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Journal of Molecular Structure 754 (2005) 71–76

Journal of MOLECULAR STRUCTURE

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Synthesis and crystal structures of two new Cd(II) complexes with 3-(2-pyridy)pyrazole-based ligand: influence of anions

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Received 27 June 2005; revised 3 July 2005; accepted 3 July 2005
Available online 18 August 2005

Abstract

Two new Cd(II) complexes with a 3-(2-pyridyl)pyrazole-based ligand, [Cd(**L**)$_2$(SCN)$_2$] (**1**) and {[Cd(**L**)$_2$N$_3$](ClO$_4$)}$_n$ (**2**) (**L**=3-(2-pyridyl)pyrazol-1-ylmethylbenzene) were synthesized and structurally characterized by elemental analyses, IR and single crystal X-ray diffraction analysis. Complex **1** crystallizes in the monoclinic system, space group $C2/c$, with $a=14.833(3)$, $b=13.790(3)$, $c=15.970(3)$ Å, $\beta=110.89(3)°$ and $Z=4$, while **2** crystallizes in the monoclinic system, space group $P2_1/c$, with $a=13.622(4)$, $b=23.286(7)$, $c=10.547(3)$ Å, $\beta=111.084(6)°$ and $Z=4$. In the two complexes, the Cd(II) centers are coordinated by six nitrogen atoms, in which four from two distinct **L** ligands and two from thiocyanato (**1**) or azido (**2**) anions. Complex **1** has a mononuclear structure, whereas **2** has a 1D chain structure bridged by azido anions. In **2**, the azido adopts a μ-1,3-*trans* coordination mode, which is not common in the azide Cd(II) complexes. In addition, in the structure of **2**, the 1D chains were further assembled into a quasi-3D supramolecular network by the C–H···O hydrogen-bonding interactions. The structural difference of the two complexes is attributable to the different anions, which have different coordination natures.

Keywords: Anion effects; Cd(II) complexes; Crystal structures; 3-(2-pyridyl)pyrazole-based ligand

1. Introduction

The synthesis of discrete complexes or coordination polymers is a rapidly developing field in current coordination and supramolecular chemistry [1,2]. One of the ultimate aim of coordination chemistry is to control the structure of the target product with tailored properties and structures. Therefore, the selection of proper ligands as 'building blocks' is a key factor in manipulating the structures of complexes. For instance, some typical chelate ligands, such as 2,2-bipyridine (bpy) and its derivatives have been well used in the synthesis of functional complexes [3], and many coordination architectures with a chelating ligand 3-(2-pyridyl)pyrazole whose structure is very similar to 2,2-bipyridine and its substituted derivatives were also reported [4]. Some complexes with 3-(2-pyridyl)pyrazole-based ligands have been found to have potential biological and catalytic activities [5].

In this paper, we synthesized a 3-(2-pyridyl)pyrazole-based ligand **L** (**L**=3-(2-pyridyl)pyrazol-1-ylmethylbenzene) (see Chart 1), in which the benzene ring acts as a directing group for π–π stacking. We report herein the syntheses and structures of two Cd(II) complexes with this ligand, [Cd(**L**)$_2$(SCN)$_2$] (**1**) and {[Cd(**L**)$_2$N$_3$](ClO$_4$)}$_n$ (**2**), and the anion effects have also been discussed.

2. Experimental

2.1. Materials and general methods

3-(2-Pyridyl)pyrazole was synthesized with reported procedures [6]. All the other reagents for synthesis were commercially available and employed as received or

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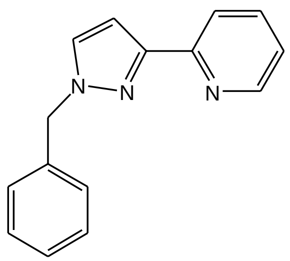
0022-2860/$ - see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.molstruc.2005.07.001



L

Chart 1.

purified by standard methods prior to use. Elemental analyses were performed on a Perkin-Elemer 240C analyzer and IR spectra on a Tensor 27 OPUS (Bruker) FT-IR spectrometer with KBr pellets. ^{1}H NMR spectra were recorded on a Bruker AC-P500 spectrometer (300 MHz) at 25 °C with tetramethylsilane as the internal reference.

2.2. Synthesis of ligand

3-(2-Pyridyl)pyrazol-1-ylmethylbenzene (**L**) A mixture of benzyl chloride (1.67 g, 13.2 mmol), 3-(2-pyridyl)-pyrazole (1.74 g, 12 mmol), benzene (52 mL), ^{n}Bu$_4$NOH (0.5 cm^3, 40% aqueous solution) and NaOH aqueous solution (10 cm^3, 10 M) was refluxed (ca. 80 °C) for ca. 48 h with vigorous stirring. After cooling to room temperature, the organic phase was separated, washed three times with H_2O, and extracted with $CHCl_3$. The organic layer was collected and dried over anhydrous $MgSO_4$. 3-(2-Pyridyl)pyrazol-1-ylmethylbenzene (**L**) was obtained as yellow solid after $CHCl_3$ was removed with a rotary evaporator and it was further purified by recrystallization from $CHCl_3$/hexane (Yield: 60%). M.p.: 93–95 °C. IR (cm^{-1}): 3050w, 2935w, 1591m, 1488m, 1454m, 1399m, 1368w, 1349w, 1298w, 1285w, 1226s, 1202w, 1145m, 1111w, 1050m, 1040m, 991w, 914w, 895w, 848w, 796w, 761vs, 726s, 692w, 621w, 579w. ^{1}H NMR ($CDCl_3$): δ 5.41 (s, 2H), 6.95 (d, 1H), 7.18–7.41 (m, 7H), 7.72 (t, 1H), 7.97 (d, 1H), 8.63 (d, 1H). Anal. Found: C, 76.11, H, 5.09, N, 17.50. Calcd for $C_{15}H_{13}N_3$: C, 76.60; H, 5.53; N, 17.87.

2.3. Preparation of complexes *1* and *2*

[Cd(**L**)$_2$(SCN)$_2$] (**1**) The reaction of **L** (47 mg, 0.2 mmol) with $Cd(ClO_4)_2\cdot 6H_2O$ (42 mg, 0.1 mmol) and NH_4SCN (15 mg, 0.2 mmol) in ethanol (10 mL) and acetonitrile (2 mL) for a few minutes afforded a yellow solid. Then, to this mixture system 10 mL acetonitrile was added and stirred for about 30 min until the solid was dissolved. The solution was filtered, and the filtrate was kept at room temperature. After several days single crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent. Yield: 42%. Anal. Found: C, 54.63; H, 3.35; N, 15.71. Calcd for $C_{32}H_{26}CdN_8S_2$: C, 54.97; H, 3.75; N, 16.03. IR (cm^{-1}): 3124w, 2359w, 2076s, 1605s, 1570m, 1499m, 1436s, 1371m, 1339s, 1231m, 1159w, 1096s, 1030w, 960w, 774s, 730s, 706m, 691m, 624m, 462w, 409w.

{[Cd(**L**)$_2$N$_3$](ClO$_4$)}$_n$ (**2**) Complex **2** was obtained as single crystals by the similar method to that for complex **1** except for using NaN_3 (7 mg, 0.1 mmol) instead of NH_4SCN. Yield: 47%. Anal. Found: C, 49.32; H, 3.44; N, 17.07. Calcd for $C_{30}H_{26}CdClN_9O_4$: C, 49.74; H, 3.62; N, 17.40. IR (cm^{-1}): 3138w, 2359m, 2040s, 1607m, 1570s, 1506w, 1438m, 1372w, 1245w, 1089s, 1028w, 777m, 723m, 705w, 692w, 623m.

Caution: Metal perchlorate and azide compounds are potentially explosive. Only a small amount of material should be prepared and handled with caution. On the other hand, cadmium compounds and their wastes are extremely toxic and must be handled carefully.

2.4. X-ray crystallographic studies

Single-crystal X-ray diffraction measurements for complexes **1** and **2** were carried out on a Bruker Smart 1000 CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection at 293(2) K. The determinations of unit cell parameters and data collections were performed with Mo–Kα radiation ($\lambda = 0.71073$ Å) and unit cell dimensions were

Table 1
Crystal data and structure refinement summary for complexes **1**–**2**

	1	**2**
Empirical formula	$C_{32}H_{26}CdN_8S_2$	$C_{30}H_{26}CdClN_9O_4$
Formula weight	699.13	724.45
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	*P*2(1)/*c*
Unit cell dimensions (Å, °)		
a	14.833(3)	13.622(4)
B	13.790(3)	23.286(7)
c	15.970(3)	10.547(3)
β	110.89(3)	111.084(6)
Volume (Å^3)	3052(1)	3121(2)
Z	4	4
D_{calcd} (g/cm^3)	1.522	1.542
μ (mm^{-1})	0.889	0.836
F (000)	1416	1464
Range of *h*, *k*, *l*	0/19, 0/17, −20/19	−17/16, −23/29, −13/11
Reflections collected/unique/observed	3419/3419/2222	18030/6429/3637
Max. & min. transmission	0.8708 and 0.8422	0.9063 and 0.8506
Data/restraints/parameters	3419/0/190	6429/0/407
Goodness-of-fit on F^2	0.952	1.061
R^a & $R_w{}^b$	0.0584 & 0.1469	0.0664 & 0.1178
Largest diff. Peak & hole (e/Å^3)	1.190 & −0.749	0.718 & −0.736

[a] $R = \Sigma||F_0| - |F_C||/\Sigma|F_0|$.

[b] $wR = [\Sigma w(F_0^2 - F_C^2)^2/\Sigma w(F_0^2)^2]^{1/2}$.

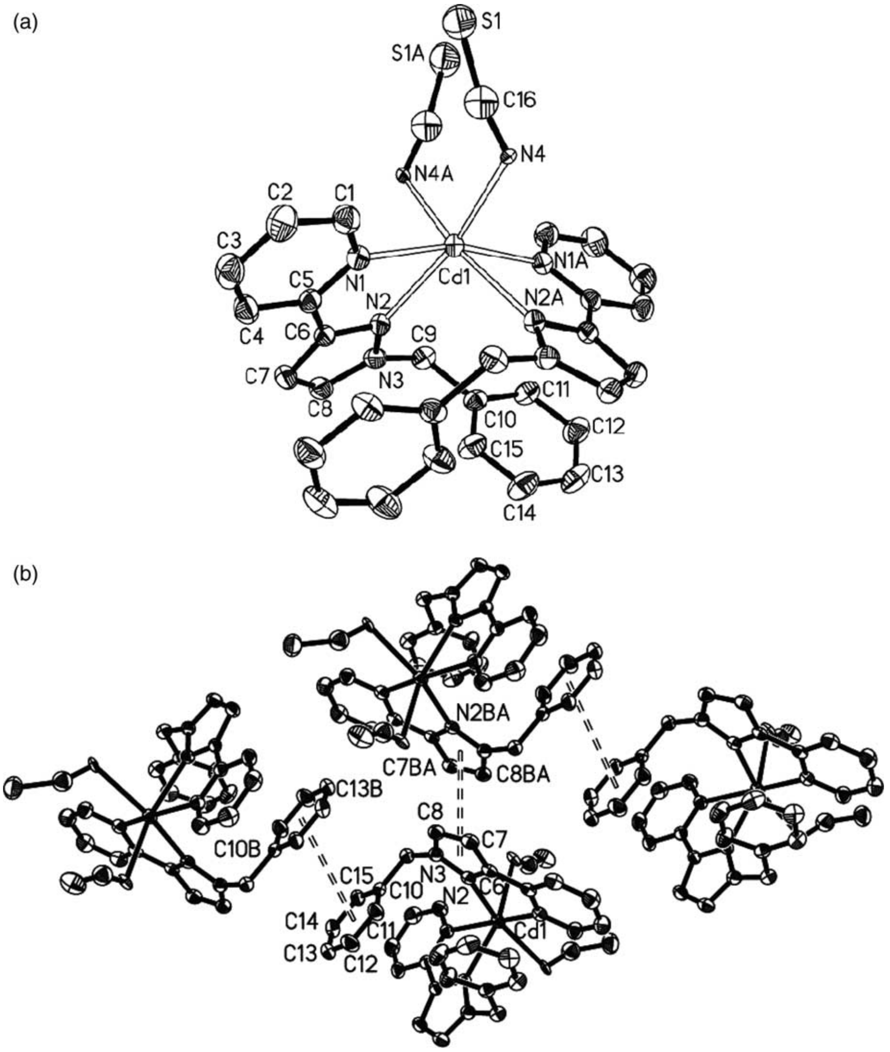


Fig. 1. (a) View of the molecular structure of **1** with 20% displacement ellipsoids probability (thiocyanate N atom have small atomic displacement parameters, but the disordered mode is not successful for it or thiocyanate group) and (b) π–π stacking diagram of **1** (symmetry code A: $-x$, y, $-z-1/2$; B: $-x$, $-y$, $-1-z$; BA: $-x-1/2$, $1/2-y$, $-1-z$).

obtained with least-squares refinements. The program SAINT [7] was used for integration of the diffraction profiles. All structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL [8]. All non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. The hydrogen atoms were added theoretically, riding on the concerned atoms and refined with fixed thermal factors. Crystallographic data and experimental details for structural analyses are summarized in Table 1. CCDC-271942 and 271943 contain the supplementary crystallographic data of complexes **1** and **2**. These data can be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk.

3. Results and discussion

3.1. Synthesis and general characterizations of complexes 1 and 2

Complex **1** was prepared by the reaction of $Cd(ClO)_4\cdot 6H_2O$, 3-(2-pyridyl)pyrazol-1-ylmethylbenzene (**L**) and NH_4SCN in 1:2:2 molar ratio in acetonitrile/ethanol system, while **2** was prepared by following an analogous procedure to that of **1** except for using NaN_3 instead of NH_4SCN and in 1:2:1 molar ratio. The IR spectra of the two complexes show absorption bands resulting from the skeletal vibrations of the aromatic rings in 1600–1400 cm^{-1} region. In complex **1**, the IR spectrum exhibits a strong and sharp band at 2076 cm^{-1}, indicating the presence of an N-bound, terminal thiocyanato ligand. The IR spectrum of **2** shows a very strong band at 2040 cm^{-1} due to $\nu_{as}(N_3)$, and this band is very similar to some complexes containing μ-1,3 bridging

Table 2
Selected bond lengths [Å] and angles [°] for **1**

Cd(1)–N(1)	2.367(4)	C(16)–N(4)	1.174(9)
Cd(1)–N(2)	2.418(4)	C(16)–S(1)	1.597(8)
Cd(1)–N(4)	2.567(4)		
N(1A)–Cd(1)–N(1)	165.2(2)	N(2)–Cd(1)–N(4)	160.2(1)
N(1)–Cd(1)–N(2)	69.4(1)	N(1)–Cd(1)–N(4A)	98.4(1)
N(1)–Cd(1)–N(2A)	100.6(1)	N(2)–Cd(1)–N(4A)	82.7(1)
N(2)–Cd(1)–N(2A)	99.0(2)	N(4)–Cd(1)–N(4A)	102.3(2)
N(1)–Cd(1)–N(4)	90.9(1)		

Symmetry code: A $-x$, y, $-z-1/2$.

azido groups [9]. In addition, the IR spectra of **2** also exhibit the characteristic bands of perchlorate anions at 1089 cm^{-1}.

3.2. Description of the crystal structures of complexes *1* and *2*

[Cd(**L**)$_2$(SCN)$_2$] **1** The crystal structure of complex **1** consists of a neutral [Cd(**L**)$_2$(SCN)$_2$] molecule. The view of the mononuclear entity in **1** with atomic labeling is given in Fig. 1(a) and the selected bond lengths and angles are listed in Table 2. Each Cd(II) center is six-coordinated to four N donors from two distinct **L** ligands and two N donors thiocyanato anions. The coordination geometry around the Cd(II) center could be described as a distorted octahedron. All the Cd–N bond lengths [from 2.367(4) to 2.567(4) Å] and the bond angles around each Cd(II) center [from 69.38(14) to 165.2(2)°] are in the normal range expected for related coordination complexes (see Table 2) [10]. In **1**, each **L** adopts typical *N*,*N*-bidentate chelating coordination mode to form a five-membered Cd–N–C–C–N chelating ring (Cd1–N1–C5–C6–N2). The thiocyanato anions adopt N-terminal mode to coordinate to the Cd(II) center. The Cd–N–C bond angle (C16–N4–Cd1) is significantly bent at 111.1(4)° and the bond angle of N4–C16–S1 is 159.9(7)°. The Cd1–N4 bond length [2.567(4) Å] is a little longer than the other Cd–N bond lengths [i.e. Cd1–N1 = 2.367(4) Å, Cd1–N2 = 2.418(4) Å], which are still on the normal ranges of distances for analogous terminal Cd–NCS complexes [11]. In addition, the bond lengths of C16–N4 [1.174(9) Å] and C16–S1 [1.597(8) Å] in the thiocyanate anions show the normal structure of the thiocyanato in complex **1** [12].

It is should be noted that, in the crystal structure of **1**, there are weak intermolecular π–π stacking interactions (Fig. 1b) [13]. The dihedral angle between two benzene rings of adjacent molecules is 0.03°, the centroid–centroid separation is 4.0985 Å and the perpendicular distance is 3.805 Å. The related values for two pyrazole rings are 0°, 3.925 and 3.360 Å. Such two types of π–π stacking interactions expend this mononuclear molecule to a 2D supramolecular sheet.

{[Cd(**L**)$_2$N$_3$](ClO$_4$)}$_n$ **2** The crystal structure of complex **2** consists of 1D {[Cd(**L**)$_2$N$_3$]$^+$}$_n$ cation chains and free ClO$_4^-$ anions. Fig. 2(a) shows the coordination environment of Cd(II) center. The selected bond lengths and angles are listed in Table 3. Similar to the complex **1**, the coordination

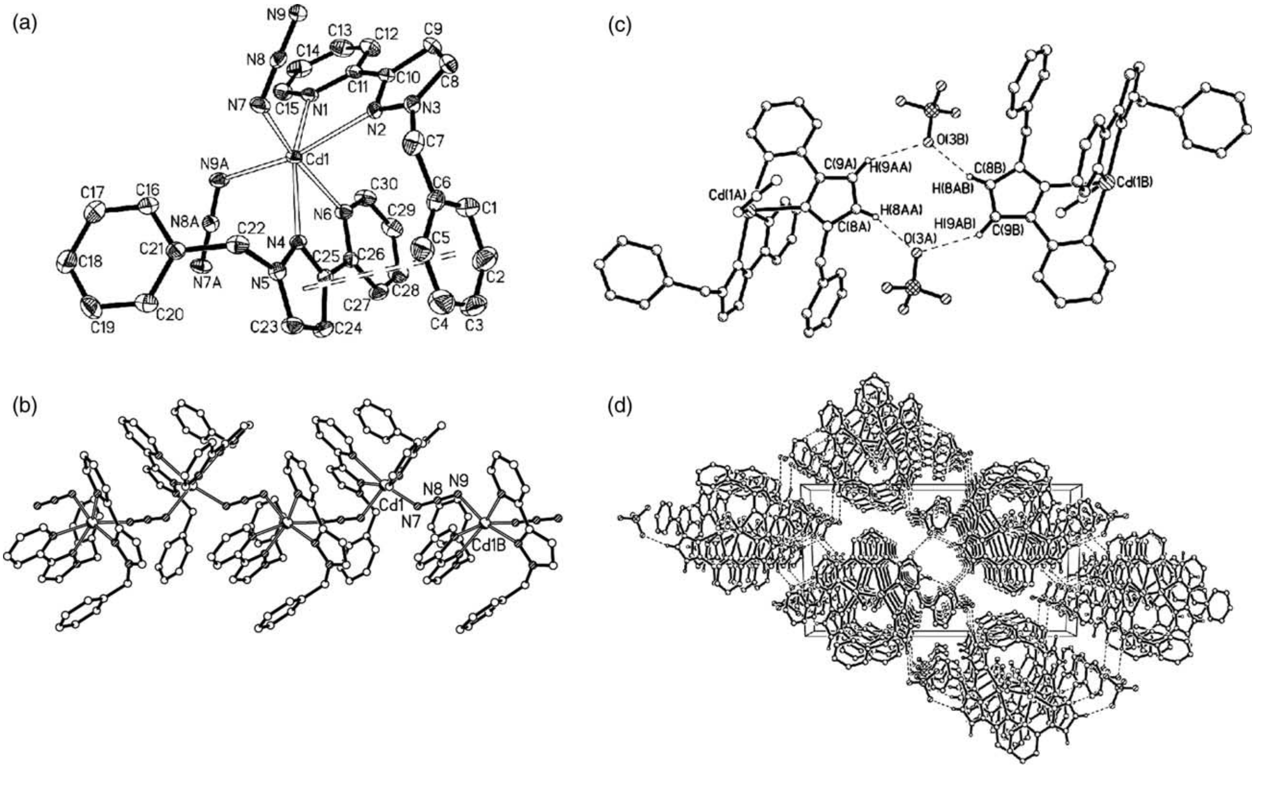


Fig. 2. (a) Coordination environment of Cd(II) in **2** with 20% displacement ellipsoids probability, (b) view of the 1D chains of **2**, (c) view of two kinds of C–H···O hydrogen bonds and (d) view of 3D supramolecular framework linked by C–H···O hydrogen bonds (symmetry code A: x, $3/2-y$, $z-1/2$; B: x, $3/2-y$, $z+1/2$).

Table 3
Selected bond lengths [Å] and angles [°] for **2**

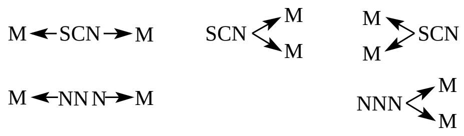
Cd(1)–N(1)	2.365(6)	Cd(1)–N(6)	2.412(5)
Cd(1)–N(2)	2.385(5)	Cd(1)–N(7)	2.291(6)
Cd(1)–N(4)	2.329(5)	Cd(1)–N(9A)	2.301(6)
N(1)–Cd(1)–N(2)	70.1(2)	N(7)–Cd(1)–N(4)	100.2(2)
N(1)–Cd(1)–N(6)	86.6(2)	N(7)–Cd(1)–N(6)	163.8(2)
N(2)–Cd(1)–N(6)	87.7(2)	N(7)–Cd(1)–N(9B)	99.9(2)
N(4)–Cd(1)–N(1)	157.4(2)	N(9B)–Cd(1)–N(1)	92.3(2)
N(4)–Cd(1)–N(2)	108.0(2)	N(9B)–Cd(1)–N(2)	162.3(2)
N(4)–Cd(1)–N(6)	70.8(2)	N(9B)–Cd(1)–N(4)	89.0(2)
N(7)–Cd(1)–N(1)	101.8(2)	N(9B)–Cd(1)–N(6)	93.4(2)
N(7)–Cd(1)–N(2)	82.4(2)		

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

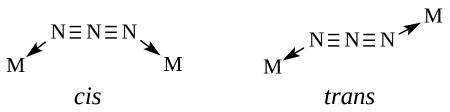
geometry around the Cd(II) center in **2** could also be described as a distorted octahedron. All the Cd–N bond lengths [region from 2.291(6) to 2.412(5) Å] are in the normal range for analogous complexes [10], and the bond angles around each Cd(II) center range from 70.1(2) to 157.38(19)°. In addition, the dihedral angles between the pyridyl-pyrazole ring and benzene ring is 9.2° in the unit around each Cd(II) center, and the centroid-centroid separation between them is 3.684 Å, indicating the presence of intramolecular π–π stacking interaction [13].

It is interesting that in **2** the azido anion acts as a bridge to link the Cd(II) ions in an end-to-end (μ-1,3) coordination mode to form a 1D chain (Fig. 2(b)), and the two coordinated azido is in *cis* positions, but for bridging azido it is a *trans* coordination mode. It is worthy to point out that the bridging mode of azide adopting *cis*-M-(μ-N_3)-M to coordinate to Cd(II) center is rare, although similar bridging mode has been observed in the structures of other metal azido complexes (i.e. $[Ni(1,2\text{-diamino-2-methylpropan})_2(\mu\text{-}N_3)]_n(PF_6)_n$ [14], $[Ni(aep)_2(\mu\text{-}N_3)]_n(ClO_4)_n$ [15]). Furthermore, the adjacent $\{[Cd(\mathbf{L})_2N_3]^+\}_n$ chains are linked through intermolecular C–H···O weak hydrogen-bonding interactions into a 3D framework (Fig. 2c and d) [C(9A)···O(3B) = 3.3593 Å, H(9AA)···O(3B) = 2.540 Å, C(9A)-H(9AA)···O(3B) = 147.1°; C(8B)···O(3B) = 3.2331 Å, H(8AB)···O(3B) = 2.332 Å, C(8B)-H(8AB)···O(3B) = 163.1°].

Both SCN^- and N_3^- anions have mono-terminal and bridging coordination modes, respectively (see Scheme 1) [12,16]. But in more examples, the former prefers to mono-terminal coordination, while the latter prefers to bridging [16,17]. Furthermore, when the N_3^- anion acts as bridging ligand, there are two typical coordination modes: end-to-end (EE or 1,3) and end-on (EO or 1,1). For the end-to-end coordination, there are also *trans* or *cis* coordination configurations (see Scheme 2) [16]. In **1**, the SCN^- adopts terminal mode to coordinate to the Cd^{II} center, while N_3^- in **2** acts as a bridge in an end-to-end (μ-1,3) coordination mode, and for each N_3^- it is a *trans* coordination configuration.



Scheme 1.



Scheme 2.

In summary, two Cd(II) complexes with 3-(2-pyridyl) pyrazole-based ligand, which have mononuclear and 1D chain structures, have been synthesized. The structural difference of the two complexes is attributed to the different anions, which have different coordination methods.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 20373028).

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