

group and stabilizes the resulting radicals. From this line of reasoning, the degree of destabilization inherent to the geminal effect is supposed to be somewhat higher, and also the removal of nitrile occurs more readily in the reactions of Eq. (2) than those of Eq. (1).

In summary, theoretical results of the geminal effects qualitatively explain the experimental observations on the decyanation of substituted nitriles.

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5. QCPE Program No. 455, Ver. 6.0. MOPAC package has been developed and distributed by J. J. P. Stewart

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Potential Precursor for Heteropolynuclear Metal Complexes. Synthesis and Crystal Structure of *cis*-Co(NCS)₂(bpym)₂ (bpym=2,2'-bipyrimidine)

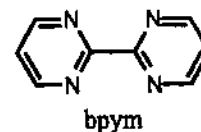
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Ligands that can serve as molecular bridges between metal centers and that also contain a delocalized π system have received considerable attention in recent years as potential electron "propagating" components for inner-sphere electron transfer reactions between metals,¹ magnetically coupled polynuclear systems,^{2,3} models for binuclear rearrangements occurring in metalloenzymes,^{4,5} and low-dimensional conducting coordination polymers.^{6,7} Among various ligands for such goals, the bridging ability of 2,2'-bipyrimidine (bpym) towards first row transition metal has yielded a remarkable class of materials containing diverse architectures and functions.⁸⁻¹⁸ In this context, the reaction of Co(NCS)₂ with bpym in a mole ratio of 2:3 in a mixture solvent of water and ethanol has been found to afford the dinuclear complex, [Co₂(bpym)₃(NCS)₄].¹⁹ In particular, the design of compounds that exhibit desired properties has been continued. In the present contribution, 2,2'-bipyrimidine as a simple bidentate ligand such as 2,2'-bipyridine or 1,10-phenanthroline was clearly demonstrated by the change of reaction conditions. We report the synthesis and

structural properties of the title complex along with potential applicability as a precursor for heteropolynuclear metal complexes.



Experimental

Materials and Instrumentation. Co(NCS)₂ and 2,2'-bipyrimidine were purchased from Aldrich and Alfa, respectively, and used without purification. Elemental analysis (C, H, N) was carried out at the Chemical Analysis Center in KIST. Infrared spectrum was obtained in 4000-400 cm⁻¹ range on a Perkin Elmer 16F PC FTIR spectrometer with sample prepared as KBr pellet.

Preparation of *cis*-Co(NCS)₂(bpym)₂. A chloroform

Table 1. Crystal Data and Structure Refinement for $\text{Co}(\text{NCS})_2(\text{bpym})_2$

Empirical formula	$\text{C}_{18}\text{H}_{12}\text{N}_{10}\text{S}_2\text{Co}$
Formula weight	491.42
Temperature, K	293(2)
Wavelength, \AA	0.71073
Crystal system	I-centered tetragonal
Space group	$I4(1)/a$ (No.88)
a, \AA	12.191(3)
c, \AA	29.014(7)
V, \AA^3	4312(2)
Z	16
d_{calc} , Mg/m^3	1.514
Absorption coefficient, mm^{-1}	1.018
F(000)	1992
Crystal size, mm	$0.4 \times 0.4 \times 0.5$
θ_{max} , deg	25
Index ranges	$-9 \leq h \leq 10, 0 \leq k \leq 14, -34 \leq l \leq 0$
Reflections collected	1363
Independent reflections	1287 [R(int)=0.0354]
Refined parameters	141
Goodness-of-fit on F^2	1.148
Final R indices [$I > 2\sigma(I)$]	R1=0.045, wR2=0.112
R indices (all data)	R1=0.046, wR2=0.1122
Largest diff peak and hole, $e \text{\AA}^{-3}$	0.517 and -0.424
R1= $\sum F_o - F_c / \sum F_o $, wR2= $\{\sum (F_o^2 - F_c^2)^2 / \sum w F_o^4\}^{1/2}$	

solution (5 mL) of bpym (78 mg, 0.5 mmol) was slowly diffused into a methanol solution (15 mL) of $\text{Co}(\text{NCS})_2$ (87 mg, 0.5 mmol). Redish brown crystals were formed in a week. Yield, 85%. mp 400 °C (dec.). Anal. found (Calcd. for $\text{C}_{18}\text{H}_{12}\text{N}_{10}\text{S}_2\text{Co}$): C, 43.10 (44.00); H, 2.39 (2.46); N, 27.90 (28.50). IR(KBr, cm^{-1}): 2096 (sh, C-N), 2083 (s, C-N), 2072 (sh, C-N), 2053 (sh, C-N), 1574 (s), 1408 (s), 1220 (w), 1142 (w), 1091 (w), 1022 (m), 818 (w), 756 (m, C-S), 750 (m, C-S), 686 (m), 670 (m), 472 (w).

X-ray Crystal Analysis. The crystal was wedged in a Lindemann capillary with mother liquor. The X-ray data were collected on an Enraf-Nonius CAD4 automatic diffractometer with graphite-monochromated $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) at ambient temperature. Unit cell dimension was based on 25 well-centered reflections by using a least-square procedure. During the data collection, three standard reflections monitored every hour did not show any significant intensity variation. The data were corrected for Lorentz and polarization effects. Absorption effects were corrected by the empirical psi-scan method. The structure was solved by Patterson method (SHELXS-86), and was refined by full-matrix least squares techniques (SHELXL-93).²⁰ All non-hydrogen atoms were refined anisotropically. Crystal parameters and procedural information corresponding to data collection and structure refinement are given in Table 1. Final atomic coordinates and isotropic thermal parameters are given in Table 2.

Results and Discussion

The reaction of $\text{Co}(\text{NCS})_2$ with bpym in the mole ratio of 1:1 afforded *cis*- $\text{Co}^{\text{II}}(\text{NCS})_2(\text{bpym})_2$ as will be confirmed later. Among various possible structures, only the adduct

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{Co}(\text{NCS})_2(\text{bpym})_2$

	x	y	z	U(eq)
Co	5000	2500	850(1)	33(1)
S	1849(2)	2821(2)	-142(1)	77(1)
N(1)	3746(4)	2436(4)	367(2)	47(1)
N(2)	3724(3)	2724(3)	1350(1)	39(1)
N(3)	4803(3)	4225(3)	880(1)	36(1)
N(4)	2363(4)	4022(4)	1568(2)	58(1)
N(5)	3438(4)	5555(4)	1040(2)	48(1)
C(1)	2956(5)	2607(4)	161(2)	42(1)
C(2)	3215(5)	1956(5)	1592(2)	56(2)
C(3)	2267(6)	2183(6)	1841(2)	69(2)
C(4)	1880(6)	3228(6)	1814(2)	76(2)
C(5)	3270(4)	3726(4)	1351(2)	39(1)
C(6)	3859(4)	4562(4)	1076(2)	35(1)
C(7)	3995(5)	6260(5)	776(2)	54(2)
C(8)	4963(5)	5993(4)	565(2)	48(1)
C(9)	5350(4)	4961(4)	628(2)	43(1)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

was obtained as crystals in high yield. Of course, since such a crystal engineering is delicately dependent on reaction conditions, the structure and nature of the title compound may be changed by the solvent used. In particular, for the bpym ligand, the present reaction produces discrete mononuclear complex instead of the formation of coordination polymers.¹⁴⁻¹⁶ Formation of a *cis*-isomer seems to be induced by the intrinsic properties of the complex. The compound is stable up to 400 °C in air and is slightly soluble in polar organic solvents.

The crystal and molecular structure of the present complex is depicted in Figure 1, and the relevant bond distances and angles are listed in Table 3. The structure consists of centrosymmetric discrete mononuclear molecules. Interestingly, the two NCS groups occupy *cis* positions to each other (N(1)-Co-N(1), 95.0(2)°). The Co-N bond length involving NCS group is much shorter than the corresponding

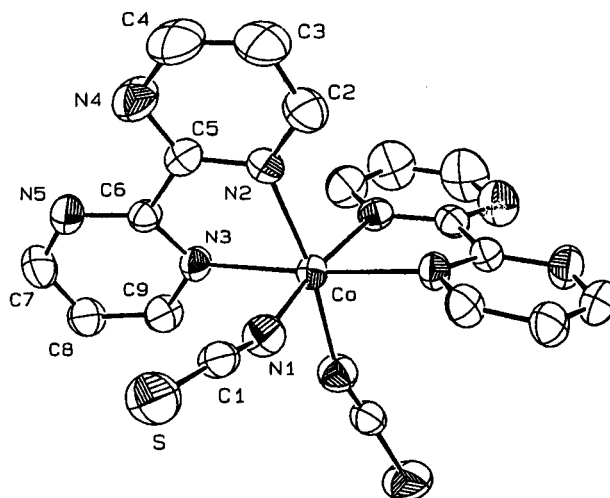
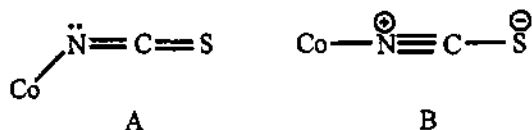
**Figure 1.** X-ray crystal structure and atomic labeling scheme of *cis*- $\text{Co}^{\text{II}}(\text{NCS})_2(\text{bpym})_2$.

Table 3. Bond Lengths (Å) and Angles (°) for Co(NCS)₂(bpym)₂

Co-N(1)	2.076(5)	Co-N(1)#1	2.076(5)
Co-N(3)#1	2.118(4)	Co-N(3)	2.118(4)
Co-N(2)	2.145(4)	Co-N(2)#1	2.145(4)
S-C(1)	1.631(6)	N(1)-C(1)	1.151(6)
N(2)-C(2)	1.323(6)	N(2)-C(5)	1.341(6)
N(3)-C(9)	1.336(6)	N(3)-C(6)	1.348(6)
N(4)-C(5)	1.323(6)	N(4)-C(4)	1.339(8)
N(5)-C(6)	1.319(6)	N(5)-C(7)	1.337(7)
C(2)-C(3)	1.390(8)	C(3)-C(4)	1.361(9)
C(5)-C(6)	1.480(7)	C(7)-C(8)	1.368(8)
C(8)-C(9)	1.355(7)		
N(1)-Co-N(1)#1	95.0(2)	N(1)-Co-N(3)#1	94.2(2)
N(1)#1-Co-N(3)#1	88.9(2)	N(1)-Co-N(3)	88.9(2)
N(1)#1-Co-N(3)	94.2(2)	N(3)#1-Co-N(3)	175.3(2)
N(1)-Co-N(2)	85.9(2)	N(1)#1-Co-N(2)	170.5(2)
N(3)#1-Co-N(2)	100.4(2)	N(3)-Co-N(2)	76.3(2)
N(1)-Co-N(2)#1	170.5(2)	N(1)#1-Co-N(2)#1	85.9(2)
N(3)#1-Co-N(2)#1	76.3(2)	N(3)-Co-N(2)#1	100.4(2)
N(2)-Co-N(2)#1	94.9(2)	C(1)-N(1)-Co	163.5(4)
C(2)-N(2)-C(5)	116.7(5)	C(2)-N(2)-Co	127.5(4)
C(5)-N(2)-Co	114.6(3)	C(9)-N(3)-C(6)	116.9(4)
C(9)-N(3)-Co	126.0(3)	C(6)-N(3)-Co	114.6(3)
C(5)-N(4)-C(4)	115.1(5)	C(6)-N(5)-C(7)	116.0(5)
N(1)-C(1)-S	178.2(5)	N(2)-C(2)-C(3)	121.6(6)
C(4)-C(3)-C(2)	116.4(6)	N(4)-C(4)-C(3)	123.7(6)
N(4)-C(5)-N(2)	126.5(5)	N(4)-C(5)-C(6)	118.3(5)
N(2)-C(5)-C(6)	115.2(4)	N(5)-C(6)-N(3)	125.4(4)
N(5)-C(6)-C(5)	119.0(4)	N(3)-C(6)-C(5)	115.6(4)
N(5)-C(7)-C(8)	122.7(5)	C(9)-C(8)-C(7)	117.5(5)
N(3)-C(9)-C(8)	121.5(5)		

bond involving the bpym ligand. In particular, the Co-N(2) (2.145(4) Å) *trans* to NCS group is significantly longer than the Co-N(3) (2.076(5) Å). This is an excellent example of the *trans* effect²¹: the NCS anion is a stronger *trans* directing ligand than the N atom of pyridine. Thus, the *cis* geometry of the title complex may result from the *trans* effect of NCS group. Among two possible linkage isomers of NCS group, an isothiocyanate mode (Co-NCS) was observed. The connection between Co atom and the isothiocyanate group is slightly bent with C(1)-N(1)-Co (163.5(4)°), indicating that the contribution of the resonance structure B



is significant. The bond lengths of N(1)-C(1) (1.151(6) Å) and C(1)-S (1.631(6) Å) are additional evidence for the contribution of the resonance structure B. The most striking feature is that the bpym ligand is coordinated to the cobalt atom in a simple bidentate mode such as bipyridine, resulting in mononuclear cobalt(II) complex. Thus, the angles of N(4)-C(5)-C(6) (118.3(5)°) and N(5)-C(6)-C(5) (119.0(4)°) are splayed out with the concomitant closing of the angles of N(2)-C(5)-C(6) (115.2(4)°) and N(3)-C(6)-C(5) (115.6(4)°). The small bite angle of the bpym ligand (76.3(2)°) is respon-

sible for the distortion of the octahedral geometry. Thus, the central cobalt atom is in a distorted octahedral environment with six nitrogen atoms.

The most relevant IR feature is those associated with the presence of linkage isomeric NCS anionic ligand. Bonding mode of metal (iso)thiocyanate complexes have been well established for whether the NCS group is bonded to thiocyanate (M-SCN) or isothiocyanate (M-NCS).²² The ν (C-N) band in the region of 2000-2200 cm⁻¹ has been used to discern the bonding fashion of the NCS anion: thiocyanate complexes exhibit very sharp ν (C-N) above 2100 cm⁻¹, whereas isothiocyanate complexes do relatively broad and intensive band around or below 2100 cm⁻¹. Strong and broad bands below 2100 cm⁻¹ of the present complex are strongly indicative of isothiocyanate bonding mode, which is well consistent with the X-ray structure. Furthermore, the *cis* isomer has been known to exhibit more bands than the *trans* isomer, expected from symmetry considerations.²³ The complicated bands of both C-N (2096 (sh), 2083 (s), 2072 (sh), and 2053 (sh)) and C-S (756 (m), 750 (m)) stretching frequencies seem to be indebted to the *cis* isomer.

In conclusion, the title complex is the first structurally characterized mononuclear (bipyrimidine)cobalt complex. Only a mononuclear complex, *cis*-Co(NCS)₂(bpym)₂, instead of coordination polymers including interpenetrating lattice was isolated in high yield by delicate change of reaction conditions. The mononuclear complex bearing additional potential chelate may be devoted to the development of rational synthetic routes to obtain novel homo- and heteropolynuclear coordination compounds that have applications as molecular-based materials or molecular building block.

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