 111 West Changjiang Road, Huai'an 223300, Jiangsu, People's Republic of China, and ^bState Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, People's Republic of China
Correspondence e-mail: overloadzz@hotmail.com

Received 22 November 2010

Accepted 9 March 2011

Online 13 April 2011

The first lanthanide mixed sulfate–sulfite inorganic coordination polymer, poly[*diaqua-μ*₄-sulfato-di-*μ*₄-sulfite-didysprosium(III)], [Dy₂(SO₃)₂(SO₄)(H₂O)₂]_n, has been obtained, in which both sulfate and sulfite groups originate from the disproportionation of S₂O₃²⁻ under hydrothermal and weakly acidic conditions. The crystal structure of the title compound exhibits a three-dimensional framework. The Dy^{III} ion is surrounded by eight O atoms from one water molecule and two sulfate and five sulfite groups. These DyO₈ polyhedra have two shared edges and form an infinite zigzag Dy–O chain. In the *bc* plane, neighbouring chains are integrated through SO₃ trigonal pyramids, forming a two-dimensional sheet. Along the *a*-axial direction, the sulfate group, with the central S atom lying on a twofold axis, links adjacent two-dimensional sheets *via* two S–O–Dy connections, thus generating the three-dimensional framework.

Comment

Over the past few decades, numerous solid inorganic materials with new topologies have been synthesized, and they have applications in ion exchange, adsorption, catalysis and radioactive waste remediation. Compared with other transition metal cations, the lanthanides have flexible bond lengths and high coordination numbers ranging from 7 to 12, which offer the possibility of forming solid-state materials with novel topological structures (Allendorf *et al.*, 2009; Feng *et al.*, 2010).

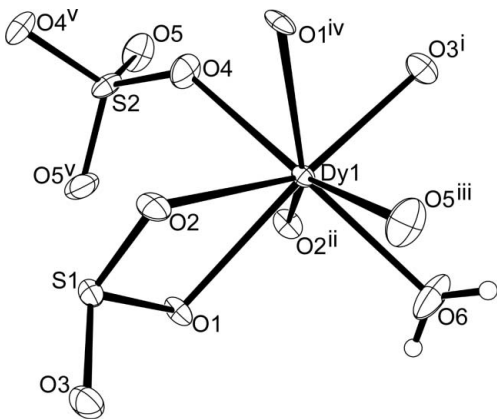
Coordination polymers, open-framework materials and hybrid compounds built up from various anions have been extensively described in the literature. The structural diversities of the anions have resulted in a variety of beautiful and topologically interesting structures, such as one-dimensional chains, two-dimensional grids, three-dimensional porous structures and interpenetrating networks. Among the

different anions, sulfate and sulfite groups are two important kinds of sulfur-centred oxyanions. Using sulfate groups as bridges, Doran *et al.* (2002), the Louer group (Bataille & Louer, 2002) and Xing *et al.* (2003) have achieved impressive geometric constructions. Our laboratory has also determined the crystal structure of oxonium neodymium bis(sulfate), (H₃O)Nd(SO₄)₂, which shows a two-dimensional layered framework assembled from SO₄ tetrahedra and NdO₉ tricapped trigonal prisms (Zhang & Zhang, 2010). In the sulfite group, the S atom is in a +4 intermediate oxidation state, which causes the sulfite anion to be readily oxidized to the sulfate ion and to appear unstable under hydrothermal and acidic conditions. For the purpose of synthesizing sulfite-containing materials, the main strategy nowadays is to introduce soft acids, for example, Cu^I, into the reactant system to stabilize the S^{IV} moieties through coordination from the soft base site (S atom) of the sulfite group to the soft acid (Li *et al.*, 2007, 2009; Li & Mao, 2008, 2010; Abrahams *et al.*, 2008). There are very few examples of metal sulfites synthesized without the assistance of soft acids (Rao & Rao, 2007). Due to this synthesis barrier, coordination polymers and open-framework structures containing both sulfate and sulfite anions are relatively rare. To the best of our knowledge, to date, only one mixed sulfate–sulfite inorganic compound has been reported, namely the mineral orschallite, Ca₃(SO₃)₂·(SO₄)·12H₂O (Weidenthaler *et al.*, 1993).

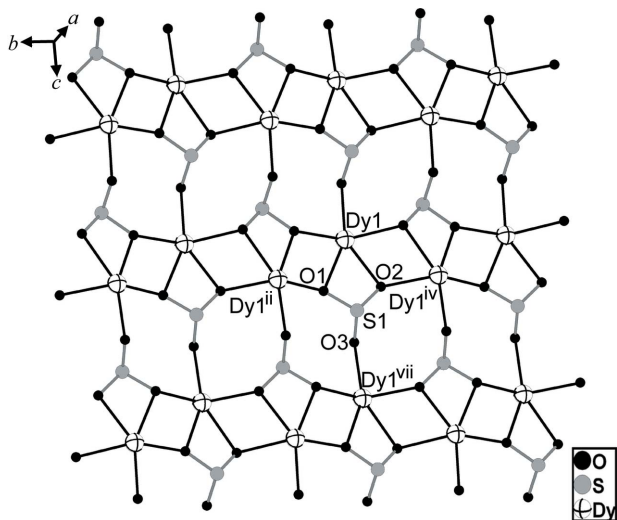
In order to synthesize sulfite-containing compounds without introducing soft acids, we therefore adopted the strategy of selecting and designating suitable sulfur sources to be used in reactions. Here, we report the synthesis and crystal structure of the first three-dimensional lanthanide mixed sulfate–sulfite inorganic coordination polymer, [Dy₂(SO₃)₂(SO₄)(H₂O)₂]_n. During the synthesis of the title compound, sodium hyposulfite, with better antioxidant ability, was chosen as the sulfur source instead of the more usual corresponding sulfite or hydrosulfite. The pH of the reactant solution was carefully controlled to be near 5.0. In this weakly acidic solution, S₂O₃²⁻ disproportionated slowly into H₂S, SO₃²⁻ and SO₄²⁻ under hydrothermal conditions and the title compound was obtained.

X-ray crystal structure analysis indicates that the asymmetric unit of Dy₂(SO₃)₂(SO₄)(H₂O)₂ contains one distinct Dy^{III} cation, one sulfite ion, one-half of the sulfate ion and one coordinated water molecule (Fig. 1). Atom Dy1 is coordinated by eight O atoms, *viz.* atom O6 of the water molecule, two sulfate O atoms (O4 and O5ⁱⁱⁱ) and five sulfite O atoms (O1, O2, O1^{iv}, O2ⁱⁱ and O3ⁱ) (symmetry codes as in Fig. 1 and Table 1). The Dy–O bond lengths are in the range 2.287 (4)–2.429 (4) Å (Table 1). The sulfite group makes five S–O–Dy linkages, where atom O3 coordinates to one Dy^{III} cation and atoms O1 and O2 each bridge two metal centres, while the sulfate group, with the central S2 atom lying on a twofold axis, makes four S–O–Dy connections where each of atoms O4 and O5 coordinates to one Dy^{III} cation.

The sulfite group bridges atoms Dy1ⁱⁱ, Dy1 and Dy1^{iv} using its two *μ*₂-O atoms (O1 and O2), forming a zigzag chain (symmetry codes as in Fig. 2). The remaining sulfite atom O3

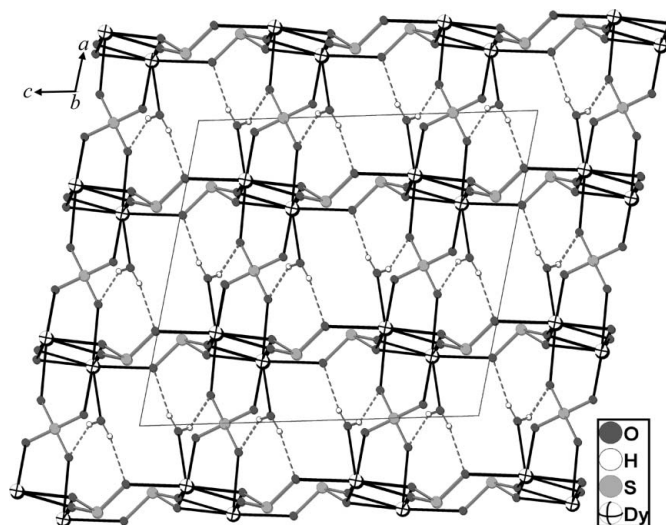

Figure 1

The asymmetric unit of $\text{Dy}_2(\text{SO}_3)_2(\text{SO}_4)(\text{H}_2\text{O})_2$, showing the atom-labelling scheme and the complete coordination environment around atom Dy1. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $x, -y, z - \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (iv) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$.]


Figure 2

The cationic sheet of $[\text{Dy}(\text{SO}_3)]^+$. [Symmetry codes: (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (iv) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (vii) $x, -y, z + \frac{1}{2}$.]

coordinates to atom Dy1^{vii} of an adjacent chain, thus forming a cationic $\text{Dy}-\text{O}-\text{S}$ sheet of composition $[\text{Dy}(\text{SO}_3)]^+$ in the bc plane (Fig. 2). A similar structure of a sulfite-bridged lanthanide-centred sheet with composition $[\text{Ln}(\text{SO}_3)]^+$ (Ln = lanthanide) has also been found in the previously reported two-dimensional open-framework compound $(\text{C}_2\text{H}_{10}\text{N}_2)[\text{Nd}(\text{SO}_3)(\text{SO}_4)(\text{H}_2\text{O})_2]$ (Rao & Rao, 2007), which also contains both sulfate and sulfite ligands. In this structure, the unique eight-coordinate lanthanide centre is surrounded by eight O atoms from one water molecule and five sulfite and two sulfate groups. The differences in the structures of these two compounds are mainly attributed to the coordination modes of the sulfate groups. In the title compound, the sulfate group simultaneously coordinates to two pairs of Dy^{III} cations from two neighbouring sheets and, as a consequence, a three-dimensional neutral framework is generated consisting of sulfate-bridged $[\text{Dy}(\text{SO}_3)]^+$ sheets (Fig. 3). In $(\text{C}_2\text{H}_{10}\text{N}_2)-$


Figure 3

A view along the b axis, showing the three-dimensional framework structure of $\text{Dy}_2(\text{SO}_3)_2(\text{SO}_4)(\text{H}_2\text{O})_2$. Hydrogen bonds are represented by dashed lines.

$[\text{Nd}(\text{SO}_3)(\text{SO}_4)(\text{H}_2\text{O})_2]$, each sulfate group coordinates to only two lanthanide atoms of the same $[\text{Nd}(\text{SO}_3)]^+$ sheet. Thus, the formation of a three-dimensional framework is terminated and a two-dimensional open framework is formed instead. The protonated organoammonium cation $\text{C}_2\text{H}_{10}\text{N}_2^{2+}$, which acts as a template in $(\text{C}_2\text{H}_{10}\text{N}_2)[\text{Nd}(\text{SO}_3)(\text{SO}_4)(\text{H}_2\text{O})_2]$, induces the formation of anionic layers of composition $[\text{Ln}(\text{SO}_3)(\text{SO}_4)(\text{H}_2\text{O})]^-$ with an eight-coordinate Ln centre. The anionic layers and organoammonium cations are stacked in the two-dimensional open framework through electrostatic forces and hydrogen bonds between the protonated amino groups and the sulfate O atoms. The occurrence of the organoammonium cation in the two-dimensional open-framework structure separates the $[\text{Ln}(\text{SO}_3)(\text{SO}_4)(\text{H}_2\text{O})]^-$ anionic layers, leading to lengthening of the distance between neighbouring $[\text{Ln}(\text{SO}_3)]^+$ sheets. The distance along the a direction is 5.8680 (15) Å in the title compound and 9.0880 (3) Å in $(\text{C}_2\text{H}_{10}\text{N}_2)[\text{Nd}(\text{SO}_3)(\text{SO}_4)(\text{H}_2\text{O})_2]$. Along the a direction, the $[\text{Nd}(\text{SO}_3)]^+$ sheets of $(\text{C}_2\text{H}_{10}\text{N}_2)[\text{Nd}(\text{SO}_3)(\text{SO}_4)(\text{H}_2\text{O})_2]$ are arranged in a parallel manner. In the title compound, all the $[\text{Dy}(\text{SO}_3)]^+$ sheets are equivalent and stack along the a axis. However, as the bridging tetragonal μ_4 -sulfate groups lie about twofold axes that run parallel to the b axis, adjacent sheets are not directly superimposable, but are related by these twofold axes. The coordinated water molecule in the title compound is fixed through $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds (Table 2).

In summary, the first lanthanide mixed sulfate-sulfite inorganic compound with a three-dimensional framework structure has been obtained by employing $\text{S}_2\text{O}_3^{2-}$ as the sulfur source, which offers a new strategy to synthesize sulfite-containing solid inorganic materials. The structure of the title compound shows that an $[\text{Ln}(\text{SO}_3)]^+$ inorganic sheet can not only occur isolated in two-dimensional open-framework compounds, as in $(\text{C}_2\text{H}_{10}\text{N}_2)[\text{Nd}(\text{SO}_3)(\text{SO}_4)(\text{H}_2\text{O})_2]$, but can also be bridged to form porous three-dimensional neutral

frameworks. Such porous frameworks would be important catalyst candidates. However, in the title compound, the sulfate group, which is the bridging ligand connecting neighbouring $[\text{Ln}(\text{SO}_3)]^+$ sheets, is rather short, which leads to a very small pore size in the framework. Further work will focus on introducing longer organic bridging ligands than the sulfate group in the title compound, in order to synthesize metal-organic frameworks (MOFs) with larger pores based on $[\text{Ln}(\text{SO}_3)]^+$ inorganic sheets.

Experimental

Crystals of $\text{Dy}_2(\text{SO}_3)_2(\text{SO}_4)(\text{H}_2\text{O})_2$ were synthesized hydrothermally. A mixture of $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$ (0.30 mmol, 0.11 g) and $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (0.10 mmol, 0.025 g) was dissolved in distilled water (8 ml). The pH was carefully adjusted to near 5.0 using 1.0 M NaOH (aqueous) and the reaction mixture was placed in a Teflon-lined stainless steel autoclave (25 ml), which was heated at 433 K for 48 h. Block-shaped colourless crystals were collected (yield 54%, based on $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$). The final solution gave off a pungent smell with little change in pH, which is undoubtedly ascribed to the formation of H_2S from the disproportionation of $\text{S}_2\text{O}_3^{2-}$ during the hydrothermal reaction.

Crystal data

$[\text{Dy}_2(\text{SO}_3)_2(\text{SO}_4)(\text{H}_2\text{O})_2]$	$V = 996.1 (4) \text{ \AA}^3$
$M_r = 617.21$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 11.736 (3) \text{ \AA}$	$\mu = 15.58 \text{ mm}^{-1}$
$b = 6.8010 (16) \text{ \AA}$	$T = 296 \text{ K}$
$c = 12.793 (3) \text{ \AA}$	$0.15 \times 0.15 \times 0.10 \text{ mm}$
$\beta = 102.686 (2)^\circ$	

Data collection

Bruker SMART APEX2 diffractometer	3145 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2000)	965 independent reflections
$T_{\min} = 0.13$, $T_{\max} = 0.22$	854 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$	78 parameters
$wR(F^2) = 0.049$	H-atom parameters constrained
$S = 1.09$	$\Delta\rho_{\text{max}} = 0.64 \text{ e \AA}^{-3}$
965 reflections	$\Delta\rho_{\text{min}} = -0.91 \text{ e \AA}^{-3}$

H atoms were located in a difference Fourier map and refined with distance restraints on the O—H bond lengths [0.85 (1) Å]. In the final stages of refinement, these atoms were refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O6})$.

Data collection: APEX2 (Bruker, 2004); cell refinement: APEX2; data reduction: APEX2; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXL97 and DIAMOND (Brandenburg & Putz, 2005); software used to prepare material for publication: SHELXL97.

Table 1

Selected bond lengths (Å).

Dy1—O1	2.429 (4)	Dy1—O3 ⁱ	2.287 (4)
Dy1—O2	2.415 (4)	Dy1—O2 ⁱⁱ	2.352 (4)
Dy1—O4	2.353 (4)	Dy1—O5 ⁱⁱⁱ	2.376 (4)
Dy1—O6	2.360 (4)	Dy1—O1 ^{iv}	2.388 (3)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O6—H6A ^v ···O3 ^v	0.85	2.00	2.843 (6)	176
O6—H6B ^v ···O4 ^{vi}	0.85	2.25	3.078 (6)	167

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

This work was supported by the Natural Science Foundation of Higher Education Colleges of Jiangsu Province (grant No. 08KJB150003), Jiangsu Planned Projects for Postdoctoral Research Funds (grant No. 1002012B) and an Industry Support Project of Huai'an City (grant No. HAG09054-9). Herein the authors extend their sincere gratitude for the support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KU3040). Services for accessing these data are described at the back of the journal.

References

- Abrahams, B. F., Haywood, M. G. & Robson, R. (2008). *Cryst. Growth Des.* **8**, 1288–1293.
- Allendorf, M. D., Bauer, C. A., Bhakta, R. K. & Houka, R. J. T. (2009). *Chem. Soc. Rev.* **38**, 1330–1352.
- Bataille, T. & Louer, D. (2002). *J. Mater. Chem.* **12**, 3487–3493.
- Brandenburg, K. & Putz, H. (2005). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Bruker (2000). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2004). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Doran, M., Norquist, A. J. & O'Hare, D. (2002). *Chem. Commun.* pp. 2946–2947.
- Feng, X., Wang, L.-Y., Wang, J.-G., Xie, C.-Z., Zhao, J.-S. & Sun, Q. (2010). *CrystEngComm*, **12**, 3476–3482.
- Li, P.-X., Hu, C.-L., Feng, M.-L. & Mao, J.-G. (2009). *Inorg. Chem.* **48**, 5454–5461.
- Li, P.-X., Jiang, H.-L., Feng, M.-L. & Mao, J.-G. (2007). *Inorg. Chem.* **46**, 8302–8308.
- Li, P.-X. & Mao, J.-G. (2008). *Cryst. Growth Des.* **8**, 3385–3389.
- Li, P.-X. & Mao, J.-G. (2010). *Dalton Trans.* pp. 107–112.
- Rao, K. P. & Rao, C. N. R. (2007). *Inorg. Chem.* **46**, 2511–2518.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Weidenthaler, C., Tillmanns, E. & Hentschel, G. (1993). *Mineral. Petrol.* **48**, 167–177.
- Xing, Y., Shi, Z., Li, G.-H. & Pang, W.-Q. (2003). *Dalton Trans.* pp. 940–943.
- Zhang, Z. & Zhang, Z. (2010). *Acta Cryst.* **C66**, i9–i11.