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Two Versatile *N,N′*-Bipyridine-Type Ligands for Preparing Organic−Inorganic Coordination Polymers: New Cobalt- and Nickel-Containing Framework Materials

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The Schiff base ligands 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (**L1**, monoclinic, $P2_1/c$, $a = 3.856(1)$ Å, $b = 11.032(2)$ Å, $c = 12.738(3)$ Å, $\beta = 92.21(3)°$, $Z = 2$) and 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene (**L2**, monoclinic, $P2_1/c$, $a = 10.885(2)$ Å, $b = 4.613(1)$ Å, $c = 14.978(3)$ Å, $\beta = 92.827(4)$ °, $Z = 2$) were used in the synthesis of four new organic−inorganic coordination polymers, each of them adopting a different structural motif. Synthesis, X-ray structural determinations, and spectroscopic and thermogravimetric analyses are presented. The reaction between $Co(NO_3)_2{\cdot}6H_2O$ and **L1** afforded a two-dimensional noninterpenetrating brick-wall structure, $[Co(C_{12}N_4H_{10})_{1.5}(NO_3)_2(H_2O)(CH_2Cl_2)_2]_n$ (**1**, triclinic, $P\bar{1}$; $a = 10.242(7)$ Å, $b = 10.802(7)$ Å, $c = 15.100(1)$ Å, $\alpha = 70.031(1)$, $\beta = 75.168(11)$, $\gamma = 76.155(11)$, $Z = 2$), while $Ni(NO_3)_2{\cdot}6H_2O$ combined with **L1** yielded an interpenetrating three-dimensional rhombus-grid polymer, $[Ni(C_{12}N_4H_{10})_2(NO_3)_2(OC_4H_8)_{1.66}(H_2O)_{0.33}]_n$ (**2**, monoclinic, $C2/c$; $a = 20.815(8)$ Å, $b = 23.427(8)$ Å, $c = 17.291(6)$ Å, $\beta = 116.148(6)$, $Z = 8$). The reaction of $Co(NO_3)_2{\cdot}6H_2O$ and **L2** was found to be solvent-sensitive and resulted in the formation of two different noninterpenetrating compounds: $[Co(C_{14}N_4H_{14})_2(NO_3)_2(C_6H_6)_{1.5}]_n$ (**3**, monoclinic, $C2/c$; $a = 22.760(2)$ Å, $b = 21.010(3)$ Å, $c = 25.521(2)$ Å, $\beta = 97.151(2)$, $Z = 8$), which adopts a two-dimensional square-grid motif formed by propeller-type modules, and $[Co(C_{14}N_4H_{14})_{1.5}(NO_3)_2(CH_2Cl_2)_2]_n$ (**4**, monoclinic, $P2_1/n$; $a = 14.432(2)$ Å, $b = 14.543(8)$ Å, $c = 15.448(4)$ Å, $\beta = 96.968(0)$, $Z = 4$), consisting of T-shaped building blocks assembled into a one-dimensional ladder-type structure. These four coordination polymers all exhibit impressive thermal stability. Thermogravimetric studies showed that after complete removal of the solvents, the frameworks are stable to temperatures between 234 °C and 260 °C.

Introduction

Synthesis of new organic−inorganic hybrid compounds is a relatively new research area that has evolved rapidly in the last several years. In particular, the formation of porous framework structures makes these materials potential candidates for use in applications ranging from catalysis and molecular recognition to selective sorption materials, while other structure types can potentially be useful in the areas of nonlinear optics, ion exchange and magnetism.[1−5] While the precise assembly of such extended structures cannot yet be fully controlled, it is nonetheless possible to apply fundamental aspects of coordination chemistry (the identity and oxidation state of the metal,[6] the length and geometry of the organic ligand,[7−11] the relative orientation of the ligand donor group[12−14]) to direct the overall architecture. For example, the choice of the ligand is clearly of great importance in determining the final topology of these materials. In this context, bipyridyl-based ligands, rigid or flexible, separated by different spacers, such as ethyne, ethane, or propane have been widely employed and have led to a large group of novel networks with various shapes and sizes of pores and channels.[15−20] The length of the organic moiety, also, has a great impact on the polymer topology, especially on the size

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Table 1. Crystallographic Data for **L1**, **L2**, **1**, **2**, **3**, and **4**

	L1	**L2**	**1**	**2**	**3**	**4**
empirical formula	$C_{12}H_{10}N_4$	$C_{14}H_{18}N_4O_2$	$C_{20}H_{19}Cl_4CoN_8O_7$	$C_{30.64}H_{33.94}NiN_{10}O_{7.99}$	$C_{55.5}H_{55.5}Co_{1.5}N_{15}O_9$	$C_{23}H_{25}Cl_4CoN_8O_6$
fw	210.24	274.32	684.16	1458.77	1165.04	710.24
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
a (Å)	3.8560(8)	10.885(2)	10.242(7)	20.815(8)	22.760(2)	14.432(3)
b (Å)	11.032(2)	4.6131(9)	10.802(7)	23.427(8)	21.010(3)	14.544(3)
c (Å)	12.738(3)	14.978(3)	15.100(1)	17.291(6)	25.521(2)	15.448(3)
α (deg)	90	90	70.03(1)	90	90	90
β (deg)	92.21(3)	92.82(7)	75.16(8)	116.14(8)	97.15(1)	96.97(3)
γ (deg)	90	90	76.15(5)	90	90	90
V (Å^3)	541.45(19)	751.2(3)	1496.4(1)	7569.(5)	12109.0(1)	3218.7(1)
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$C2/c$	$C2/c$	$P2_1/n$
Z value	2	2	2	8	8	4
ρ_{calc} (g/cm^3)	1.29	1.21	1.51	1.28	1.27	1.46
μ (Mo Kα) (cm^{-1})	0.0082	0.0084	0.0982	0.057	0.0481	0.0914
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
temp (°C)	20	20	−80	20	20	20
residuals:[a] R1, wR2	0.039; 0.101	0.060; 0.170	0.061; 0.142	0.067; 0.2019	0.063; 0.191	0.056; 0.148

[a] $R1 = \sum||F_o| - |F_c||/\sum |F_o|$. $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $GOF = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$ (n = no. refl; p = no. refined parameters). $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where P is $[2F_c^2 + \max(F_o^2, 0)]/3$.

Table 2. Interatomic Distances (Å) and Bond Angles (deg) with esds (in parentheses) for **1**, **2**, **3**, and **4**

	$C_{20}H_{19}Cl_4CoN_8O_7$, **1**		
Co−N(1)	2.129(4)	N(1)−Co−N(3)	99.75(1)
Co−N(3)	2.129(4)	N(1)−Co−N(5)	86.02(1)
Co−N(5)	2.168(4)	N(1)−Co−O(1)	83.57(1)
Co−O(1)	2.372(4)	N(1)−Co−O(4)	85.86(1)
Co−O(2)	2.129(4)	O(1)−Co−O(2)	56.42(1)
Co−O(4)	2.223(4)	O(4)−Co−O(5)	56.92(1)
Co−O(5)	2.280(4)		
N(2)−N(2A)	1.418(8)		
	$C_{30.64}H_{33.94}NiN_{10}O_{7.99}$, **2**		
Ni(1)−N(1)	2.134(3)	N(1)−Ni(1)−N(1A)	85.52(1)
Ni(1)−N(2)	2.145(3)	N(1)−Ni(1)−N(2)	95.07(1)
Ni(1)−O(1)	2.085(3)	O(1)−Ni(1)−N(2)	85.53(1)
N(11)−N(21)	1.411(5)	N(4)−Ni(2)−N(4A)	93.75(1)
Ni(2)−N(4)	2.100(3)	N(5)−Ni(2)−N(5A)	90.69(1)
Ni(2)−N(5)	2.115(3)	N(4)−Ni(2)−O(4)	98.97(1)
Ni(2)−O(4)	2.102(4)		
	$C_{55.5}H_{55.5}Co_{1.5}N_{15}O_9$, **3**		
Co(1)−N(1)	2.159(1)	N(1)−Co(1)−N(1B)	92.44(5)
Co(1)−N(4)	2.166(1)	N(4)−Co(1)−N(4B)	91.91(5)
Co(1)−O(1)	2.100(1)	O(1)−Co(1)−O(1B)	175.35(6)
Co(2)−N(6)	2.166(1)	N(1)−Co(1)−O(1)	95.8(1)
Co(2)−N(9)	2.142(1)	N(9)−Co(2)−N(13)	92.1(1)
Co(2)−N(10)	2.145(1)	N(9)−Co(2)−N(10)	87.9(1)
Co(2)−N(13)	2.143(1)	N(6)−Co(2)−N(13)	89.3(1)
Co(2)−O(4)	2.094(1)	O(4)−Co(2)−O(7)	175.89(6)
Co(2)−O(7)	2.107(1)	O(4)−Co(2)−N(6)	91.0(1)
N(2)−N(3)	1.391(1)		
	$C_{23}H_{25}Cl_4CoN_8O_6$, **4**		
Co−N(1)	2.156(3)	N(1)−Co−N(5)	89.08(1)
Co−N(3)	2.120(3)	N(1)−Co−N(3)	91.52(1)
Co−N(5)	2.141(3)	O(1)−Co−O(2)	56.56(1)
Co−O(1)	2.247(3)	O(4)−Co−O(5)	56.13(1)
Co−O(2)	2.239(3)		
Co−O(4)	2.338(3)		
Co−O(5)	2.187(3)		

of pores or channels, and on whether the structure is interpenetrating or noninterpenetrating.[21,22] Consequently, we have chosen two long, rigid bipyridyl-based ligands, 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (**L1**) and 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene (**L2**) to react with $Co(NO_3)_2{\cdot}6H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$ to direct the formation of organic−inorganic coordination polymers with large channels. The nitrate anion was chosen because it is known to promote T-shaped building blocks, which further assemble into several different commonly observed structural motifs: ladder, brick wall, parquet, and 3D frameworks.[8,13,23−28] In addition, the T-shaped module can sometimes convert to a propeller type building block that forms extended square-grid and rhombus-grid patterns.[29−34] In this work we report the synthesis, crystal structures, and thermogravimetric analysis of four new organic−inorganic polymers. Two coordination polymers have been obtained with the **L1** ligand, $[Co(C_{12}N_4H_{10})_{1.5}(NO_3)_2(H_2O)(CH_2Cl_2)_2]_n$ (**1**) and $[Ni(C_{12}N_4H_{10})_2(NO_3)_2(OC_4H_8)_{1.66}(H_2O)_{0.33}]_n$ (**2**), which form a noninterpenetrating brick-wall framework (**1**), and an interpenetrating rhombus-grid framework (**2**), respectively. Two other coordination polymers were synthesized with the **L2** ligand, $[Co(C_{14}N_4H_{14})_2(NO_3)_2(C_6H_6)_{1.5}]_n$ (**3**) and $[Co(C_{14}N_4H_{14})_{1.5}(NO_3)_2(CH_2Cl_2)_2]_n$ (**4**) which form a square-grid structure (**3**) and a ladder-type network (**4**), respectively.

Experimental Section

Materials and Methods. $Co(NO_3)_2{\cdot}6H_2O$ (Aldrich, 98%), $Ni(NO_3)_2{\cdot}6H_2O$ (Alfa Aesar, Technical Grade), pyridine-4-carboxaldehyde (Avocado, 98%), 4-acetylpyridine (Avocado, 98%), hydrazine (Aldrich, 35 wt % solution in water), were used without further purification. IR

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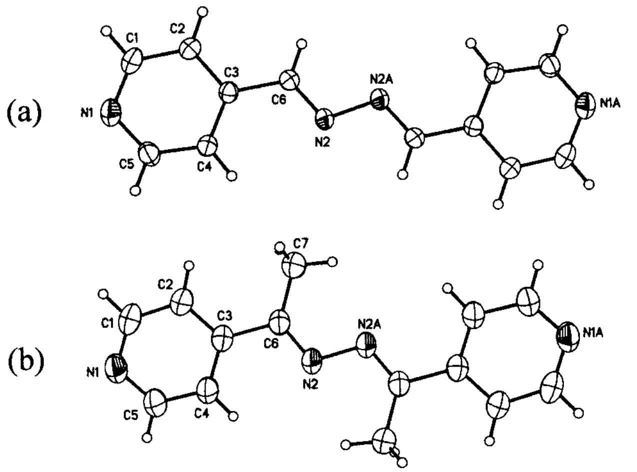

Figure 1. ORTEP representation of (a) 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene, **L1**, and (b) 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene, **L2**. Ellipsoids are shown with 30% probability.

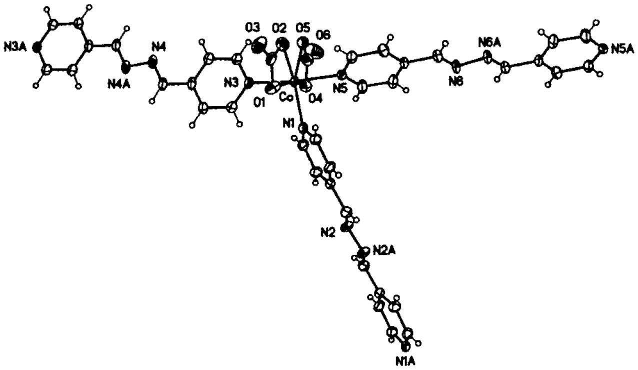

Figure 2. The "T-shaped" environment at the cobalt center in **1**, drawn with 30% probability ellipsoids.

spectra were recorded on a Nicolet 740 FTIR spectrometer as KBr pellets in the 4000−400 cm^{-1} range. Thermogravimetric anlyses were carried out on a TA Instruments SDT 2960 simultaneous DTA-TGA under flowing helium. Compounds **1**, **2**, **3**, and **4** were heated from 50 to 500 °C at a rate of 5 °C/min. Elemental analysis was performed by Robertson Microlit Laboratories. Since compounds **1**, **2**, **3**, and **4** lose solvent when removed from the mother liquors, analyses were performed on samples heated gently (below 60 °C) until a constant weight was achieved.

X-ray Structure Determinations. Crystal data and refinement statistics for ligands **L1**[35] and **L2** and for compounds **1**−**4** are given in Table 1. All crystals were mounted on the tips of glass fibers with epoxy; measurements were carried out at room temperature except for **1**, which was unstable with respect to solvent loss. Therefore **1** was coated in inert oil and quickly transferred to a cold N_2 stream; data were collected at −80 °C.

L1 and 4. Data were collected on a Rigaku AFC6s diffractometer (Mo Kα, $\lambda = 0.71073$ Å). Crystal quality and unit cell parameters were initially determined based on 25 reflections located with a random search-and-center routine and subsequently refined using 25 high-angle reflections after data collection. Three standard reflections measured every 150 reflections showed no significant decay in either case. Corrections for Lorentz and polarization effects were made during data processing, and subsequently the structures were solved by direct methods and refined by full matrix least squares against F^2, using SHELXTL.[36] After locating and refining all non-hydrogen atoms with isotropic displacement parameters, an absorption correction (DIFABS[37]) was applied to **4**; no correction for absorption was made for **L1**. All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were placed in calculated positions and refined using a riding model.

1, 2, 3 and L2. In each case, hemispheres of X-ray intensity data were collected on Bruker SMART CCD-based diffractometers (SMART 1000 for **1** and **2**, SMART APEX for **L2** and **3**), equipped with Mo Kα radiation ($\lambda = 0.71073$ Å). The first 50 frames were re-collected at the end of the process to monitor crystal decay; no significant decay was observed in any case. The raw frame data for **1**, **2**, **3**, and **L2** were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT.[38] Corrections for incident and diffracted beam absorption effects were applied using SADABS[38] except in the case of **L2**, where no absorption correction was applied. All structures were solved by direct methods and refined against F^2 by the full-matrix least squares technique. Hydrogen atoms were calculated and refined as riding atoms; all non-hydrogen atoms were refined with anisotropic displacement parameters. Relevant interatomic bond distances and bond angles for all compounds are given in Table 2.

Synthesis. 1,4-Bis(4-pyridyl)-2,3-diaza-1,3-butadiene (L1). 1 mL (11 mmol) of hydrazine was added dropwise to a solution of pyridine-4-carboxaldehyde (2.2 mL, 22 mmol) dissolved in ethanol (15 mL). Two drops of formic acid were added and the mixture was stirred at room temperature for 24 h. The yellow solid that formed was filtered and washed several times with ethanol/ether (1:1). Yield, 86%.

2,5-Bis(4-pyridyl)-3,4-diaza-2,4-hexadiene (L2). Ligand **L2** was obtained similarly to **L1**, except that 4-acetylpyridine was used instead of pyridine-4-carboxaldehyde. The mixture was slightly warmed and

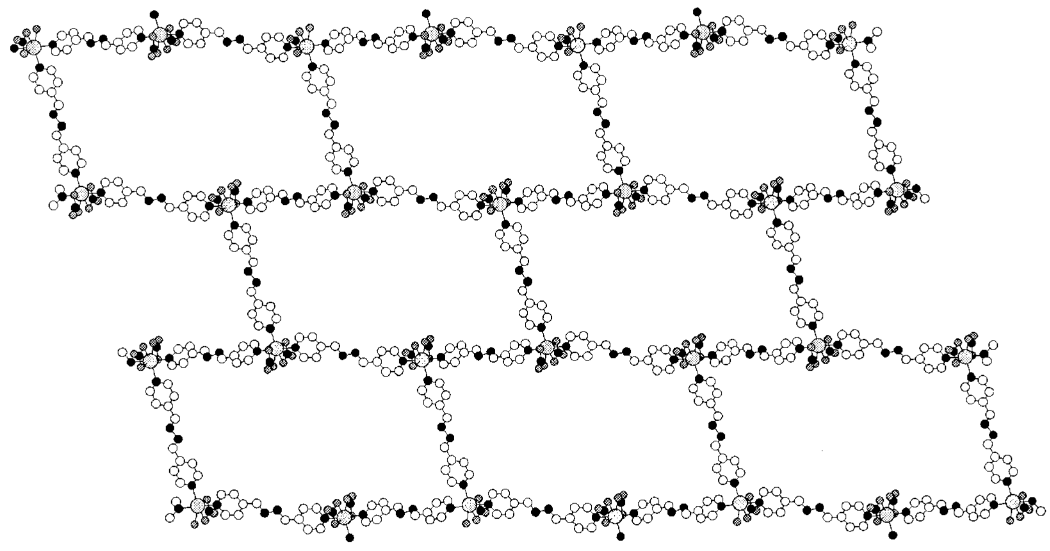

Figure 3. View of **1** down the *c* axis, perpendicular to the brick wall layers. Co atoms are shown as larger shaded circles; N atoms, black circles; O atoms, smaller shaded circles; C atoms, white circles.

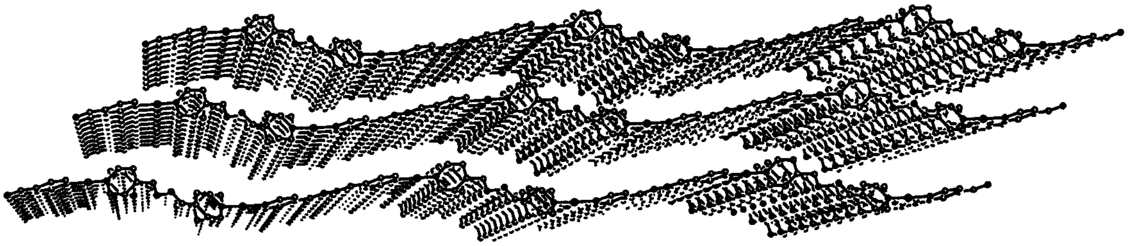

Figure 4. Perspective view of the packing of the undulating brick wall layers in **1**. Nitrates and molecules of solvent have been omitted for clarity (Co centers are shown as black circles).

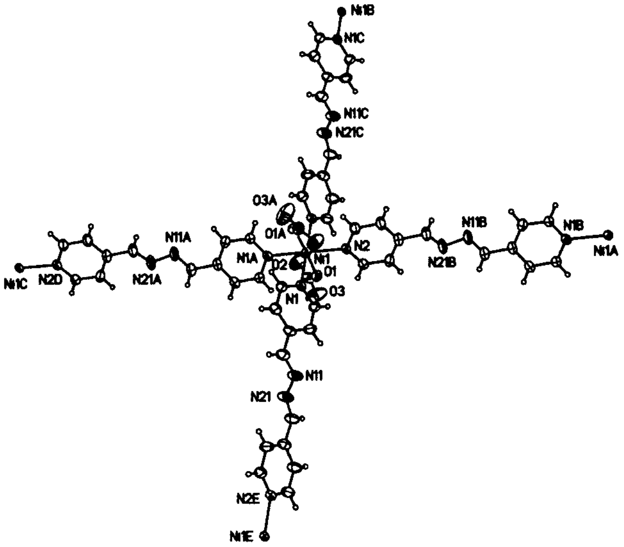

Figure 5. Propeller type environment around the nickel center in **2**. Atoms are shown as ellipsoids at 30% probability.

then allowed to cool to room temperature. A yellow-orange crystalline solid formed and was isolated by filtration. Yield, 30%.

$[Co(C_{12}N_4H_{10})_{1.5}(NO_3)_2(H_2O)(CH_2Cl_2)_2]_n$ (1). An ethanol solution of $Co(NO_3)_2 \cdot 6H_2O$ (0.2 mmol, 6 mL) was mixed with 0.4 mmol of **L1** dissolved in methylene chloride (8 mL) and allowed to sit at room temperature. After 3 days, red crystals formed in 78% yield based on cobalt nitrate. IR (KBr, cm^{-1}): 1609 (s), 1552 (w), 1465 (m), 1424 (s), 1383 (s), 1301 (s), 1235 (m), 1061 (m), 1015 (m), 953 (w), 871 (w). Anal. Calcd: C, 39.77%; H, 3.24%. Found: C, 39.86%; H, 3.93%.

$[Ni(C_{12}N_4H_{10})_2(NO_3)_2(OC_4H_8)_{1.66}(H_2O)_{0.33}]_n$ (2). 0.2 mmol of $Ni(NO_3)_2 \cdot 6H_2O$ was dissolved in 6 mL of ethanol, then carefully layered onto a solution of **L1** in tetrahydrofuran (0.4 mmol, 8 mL) and allowed to stand at room temperature. In approximately two weeks, green crystals grew at the interface of the above solutions in 80% yield based on nickel nitrate. IR (KBr, cm^{-1}): 1761 (w), 1613 (m), 1548 (m), 1498 (w), 1414 (m), 1382 (s), 1308 (m), 1234 (m), 1058 (m), 1016 (m), 947 (w). Anal. Calcd: C, 48.70%; H, 3.95%. Found: C, 48.37%; H, 3.31%.

$[Co(C_{14}N_4H_{14})_2(NO_3)_2(C_6H_6)_{1.5}]_n$ (3). Compound **3** was synthesized in a similar way to **2**, except that ligand **L1** was replaced by **L2**, tetrahydrofuran by benzene, and $Ni(NO_3)_2 \cdot 6H_2O$ by $Co(NO_3)_2 \cdot 6H_2O$. Also, methanol was used instead of ethanol. In 4 days, deep red crystals were obtained in 80% yield based on cobalt nitrate. IR (KBr, cm^{-1}): 1614 (s), 1542 (w), 1414 (m), 1383 (s), 1291 (m), 1219 (m), 1061 (m), 1015 (m), 825 (m). Anal. Calcd: C, 52.49%; H, 4.37%. Found: C, 52.06%; H, 4.16%.

$[Co(C_{14}N_4H_{14})_{1.5}(NO_3)_2(CH_2Cl_2)_2]_n$ (4). Compound **4** was synthesized using a procedure similar to that for **3**, but this time the ligand **L2** was dissolved in methylene chloride. Deep red crystals were obtained in 81% yield based on cobalt nitrate. IR (KBr, cm^{-1}): 1609 (s), 1542 (w), 1434 (s), 1368 (m), 1291 (s), 1219 (m), 1061 (m), 1015 (s), 830 (m). Anal. Calcd: C, 39.83%; H, 3.57%. Found: C, 39.51%; H, 3.68%.

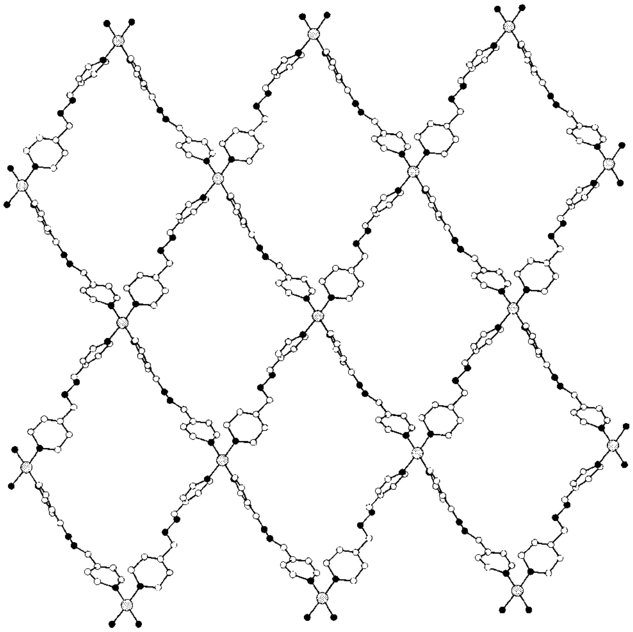

Figure 6. View of the rhombus grid layer in **2**, with nitrates omitted for clarity. (Co atoms, dark gray; N atoms, black; C atoms, white.)

Results and Discussion

The two ligands **L1** and **L2** have been synthesized using a Schiff base condensation reaction with 4-pyridyl aldehyde (**L1**), 4-acetylpyridine (**L2**), and hydrazine as starting materials. Although their synthesis was reported by Chen et al. and more recently again by Baer and Macartney using a synthetic approach different from ours,[39a,b] to our knowledge, these ligands haven not been utilized in the preparation of organic−inorganic frameworks. We were able to grow crystals of **L1** by dissolving the polycrystalline material in methylene chloride and allowing the solvent to evaporate at room temperature. Crystals of **L2** were obtained in the synthesis process while the reaction mixture was cooling to room temperature. The solid-state molecular structures of **L1** and **L2** were determined using single-crystal X-ray diffraction. In both cases, the two pyridyl rings are coplanar, and are linked at the *para* position by a zigzag $-HC{=}N{-}N{=}CH-$ spacer in the case of **L1**, and by its homologue $-(CH_3)C{=}N{-}N{=}C(CH_3)-$ in the case of **L2** (Figure 1a and 1b).

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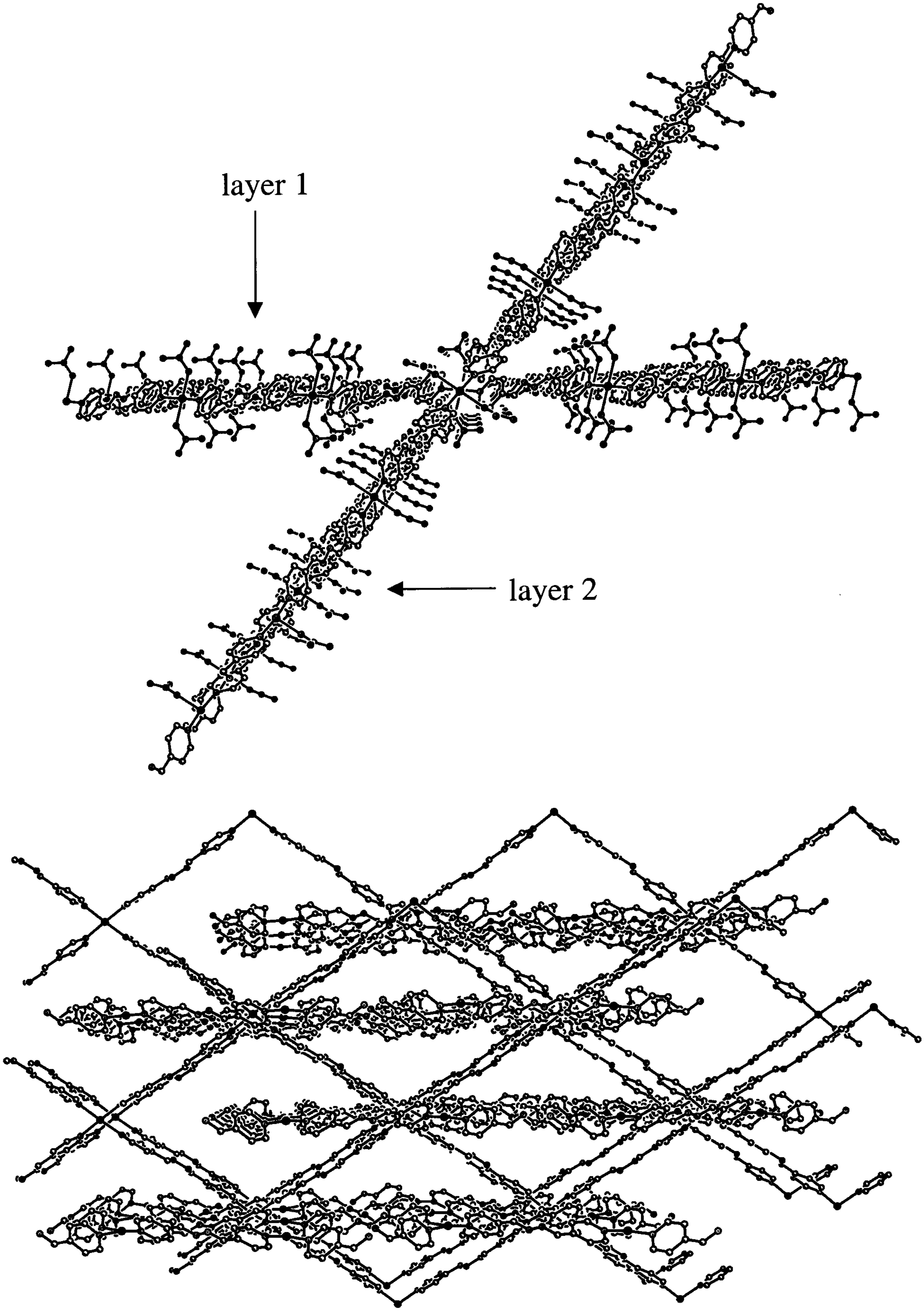

Figure 7. Top: Interpenetration of two rhombus grid layers in **2**. Bottom: Perspective view of the interpenetrating three-dimensional network of **2**. Molecules of methylene chloride and water have been omitted for clarity.

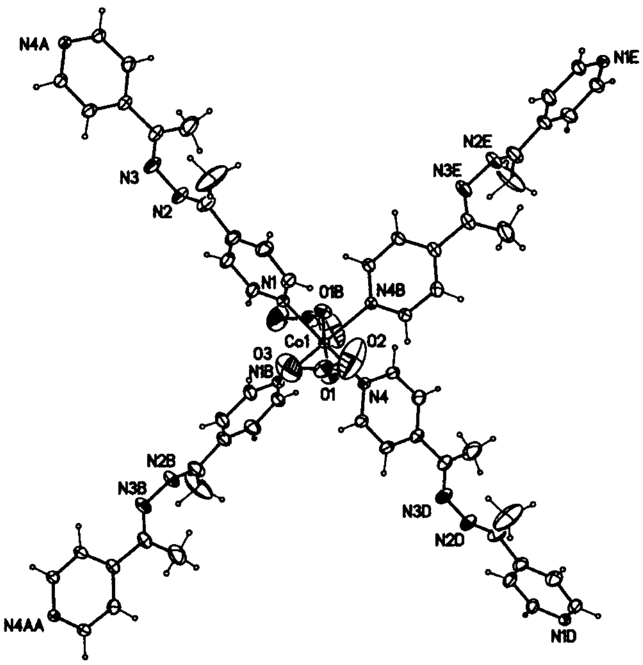

Figure 8. Propeller type environment around the cobalt center in **3**. Atoms are shown with 30% probability thermal ellipsoids.

Compound **1** was obtained by mixing a solution of $Co(NO_3)_2 \cdot 6H_2O$ dissolved in ethanol with a solution of **L1** dissolved in methylene chloride. The metal-to-ligand ratio and the solvent[40−43] both proved to have a direct influence in the synthesis of the polymeric structure of **1**. Although several different ratios (1:2, 1:3, 1:4) and solvents (chloroform, acetonitrile) were tried, only in the case of a 1:2 ratio and the use of methylene chloride as the solvent did the reaction result in an isolatable product.

The slow diffusion of a solution of $Ni(NO_3)_2 \cdot 6H_2O$ in ethanol into a solution of **L1** dissolved in tetrahydrofuran resulted, in approximately two weeks, in the formation of green crystals of **2**. In contrast with the cobalt/**L1** system, the nickel/**L1** system yielded the same product regardless of the metal-to-ligand ratio (1:1.5, 1:2, 1:3, 1:4) or the solvent (methylene chloride, tetrahydrofuran, chloroform) used.

Compounds **3** and **4** were obtained by the slow diffusion of a methanolic $Co(NO_3)_2 \cdot 6H_2O$ solution into a solution of **L2** in benzene or methylene chloride, respectively. Interestingly, the solvent system had a dramatic impact on the resulting extended structures; when benzene was used, a two-dimensional square-grid framework was obtained while methylene chloride gave a one-dimensional ladder-type structure.

Compounds **1**, **2**, **3**, and **4** are insoluble in water and common organic solvents. Exposed to air, crystals of **1**, **2**, **3**, and **4** lose molecules of solvent and become opaque within minutes. Although the general aspect of the crystal framework is preserved upon solvent loss, such crystals can no longer be used for single crystal studies. Consequently, for single crystal diffraction studies, suitable crystals were encased in epoxy, effectively sealing in the solvent and stabilizing the crystals for days to weeks.

Crystal Structure of 1. Each Co(II) atom adopts a distorted pentagonal bipyramid geometry (Figure 2). This heptacoordinate environment is generated by three **L1** ligands bound in a T-joint fashion and two nitrates coordinated in bidentate modes. The Co−O bond lengths range between 2.129(4) Å and 2.280(4) Å, while the Co−N bond length range is 2.129(4)−2.168(4) Å, all consistent with values reported in the literature.[30,41,44,45] The angles of the T-joint around the cobalt centers reflect a slightly distorted geometry N(3)−Co−N(1) = 99.75(1)°, N(1)−Co−N(5) = 86.02(1)°, N(5)−Co−N(3) = 173.69(1)°. Nevertheless, the self-assembly of the T-joint building blocks results in a brick wall type pattern (Figure 3); these brick wall layers contain pores of relatively large dimensions, ca. 30×15 Å^2. A deviation from planarity is observed among the pyridyls that coordinate the cobalt centers. The dihedral angles formed by the planes of adjacent coordinated pyridyls from two adjacent ligands are 62.2° or 65.9°. As shown in Figure 4, the undulating brick wall layers stack in three dimensions to give a noninterpenetrating open framework; large channels run perpendicular to the plane of these layers. The nitrate ions point into the channels and occupy the "axial" positions around the cobalt atoms, while the ligands are occupying the "equatorial" positions. The channels are filled with two molecules of methylene chloride and one molecule of water per each cobalt center.

Crystal Structure of 2. Figure 5 shows the pseudo-octahedral six-coordinated Ni(II) centers. Four **L1** ligands, occupying "equatorial" positions, coordinate the metal ions via pyridyl nitrogen atoms to form a distorted square planar geometry

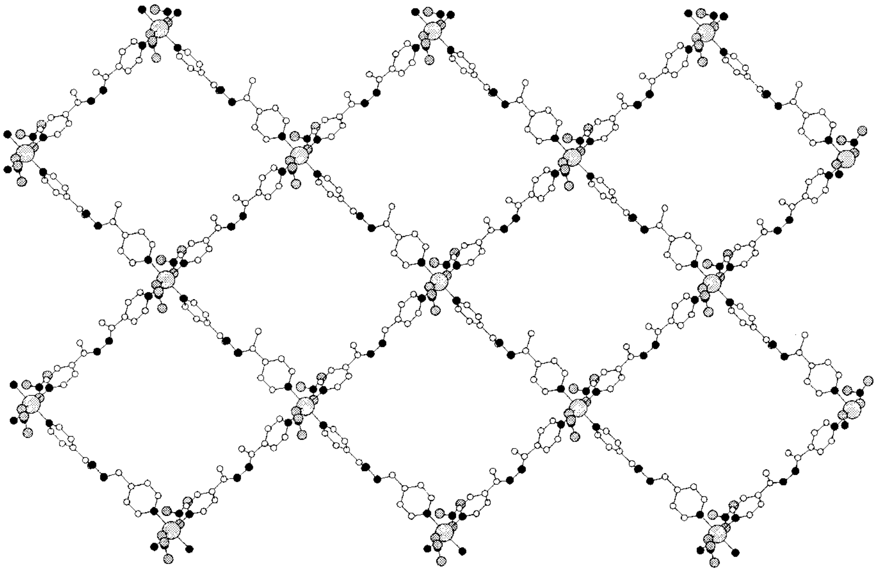

Figure 9. View perpendicular to a square grid layer of **3**. Co atoms are shown as larger shaded circles; N atoms, black circles; O atoms, smaller shaded circles; C atoms, white circles.

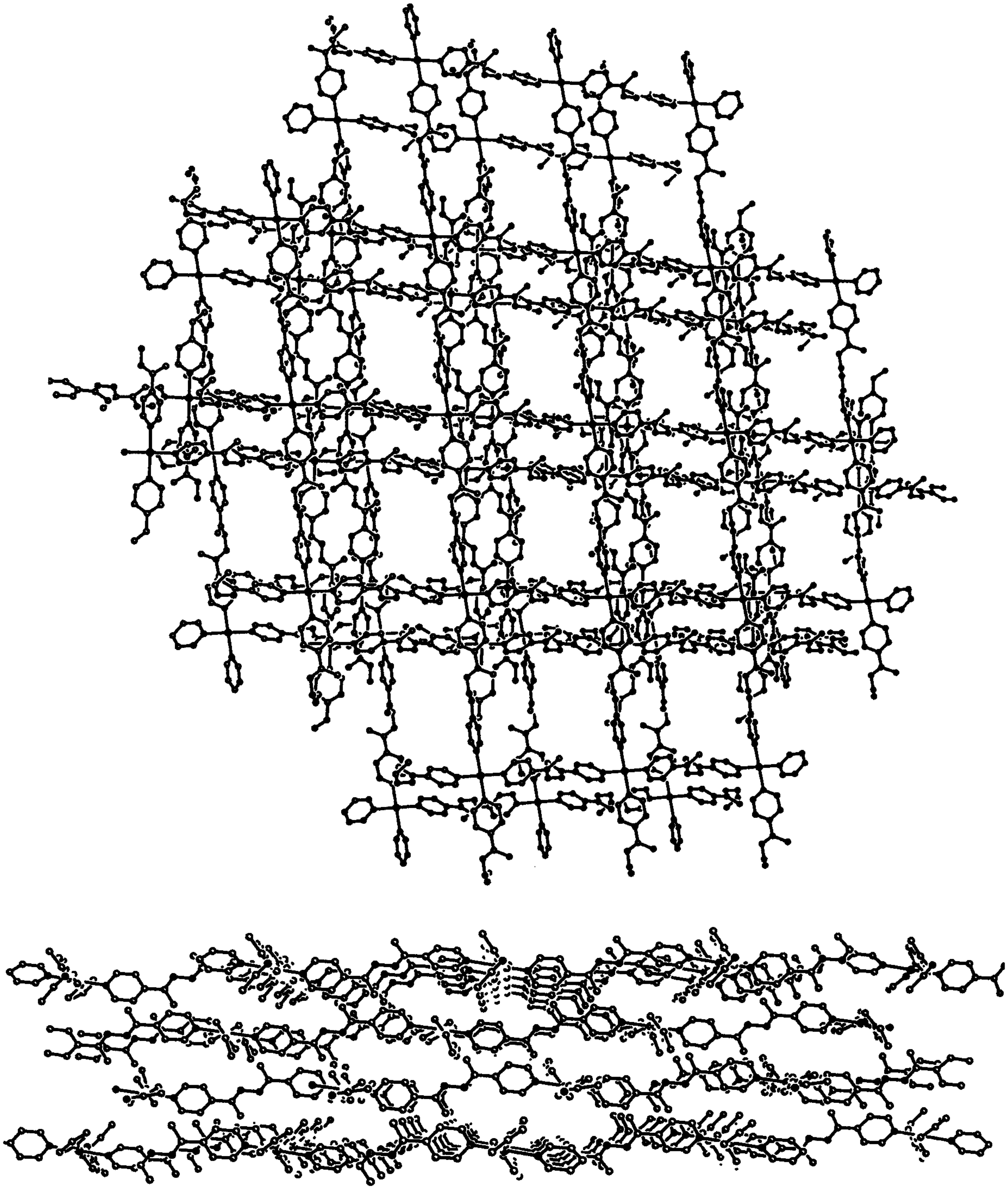

Figure 10. Top: Repeating ABBA sequence of the square grid layers in **3**. Bottom: Perspective view of the packing of the square grids.

(N(1)−Ni(1)−N(2) = 95.07(1)°, N(1)−Ni(1)−N(1A) = 85.52(1)°). The two pyridyls in the individual **L1** molecules are coplanar but are twisted by an angle of 65.6° with respect to the pyridyls of adjacent coordinated **L1** molecules. The Ni coordination sphere is completed by two monodentate nitrate ions occupying the "axial" positions. The Ni−N bond lengths range from 2.100(3)−2.145(3) Å and the Ni−O bond lengths range from 2.085(3)−2.102(4) Å. Modules of [Ni(**L1**)$_{4/2}$] are assembled in two-dimensional rhombus-grid layers (Figure 6), which stack to form a porous layer framework with pore dimensions of ca. 15.5 × 15.5 Å. However, the accessible pore dimensions of the full three-dimensional structure is drastically reduced by interpenetration. There are two crystallographically independent but topologically identical rhombus-grid layers in the structure. One set of layers runs parallel to the crystallographic *ab* plane and the second set cuts through the first layer at a 65.6° angle, parallel to the crystallographic (1 0−1) plane, generating a three-dimensional interpenetrating structure (Figure 7). Despite this interpenetration and the presence of solvent and water molecules in the cavities (two molecules per metal center), a small amount of the entire polymer volume (7.3%, as calculated with PLATON[46]) is still solvent accessible.

Crystal Structure of 3. In compound **3** each cobalt(II) center adopts a distorted pseudo-octahedral geometry (Figure 8). Four **L2** ligands are coordinated to the metal ions in a propeller type fashion in the "equatorial" positions, while two monodentate "axial" nitrate anions complete the Co coordination sphere. The bond distances between the cobalt and the pyridyl nitrogen

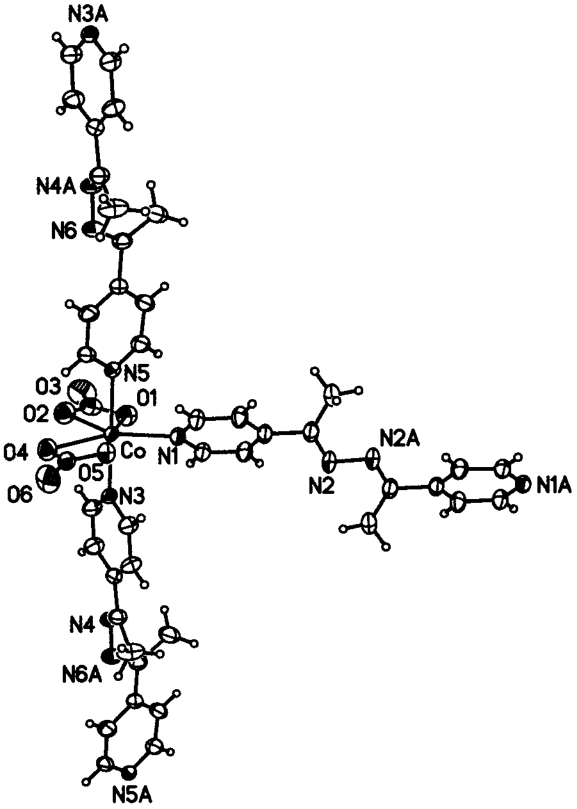

Figure 11. The T-shaped coordination environment around the cobalt centers in **4**.

atoms vary between 2.142(1)−2.166(1) Å, while the cobalt−oxygen bond lengths are shorter, 2.094(1)−2.107(1) Å. These distances are all consistent with literature values. In each individual **L2** ligand, the pyridyl rings are rotated with respect to one another and have become nearly perpendicular (106.9°) rather than the usual coplanar arrangement. Similar to compound **2**, the [Co(**L2**)$_{4/2}$] units assemble in two-dimensional square grid nets (Figure 9), which stack along the crystallographic *c* axis in an (...ABBA...) fashion. Two crystallographically different cobalt ions, Co(1) and Co(2), form two noninterpenetrating nets which, although identical in size (15.48 × 15.48 Å), are arranged slightly differently. The Co(1) sheets, with a perpendicular interlayer distance of 12.92 Å, are separated by two interleaving Co(2) sheets with a perpendicular interlayer distance of 9.22 Å. The Co(2) sheets are slightly shifted with respect to the Co(1) sheets (Figure 10) and, consequently, the size of the cavities in the overall structure is reduced to approximately 11 × 11 Å^2. The pores are partially filled with benzene, 1.66 molecules per each metal center.

Crystal Structure of 4. The cobalt(II) centers have the same pentagonal bipyramidal geometry as observed in compound **1**, with two bidentate nitrates, one **L2** ligand in the basal plane and two other **L2** ligands in trans positions (Figure 11). The **L2** ligands, arranged in a T-joint fashion (N(3)−Co−N(1) = 91.52(1)°, N(1)−Co−N(5) = 89.08(1)°), give rise to a one-dimensional ladder type structure (Figure 12). All pyridyls within the individual **L2** molecules are coplanar, while the three pyridyls from the three **L2** ligands immediately surrounding the cobalt atoms are rotated by 55.1°and 64.8° angles with respect to each other. The ladders run along the crystallographic *c* axis. Two groups of ladders are packed together in a herringbone type structure, as shown in Figure 13. Two molecules of methylene chloride per metal center partially fill the space between ladders.

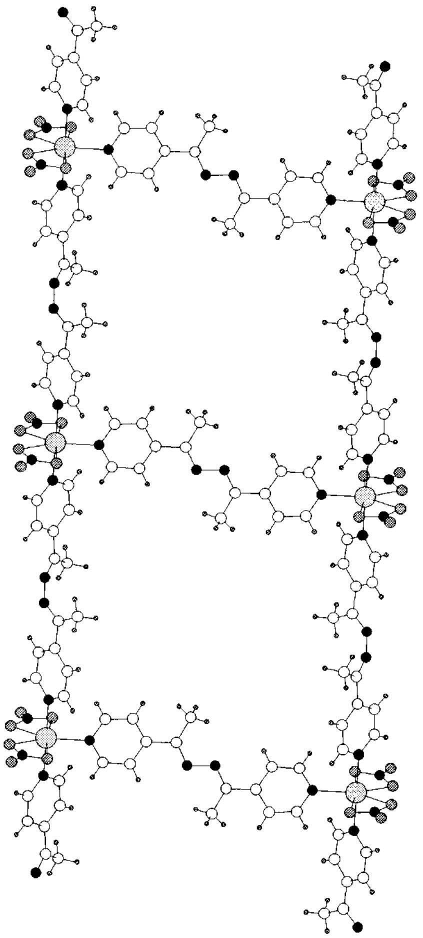

Figure 12. View of a single ladder in **4**. Co atoms are shown as larger shaded circles; N atoms, black circles; O atoms, smaller shaded circles; C atoms, white circles.

Thermogravimetric Analyses. Thermogravimetric analyses (TGA) have been performed on compounds **1**−**4** by heating each compound to 500 °C in an atmosphere of flowing helium. TGA for **1** showed the loss of methylene chloride between 70 °C and 234 °C (calculated 7.60%, observed 7.58%). Between 234 °C and 286 °C a significant mass loss occurred, corresponding to the removal of the water molecule, all the **L1** ligand molecules, and one nitrate (calculated 78.40%, observed 78.69%). A black residue remained. The framework of compound **2** was stable up to 255 °C. The first weight loss took place between 90 °C and 255 °C and was associated with the loss of the tetrahydrofuran, the water, and the two nitrate anions (calculated 27.03%, observed 27.13%). Above 255 °C a massive weight loss was observed, corresponding to the decomposition of the framework. TGA for **3** shows that the benzene molecules and the two nitrate ions were lost in the temperature range of 90−257 °C (calculated 21.86%, observed 21.65%). Above that temperature the **L2** ligands were lost (calculated 73.98%, observed 73.83%) and a black solid remained. In compound **4**, the framework is stable up to 260 °C. The first weight loss, between 65 °C and 165 °C, is due to the loss of all methylene chloride molecules (calculated 24.74%, observed 24.70%). Starting around 260 °C the **L2** ligands decompose and leave a black solid behind.

Effect of Ligands on Structure: The synthesis of these four coordination polymers is part of an extended project currently underway in our group, one goal of which is the synthesis of novel, multifunctional rigid pyridyl-based ligands with long spacers between the pyridyl rings. Coordinated to different

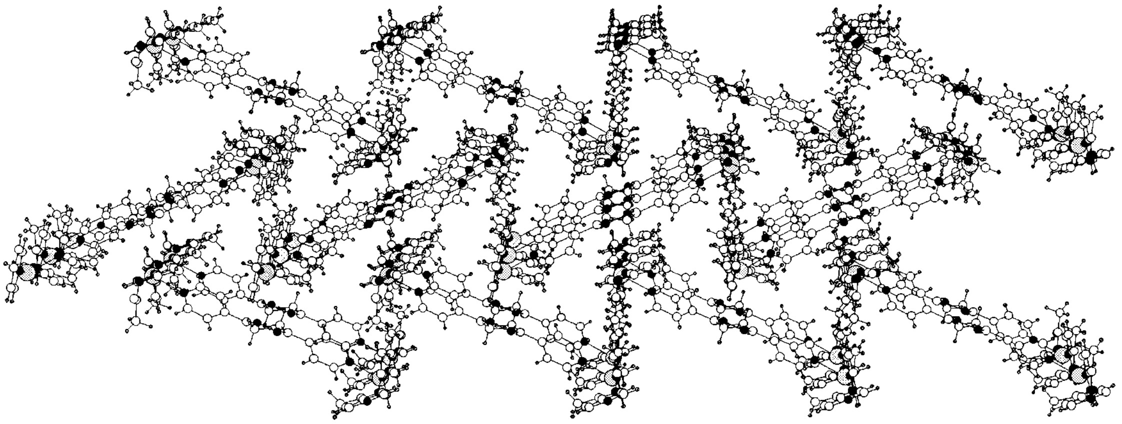

Figure 13. Perspective view of ladders packed together in the herringbone type structure of **4** (molecules of methylene chloride have been omitted).

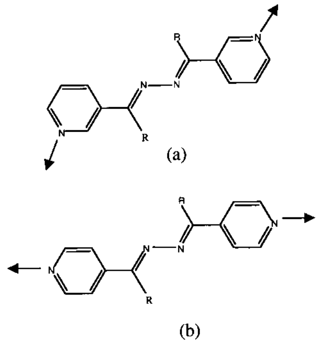

Figure 14. (a) 1,4-Bis(3-pyridyl)-2,3-diaza-1,3-butadiene (R═H), **L3**, or 2,5-bis(3-pyridyl)-3,4-diaza-2,4-hexadiene (R═CH_3), **L4**; (b) **L1** (R═H) or **L2** (R═CH_3).

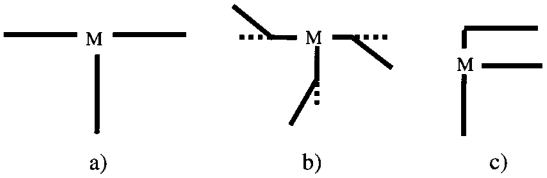

Figure 15. Schematic view of a common T-joint (a), a distorted T-joint (b), and an F-joint (c).

metals, these ligands may eventually lead to new organic−inorganic polymeric frameworks having sizable pores and channels, although it is known that longer organic spacers may result in higher degree of interpenetration. The relative orientation of the pyridyl nitrogen donors can be changed, and in this context we have already reported the synthesis and crystal structure of two new ligands: 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene (**L3**), in which the $-HC{=}N{-}N{=}CH-$ spacer links the pyridyls at the *meta* position and its homologue, 2,5-bis(3-pyridyl)-3,4-diaza-2,4-hexadiene (**L4**), with $-(CH_3)C{=}N{-}N{=}C(CH_3)-$ as the spacer, linking the pyridyls at the same *meta* position (Figure 14a). These ligands have been successfully combined with $Co(NO_3)_2{\cdot}6H_2O$ and $Cd(NO_3)_2{\cdot}6H_2O$ to produce several unusual one- and two-dimensional coordination polymers with large pores.[12,13] 1,4-Bis(3-pyridyl)-2,3-diaza-1,3-butadiene (**L3**) afforded interpenetrating and noninterpenetrating two-dimensional brick-wall structures, similar to compound **1**, as well as new polycyclohexane networks. However, no square grids or rhombus grids were obtained and the building blocks consisted of distorted T-joint or F-joint units (Figure 15b,c), with exclusively heptacoordinated environments around the metal centers. The pyridine groups in the ligands were coplanar, except for one cadmium-containing compound in which two of the three ligands in the T-shaped building block had the terminal pyridine groups rotated by 90° with respect to one another, while the pyridine in the third ligand was strictly coplanar. The nonlinear orientation of the N-donor in **L3** and **L4** (Figure 14a) appears to be capable of directing the formation of more structurally complex frameworks[12,13] than are **L1** and **L2** (Figure 14b), which might be thought of simply as longer versions of 4,4′-bipyridine. **L1** and **L2**, as shown herein, have resulted in relatively "orthogonal" frameworks (square grid, rectangular brick wall, and planar rhombus), which are not unexpected based on the linear, opposite N-donor nature of these ligands.

In previous cobalt- and cadmium-containing examples, the use of 2,5-bis(3-pyridyl)-3,4-diaza-2,4-hexadiene (**L2**) lowered the dimensionality of polymers to one-dimensional chains, which may be explained as a steric effect caused by the extra methyl group in the spacer. In the cobalt examples reported herein (**1**, **3**, and **4**), the steric effect (presumably) of the methyl group is less well-defined, as it altered the structural motif from a 2-D brick wall (**1**, no methyl) to a 2-D square grid (**3**) and also to a 1-D ladder motif (**4**). In the case of nickel, preliminary results indicate that the use of methylated **L2** results in a noninterpenetrating square-grid structure similar to the square grid structure of compound **3**, and quite different from the interpenetrating rhombus-grid structure obtained from nickel and nonmethylated **L1** (compound **2**). Unfortunately, crystals of high enough quality to report have not been obtained.

Conclusions

Three new cobalt coordination polymers and one nickel polymer have been synthesized by the reaction of the long Schiff base ligands 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene and 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene with $Co(NO_3)_2{\cdot}6H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$. All the new compounds were structurally characterized by single-crystal X-ray diffraction. It was observed that the solvent system has a significant influence on the coordination geometry and finally on the overall extended

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structure. The two-dimensional and three-dimensional polymers have open frameworks with large pores, partially filled with solvent molecules. Thermogravimetric analysis showed that the frameworks have a remarkably thermal stability, surviving up to 260 °C.

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Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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