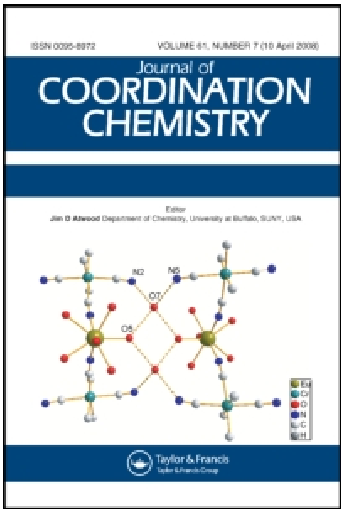

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and characterization of a two-dimensional calcium complex with (1,3,4-thiadiazole-2,5-diyldithio)diacetic acid

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First published on: 22 September 2010

To cite this Article Wang, Yuting , Yin, Mingcai , Fan, Yaoting and Hou, Hongwei(2008) 'Synthesis and characterization of a two-dimensional calcium complex with (1,3,4-thiadiazole-2,5-diyldithio)diacetic acid', Journal of Coordination Chemistry, 61: 6, 907 — 916, First published on: 22 September 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958970701413250

URL: http://dx.doi.org/10.1080/00958970701413250

Journal of Coordination Chemistry
Vol. 61, No. 6, 20 March 2008, 907–916

Synthesis and characterization of a two-dimensional calcium complex with (1,3,4-thiadiazole-2,5-diyldithio)diacetic acid

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(*Received 9 January 2007; in final form 15 May 2007*)

A two-dimensional coordination polymer $\{[Ca_2(tzda)_2(H_2O)_4] \cdot 3H_2O\}_n$, where H_2tzda is a flexible carboxylate ligand (1,3,4-thiadiazole-2,5-diyldithio)diacetic acid, was synthesized and characterized by X-ray crystallography, IR, TGA and photoluminescence. The results show that there are two crystallographically independent Ca atoms in the structure, which are both seven-coordinate, but with different coordination environments. Two kinds of $tzda^{2-}$ ligands with identical coordination mode exist in $\{[Ca_2(tzda)_2(H_2O)_4] \cdot 3H_2O\}_n$. The η^2-bridging O3 and O8 atoms link the Ca1 atoms into a 1-D chain, which are further connected by the $tzda^{2-}$ ligands forming a 2-D network. A series of hydrogen bonds link the 2-D network to form a 3-D architecture. The solid state luminescence behavior of $\{[Ca_2(tzda)_2(H_2O)_4] \cdot 3H_2O\}_n$ exhibits one intense emission band at 375 nm upon excitation at 315 nm which can be attributed to the intraligand emission.

Keywords: Calcium complex; (1,3,4-Thiadiazole-2,5-diyldithio)diacetic acid; Synthesis; Crystal structure

1. Introduction

Synthesis and characterization of coordination polymers have been studied due to their fascinating architectures and applications [1–4]. Selection of appropriate organic bridging ligands provides a route to achieve intriguing polymeric structures [5–8]. Many multidentate ligands, such as pyrazine [9, 10], 4,4′-bipyridine [11, 12], imidazole [13, 14], 1,4-benzenedicarboxylic acid [15–17], 1,3,5-benzenetricarboxylate acid (H_3btc) [18–23], 4,4′-biphenyldicarboxylic acid [24] and 1,2,4,5-benzenetetracarboxylic acid [25–28], have been used with carboxylate-containing ligands having versatile coordination modes [15–28]. However, most of the bridging ligands used are rigid [29–32]. Flexible carboxylate-containing ligands in construction of metal-organic frameworks are rare, possibly due to the difficulties in predicting the resulting framework structures [33, 34]. Most reports center on transition metal polymers with research on alkaline earth

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970701413250

polymeric complexes less common [35]. Herein, we report the synthesis and structural characterization of a two-dimensional complex $\{[Ca_2(tzda)_2(H_2O)_4]\cdot 3H_2O\}_n$, where H_2tzda is a flexible carboxylate ligand (1,3,4-thiadiazole-2,5-diyldithio)diacetic acid, which possesses two $-SCH_2-$ spacers between the thiadiazole ring and carboxyl groups. The spectra and thermogravimetric properties have also been discussed in this article.

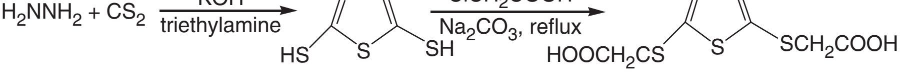
2. Experimental

2.1. *Materials and methods*

All chemicals were reagent grade and obtained from commercial sources and used without further purification. Elemental analyses (C, H, N) were performed on a Carlo-Erba 1160 Elemental Analyzer. IR spectra were recorded in the region of 4000–400 cm^{-1} on a FTS-40 infrared spectrophotometer with pressed KBr pellets. ^1H NMR spectrum was recorded at room temperature on Bruker DPX 400 spectrometer. Thermogravimetric analysis was carried out with a NETZSCH STA 409 unit at a heating rate of 10°C min^{-1} under nitrogen. Emission spectrum was recorded on a HITACHI F-4500 fluorescence spectrophotometer.

2.2. *Synthesis of (1,3,4-thiadiazole-2,5-diyldithio)diacetic acid (H_2tzda)*

2,5-Dimercapto-1,3,4-thiadiazole was prepared according to the literature [36–38]. Elemental analysis, IR and ^1H NMR spectra were consistent with those previously reported. The target ligand H_2tzda was synthesized as follows (scheme 1): 2,5-dimercapto-1,3,4-thiadiazole (1.5 g, 10 mmol) was slowly added to a 30 mL aqueous solution of chloroacetic acid (1.89 g, 20 mmol) and sodium carbonate (3.12 g, 20 mmol), and refluxed for 3 h under stirring. The mixture was then cooled to room temperature and concentrated hydrochloric acid was introduced with stirring until pH = 2. A white precipitate formed and was collected; after washing with water and drying, 2.2 g (83%) product was isolated. m.p. 164–165°C. Anal. Cacld for $C_6H_6N_2O_4S_3$ (%): C, 27.07; H, 2.26; N, 10.53. Found: C, 27.62; H, 2.18; N, 10.09. IR data (cm^{-1}): 3082 (m), 2983 (m), 2927 (m), 1735 (s), 1712 (s), 1384 (s), 1364 (m), 1299 (m), 1202 (s), 1182 (s), 1050 (s), 893 (m), 780 (m), 709 (m). ^1H NMR (300 MHz, DMSO, 25°C): $\delta = 13.0479$ (s, 2H, COOH), 4.1414 (s, 4H, CH_2). This ligand is soluble in common organic solvents such as methanol, ethanol, DMF and DMSO, and in hot water.



Scheme 1. The synthesis route of ligand H_2tzda.

2.3. *Preparation of* $\{[Ca_2(tzda)_2(H_2O)_4]\cdot 3H_2O\}_n$

H_2tzda (9.0 mmol) was dissolved in ethanol (30 mL) and diluted with water (15 mL). $CaCl_2\cdot 2H_2O$ (4.5 mmol) dissolved in water (25 mL) was added to the above solution. To this mixture aqueous NH_3 (25%) (15 mL) was added dropwise till the reaction mixture became slightly basic. The resulting solution was concentrated to half of its original volume on a water bath, filtered, and kept for crystallization. Colorless crystals suitable for diffraction studies were obtained after two days in ca. 23% yield (based on Ca). Anal. Cacld for $C_{12}H_{22}Ca_2N_4O_{15}S_6$ (%): C, 19.60; H, 2.99; N, 7.62. Found: C, 19.69; H, 2.90; N, 7.56. IR (KBr, cm^{-1}): 3390 (m), 1635 (s), 1589 (s), 1414 (s), 1384 (s), 1225 (m), 1208 (m), 1062 (m), 934 (w), 914 (m), 700 (m), 686 (m), 598 (m).

2.4. *X-ray diffraction studies*

The X-ray diffraction measurement was carried out on a Bruker SMART APEX II CCD diffractometer equipped with a graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) by using ω–2θ scan technique at 291(2) K. 8373 reflections were measured over the ranges $5.4 \le 2\theta \le 55°$, $-10 \le h \le 9$, $-18 \le k \le 18$, and $-13 \le l \le 18$, yielding 5929 unique reflections. Raw data were corrected and the structure was solved by direct methods using the SHELXS-97 program. Non-hydrogen atoms were located by direct phase determination and subjected to anisotropic refinement. Full-matrix least-squares calculation on F^2 was applied on the final refinement. The crystal parameters, data collection, and refinement results are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

Table 1. Crystal data and structure refinement parameters.

Formula	$C_{12}H_{22}Ca_2N_4O_{15}S_6$
Formula weight	734.86
Temperature (K)	291(2)
Wavelength (Å)	0.71073
Crystal sizes (mm)	0.49 × 0.39 × 0.23
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	7.7318(6)
b (Å)	14.1534(10)
c (Å)	14.3828(10)
α (°)	61.1550(10)
β (°)	81.1570(10
γ (°)	78.2950(10)
V (Å^3)	1347.11(17)
Z	2
D_c ($g\,cm^{-3}$)	1.812
Absorption coefficient (mm^{-1})	None
$F(000)$	756
Reflections collected/unique	8373/5929 [$R_{(int)} = 0.0080$]
Data/restraints/parameters	5929/21/352
Goodness-of-fit on F^2	1.018
R_1, wR_2 [$I > 2\sigma(I)$]	0.0231, 0.0586
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ (e Å^{-3})	0.324, −0.305

$R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$, $wR_2 = \{\sum w(|F_o| - |F_c|)^2/\sum wF_o^2\}^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (°).

Ca(1)–O(5)#1	2.310(1)	Ca(2)–O(7)	2.298(1)
Ca(1)–O(2)#2	2.358(1)	Ca(2)–O(11)	2.383(1)
Ca(1)–O(8)	2.386(1)	Ca(2)–O(4)	2.426(1)
Ca(1)–O(12)	2.395(1)	Ca(2)–O(10)	2.426(1)
Ca(1)–O(3)#3	2.414(1)	Ca(2)–O(9)	2.437(1)
Ca(1)–O(3)	2.452(1)	Ca(2)–O(6)#1	2.483(1)
Ca(1)–O(8)#4	2.676(1)	Ca(2)–O(1)#5	2.515(1)
Ca(1)–Ca(1)#3	4.0174(6)	Ca(1)–Ca(1)#4	4.1225(6)
O(5)#1–Ca(1)–O(2)#2	89.13(4)	O(7)–Ca(2)–O(11)	171.92(4)
O(5)#1–Ca(1)–O(8)	100.68(4)	O(7)–Ca(2)–O(4)	102.80(4)
O(2)#2–Ca(1)–O(8)	158.89(4)	O(11)–Ca(2)–O(4)	80.10(3)
O(5)#1–Ca(1)–O(12)	139.34(4)	O(7)–Ca(2)–O(10)	87.66(4)
O(2)#2–Ca(1)–O(12)	78.11(4)	O(11)–Ca(2)–O(10)	85.60(4)
O(8)–Ca(1)–O(12)	82.37(4)	O(4)–Ca(2)–O(10)	142.71(4)
O(5)#1–Ca(1)–O(3)#3	144.27(4)	O(7)–Ca(2)–O(9)	102.00(4)
O(2)#2–Ca(1)–O(3)#3	92.68(4)	O(11)–Ca(2)–O(9)	80.22(4)
O(8)–Ca(1)–O(3)#3	90.13(4)	O(4)–Ca(2)–O(9)	136.95(4)
O(12)–Ca(1)–O(3)#3	75.50(4)	O(10)–Ca(2)–O(9)	72.58(4)
O(5)#1–Ca(1)–O(3)	75.96(4)	O(7)–Ca(2)–O(6)#1	91.00(4)
O(2)#2–Ca(1)–O(3)	84.31(4)	O(11)–Ca(2)–O(6)#1	82.53(4)
O(8)–Ca(1)–O(3)	116.08(4)	O(4)–Ca(2)–O(6)#1	73.81(3)
O(12)–Ca(1)–O(3)	139.13(4)	O(10)–Ca(2)–O(6)#1	70.28(4)
O(3)#3–Ca(1)–O(3)	68.74(4)	O(9)–Ca(2)–O(6)#1	139.95(4)
O(5)#1–Ca(1)–O(8)#4	71.55(4)	O(7)–Ca(2)–O(1)#5	78.43(4)
O(2)#2–Ca(1)–O(8)#4	94.84(4)	O(11)–Ca(2)–O(1)#5	109.63(4)
O(8)–Ca(1)–O(8)#4	71.12(4)	O(4)–Ca(2)–O(1)#5	76.03(3)
O(12)–Ca(1)–O(8)#4	71.31(4)	O(10)–Ca(2)–O(1)#5	141.22(4)
O(3)#3–Ca(1)–O(8)#4	143.55(3)	O(9)–Ca(2)–O(1)#5	75.21(4)
O(3)–Ca(1)–O(8)#4	147.51(3)	O(6)#1–Ca(2)–O(1)#5	144.84(3)

Symmetry transformations used to generate equivalent atoms: #1: $x, y, z+1$; #2: $-x+2, -y+1, -z+2$; #3: $-x+2, -y+1, -z+1$; #4: $-x+1, -y+1, -z+1$; #5: $x, y, z-1$.

3. Results and discussion

3.1. *Crystal structure of* $\{[Ca_2(tzda)_2(H_2O)_4]\cdot 3H_2O\}_n$

In $[Ca_2(tzda)_2(H_2O)_4\cdot 3H_2O]_n$, there are two crystallographically independent Ca atom centers (Ca1, Ca2), which have the same coordination number but different coordination environments, as shown in figure 1.

Ca1 is coordinated by seven oxygen atoms: six (O2A, O3, O3A, O5A, O8, O8A) from six carboxylate groups of six tzda^{2-} ligands and one (O12) from a water molecule. The Ca2 atom is also surrounded by seven oxygen atoms, four (O1A, O4, O6A, O7) are provided by four carboxylate groups of four tzda^{2-} ligands and three (O9, O10, O11) are from three water molecules. The coordination polyhedron of either Ca1 or Ca2 can be described as a heavily distorted pentagonal bipyramid. For Ca1, O8 and O2A occupy the apical positions and the severely distorted equatorial plane is defined by O5A, O3, O3A, O12 and O8A with the largest deviation of O12 at 0.3418 Å. The dihedral angles between the equatorial plane and two thiadiazole rings are 87.8° (ring composed of S2, C4, N2, N1, C3, defined as plane **A**) and 94.0° (ring composed of S5, C10, N3, N4, C9, defined as plane **B**), respectively. For Ca2, the apical positions are occupied by O11 and O7, and the severely distorted equatorial plane is constructed by O1A, O4, O6A, O10 and O9 with the largest deviation of O1A at 0.5373 Å.

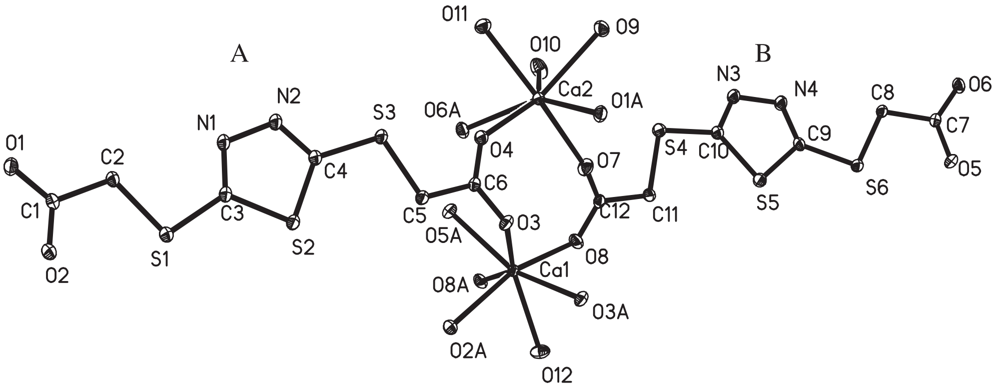


Figure 1. Coordination environments of Ca(II) atoms in the title complex, the hydrogen atoms and uncoordinated water molecules are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

The dihedral angles between it and the two thiadiazole rings are 65.1° (plane **A**) and 60.5° (plane **B**), respectively. The Ca1–O bond distances range from 2.3101 to 2.6766 Å and the Ca2–O bond length varies in the range of 2.2987–2.5158 Å, which are similar to those observed in other calcium carboxylate complexes [39–40]. The O–Ca–O bond angles vary from 68.74 to 158.89° (Ca1) or from 70.28 to 171.92° (Ca2), as displayed in table 2.

There are two kinds of tzda^{2-} ligands in $\{[Ca_2(tzda)_2(H_2O)_4] \cdot 3H_2O\}_n$. Each bonds to five Ca atoms (three Ca1 and two Ca2) with two carboxylate groups adopting μ_3-η^2: η^1 (one oxygen atom coordinating to two metal atoms, the other one coordinating to one metal atom and the carboxylic group coordinates to three metal atoms altogether) and μ_2-η^1: η^1 (each oxygen atom bonds to one metal atom) bridging mode, as shown in figure 2(a). The Ca1 atoms and bridging O3 and O8 atoms form an infinite zig-zag chain running along *a* direction with Ca1B–Ca1–Ca1A bond angle of 143.557°; Ca1 and Ca1A are bridged by O8 and O8A with a separation of 4.1233 Å and the distance between Ca1 and Ca1B bridged by O3 and O3A is 4.017 Å. The Ca2 atoms sit on the both sides of the chain, linked by coordination of carboxylate (O4, O6, O1) and so the Ca1 and Ca2 atoms form a centipede-like chain (figure 2b).

The tzda^{2-} ligands link these one-dimensional (1-D) centipede-like chains to generate a 2-D network on the *ac* plane (figure 3a), in which the ligands are arranged as follows: the thiadiazole planes **B** are parallel and the centroid–centroid distance between adjacent ones is 5.951 Å, similarly the thiadiazole planes **A** are parallel to each other with separation of adjacent planes 6.074 Å. The centroid–centroid distance between the adjacent **A** and **B** planes is 6.483 Å with the dihedral angle being 8.0°. The Ca1 $\cdots$ Ca1 or Ca2 $\cdots$ Ca2 distance of two adjacent chains is 14.383 Å. The Ca polyhedra and the bridging tzda^{2-} ligands construct 1-D channels along the *a* axis (figure 3b), however, the cavities are almost completely occupied by the ligand atoms as shown by the space-filling diagram.

Besides the coordinated water molecules, uncoordinated water molecules (OW13, OW14 and OW15) exist. A series of hydrogen bonds are formed between the uncoordinated water and the thiadiazole N atom, between the uncoordinated water and the carboxylate oxygen atom, between the uncoordinated water and the coordinated

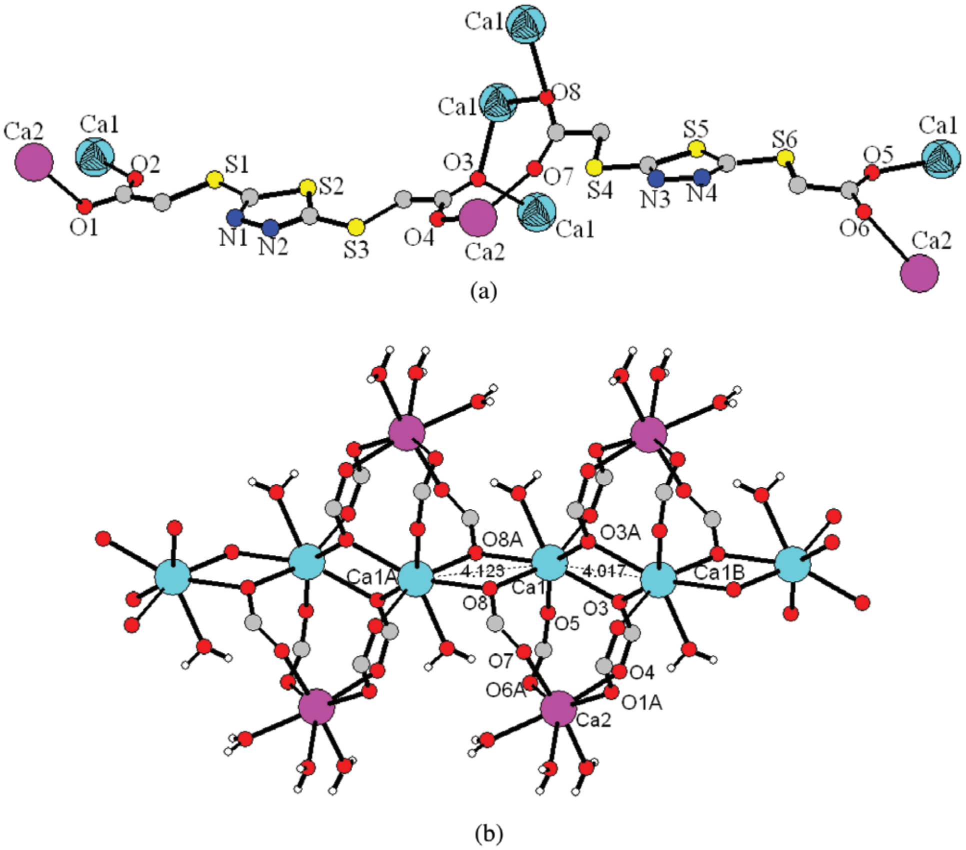
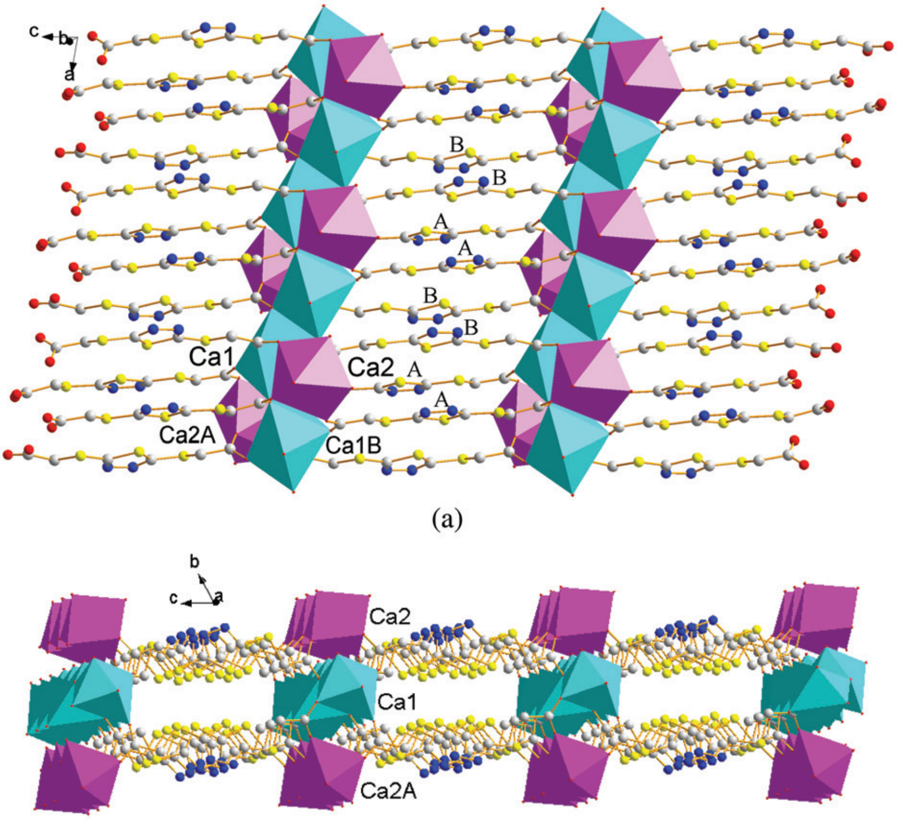


Figure 2. (a) The coordination modes of two tzda^{2-} ligands in $\{[Ca_2(tzda)_2(H_2O)_4] \cdot 3H_2O\}_n$. (b) The one-dimensional centipede-like chain formed by Ca1, Ca2 and O atoms with most of the ligands omitted for clarity.

water molecules, between the coordinated water and the thiadiazole N atom, between the coordinated water and the carboxylate oxygen atom, between the coordinated water the and thiadiazole N atom, and between the uncoordinated water and S atom (table 3), which connect the 2-D networks to 3-D supramolecular architecture (figure 4).

3.2. *IR spectrum*

The infrared spectrum determined in the range of 4000–400 cm^{-1} is consistent with the results of X-ray analyses. The absence of band in the region 1690–1730 cm^{-1} indicates complete deprotonation of the –COOH groups. The asymmetric and symmetric stretching bands of CO_2^- groups appear at 1635, 1589 cm^{-1}, and 1414, 1384 cm^{-1}, respectively, suggesting the CO_2^- groups function in different coordination modes [41]. The broad band at about 3390 cm^{-1} indicates the presence of water. The absorption bands at 1062 and 700 cm^{-1} can be attributed to the vibrations of thiadiazole ring and ν(C–S), respectively [42].



(a)

(b)

Figure 3. The 2-D network formed by 1-D chains and bridging tzda^{2-} ligands viewed along the *b* axis (a) and *a* axis (b).

Table 3. The hydrogen bonds (Å) and angles (°) in the title complex.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O(15)–H(14W)···S(3)#3	0.82	2.99	3.584(1)	130.9
O(15)–H(14W)···O(4)#3	0.82	2.16	2.959(2)	165.6
O(15)–H(13W)···O(11)#3	0.82	2.62	3.036(2)	112.6
O(15)–H(13W)···N(2)#6	0.82	2.11	2.888(2)	156.5
O(14)–H(12W)···O(1)#7	0.84	2.24	3.067(2)	168.7
O(14)–H(11W)···N(1)#4	0.84	2.14	2.981(2)	174.5
O(13)–H(10W)···O(6)#1	0.84	2.22	2.978(2)	150.3
O(13)–H(9W)···O(15)#4	0.84	2.02	2.794(2)	152.3
O(12)–H(8W)···O(6)#8	0.83	2.13	2.942(2)	168.2
O(12)–H(7W)···O(1)#2	0.83	2.06	2.841(2)	157.5
O(11)–H(5W)···N(4)#9	0.83	2.12	2.944(2)	171.8
O(11)–H(6W)···O(13)#10	0.83	1.91	2.744(2)	172.4
O(10)–H(4W)···O(15)#4	0.83	1.98	2.809(2)	170.9
O(9)–H(2W)···O(14)#8	0.84	2.04	2.856(2)	164.1
O(9)–H(1W)···N(3)#9	0.83	2.04	2.870(2)	174.2

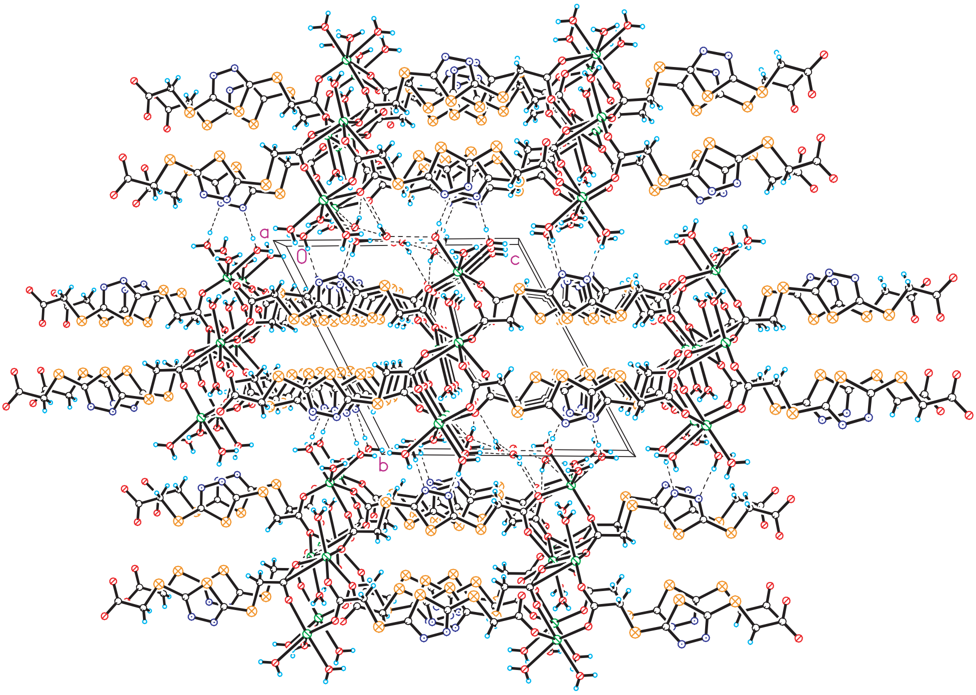


Figure 4. Packing diagram of $\{[Ca_2(tzda)_2(H_2O)_4]\cdot 3H_2O\}_n$ viewed along the *a*-axis.

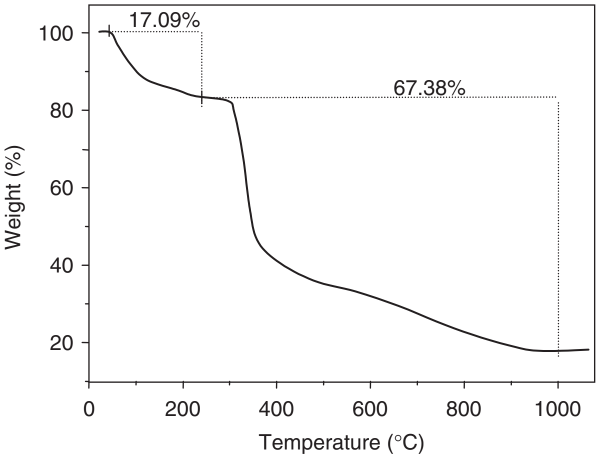


Figure 5. TGA curve of $\{[Ca_2(tzda)_2(H_2O)_4]\cdot 3H_2O\}_n$.

3.3. *Thermogravimetric analysis (TGA)*

Thermal analysis was carried out in an atmosphere of nitrogen to establish the content of coordinated and uncoordinated water molecules in the complex. The TGA curve exhibits two steps of weight loss, as depicted in figure 5. The first, in the range 50–230°C, (observed 17.09%) corresponds to loss of lattice and coordinated water

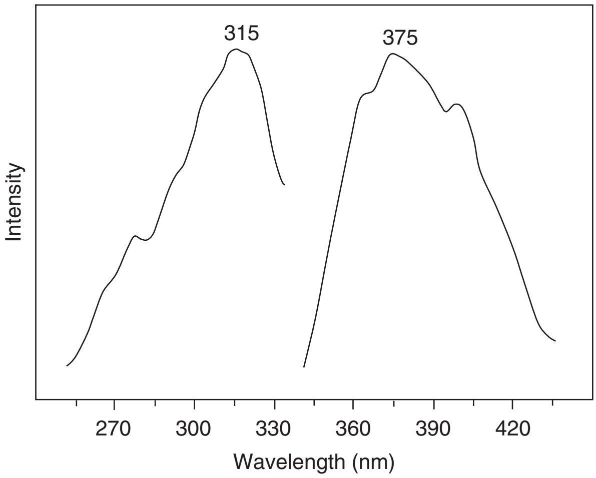


Figure 6. The excitation and emission spectra of $\{[Ca_2(tzda)_2(H_2O)_4]\cdot 3H_2O\}_n]_n$ in the solid state at room temperature.

molecules (calculated 17.15%). The second weight loss occurs from 230 to 1000°C, probably due to breaking the organic moieties and release of N_2, CO_2 and SO_2. The remaining weight of 15.53% (observed) corresponds to the percentage of Ca and O components (calculated 15.24%), indicating that the final product is CaO [43].

3.4. *Photoluminescence*

The luminescent properties of free ligand H_2tzda and the title complex were investigated in the solid state at room temperature. Upon excitation at 315 nm, the complex exhibits one intense emission band at about 375 nm, as shown in figure 6, which can be attributed to the intraligand emission since the free ligand H_2tzda is observed similar photoemissions at 374 nm at the same photoexcitation condition.

Supplementary data

X-ray crystallographic file in CIF format has been deposited to the Cambridge Crystallographic Data Center (CCDC No. 631605).

Acknowledgements

This work was sponsored by the National Natural Science Foundation of China (No. 20471053), the China National Key Basic Research Special Funds (No. 2003CB214500) and the Energy & Technology Program from Zhengzhou University.

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