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# Unprecedented N-Inserted Disulfide Ligand Stabilized by Coordination to the Electropositive Co$^{III}$ Center

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The reaction of Co$^{II}$ and 2,2′-dipyridyldisulfide (PySSPy) in the presence of azide produced a peculiar monomeric complex [Co$^{III}$(PyS)(PyS-N-SPy)(N$_3$)] (**1**). In this reaction, redox chemistry takes place, which is associated mainly with the oxidation of Co$^{II}$ to Co$^{III}$ and the reduction of PySSPy. During the reaction, the azide ion decomposes and donates a nitrogen atom to PySSPy. The crystal structure of **1** provides evidence that the unusual, N-inserted ligand PyS-N-SPy can be stabilized through coordination to the electropositive Co$^{III}$ ion.

## Introduction

Sulfur-containing ligands have shown not only a diverse chemistry but also a broad relevance to organic, inorganic, and biological systems.[1] Pyridine 2-thiol was frequently used to create metal thiolates, and several related structural types have been characterized.[2] Another efficient strategy for metal–sulfur compounds is to utilize organic disulfides that can be incorporated into molecular assemblies by oxidative addition to metal centers under UV, thermal treatment, and at ambient conditions.[3] The redox events help to generate coordination systems with high oxidation states.[4] Among disulfides, pyridine disulfides are of high interest in terms of supramolecular chemistry and the chemical diversity (binding patterns and redox reactions) of the compounds prepared with them.[5,6] For instance, 2,2′-dipyridyldisulfide (PySSPy) functions as a monodentate, bidentate, or tridentate chelating ligand, depending on the binding affinity of the donor atoms in PySSPy.[6] The disulfide can also be dissembled and reassembled in the presence of suitable reaction conditions to give transformed products.[6] In addition, the 2-pyridinethiolate ligand (PyS$^-$) containing N,S-donors can be produced from the decomposition of PySSPy. The generated PyS$^-$ anion is chelated to form monomeric metal entities and lanthanide complexes, which comprise sterically strained four-membered rings.[7,8] In some cases, oxidation of PySSPy to pyridine-2-sulfinate in the presence of Cu$^{II}$ ions occurs under aerobic conditions.[9] Normally, the oxidation of the ligands proceeds with a strong oxidant such as H$_2$O$_2$ or a halogen.[10] Because of the aforementioned diversity derived from PySSPy, it is desirable to seek a new system that provides more insight into this adventurous ligand.

We report the synthesis, crystal structure, and physical properties of [Co$^{III}$(PyS)(PyS-N-SPy)(N$_3$)] (**1**), which accommodates the singular, N-inserted ligand PyS-N-SPy stabilized through coordination to the oxidized Co$^{III}$ ion.

## Results and Discussion

The reaction of Co(ClO$_4$)$_2$·6H$_2$O/PySSPy/NaN$_3$ in a 1:1.5:2 ratio afforded brown crystals of **1** in 44% yield. The color of the product is identical to the complex [Co(en)$_2$(PyS)]$^{2+}$ (en = ethylenediamine) containing the Co$^{III}$ ion and the 2-pyridinethiolato (PyS$^-$) ligand.[7a] In the synthesis, mixing Co$^{II}$ ions and PySSPy did not affect the color of the reaction solution. Upon adding NaN$_3$ to the resultant solution, the color of the solution immediately changed from pink to brown. The UV/Vis spectra (Figure 1) show that the characteristic d–d bands of an octahedral Co$^{II}$ center are observed in the presence of Co$^{II}$ or Co$^{II}$/PySSPy. The addition of azide to the Co$^{II}$/PySSPy solution drastically promoted the reaction, and after around ten hours, the spectra were virtually not altered but akin to that of the product, demonstrating that Co$^{II}$ was oxidized to Co$^{III}$ in solution. Moreover, the exact stoichiometric ratio of 1:1.5:2 for Co$^{2+}$/PySSPy/N$_3$$^-$ in the reaction mixture should be used in order to obtain the maximal yield. These observations strongly support that azide plays a key role in the evolution of the reaction.

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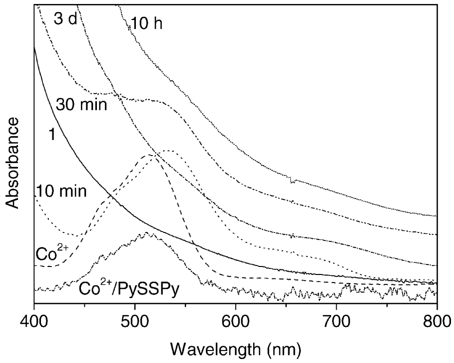

Figure 1. UV/Vis spectra at various time intervals after the beginning of the reaction in the simultaneous presence of $Co^{2+}$, PySSPy, and $N_3^-$ in MeOH. The spectra for compound **1**, $Co(ClO_4)_2·6H_2O$, and $Co^{2+}$/PySSPy were included for comparison.

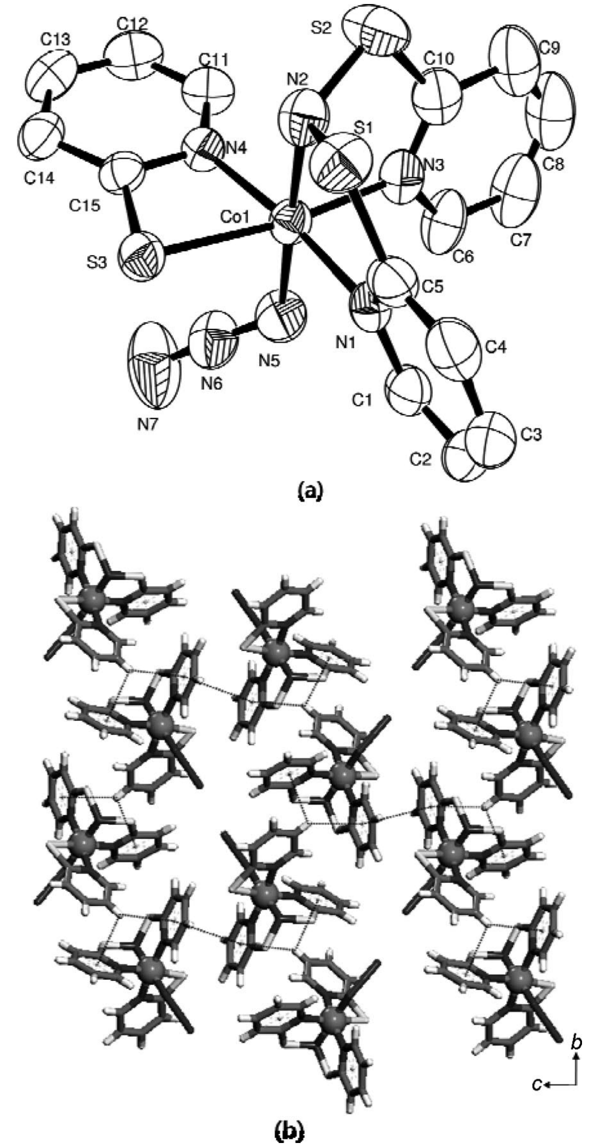

Figure 2. (a) Molecular view of **1** showing the atom-labeling scheme. (b) Extended two-dimensional structure including CH–π and π–π interactions (dotted lines).

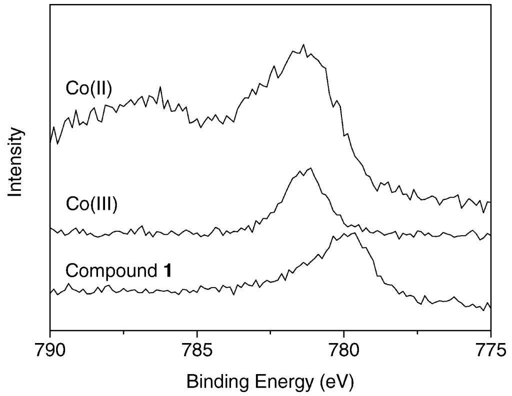

Figure 3. X-ray photoelectron spectra for $CoCl_2·6H_2O$, $K_3[Co(CN)_6]$, and compound **1**.

Compound **1** crystallizes in the monoclinic system as determined by X-ray crystallography. As shown in Figure 2a, the Co center adopts a distorted octahedral environment consisting of three N atoms from $(PyS)_2N^–$, one S and one N atom from $PyS^–$, and one N atom from the terminal azide. The Co–N lengths span from 1.908 to 1.983 Å, which fall in the usual range of N-surrounded $Co^{III}$ systems.[8,11] The $Co^{II}$–N distances are much longer, being around 2.1 Å.[11,12] The N and S atoms of the $PyS^–$ ligand are coordinated to the Co ion, resulting in the formation of a four-membered ring. The bond angle [72.35(10)°] of N4–Co1–S3 is significantly smaller than the other angles, which are close to 90° around the Co coordination sphere. This unusual binding pattern was also observed in $Cu^{2+}$, $Hg^{2+}$, $Ag^+$, and $Ru^{2+}$ species surrounded by neutral N and S atoms.[6a,13] The anionic sulfur atom on $PyS^–$ is directly bonded to the Co ion with a distance of 2.2901(12) Å, which was found in $Li^+$, $K^+$, $W^{2+}$, $Ir^+$, $Rh^+$, $Re^{5+}$, and $Ln^{3+}$ complexes with steric strains.[2b,7b,8,14] The dihedral angles between the pyridyl groups of $(PyS)_2N^–$ are almost right angles [88.76(15)°]. In comparison, the other dihedral angles correspond to 78.00(13)° for N3- and N4-containing rings, and 75.40(14)° for N1- and N4-containing rings.

The extended structure of **1** in the *bc* plane is displayed in Figure 2b. One pyridyl hydrogen atom (H12) on $PyS^–$ builds the noncovalent CH–π contacts with the centroids of two pyridyl rings on $(PyS)_2N^–$ along the *b* axis (Figure S1), leading to the construction of a one-dimensional chain. The distances between H12 and the aromatic groups are 3.209 Å for the N1-containing ring and 3.169 Å for the N3-containing ring, which are consistent with the $Ni^{II}$ complex capped with pyrazoles.[15] On the other hand, the π–π interactions are established between the pyridyl rings of $(PyS)_2N^–$ with a centroid distance of 3.839 Å (Figure S2). The combined noncovalent forces lead to the formation of a two-dimensional supramolecular entity, and the layered structure is depicted in Figure S3.

To determine the oxidation state of Co, we carried out an X-ray photoelectron (XPS) experiment (Figure 3). Binding energies quite similar to that of the Co $2p_{3/2}$ peak are detected for cobalt systems such as CoO, $Co_2O_3$, $Co(OH)_2$, and CoOOH.[16] In the XPS data, the Co $2p_{3/2}$ peaks are at 781.3 eV for $CoCl_2{\cdot}6H_2O$. The additional satellite peak is positioned at about 786.5 eV, which is typical for paramagnetic $Co^{II}$ species.[16] The binding energy for $K_3[Co(CN)_6]$ has a well-resolved asymmetric band at 781.3 eV. Compound **1** shows a peak at 779.9 eV, which is analogous to the signal of $K_3[Co(CN)_6]$ and hence assignable to $Co^{III}$. The difference between the peak positions of **1** and $K_3[Co(CN)_6]$ is presumably due to the dissimilar environments of the Co atoms.[17] Therefore, the valence of the Co atom in **1** is determined to be 3+, and the oxidation of $Co^{II}$ to $Co^{III}$ is confirmed. The cyclic voltammogram shows that an irreversible event is observed at $E_{pc} = -0.92$ V, which lies in the range for the $Co^{III}/Co^{II}$ couple (Figure S4).[18]

From synthetic conditions and other data, a possible chemical reaction in the present system can be written as

$$Co^{II} + 1.5PySSPy + 2N_3^- \rightarrow [Co^{III}(PyS)(PySNSPy)(N_3)] + N_2.$$

A most notable feature for **1** is the presence of the N atom between the disulfide on $(PyS)_2N^-$. This indicates that an N atom intrudes into the disulfide bond in the course of the reaction. The role of the azide appears to be crucial, because the product was not generated in the absence of azide. During the reaction process, the chemistry involved seems rather complex; the $Co^{II}$ ion is oxidized to $Co^{III}$, and PySSPy undergoes reduction to $PyS^-$, while the azido ligand is fragmented into $N_2$ and $N^-$. The generated nitride is likely incorporated into the –S–S– bond of PySSPy. It is reasoned that the driving force of the insertion may be associated with both the expansion from the strained four-membered to the strain-free five-membered ring and the subsequent stabilization of the N-inserted ligand by coordination to the electropositive $Co^{III}$ ion. It is worth noting that the $(PyS)_2N^-$ ligand is created and successfully characterized for the first time.

## Conclusions

We prepared a $Co^{III}$ monomer $[Co^{III}(PyS)(PyS\text{-}N\text{-}SPy)(N_3)]$ (**1**) by the reaction of $Co^{II}$, PySSPy, and azide. The crystal structure clearly reveals that the unique N-inserted species PyS-N-SPy is stabilized by coordination to the $Co^{III}$ center. The current results indicate that creating and stabilizing chemically unstable organic species may be possible by applying the principles of coordination chemistry as exemplified in this case.

## Experimental Section

**Materials:** All the chemicals and solvents in the synthesis were of reagent grade and used as received.

**Preparation of Compound 1:** A methanol solution (10 mL) of $Co(ClO_4)_2{\cdot}6H_2O$ (0.50 mmol) was mixed with 2,2′-dipyridyldisulfide (0.75 mmol) dissolved in MeOH (10 mL). The pink solution was treated with $NaN_3$ (1.0 mmol) in MeOH (10 mL), allowing for the color change from deep pink to pale pink and then to brown. After being stirred for 20 min, the resulting mixture was filtered and concentrated slowly, producing brown crystals with a yield of 44%. $C_{15}H_{12}CoN_7S_3$ (445.43): calcd. C 40.45, H 2.72, N 22.01, S 21.60; found C 40.46, H 2.71, N 21.92, S 21.62.

**Physical Measurements:** Elemental analyses for C, H, and N were performed at the Elemental Analysis Service Center of Sogang University. UV/Vis spectra were obtained with a Sinco S-3150 spectrometer. A cyclic voltammogram was recorded with a CHI600C potentiostat equipped with a C-3 cell stand.

**Crystal Data for 1:** $C_{15}H_{12}CoN_7S_3$, $M_r = 445.43$, monoclinic, space group $P2_1/n$, $a = 7.48990(10)$ Å, $b = 12.8243(3)$ Å, $c = 18.4334(4)$ Å, $\beta = 93.6200(10)°$, $V = 1767.05(6)$ Å$^3$, $Z = 4$, $\rho_{calcd.} = 1.674$ g cm$^{-3}$, $\mu = 1.341$ mm$^{-1}$, 31071 reflections collected, 4378 unique ($R_{int} = 0.0575$), $R1 = 0.0531$, $wR2 = 0.1346$ [$I > 2\sigma(I)$]. CCDC-686325 contains the supplementary crystallographic data for **1**. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Supporting Information** (see footnote on the first page of this article): Relevant crystal structures and CV of **1**.

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