

含有双甜菜碱衍生物/SCN⁻混合配体的 镉配合物的合成及晶体结构分析

蒋宁懿 李松林*

(天津大学理学院化学系, 天津 300072)

关键词: 1,3-二-(4-羧基吡啶基)丙烷; 双甜菜碱衍生物; 硫氰酸盐; Cd(II)配位聚合物

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Synthesis and Structural Characterization of a New Cadmium(II) Coordination Networks Derived from Mixed Double Betaine Derivate/SCN⁻ Ligands

JIANG Ning-Yi LI Song-Lin*

(Department of Chemistry, School of Science, Tianjin University, Tianjin 300072)

Abstract: A new coordination polymer of Cd(II) was prepared by the reaction of Cd(ClO₄)₂·6H₂O with mixed ligands, namely, neutral double betaine derivative 1,3-bis(pyridinio-4-carboxylato)propane and SCN⁻ anion in aqueous solution. The crystal structure of **1** has been determined by single-crystal X-ray diffraction methods. Crystal data for **1**: orthorhombic, space group *P*2₁2₁2₁, *a*=1.050 9(2), *b*=1.162 8(2), *c*=1.649 5(3) nm, *V*=2.015 7(7) nm³, *Z*=4, *F*(000)=1 064, *D*_c=1.756 g·cm⁻³, the final *R*=0.050 8 and *wR*=0.130 1 for 3 530 observed reflections [*I*>2σ(*I*)]. Crystal structure of **1** indicates that the (μ-1,3-NCS) bridging NCS⁻ ligand connects neighboring cadmium atoms, leading to a single strand helical chain which propagates along crystallographic *a* axis. The metallic nodes of adjacent helical chains are linked by monodentate-monodentate coordination mode of both carboxylate groups in L molecules to generate 2D coordination sheet which parallels to the (001) plane. Adjacent layers are further joined by C—H···O hydrogen bonds; the structure thus expanded into a three-dimensional network. CCDC: 612657.

Key words: 1,3-bis(pyridinio-4-carboxylato)propane; double betaine derivative; thiocyanate; cadmium(II) coordination polymer

Supramolecular metal coordination compounds formed by self-assembly are a frontier field in research because of their potential applications in catalyses, molecular recognition, molecular electronics and photonic materials etc.^[1]. Crystal engineering of metal coordination compounds, especially coordination polymers are usually achieved by using bi- or multidentate ligands to bind the metal centers^[2,3]. Many one-, two- or three-dimensional polymers coordination solids have been obtained by two types ligands, neutral organic 4,

4'-bipyridine, pyrazine, betaines, etc.^[4-6] and anionic e. g. thiocyanate, azide, polyaromatic acids^[1,7-10] etc.

Among the anionic ligands, the pseudohalide NCS⁻ is known to coordinate to metals in both terminal and bridging modes. As bridging ligand, the thiocyanate can link a pair of metal centers in either an end-on (μ-1,1-NCS, μ-1,1-SCN) or end-to-end (μ-1,3-NCS) configuration^[11]. Particularly cadmium-thiocyanate coordination solids are of considerable interest owing to their topological aspects^[8]; potential use as optical

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*通讯联系人. E-mail: slitju@yahoo.com.cn

第一作者: 蒋宁懿, 女, 30 岁, 硕士生; 研究方向: 结构化学。

materials effective in blue light emission^[12] and the second harmonic generation (SHG)^[13].

Among the neutral ligands which display versatile coordination capability, double betaines represent a good choice because of their zwitterionic properties of permanent bipolarity and overall charge neutrality. Double betaine compounds can be expected to widen structural varieties of metal dicarboxylates, such as complexes with metal centers bearing additional anionic ligands, and those with variable metal to dicarboxylate molar ratios^[14].

To explore the combination effects of neutral double betaine ligand 1,3-bis(pyridinio-4-carboxylato)propane (L) and anionic thiocyanate ligand, we synthesize a coordination polymer of Cd(II) containing these ligands, namely $[\text{Cd}(\text{H}_2\text{O})\text{L}(\text{SCN})_2]_n$ (**1**). Reported herein are the details of the synthesis, crystal structure and other relevant physicochemical studies of **1**.

1 Experimental

All chemicals and solvents obtained from commercial sources were of A.R. grade and used without further purification. Elemental analyses data of C, H, N were determined by a Vanio-EL elemental analyzer. The IR spectra were recorded from KBr pallet in the range of 4 000 ~400 cm^{-1} on a Bio-Rad Exalibur FTS3000 spectrometer.

1.1 Synthesis of $[\text{Cd}(\text{H}_2\text{O})\text{L}(\text{SCN})_2]_n$ (**1**)

The flexible ligand 1,3-bis(pyridinio-4-carboxylato)propane tetrahydrate ($\text{L} \cdot 4\text{H}_2\text{O}$) was synthesized similar to the method described previously^[15]. However, we adopted 1,2-epoxypropane to remove the bromide and chloride ions in the product other than silver(I) oxide. $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was prepared by the reaction of freshly precipitated CdCO_3 with HClO_4 (70% aqueous solution) and re-crystallized in water. The preparation of **1** was achieved via the following route. Dissolve $\text{L} \cdot 4\text{H}_2\text{O}$ (360 mg, 1 mmol) and $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$

(419 mg, 1 mmol) in distilled water (*c.a.* 8 cm^3), and the solution obtained was stirred at *c.a.* 60 °C for about 15 min. The solution was filtrated to a test tube and carefully covered with NaSCN aqueous solution (162 mg, 2 mmol in *c.a.* 5 cm^3 distilled water). The pale yellow crystals of **1** available for X-ray structure analysis were obtained in (440 mg) 83% yield after standing the filtration at ambient temperature for 4 hours. Anal. Calcd. (%) for $\text{C}_{17}\text{H}_{16}\text{N}_4\text{O}_5\text{S}_2\text{Cd}$: C, 38.32; H, 3.03; N, 10.51. Found (%): C, 37.72; H, 3.17; N, 10.78.

1.2 Crystal structure determination

The intensities for **1** (pale yellow prism, 0.25 mm \times 0.22 mm \times 0.22 mm) were collected at 293(2) K in ω -scan mode on a Siemens P4 four-circle diffractometer using Mo $K\alpha$ radiation ($\lambda=0.071\ 073$ nm) operating at 50 kV, 25 mA^[16]. The structure was solved by the direct method, and the non-hydrogen atoms were refined anisotropically by full-matrix least squares techniques on F^2 using SHELXTL program package^[17]. For **1**, $w=1/[\sigma^2 F_o^2 + (0.079\ 3P)^2 + 0.414\ 4P]$ where $P=(F_o^2 + 2F_c^2)/3$; all H atoms were positioned geometrically and refined as riding (C-H=0.093~0.097 nm). The U_{iso} (H) values other than hydrogen atoms on water molecules were set equal to 1.2 U_{eq} (carrier atoms). The H atoms of water molecules were located on difference Fourier map and allowed to ride on their respective parent oxygen atoms with $U_{\text{iso}}(\text{H})=1.5\ U_{\text{iso}}(\text{O})$. At the end of the least-squares refinement, the racemic twinning model was introduced, giving a better convergence with the Flack^[18] absolute structure parameter x of 0.39(4).

Crystallographic data; the selected bond lengths and bond angles; distance and angles involving hydrogen bonding for **1** are given in Tables 1 to 3, respectively.

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Table 1 Crystal data and structure refinement parameters for **1**

Empirical formula	$\text{C}_{17}\text{H}_{16}\text{CdN}_4\text{O}_5\text{S}_2$	Method of collecting reflections	ω scan
Formula weight	532.86	Transmission coefficient	0.732 5~0.758 8
Temperature / K	293(2)	θ range for data collection / (°)	2.30~25.53
Wavelength / nm	0.071 073	Measured reflections	6 657

Continued Table 1

Crystal system	Orthorhombic	Independent reflections	3 648
Space group	$P2_12_12_1$	Observed reflections	3 530 ($I > 2\sigma(I)$)
a / nm	1.050 9(2)	R_{int}	0.059 8
b / nm	1.162 8(2)	Data / restraint / parameters	3 648 / 0 / 264
c / nm	1.649 5(3)	GOOF	1.043
Volume / nm^3	2.015 7(7)	R, wR ($I > 2\sigma(I)$)	0.050 8, 0.130 1
Z	4	(All data)	0.054 1, 0.133 7
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.756	$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}} / (\text{e} \cdot \text{nm}^{-3})$	946, -802
μ / mm^{-1}	1.328	$(\Delta/\sigma)_{\text{max}}$	0.000
$F(000)$	1 064	Flack parameter	0.39(4)
Crystal size / mm	$0.25 \times 0.22 \times 0.22$	Extinction coefficient	0.018(2)

$$^a R_1 = \sum (|F_o| - |F_c|) / \sum |F_o|, ^b wR_2 = [\sum w[(F_o^2 - F_c^2)] / \sum w[(F_o^2)]]^{0.5}, w = 1 / [\sigma^2 F_o^2 + (0.079 3 P)^2 + 0.414 4 P], P = (F_o^2 + 2 F_c^2) / 3.$$

Table 2 Selected bond lengths (nm) and bond angles ($^\circ$) for **1**

Cd1-O1	0.223 8(4)	Cd1-N3#2	0.237 8(5)	C15-O4	0.124 5(7)
Cd1-N4	0.229 9(5)	Cd1-S1	0.273 5(2)	C15-O3	0.124 7(7)
Cd1-O1W	0.230 7(4)	O1-C1	0.126 3(8)		
Cd1-O3#1	0.231 3(4)	O2-C1	0.122 8(8)		
O1-Cd1-N4	93.7(2)	O1W-Cd1-N3#2	91.43(17)	N4-C17-S2	179.1(7)
O1-Cd1-O1W	173.14(17)	O3#1-Cd1-N3#2	86.51(18)	C17-N4-Cd1	159.4(6)
N4-Cd1-O1W	80.45(18)	O1-Cd1-S1	94.74(14)	C1-O1-Cd1	120.8(4)
O1-Cd1-O3#1	100.46(18)	N4-Cd1-S1	104.57(17)	C15-O3-Cd1#3	145.4(5)
N4-Cd1-O3#1	165.2(2)	O1W-Cd1-S1	90.17(11)	O2-C1-O1	127.0(6)
O1W-Cd1-O3#1	85.16(17)	O3#1-Cd1-S1	78.87(14)	O4-C15-O3	128.5(6)
O1-Cd1-N3#2	85.05(18)	N3#2-Cd1-S1	165.11(14)		
N4-Cd1-N3#2	90.3(2)	N3-C16-S1	177.6(6)		

Symmetry codes: #1: $-1+x, 1+y, z$; #2: $1/2+x, 3/2-y, 1-z$; #3: $1+x, -1+y, z$.

Table 3 Distances and angles involving hydrogen bonding of **1**

D-H...A	D-H / nm	H...A / nm	D...A / nm	D-H...A / ($^\circ$)
O1W-H1WA...O1#1	0.097	0.178	0.274 9(6)	179.9
O1W-H1WB...O4#2	0.097	0.166	0.263 1(6)	179.8
C5-H5...O1W#3	0.093	0.247	0.330 0(7)	148.5

Symmetry codes: #1: $-1/2+x, 3/2-y, 1-z$; #2: $-3/2+x, 1/2-y, 1-z$; #3: $3/2-x, 1-y, 1/2+z$.

2 Result and discussion

2.1 IR spectra

The position of the IR-bands corresponding to the stretching frequency of the thiocyanate group and carboxylate group can be used for characterization of the mode of coordination to the metal. The strong $\nu(\text{CN})$ stretching vibration of a bridging thiocyanate is usually found to be around $2\,100\text{ cm}^{-1}$ [3,19,20], whereas the terminally nitrogen-bonded NCS^- group occurs at around

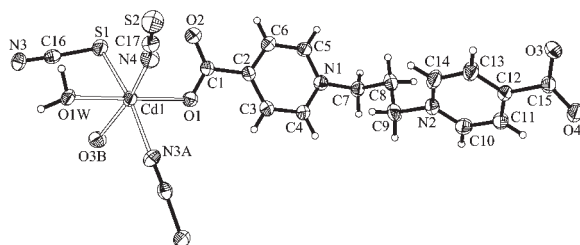
$2\,050\text{ cm}^{-1}$ [20,21]. In IR spectra two well resolved $\nu(\text{CN})$ bands (at $2\,073, 2\,095\text{ cm}^{-1}$) in **1** are observed indicating the existence of different force constants of the thiocyanato groups in the crystal lattice. The band corresponding to the $\nu(\text{CS})$ stretching frequency appears at 751 cm^{-1} ; bands belonging to the deformation frequency $\delta(\text{NCS})$ are found as doublets at $469, 429\text{ cm}^{-1}$.

The stretching bands of carboxylate ions are also evident in the FTIR spectrum. Both antisymmetric ($1\,646, 1\,615\text{ cm}^{-1}$) and symmetric ($1\,375, 1\,347\text{ cm}^{-1}$)

stretching bands are split into two peaks, which indicate the difference of two carboxylate groups. The respective $\Delta[\nu_{\text{asym}}(\text{CO}_2) - \nu_{\text{sym}}(\text{CO}_2)]$ values clearly indicate the presence of monodentate coordination mode (271, 268 cm^{-1}) of carboxylate groups^[20], as is shown by the crystal structure.

2.2 Crystal structure of $[\text{Cd}(\text{H}_2\text{O})\text{L}(\text{SCN})_2]_n$ (**1**)

Compound **1** crystallizes in space group $P2_12_12_1$. As it can be seen from Fig.1, each cadmium atom is six-coordinated in distorted octahedron geometry, surrounded by two nitrogen atoms from one bridging thiocyanate ligand (μ -1,3-NCS) and one terminal thiocyanate ligand; one sulfur atom from one bridging thiocyanate ligand (μ -1,3-NCS); three oxygen atoms from two symmetrically related bridging L ligands and one aqua ligand.



The thermal ellipsoids are at 30% probability level

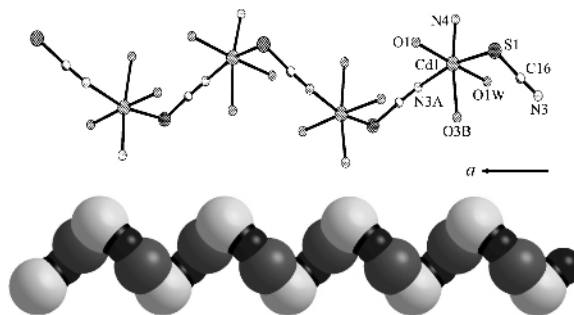
Symmetry code: A: $1/2+x, 3/2-y, 1-z$; B: $-1+x, 1+y, z$

Fig.1 Coordination environment of compound **1**

The Cd1-N4 bond distance is 0.229 9 (5) nm, in the middle of the published ranges of analogous distances for terminal CdNCS groups^[8,22-25]. As to the end-to-end bridging SCN^- groups, The Cd-NCS bond distance (Cd1-N3A) is 0.237 8 (5) nm, and the Cd-SCN (Cd1-S1) bond distance is 0.273 5(2) nm, both typical for the μ -NCS-S,N bridging ligands coordinated with cadmium(II)^[1,3,26]. The bridging Cd-N bond length is slight longer than that of terminal N-coordinated SCN^- groups and the difference is 0.079 nm. The probable reason is the terminal thiocyanate ion is more strongly bound compared to the bridging thiocyanate in coordination polymer^[7]. The M-N-C angles vary from 154.3° [Cd1-N3#1-C16#1 (#1: $1/2+x, 3/2-y, 1-z$)] to 159.4° (Cd1-N4-C17), also resulting from the different coordination modes of SCN^- ligands. Besides, both bridging and terminal pseudohalide SCN^- do not show ob-

vious deviation from linearity [S1-C16-N3 $177.6(6)^\circ$; S2-C17-N4 $179.1(7)^\circ$], and distances about SCN (C-N, C-S) differ only by 0.001 3~0.003 0 nm. The Cd-O bond lengths are in the range of 0.223 8(4)~0.231 3(4) nm, comparable with those found in other cadmium(II) octahedral complexes^[6,27,28]. The range of cisoid angles [$80.5(2)^\circ \sim 104.6(2)^\circ$] and that of transoid angles [$165.1(1)^\circ \sim 173.1(2)^\circ$], reflect the degrees of distortion from the ideal octahedral geometry.

The (μ -1, 3-NCS) bridging NCS^- ligand connect neighboring cadmium atoms, leading to a single strand helical chain which propagates along crystallographic a axis. The Cd...Cd distance bridged by a NCS^- anion is about 0.567 7 nm, and the pitch of the helix is about 1.050 9 nm, shown as Fig.2.



Symmetry code: A: $1/2+x, 3/2-y, 1-z$; B: $-1+x, 1+y, z$

Fig.2 View of the helical chain formed by cadmium(II) and SCN^- anions (top) and space-filling representation of the helix with **1** (below)

Furthermore, the metallic nodes of adjacent helical chains are linked by monodentate-monodentate coordination mode of both carboxylate groups in L ligands to generate two mutually perpendicular 1D wavelike chains extending along $[110]$ and $[1\bar{1}0]$ directions. It is noteworthy that the C-O lengths for one carboxylate group are very similar, within the experimental errors, [C15-O4: 0.124 5 (7) nm; C15-O3: 0.124 7 (7) nm], while for the other one, C-O lengths are not equivalent [C1-O1: 0.126 3(8) nm; C1-O2: 0.122 8(8) nm] with a difference of 0.003 8 nm. The probable reason is that the thiocyanate group is a π conjugated system so that it can exert some influence on the carboxylate group [O(3)C(15)O(4)] located in its trans position, resulting in the equalization of C-O lengths. The difference of two carboxylate groups is also evidenced by the pres-

ence of peak splitting in the infrared spectra.

Through the versatile bridging nature of thiocyanate groups and carboxylate groups, the 1D chains are self-assembled into 2D coordination sheet parallel to the (001) plane (Fig.3).

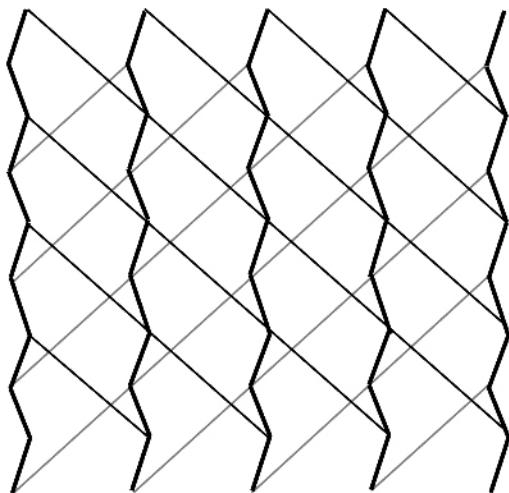


Fig.3 Schematic representation of the 2D coordination layer

Besides, the hydrogen bond between aqua ligand and carboxylate O atoms further stabilized the structure: O1W...O1#2 0.274 9 (6) nm, O1W-H1WA-O1#2 179.9°; O1W...O4#3 0.263 1 (6) nm, O1W-H1WB-O4#3 179.8° [#2: $-1/2+x, 3/2-y, 1-z$; #3: $-3/2+x, 1/2-y, 1-z$]. Adjacent layers are further joined by C-H...O hydrogen bonds [H...O 0.247 nm, C...O 0.330 0(7) nm; C-H...O 148.5°; thus expand the structure into a three-dimensional hydrogen bonded network.

3 Conclusion

A new coordination polymer of Cd(II) has been constructed by adopting a double betaine derivative and the pseudohalide SCN⁻ anion. The results indicate that with the zwitterionic properties of betaine derivative, the metal centers can accommodate additional anionic ligands, and double betaines represent a good choice to construct networks with mixed ligands.

References:

[1] Chand B, Ray U, Mostafa G. et al. *Polyhedron*, **2004**,**23**: 1669~1676

[2] Ye B H, Tong M L, Chen X M. *Coord. Chem. Rev.*, **2005**,**249**: 545~565
 [3] Banerjee S, Drew M G B, Ghosh A. *Polyhedron*, **2003**,**22**: 2933~2941
 [4] (a)Tong M L, Chen X M, Yu X L, et al. *J. Chem. Soc., Dalton Trans.*, **1998**:5~6
 (b)Lightfoot P, Snedden A. *J. Chem. Soc., Dalton Trans.*, **1999**: 3549~3551
 [5] (a)Tong M L, Lee H K, Chen X M, et al. *J. Chem. Soc., Dalton Trans.*, **1999**:3657~3659
 (b)Wagner B D, McManus G J, Moulton B, et al. *Chem. Commun.*, **2002**:2176~2177
 [6] (a)Li S L, Mak T C W. *J. Chem. Soc. Dalton Trans.*, **1995**: 1519~1524
 (b)Wu A Q, Li Y, Zheng F K. *Cryst. Growth Des.*, **2006**,**6**: 444~450
 [7] Sailaja S, Rajender R K, Rajasekharan M V, et al. *Inorg. Chem.*, **2003**,**42**:180~186
 [8] Bose D, Banerjee J, Rahaman S H, et al. *Polyhedron*, **2004**, **23**:2045~2053
 [9] Livage C, Egger C, Nogues M, et al. *J. Mater. Chem.*, **1998**, **8**:2743~2747
 [10]Evans O R, Lin W. *Inorg. Chem.*, **2000**,**39**:2189~2198
 [11]Goher M A S, Yang Q C, Mak T C W. *Polyhedron*, **2000**,**19**: 615~621
 [12]Zhu H, Ströbele M, Yu Z, et al. *Inorg. Chem. Commun.*, **2001**,**4**:577~581
 [13]da Silva P B, Frem R C G, Netto A V G, et al. *Inorg. Chem. Commun.*, **2006**,**9**:235~238
 [14]Zhang L P, Song H B, Wang Q M, et al. *Polyhedron*, **2003**, **22**:811~818
 [15]Mao J G, Wu H T, Mak T C W, et al. *Chinese J. Struct. Chem.*, **1998**,**17**:353~360
 [16]Siemens. XSCANS. Version 2.1, Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, **1994**.
 [17]Sheldrick G M. *SHELXTL Version 5*, Siemens Industrial Automation Inc. Madison, WI, **1995**.
 [18]Flack H D. *Acta Cryst.*, **1983**,**A39**:876~881
 [19]Luo J H, Hong M C, Wang R H, et al. *Eur. J. Inorg. Chem.*, **2003**:1778~1784
 [20]Nakamoto K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed. New York: John Wiley, **1986**.231~286
 [21]Suen M C, Keng T C, Wang J C. *Polyhedron*, **2002**,**21**:2705~2710
 [22]Reger D L, Wright T D, Smith M D, et al. *Polyhedron*, **2002**, **21**:1795~1807

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- [23] Li S L, Zhang Z Z, Mak T C W. *Inorg. Chim. Acta*, **1998**, **268**:177~187
- [24] Baggio R, Frigerio A, Halac E B, et al. *J. Chem. Soc., Dalton Trans.*, **1992**:549~554
- [25] Kuang S M, Zhang Z Z, Wu B M, et al. *J. Organomet. Chem.*, **1997**, **540**:55~60
- [26] Bose D, Rahaman S H, Ghosh R, et al. *Polyhedron*, **2006**, **25**:645~653
- [27] Li X J, Cao R, Bi W H, et al. *Polyhedron*, **2005**, **24**:2955~2962
- [28] Choi K Y, Jeon Y M, Lee K C. *J. Chem. Crystallogr.*, **2004**, **34**:591~596