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Crystal structures of two- and three-dimensional polymeric complexes assembled by metal pseudohalides and 4-aminobenzoic acid via hydrogen bonds and covalent bonds

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Abstract

Four polymeric complexes $[M(SCN)_2(4-abaH)_2]_n$ [M = Co(II) (1) or Cd(II) (2), 4-abaH = 4-aminobenzoic acid], $[Zn(N_3)(4-aba)]_n$ (3) and $[Cd(N_3)(4-aba)(H_2O)]_n$ (4) were prepared from the reactions of 4-abaH with $M(SCN)_2$ [M = Co(II) or Cd(II)] and $M(N_3)_2$ [M = Zn(II) or Cd(II)] at different pH values. Their crystal structures have been determined by single-crystal X-ray diffraction. Both 1 and 2 consist of one-dimensional chains $[M(\mu-1,3-SCN)_2(4-abaH)_2]_n$, in which each pair of the lateral carboxylic groups form double hydrogen bonds to furnish infinite two-dimensional sheets. In 3, the Zn(II) atoms are bridged by μ -1,1-azide groups and μ_2 -carboxylate-O,O' groups into an infinite zigzag chain featuring six-membered $(Zn-N-Zn-O-C-O-)_n$ rings, which are further connected by the 4-aba-N,O,O' groups to generate a two-dimensional network. In 4, however, adjacent Cd(II) atoms are bridged by μ -1,1,3-azide groups to form an infinite chain with both four-membered Cd₂(μ -1,1-N₃)₂ and eight-membered Cd₂(μ -1,3-N₃)₂ rings. These chains are further connected by the 4-aba-N,O groups to generate a three-dimensional brickwall-like network. The results show significant effect of pH on the formation of the network structures. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: 4-Aminobenzoic acid; Transition metal pseudohalides; Coordination polymers; Self-assembly; Hydrogen bonding

1. Introduction

Crystal engineering of metal-organic framework materials has evolved rather rapidly in recent years because this kind of materials may have interesting physicochemical properties and potential applications such as adsorption, ion exchange, shape-selective catalysis, non-linear optical and magnetic materials [1]. A number of organic spacers (such as pyrazine [2], 4,4'bipyridine [2b,3], 1,4-bis(4-pyridyl)benzene [4], 1,4bis(imidazol-1-yl-methyl)benzene [5], 3,6-di(4-pyridyl)-1,2,4,5-tetrazine [6], 1,4-bis(4-pyridyl)butadiyne [7], 1,3bis(4-pyridyl)propane [8], 1,2-bis(4-pyridyl)ethane [9], etc.) have been used to produce a large number of metal-organic materials exhibiting interesting topologies, including infinite one-, two- or three-dimensional frameworks including helical [6,8], diamondoid and honeycomb [2b], square [3c] or rectangular [2a] grid, T-shaped [3d], ladder [2a,4,7] and other uncommon frameworks. Generally, the construction of frameworks can been achieved by using either covalent bonds or weaker intermolecular forces, e.g. hydrogen bonds, aryl-aryl interactions, etc. [10].

As part of our investigation on rational design and preparation of functional coordination frameworks, we have recently reported a number of transition metal coordination polymers with the organic spacers such as imidazole, 4,4'-bipyridine and 4,4'-oxydianiline [11]. We found that besides the linear pyridyl-like ligands, aniline-like ones are also effective organic spacers to construct coordination supramolecular frameworks even though they are weaker in coordination ability than the pyridyl ones [11c,12]. We now extend our work to include another bifunctional organic ligand 4aminobenzoic acid (4-abaH), and report herewith two

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layer networks, namely $[M(SCN)_2(4-abaH)_2]_n$ [M = Co(II) (1) or Cd(II) (2)], assembled simultaneously by covalent bonds and hydrogen-bonded carboxylic dimers as the supramolecular synthons [10a,b,g], as well as two new polymeric covalent networks $[ZnN_3(4-aba)]_n$ (3) and $[CdN_3(4-aba)(H_2O)]_n$ (4) featuring mixed bridging azide and carboxylate groups.

2. Experimental

2.1. Materials and instrumentation

All the reagents were commercially available and used as received. The C, H, N microanalyses were carried out with a Perkin–Elmer 240 elemental analyser. The IR spectra were recorded from KBr pellets in the range 4000-400 cm⁻¹ on a Nicolet Impact 420 FT-IR spectrometer.

Caution! Metal azide complexes are potentially explosive. Only a small amount of material should be prepared and should be handled with caution.

2.2. Synthesis

2.2.1. $[Co(SCN)_2(4-abaH)_2]_n$ (1)

A hot aqueous solution (10 cm³) of Co(NO₃)₂·6H₂O (1.06 mmol) and NH₄SCN (2.03 mmol) was added slowly to a hot ethanol solution (10 cm³) of 4-abaH (1.02 mmol). After vigorous stirring, the pH of the resulting solution was adjusted to 4.5 by addition of dilute HNO₃ solution. The mixture was then allowed to evaporate at room temperature (r.t.). Violet crystals of 1 suitable for X-ray diffraction were deposited in a week (78% yield). Calc. for C₁₆H₁₄CoN₄O₄S₂: C, 42.76, H, 3.14, N, 12.47, S, 14.27. Found: C, 42.69, H, 3.21, N, 12.49, S, 14.28%. IR data (cm⁻¹): 3355m, 3274m, 3071w, 2981w, 2116vs, 1681vs, 1606vs, 1514w, 1418m, 1317s, 1289s, 1247s, 1178m, 1010w, 929s, 835m, 691w, 615m, 551m, 506w.

2.2.2. $[Cd(SCN)_2(4-abaH)_2]_n$ (2)

Complex **2** was prepared in the same way as for **1** using $Cd(NO_3)_2 \cdot 4H_2O$ in place of $Co(NO_3)_2 \cdot 6H_2O$, and the resulting clear solution was then allowed to evaporate at r.t. Pale yellow crystals of **2** suitable for X-ray diffraction were deposited in a week (75% yield). Calc. for $C_{16}H_{14}CdN_4O_4S_2$: C, 38.22, H, 2.81, N, 11.14, S, 12.75. Found: C, 38.26, H, 2.79, N, 11.19, S, 12.71%. IR data (cm⁻¹): 3353m, 3273m, 3072w, 2979w, 2116vs, 1680vs, 1606vs, 1513w, 1419m, 1317s, 1289s, 1248s, 1177m, 1013w, 928s, 836m, 692w, 616m, 552m, 506w.

2.2.3. $[ZnN_3(4-aba)]_n$ (3)

An aqueous solution (5 cm³) of $Zn(NO_3)_2 \cdot 6H_2O$ (1.00 mmol) was added to an ethanol solution (8 cm³) of

4-abaH (1.00 mmol). After mixing for 5 min, an aqueous solution (2 cm³) of NaN₃ (1.02 mmol) was slowly added and the pH of the reaction mixture was adjusted to approximately 7. The resulting mixture was stirred for 10 min at r.t. and was then allowed to evaporate at r.t. Colourless crystals of **3** suitable for X-ray diffraction were deposited in a week (56% yield). Calc. for C₇H₆N₄O₂Zn: C, 34.52, H, 2.48, N, 23.01. Found: C, 34.48, H, 2.50, N, 23.04%. IR data (cm⁻¹): 3373w, 3327m, 3261m, 3160w, 2093vs, 1607vs, 1550vs, 1399vs, 1300m, 1227w, 1176w, 1060s, 851m, 783m, 695m, 627m, 566w, 518w.

2.2.4. $[CdN_3(4-aba)(H_2O)]_n$ (4)

Complex 4 was prepared in the same way as for 3 using Cd(NO₃)₂·4H₂O instead of Zn(NO₃)₂·6H₂O. Pale yellow crystals of 4 suitable for X-ray diffraction were obtained in a week (66% yield). Calc. for C₇H₈CdN₄O₃: C, 27.25, H, 2.61, N, 18.16. Found: C, 27.38, H, 2.59, N, 18.17%. IR data (cm⁻¹): 3385m, 3271m, 3159m, 2063vs, 1612vs, 1529vs, 1503vs, 1385s, 1253m, 1294m, 1289s, 1182m, 1143w, 1037s, 856m, 783m, 699m, 636m, 575w, 513w.

2.3. Crystallography

The collections of crystallographic data for the four complexes were carried out on a Siemens R3m diffractometer using graphite-monochromated Mo K α (λ 0.71073 Å) radiation at 293(2) K; the determinations of the crystal class, orientation matrix, and cell dimensions were performed according to the established procedures. The intensity data were collected using the ω scan mode. Absorption corrections were applied by fitting a pseudoellipsoid to the ψ -scan data of selected strong reflections over a range of 2θ angles [13]. The structure solutions and full-matrix least-squares refinements based on F^2 were performed with the SHELXS-97 and SHELXL-97 program packages, respectively [14,15]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of organic ligands were generated geometrically (C-H 0.96 Å); all the hydrogen atoms were assigned isotropic thermal parameters and included in the structure-factor calculations. Analytical expression of neutral-atom scattering factors was employed and anomalous dispersion corrections incorporated [16]. Drawings were produced with SHELXTL [17]. The crystal data are given in Table 1, and the selected bond distances and bond angles are listed in Table 2.

3. Results and discussion

3.1. Structural descriptions

3.1.1. $[Co(SCN)_2(4-abaH)_2]_n$ (1)

A fragment of the crystal structure of 1 is shown in

Fig. 1. The structure of 1 consist of $[M(SCN)_2]_n$ chains running along the a-axis. The Co(II) atom, being located at an inversion centre, is hexa-coordinated in a trans fashion by a pair of sulphur atoms from two SCN^- groups [Co(1)–S(1) 2.552(1) Å], a pair of nitrogen atoms from another two SCN⁻ groups [Co(1)-N(1a) 2.035(2) Å], and a pair of nitrogen atoms from two 4-abaH ligands [Co(1)-N(2) 2.206(2) Å] in an octahedral geometry with the most distorted bond angle being 92.6(1)°. Each pair of adjacent metal atoms are alternately bridged by a pair of SCN- groups through both ends, resulting in a chain-like structure with eight-membered (-N-C-S-M)₂ rings in a chair conformation. As expected, each pair of the carboxylic groups from adjacent chains form a pair of hydrogen bonds with each other to generate a hydrogen-bonded layer with 17.9×5.7 Å internal dimensions, as shown in Fig. 2. The doubly hydrogen-bonded carboxylic groups may be regarded as the supramolecular synthons which have a graph set [18,19] of $R_2^2(8)$ [O...O, 2.635(3) Å; O–H···O, 156.5(4)°]. Similar supramolecular synthons of doubly hydrogen-bonded carboxylic groups have been documented in a few previous work [10a,b,g]. There is no significant aryl-aryl interactions between neighbouring layers in 1, similar to those reported previously [10a,b]. On the other hand, each 4-aba amine group donates a weak hydrogen bond to the thiocyanate sulphur atoms (N...S 3.604(3) Å), and these hydrogen bonds extend the two-dimensional layers into the three-dimensional solid-state structure.

Crystal data and structure refinement parameters for complexes 1-4

Table 1

3.1.2. $[Cd(SCN)_2(4-abaH)_2]_n$ (2)

The coordination geometry and three-dimensional structure of **2** are very similar to those of **1**, as shown in Figs. 2 and 3. Due to the larger ionic radius of Cd(II) as compared to that of Co(II), the metal-ligand bonds in 2 are significantly longer than the corresponding ones in 1. Different from that of 1, the inversion centre is located between the Cd(II) atoms rather than on the Cd(II) atoms. Consequently, the lengths of each pair of the trans-related metal-ligand bonds are slightly different as compared in Table 2. The non-bonded Cd…Cd separations are also different with Cd(1)...Cd(1a) and Cd(1)...Cd(1b) at 5.822(1) and 5.961(1) Å, respectively. Similar to those of 1, the hydrogen-bonded dicarboxylic supramolecular synthons [O···O, 2.664(6) Å; O–H···O, 172.4(4)°] extend the chains into infinite two-dimensional networks (with the 18.1×5.8 Å internal dimensions) in the solid of 2.

3.1.3. $[ZnN_3(4-aba)]_n$ (3)

The crystal structure of **3** is different from those of **1** and **2**, featuring covalent bridges of the deprotonated 4-aba groups which interconnect the polymeric $[ZnN_3]_n$ chains. In **3**, the Zn(II) atom is penta-coordinated in a distorted trigonal-bipyramidal environment with two carboxylic oxygen atoms (Zn–O 2.042(2), 2.089(2) Å) from two deprotonated 4-aba groups at the apical positions and three nitrogen atoms (Zn–N 2.063(2)–2.112(2) Å) from two azide groups and one from a 4-aba group at the equatorial plane (Fig. 4(a)). The adjacent Zn(II) atoms are interconnected through μ -1,1-bound-azide groups (Zn–N–Zn 118.0(1)°) and μ_2 -

Complexes	1	2	3	4
Empirical formula	$C_{16}H_{14}CoN_4O_4S_2$	$C_{16}H_{14}CdN_4O_4S_2$	$C_7H_6N_4O_2Zn$	C7H8CdN4O3
Formula weight	449.36	502.83	243.54	308.57
Crystal system	triclinic	triclinic	monoclinic	monoclinic
Space group	$P\overline{1}$	$P\overline{1}$	$P2_{1}/c$	$P2_1/n$
Unit cell dimensions				• /
a (Å)	5.653(3)	6.389(3)	9.279(2)	6.541(2)
b (Å)	6.273(4)	11.698(7)	6.281(1)	20.180(9)
c (Å)	12.932(9)	12.758(8)	14.343(3)	7.204(2)
α (°)	82.630(3)	88.790(4)	90	90
β (°)	89.300(4)	84.710(6)	93.53(3)	97.18(2)
γ (°)	86.100(1)	87.030(1)	90	90
$V(Å^3)$	453.7(5)	948.0(9)	834.3(3)	943.5(6)
Z	1	2	4	4
$D_{\rm c} ({\rm g} {\rm cm}^{-3})$	1.645	1.761	1.939	2.172
μ (Mo K α) (mm ⁻¹)	1.207	1.402	2.919	2.307
<i>F</i> (000)	229	500	488	600
θ range (°)	3.2-29.0	2.4-26.0	4.1-30.0	3.0-28.0
Goodness-of-fit on F^2	1.052	1.051	1.035	1.039
$R_1 w R_2 [I > 2\sigma(I)]^a$	0.0428, 0.1109	0.0472, 0.1071	0.0457, 0.1273	0.0251, 0.0705
R_1 , wR_2 (all data) ^a	0.0518, 0.1170	0.0725, 0.1176	0.0518, 0.1325	0.0283, 0.0722

^a $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|, \ wR_2 = [\Sigma w (|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}, \ w = [\sigma^2 (F_o)^2 + (0.1(\max(0, F_o^2) + 2F_c^2)/3)^2]^{-1}.$

Table 2

Selected bond lengths (Å) and bond angles (°) for complexes 1-4

Complex 1			
Co(1)-N(1a)	2.035(2)	Co(1) - S(1)	2.552(1)
$C_0(1) - N(2)$	2.206(2)		
N(1a)-Co(1)-N(2)	87.5(1)	N(1)-C(1)-S(1)	179.6(2)
N(1b)-Co(1)-N(2)	92.5(1)	C(6)-N(2)-Co(1)	121.6(2)
N(1a)-Co(1)-S(1)	87.9(1)	C(1)-S(1)-Co(1)	102.0(1)
N(1b)-Co(1)-S(1)	92.1(1)	C(1)-N(1)-Co(1a)	165.8(2)
N(2)-Co(1)-S(1)	92.7(1)		
O(1)…O(2c)	2.635(3)	O(1)-H(1)O(2c)	156.5(4)
Complex 2			
Cd(1)-N(4a)	2.278(5)	Cd(1)-N(2)	2.448(5)
Cd(1)-N(3b)	2.305(4)	Cd(1)-S(1)	2.682(4)
Cd(1)–N(1)	2.440(5)	Cd(1)-S(2)	2.693(4)
$N(A_{-}) \subset I(1) \setminus N(2L)$	177.5(2)	$N(2h) = C_1(1) = C(2h)$	95 0(1)
N(4a) = Cu(1) = N(3b)	1/1.3(2)	N(30) = Cu(1) = S(2)	03.9(1)
N(4a) - Cd(1) - N(1)	94.3(2)	N(1) - Cd(1) - S(2)	94.0(1)
N(4a) - Cd(1) - S(1)	90.4(1)	N(1) - Cd(1) - N(2)	1/4.2(1)
N(4a)-Cd(1)-N(2)	91.3(2)	N(1)-Cd(1)-S(1)	85.6(1)
N(4a)-Cd(1)-S(2)	91.8(1)	N(2)-Cd(1)-S(1)	92.9(1)
N(3b)-Cd(1)-N(1)	86.5(2)	N(2)-Cd(1)-S(2)	87.3(1)
N(3b)-Cd(1)-N(2)	87.9(2)	S(1)-Cd(1)-S(2)	177.8(1)
N(3b)-Cd(1)-S(1)	91.9(1)		
$O(3) \cdots O(1d)$	2,629(6)	O(3) - H(3) - O(1d)	167 6(7)
$O(2) \cdots O(4c)$	2.664(6)	$O(2)-H(4b)\cdots O(4c)$	172.4(4)
	2.00 .(0)		1/200(1)
Complex 3			
Zn(1) = O(1)	2.089(2)	Zn(1)-N(2a)	2.063(2)
Zn(1)-N(2)	2.064(3)	N(2)-N(3)	1.213(3)
Zn(1)-N(1b)	2.112(2)	N(3) - N(4)	1.140(4)
Zn(1)-O(2a)	2.042(2)		
O(2a) - Zn(1) - O(1)	175.7(1)	N(2)-Zn(1)-O(1)	94.7(1)
O(2a) - Zn(1) - N(2a)	87.0(1)	N(2) - Zn(1) - N(1b)	116.8(1)
O(2a) - Zn(1) - N(2)	88.0(1)	O(1)-Zn(1)-N(1b)	90.4(1)
O(2a) - Zn(1) - N(1b)	91.4(1)	Zn(1c) - N(2) - Zn(1)	118.0(1)
N(2a) = Zn(1) = N(2)	129 4(1)	N(4) - N(3) - N(2)	177.9(4)
N(2a) = Zn(1) = N(1b)	1137(1)	N(3) - N(2) - Zn(1)	1201(2)
N(2a) = Zn(1) = O(1)	88 7(1)	$\Pi(3) \Pi(2) \Sigma \Pi(1)$	120.1(2)
	00.7(1)		
Complex 4	2 2 () ()		0.051(0)
Cd(1)-N(1)	2.368(3)	Cd(1) = O(2a)	2.271(3)
Cd(1)-N(2)	2.474(3)	Cd(1)-O(1w)	2.270(3)
Cd(1)-N(2c)	2.469(3)	N(3)-N(2)	1.191(4)
Cd(1)–N(4b)	2.404(3)	N(3)–N(4)	1.158(4)
O(1w) - Cd(1) - N(1)	102.5(1)	N(1)-Cd(1)-N(2)	76.6(1)
O(1w) - Cd(1) - N(2)	165.6(1)	N(1)-Cd(1)-N(4b)	79.7(1)
O(1w) - Cd(1) - N(2c)	89 5(1)	N(1)-Cd(1)-N(2c)	81 9(1)
O(1w)-Cd(1)-N(4b)	83 4(1)	N(4b)-Cd(1)-N(2c)	158 3(1)
O(1w) - Cd(1) - O(2w)	02.7(1)	N(4b) = Cd(1) N(2)	110.3(1)
O(2a) Cd(1) - O(2a)	$\frac{92.3(1)}{117.7(1)}$	N(2a) Cd(1) N(2)	76.1(1)
O(2a) = Cu(1) = IN(4D) O(2a) = Cd(1) = IN(2)	25 2(1)	IN(20) = Cu(1) = IN(2) Cd(1a) = N(2) = Cd(1)	1020(1)
O(2a) = O(1) = N(2)	03.2(1)	U(10) - IN(2) - U(1)	103.9(1)
O(2a) - Ca(1) - N(1) O(2a) - Cd(1) - N(2a)	138.7(1) 82.0(1)	N(3) - N(2) - Cd(1) N(4) - N(2) - N(2)	$121.\delta(2)$ 170.4(2)
-(2a) - (u(1) - in(2c))	05.0(1)	$11(7)^{-11}(3)^{-11}(2)$	179.4(3)

Symmetry codes for: 1 (a) -x, -y, -z; (b) -x-1, -y, -z; (c) -x-2, -y-1, -z+1. 2 (a) -x, -y, -z+1; (b) -x, -y+1, -z+1; (c) x-1, y-1, z+1; (d) x+1, y+1, z-1. 3 (a) -x+2, y+1/2, -z+1/2; (b) x-1, y, z. 4 (a) -x, -y+2, -z+1; (b) -x+1, -y+2, -z+1; (c) -x+1/2, y+1/2, -z+3/2.

carboxylate-O,O' groups in a *trans* fashion to generate an infinite zigzag chain with the $(Zn-N-Zn-O-C-O-)_n$ six-membered rings. Each deprotonated 4-aba group exhibits a tridentate (μ_3 -N,O,O') coordination mode to bridge three metal centres (Zn…Zn 3.5 × 9.3 Å) and extends the chains into a two-dimensional network, as illustrated in Fig. 4(b).

3.1.4. $[CdN_3(4-aba)(H_2O)]_n$ (4)

Similar to that of 3, the crystal structure of 4 is also constructed from covalent bridges of the deprotonated 4-aba groups which interconnect the polymeric $[CdN_3]_n$ chains. In 4, each Cd(II) atom is coordinated in a distorted octahedral environment by three azide nitrogen atoms (Cd-N 2.404(3)-2.474(3) Å), one aqua ligand (Cd-O 2.270(3) Å), one carboxy oxygen atom (Cd–O 2.271(3) Å) of a 4-aba ligand, and one amine nitrogen atom (Cd-N 2.368(3) Å) of another 4-aba ligand (Fig. 5(a)). The bond lengths and bond angles at the metal centre are typical for azide and 4-aba coordination. Each azide ligand acts in a μ -1,1,3-briding mode to link three Cd(II) atoms, generating an infinite onedimensional staircase-like chain, which is constructed by alternate interconnection of four-membered Cd₂(µ- $1,1-N_3)_2$ and eight-membered Cd₂(μ -1,3-N₃)₂ rings (Fig. 5(b)) with the intra-ring Cd···Cd distances of 3.892(1)and 5.073(1) A, respectively. As the carboxylate group of the 4-aba ligand acting in a monodentate mode, both ends of the organic ligand participates in the coordination to the metal atoms in a μ_2 -N,O mode, the azidobridged chains are further interlinked through the organic spacers into a new three-dimensional, irregular brickwall-like network (see Fig. 6).

3.2. Discussions

A few one-dimensional polymers of cadmium thiocyanates $[Cd(SCN)_2L_2]_n$ (L = benzylamine, dibenzylamine, tri-m-tolyphosphine or 1H-1,2,4-triazole) have been reported in the past decades [20]. All of these complexes exhibit chain structures, where each pair of adjacent Cd(II) atoms are bridged by two inversely related μ_2 -SCN-N,S ligands and the remaining coordination sites are occupied by the monodentate organic ligands. We have recently found that imidazole and nicotinic derivatives can extend the $[Cd(SCN)_2]_n$ chains into two-dimensional networks through hydrogen bonding [10g,12]. Therefore, we may conclude that the $[M(\mu_2-SCN-N,S)_2]_n$ chain structure is quite stable and introduction of organic ligands capable of both proton donation and acceptance may extend the chains into higher dimensional structures, as demonstrated by 1 and 2. An acidic reaction solution is essential for the formation of the hydrogen-bonded carboxylic dimer. This conclusion is also supported by the fact that hydrogen-bonded carboxylic dimers do not formed at higher pH (ca. 7); instead, the carboxylic groups are deprotonated and participate in coordination to the metal atoms, as shown in both 3 and 4. On the other



Fig. 1. Perspective view of the one-dimensional chains showing the coordination environment in 1.



Fig. 2. Perspective views of the layer formed by the hydrogen-bonded $[M(SCN)_2(4-abaH)_2]_n$ chains in 1 or 2.



Fig. 3. Perspective view of the one-dimensional chains showing the coordination environment in 2.





Fig. 4. Perspective views of the coordination environment of the Zn(II) atom (a) and the two-dimensional framework (b) in $[ZnN_3(4-aba)]_n$ (3).

hand, our attempt to assemble the $M(SCN)_2$ with 4-aba through covalent bonds and manganese(II)/nickel(II) thiocyanates with 4-aba through supramolecular synthon did not success.

It has been found that SCN^- group can exhibit two types of terminal coordination modes, *S*-coordinated and *N*-coordinated, as well as 13 bridging modes with the metal ions [21]. The μ_2 -SCN-*N*,*S* coordination mode for Cd(II) atoms is one of the usual fashion since Cd(II) atom is between hard base and soft base according to the hard–soft acid–base concept [22]. On the other hand, such μ_2 -SCN-*N*,*S* coordination mode for the Co(II) atoms in **1** is less common [22], since Co(II) ion is a hard acid and expected to exhibit *N*coordination.

Azide group is a versatile bridging ligand in coordination to transition metal centres in the μ -1,3 or μ -1,1 fashions (Scheme 1), which has been widely investigated as the study of ferro- or antiferromagnetic materials [23]. In contrast, the μ -1,1,3-bound mode, as well as the accompanying infinite one-dimensional staircase-like chain $[MN_3]_n$ found in 4 has not been documented in the literature. The IR spectrum of 3 shows a sharp band at 2093(vs) cm⁻¹, which agrees with the μ -1,1azide group [23a-c]. However, the IR spectrum of 4 shows a sharp band at 2063 cm⁻¹, which is located between 2056 cm⁻¹ for μ -1,3-azide and 2094 cm⁻¹ for μ -1,1-azide [23d]. This absorption should be ascribed to the occurrence of μ -1,1,3-azide group. A few two-dimensional brickwall-like sheets (Scheme 2) or their triple interpenetrating sheets have been reported, in which the metal centres are T-shaped [3b,24]. In order to extent the two-dimensional brickwall-like sheets into a three-dimensional brickwall network, a neutral bidentate ligand must be introduced and the metal atoms should exhibit a penta-coordination fashion. At neutral



Fig. 5. Perspective views of the coordination environment of the Cd(II) atom (a) and staircase-like chain constructed by μ -1,1,3-azide ligands with Cd(II) atoms (b) in [CdN₃(4-aba)(H₂O)]_n (4).



Fig. 6. Perspective view of the brickwall-like three-dimensional framework of 4. The aqua ligands are omitted for clarity.

condition, the polymeric $[CdN_3]_n$ chains are interconnected by the deprotonated 4-aba spacers to produce a three-dimensional brickwall network (Scheme 2). Attempt to assemble the $M(N_3)_2$ with 4-abaH through





Scheme 2. Schematic diagram of the three-dimensional brickwall network.

hydrogen bonds did not success as NaN_3 decomposes in an acidic solution.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 156833–156836 for compounds 1–4. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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