Solvent-Dependent Structures of Co(NO₃)₂ with 1,2-Bis(4-pyridyl)ethylene. Interconversion of Molecular Ladders versus Mononuclear Complexes

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Received March 12, 1998

Studies have been carried out on two solvent-dependent structures of $Co(NO_3)_2$ with *trans*-1,2-bis(4-pyridyl)-ethylene (bpee) and their interconversions. X-ray analyses disclose that the molecule obtained in MeOH/CHCl₃ is an infinite ladder structure, $[Co(NO_3)_2(bpee)_{1.5} \cdot 3CHCl_3]_n$ (triclinic $P\bar{1}$; $a = 10.415(4)$ Å, $b = 13.425(4)$ Å, $c = 14.212(4)$ Å, $\alpha = 110.41(3)°$, $\beta = 109.06(3)°$, $\gamma = 97.20(3)°$, $Z = 2$), whereas the compound afforded in H₂O/EtOH is a mononuclear structure, $[Co(H_2O)_4(bpee)_2](NO_3)_2 \cdot ^8/_3H_2O \cdot ^2/_3bpee$ (triclinic $P\bar{1}$; $a = 9.625(3)$ Å, $b = 14.597(5)$ Å, $c = 20.544(5)$ Å, $\alpha = 87.52(3)°$, $\beta = 83.34(2)°$, $\gamma = 75.94(3)°$, $Z = 2$). For $[Co(NO_3)_2(bpee)_{1.5} \cdot 3CHCl_3]_n$, the local geometry around the cobalt(II) atom approximates to a heptacoordinate environment with four oxygens and three nitrogens. The four oxygen sites are occupied by an isobidentate and an anisobidetate nitrate ligand. Each bpee spacer connects two cobalt(II) atoms defining a T-shaped arrangement at the metal atom. For $[Co(H_2O)_4(bpee)_2](NO_3)_2 \cdot ^8/_3H_2O \cdot ^2/_3bpee$, the cobalt atom is in a typical octahedral arrangement with two bpee ligands and four water molecules. The bpee ligand is coordinated to the cobalt atom in a monodentate mode with a dangling pyridine group. Thermal and IR analyses of the present two complexes show that in the solid state the mononuclear complex is changed to the ladder structure at temperatures above 150 °C. Moreover, the ladder structure slowly shifts to the mononuclear complexes at sufficient moisture condition. Thus, either the ladder structure or the mononuclear complex exists depending on the presence or absence of moisture.

Introduction

Molecular architecture constructed by metal based coordination is an expanding field, offering the potential for the development of desirable functional materials or properties such as inner-sphere electron transfer between metals,[1] magnetically coupled polynuclear complexes,[2] models for binuclear rearrangements occurring in metalloenzymes,[3] low-dimensional conducting polymers,[4] crystal bending effect,[5] and inorganic−organic composites.[6] In particular, open framework structures in various coordination polymers are of great interest due to their intriguing structures and their mimicry of microporous solids useful for molecular adsorption,[7] host−guest chemistry,[8] etc. The structural topology of coordination polymers can be

specifically designed according to the selection of the coordination geometry of metals, the structure of spacer ligands, counterions, and reaction conditions.[9−11] To date, of diverse elegant efforts to find key factors in the development of the polymers, the main rational synthetic strategy has been the use of unique spacer ligands. It has been shown, however, that crystallization media such as solvent and template can influence the nucleation and architecture of coordination polymers.[10b] For instance, the type of solvent has been found to play an important role in an isomerism via conformational freedom.[12]

Ligands that can serve as molecular bridges between metal centers and that also contain a delocalized π system have been applied as potential electron "propagating" components.[13]

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Recently, exploitation of *trans*-1,2-bis(4-pyridyl)ethylene (bpee)
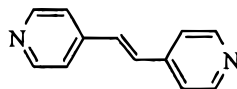
bpee

as a spacer ligand has been explored, resulting in a remarkable class of materials containing diverse architectures and functions.[14] In this context, aesthetic compounds that exhibit desirable properties have been designed and synthesized for new materials, but direct results both on solvent effects and on interconversion properties have remained unexplored. In this paper, we report two crystal structures of $Co(NO_3)_2$ with bpee along with their interconversion properties via thermal and solvent effects.

Experimental Section

Materials and Instrumentation. $Co(NO_3)_2 \cdot 6H_2O$ and *trans*-1,2-bis(4-pyridyl)ethylene were purchased from Hayashi and Aldrich, respectively, and used without purification. Elemental analysis (C, H, N) was carried out at the Chemical Analysis Center at KIST. Infrared spectra were obtained in the $4000-400$ cm^{-1} range on a Perkin-Elmer 16F PC FTIR spectrometer with the sample prepared as a KBr pellet. Thermal analyses were performed on a Stanton Red Croft TG 100 with a scanning rate of 10 °C/min when heating.

Preparation of $[Co(NO_3)_2(bpee)_{1.5}\cdot 3CHCl_3]_n$. A methanolic solution (10 mL) of $Co(NO_3)_2 \cdot 6H_2O$ (146 mg, 0.5 mmol) was slowly diffused into a chloroform solution (10 mL) of bpee (182 mg, 1.0 mmol). Pink crystals formed as chloroform solvate in a week. The yield was 70% based on $Co(NO_3)_2 \cdot 6H_2O$. IR (KBr, cm^{-1}): 1704 (w), 1610 (s), 1558 (w), 1510 (sh), 1461 (s), 1428 (s), 1384 (s), 1304 (s), 1220 (m), 1210 (m), 1068 (m), 1018 (s), 978 (m), 832 (s), 554 (s).

Preparation of $[Co(H_2O)_4(bpee)_2](NO_3)_2\cdot^8/_3H_2O\cdot^2/_3bpee$. The reaction was carried out in the similar procedure besides solvents used: an ethanolic solution (5 mL) of bpee (364 mg, 2.0 mmol) was slowly diffused into an aqueous solution (5 mL) of $Co(NO_3)_2 \cdot 6H_2O$ (291 mg, 1.0 mmol). Light pink crystals were obtained in a week. Yield, 60%. IR (KBr, cm^{-1}): 3348 (br, s), 1666 (w), 1612 (s), 1602 (s), 1560 (m), 1504 (w), 1426 (s), 1390 (s), 1360 (s), 1252 (w), 1220 (m), 1210 (w), 1094 (w), 1068 (m), 1020 (m), 1006 (m), 972 (m), 835 (sh), 826 (s), 738 (m), 550 (s). Elemental analysis (C, H, N) of $[Co(H_2O)_4(bpee)_2](NO_3)_2\cdot^8/_3H_2O\cdot^2/_3bpee$ gave satisfactory results, but for $[Co(NO_3)_2(bpee)_{1.5}\cdot 3CHCl_3]_n$, partial evaporation of chloroform molecules resulted in erratic chemical analysis.

X-ray Crystallography. Each crystal was wedged in a Lindemann capillary with mother solvent. All X-ray data were collected on an Enraf-Nonius CAD4 automatic diffractometer with graphite-mono-chromated Mo Kα ($\lambda = 0.710\ 73$ Å) at ambient temperature. Unit cell dimensions were based on 25 well-centered reflections by using a least-squares procedure. During the data collection, three standard reflections monitored every hour did not show any significant intensity variation. All data were collected with the $\omega/2\theta$ scan mode. The data were corrected for Lorentz and polarization effects. Absorption effects were corrected by the empirical ψ-scan method. The structures were solved by the Patterson method (SHELXS-86) and refined by full-matrix least squares techniques (SHELXL-93).[14] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added at calculated positions. For $[Co(NO_3)_2(bpee)_{1.5}\cdot 3CHCl_3]_n$, two chlorine atoms (Cl(3) and Cl(5)) were disordered. For the two crystals, crystal parameters and procedural information corresponding to data collection and structure refinement are given in Table 1.
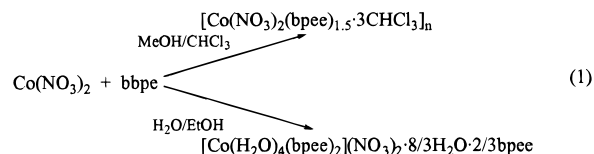
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Table 1. Crystallographic Data for $[Co(NO_3)_2(bpee)_{1.5}\cdot 3CHCl_3]_n$ and $[Co(H_2O)_4(bpee)_2](NO_3)_2\cdot^8/_3H_2O\cdot^2/_3bpee$

empirical formula	$C_{18}H_{15}N_5O_6Co\cdot 3CHCl_3$	$C_{48}H_{60}N_{11}O_{19}Co_{1.5}$
fw	814.38	1183.46
space group	$P\bar{1}$	$P\bar{1}$
a, Å	10.415(4)	9.625(3)
b, Å	13.425(4)	14.597(5)
c, Å	14.212(4)	20.544(5)
α, deg	110.41(3)	87.5293(3)
β, deg	109.06(3)	83.34(2)
γ, deg	97.20(3)	75.94(3)
V, Å^3	1695(1)	2781(2)
Z	2	2
d_{calcd}, g cm^{-3}	1.596	1.413
absorption coeff, mm^{-1}	1.258	0.535
final R indices $\{I > 3\sigma(I)\}^a$	R1 = 0.0853	R1 = 0.0714
	wR2 = 0.2124	wR2 = 0.1891

^{a} R1 $= \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} wR2 $= \sum w(F_o^2 - F_c^2)^2/\sum wF_o^4)^{1/2}$, where $w = 1/\{\sigma^2F_o^2 + (aP)^2 + bP\}$ and where $P = \{Max(F_o^2,0) + 2F_c^2\}/3$.

Results

Synthesis. Slow diffusion of $Co(NO_3)_2$ in methanol with the present spacer ligand, bpee in chloroform afforded an infinite coordination polymer of $[Co(NO_3)_2(bpee)_{1.5}\cdot 3CHCl_3]_n$ (pink crystals). The product may depend on the mole ratio of metal-to-ligand, but the reaction was not significantly affected by the change of the mole ratio (bpee/$Co(NO_3)_2 = 1.5-3$). Nevertheless, the reaction product was very dependent on the solvents used. That is, a similar diffusion of $Co(NO_3)_2$ in water with bpee in ethanol gave a discrete structure with the composition of $[Co(H_2O)_4(bpee)_2](NO_3)_2\cdot^8/_3H_2O\cdot^2/_3bpee$ (light pink crystals) instead of the possible multinuclear species even though the reaction was conducted in the same mole ratio (eq 1). For the

$$Co(NO_3)_2 + bbpe \nearrow^{MeOH/CHCl_3} [Co(NO_3)_2(bpee)_{1.5}\cdot 3CHCl_3]_n$$
$$\searrow_{H_2O/EtOH} [Co(H_2O)_4(bpee)_2](NO_3)_2\cdot 8/3H_2O\cdot 2/3bpee \quad (1)$$

reaction, the increase of the mole ratio (bpee/$Co(NO_3)_2 > 2.0$) expectedly resulted in somewhat high yields. Formation of a discrete monomeric species with the nitrates as counteranions seems to be due to the properties of the solvents used. In this case, the product may have been induced by the degree of dissociation of $Co(NO_3)_2$ in water. Of course, the molecular structure via such a slow diffusion may be delicately dependent on the order of slow diffusion, but several attempts gave the same results. Both compounds were directly isolated as pink crystals suitable for X-ray diffraction. The present compounds were insoluble solids in common organic solvents, but they changed in appearance slowly in water. The crystals of $[Co(NO_3)_2(bpee)_{1.5}\cdot 3CHCl_3]_n$ lose chloroform immediately after the crystals are removed from mother liquor.

Crystal Structure Descriptions. The ORTEP and infinite ladder structure of $[Co(NO_3)_2(bpee)_{1.5}\cdot 3CHCl_3]_n$ are depicted in Figures 1 and 2, respectively, and the relevant bond distances and angles are listed in Table 2. X-ray structural analyses reveal that the local geometry of the cobalt atom is a pseudo-heptacoordinate environment with three nitrogen and four oxygen donating atoms. Three pyridyl moieties form a T-shaped arrangement at the metal atom:[16] the geometry of the pyridyl groups around the cobalt(II) atom is slightly deviated from an ideal T shape (N(3)−Co−N(4), 93.1(2)°; N(3)−Co−N(5), 96.0(2)° N(4)−Co−N(5), 169.8(3)°). The remaining four
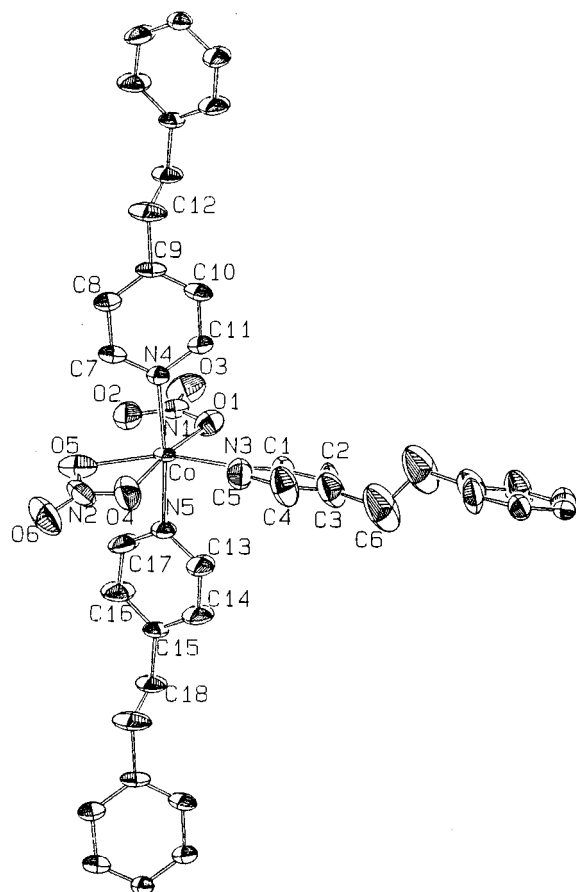
Figure 1. ORTEP view of $[Co(NO_3)_2(bpee)_{1.5} \cdot 3CHCl_3]_n$.

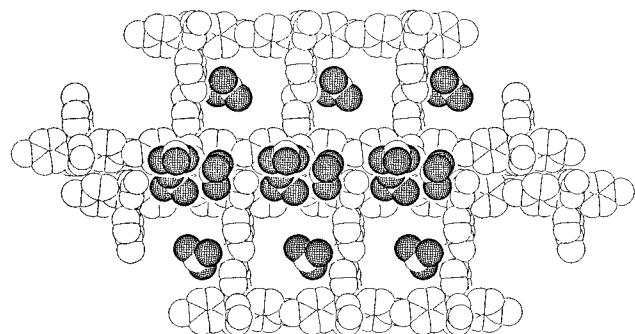**Figure 2.** Space-filling view of infinite ladder structure of $[Co(NO_3)_2$-$(bpee)_{1.5} \cdot 3CHCl_3]_n$.

oxygen sites are occupied by two bidentate nitrate groups: one is isobidentate (Co−O(4), 2.206(8) Å; Co−O(5), 2.255(9) Å) whereas the other is anisobidetate (Co−O(1), 2.148(7) Å; Co−O(2), 2.521(6) Å). The anisobidentate nitrate is responsible for the pseudo-heptacoordinate arrangement. The most interesting feature is that an infinite molecular ladder is formed in which the T-shaped units are linked to each other. Such bidentate nitrates seem to prevent the formation of a square grid polymeric motif, instead forming an infinite ladder structure involving a large 44-membered ring (13.4 × 13.6 Å). There are three crystallographically independent molecules of $CHCl_3$ per cobalt(II) metal atom. One solvate chloroform molecule sits in

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Table 2. Selected Bond Lengths (Å) and Bond Angles (deg)

$[Co(NO_3)_2(bpee)_{1.5} \cdot 3CHCl_3]_n$		$[Co(H_2O)_4(bpee)_2](NO_3)_2 \cdot {}^8/_3H_2O \cdot {}^2/_3bpee$	
Co−N(2)	2.146(7)	Co(1)−N(1)	2.142(5)
Co−N(3)	2.144(6)	Co(1)−N(2)	2.152(5)
Co−N(4)	2.163(6)	Co(2)−N(5)	2.158(5)
Co−O(1)	2.148(7)	Co(2)−N(5)′	2.158(5)
Co−O(2)	2.521(6)	Co(1)−O(1)	2.106(4)
Co−O(4)	2.206(8)	Co(1)−O(2)	2.117(4)
Co−O(5)	2.255(9)	Co(1)−O(3)	2.110(4)
		Co(1)−O(4)	2.098(4)
N(3)−Co−N(4)	93.1(2)	Co(2)−O(5)	2.084(4)
N(4)−Co−O(1)	87.5(3)	Co(2)−O(5)′	2.084(4)
N(3)−Co−O(1)	87.4(3)	Co(2)−O(6)	2.130(4)
N(4)−Co−N(5)	169.8(3)	Co(2)−O(6)′	2.130(4)
N(3)−Co−N(5)	96.0(2)		
O(1)−Co−N(5)	88.3(3)	N(1)−Co(1)−N(2)	176.2(2)
N(4)−Co−O(4)	96.4(3)	O(3)−Co(1)−O(4)	175.3(2)
N(3)−Co−O(4)	87.0(3)	O(1)−Co(1)−O(2)	176.2(2)
O(1)−Co−O(4)	173.3(3)	O(1)−Co(1)−N(1)	93.5(2)
N(5)−Co−O(4)	88.7(3)	N(5)−Co(2)−N(5)′	180.0
N(4)−Co−O(5)	90.5(3)	O(5)−Co(2)−O(5)′	180.0
N(3)−Co−O(5)	143.0(3)	O(6)−Co(2)−O(6)′	180.0
O(1)−Co−O(5)	129.3(3)	O(5)−Co(2)−N(5)′	88.8(2)
N(5)−Co−O(5)	85.0(3)		
O(4)−Co−O(5)	56.0(3)		

the square void, whereas the other two chloroform molecules are positioned outside.

The ORTEP and packing diagram of $[Co(H_2O)_4(bpee)_2]$-$(NO_3)_2 \cdot {}^8/_3H_2O \cdot {}^2/_3bpee$ are shown in Figures 3 and 4, respectively, and relevant bond distances and angles are listed in Table 2. The X-ray structure exhibited something complicated: the crystal consisted of monomeric cobalt(II) complexes, counteranions, solvate water molecules, and free bpee ligands. The cobalt atom has a typical octahedral environment with two nitrogen and four oxygen donating atoms. The interesting feature is that the bpee ligand is coordinated to the cobalt atom in a monodentate mode with a dangling pyridine group, resulting in a mononuclear cobalt(II) complex with each nitrogen atom in the trans position. In contrast to the above ladder structure, the two nitrate groups are positioned as counteranions and the four water molecules are coordinated to the cobalt(II) atom. The structural analysis indicates weak interactions among aqua ligands, solvate water molecules, and nitrates. The intermolecular interactions such as hydrogen bonding and interdigited interaction stabilize the crystal lattice.

Thermal Behaviors. When the crystals of $[Co(NO_3)_2$-$(bpee)_{1.5} \cdot 3CHCl_3]_n$ were removed from mother solution, they immediately lost partial chloroform molecules. Thus, TGA and DSC traces of the ladder structure depicted in Figure 5 were measured after the solvate molecules were evaporated. However, even for the sample containing partial solvent molecules, a weight loss corresponding to the solvate molecules was observed in the wide temperature range of 25−140 °C. The wide range is not characteristic of a phase transition but rather with the process of evaporating chloroform molecules.[17] The wide range may be additional evidence for the coexistence of inner- and outer-solvate molecules of the ladder cavities. However, the skeleton of the ladder structure is stable up to 280 °C: the absence of a phase transition suggests that the integrity of the ladder structure is preserved during and after the liberation of chloroform molecules. The drastic loss in weight corresponding to bpee ligands (obsd 61.1%, calcd 59.9% by TGA) was observed at 293 °C. For the thermograms of

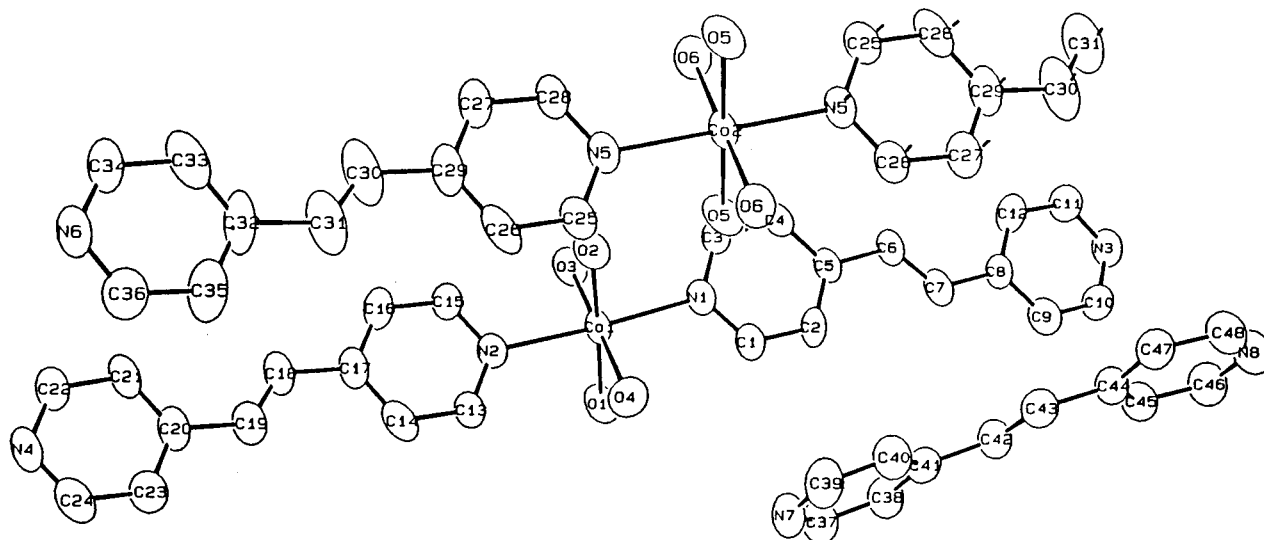(17) Gardner, G. B.; Kiang, Y.-H.; Lee, S.; Asgaonkar, A.; Venkataraman, D. *J. Am. Chem. Soc.* **1996**, *118*, 6946.

Figure 3. ORTEP view of $[Co(H_2O)_4(bpee)_2](NO_3)_2 \cdot {}^8/_3H_2O \cdot {}^2/_3bpee$.

Figure 4. Packing diagram of $[Co(H_2O)_4(bpee)_2](NO_3)_2 \cdot {}^8/_3H_2O \cdot {}^2/_3bpee$.

$[Co(H_2O)_4(bpee)_2](NO_3)_2 \cdot {}^8/_3H_2O \cdot {}^2/_3bpee$ (Figure 6), appearance of two endotherms at 111 and 130 °C seems to be due to the evaporation of solvate water molecules and aqua ligands, respectively (obsd 15.4%, calcd 15.2% weight loss by TGA). An endothermic peak at 245 °C seems to be responsible for the evaporation of the dissociated bpee ligand. The most significant thermal behavior is that the curves of the two compounds at above 150 °C are identical, implying that they are the same structure at above the temperature. The mononuclear complex at above 150 °C is changed to the ladder structure (eq 2): for

$$[Co(H_2O)_4(bpee)_2](NO_3)_2 \cdot {}^8/_3H_2O \cdot {}^2/_3bpee \xrightarrow[150\,°C]{}$$
$$[Co(NO_3)_2(bpee)_{1.5}]_n + 20/3H_2O + {}^7/_6bpee \quad (2)$$
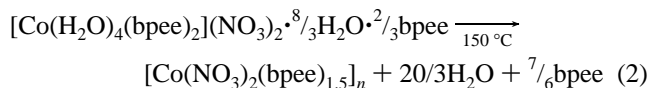
the mononuclear complex, the counteranionic nitrates were
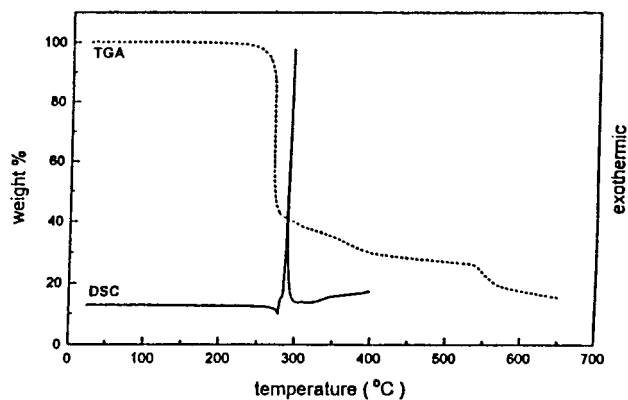
Figure 5. Overlay of TGA and DSC traces of $[Co(NO_3)_2(bpee)_{1.5}]_n$, each recorded at a heating rate of 10 °C min^{-1}.
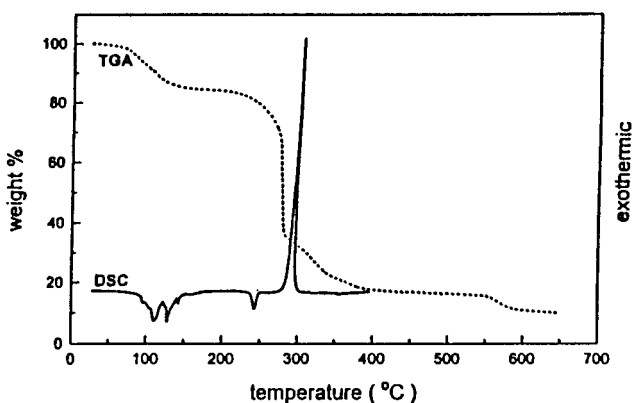
Figure 6. Overlay of TGA and DSC traces of $[Co(H_2O)_4(bpee)_2]$-$(NO_3)_2 \cdot {}^8/_3H_2O \cdot {}^2/_3bpee$, each recorded at a heating rate of 10 °C min^{-1}.

coordinated to the cobalt(II) atom after aqua ligands were dissociated at high temperature. A small DSC peak at around 150 °C may be indebted to such a structural change. The conversion processes could be observed from the IR spectra measured for the mononuclear sample both at room temperature and after heating at 250 °C (Figure 7). When the sample of the ladder structure was heated to 250 °C, the bands of solvate chloroform molecules disappeared, indicating that solvate chloroform molecules were evaporated without the collapse of the skeletal ladder structure. After the heated sample was left in chloroform, the IR spectrum is consistent with the original
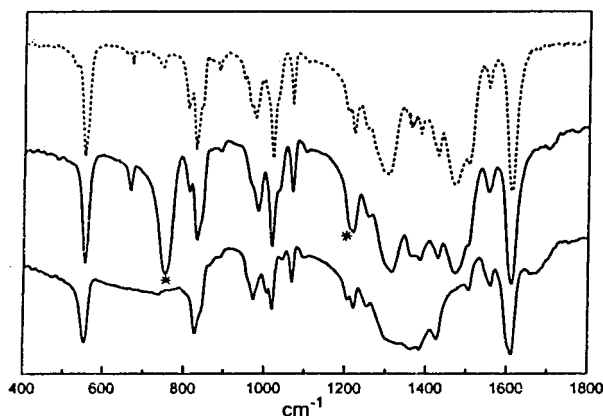
Figure 7. IR spectra of [Co(H$_2$O)$_4$(bpee)$_2$](NO$_3$)$_2$·$^8/_3$H$_2$O·$^2/_3$bpee heated to 250 °C (top), [Co(NO$_3$)$_2$(bpee)$_{1.5}$·3CHCl$_3$]$_n$ (middle), where asterisks mark bands induced by solvate chloroform molecules and [Co(H$_2$O)$_4$-(bpee)$_2$](NO$_3$)$_2$·$^8/_3$H$_2$O·$^2/_3$bpee (bottom).
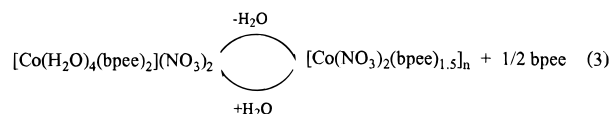
room-temperature spectrum, disclosing that chloroform molecules were reversibly dissociated and associated from the ladder structure. IR spectra of the mononuclear complex show prominent temperature dependence: the spectrum of the sample heated to 250 °C was quite different from that of the room-temperature sample. IR spectrum of the heated sample is consistent with that of the ladder structure except for the bands induced by chloroform molecules, meaning the mononuclear complex transforms into the ladder structure at high temperature. Furthermore, the most relevant IR feature is those associated with the presence of a nitrate ligand. The bonding mode of metal nitrate complexes, depending on whether the NO$_3$ anion is bonded to monodentate, bidentate, or free ligand, has been well established.[18] A sample with a single $\nu(N-O)$ band (1360 cm^{-1}) at room temperature and two strong bands (1470 and 1306 cm^{-1}) at high temperature indicates free ion and bidentate bonding mode, respectively, which is consistent with the X-ray structure and thermal analyses.

Discussion

The structure of [Co(NO$_3$)$_2$(bpee)$_{1.5}$·3CHCl$_3$]$_n$ is an open framework molecular ladder connected by a 44-membered ring square unit. Related structures were obtained in [Co(NO$_3$)$_2$-(1,2-bis(4-pyridyl)ethane)$_{1.5}$]$_n$[12] and [Co(NO$_3$)$_2$(4,4′-bpy)$_{1.5}$]$_n$.[16] For [Co(NO$_3$)$_2$(1,2-bis(4-pyridyl)ethane)$_{1.5}$]$_n$, one of three conformational isomers was also found to be a similar ladder structure. [Co(NO$_3$)$_2$(4,4′-bpy)$_{1.5}$]$_n$ also showed eithor a ladder structure with hydrophobic cavities or a three-dimensional framework with channeling cavities of 36-membered rings. Thus, both nitrates and bipyridine linkers are essential building blocks in the formation of an infinite ladder structure via T-shape. However, when water was used in the crystallization,

a discrete cationic mononuclear complex with nitrate groups as counteranions was obtained. Dissociated NO$_3^-$ species in water seemed to be retained even in its crystalline state while water molecules were coordinated to the central cobalt atom, meaning the solvent effect of water may be an obstacle to formation of the ladder structure. This species involving the counteranionic nitrate group is a rare case in the cobalt nitrate—pyridine system. The isolation of the mixed complex—bpee pair is particularly fortuitous because it permits the preparation of "molecular inorganic—organic composites".[6] Thus, reaction media can affect nucleation of coordination polymers, which is a good example of solvent media tailored hosts.

Temperature-dependent IR and thermal analyses could be used to follow shifts that occur in the solid state. The ladder structure composed by a 44-membered ring is very favorable in the absence of water even at high temperature, indicating that the compound is a thermodynamically stable species. Why does the mononuclear complex shift to the ladder structure at high temperatures? The question about such a change can be answered as follows: at high temperature aqua ligands are evaporated and then immediately replaced by nitrate groups, i.e., the transformation of mononuclear complex into the ladder structure. Moreover, on standing at sufficient moisture condition, the ladder structure is slowly converted back to the mononuclear complex. This fact is direct evidence that the structure changes depending on the absence or presence of water, not because of temperature conditions. Thus, eq 2 can be generalized in eq 3:

$$[Co(H_2O)_4(bpee)_2](NO_3)_2 \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} [Co(NO_3)_2(bpee)_{1.5}]_n + 1/2 \text{ bpee} \quad (3)$$

Conclusion

For the present system, the formation of an infinite ladder structure is very favorable regardless of the reaction mole ratio in organic solvents, whereas a discrete mononuclear structure is formed in an aqueous solution. The molecular ladder structure is capable of chloroform evacuation without destruction of the network connectivity. This study exhibited a rare example of a transformation by thermal rearrangement (at 150 °C) in a solid state of a mononuclear complex into a ladder structure with a 44-membered ring. Such interconversion properties may be devoted to the development of rational synthetic strategies that are not possible by general methods.

(18) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; John Wiley & Sons: New York, 1986.