

Structure of $[\text{CoL}_2(\text{MeOH})(\text{NO}_3)_2]$ [$\text{L} = \text{N1-(1-(pyridin-4-yl)ethylidene)naphthalene-1,5-diamine}$]

Sung Hoon Kim, Hyun Sue Huh and Soon W. Lee

Department of Chemistry (BK21), Sungkyunkwan University, Natural Science Campus,
Suwon 440-746, Republic of Korea

$[\text{CoL}_2(\text{MeOH})(\text{NO}_3)_2]$ 의 구조 [$\text{L} = \text{N1-(1-(pyridin-4-yl)ethylidene)naphthalene-1,5-diamine}$]

김성훈 · 허현수 · 이순원
성균관대학교 화학과

Abstract

When a CH_2Cl_2 solution of the dipyriddy species L' (N,N' -bis-(1-pyridin-4-yl-ethylidene)-naphthalene-1,5-diamine) was layered onto the top of a MeOH solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, a molecular cobalt compound $[\text{CoL}_2(\text{MeOH})(\text{NO}_3)_2]$ (**1**), not a coordination polymer, was formed. X-ray structural analysis of compound **1** revealed that it contains the pyridyl-amine ligand L ($N1$ -(4-imino-1-methyl-but-2-enylidene)-naphthalene-1,5-diamine), instead of L' . Structure of compound **1** strongly suggests that the original ligand L' has been hydrolyzed to ligand L during the reaction.

요 약

Dipyriddy 리간드 L' (N,N' -bis-(1-pyridin-4-yl-ethylidene)-naphthalene-1,5-diamine) 을 함유한 CH_2Cl_2 용액을 $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 을 함유한 MeOH 용액 위에 깔았을 때, 배위 고분자가 아닌, 분자성 코발트 화합물 $[\text{CoL}_2(\text{MeOH})(\text{NO}_3)_2]$ (**1**) 이 형성되었다. 화합물 **1** 의 X-ray 구조 분석 결과, 이 화합물은 pyridyl-amine 리간드 L ($N1$ -(4-Imino-1-methyl-but-2-enylidene)-naphthalene-1,5-diamine) 을 함유하고 있었다. 반응 중에 리간드 L' 이 리간드 L 로 가수분해되었다는 것을 화합물 **1** 의 구조가 강하게 암시하고 있다.

1. Introduction

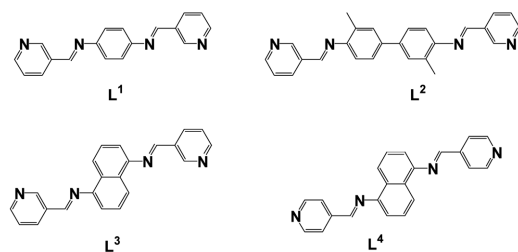
The design and synthesis of infinite coordination polymers (or metal-organic frameworks), which are formed by coordinative covalent bonds, are currently under intensive study due to their useful properties applicable to catalysis, chirality, conductivity, luminescence, magnetism, adsorption, and gas storage.¹⁻¹¹⁾ Carboxylates and pyridyls are commonly used as linking ligands (or organic spacers) in preparing these polymers. For the past few years, our research group has prepared several coordina-

tion polymers based on dicarboxylates or dipyriddyds under hydrothermal or solvothermal conditions.¹²⁻¹⁶⁾

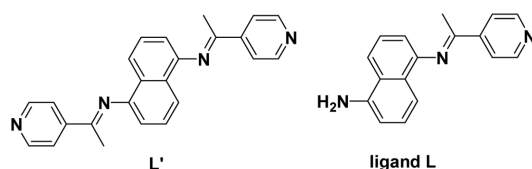
Very recently, we prepared several long dipyriddy-type ligands $\text{L}^1 \sim \text{L}^4$ by Schiff-base condensation and their coordination polymers: $[\text{Zn}(\text{H}_2\text{O})_4\text{L}^1] \cdot (\text{MeOH})$, $[\text{Zn}(\text{NO}_3)(\text{H}_2\text{O})_2\text{L}^1] \cdot (\text{NO}_3) \cdot (\text{H}_2\text{O})_2$, $[\text{ZnL}^2(\text{NO}_3)_2]$, $[\text{CoL}^2_{1,3}(\text{NO}_3)_2]$, $[\text{CoL}^2_2(\text{NO}_3)_2] \cdot \text{X}$ (X = benzene or toluene), $[\text{ZnL}^3(\text{NO}_3)_2]$, $[\text{ZnL}^4(\text{NO}_3)_2]$, $[\text{CdL}^4_{1,5}(\text{NO}_3)_2]$, and $[\text{CoL}^4(\text{bpdc})] \cdot (\text{EtOH})$ ($\text{bpdcH}_2 = \text{biphenyl-4,4'-dicarboxylic acid}$) (Chart 1).¹⁷⁻²⁰⁾

Recently, zur Loye and co-workers reported a novel dipyriddy-type ligand L' ,²¹⁾ whose structure is

Chart 1



closely related to that of ligand **L**⁴ we previously prepared. For a comparative study, we made an attempt to prepare coordination polymers by using ligand **L'**. When a dichloromethane solution of **L'** was layered onto the top of a methanol solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, a molecular cobalt compound $[\text{CoL}_2(\text{MeOH})(\text{NO}_3)_2]$ (**1**), not a coordination polymer, was formed. The structure of ligand **L** in compound **1** tells us that the original ligand **L'** has been hydrolyzed to ligand **L** during the reaction. We herein report the isolation and structure of $[\text{CoL}_2(\text{MeOH})(\text{NO}_3)_2]$ (**1**).



2. Experimental Section

All solid chemicals were purified by recrystallization, and all solvents were distilled and stored over molecular sieves. Ligand **L'** was prepared by the literature method.²¹⁾ IR spectra were recorded with a Nicolet 320 FTIR spectrophotometer.

Preparation of $[\text{CoL}_2(\text{MeOH})(\text{NO}_3)_2]$ (1**)** A dichloromethane solution (7 ml) of **L'** (60.0 mg, 0.230 mmol) was layered onto the top of a methanol solution (7 ml) of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (60.0 mg, 0.206 mmol). Brown crystals of compound **1** formed in 5 days (73.0 mg, 0.098 mmol, 48%). IR (KBr, cm^{-1}): 3380 (m), 1622 (m), 1484 (s), 1379 (s), 1289 (s),

1016(m), 826 (m), 775 (m), 737 (m), 575 (m), 515 (m).

X-ray structure determination. All X-ray data were collected with the use of a Siemens P4 diffractometer equipped with a Mo X-ray tube. Details on crystal data and intensity data are given in Table 1. The orientation matrix and unit-cell parameters were determined by least-squares analyses of the setting angles of 25 reflections in the range $15.0^\circ < 2\theta < 25.0^\circ$. The intensity data were empirically corrected for absorption with ψ -scan data. All calculations were carried out with the SHELXTL programs.²²⁾

A brown crystal of **1** of approximate dimensions $0.28 \times 0.24 \times 0.18$ mm, shaped as a block, was used for crystal and intensity data collection. The unit-cell parameters indicated a triclinic unit cell with the two possible space groups: *P*1 and *P*-1. A sta-

Table 1. X-ray data collection and structure refinement details

formula	$\text{C}_{35}\text{H}_{34}\text{CoN}_8\text{O}_7$
fw	737.63
temperature, K	293(2)
crystal system	triclinic
space group	<i>P</i> -1
<i>a</i> , Å	8.087(2)
<i>b</i> , Å	14.712(2)
<i>c</i> , Å	15.497(3)
α , deg	68.64(1)
β , deg	75.95(1)
γ , deg	89.83(1)
<i>V</i> , Å ³	1658.1(6)
<i>Z</i>	2
d_{calc} , g cm ⁻³	1.477
μ , mm ⁻¹	0.581
T_{min}	0.6726
T_{max}	0.9056
<i>F</i> (000)	766
No. of reflections measured	6136
No. of reflections unique	5693
No. of reflections with $I > 2\sigma(I)$	3692
No. of parameters refined	477
2θ range (°)	3.5~50.0
GOF (goodness-of-fit on F^2)	1.027
Max., min. in $\Delta\rho$ (e Å ⁻³)	0.648, -0.251
$R1^a$	0.0570
$wR2^b$	0.1223

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b wR2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$$

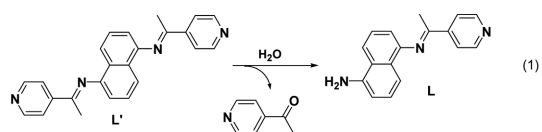
Table 2. Atomic ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^4$)

Co1	7543(1)	7553(1)	4930(1)	43(1)
O1	6852(4)	6019(2)	5243(2)	61(1)
O2	9319(4)	6378(2)	5384(2)	61(1)
O3	8383(5)	4850(3)	5834(2)	82(1)
O4	7459(4)	9133(2)	4610(2)	59(1)
O5	9929(4)	8622(2)	4554(2)	62(1)
O6	9691(5)	10189(3)	4059(3)	87(1)
O7	4970(4)	7827(3)	4833(2)	76(1)
N1	6837(4)	7287(2)	6430(2)	43(1)
N2	6673(5)	6802(3)	9820(2)	51(1)
N3	7724(8)	4901(5)	13857(3)	92(2)
N4	8425(4)	7783(2)	3438(2)	43(1)
N5	11572(4)	8191(2)	71(2)	48(1)
N6	16309(6)	10266(4)	-4007(3)	64(1)
N7	8199(6)	5716(3)	5505(2)	57(1)
N8	9056(5)	9344(3)	4392(2)	55(1)
C1	5541(6)	6637(3)	7014(3)	53(1)
C2	5050(6)	6393(3)	7993(3)	50(1)
C3	5952(5)	6821(3)	8416(3)	39(1)
C4	7314(5)	7507(3)	7802(3)	46(1)
C5	7712(5)	7716(3)	6832(3)	47(1)
C6	5509(5)	6566(3)	9489(3)	42(1)
C7	3804(5)	6018(3)	10072(3)	49(1)
C8	6326(5)	6610(3)	10819(3)	46(1)
C9	5089(6)	7056(3)	11258(3)	61(1)
C10	4795(6)	6870(4)	12239(3)	63(1)
C11	5693(6)	6230(3)	12780(3)	54(1)
C12	8022(6)	5120(3)	12893(3)	55(1)
C13	9275(6)	4689(4)	12448(3)	63(1)
C14	9613(6)	4897(4)	11469(3)	61(1)
C15	8703(5)	5528(3)	10918(3)	51(1)
C16	7368(5)	5982(3)	11348(3)	46(1)
C17	7023(5)	5779(3)	12355(3)	46(1)
C18	7756(6)	8453(3)	2809(3)	57(1)
C19	8239(6)	8669(3)	1835(3)	57(1)
C20	9515(5)	8198(3)	1448(3)	41(1)
C21	10227(5)	7500(3)	2101(3)	49(1)
C22	9660(5)	7323(3)	3066(3)	48(1)
C23	10093(5)	8428(3)	392(3)	42(1)
C24	8932(5)	8973(3)	-207(3)	53(1)
C25	12201(5)	8382(3)	-929(3)	46(1)
C26	11421(6)	7919(3)	-1372(3)	55(1)
C27	12051(6)	8112(3)	-2355(3)	58(1)
C28	13441(6)	8781(3)	-2887(3)	52(1)
C29	15762(5)	9958(3)	-2988(3)	48(1)
C30	16585(6)	10384(3)	-2531(3)	56(1)
C31	15984(6)	10138(4)	-1534(3)	57(1)
C32	14589(6)	9489(3)	-1004(3)	50(1)
C33	13702(5)	9033(3)	-1453(3)	43(1)
C34	14310(5)	9255(3)	-2462(3)	42(1)
C35	3686(9)	7328(5)	4766(6)	130(3)

tistical analysis of reflection intensities suggested a centrosymmetric space group, and the structure analysis converged only in *P*-1. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. The methanol OH hydrogen could not be located, and the remaining hydrogen atoms were generated in idealized positions and refined in a riding model. Final atomic coordinates for **1** are given in Table 2. Selected bond lengths and angles are given in Table 3.

3. Results and Discussion

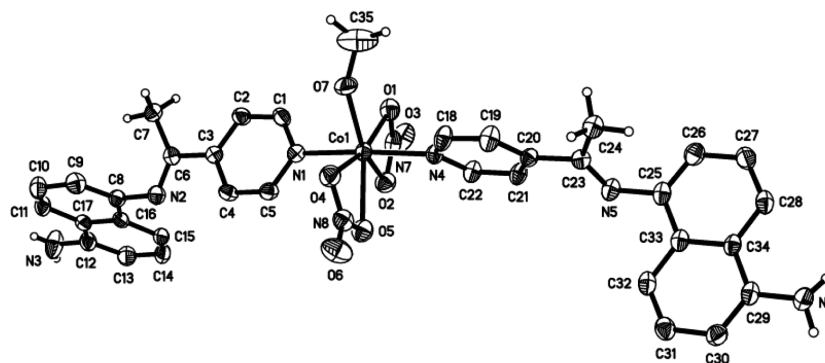
Preparation. Compound **1** was isolated from the reaction of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with **L'** (*N,N'*-bis-(1-pyridin-4-yl-ethylidene)-naphthalene-1,5-diamine), a dipyridyl species. When a dichloromethane solution of **L'** was layered onto the top of a methanol solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, a molecular cobalt compound $[\text{CoL}_2(\text{MeOH})(\text{NO}_3)_2]$ (**1**), not a coordination polymer, was formed. X-ray structural analysis of compound **1** revealed that it contains **L** (a pyridyl-amine species, *N*1-(4-Imino-1-methyl-but-2-enylidene)-naphthalene-1,5-diamine), instead of **L'**. The structure of **L** in compound **1** strongly suggests that the original ligand **L'** has been hydrolyzed to **L** during the reaction, concurrently with the liberation of 4-pyridyl-aldehyde (eq 1). However, we do not know whether the hydrolysis occurred before or after the coordination of **L'** to the cobalt metal. Furthermore, we did not identify the 4-pyridyl-aldehyde in the reaction mixture.



Structure. The molecular structure of compound **1** with the atom-numbering scheme is shown in Fig. 1. The coordination sphere of Co can be described as a trigonal bipyramid, with two η^2 -nitrate ligands, one two **L** ligands, and one methanol ligand. The formal oxidation state of the Co metal is +2 (d^7). Because of the two η^2 -nitrate ligands, compound **1** can also be described as having a 7-coordinate co-

Table 3. Selected bond lengths (Å) and bond angles (°)

Co1-N1	2.141(3)	Co1-N4	2.144(3)	Co1-O7	2.149(3)
Co1-O1	2.172(3)	Co1-O4	2.198(3)	Co1-O2	2.265(3)
Co1-O5	2.311(3)	O1-N7	1.276(5)	O2-N7	1.262(5)
O3-N7	1.212(4)	O4-N8	1.262(5)	O5-N8	1.255(4)
O6-N8	1.219(5)	O7-C35	1.319(7)	N3-C12	1.367(6)
N6-C29	1.427(5)				
N1-Co1-N4	175.9(1)	N1-Co1-O7	91.3(1)	N4-Co1-O7	92.7(1)
N1-Co1-O1	90.3(1)	N4-Co1-O1	89.2(1)	O7-Co1-O1	88.0(1)
N1-Co1-O4	89.4(1)	N4-Co1-O4	92.2(1)	O7-Co1-O4	75.4(1)
O1-Co1-O4	163.4(1)	N1-Co1-O2	82.4(1)	N4-Co1-O2	93.9(1)
O7-Co1-O2	145.0(2)	O1-Co1-O2	57.8(1)	O4-Co1-O2	138.5(1)
N1-Co1-O5	95.7(1)	N4-Co1-O5	82.1(1)	O7-Co1-O5	130.8(1)
O1-Co1-O5	140.3(1)	O4-Co1-O5	56.2(1)	O2-Co1-O5	84.1(1)
C35-O7-Co1	134.9(4)				

**Fig. 1.** Ortep drawing of compound 1.

ordination environment. All amine hydrogen atoms are involved in intermolecular N-H \cdots O hydrogen bonds. All Co-O and Co-N distances are normal single bonds.

In summary, we isolated [CoL₂(MeOH)(NO₃)₂] (**1**) (L = N1-(4-imino-1-methyl-but-2-enylidene)-naphthalene-1,5-diamine) from the reaction of Co(NO₃)₂·6H₂O with a dipyridyl ligand L' (N,N'-bis-(1-pyridin-4-yl-ethylidene)-naphthalene-1,5-diamine). The original ligand (L') is a dipyridyl species, whereas the ligand (L) in compound **1** is a pyridylamine species. Ligand L in the product is believed to be formed by hydrolysis of L' during the reaction.

References

- 1) Swiergers, G. F. and Malefetse, T. J., *Chem. Rev.*, **100**, 3483 (2000).
- 2) Moulton, B. and Zaworotko, M. J., *Chem. Rev.*, **101**, 1629 (2001).
- 3) Eddaoudi, M., Moler, D. B., Li, H., Chen, B., Reineke, T. M., O'Keeffe, M. and Yaghi, O. M., *Acc. Chem. Res.*, **319**, 34 (2001).
- 4) Eddaoudi, M., Kim, J., Rosi, N., Vodak, D., Wachter, J., O'Keeffe, M. and Yaghi, O. M., *Science*, **295**, 469 (2002).
- 5) Janiak, C., *Dalton Trans.*, 2781 (2003).
- 6) Kesanli, B. and Lin, W., *Coord. Chem. Rev.*, **246**, 305 (2003).
- 7) Barnett, S. A. and Champness, N. R., *Coord. Chem. Rev.*, **246**, 145 (2003).
- 8) Rowsell, J. L. C. and Yaghi, O. M., *Micropor. Mesopor. Mater.*, **73**, 3 (2004).
- 9) Ockwig, N. W., Friedrichs, O. D., O'Keeffe, M. and Yaghi, O. M., *Acc. Chem. Res.*, **38**, 176 (2005).

- 10) Robin, A. Y. and Fromm, K. M., *Coord. Chem. Rev.*, **250**, 2127 (2006).
- 11) Vittal, J. J., *Coord. Chem. Rev.*, **251**, 1781 (2007).
- 12) Baeg, J.-Y. and Lee, S. W., *Inorg. Chem. Commun.*, **6**, 313 (2003).
- 13) Lee, Y. K. and Lee, S. W., *Bull. Korean Chem. Soc.*, **24**, 7 (2003).
- 14) Kim, H. J., Lee, Y. K., Park, K., Son, J. H., Kwon, Y.-U. and Lee, S. W., *Inorg. Chim. Acta*, **353**, 151 (2003).
- 15) Lee, H. K., Min, D., Cho, B.-Y. and Lee, S. W., *Bull. Korean Chem. Soc.*, **25**, 1955 (2004).
- 16) Choi, E.-Y., Park, K., Yang, C.-M., Kim, H. J., Son, J.-H., Lee, S. W., Lee, Y. H., Min, D. and Kwon, Y.-U., *Chem. Eur. J.*, **10**, 5535 (2004).
- 17) Kim, H. N., Lee, H. K. and Lee, S. W., *Bull. Korean Chem. Soc.*, **26**, 6 (2005).
- 18) Min, D., Cho, Y.-B., Lee, H. K. and Lee, S. W., *Inorg. Chim. Acta*, **359**, 577, (2006).
- 19) Cho, Y.-B., Min, D., Lee, H. K. and Lee, S. W., *Cryst. Growth Des.*, **6**, 342 (2006).
- 20) Kim, S. H., Huh, H. S. and Lee, S. W., *J. Mol. Struct.*, **841**, 78 (2007).
- 21) Dong, Y.-B., Smith M. D. and zur Loye, H.-C., *Inorg. Chem.*, **39**, 4927 (2000).
- 22) Bruker, SHELXTL, Structure Determination Software Programs, Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA (1997).