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Unexpected Formation of a Disulfide from 2-Mercaptopyridine and Co(II).

Phimphaka HARDING[1], David J. HARDING[1],
and Chaveng PAKAWATCHAI[2]

[1]*Department of Chemistry, School of Science, Walailak University,*
Thasala, Nakhon Si Thammarat 80160, Thailand
[2]*Department of Chemistry, Faculty of Science,*
Prince of Songkla University, Songkhla, 90112, Thailand

ABSTRACT

The reaction between the Co(II) ion and 2-mercaptopyridine in the presence of base yields a disulfide Co(II) complex, namely [$CoCl_2$(2,2′-dipyridyldisulfide)] **1**. The structure has been determined by single crystal X-ray crystallography. The Co(II) ion coordinates to two chlorine atoms and two nitrogen atoms in a tetrahedral fashion. This result provides insight into the formation of 2,2′-dipyridyldisulfide from 2-mercaptopyridine.

Keywords: Co(II), 2-Mercaptopyridine, X-ray structure, Disulfide

INTRODUCTION

2-Mercaptopyridine (pySH) and its anion 2-mercaptopyridinate are versatile coordination ligands acting as chelating, bridging and chelating, bridging groups [1-4] (**Figure 1**). Although, pySH generally acts as an innocent ligand it can undergo a number of reactions resulting in modification of the original unit [3,4]. For instance, under the appropriate conditions pySH may be oxidized to yield pyridine-2-sulfenato or pyridine-2-sulfanato [5].

In this paper we report the formation of 2,2′-dipyridyldisulfide (dpds) from the reaction between 2-mercaptopyridinate and Co(II) chloride, instead of the expected paddlewheel complex [$Co_2(pyS)_4$].

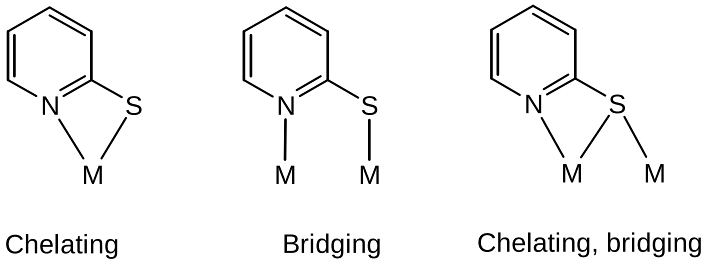


Figure 1 The bonding modes of 2-mercaptopyridine.

MATERIALS AND METHODS

2-mercaptopyridine, $CoCl_2.6H_2O$, triethylamine (NEt_3) and solvents were purchased from Fluka Chemical Co. and were used as received.

Synthesis of [$CoCl_2$(2,2′-dipyridyldisulfide)] 1.

To a solution of 2-mercaptopyridine (144.8 mg, 1.30 mmol) in acetonitrile (5 ml) was added NEt_3 (180 μl, 1.30 mmol). In a separate flask $CoCl_2.6H_2O$ (155 mg, 0.65 mmol) was dissolved in acetonitrile (20 ml) yielding a green solution. Addition of the mercaptopyridine solution to the Co(II) solution resulted in a deep green solution that was stirred for 1 hour. During this time a dark green solid precipitated which was filtered off and air-dried (191.5 mg, 84 %). IR (KBr; cm^{-1}): 1583, 1552, 1450, 1407, 1018, 646, 494, 483. Anal. Calc. for $C_{10}H_8Cl_2N_2S_2Co$: C, 34.30; H, 2.31; N, 8.00 %. Found: C, 34.64; H, 2.71; N, 7.47 %. Crystals suitable for X-ray diffraction were grown by slow evapouration of a saturated solution of 1 in EtOH at room temperature.

X-ray Data Collection and Reduction

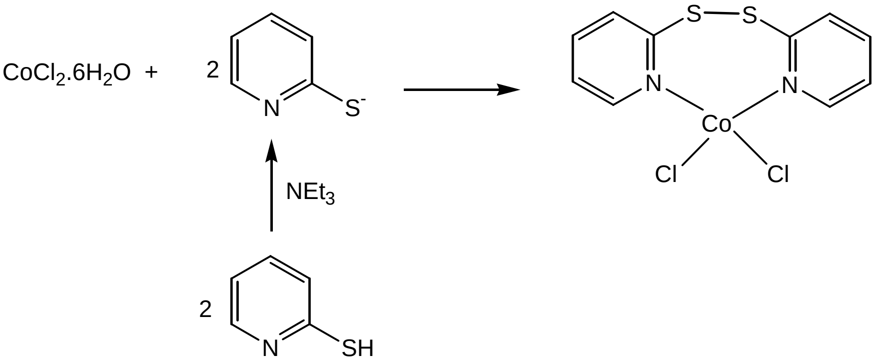
X-ray data of a blue square crystal of [$CoCl_2$(dpds)] **1** were collected on a Bruker APEX diffractrometer at 293 K for $1.82 < \theta < 26.02$ with $\lambda = 0.71073$ Å. The structure was solved by direct methods and refined by least-squares against all F^2 values corrected for absorption [6]. A summary of the crystal data, experimental details and refinement results are listed in **Table 1**.

Table 1 Crystal data and structure refinement for [CoCl$_2$(2,2′-dipyridyldisulfide)] **1**.

Empirical formula	$C_{10}H_8Cl_2CoN_2S_2$
Formula weight	350.13
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 7.8210(14) Å α = 94.503(3)° b = 8.1492(15) Å β = 107.223(3)° c = 12.082(2) Å γ = 114.835(2)°
Volume	648.9(2) Å
Z	2
Density (calculated)	1.792 Mg/m^3
Absorption coefficient	2.031 mm^{-1}
F(000)	350
Crystal size	0.31 x 0.223 x 0.132 mm^3
Theta range for data collection	1.82 to 26.02°
Index ranges	$-9 \le h \le 9$, $-10 \le k \le 9$, $-14 \le l \le 14$
Reflections collection	6707
Independent reflections	2540 [R(*int*) = 0.0129]
Completeness to theta = 26.02°	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.760 and 0.612
Refinement method	Full-matrix least-square on F^2
Data/restraints/parameters	2540/0/186
Goodness-of-fit on F^2	1.053
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0212, wR_2 = 0.0569
R indices (all data)	R_1 = 0.0227, wR_2 = 0.0579
Largest diff. peak and hole	0.282 and -0.187 e. Å^{-3}

RESULTS AND DISCUSSION

We attempted to prepare a paddlewheel complex [Co_2(2-mercaptopyridine)$_4$] in which 2-mercaptopyridine acts as a bridging ligand by reacting pyS^- with Co(II) chloride (**Scheme 1**). Crystallization of the resulting solid and subsequent X-ray crystallographic analysis reveal that the product is an unexpected 2,2′-dipyridyldisulfide complex, [$CoCl_2$(2,2′-dipyridyldisulfide)] **1**. The structure of **1** is shown in **Figure 2**, while selected bond lengths and angles are listed in **Table 2**. The cobalt coordination sphere is approximately tetrahedral with the metal coordinated by two chloride atoms and two pyridyl nitrogen atoms of the dpds ligand. The Co-Cl and Co-N bond lengths are typical of Co(II) and require no further comment.



Scheme 1 The reaction between deprotonated 2-mercaptopyridine and Co(II) ion.

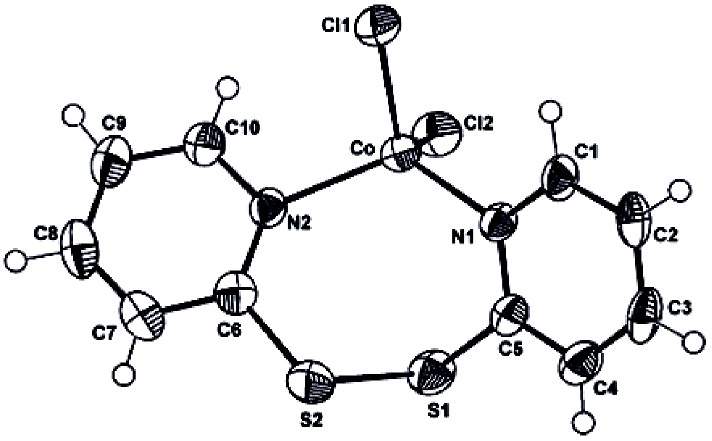


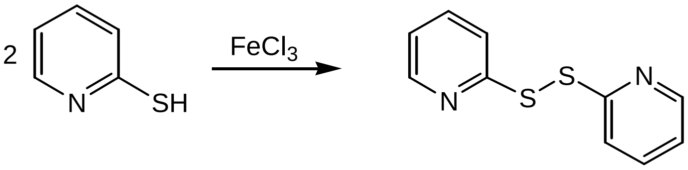
Figure 2 ORTEP view of [CoCl$_2$(2,2′-dipyridyldisulfide)] **1**. Ellipsoids are drawn at the 50% probability level.

Table 2 Selected bond distances (Å) and angles (°) of [CoCl$_2$(2,2′-dipyridyldisulfide)] **1**.

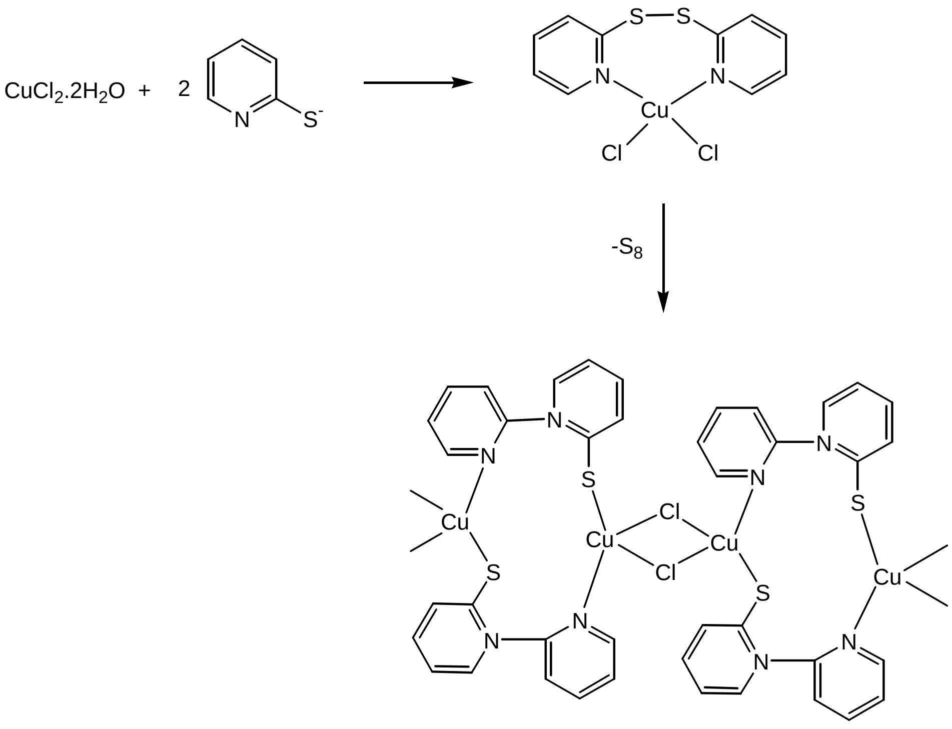
Co-N(1)	2.0287(14)
Co-N(2)	2.0607(14)
Co-Cl(2)	2.2365(6)
Co-Cl(1)	2.2552(5)
S(1)-C(5)	1.7824(18)
S(1)-S(2)	2.0455(8)
S(2)-C(6)	1.7805(18)
N(1)-Co-N(2)	117.73(6)
N(1)-Co-Cl(2)	113.51(4)
N(2)-Co-Cl(2)	104.51(4)
N(1)-Co-Cl(1)	101.97(4)
N(2)-Co-Cl(1)	100.61(4)
Cl(2)-Co-Cl(1)	118.47(2)

Although the structure of [CoCl$_2$(dpds)] **1** has been reported previously, the compound was originally prepared by reaction of dpds and Co(II) chloride [7,8]. In this work, dpds forms as the result of oxidation of two 2-mercaptopyridinate anions. The formation of disulfide from pySH is known in the case of Fe^{3+} but has never previously been observed for cobalt [9] (**Scheme 2**). It is also interesting to note that the reaction of $CuCl_2$ with pyS^- leads to the formation of a 1D polymer $[Cu(\mu\text{-}Cl)(\mu\text{-}ppt)]_n$ {ppt = 1-(2-pyridine)pyridinium-2-thiolate} [10]. This is thought to occur in two steps; first formation of dpds and second modification of the dpds ligand at the metal centre to give ppt (**Scheme 3**) [10,11]. Given that $[CoCl_2(dpds)]$ **1** is the only product from this reaction it would seem that cobalt(II) is not a strong enough Lewis acid to active the dpds ligand to yield 1-(2-pyridine)pyridinium-2-thiolate.

The resonances in the IR spectrum of **1** are essentially the same as those reported in the literature [7,8]. The FAB Mass spectrum of complex **1** shows two peaks at 316 and 280 consistent with $[CoCl(2,2'\text{-}dipyridyldisulfide)]^+$ and $[Co(2,2'\text{-}dipyridyldisulfide)]^+$ respectively, confirming that the structurally characterized compound is representative of the bulk solid.



Scheme 2 The disulfide formation of 2-mercaptopyridine.



Scheme 3 Formation of ppt from pyS$^-$ and Cu(II) chloride.

CONCLUSIONS

In conclusion, a new preparative methodology for the known cobalt(II) complex, [$CoCl_2$(2,2′-dipyridyldisulfide)] provides interesting insights into the formation of 2,2′-dipyridyldisulfide from 2-mercaptopyridine. It is clear from this study that formation of dpds occurs readily at metal centres and that if the metal centre is not too Lewis acidic complexes containing the dpds ligand can be isolated.

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Supporting Information Available: X-ray crystallographic details (CIF) of **1** are available free of charge by contacting the authors.

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บทคัดย่อ

พิมผกา ฮาร์ดิง[1] เดวิด ฮาร์ดิง[1] และ เชวง ภัควัตชัย[2]

การเกิดไดซัลไฟด์จาก 2-เมอร์แคปโทไพริดีนและโคบอลต์(II)

ปฏิกิริยาระหว่างไอออนโคบอลต์(II) และ 2-เมอร์แคปโทไพริดินในสภาวะที่เป็นเบส ทำให้เกิดสารประกอบเชิงซ้อนของโคบอลต์ไดซัลไฟด์, [CoCl$_2$(2,2′-dipyridyldisulfide)] **1** เมื่อศึกษาโครงสร้างของสารประกอบเชิงซ้อนโดยเทคนิคเอกซ์เรย์แบบผลึกเดี่ยว พบว่ามีรูปทรงแบบทรงสี่หน้าโดยไอออนโคบอลต์โคออร์ดิเนตกับอะตอมคลอรีนจำนวน 2 อะตอมและอะตอมไนโตรเจนจำนวน 2 อะตอม ผลจากการศึกษาโครงสร้างนี้ทำให้ทราบถึงการเกิด 2,2′-ไดไพริดิลไดซัลไฟด์จาก 2-เมอร์แคปโทไพริดิน

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[1] สำนักวิชาวิทยาศาสตร์ มหาวิทยาลัยวลัยลักษณ์ อำเภอท่าศาลา จังหวัดนครศรีธรรมราช 80160

[2] ภาควิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยสงขลานครินทร์ อำเภอหาดใหญ่ จังหวัดสงขลา 90112