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A Novel Layer Crystal Structure of Sr(II) Complex Based on 2-Methyl-1*H*-Imidazole-4,5-Dicarboxylate Ligand[1]

K. Zhou[a], F. Yue[a], *, H. M. Chen[a], T. T. Liu[b], and J. D. Wang[a], *

[a]*Key Laboratory of Oil and Gas Fine Chemicals, Ministry of Education and Xinjiang Uygur Autonomous Region, College of Chemistry and Chemical Engineering of Xinjiang University, Urumqi, 830046 P.R. China*

[b]*Xinjiang Shihezi Vocational Technical College, Shihezi, 832000 P.R. China*

**e-mail: xjyuefan@163.com*

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Abstract—A layer coordination polymer of $[Sr(H_2MIDC)_2(H_2O)_2]_n$, ($H_3MIDC$ = 2-methyl-1*H*-imidazole-4,5-dicarboxylate) has been synthesized and characterized. Single X-ray structural analysis indicates the title compound crystallizes in a monoclinic lattice, $P2_1/n$ with $a = 6.902(1)$ $b = 14.469(3)$, $c = 16.641(3)$ Å, $\beta = 98.58(3)°$, $Z = 4$, $V = 1643.2(6)$ Å^3, $\rho_c = 1.867$ g/cm^3, $F(000) = 928$, $S = 1.079$, $R_1 = 0.1346$, $wR_2 = 0.3892$ (CIF file CCDC no. 791212). Crystal structure analysis reveals that Sr^{2+} ion is eight-coordinate and lies in a bicapped tetragonal bipyramid environment with one nitrogen atom and seven oxygen atoms. For the variaties of the ligand's coordination modes and the bridging oxygen atom in carboxylate group, the structure presents a two-dimensional layer molecular network. This coordination polymer exhibited intense fluorescent emissions in the solid state at room temperature.

Keywords: 2-methyl-1*H*-imidazole-4,5-dicarboxylate, strontium, coordination polymer

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INTRODUCTION

Design and synthesis of metal coordination polymers (MCPs) via inorganic connectors (metal ions or polynuclear clusters) and neutral or anionic organic ligands have been developed into one of the most attractive topics [1, 2]. For the strong X-ray absorbtion and unique physical and chemical properties, strontium [3, 4] was widely used in many field such as electronic, chemistry engineering, metallurgy, war industry, light industry, medicine and optics etc. Strontium occurs as a trace element in a number of biological systems and has a similar metabolism process with calcium [5]. Strontium(II) possesses a relative large radius and flexible coordination environment [6], which provides unique opportunity for the constructions of novel frameworks. In the past few years, much attention has been put into imidazole 4,5-dicarboxylic acid (H_3IDC) [7, 8], considering its abundant coordination fashions and results in the formation of the structures of higher dimensions. Prompted by these interesting findings, some groups have synthesized ligands of 2-methyl-1*H*-imidazole-4,5-dicarboxylic acid (H_3MIDC) [9, 10] to build up desired complexes. H_3MIDC is a kind of multidentate N- or O-donor ligand deprotonated to generate H_2MIDC^-, $HMIDC^{2-}$ and $MIDC^{3-}$ with versatile metal-binding and hydrogen-bonding capabilities, and it has recently drawn extensive attention in the construction of frameworks with fascinating structures [9–14]. These properties are illustrated by the structure of Sr(II) complex $[Sr(H_2MIDC)_2(H_2O)_2]_n$ (**I**) with five-membered heterocyclic carboxylate ligand as H_2MIDC^- and water ligand. The two-dimensional structure of complex with the ligand contains two symmetry independent Sr^{2+} ion located in general positions. Two Sr^{2+} situated on the two-fold axes, both with coordination number 8. Herein, this article focuses on the structure aspects of MCPs and reveals the structure of $[Sr(H_2MIDC)_2(H_2O)_2]_n$.

EXPERIMENTAL

Synthesis of complex I. The ligand H_3MIDC was prepared according to the literature method [15]. Strontium nitrate ($Sr(NO_3)_2$) (0.071 g, 1.0 mmol) and ligand (0.071 g, 1.0 mmol) was added to a distilled solution (25 mL), and then adjusted its pH to about 7 with 1 mol/L NaOH (0.3 mL, 0.65 mol/L). The reaction mixture was refluxed 2 h with stirring. The resulting clear solution filtrated keeping hot, and then evaporates the mother solution. Two weeks later colorless crystals were collected, washed with water, then dried in air, the yield was 45%.

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[1] The article is published in the original.

Table 1. Crystallografical data and structure refinement details for compound **I**

Parameter	Value
Empirical formula	$C_{12}H_{14}N_4O_{10}Sr$
Formula weight	461.89
Temperature, K	293(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions:	
a, Å	6.902(1)
b, Å	14.469(3)
c, Å	16.641(3)
β, deg	98.58(3)
V, Å^3	1643.2(6)
Z	4
ρ_{calcd}, g/cm^3	1.867
μ, mm^{-1}	3.347
F(000)	928
Crystal size, mm	0.53 × 0.11 × 0.06
2θ Range for data collection, deg	3.06–27.48
Indices range	$-8 \le h \le 8$, $-16 \le k \le 18$, $-21 \le l \le 21$
Reflections collected	15436
Unique reflections	3752
Reflections observed	2561
Goodness of fit on F^2	1.079
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.1346$, $wR_2 = 0.3892$
Largest diff. peak and hole, e/Å^3	3.84, – and 1.52

IR (ν, cm^{-1}): 3300 ν(C–C), 1260 ν(C–N), 1115 ν(C–O), 1543 ν(C=O), 409 ν(Sr–N,O).

IR spectra of **I** were recorded on a VERTEX 70 Bruker spectrophotometer with KBr pellets in the 400–4000 cm^{-1} region. Powder X-ray diffraction (PXRD) data were collected on a BRUKER-AXS diffractometer, the scanning speed of 2°/min, collecting data in the 2θ angle range of 5°–50°. The fluorescence spectra were obtained on a Shimadzu RF-5301 fluorescence spectrophotometer. The fluorescent light source is a Xe lamp. The excitation spectrum is obtained by a given excitation wavelength and scanning in the wavelength range 250 to 400 nm. The emission wavelength was set according to the position of the excitation peak, and the emission spectra of the coordination polymer were measured in the wavelength range 400 to 600 nm.

X-ray diffraction analyses. Experimental data were collected at room temperature using R-AXIS SPIDER diffractometer with MoK_α ($\lambda = 0.71073$ Å). The structure was solved primary by direct method by SHELX-97 [16] and refined by the full-least-squares method on F^2. The nonhydrogen atoms were refined anisotropically, and all hydrogen atoms were placed in calculated positions. Crystallographic data for compound **I** are given in Table 1. Selected bond lengths and angles are listed in Table 2, hydrogen bonds parameters are given in Table 3.

Supplementary material for structure **I** has been deposited with the Cambridge Crystallographic Data Centre (no. 791212; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The structure of the title compound is composed of molecular layers in which Sr^{2+} ions are bridged by mono-deprotonated ligand molecules. However, each Sr^{2+} ion, being situated on a two-fold axis, exibits a unique coordination mode: one of each H_2MIDC^- ligand coordinates a Sr^{2+} ion using its N,O bonding moiety consisting of a hetero-ring nitrogen atoms (N(1)) and an oxygen atom (O(5)) in a carboxylate group. Another H_2MIDC^- ligand using its two oxygen

Table 2. Selected bond lengths (Å) and bond angles (deg) for compound **I***

Bond	d, Å	Bond	d, Å
Sr(1)–O(2)	2.509(1)	Sr(1)–O(5)	2.638(1)
Sr(1)–O(3)	2.711(1)	Sr(1)–O(10)	2.399(2)
Sr(1)–O(4)	2.83(1)	Sr(1)–N(1)	2.672(1)
Sr(1)–O(4)$^{\#1}$	2.55(1)	Sr(1)–O(9)$^{\#2}$	2.639(1)
Angle	ω, deg	Angle	ω, deg
O(2)Sr(1)O(3)	70.7(4)	O(5)Sr(1)O(4)	156.1(3)
O(2)Sr(1)O(4)	85.8(4)	O(5)Sr(1)O(4)$^{\#1}$	99.5(4)
O(2)Sr(1)O(5)	114.9(4)	O(5)Sr(1)O(9)$^{\#2}$	69.4(3)
O(2)Sr(1)N(1)	76.1(4)	O(10)Sr(1)O(4)$^{\#1}$	148.3(4)
O(2)Sr(1)O(10)	133.2(4)	O(10)Sr(1)O(9)$^{\#2}$	79.2(4)
O(2)Sr(1)O(4)$^{\#1}$	74.8(4)	O(10)Sr(1)O(5)	82.6(5)
O(2)Sr(1)O(9)$^{\#2}$	147.0(4)	O(10)Sr(1)O(3)	73.9(4)
O(3)Sr(1)O(4)	47.0(3)	O(10)Sr(1)O(4)	92.0(4)
O(3)Sr(1)O(4)$^{\#1}$	111.3(4)	N(1)Sr(1)O(3)	92.4(4)
O(3)Sr(1)O(5)	148.8(4)	N(1)Sr(1)O(5)	61.7(4)
O(3)Sr(1)O(9)$^{\#2}$	123.9(3)	N(1)Sr(1)O(4)	139.3(3)
O(4)Sr(1)O(4)$^{\#1}$	73.3(4)	N(1)Sr(1)O(10)	75.8(4)
O(4)Sr(1)O(9)$^{\#2}$	86.7(3)	N(1)Sr(1)O(9)$^{\#2}$	127.1(4)
O(4)$^{\#1}$Sr(1)O(9)$^{\#2}$	72.2(4)	N(1)Sr(1)O(4)$^{\#1}$	133.2(4)

Table 3. Geometric parameters of hydrogen bonds for compound **I***

D–H···A	Distance, Å			Angle DHA, deg
	D–H	H···A	D···A	
O(2)–H(2*wA*)···O(1)^{a}	0.82	2.02	2.765	150
O(2)–H(2*wB*)···N(4)^{b}	0.82	2.01	2.767	154
O(2)–H(2*wB*)···O(8)^{b}	0.82	2.48	2.944	117
O(6)–H(6*D*)···O(1)	0.82	1.61	2.434	180
O(7)–H(7*A*)···O(3)	0.82	1.70	2.521	179
O(10)–H(1*wA*)···O(9)^{c}	0.82	2.21	3.002	161
O(10)–H(1*wB*)···O(2)^{d}	0.81	2.40	3.028	135
O(10)–H(1*wB*)···O(4)^{e}	0.81	2.42	2.910	119
N(3)–H(3*A*)···O(8)^{f}	0.86	1.92	2.771	171
N(2)–H(2*A*)···O(5)^{g}	0.86	2.01	2.862	169

* Symmetry codes: $^{a}\,x-1/2, -y+3/2, z+1/2$; $^{b}\,x-1/2, -y+3/2, z-1/2$; $^{c}\,x+1/2, -y+3/2, z+1/2$; $^{d}\,x+1, y, z$; $^{e}\,-x+1, -y+1, -z+1$; $^{f}\,-x+1/2, y-1/2, -z+3/2$; $^{g}\,-x+1/2, y+1/2, -z+1/2$.

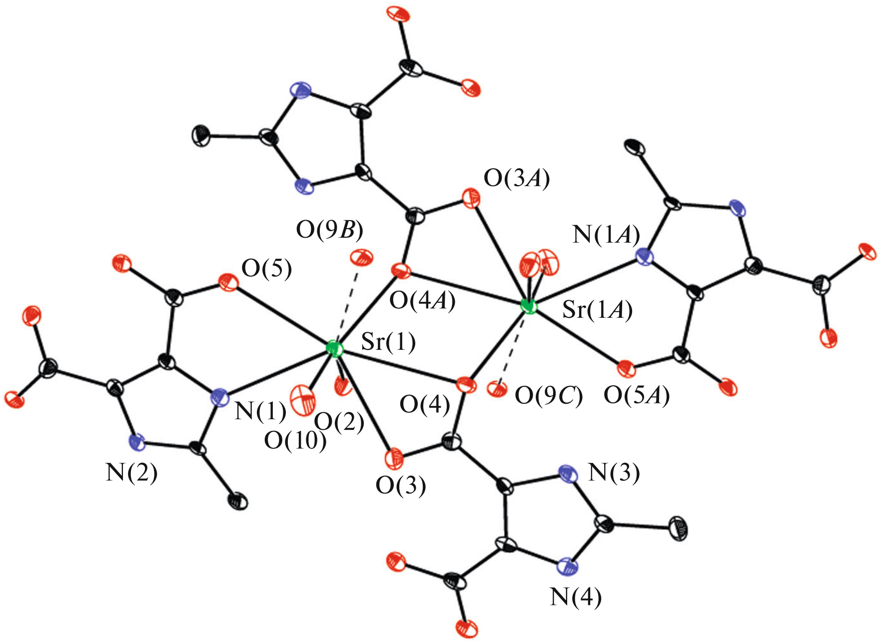
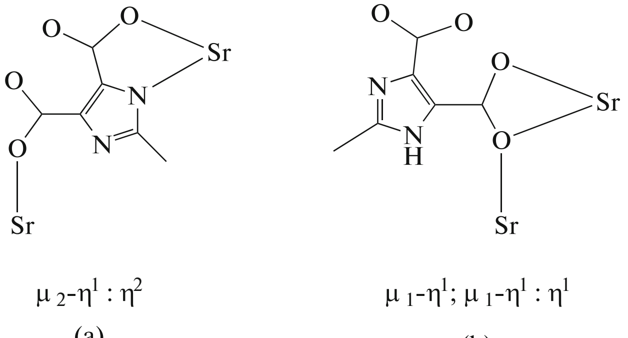


Fig. 1. A fragment of the molecular layer constituting the structure of $[Sr(H_2MIDC)_2(H_2O)_2]$ (hydrogen atoms are omitted for clarity).

atoms (O(3),O(4)) in a carboxylate group and one oxygen atom (O(9*B*)) in the third carboxylate group as well as two oxygen atoms (O(2),O(10)) in water molecules coordinates with the same Sr^{2+} ion. The two Sr^{2+} ion have the same coordinate environment, each Sr^{2+} is eight-coordinate and appears bicapped tetragonal bipyramid geometry. The vertex are occupied by four oxygen atoms nearly equatorial plan (two oxygen atoms (O(4*A*),O(9*B*)) from two carboxylate ligands, two oxygen atoms from water molecules) and two oxgen atoms (O(4),O(5)) from two different ligand in axis. The bicapped positions are occupied by one hetero-ring nitrogen atoms (N(1)) from the H_2MIDC^- ligand and one oxygen atoms (O(3)) from a carboxylate group. The nearly equatorial plan angle is 17.2°, the imidazole ring of the ligand molecules is planar. The plans of the C(11),O(5),O(6) and C(12),O(1),O(9) of carboxylate group make dihedral angles with the plan of the imidazole ring of 4.9° and 5.8°, respectively. The dihedral angle between two carboxylate groups is 9.3°. It means that the whole ligand molecule is almost coplanlar include the methyl C(10). One of an oxygen atom O(4) (or O(4*A*)) in carboxylate group bridges the neighbour metal ion, thus extend the structure into a two-dimensional layer network (Fig. 1).

In this stucture, there are two coordination modes for the H_2MIDC^- ligand as illustrate in Scheme 1. Scheme 1a shows only one carboxylate group involved in coordiantion, two bidentate oxygen atoms coordinate with a Sr^{2+} ion, one of a oxygen coordinate with the adjacent Sr^{2+} ion. The ligand adopts μ_2-η^1 : η^2 bridging modes to coordinate with two metal ions. Scheme 1b shows two carboxylate groups coordinate with two metal ions and N,O moiety coordinate with the same Sr^{2+} ion, the other ligand adopts μ_1-η^1 : η^1 bridging modes.

Although, there exist above two coordination modes in the structure, only the (a) mode bridge the distant Sr^{2+} ion. The shortest Sr(II)–Sr(II) distance is 4.32(2)Å, while the farthest is 9.353(2) Å. The Sr^{2+} ion as nodes form (4,4)-connectivity 2D layer structure, as illustrate in Fig. 2.



μ_2-η^1 : η^2

(a)

μ_1-η^1; μ_1-η^1 : η^1

(b)

Scheme 1.

Moreover, the face-to-face π–π stacking function between the imidazole molecules play an important role in stabilizing the structure. The face centered distance between the imidazole molecules are 3.677 Å, and the vertical distance is 3.328 Å, the dislocation angle is about 25.2°. For abundent hydrogen bond of inter-molecular and intra-molecular, the structure

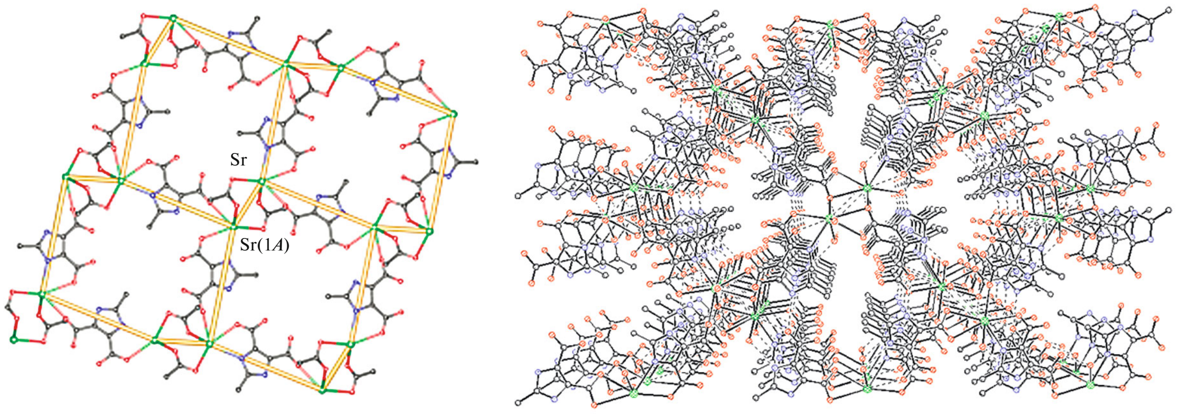


Fig. 2. The 2D topology network for compound **I** with (4,4)-connectivity.

based on these hydrogen bond is also a 2D 4,4-connectivity network.

The phase purity of compound **I** was determined by XRPD. The peak positions of the experimental and simulated XRPD patterns are in good agreement, demonstrating that compound was a pure crystalline phase.

The photoluminescent properties of compound **I** and H_3MIDC ligand were determined in the solid state at room temperature (Fig. 3). The coordination polymer showed blue fluoresence under experimental conditions, and exhibited with emission spectra at 451 nm upon excitation at 341 nm. In the case of ligand, a similar fluoresence with emission spectra at 424 nm upon excitation at 322 nm was observed. Comparing intenisity of the ligand and complex, we observed a significant enhancement of intensity in the complex than in the ligand. This may assigned to the rigidity of the complex after the ligand coordinate with the metal ion, as a result decreases the vibration energy lost. Besides, the red-shift of ligand to complex is slightly, this may because the emission is associated with transition of electrons located predominantly within the organic part of the molecule. Nevertheless, the fluorescent intenisity of complex is obviously not strong, for this may be caused by inter-system crossing which is very efficient in compounds containing heavy atoms [17].

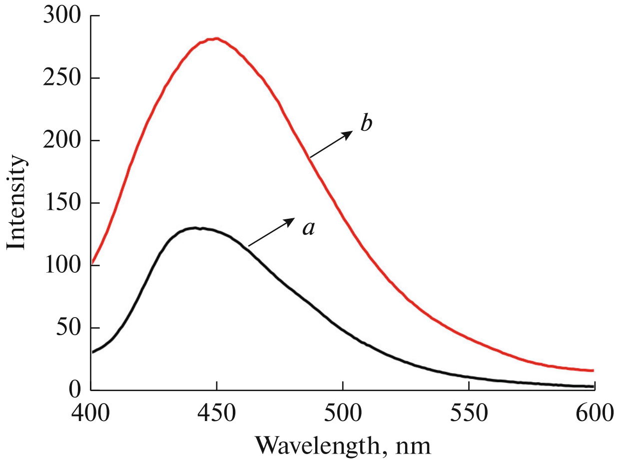


Fig. 3. Fluorescent emmission spectra of the ligand (*a*) and compound **I** (*b*) in solid state at room temperature.

In summary, we have successfully synthesized an interesting Sr(II) coordination polymer through crystal engineering strategies with hydrothermal synthesis technique and characterized it structurally. This work may provide a useful approach for the layer coordination polymer design and construction, which can further help us understand the relationships between structures and properties of $[Sr(H_2MIDC)_2(H_2O)_2]_n$.

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REFERENCES

1. Zhong, R.Q., Zou, R.Q., Du, M., et al., *Cryst. Eng. Commun.*, 2008, vol. 10, no. 9, p. 1175.
2. Zhou, H.C., Long, J.R., Yaghi, O.M., et al., *Chem. Rev.*, 2012, vol. 112, no. 2, p. 673.
3. Hanusa, T.P., *Coord. Chem. Rev.*, 2000, vol. 210, no. 1, p. 329.
4. Gilman, H., Meals, R.N., O'Donnell, G., et al., *J. Am. Chem. Soc.*, 2002, vol. 65, no. 2, p. 268.
5. Starosta, W., Janusz, L., Thathan, P., et al., *Coord. Chem.*, 2006, vol. 59, no. 5, p. 557.
6. Li, H., Feng, H., Xie, Y., et al., *Chemistry*, 2016, vol. 22, no. 42, p. 15019.
7. Yu, X.Y., Zhang, X., Liu, Z.G., et al., *J. Mol. Struct.*, 2017, vol. 1147, p. 747.

8. Li, Y., Lu, X., Jing, H., et al., *Inorg. Chim. Acta*, 2017, vol. 467, p. 117.
9. Dang, F., Wang, X., Han, G., et al., *Monatsh. Chem.*, 2009, vol. 140, no. 6, p. 615.
10. Gao, Y.C., Liu, Q.H., Zhang, F.W., et al., *Polyhedron*, 2011, vol. 30, no. 1, p. 1.
11. Wang, Y.L., Yuan, D.Q., Bi, W.H., et al., *Cryst. Growth Des.*, 2005, vol. 5, no. 5, p. 1849.
12. Gu, Z.G., Li, G.Z., Yin, P.Y., et al., *Inorg Chem. Commun.*, 2011, vol. 14, no. 9, p. 1479.
13. Chen, N., Wang, C.J., Guo, M.W., et al., *Synt. React. Inorg. Met.-Org. Chem.*, 2012, vol. 42, no. 7, p. 981.
14. Cook, T.R., Zheng, Y.R., and Stang, P.J., *Chem. Inform.*, 2013, vol. 113, no. 1, p. 734.
15. Andson, W.K., Bhattacharjee, D., and Houston, D.M., *J. Med. Chem.*, 1989, vol. 32, no. 1, p. 119.
16. Sheldrick, G.M., *SHEIXIL NT, Version 5.1, Program for Solution and Refinement of Crystal Structures*, Göttingen: Univ. of Göttingen, 1997.
17. Cui, P., Chen, Z., Gao, D.L., et al., *Cryst. Growth Des.*, 2010, vol. 10, no. 10, p. 4370.