metal-organic papers

catena-Poly[[[diaqua(pyrimidin-2-ylsulfanyl-acetato)lanthanum(III)]-di-*μ*-pyrimidin-2-yl-sulfanylacetato] trihydrate]

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The La atom is ten-coordinate in a capped square–antiprismatic geometry in the title polymeric chain structure, $\{[La(C_6H_5N_2O_2S)_3(H_2O)_2]\cdot 3H_2O\}_n$. Adjacent chains are linked by hydrogen bonds to give a layer structure.

Comment

We have reported several metal derivatives of 4-pyridylthio-acetic acid (Fang *et al.*, 2004; Huang, Zhang, Chen & Ng, 2004; Huang, Zhang, Chen, Zhou *et al.*, 2004; Zhang *et al.*, 2003, 2004*a,b*); the pyridyl N atoms in these complexes typically interact through hydrogen bonds. The studies continue with the 2-pyrimidinyl analog of this heteroarylthioacetic acid; few metal derivatives of this carboxylic acid have been reported (Ng *et al.*, 1993; Ma *et al.*, 2004). The present lanthanum(III) derivative, (I), is chelated by the carboxylate portion of the pyrimidin-2-ylsulfanylacetate, but coordination by water molecules as well as two bridging interactions lead to a ten-coordinate environment of the metal atom (Fig. 1). The geometry is better regarded as capped square–antiprismatic (Fig. 2); the capping O atoms are farther away than the other eight O atoms that comprise the square antiprism (Table 1). The compound adopts a chain motif arising from carboxylate bridging (Fig. 3); adjacent chains are linked through hydrogen bonds involving the uncoordinated water molecules (Table 2) to give layers.

(I)
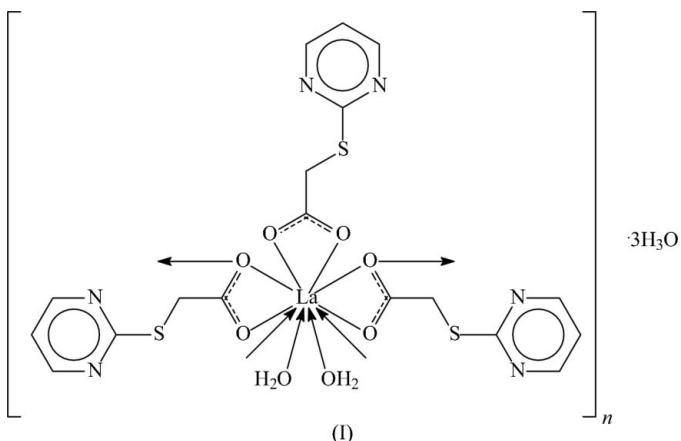
Experimental

Pyrimidin-2-ylsulfanylacetic acid (102 mg, 0.6 mmol) was suspended in a small volume of water–ethanol (2:1 *v/v*) and a few drops of aqueous ammonia was added dropwise until it dissolved completely. Lanthanum nitrate (86 mg, 0.2 mmol) was added and the mixture was transferred into a Teflon-lined Parr bomb. The bomb was heated at
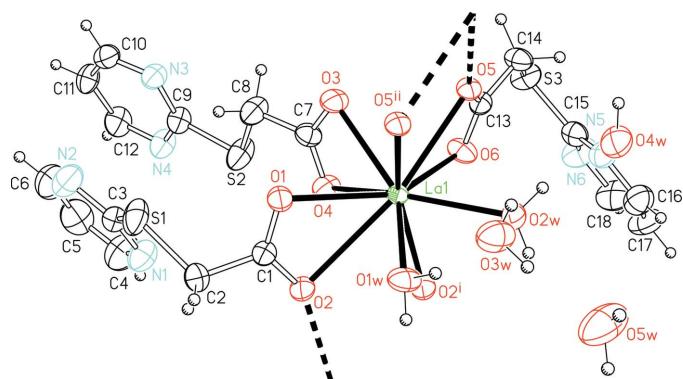
Figure 1
ORTEPII (Johnson, 1976) plot of a portion of the polymeric structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms as spheres of arbitrary radii. [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $-x, 1 - y, 1 - z$.]
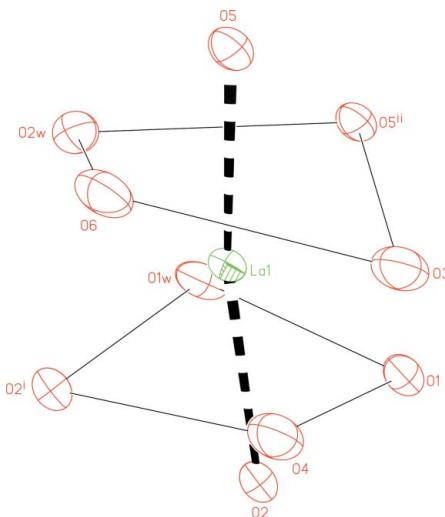

Figure 2
ORTEPII (Johnson, 1976) plot of the capped square–antiprismatic geometry of La in (I). [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $-x, 1 - y, 1 - z$.]
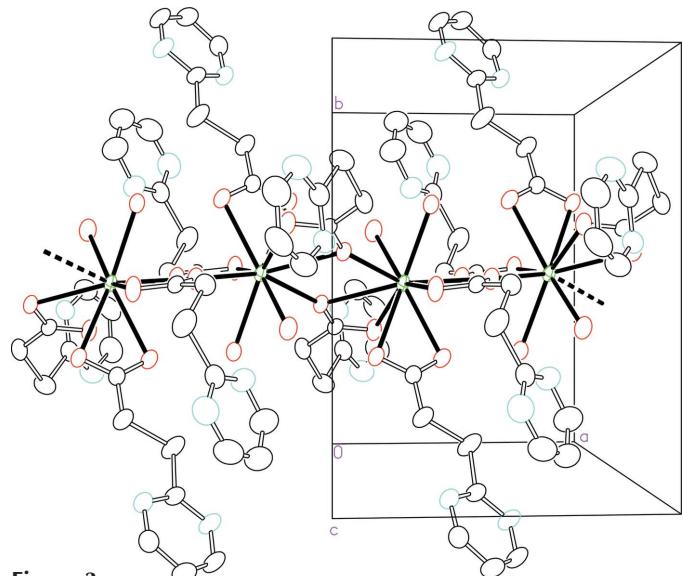

Figure 3
ORTEPII (Johnson, 1976) of the chain structure. The uncoordinated water molecules have been omitted.

413 K for 100 h. The cooled contents were filtered; colorless plates separated after two weeks. Elemental analysis found (calculated) for $C_{18}H_{25}LaN_6O_{11}S_3$: C 29.26 (29.35), H 3.40 (3.42), N 11.32% (11.41%). IR (KBr): 3410, 1601, 1535, 1487, 1426, 622, 550, 472 cm^{-1}.

Crystal data

$[La(C_6H_5N_2O_2S)_3(H_2O)_2]\cdot3H_2O$	$D_x = 1.827$ Mg m^{-3}
$M_r = 736.53$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 7684
$a = 8.8145$ (3) Å	reflections
$b = 11.8211$ (5) Å	$\theta = 2.3–28.6°$
$c = 25.887$ (1) Å	$\mu = 1.90$ mm^{-1}
$\beta = 97.046$ (1)°	$T = 295$ (2) K
$V = 2677.0$ (2) Å^3	Block, colorless
$Z = 4$	$0.50 \times 0.22 \times 0.14$ mm

Data collection

Bruker APEX area-detector diffractometer	6110 independent reflections
	5749 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.029$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 27.5°$
$T_{min} = 0.504$, $T_{max} = 0.777$	$h = -9 \rightarrow 11$
15909 measured reflections	$k = -15 \rightarrow 12$
	$l = -33 \rightarrow 32$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0499P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.044$	$+ 4.1463P]$
$wR(F^2) = 0.110$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.16$	$(\Delta/\sigma)_{max} = 0.001$
6110 reflections	$\Delta\rho_{max} = 1.19$ e Å^{-3}
382 parameters	$\Delta\rho_{min} = -0.75$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

La1—O1	2.590 (3)	La1—O5	2.687 (3)
La1—O2	2.838 (3)	La1—O5^{ii}	2.469 (2)
La1—O2^i	2.466 (3)	La1—O6	2.583 (3)
La1—O3	2.584 (3)	La1—O1w	2.556 (3)
La1—O4	2.560 (3)	La1—O2w	2.518 (3)
O1—La1—O2	46.9 (1)	O2^i—La1—O2w	76.7 (1)
O1—La1—O2^i	111.0 (1)	O3—La1—O4	50.1 (1)
O1—La1—O3	69.5 (1)	O3—La1—O5	68.3 (1)
O1—La1—O4	72.2 (1)	O3—La1—O5^{ii}	80.8 (1)
O1—La1—O5	125.2 (1)	O3—La1—O6	75.3 (1)
O1—La1—O5^{ii}	74.7 (1)	O3—La1—O1w	143.3 (1)
O1—La1—O6	141.8 (1)	O3—La1—O2w	136.8 (1)
O1—La1—O1w	76.6 (1)	O4—La1—O5	104.1 (1)
O1—La1—O2w	143.1 (1)	O4—La1—O5^{ii}	127.8 (1)
O2—La1—O2^i	64.2 (1)	O4—La1—O6	74.1 (1)
O2—La1—O3	99.2 (1)	O4—La1—O1w	130.5 (1)
O2—La1—O4	65.3 (1)	O4—La1—O2w	142.4 (1)
O2—La1—O5	167.5 (1)	O5—La1—O5^{ii}	65.5 (1)
O2—La1—O5^{ii}	114.9 (1)	O5—La1—O6	48.6 (1)
O2—La1—O6	129.0 (1)	O5—La1—O1w	125.3 (1)
O2—La1—O1w	65.3 (1)	O5—La1—O2w	68.6 (1)
O2—La1—O2w	123.8 (1)	O5^{ii}—La1—O6	114.1 (1)
O2^i—La1—O3	125.35 (1)	O5^{ii}—La1—O1w	77.0 (1)
O2^i—La1—O4	77.1 (1)	O5^{ii}—La1—O2w	84.2 (1)
O2^i—La1—O5^{ii}	153.8 (1)	O6—La1—O1w	140.8 (1)
O2^i—La1—O5	121.5 (1)	O6—La1—O2w	74.5 (1)
O2^i—La1—O6	77.9 (1)	O1w—La1—O2w	69.3 (1)
O2^i—La1—O1w	79.6 (1)		

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

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

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
O1w—H1w1$\cdots$O3w	0.85 (1)	1.92 (1)	2.749 (5)	165 (4)
O1w—H1w2$\cdots$O4^i	0.85 (1)	1.93 (2)	2.751 (4)	164 (4)
O2w—H2w1$\cdots$N1^i	0.85 (1)	2.05 (2)	2.852 (5)	158 (4)
O2w—H2w2$\cdots$O4w	0.85 (1)	1.88 (2)	2.709 (5)	167 (4)
O3w—H3w1$\cdots$O5w	0.85 (1)	1.89 (2)	2.718 (5)	166 (6)
O3w—H3w2$\cdots$O3^{ii}	0.85 (1)	2.03 (2)	2.840 (5)	158 (5)
O4w—H4w1$\cdots$O1^{ii}	0.85 (1)	2.01 (2)	2.823 (4)	160 (5)
O4w—H4w2$\cdots$N5	0.85 (1)	2.13 (3)	2.918 (5)	154 (5)
O5w—H5w1$\cdots$O3w^{iii}	0.85 (1)	2.09 (2)	2.903 (6)	162 (6)
O5w—H5w2$\cdots$N4^i	0.85 (1)	2.08 (2)	2.918 (6)	169 (6)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, -y+1, -z+1$; (iii) $-x, -y+2, -z+1$.

The methylene and aromatic H atoms were positioned geometrically (C—H = 0.97 and 0.93 Å) and were included in the refinement in the riding-model approximation, with U_{iso}(H) values set at $1.2U_{eq}$(C). The water H atoms were located in difference Fourier maps and were refined with distance restraints of O—H = 0.85 (1) Å and H$\cdots$H = 1.39 (1) Å; their displacement parameters were similarly tied to those of the parent atoms. The final difference Fourier map has a large peak at about 1 Å from atom La1.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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