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Coordination Networks Self-assembled by Transition Metal Salts With 4,4'-oxydianiline (4,4'-oda). Syntheses and Structures of ∞ 1 [Ni(NCS) 2 (4,4'-oda) 2], ∞ 2 [Co(NCS) 2 (4,4'-oda) 2] and ∞ 2 [M(N 3)(4,4'-oda) 2]NO 3 (M=Cd II or Co II)

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Coordination Networks Self-assembled by Transition Metal Salts With 4,4′-oxydianiline (4,4′-oda). Syntheses and Structures of ${}^{1}_{\infty}[\mathrm{Ni(NCS)_2(4,4'\text{-}oda)_2}]$, ${}^{2}_{\infty}[\mathrm{Co(NCS)_2(4,4'\text{-}oda)_2}]$ and ${}^{2}_{\infty}[\mathrm{M(N_3)(4,4'\text{-}oda)_2}]\mathrm{NO_3}$ ($\mathrm{M = Cd^{II}}$ or $\mathrm{Co^{II}}$)

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Four infinite complexes ${}^{1}_{\infty}[\mathrm{Ni(NCS)_2(4,4'\text{-}oda)_2}]$, ${}^{2}_{\infty}[\mathrm{Co(NCS)_2(4,4'\text{-}oda)_2}]$ and ${}^{2}_{\infty}[\mathrm{M(N_3)(4,4'\text{-}oda)_2}]\mathrm{NO_3}$ [M = $\mathrm{Cd^{II}}$ (3) **or $\mathrm{Co^{II}}$ (4)] were obtained by reactions 4,4′-oxydianiline (4,4′-oda) with $\mathrm{Ni(SCN)_2}$, $\mathrm{Co(SCN)_2}$, $\mathrm{Cd(N_3)_2}$ and $\mathrm{Co(N_3)_2}$, respectively which have been structurally established by single-crystal X-ray diffraction. Complex 1 contains one-dimensional double-stranded chains comprising 24-membered $\mathrm{Ni_2(4,4'\text{-}oda)_2}$ macrocycles, each formed by two 4,4′-oda ligands and two octahedral $\mathrm{Ni^{II}}$ centers. Complex 2 exhibits two-dimensional non-interpenetrating networks consisting of large 48-membered macrocycles each formed by four 4,4′-oda ligands and four octahedral $\mathrm{Co^{II}}$ centers. The crystal structures of 3 and 4 are isomorphous and both contain one-dimensional double-stranded chains comprising 24-membered $\mathrm{M_2(4,4'\text{-}oda)_2}$ macrocycles, which are interlinked by μ-1,3-azide groups to generate cationic two-dimensional sheets. These sheets are further connected by hydrogen bonds between the amine groups and nitrate ions to furnish three-dimensional networks. Crystal data: complex 1 crystallizes in the monoclinic space group $P2_1/c$ with $a = 11.990(4)$ Å, $b = 9.413(4)$ Å, $c = 12.827(4)$ Å, $\beta = 116.32(2)°$, $V = 1297.6(8)$ Å^3 and $Z = 2$; complex 2 crystallizes in the orthorhombic space group $Pbca$ with $a = 9.583(2)$ Å, $b = 12.738(3)$ Å, $c = 21.039(4)$ Å, $V = 2568.2(9)$ Å^3 and $Z = 4$; complex 3 crystallizes in the monoclinic space group $C2/c$ with $a = 23.036(5)$ Å, $b = 5.920(1)$ Å, $c = 17.800(4)$ Å, $\beta = 92.67(3)°$, $V = 2424.8(9)$ Å^3 and $Z = 4$; complex 4 crystallizes in the monoclinic space group $C2/c$ with $a = 22.861(5)$ Å, $b = 5.812(1)$ Å, $c = 17.720(4)$ Å, $\beta = 93.00(3)°$, $V = 2351.2(8)$ Å^3 and $Z = 4$.**

Keywords: Solid state coordination polymer; Ligands; 4,4′-oxydianiline; Self-assembly

INTRODUCTION

There has been an increasing interest in construction of solid state coordination polymers by molecular self-assembly over the past decade because of their intriguing structural diversity, physical properties and potential applications such as adsorption, ion exchange, magnetism and shape-selective catalysis [1–8]. Previous reports have demonstrated that the self-assembly of these frameworks is highly influenced by many factors such as the organic spacers, solvent, template, the pH value of the solution and even the counterion [1–18], therefore much work is required to extend the knowledge of the relevant structural types and establish proper synthetic strategies leading to the desired species. So far, a large number of rigid rod-like bidentate ligands, such as pyrazine (pz) [9–12], 4,4′-bipyridine (bpy) [7,9,13–18], 1,4-bis(4-pyridyl)benzene (bpb) [19], 1,4-bis(imidazol-1-yl-methyl)benzene (bix) [20] and 3,6-di(4-pyridyl)-1,2,4,5-tetrazine (ptyz) [22], together with a few flexible bidentate ligands including 1,2-bis(4-pyridyl)butadiyne (bpbd) [23], 1,3-bis(4-pyridyl)propane (bpp) [24] and 1,2-bis(4-pyridyl)ethane (bpe) [25,26], have been employed in the construction of these materials, which are infinite one-, two- or three-dimensional frameworks including helical chains [22,24], diamondoid and honeycomb networks [9], square [15] or rectangular [10] grids, T-shaped networks [14], ladders [13,19,23]. In

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TABLE I Crystallographic data for **1**, **2**, **3** and **4**

Complex	**1**	**2**	**3**	**4**
Empirical formula	$C_{26}H_{24}N_6NiO_2S_2$	$C_{26}H_{24}CoN_6O_2S_2$	$C_{24}H_{24}CdN_8O_5$	$C_{24}H_{24}CoN_8O_5$
M	575.34	575.56	616.91	563.44
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group (no.)	$P2_1/c$	Pbca	$C2/c$	$C2/c$
a (Å)	11.990(4)	9.583(2)	23.036(5)	22.861(5)
b (Å)	9.413(4)	12.738(3)	5.920(1)	5.812(1)
c (Å)	12.827(4)	21.039(4)	17.800(4)	17.720(4)
β (°)	116.32	90	92.67(3)	93.00(3)
V (Å^3)	1297.6(8)	2568.2(9)	2424.8(9)	2351.2(8)
Z	2	4	4	4
D_c (g cm^{-3})	1.473	1.498	1.690	1.592
μ(Mo–Kα) (mm^{-1})	0.945	0.868	0.955	0.786
Goodness-of fit on F^2	1.048	1.031	1.120	1.003
Data/parameters	2551/169	3662/170	3446/166	3412/177
$R1[I > 2\sigma(I)]$	0.0440	0.0380	0.0471	0.0486
$wR2$ (all data)	0.1205	0.1104	0.1452	0.1422
T (K)	293(2)	293(2)	293(2)	293(2)

contrast, flexible dianiline-like ligands have virtually been unexploited for this purpose [27], although this type of ligands may be employed to construct interesting coordination polymers in solid state. As part of our study in the chemistry of this field [28,29], we used 4,4′-oxydianiline (4,4′-oda) as an organic spacer and metal ions to construct solid state coordination polymers, and report here, the crystal structures of four solid state coordination polymers, namely $[M(NCS)_2(4,4'\text{-oda})_2]$ [M = Ni^{II} (**1**) or Co^{II} (**2**)] and $[M(N_3)(4,4'\text{-oda})_2]NO_3$ [M = Cd^{II} (**3**) or Co^{II} (**(4)**], as well as the thermal behaviors of **1** and **2**.

EXPERIMENTAL

Materials and Physical Techniques

Nickel(II) nitrate hexahydrate, cobalt(II) nitrate hexahydrate, cadmium (II) nitrate tetrahydrate, 4,4′-oxydianiline, ammonium thiocyanate and sodium azide were purchased from commercial sources and used as received. The C, H, N and S microanalyses were carried out with a VARIO elemental analyzer. The IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Bruker EQUINOX-55 FT-IR spectrometer. Thermogravimetric data were collected on a Perkin–Elmer TGS-2 analyzer in flowing dinitrogen at a heating rate of 10°C per minute.

Synthesis of the Complexes

$^1_\infty[Ni(NCS)_2(4,4'\text{-oda})_2]$ 1

A hot alcohol solution (25 cm^3) of 4,4′-oda (2.0 mmol) was added to a hot aqueous solution (15 cm^3) of nickel(II) nitrate hexahydrate (1.0 mmol) and ammonium thiocyanate (2.0 mmol). Green microcrystals of **1** were precipitated after cooling the mixture to room temperature, were collected by filtration and washed with methanol and diethyl ether (yield ca. 46%). Prismatic crystals of **1** suitable for X-ray diffraction were produced by slow evaporation of the above filtrate in a week. Calc. For $C_{26}H_{24}NiN_6O_2S_2$: C, 54.27; H, 4.20; N, 14.61; S, 11.14%. Found: C, 54.19; H, 4.27; N, 14.57; S, 11.11%. IR data (cm^{-1}): 3332s, 3298m, 3250s, 3163m, 2090vs, 1594m, 1498vs, 1222s, 1055s, 1029s, 874w, 825s, 787m, 522m.

$^2_\infty[Co(NCS)_2(4,4'\text{-oda})_2]$ 2

This compound was prepared as for **1** by using cobalt(II) nitrate hexahydrate in place of nickel(II) nitrate hexahydrate. The yield was ca. 67%. Violet prismatic crystals of **2** suitable for X-ray diffraction were obtained by slow evaporation of the above filtrate in week, Calc. for $C_{26}H_{24}CoN_6O_2S_2$: C, 54.25; H, 4.20; N, 14.60; S, 11.14%. Found: C, 54.22; H, 4.18; N, 14.48; S, 11.17%. IR data (cm^{-1}): 3332s, 3298m, 3250s, 3160m, 2081vs, 1592s, 1497vs, 1222s, 1042s, 1018s, 873w, 824s, 785m, 518m.

$^2_\infty[Cd(N_3)(4,4'\text{-oda})_2]NO_3$ 3

An acetonitrile solution (25 cm^3) of 4,4′-oda (2.0 mmol) was added to a hot aqueous solution (15 cm^3) containing cadmium(II) nitrate tetrahydrate (1.0 mmol) and sodium azide (1.1 mmol). The pH of the mixture was adjusted to five by addition of dilute HNO_3. Yellow microcrystals of **3** were deposited after cooling the mixture solution to room temperature, and collected by filtration and washed with methanol and diethyl ether (yield ca. 70%). Crystals of **3** suitable for X-ray diffraction were isolated after slow evaporation of the above filtrate in a week. Calc. for $C_{24}H_{24}CdN_8O_5$: C, 46.72; H, 3.92; N, 18.17%. Found: C, 46.69; H, 3.98; N, 18.18%. IR data (cm^{-1}):

TABLE II Selected bond lengths (Å) and bond angles (°) for **1**, **2**, **3** and **4** (symmetric codes: (a) x + 1, y, z for **1**; (a) −x, −y, −z for **2**; (a) −x, −y, −z for **3**; (a) −x, −y − 1, −z; (b) −x − 1/2, −y − 1/2, −z; (c) −x, −y, −z for **4**

Complex ***1***			
Ni(1)–N(3)	2.023(3)	N(2)–C(1)	1.438(4)
Ni(1)–N(2)	2.195(3)	N3(2)–C(1)	1.156(4)
Ni(1)–N(1)	2.196(3)	C(13)–S(1)	1.633(3)
N(1)–C(1)	1.439(4)	O(1)–C(7)	1.396(4)
N(3)–Ni(1)–N(2)	88.36(1)	N(2)–Ni(1)–N(1)	85.38(1)
N(3)–Ni(1)–N(2a)	91.64(1)	N(2)–Ni(1)–N(1a)	94.62(1)
N(3)–Ni(1)–N(1)	87.59(1)	C(7)–O(1)–C(4)	116.5(3)
N(3)–Ni(1)–N(1a)	92.41(1)		
Complex **2**			
Co(1)–N(3)	2.043(2)	N(2)–C(1)	1.436(2)
Co(1)–N(2)	2.211(2)	N(3)–C(1)	1.153(3)
Co(1)–N(1)	2.252(2)	C(13)–S(1)	1.622(2)
N(1)–C(1)	1.439(2)	O(1)–C(7)	1.385(2)
N(3)–Co(1)–N(2)	91.90(7)	N(2)– Co(1)–N(1)	85.88(6)
N(3)–Co(1)–N(2a)	88.10(7)	N(2)–Co(1)–N(1a)	94.12(6)
N(3)–Co(1)–N(1)	86.30(6)	C(2)–O(1)–C(4)	118.77(2)
N(3)–Co(1)–N(1a)	93.70(6)		
Complex**3**			
Cd(1)–N(3)	2.294(3)	N(1)–C(1)	1.434(4)
Cd(1)–N(2)	2.421(3)	N(2)–C(1)	1.430(5)
Cd(1)–N(1)	2.413(3)	O(1)–C(7)	1.393(5)
N(3)–N(4)	1.166(4)	O(1)–C(4)	1.388(4)
N(3)–Cd(1)–N(1)	87.63(1)	N(2)–Cd(1)–N(1a)	93.36(1)
N(3)–Cd(1)–N(1a)	92.37(1)	N(4)–N(3)–Cd(1)	113.6(2)
N(3)–Cd(1)–N(2)	92.00(1)	C(1)–N(1)–Cd(1)	119.9(2)
N(3)–Cd(1)–N(2a)	88.00(1)	C(10)–N(2)–Cd(1)	113.4(2)
N(2)–Cd(1)–N(1)	86.64(1)	C(4)–O(1)–C(7)	116.0(2)
Complex **4**			
Co(1)–N(3)	2.076(2)	C(1)– N(1)	1.438(3)
Co(1)–N(2)	2.235(2)	C(10)– N(2)	1.434(4)
Co(1)–N(1)	2.235(2)	C(4)– O(1)	1.392(3)
N(3)–N(4)	1.179(2)	O(1)– C(7b)	1.395(3)
N(3)–Co(1)–N(1)	92.06(9)	N(2)– Co(1)– N(1c)	86.45(8)
N(3)–Co(1)–N(1c)	87.94(9)	N(4)– N(3)– Co(1)	124.13(2)
N(3)–Co(1)–N(2)	92.06(9)	C(1)– N(1)– Co(1)	122.41(2)
N(3)–Co(1)–N(2c)	87.94(9)	C(10)– N(2)– Co(1)	118.13(2)
N(2)–Co(1)–N(1)	93.55(8)	C(4)– O(1)– C(7b)	115.81(2)

3337s, 3303m, 3261m, 3161m, 2047vs, 1612m, 1585m, 1499vs, 1404s, 1316s, 1220s, 1163m, 1048m 997s, 825s, 779s, 518w.

${}^{2}_{\infty}[Co(N_3)(4,4'\text{-}oda)_2]NO_3$ **4**

This compound was prepared as for **3** using cobalt(II) nitrate hexahydrate in place of cadmium(II) nitrate hexahydrate (yield was ca. 76%). Prismatic crystals of **4** suitable for X-ray diffraction were obtained by slow evaporation of the above filtrate in a week, Calc. for $C_{24}H_{24}CoN_8O_5$: C, 51.16; H, 4.29; N, 19.89%. Found: C, 50.98; H, 4.32; N, 19.88%. IR data (cm^{-1}): 3323m, 3301m, 3260s, 3164, 2071vs, 1616m, 1592m, 1500vs, 1387s, 1319s, 1222s, 1165m 1085m, 1034s, 856m, 827s, 781s, 522w.

Crystallography

Crystallographic data for the four complexes are summarized in Table I and the selected bond lengths and bond angles are given in Table II. The diffraction data for the complexes were carried out on a Siemens R3m diffractometer using graphite-monochromated Mo–Kα($\lambda = 0.71073$ 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 [30]. The structure solution sand full-matrix least-squares refinement based on F^2 were performed with the SHELXS-97 and SHELEXL-97 program packages, respectively [31,32]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of organic ligands were generated geometrically (C–H 0.96 Å), assigned isotropic thermal parameters and included in the structure-factor calculations. Anomalous dispersion corrections incorporated [33] and the drawings were produced with SHELXTL [34].

RESULTS AND DISCUSSION

Structural Descriptions

${}^{1}_{\infty}[Ni(NCS)_2(4,4'\text{-}oda)_2]$ **1**

The crystal structure of **1** consists of covalently linked one-dimensional double-stranded chains with the $Ni(NCS)_2(4,4'\text{-}oda)_2$ fragments as a repeating unit, as illustrated in Fig. 1. The Ni^{II} atom is in a compressed octahedral environment with two nitrogen atoms from a pair of *trans*-related thiocyanate groups at the axial positions (Ni–N = 2.023(3) Å) and four nitrogen atoms from different 4,4′-oda ligands at the equatorial plane (Ni–N = 2.195(3)–2.196(3) Å). A pair of 4,4′-oda ligands interconnect two adjacent Ni^{II} atoms to give a

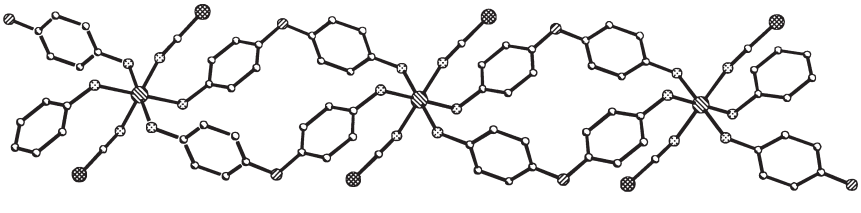

FIGURE 1 A perspective view of the infinite double-stranded chain structure **1**.

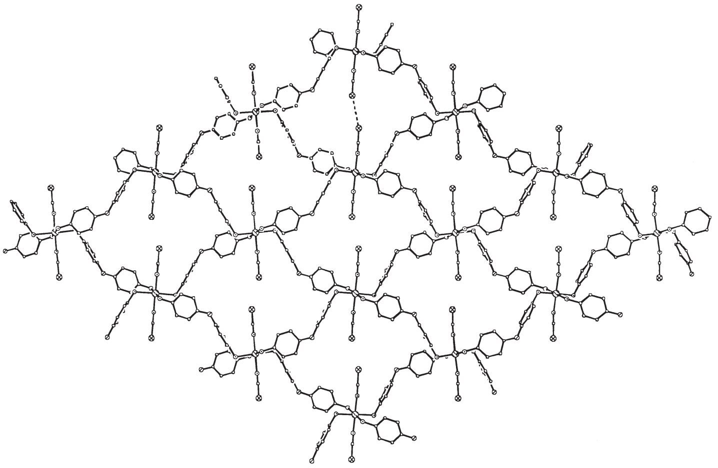

FIGURE 2 A top-view of the infinite two-dimensional sheet of **2**.

24-membered macrocyclic structure, which is repeated to generate a one-dimensional double-stranded chain with a period of 11.99 Å.

The connection between a 4,4′-oda ligand and a Ni^{II} atom is bent with the C–N–Ni angle of 121.7(2)–124.7(2)°, indicating that the amine nitrogen is sp^3 hybridized. The 4,4′-oda ligands is in a V-shape configuration and two phenyl rings of the 4,4′-oda ligand are not coplanar as indicated by the C(7)–O(1)–C(4) bond angle of 116.5(3)° and phenyl/phenyl dihedral angle of 73.4°. The thiocyanate group is linear (N–C–S = 178.1(3)°), however, its connection with the Ni^{II} atom is slightly bent with a C–N–Ni angle of 164.3(2)°.

$^{2}_{\infty}[Co(NCS)_2(4,4'\text{-}oda)_2]$ 2

The crystal structure of **2** consists of covalently lined two-dimensional frameworks with the [Co(NCS)$_2$(4,4′-oda)$_2$] fragments as building blocks, as illustrated in Fig. 2. The Co^{II} atom exhibits a centrosymmetrically compressed octahedral CoN$_6$ coordination geometry formed with four nitrogen atoms (Co–N = 2.211(2)and2.252(2) Å) from four 4,4′-oda ligands at the equatorial plane and two nitrogen atoms (Co–N = 2.043(2) Å) from two thiocyanate groups at the axial positions. The 4,4′-oda ligand in **2** exhibits a very similar V-shape configuration to that in **1**, and the coordination mode of the thiocyanate group in **2** is also similar to that in **1**.

Interconnection of the four 4,4′-oda ligands ligating a metal center to four adjacent metal centers extends the structure into a neutral two-dimensional layer. The two-dimensional network of **2** is distorted to the largest extent among the related structures, and each building block of which consists of a large 48-membered Co$_4$(4,4′-oda)$_4$ rings. However a significant S···S contact (3.505(2) Å) is found between two sulfur atoms of the thiocyanate groups within each ring, which may play a role in the formation of the rhombic structure. These two-dimensional layers are packed in a staggered fashion so that the Co^{II} atoms in one layer sit above or below the rhombs of the adjacent layers.

$^{2}_{\infty}[Cd(N_3)(4,4'\text{-}oda)_2]NO_3$ 3 and $^{2}_{\infty}[Co(N_3)(4,4'\text{-}oda)_2]NO_3$ 4

Complexes **3** and **4** crystallizes isomorphously in the monoclinic space group *C*2/*c*. Their structures contain primarily one-dimensional double-stranded chains running along the *a*-axis direction, which comprise 24-membered M$_2$(4,4′-oda)$_2$ macrocycles similar to those found in **1**. These chains are interlinked by μ-1,3-azide groups to generate cationic two-dimensional sheets containing 32-membered M$_4$(N$_3$)$_2$(4,4′-oda)$_2$ macrocycles. In both **3** and **4**, the metal atom exhibits a compressed octahedral MN$_6$ coordination geometry, being surrounded by four nitrogen atoms (M–N = 2.421(3) and 2.413(3) Å for **3**, 2.211(2) and 2.252(2) Å for **4**) from four 4,4′-oda ligands at the equatorial positions and two *trans*-related nitrogen atoms (2.294(3) Å for **3** and 2.043(2) Å for **4**) from two azide groups at the axial positions, as shown in Fig. 3. However, the angle

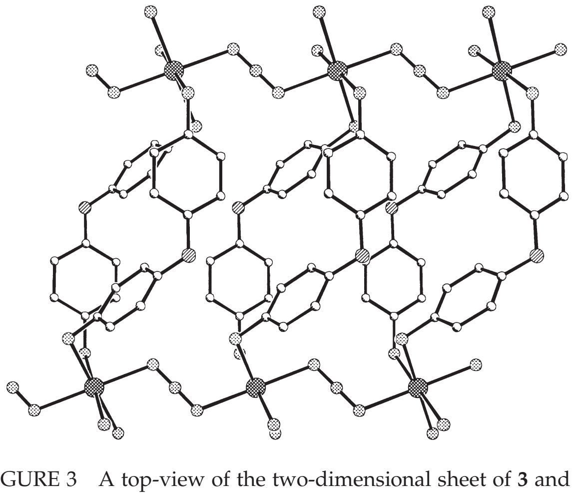

FIGURE 3 A top-view of the two-dimensional sheet of **3** and **4**.

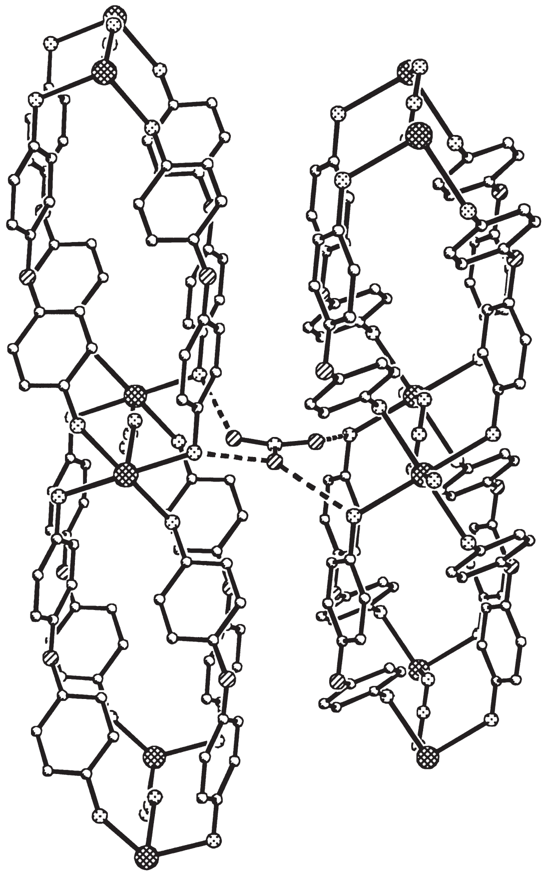

FIGURE 4 A side-view of the three-dimensional networks of **3** and **4**.

deviations from an idealized octahedron are relatively small, as shown in Table II.

In the two-dimensional sheets, adjacent metal atoms are interconnected by both 4,4′-oda and azide spacers at distances of 5.9 × 11.9 and 5.8 × 11.8 Å for **3** and **4** respectively. The 4,4′-oda ligand behaves very similar to those in **1** and **2**. Since the central nitrogen atoms of the azide groups in **3** and **4** are located at the crystallographic inverse centers, the azide groups are exactly linear and coordinate to a pair of metal atoms in a *trans*-1,3-bridging fashion. The connection between an azide group and a metal atom is bent with N–N–Cd angle of 113.6(2)°and N–N–Co angle of 124.1(2)° for **3** and **4**, respectively. It is interesting to note that hydrogen bonding plays an important role in consolidating the crystal structures of **3** and **4**. Each nitrate group forms four acceptor hydrogen bonds with the amine groups ($N\cdots O = 3.060–3.189$ Å). The two-dimensional sheets are thus interconnected by these hydrogen bonds to furnish a three-dimensional network, as shown in Fig. 4.

Thermogravimetric Analysis

Complexes **1** and **2** were heated up to 600°C in N_2 gas. The TGA curve for **1** shows that the first weight loss at 262–285°C corresponds possibly to two HNCS molecules (observed 79.8%, calculated 79.8%), implying that the infinite double-stranded chain is still kept thermally stable). Upon further heating, the chain and the 4,4′-oda ligand decomposed between 350 and 600°C. The TGA curve for **2** shows that the first weight loss corresponds possibly to one HNCS molecule (observed 89.24%, calculated 89.91%) from 221–245°C. Upon further heating, decomposition occurred in 278–555°C.

Discussion

Different from the double chain structure of $[Ag(pytz)(MeCN)]PF_6$ [22] and the chains of equispaced loops/rings of $[Ag_2(bix)_3](NO_3)_2$ [20,21] and α-$[Co(dpe)_{1.5}(NO_3)_2]$ [25,26], the infinite chain of **1** features a double-stranded fashion similar to the one-dimensional chain $[Co(Py_2S)_2(NCS)_2]$ (Py_2S = 4,4′-dipyridyl sulfide) [35]. It is noteworthy that such double helix-like chains are rarely observed in the currently very active field of crystal engineering of solid state coordination polymers. The reason for the different structures between **1** and **2**, which have the same empirical formula and very similar octahedral metal centers, is unclear; yet it may be mainly attributed to the metal ions together with the fact that solid state coordination polymers of the flexible V-shaped organic spacers may exhibit drastic topological differences [35]. These observations strongly suggest that the rational design and assembly of solid-state coordination polymers is yet a challenge and that solid state coordination polymers of the flexible organic spacers may exhibit interesting topological diversity. The non-penetrating two-dimensional network of **2** is different from the interpenetrating two-dimensional networks of $[Cu(4,4'\text{-}bpy)(pyz)(H_2O)_2](PF_6)_2$ [9] $[Co(Py_2S)_2(Cl)_2]$ [35], $[Co(NCS)_2(bpy)_2]$ [36] and $[Co(bpy)_2(NO_3)2]\cdot 2C_6H_4Br_2$ [15].

When azide groups were used, we isolated the two-dimensional networks of **3** and **4**, constructed from the one-dimensional double-stranded chains in **1** and the 1,3-bridging azide groups. These observations indicate that the double-stranded chains in **1** may be used as building blocks in construction of higher dimensional architectures with suitable bridging ligands, and the azide is a very good inorganic bridge for construction of solid-state homometallic coordination polymers compared to thiocyanate, since the latter anion has both soft sulfur and hard nitrogen ends; and the soft end is not usually suitable for ligation of a hard metal center, according to the hard–soft acid-base concept [38]. Consequently, thiocyanate group usually utilizes only the nitrogen end in coordination to hard metal ions such as Ni^{II} and Co^{II}, as observed in **1**, **2** and the related complexes [35,37].

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