Synthesis and Crystal Structure of a 3D Samarium-Organic Framework Containing Vacant Chelating Sites

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Metal organic frameworks (MOFs) have been intensely studied over the last few decades[1] because their pores and optical properties can be employed in various applications including gas storage, ion-exchange, catalysis, and fluorescence technology.[2] The characteristics of MOFs depend greatly on the properties of their metal ions and organic linker compounds, and thus a proper choice of the building blocks is of significant importance in preparation of functional MOFs. While most transition metal ions can be used as the framework metal centers, not all organic compounds can be utilized as the linker compounds. The organic linker compounds are usually multidentate aromatic carboxylic acids possessing high thermal stability because they are typically made through thermal solvolysis. This characteristic of the organic linkers, however, has restricted the diversity of MOFs because the aromatic carboxylic acids have limitations to their flexible modification for specific functions such as incorporation of additional guest-recognition sites.

Recently, the modification of MOFs after their syntheses ("the post-synthetic modification") has been explored to expand the scope of the applications of MOFs.[3,4] The most modifications of MOFs are focused on the covalent conjugation of the organic linker compounds rather than incorporation of another metal ion to the MOFs because it is more challenging to maintain the vacant metal-binding sites in organic linkers during the preparation of MOFs.[5] The preparation of MOFs containing the vacant metal-binding sites probably expands the range of the applications of MOFs through the incorporation of the second metal ions. A rare and successful example is the incorporation of $Ti(O^iPr)_4$ to a MOF composed of Cd^{II} and (*R*)-6,6'-dichloro-2,2'-dihydroxy-1,1'-binaphthyl-4,4'-bipyridine, affording an enantioselective asymmetric catalyst.[6]

Despite this promising result, the examples for the MOFs containing unbound chelating ligands are still rare.[7] Maintaining unbound chelating ligand during the preparation of MOFs may be achieved by using the organic linker compounds with two distinct kinds of coordination atoms and a particular metal ion possessing a tendency to prefer binding to the particular atoms. For example, an organic linker compound with multiple metal-binding sites composed of oxygen as well as of nitrogen atoms can provide specific

coordination properties toward oxophilic metal ions. The oxophilic metal ions solely bind to the oxygen atoms and then the binding sites composed of nitrogen atoms perhaps remains as uncoordinated. Herein, we exploited this idea and report the preparation of a samarium three-dimensional MOF containing unbound metal-chelating sites.

We chose 2,2'-bipyridine-5,5'-dicarboxylic acid (bpydc) as a linker compound because bpydc contains two different types of functional groups: a bipyridine and two carboxylates (Chart 1). Recently, we reported two-dimensional coordination polymers using bpydc and zinc(II) ion.[2(f)] The zinc ions coordinate to both functional groups. Presumably zinc(II) ion does not have enough selectivity toward oxygen atoms. More oxophilic metal ions may solely bind to the carboxylate group and therefore bipyridine group remains as uncoordinated. We chose samarium(III) ion instead of zinc(II) ion in this study because trivalent lanthanides possess high oxophilicity.[8] A similar idea has been recently demonstrated by a MOF built from Al(III) ions and bpydc, where the oxophilic Al ions are only bound to the bpydc carboxylates.[7(c)]

Samarium nitrate hexahydrate (0.05 mmol) was mixed with bpydc (0.075 mmol) in *N,N*-diethylformamide (DEF, 3 mL) and heated at 100 °C for three days. After cooling to the room temparature, crystals suitable for X-ray crystallography were obtained. However, the crystals were not stable and cracked when they were taken out of the mother liquor at room temperature. Instability of the crystals causes slight change in the XRD pattern compared to the simulated one (see Figure 3). Thus, X-ray crystallographic analysis was performed at 170 K and revealed the product was constructed as a three-dimensional framework (Sm-MOF, $[Sm_2(bpydc)_3(H_2O)_2(DEF)]\cdot2DEF$).[9] A samarium ion is solely coordinated by six carboxylate groups, and the bipyrine remains as unbound as we expected. Two samarium ions are bridged by four carboxylate groups from four bpydc ligands to form pseudo-paddle wheel dinuclear units (Figure 1). In a dinuclear
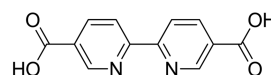
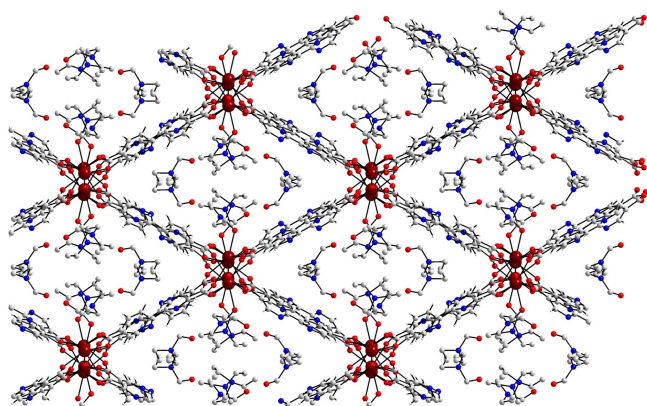**Chart 1.** Structure of 2,2'-bipyridine-5,5'-dicarboxylic acid (bpydc).
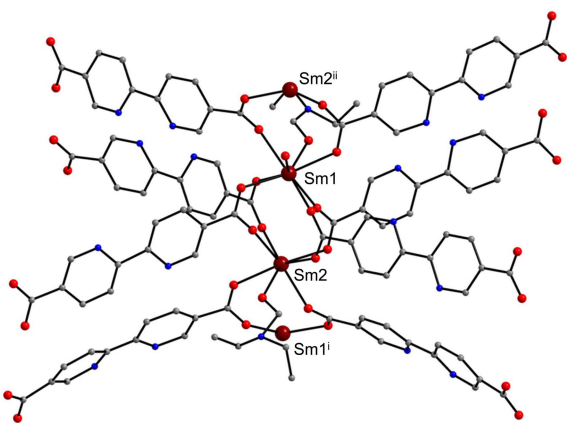
Figure 1. A fragment containing pseudo-paddlewheel units. Hydrogen atoms were ommitted for clarity. Symmetry operations: (i) (x, −y+3/2, z−1/2), (ii) (x, −y+3/2, z+1/2).

unit, one samarium ion (Sm1) is coordinated by eight oxygen atoms from six carboxylates, a DEF molecule, and a water molecule with the bond lengths from 2.34 to 2.44 Å for Sm1-$O_{carboxylate}$, 2.550(17) Å for Sm1-O_{DEF} (Sm1-O51), and 2.44(2) Å for Sm1-O_{water} (Sm1-O1), respectively (Table 1). The other samarium ion (Sm2) is coordinated by seven oxygen atoms from six carboxylates and a coordinated DEF molecule. The Sm2-$O_{carboxylate}$ bond distances range from 2.33 to 2.43 Å, and the Sm2-O_{DEF} (Sm2-O61) distance is 2.40(2) Å (Table 1). The pseudo-paddlewheel units were connected by two carboxylates to form one-dimensional arrays. The Sm⋯Sm distances are 4.227(2) and 4.740(2) Å. The arrays were again joined by bpydc ligands forming three-dimensional networks possessing one-dimensional channels (Figure 2). All carboxylates coordinate samarium(III) ions in bridging (η^1:η^1:μ_2) mode.

Table 1. Selected bond lengths [Å] and angles [º] for Sm-MOF

Sm(1)-O(23)#1	2.348(16)	Sm(1)-O(11)	2.389(17)
Sm(1)-O(41)	2.398(16)	Sm(1)-O(43)#2	2.421(17)
Sm(1)-O(31)	2.425(16)	Sm(1)-O(51)	2.44(2)
Sm(1)-O(21)	2.450(17)	Sm(1)-O(1)	2.550(17)
Sm(2)-O(44)#3	2.332(16)	Sm(2)-O(32)	2.354(18)
Sm(2)-O(22)	2.367(18)	Sm(2)-O(61)	2.40(2)
Sm(2)-O(24)#4	2.418(18)	Sm(2)-O(12)	2.436(18)
Sm(2)-O(42)	2.437(15)	Sm(2)-O(41)	2.925(18)
Sm(2)-C(41)	3.05(2)	O(23)-Sm(1)#1	2.348(16)
O(24)-Sm(2)#5	2.418(18)	O(43)-Sm(1)#2	2.421(17)
O(44)-Sm(2)#6	2.332(16)	O(1)-Sm(2) #7	2.976(19)
Sm(1)-Sm(2)	4.227(2)	Sm(2)-Sm(1)#8	4.740(2)
O(23)#1-Sm(1)-O(11)	142.7(6)	O(23)#1-Sm(1)-O(41)	146.3(6)
O(11)-Sm(1)-O(41)	71.0(6)	O(23)#1-Sm(1)-O(43)#2	99.4(6)
O(11)-Sm(1)-O(43)#2	75.2(6)	O(41)-Sm(1)-O(43)#2	87.9(6)
O(23)#1-Sm(1)-O(31)	73.7(7)	O(11)-Sm(1)-O(31)	85.7(6)
O(41)-Sm(1)-O(31)	121.3(6)	O(43)#2-Sm(1)-O(31)	137.6(6)
O(23)#1-Sm(1)-O(51)	74.3(7)	O(11)-Sm(1)-O(51)	133.6(6)
O(41)-Sm(1)-O(51)	77.4(6)	O(43)#2-Sm(1)-O(51)	70.5(7)
O(31)-Sm(1)-O(51)	140.4(7)	O(23)#1-Sm(1)-O(21)	79.2(6)
O(11)-Sm(1)-O(21)	127.2(6)	O(41)-Sm(1)-O(21)	75.6(6)
O(43)#2-Sm(1)-O(21)	143.0(6)	O(31)-Sm(1)-O(21)	78.0(7)
O(51)-Sm(1)-O(21)	73.6(7)	O(23)#1-Sm(1)-O(1)	72.0(6)
O(11)-Sm(1)-O(1)	71.5(6)	O(41)-Sm(1)-O(1)	140.1(5)
O(43)#2-Sm(1)-O(1)	70.0(6)	O(31)-Sm(1)-O(1)	68.2(6)
O(51)-Sm(1)-O(1)	121.8(7)	O(21)-Sm(1)-O(1)	140.3(5)
O(44)#3-Sm(2)-O(32)	154.2(6)	O(44)#3-Sm(2)-O(22)	130.4(6)
O(32)-Sm(2)-O(22)	74.7(6)	O(44)#3-Sm(2)-O(61)	76.4(7)
O(32)-Sm(2)-O(61)	79.6(7)	O(22)-Sm(2)-O(61)	138.2(7)
O(44)#3-Sm(2)-O(24)#4	93.7(6)	O(32)-Sm(2)-O(24)#4	87.3(6)
O(22)-Sm(2)-O(24)#4	75.3(7)	O(61)-Sm(2)-O(24)#4	71.0(8)
O(44)#3-Sm(2)-O(12)	84.2(6)	O(32)-Sm(2)-O(12)	80.5(6)
O(22)-Sm(2)-O(12)	130.9(6)	O(61)-Sm(2)-O(12)	74.8(7)
O(24)#4-Sm(2)-O(12)	145.2(7)	O(44)#3-Sm(2)-O(42)	73.5(6)
O(32)-Sm(2)-O(42)	123.3(6)	O(22)-Sm(2)-O(42)	79.6(6)
O(61)-Sm(2)-O(42)	142.2(7)	O(24)#4-Sm(2)-O(42)	132.9(7)
O(12)-Sm(2)-O(42)	79.8(6)	O(44)#3-Sm(2)-O(41)	115.9(5)
O(32)-Sm(2)-O(41)	76.1(5)	O(22)-Sm(2)-O(41)	67.6(6)
O(61)-Sm(2)-O(41)	136.1(7)	O(24)#4-Sm(2)-O(41)	142.1(7)
O(12)-Sm(2)-O(41)	65.6(5)	O(42)-Sm(2)-O(41)	47.4(5)

Symmetry transformations used to generate equivalent atoms: #1 −x+2, −y+1, −z+2, #2 −x+1, −y+1, −z+2, #3 −x+1, y+1/2, −z+3/2, #4 −x+2, y+1/2, −z+3/2, #5 −x+2, y−1/2, −z+3/2, #6 −x+1, y−1/2, −z+3/2, #7 x, −y+3/2, z−1/2, #8 x, −y+3/2, z−1/2

Notes

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Figure 2. The packing diagram along c-axis of the Sm-MOF.

Figure 4. Microscopic images of Sm-MOF. Left column: an optical microscopic image. Right column: a fluorescence microscopic image of the same region.
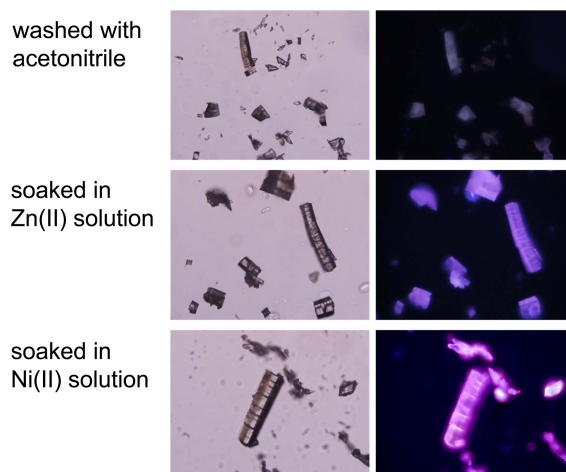
The internal channel of the framework is occupied by disordered DEF molecules and three uncoordinated DEF molecules were found around the pseudo-paddlewheel units. The TG profile indicated that two DEF molecules are solvated and one DEF molecule is coordinated to samarium ion (Figure S1 in the supporting information). The voids without the solvated DEF molecules was calculated as 40.7%, while the solvent accessible void with the DEF molecules were calculated as 3.6% from the PLATON calculation.[10] It implies that the internal cavities of the Sm-MOF were fully occupied by DEF molecules.

We attempted to incorporate another divalent metal ions, such as copper(II), cobalt(II), mercury(II), nickel(II), and zinc(II) ions, into Sm-MOF. Because the cavities of Sm-MOF are occupied by DEF molecules, we first tried to remove the occupied DEF molecules by washing with a polar solvent, such as acetonitrile, ethyl alcohol, or water, in which metal ions can be dissolved. Unfortunately, cracks were observed when the crystals were soaked in such solvents. In addition, PXRD analyses showed that the crystallinity of Sm-MOF was altered by washing with acetonitrile, ethanol, or water (Figure 3). Presumably, the coordinated DEF molecules are removed by the solvent exchange step or the oxygen atoms of protic solvents (*i.e.* ethanol or water) coordinate to samarium ions, and thus the crystallinity of MOFs was altered.

Although the crystallinity of Sm-MOF was changed, we

soaked the crystals in an acetonitrile solution of a metal ion to incorporate metal ions into the Sm-MOF, and analyzed the soaked crystals by a fluorescence microscope and a fluorescence spectrometer. Interestingly, we observed fluorescence from the crystals soaked in the nickel and zinc ion solutions, whereas the crystals washed with acetonitrile did not show fluorescence (Figure 4). The incorporated metal ions coordinate to the bipyridyl group and the incorporation presumably causes the metal-perturbed intraligand fluorescent emission.[2(f)] However, fluorescence spectroscopic analyses did not provide intense spectra (data not shown). Presumably, the enough amount of the second metal ions were not incorporated to produce intense fluorescence because the solvated DEF molecules were not completely removed to provide sufficient space for metal incorporation, or the orientation of the chelating group (*i.e.* bipyridine group) is not proper to accept a metal ion. This may cause only small portion of the second metal ions to incorporate and afford weak fluorescence. Although the soaked crystals did not provide intense fluorescence to detect the second metal ions by fluorescence spectroscopic analysis, this current strategy for synthesis of MOF containing vacant chelating sites can be used for developing a sensing system of metal ions. We are expanding this work to other oxophilic metal ions including lanthanide ions, which will produce MOFs having both improved framework rigidity and metal-binding affinity.

Experimental Section

Preparation of Sm-MOF. Samarium(III) nitrate hexahydrate (22.2 mg, 0.05 mmol) and bpydc (18.3 mg, 0.75 mmol) were suspended in *N,N*-diethylformamide (3 mL) and heated at 100 °C for 3 days. Crystals were collected after cooled at room temperature and analyzed by x-ray crystallography. FT-IR (KBr pellet, 4500-600 cm⁻¹): 2978 (br, w), 1648 (w), 1621 (w), 1575 (vs), 1529 (m), 1394 (vs), 1265 (w), 1246 (w), 1212 (m), 1160 (m), 1119 (m), 946 (w), 862

Figure 3. PXRD patterns of Sm-MOF.

(m), 814 (w), 779 (s), 697 (m), 643 (m). Anal. Calcd. for $C_{51}H_{55}N_9O_{17}Sm_2$: C, 44.82; H, 4.06; N, 9.22. Found: C, 43.94; H, 3.32; N, 8.42.

X-Ray Crystallography. The X-ray diffraction data for the compound were collected on a Bruker SMART APX diffractometer equipped with a monochromater in the Mo $K\alpha$ (λ = 0.71073 Å) incident beam. A crystal was mounted on a glass fiber. The CCD data were integrated and scaled using the Bruker-SAINT software package, and the structure was solved and refined using SHEXTL V6.12. All hydrogen atoms were placed in the calculated positions. The crystallographic data (CIF) for Sm-MOF has been provided to the Cambridge Crystallographic Data Centre, CCDC No. 841978. Copies of the data can be obtained free of charge by contacting CCDC, 12 Union road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk), or electronically via www.ccdc.cam.ac.uk/data_request/cif.

Incorporation of Metal Ions into Sm-MOF. The Sm-MOF (50 mg) was washed three times with acetonitrile (1 mL × 3). The washed Sm-MOF was soaked in an acetonitrile solution (1 mM) of metal ions ($ZnCl_2$ or $NiCl_2 \cdot 6H_2O$) and kept at room temperature for 16 h. The soaked crystals were isolated by filtrations and washed three times with acetonitrile (1 mL × 3).

References

1. (a) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276. (b) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469. (c) Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2003**, *300*, 1127. (d) Kitagawa, S.; Kitaura, R.; Noro, S.-I. *Angew. Chem. Int. Ed.* **2004**, *43*, 2334. (e) Rowsell, J. L. C.; Millward, A. R.; Park, K. S.; Yaghi, O. M. *J. Am. Chem. Soc.* **2004**, *126*, 5666. (f) Rowsell, J. L. C.; Yaghi, O. M. *Angew. Chem. Int. Ed.* **2005**, *44*, 4670. (g) Matsuda, R.; Kitaura, R.; Kitagawa, S.; Kubota, Y.; Belosludov, R. V.; Kobayashi, T. C.; Sakamoto, H.; Chiba, T.; Takata, M.; Kawazoe, Y.; Mita, Y. *Nature* **2005**, *436*, 238. (g) Park, G.; Kim, H.; Lee, G. H.; Park, S.-K.; Kim, K. *Bull. Korean Chem. Soc.* **2006**, *27*, 443. (h) Ma, S.; Sun, D.; Simmons, J. M.; Collier, C. D.; Yuan, D.; Zhou, H.-C. *J. Am. Chem. Soc.* **2008**, *130*, 1012. (i) Banerjee, R.; Phan, A.; Wang, B.; Knobler, C.; Furukawa, H.; O'Keeffe, M.; Yaghi, O. M. *Science* **2008**, *319*, 939.

2. (a) review: Kuppler. R. J.; Timmons, D. J.; Fang, Q.-R.; Li, J. R.; Makal, T. A.; Young, M. D.; Yuan, D.; Zhao, D.; Zhuang, W.; Zhou, H. C. *Coord. Chem. Rev.* **2009**, *253*, 3042. (b) Qiu, L.-G.; Li, Z.-Q.; Wu, Y.; Wang, W.; Xu, T.; Jiang, X. *Chem. Commun.* **2008**, 3642. (c) Qiu, L.-G.; Li, Z.-Q.; Wu, Y.; Wang, W.; Xu, T.; Jiang, X. *Inorg. Chem. Commun.* **2008**, *11*, 727. (d) Chen, B.; Wang, L.; Zapata, F.; Qian, G.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **2008**, *130*, 6718. (e) Lan, A.; Li, K.; Wu, H.; Olson, D. H.; Emge, T. J.; Ki, W.; Hong, M.; Li, J. *Angew. Chem., Int. Ed.* **2009**, *48*, 2334. (f) Huh, S.; Jung, S.; Kim, Y.; Kim, S.-J.; Park, S. *Dalton Trans.* **2010**, *39*, 1261.

3. Wang, Z.; Cohen, S. M. *J. Am. Chem. Soc.* **2007**, *129*, 12368.

4. (a) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982. (b) Wang, Z.; Cohen, S. M. *Angew. Chem. Int. Ed.* **2008**, *47*, 4699. (c) Tanabe, K. K.; Wang, Z.; Cohen, S. M. *J. Am. Chem. Soc.* **2008**, *130*, 8508. (d) Ingelson, M. J.; Barrio, J. P.; Guilbaud, J.-B.; Khimyak, Y. Z.; Rosseinsky, M. J. *Chem. Commun.* **2008**, 2680. (e) Costa, J. S.; Gamez, P.; Black, C. A.; Roubeau, O.; Teat, S.; Reedijk, J. *Eur. J. Inorg. Chem.* **2008**, 1551. (f) Burrows, A. D.; Frost, C. G.; Mahon, M. F.; Richardson, C. *Angew. Chem. Int. Ed.* **2008**, *47*, 8482. (g) Gadzikwa, T.; Lu, G.; Stern, C. L.; Wilson, S. R.; Hupp, J. T.; Nguyen, S. T. *Chem. Commun.* **2008**, 5493. (h) Wang, Z.; Tanabe, K. K.; Cohen, S. M. *Inorg. Chem.* **2009**, *48*, 296. (i) Teppei, Y.; Kitagawa, H. *J. Am. Chem. Soc.* **2009**, *131*, 6312. (j) Taylor-Pashow, K. M. L.; Rocca, J. D.; Xie, Z.; Tran, S.; Lin, W. *J. Am. Chem. Soc.* **2009**, *131*, 14261. (k) Jung, S.; Kim, Y.; Kim, S.-J.; Kwon, T.-H.; Huh, S.; Park, S. *Chem. Commun.* **2011**, *47*, 2904. (l) Ko, N.; Kim. J. *Bull. Korean Chem. Soc.* **2011**, *32*, 2705.

5. Wang, Z.; Cohen, S. M. *Chem. Soc. Rev.* **2009**, *38*, 1315.

6. Wu, C.-D.; Hu, A.; Zhang, L.; Lin, W. *J. Am. Chem. Soc.* **2005**, *127*, 8940.

7. (a) Jia, J.; Lin, X.; Blake, A. J.; Champness, N. R.; Hubberstey, P.; Shao, L.; Walker, G.; Wilson, C.; Schröder, M. *Inorg. Chem.* **2006**, *45*, 8838. (b) Chen, B.; Wang, L.; Xiao, Y.; Fronczek, F. R.; Xue, M.; Cui, Y.; Qian, G. *Angew. Chem. Int. Ed.* **2009**, *48*, 5. (c) Bloch, E. D.; Britt, D.; Doonan, C. J.; Uribe-Romo, F. J.; Furukawa, H.; Long, J. R.; Yaghi, O. M. *J. Am. Chem. Soc.* **2010**, *132*, 14382-14384.

8. *Lanthanides: Chemistry and Use in Organic Synthesis*; Kobayashi, S., Ed.; Springer-Verlag: Berlin, 1999.

9. (a) Crystal data for the title compound: monoclinic, $P2_1/c$, a = 25.475(2) Å, b = 15.5864(14) Å, c = 17.0301(16) Å, α = 90.00°, β = 98.428(2)°, γ = 90.00°, V = 6689.0(11) Å^3, Z = 4, D_c = 1.394 g/cm^3, $F(000)$ = 696.36319 reflections measured with 12994 unique reflections. The final R = 0.0613, wR = 0.1558 for 12994 observed reflections ($I > 2\sigma(I)$). Data were collected on a Bruker SMART APEX diffractometer, $\lambda(MoK\alpha)$ = 0.71073 Å, T = 170(2) K, and refined by full-matrix least-squares refinements on F^2 using all data with SHELXTL programs. (b) The molecular formula is calculated from the TG analysis (see the supporting information).

10. Spek, A. L. *Acta Cryst.* **2009**, *D65*, 148.