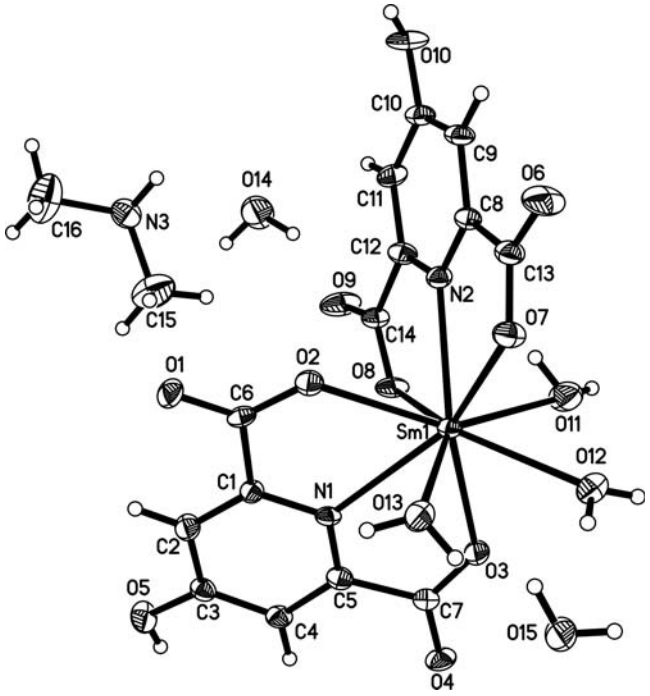
Crystal structure of dimethylammonium triaquabis(4-hydroxypyridine-2,6-dicarboxylato)samarium(III) dihydrate, $[C_2H_8N][Sm(H_2O)_3(C_7H_3NO_5)_2] \cdot 2H_2O$

Xun Feng*, Jing Liu, Tie-Fu Li and Peng-Peng Lei

Luoyang Normal University, College of Chemistry and Chemical Engineering, Luoyang 471022, Henan, P. R. China

Received November 17, 2010, accepted and available on-line December 11, 2010; CCDC no. 1267/3289



Abstract

$C_{16}H_{24}N_3O_{15}Sm$, triclinic, $P\bar{1}$ (no. 2), a = 10.276(2) Å, b = 10.403(2) Å, c = 11.951(2) Å, α = 92.358(2)°, β = 91.168(2)°, γ = 117.310(2)°, V = 1133.1 Å^3, Z = 2, $R_{gt}(F)$ = 0.047, $wR_{ref}(F^2)$ = 0.123, T = 293 K.

Source of material

The mixture of $Sm(NO_3)_3 \cdot 6H_2O$ (0.085 g, 0.2 mmol) and 4-hydroxypyridine-2,6-dicarboxylic acid (H_3CAM, 0.074 g, 0.4 mmol) was stirred into 15 ml aqueous solution and the pH value was adjusted to approx. 5 with 1.0 M ammonia. Then 5 mL ethanol solution of *N*,*N*-dimethylformamide (DMF, 1.0 mL) was added. The reaction mixture was heated on a water bath for 10 h at 70 °C, then filtered. The resulting clear solution was diffused with diethyl ether vapor at room temperature for two weeks, block-shaped colourless crystals insoluble in water were obtained (yield 0.049 g, 36 %). Elemental analysis — found: C, 32.67 %; H, 3.19 %; N, 6.17 %; calculated: C, 32.95 %; H, 3.20 %; N, 6.06 %. IR data are available in the CIF.

Discussion

During the past two decades, there has been growing interest in lanthanoids and their compounds because of the emergence of novel structure features and functional properties in different application fields [1-3]. The current attention is focused on the construction of rear earth metal-organic frameworks (MOFs) with novel topology and on the crystal engineering of molecular architectures organized by coordination bonds and supramolecular contacts (such as hydrogen bonding, π-π stack interactions, etc.) [4,5]. In this work, 4-hydroxypyridine-2,6-dicarboxylic acid (H_3CAM) was employed as the major ligand because it has a unique configuration, which can potentially provide more coordination features [6,7].

The title crystal structure is composed of one Sm(III) ion, two $HCAM^{2-}$ ligands, three coordinating water molecules, and two lattice water molecules as well as one dimethylammonium cation (DMA), which is *in situ* generated through the DMF solvent under the hydrothermal condition [8,9]. Each Sm(III) is nine-coordinated and exhibits a tricapped trigonal prismatic environment formed by four oxygen atoms from the two carboxylate groups of $HCAM^{2-}$ ligands, two nitrogen atoms from two pyridine rings, and three oxygen atoms from water molecules. Each $HCAM^{2-}$ ligand adopts a tri-dentate coordination mode, employing one nitrogen and two oxygen atoms to chelate Sm(III) ion. The dimethylamine does not participate in the coordination due to its protonation under the acidic condition. This coordination mode can also be observed in the analogous lanthanide complexes [10]. The $[Sm(HCAM)_2]$ unit carries one negative charge, while DMA bears one positive charge, thus maintaining the charge balance. The d(Sm—O) range from 2.416(4) to 2.624(2) Å, and d(Sm—N) range from 2.555(3) to 2.594(5) Å, which are within normal ranges [12]. The dihedral angle between the two pyridyl rings attached to the central Sm ion is 70.20°, and the angle of N1–Sm–N2 is 118.25°. Both the pyridine ring and the dicarboxylate group of HCAM ligands are almost coplanar, and the atoms in the pyridine deviate from the least square plane defined by the pyridine ring by less than 0. 020 Å. Deviation from the mean plane defined by the pyridine ring are observed for both of carboxylic groups with values ranging from O2 –0.156(7) to O1 +0.153(7) Å.

All the hydrogen atoms of lattice water participate in the hydrogen bond, contributing to packing stability. The adjacent $[Sm(HCAM)_2(H_2O)_3]$ units are connected into a dimer unit via the hydrogen bond O13^{i}–H4W···O1 [d(O···O) = 2.847(6) Å, ∠O–H···O = 168.4°] as well as hydrogen bond involing to the nitrogen atom of DMA unit, N3–H3A···O6^{iii}, [d(O···N) =

* Correspondence author (e-mail: fengx@lynu.edu.cn)

2.746(7) Å, ∠O–H···O = 165.6°], with the Sm···Sm separation of 8.508 Å; symmetry codes i: –*x*,–*y*+1,–*z*+1; ii: –*x*+1,–*y*+1,–*z*; iii: –*x*,–*y*,–*z*+1; iv: –*x*+1,–*y*+1,–*z*+1; v: *x*,*y*+1,*z*. These dimers are further grafted onto a zigzag chain along [100] by the hydrogen bond O14–H6W···O12^{ii}, [*d*(O···O) = 2.975(7) Å, ∠O–H···O = 167.8°]. Then these 1D chains were further linked into a supramolecular architecture through a series of hydrogen bond interactions O10–H10···O2^{iii} [*d*(O···O) = 2.659(6) Å, ∠O–H···O =138.1°], O5–H5···O8^{v} [*d*(O···O) = 2.595(6) Å, ∠O–H···O =160.2°], and O15–H7W···O3^{iv} [*d*(O···O) = 2.711(7) Å, ∠O–H···O = 156.0°].

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.14 × 0.15 × 0.21 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	26.73 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8635, 4172
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3607
$N(param)_{refined}$:	320
Programs:	SHELXS-97, SHELXL-97 [12]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(5)	2*i*	0.0797	0.6212	0.7043	0.052
H(10)	2*i*	0.4662	0.5837	–0.2079	0.055
H(11A)	2*i*	0.0155	0.1477	0.1068	0.064
H(11B)	2*i*	–0.1302	0.0489	0.0960	0.064
H(1W)	2*i*	–0.0121	–0.1373	0.2400	0.048
H(2W)	2*i*	0.1116	–0.0921	0.3136	0.048
H(3W)	2*i*	0.2665	0.0745	0.4376	0.049
H(4W)	2*i*	0.3664	0.2223	0.4581	0.049
H(5W)	2*i*	0.0978	0.7352	0.0542	0.078
H(6W)	2*i*	0.1224	0.8681	0.1045	0.078
H(7W)	2*i*	0.1906	0.0699	0.6750	0.073
H(8W)	2*i*	0.2844	0.2192	0.6713	0.073
H(3A)	2*i*	0.4782	0.9174	0.1153	0.040
H(3B)	2*i*	0.3941	0.9912	0.1508	0.040
H(2)	2*i*	0.3678	0.6862	0.5542	0.031
H(4)	2*i*	–0.0285	0.3803	0.6343	0.028
H(9)	2*i*	0.4278	0.3489	–0.1320	0.030
H(11)	2*i*	0.2229	0.5883	–0.0516	0.030
H(15A)	2*i*	0.4559	0.8179	0.2842	0.087
H(15B)	2*i*	0.3015	0.7728	0.2265	0.087
H(15C)	2*i*	0.3641	0.8966	0.3217	0.087
H(16A)	2*i*	0.5713	1.1378	0.2749	0.098
H(16B)	2*i*	0.6365	1.1480	0.1562	0.098
H(16C)	2*i*	0.6604	1.0535	0.2453	0.098

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*	0.16698(3)	0.21094(3)	0.26580(2)	0.0207(2)	0.0209(2)	0.0174(2)	0.0087(2)	0.0068(1)	0.0026(1)
O(1)	2*i*	0.5332(5)	0.6470(5)	0.4058(4)	0.022(2)	0.026(2)	0.035(3)	0.001(2)	0.010(2)	–0.003(2)
O(2)	2*i*	0.3969(5)	0.4397(5)	0.3080(4)	0.026(2)	0.027(2)	0.025(2)	0.010(2)	0.009(2)	0.001(2)
O(3)	2*i*	–0.0423(5)	0.1121(5)	0.3875(4)	0.027(2)	0.024(2)	0.026(2)	0.004(2)	0.011(2)	–0.000(2)
O(4)	2*i*	–0.1659(5)	0.1205(5)	0.5361(4)	0.025(2)	0.032(3)	0.029(3)	0.010(2)	0.014(2)	0.009(2)
O(5)	2*i*	0.1612(5)	0.6529(5)	0.6783(4)	0.029(3)	0.033(3)	0.037(3)	0.011(2)	0.013(2)	–0.012(2)
O(6)	2*i*	0.4328(7)	0.1485(6)	–0.0083(5)	0.073(4)	0.046(3)	0.041(3)	0.044(3)	0.031(3)	0.012(2)
O(7)	2*i*	0.3117(5)	0.1385(5)	0.1465(4)	0.037(3)	0.031(3)	0.024(2)	0.021(2)	0.009(2)	0.007(2)
O(8)	2*i*	0.0759(5)	0.3838(5)	0.2245(4)	0.030(2)	0.037(3)	0.024(2)	0.022(2)	0.015(2)	0.011(2)
O(9)	2*i*	0.0797(6)	0.5668(6)	0.1328(4)	0.055(3)	0.048(3)	0.044(3)	0.039(3)	0.029(3)	0.024(3)
O(10)	2*i*	0.3790(5)	0.5598(6)	–0.2003(4)	0.036(3)	0.056(3)	0.031(3)	0.030(3)	0.022(2)	0.023(2)
O(11)	2*i*	–0.0494(6)	0.0740(6)	0.1343(4)	0.038(3)	0.044(3)	0.032(3)	0.006(2)	–0.005(2)	0.009(2)
O(12)	2*i*	0.0698(5)	–0.0676(5)	0.2627(4)	0.029(2)	0.028(3)	0.038(3)	0.012(2)	0.006(2)	0.007(2)
O(13)	2*i*	0.3111(5)	0.1566(5)	0.4096(4)	0.033(3)	0.027(3)	0.032(3)	0.009(2)	0.000(2)	0.004(2)
O(14)	2*i*	0.1290(7)	0.8249(6)	0.0446(5)	0.075(4)	0.042(3)	0.040(3)	0.028(3)	–0.003(3)	0.006(3)
O(15)	2*i*	0.2241(6)	0.1524(6)	0.7099(4)	0.038(3)	0.042(3)	0.037(3)	–0.006(3)	0.013(2)	–0.003(2)
N(1)	2*i*	0.1795(5)	0.3637(5)	0.4419(4)	0.021(3)	0.023(3)	0.016(2)	0.011(2)	0.007(2)	0.004(2)
N(2)	2*i*	0.2393(5)	0.3348(5)	0.0845(4)	0.024(3)	0.021(3)	0.021(3)	0.011(2)	0.007(2)	0.004(2)
N(3)	2*i*	0.4582(7)	0.9604(6)	0.1746(5)	0.038(3)	0.036(3)	0.032(3)	0.022(3)	0.003(3)	–0.001(3)
C(1)	2*i*	0.2905(6)	0.4963(6)	0.4617(5)	0.020(3)	0.019(3)	0.021(3)	0.009(3)	0.007(2)	0.000(2)
C(2)	2*i*	0.2884(7)	0.5945(7)	0.5426(5)	0.020(3)	0.026(3)	0.027(3)	0.007(3)	0.005(3)	–0.002(3)
C(3)	2*i*	0.1650(7)	0.5532(7)	0.6062(5)	0.020(3)	0.029(3)	0.019(3)	0.012(3)	0.002(2)	0.000(3)
C(4)	2*i*	0.0526(7)	0.4134(7)	0.5898(5)	0.024(3)	0.027(3)	0.021(3)	0.013(3)	0.009(3)	0.002(3)
C(5)	2*i*	0.0635(7)	0.3238(7)	0.5053(5)	0.022(3)	0.027(3)	0.020(3)	0.013(3)	0.003(3)	0.002(3)
C(6)	2*i*	0.4193(6)	0.5333(7)	0.3862(5)	0.015(3)	0.025(3)	0.022(3)	0.009(3)	0.008(2)	0.008(3)
C(7)	2*i*	–0.0583(7)	0.1726(7)	0.4747(5)	0.026(3)	0.025(3)	0.019(3)	0.011(3)	0.004(3)	0.004(3)
C(8)	2*i*	0.3207(7)	0.3037(7)	0.0129(5)	0.022(3)	0.025(3)	0.020(3)	0.011(3)	0.007(2)	0.001(2)
C(9)	2*i*	0.3710(7)	0.3737(7)	–0.0848(5)	0.022(3)	0.034(4)	0.018(3)	0.011(3)	0.007(3)	0.004(3)
C(10)	2*i*	0.3339(7)	0.4823(7)	–0.1101(5)	0.020(3)	0.034(4)	0.019(3)	0.011(3)	0.006(3)	0.006(3)
C(11)	2*i*	0.2491(7)	0.5161(7)	–0.0367(5)	0.028(3)	0.026(3)	0.027(3)	0.016(3)	0.007(3)	0.012(3)
C(12)	2*i*	0.2048(7)	0.4395(7)	0.0590(5)	0.020(3)	0.033(4)	0.021(3)	0.015(3)	0.007(2)	0.004(3)
C(13)	2*i*	0.3597(7)	0.1879(7)	0.0520(5)	0.035(4)	0.027(4)	0.022(3)	0.016(3)	0.010(3)	0.003(3)
C(14)	2*i*	0.1128(7)	0.4683(7)	0.1426(5)	0.025(3)	0.028(4)	0.021(3)	0.014(3)	0.008(3)	0.006(3)
C(15)	2*i*	0.389(1)	0.853(1)	0.2592(8)	0.053(5)	0.060(6)	0.063(6)	0.025(5)	0.010(5)	0.026(5)
C(16)	2*i*	0.593(1)	1.086(1)	0.216(1)	0.046(5)	0.046(5)	0.096(8)	0.015(5)	–0.014(5)	0.000(5)

Acknowledgments. We gratefully acknowledge financial support of this work by the National Natural Science Foundation of China (grant no. 20971104), the Tackle Key Problem of Science and Technology Project of Henan Province (grant no. 102102210450), and the Foundation of Education Committee of Henan province (grant no. 2010A150016).

References

1. Feng, X.; Sun, Q. Q.; Shi, X. G.; Wang, L. Y.; Zhao, J. S.: Hydrothermal synthesis and properties of a New 3D lanthanum supramolecule based on the 4-hydroxypyridine 2,6-dicarboxylate and water ligands. Russ. J. Coord. Chem. **37** (2011) 57-63.
2. Luo, F.; Batten, S. R.; Che, Y. X.; Zheng, J. M.: Synthesis, structure,and characterization of three series of 3-4*f* metal-organic frameworks based on rod-shaped and (6,3)-sheet metal carboxylate substructures. Chem. Eur. J. **13** (2007) 4948-4955.
3. Feng, X.; Zhao, J.-S.; Wang, L.-Y.; X.-G. Shi, X.-G.: An anion-directed unprecedent three-dimensional array with erbium(III) based on the 2,6-pyridinedicarboxylate. Inorg. Chem. Commun. **12** (2009) 388-391.
4. Bie, H. Y.; Yu, J.-H.; Wang,T. G.; Lu, J.; Xu, J. Q .: Fluorescent property of a three-dimensional supramolecular compound assembled through combined weak intermolecular interactions. Mater. Lett. **60** (2006) 2475-2479.
5. Brycki, B.; Kowalczyk, I.; Werner, J.; Borowiak, T.; Wolska, I.: Polyamines. I. spectroscopic properties of *N*,*N*-bis(phthalimidopropyl)-*N*-propylamine and supramolecular interactions in its crystals. J. Mol. Struct. **791** (2006) 137-143.
6. Chen, Z.; Fang, M.; Ren, P.; Li, B. H.; Zhao, B.; Wei, S.; Cheng, P.: Synthesis, structure and luminescent property of two new 2D metal-organic frameworks containing lanthanide ions. Z. Anorg. Allg. Chem. **634** (2008) 382-386.
7. Gao, H.-L.; Yi, L.; Zhao, B.; Zhao, X.-Q.; Cheng, P.; Liao, D.-Z.; Yan, S.-P.: Synthesis and characterization of metal-organic frameworks based on 4-hydroxypyridine-2,6-dicarboxylic acid and pyridine-2,6-dicarboxylic acid ligands. Inorg. Chem. **45** (2006) 5980-5988.
8. Hall, A. K.; Skelton, B. W.; White, A. H.; Harrowfield, J. M.: The sodium salt of a tris(tridentate anion)gadolinium(III) complex: pentasodium bis-[chelidamato(3–)][chelidamato(2–)]gadolinate(III) hexadecahydrate. Acta Crystallogr. **C56** (2000) 407-411.
9. Shi, F.-N.; Silva, L. C.; Trindade, T.; Paz, F. A. A.; Rocha, J.: Three-dimensional lanthanide organic frameworks based on di-, Ttetra-, and hxameric clusters. Cryst. Growth Des. **9** (2009) 2098.
10. Ghosh, S. K.; Bharadwaj, P. K.: Self-Assembly of Lanthanide Helicate Coordination Polymers into 3D Metal-Organic Framework Structures. Inorg. Chem. **43** (2004) 2293-2298.
11. Feng, X.; Wang, L.-Y.; Zhao, J. S.; Wang, J. G.; Weng, N. S.; Liu, B.; Shi, X. G.: Series of anion-directed lanthanide-rigid-flexible frameworks: syntheses, structures, luminescence and magnetic properties. CrystEngComm **12** (2010) 774-783.
12. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.