



N,N'-双(4-甲基-2-苯并噻唑基)-2,6-吡啶二酰胺钴(II) 配合物的合成和晶体结构

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The Synthesis and Crystal Structure of An *N,N'*-bis(4-methyl-2-benzothiazolyl)- 2, 6-pyridicarboxamide Co(II) Complex

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Abstract: Treatment of deprotonated *N,N'*-bis(4-methyl-2-benzothiazolyl)-2, 6-pyridicarboxamide (L^{2-}) with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ yields the mononuclear complex, $(\text{Et}_4\text{N})_2[\text{CoL}_2] \cdot 0.5\text{H}_2\text{O}$. Single crystal X-ray structural determination has been carried out for the complex, crystal system: Monoclinic, space group: $P2_1/c$, $a=1.444(1)$ nm, $b=1.969(1)$ nm, $c=2.448(1)$ nm, $\beta=118.02(1)^\circ$, $V=6.143\ 0(15)$ nm³, $Z=4$. In this complex, the central Co(II) atom is in an octahedron environment, with four deprotonated amide-N atoms in the equatorial plane and two pyridine-N atoms in the axial positions. CCDC: 252558.

Key words: 2,6-pyridicarboxamide; cobalt complex; synthesis; crystal structure

0 Introduction

Cobalt complexes with nonmacrocyclic chelating ligands containing the amide functionality have received much attention in past years^[1-3]. Some studies have revealed that deprotonated nitrogens of organic amides, being anionic in nature, are capable of stabilizing the trivalent oxidation state to a considerable extent^[4-6]. Recently, there has been an increasing interest in the chemistry of deprotonated carboxamide toward transition metal ions due to their striking catalytic activities^[7-9]. In order to develop further the coordination chemistry of pyridine amide ligands to-

ward transition metal ions, as a preliminary studies of this project, herein we describe the synthesis, crystal structure of a new Co(II) complex based on *N,N'*-bis(4-methyl-2-benzothiazolyl)-2,6-pyridicarboxamide (L^{2-}), $(\text{Et}_4\text{N})_2[\text{CoL}_2] \cdot 0.5\text{H}_2\text{O}$.

1 Experimental section

1.1 Materials and physical measurements

Pyridine-2, 6-dicarboxylic acid, thionyl chloride were obtained from commercial sources and used without further purification. 8-methyl-2-aminobenzothiazole was purchased from ACROS Company. CH_2Cl_2 and DMF were dried over CaH_2 and distilled before use.

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The analyses (C, H and N) were measured on a Perkin-Elmer 240C elemental analyzer. ^1H NMR spectroscopic measurements were carried out on a Bruker AM-500 NMR spectrometer, using TMS (SiMe_4) as an internal reference. The solid infrared spectra (IR) were obtained from a Bruker IFS66V vacuum-type FTIR spectrophotometer using KBr pellets.

1.2 Preparation of N,N' -bis(4-methyl-2-benzothiazolyl)2,6-pyridicarboxamide(H_2L)

Pyridine-2, 6-dicarboxylic acid (1.67 g, 10 mmol) was refluxed in thionyl chloride (10 ml) for 8 h. Excess thionyl chloride was removed under vacuum. After cooling to room temperature, 4-methyl-2-aminobenzothiazole (3.28 g, 20 mmol) and triethylamine (3 mL) in 40 mL of CH_2Cl_2 were added to the solution of the residue in CH_2Cl_2 (30 mL). The mixture was further stirred for 2 h at ambient temperature. The white solid was collected by filtration, washed with water and dried in vacuo (yield: 4.25 g, 79.7%). Analysis calculated for $\text{C}_{26}\text{H}_{24}\text{N}_6\text{O}_3\text{S}_2$ (%): C, 58.58, H, 4.54, N, 15.77. Found(%): C, 58.55, H, 4.56, N, 15.71. IR (cm^{-1}): 3 452, 3 170, 2 921, 3 178, 1 676, 1 655, 1 586, 1 534, 1 427, 1 257, 1 119, 1 072, 999, 768, 741.

1.3 Preparation of complex $(\text{Et}_4\text{N})_2[\text{CoL}_2] \cdot 0.5\text{H}_2\text{O}$

The ligand H_2L (533 mg, 10 mmol) and NaH (48 mg, 20 mmol) in DMF (15 mL) were added to a solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (237 mg, 10 mmol) in DMF (5 mL). The resulting solution was magnetically stirred for 15 minutes, then excess $[\text{Et}_4\text{N}]\text{Cl} \cdot x\text{H}_2\text{O}$ was added, and continued to stir for about 1 h. Exposure of this solution to air for a week gave red single crystals that are suitable for structural studies (yield: 0.83 g, 66.9%). Analysis calculated for $\text{C}_{62}\text{H}_{71}\text{N}_{12}\text{O}_{4.5}\text{S}_4\text{Co}$: C, 59.83%, H, 5.76%, N, 13.52%. Found: C, 59.86%, H, 5.71%, N, 13.57%. IR (cm^{-1}): 3444, 2921, 1630, 1564, 1478, 1371, 1204, 764.

1.4 X-ray crystallographic determination

Single crystal X-ray structure determination for complex was performed on an Enraf Noius CAD4/PC equipped with graphite monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\,073\text{ nm}$) at 293 K, operating at 50 kV and 30 mA. Intensity data were collected using the θ - 2θ scan mode in the range of $2.01^\circ \leq \theta \leq 50.00^\circ$. Empirical absorption corrections based on Ψ -scan measurements were applied by XPREP program. The

structure was solved by direct method, and refined by full-matrix least-squares based on F^2 . All non-hydrogen atoms in structure were refined with anisotropic displacement parameters. All hydrogen atoms were theoretically added. The crystal data are summarized in Table 1.

Table 1 Crystallographic Data for $(\text{Et}_4\text{N})_2[\text{CoL}_2] \cdot 0.5\text{H}_2\text{O}$

Formula	$\text{C}_{62}\text{H}_{71}\text{N}_{12}\text{O}_{4.5}\text{S}_4\text{Co}$
M_r	1 243.52
Crystal system	Monoclinic
Space group	$P2_1 / c$
a / nm	1.443 9(3)
b / nm	1.968 80(1)
c / nm	2.447 8(2)
$\beta / (^\circ)$	118.2(1)
V / nm^3	6.1430(1)
Z	4
$D_{\text{calc}} / (\text{Mg} \cdot \text{m}^{-3})$	1.345
$\mu(\text{Mo } K\alpha) / \text{mm}^{-1}$	0.474
$F(000)$	2616
Crystal dimensions / mm	$0.25 \times 0.25 \times 0.32$
2θ range / $(^\circ)$	2.01 to 50.00
Reflections collected / unique	13 822 / 10 790 [$R_{\text{int}}=0.045$]
Index ranges	$-16 \leq h \leq 17$, $-23 \leq k \leq 19$, $-29 \leq l \leq 29$
observed data [$I > 2.0\sigma(I)$]	7 637
Data / restraints / parameters	10 790 / 0 / 767
$R / wR_2 / S$	0.047 5 / 0.107 9 / 1.00
Largest diff. peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	224 and -220

CCDC: 252558.

2 Results and discussion

2.1 Synthesis, IR and UV spectra for the title complex

The molecule H_2L is conveniently prepared by reaction of 2,6-pyridinedicarbonylchloride with 4-methyl-2-aminobenzothiazole. In the IR spectrum, a broad band at $3\,452\text{ cm}^{-1}$ is assigned to $\nu(\text{NH})$ of amide groups. The complex was obtained from the reaction of deprotonated ligand (L^{2-}) with CoCl_2 in DMF solution. Addition of tetraethyl ammonium salts as counter ions resulted the isolation of the air-stable metal complex. In its IR spectrum, the absence of the $\nu(\text{NH})$ confirm that the ligands are coordinated to Co(II) ions in the deprotonated form. The complex shows a

peak at 348 nm in its UV spectrum, which is caused by ligand-to-metal charge transfer transition (LMCT).

2.2 Description of the structure of the complex

It consists of discrete monomeric cobalt complex anion $[\text{CoL}_2]^{2-}$ and two tetrabutylammonium cations. View of the anion of the complex is presented in Fig. 1. The cobalt atom sits on an imposed C_2 axis and is coordinated by four deprotonated amide nitrogens in the equatorial plane and two pyridyl nitrogens in the axial positions. The plane(I) (N1, N2, N4, Co1, r.m.s. deviation=0.038) and the plane(II) (N4, N6, N9, Co1, r.m.s. deviation=0.044) make an angle of 75.5° . The two arm benzothiazole rings of the same ligand make an angle of 13.8° . The geometry of the MN_6 coordination is appreciably compressed octahedral. The significant deviation from 90° of the bond angles involving the chelation is observed (Table 2), which is presumably due to formation of five-membered chelate rings with extended conjugation. The average bond length of

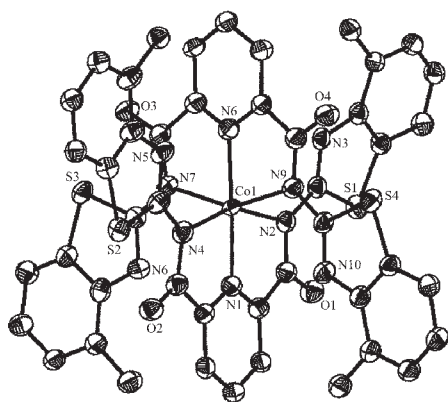


Fig.1 Molecular structure of $(\text{Et}_4\text{N})_2[\text{CoL}_2] \cdot 0.5\text{H}_2\text{O}$ (the counter ions and solvents are omitted for clarity)

Table 2 Selected bond lengths (nm) and angles ($^\circ$) for $(\text{Et}_4\text{N})_2[\text{CoL}_2] \cdot 0.5\text{H}_2\text{O}$

Co1-N1	0.203 0(3)	Co1-N2	0.219 8(3)
Co1-N4	0.220 2(3)	Co1-N6	0.201 4(3)
Co1-N7	0.228 3(3)	Co1-N9	0.218 9(3)
N1-Co1-N2	77.42(1)	N1-Co1-N4	75.99(1)
N1-Co1-N6	177.23(1)	N1-Co1-N7	101.24(1)
N1-Co1-N9	105.65(1)	N2-Co1-N4	153.02(1)
N2-Co1-N6	102.99(1)	N2-Co1-N7	91.15(1)
N2-Co1-N9	94.14(1)	N4-Co1-N6	103.79(1)
N4-Co1-N7	98.36(1)	N4-Co1-N9	88.70(1)
N6-Co1-N7	76.03(1)	N6-Co1-N9	77.09(1)
N7-Co1-N9	153.11(1)		

$\text{Co-N}_{\text{amide}}$ (0.202 2(3) nm) is longer than that of Co-N_{py} (0.221 8(3) nm), which is the result of steric predominance over electronic effects in this complex. The similar feature was observed in other complex^[4]. All of the Co-N bonds of this complex are longer than those of other CoN_6 complex^[4,10], which is resulted from that benzothiazole ring has stronger conjugation than benzene ring. The molecular packing diagram is shown in Fig.2. The tetrabutylammonium cations are included in the cavity formed by the ligands of the adjacent complex.

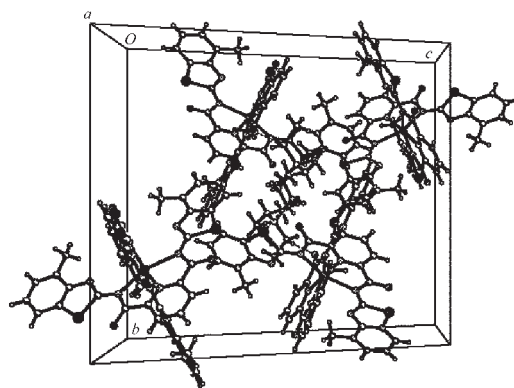


Fig.2 Packing diagram of the complex

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