Crystal structure of tetra-aqua-bis(μ_2-thiophene-3,4-dicarboxylato-κ^4*O,O':O'',O'''*)-bis(thiophene-3-carboxyl-4-carboxylato-κ^1*O*)-bis(1,10-phenantroline-κ^2*N,N'*)disamarium(III), $C_{24}H_{17}N_2O_{10}S_2Sm$

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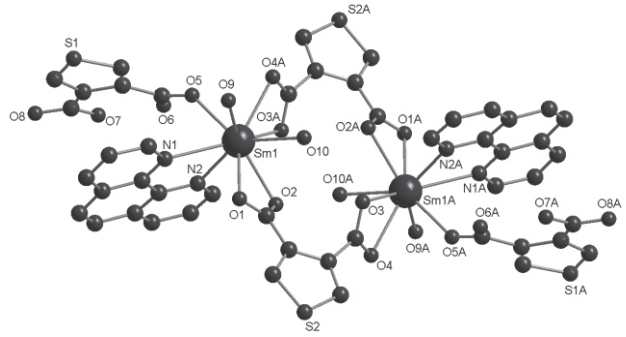

Abstract

$C_{24}H_{17}N_2O_{10}S_2Sm$, triclinic, $P\bar{1}$ (no. 2), a = 10.135(5) Å, b = 10.697(5) Å, c = 11.823(7) Å, α = 94.676(5)°, β = 98.927(5)°, γ = 101.736(4)°, V = 1231.3 Å^3, Z = 2, $R_{gt}(F)$ = 0.0184, $wR_{ref}(F^2)$ = 0.0455, T = 296 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.22×0.30×0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	26.18 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9576, 4808
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4335
$N(param)_{refined}$:	357
Programs:	SHELX [7]

Source of material

A mixture of $Sm(NO_3)_3{\cdot}6H_2O$ (0.1331 g, 0.3 mmol), KSCN (0.0146 g, 0.15 mmol), thiophene-3,4-dicarboxylic acid (0.50 mmol, 0.086 g), 1,10-phenanthroline monohydrate (0.0198 g, 0.1 mmol) was dissolved in 10 mL H_2O. Then the solution was heated in a 25 mL Teflon-lined autoclave under autogenous pressure at 423 K for three days. After cooling to room temperature, the colourless block-shaped crystals that formed were collected. The crystals suitable for X-ray diffraction analysis were collected.

Experimental details

On the thiophene ring, the hydrogen atoms were assigned with U_{iso}(H) = 1.2 U_{eq}(C), and included in the final refinement by using geometrical restraints, with d(C–H) = 0.93 Å.

Discussion

Metal-organic coordination polymers, also known as metal-organic frameworks are hybrid compounds that extend one, two, or three dimensions via a coordination bond. The design and synthesis of these compounds have attracted considerable interest due to their intriguing structures and potential applications as functional materials in luminescence, magnetism, host-guest chemistry, catalysis and gas adsorption and separation [1–4]. In recent years, a number of lanthanide coordination polymers based on pyridinedicarboxylic acid have been synthesized under hydrothermal conditions [5]. By contrast with these lanthanide complexes containing only rigid pyridinedicarboxylic ligands, the high-dimensional coordination complexes of 4*f* metal-organic frameworks formed by thiophene-3,4-dicarboxylic acid (H_2tdc) is still scarce [6]. In the title structure four water ligands, two 1,10-phenantroline ligands, two thiophene-3-carboxyl-4-carboxylato ligands as well as two bridging thiophene-3,4-dicarboxylato ligands (*tdc*) are connected to two Sm(III) metal centers to give a dinuclear complex (see the figure). Each Sm^{3+} ion is eight-coordinated, and the coordination is close to that of a distorted triangular dodecahedral coordination polyhedron geometry. The Sm–O bond lengths are 2.4316(19) Å, 2.477(2) Å, 2.492(2) Å, 2.4829(19) Å, 2.553(2) Å, 2.3794(19) Å, 2.499(2) Å, respectively. Two nitrogen atom (N1 and N2) from the 1,10-phenanthroline ligand show N–Sm bond lengths of 2.656(2) Å, and 2.586(2) Å, respectively, which are expected as those observed in reported Sm^{3+} complexes. The bond angles of O–Sm–O are in the range of 52.06(6)° to 146.42(7)°. There are intra- and intermolecular hydrogen bonding interactions between the coordinated water molecules and the uncoordinated carboxylate oxygen atom. Some are listed as follows: O10–H4W···O3, [O···O = 3.001(3) Å, O–H···O = 172.2°]; O2–H4W···O4#2, [O···O = 2.845(3) Å, O–H···O = 171.3°]; O2–H3W···O3#1, [O···O = 2.667(3) Å, O–H···O = 174.8°]; O1–H2W···O3#1, [O···O = 2.744(3) Å, O–H···O = 173.4°]. Symmetry codes: #1: $-x+1, -y, -z+1$ #2 $x, y-1, z$ #3 $x-1, y, z$. The dinuclear complexes are further assembled by the intermolecular hydrogen bonding interaction leading to the formation of a 3D framework.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(9A)	2*i*	–0.0372	–0.0696	0.3713	0.046
H(9B)	2*i*	0.0152	–0.1625	0.3194	0.046
H(10A)	2*i*	0.2554	–0.2122	0.4179	0.059
H(10B)	2*i*	0.3833	–0.1440	0.4418	0.059
H(1)	2*i*	–0.0493	–0.0043	0.1615	0.038
H(2)	2*i*	–0.1717	0.0609	0.0027	0.048
H(3)	2*i*	–0.0853	0.2520	–0.0624	0.048
H(8)	2*i*	0.4839	0.6193	0.2440	0.051
H(9)	2*i*	0.5957	0.5379	0.3964	0.046
H(10)	2*i*	0.5098	0.3309	0.4337	0.037
H(11)	2*i*	0.1003	0.4562	–0.0356	0.055

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Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(12)	2*i*	0.2920	0.5830	0.0712	0.058
H(15)	2*i*	0.4072	–0.1281	0.0219	0.043
H(16)	2*i*	0.7703	–0.2232	0.1972	0.037

Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(21)	2*i*	–0.1467	0.1575	0.3441	0.040
H(22)	2*i*	–0.2411	0.4867	0.1973	0.04
H(6)	2*i*	0.158(4)	0.517(4)	0.433(3)	0.09(1)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sm(1)	2*i*	0.24419(2)	0.07067(2)	0.37729(2)	0.01716(7)	0.01706(7)	0.02054(8)	0.00357(5)	–0.00010(4)	0.00317(4)
N(1)	2*i*	0.1058(2)	0.1428(2)	0.1935(2)	0.025(1)	0.026(1)	0.022(1)	0.0066(8)	0.0006(8)	0.0002(8)
N(2)	2*i*	0.3484(2)	0.2892(2)	0.3131(2)	0.024(1)	0.025(1)	0.024(1)	0.0058(8)	0.0026(8)	0.0047(8)
O(1)	2*i*	0.2947(2)	–0.0370(2)	0.2005(2)	0.034(1)	0.077(2)	0.032(1)	0.030(1)	–0.0071(8)	–0.012(1)
O(2)	2*i*	0.4734(2)	0.0531(2)	0.3348(2)	0.0274(9)	0.0257(9)	0.0303(9)	0.0064(7)	0.0055(7)	–0.0001(7)
O(3)	2*i*	0.5927(2)	–0.1573(2)	0.4408(1)	0.0243(9)	0.0300(9)	0.0231(9)	–0.0012(7)	0.0035(7)	0.0053(7)
O(4)	2*i*	0.7955(2)	–0.0511(2)	0.4162(1)	0.0192(8)	0.0295(9)	0.0278(9)	0.0014(7)	0.0014(7)	0.0060(7)
O(5)	2*i*	0.1070(2)	0.2181(2)	0.4358(2)	0.045(1)	0.032(1)	0.031(1)	0.0200(9)	0.0105(8)	0.0100(8)
O(6)	2*i*	0.1788(2)	0.4288(2)	0.4655(2)	0.039(1)	0.032(1)	0.042(1)	0.0128(9)	–0.0081(9)	–0.0020(9)
O(7)	2*i*	0.1236(2)	0.6171(2)	0.3858(2)	0.041(1)	0.024(1)	0.056(1)	–0.0005(8)	–0.009(1)	0.0026(9)
O(8)	2*i*	–0.0350(2)	0.6697(2)	0.2583(2)	0.054(1)	0.0226(9)	0.050(1)	0.0080(9)	–0.003(1)	0.0101(8)
O(9)	2*i*	0.0323(2)	–0.0830(2)	0.3442(2)	0.0209(9)	0.0241(9)	0.044(1)	0.0004(7)	0.0057(8)	0.0002(8)
O(10)	2*i*	0.3010(2)	–0.1350(2)	0.4332(2)	0.0253(9)	0.0236(9)	0.068(1)	0.0052(7)	0.0006(9)	0.0136(9)
S(1)	2*i*	–0.28722(7)	0.27247(7)	0.23728(7)	0.0284(4)	0.0344(4)	0.0575(5)	0.0000(3)	0.0019(3)	0.0054(3)
S(2)	2*i*	0.60382(8)	–0.21597(8)	0.03467(6)	0.0435(4)	0.0587(5)	0.0257(3)	0.0184(4)	0.0073(3)	–0.0076(3)
C(1)	2*i*	–0.0135(3)	0.0737(3)	0.1365(2)	0.031(1)	0.031(1)	0.031(1)	0.006(1)	–0.001(1)	–0.000(1)
C(2)	2*i*	–0.0885(3)	0.1125(3)	0.0400(2)	0.032(2)	0.052(2)	0.032(2)	0.010(1)	–0.006(1)	–0.003(1)
C(3)	2*i*	–0.0380(3)	0.2260(3)	0.0022(2)	0.041(2)	0.057(2)	0.025(1)	0.023(1)	–0.003(1)	0.007(1)
C(4)	2*i*	0.0867(3)	0.3042(3)	0.0616(2)	0.041(2)	0.039(2)	0.025(1)	0.018(1)	0.005(1)	0.009(1)
C(5)	2*i*	0.1554(2)	0.2580(2)	0.1579(2)	0.029(1)	0.029(1)	0.020(1)	0.012(1)	0.006(1)	0.0040(9)
C(6)	2*i*	0.2815(2)	0.3369(2)	0.2220(2)	0.028(1)	0.026(1)	0.024(1)	0.010(1)	0.008(1)	0.0060(9)
C(7)	2*i*	0.3310(3)	0.4602(3)	0.1911(2)	0.043(2)	0.028(1)	0.036(2)	0.010(1)	0.011(1)	0.013(1)
C(8)	2*i*	0.4501(3)	0.5364(3)	0.2600(3)	0.048(2)	0.027(1)	0.049(2)	–0.003(1)	0.013(1)	0.009(1)
C(9)	2*i*	0.5164(3)	0.4885(3)	0.3506(2)	0.034(2)	0.034(1)	0.041(2)	–0.004(1)	0.004(1)	0.001(1)
C(10)	2*i*	0.4627(3)	0.3635(2)	0.3732(2)	0.028(1)	0.030(1)	0.032(1)	0.002(1)	0.002(1)	0.003(1)
C(11)	2*i*	0.1435(3)	0.4276(3)	0.0295(3)	0.056(2)	0.052(2)	0.036(2)	0.022(2)	0.005(1)	0.024(1)
C(12)	2*i*	0.2585(3)	0.5023(3)	0.0922(3)	0.061(2)	0.038(2)	0.049(2)	0.012(2)	0.011(2)	0.027(1)
C(13)	2*i*	0.4199(3)	–0.0220(2)	0.2442(2)	0.029(1)	0.033(1)	0.024(1)	0.014(1)	0.005(1)	0.007(1)
C(14)	2*i*	0.5062(2)	–0.0984(2)	0.1887(2)	0.025(1)	0.029(1)	0.023(1)	0.008(1)	0.003(1)	0.003(1)
C(15)	2*i*	0.4817(3)	–0.1399(3)	0.0734(2)	0.034(1)	0.049(2)	0.025(1)	0.016(1)	0.000(1)	0.003(1)
C(16)	2*i*	0.6904(3)	–0.1949(3)	0.1742(2)	0.026(1)	0.037(1)	0.029(1)	0.009(1)	0.004(1)	–0.000(1)
C(17)	2*i*	0.6275(2)	–0.1315(2)	0.2474(2)	0.022(1)	0.023(1)	0.022(1)	0.0037(9)	0.0040(9)	0.0042(9)
C(18)	2*i*	0.6747(2)	–0.1110(2)	0.3756(2)	0.022(1)	0.018(1)	0.026(1)	0.0079(9)	0.0028(9)	0.0039(9)
C(19)	2*i*	0.0890(3)	0.3282(2)	0.4209(2)	0.034(1)	0.031(1)	0.023(1)	0.015(1)	0.008(1)	0.003(1)
C(20)	2*i*	–0.0416(2)	0.3419(2)	0.3488(2)	0.029(1)	0.022(1)	0.025(1)	0.009(1)	0.007(1)	0.0034(9)
C(21)	2*i*	–0.1488(3)	0.2381(2)	0.3206(2)	0.037(2)	0.024(1)	0.042(2)	0.008(1)	0.011(1)	0.007(1)
C(22)	2*i*	–0.2031(3)	0.4271(3)	0.2366(2)	0.034(1)	0.031(1)	0.038(2)	0.011(1)	0.002(1)	0.009(1)
C(23)	2*i*	–0.0735(3)	0.4545(2)	0.3000(2)	0.030(1)	0.022(1)	0.026(1)	0.010(1)	0.006(1)	0.0033(9)
C(24)	2*i*	0.0100(3)	0.5894(2)	0.3142(2)	0.038(2)	0.023(1)	0.032(1)	0.008(1)	0.008(1)	0.002(1)

References

1. Liang, Y.C.; Cao, R.; Su, W. P.; Hong, M. C.; Zhang, W. J.: Syntheses, structures, and magnetic properties of two gadolinium(III)-copper(II) coordination polymers by a hydrothermal reaction. Angew. Chem. Int. Ed. **39** (2000) 3304–3307.
2. Zhao, B.; Cheng, P.; Chen, X. Y.; Cheng, C.; Shi, W.; Liao, D. Z.; Yan, S. P.; Jiang, Z. H.: Design and synthesis of 3*d*-4*f* metal-based zeolite-type materials with 3D nanotublar structure capsulated water pipe. J. Am. Chem. Soc. **126** (2004) 3012–3013.
3. He, Z.; Gao, E. Q.; Wang, Z. M.; Yan, C. H.; Kurmoo, M.: Coordination polymers based on inorganic lanthanide(III) sulfate skeletons and an organic isonicotinate N-oxide connector: segregation into three structural types by the lanthanide contraction effect. Inorg. Chem. **44** (2005) 862–874.
4. Kong, Z. G.; Guo, S. N.; Zhao, Y. X.; Song, D.: A new cadmium(II) coordination polymer constructed by 2-(2-chloro-6-fluorophenyl)-1*H*-imidazo-[4,5-*f*] [1,10]phenanthroline and 1,3-benzenecarboxylate: synthesis, crystal structure, thermal behavior and luminescent property. J. Serb. Chem. Soc. **79** (2014) 669–676.
5. Zhao, B.; Cheng, P.; Dai,Y.; Cheng, C.; Liao, D. Z.; Yan, S. P.; Jiang, Z. H.; Wang, G. L.: A nanotubular 3D coordination polymer based on a 3*d*-4*f* heterometallic assembly. Angew. Chem. Int. Ed. **42** (2003) 934–936.
6. Wang, J. G., Huang, C. C., Huang, X. H., Liu, D. S.: Three-dimensional lanthanide thiophenedicarboxylate framework with an unprecedented (4,5)-connected topology. Cryst. Growth Des. **8** (2008) 795–798.
7. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.