

SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURES OF 2,2'-BIPYRIDINE COMPLEXES OF CHROMIUM(III)

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ABSTRACT

Reaction of $\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$ with 2,2'-bipyridine (bipy) in ethanol in the mole ratio of 1:1 and 1:2 at ambient temperature and pressure results in the formation of the cationic complexes $[\text{Cr}(\text{bipy})(\text{H}_2\text{O})_2\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$ ($1 \cdot \text{H}_2\text{O}$) and $[\text{Cr}(\text{bipy})_2\text{Cl}_2]\text{Cl} \cdot 2 \text{H}_2\text{O}$ ($2 \cdot 2 \text{H}_2\text{O}$), respectively. The crystal structures were determined by X-ray diffraction. **1** crystallized in the orthorhombic space group *Pccn* with $a = 6.8781$ (6) Å, $b = 11.9147$ (11) Å, $c = 20.2969$ (18) Å, and $\alpha = \beta = \gamma = 90^\circ$ with $Z = 4$. **2** crystallized in the triclinic space group *P-1* with $a = 7.0360$ (5) Å, $b = 12.3914$ (10) Å, $c = 13.0311$ (10) Å, and $\alpha = 90.70000$ (10)°, $\beta = 93.5140$ (10)°, $\gamma = 100.0230$ (10)° with $Z = 2$. The complexes are six-coordinated and have normal planarity. Both complexes were characterized by spectrophotometry and the chromium center appears as an oxidation state of +3 approved by effective magnetic moment.

KEYWORDS: chromium, 2, 2'-bipyridine

1. INTRODUCTION

Chromium compounds have been extensively used in organic synthesis both stoichiometrically and catalytically [1,2]. Among the catalysts for ethylene polymerization, the Phillips catalyst which is an inorganic chromium catalyst supported on silica ($\text{CrO}_3/\text{SiO}_2$) [3] and the Union Carbide catalyst which is an organochromium catalyst supported on silica ($\text{Cp}_2\text{Cr}/\text{SiO}_2$) are extensively used [4]. Recently active homogeneous chromium-based polymerization catalysts have been discovered. This has led to a better understanding of the chromium in the active site and the mechanism of polymerization in chromium-based heterogeneous systems [5,6]. However, the interest in the development of efficient catalysts for desired properties of polymer has been continuously studied in both academic and industrial fields. Also, N,N-, and N,O-chelating ligands have been reported to act as good ligands for chromium catalysts for ethylene polymerization [7-9]. N is a good donor atom and able to stabilize transition metal center. This encouraged us to study chromium complexes having nitrogen atoms as donor ligands. In this article we present full synthetic, characterization details, and crystal structures of chromium complexes containing 2,2'-bipyridine.

2. MATERIALS AND METHODS

General Techniques : All handles of compounds were performed in an ambient condition. $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ was purchased from Unilab Company, and 2,2'-bipyridine was purchased from Acros Organics. Melting point was measured by an Electrothermal IA 9100 series digital melting point. FTIR spectra were recorded on a Spectrum One spectrophotometer, Perkin Elmer. Magnetic susceptibilities were determined by a vibrating sample magnetometer (VSM), Lakeshore 7404. Elemental analysis was sent to analyze by using CHNS/O Analyser, Perkin Elmer PE2400 SeriesII, from Scientific and Technological Research Equipment Center, Chulalongkorn University.

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Crystal structures were characterized by using single-crystal X-ray diffractometer and SHELXTL-PC 6.12 programs from Department of Chemistry, Faculty of Science, Prince of Songkla University.

Synthesis and Characterization

[Cr(bipy)(H₂O)₂Cl₂]Cl · H₂O (1 · H₂O) 0.3023 g (1.9354 mmol) of bipy was added to a stirred solution of 0.5143 g (1.9320 mmol) of CrCl₃ · 6 H₂O in 50 mL of ethanol at room temperature. The reaction mixture turned to dark green and was stirred for 8 hours. Then the homogeneous green solution was evaporated under vacuum and allowed to evaporate slowly at room temperature. After a week, the product was filtered and washed with cold ethanol for several times to obtain a blue green crystal of 1 · H₂O (0.5063 g, 1.3736 mmol, 71.12 % yield). IR (KBr): 3529 (br), 3079 (br), 1626 (s), 1570 (w), 1469 (m), 1442 (s), 1309 (m), 1242 (w), 1154 (m), 1038 (w), 771 (s) and 651 (m) cm⁻¹. Mp: 275.5 °C (dec.). μ_{eff} (293 K) = 3.57 μ_{B} . Anal. Calcd for C₁₀H₁₄CrO₃N₂Cl₃: C, 32.59; H, 3.83; N, 7.60; Cr, 14.11. Found: C, 32.42; H, 3.89; N, 7.63.

[Cr(bipy)₂Cl₂]Cl · 2H₂O (2 · 2 H₂O) 0.5927 g (3.7947 mmol) of bipy was added to a stirred solution of 0.5046 g (1.8938 mmol) of CrCl₃ · 6 H₂O in 50 ml of ethanol at room temperature. The reaction mixture turned to dark green and was refluxed for 24 hours. Then the mixture of red green solution and a small amount of brown green solid was filtered. The filtrate was evaporated slowly at room temperature. After 2 weeks, the product was filtered and washed with cold ethanol to yield red brown crystals. Recrystallization of these crystals in DMF gave a red brown crystal of 2 · 2 H₂O (0.7153 g, 1.4115 mmol, 74.52 % yield). IR (KBr): 3369 (s), 3028 (m), 1602 (s), 1564 (w), 1472 (m), 1445 (s), 1316 (m), 1246 (w), 1157 (m), 1032 (s), 903 (w), 773 (s) and 650 (m) cm⁻¹. Mp: 210.5 °C (dec.). μ_{eff} (293K) = 3.78 μ_{B} . Anal. Calcd for C₂₀H₂₀CrO₂N₄Cl₃: C, 47.40; H, 3.98; N, 11.06; Cr, 10.26; Found: C, 47.40; H, 3.98; N, 11.06; Cr, 10.73.

3. RESULTS AND DISCUSSION

Reaction of 1 equiv of CrCl₃ · 6 H₂O with 1 equiv of bipy in Et₂OH at ambient temperature and pressure gave a dark green solution. The solution was stirred and slowly evaporated at room temperature producing [Cr(bipy)(H₂O)₂Cl₂]Cl · H₂O (1 · H₂O) which was crystallized in high yield as an air stable blue green crystal. When 2 equiv of bipy was added into a EtOH solution of 1 equiv of CrCl₃ · 6H₂O, the solution became dark green as the same color as the reaction in the mole ratio of 1:1. After the solution was refluxed for a day, its color changed from dark green to red green and formation of a trace amount of brown green precipitate. The solid was filtered and the red green solution was slowly evaporate at room temperature yielding [Cr(bipy)₂Cl₂]Cl · 2 H₂O (2 · 2 H₂O) as a red brown crystal in a reasonable amount. Indeed, this compound was synthesized before [10,11].

Solid state IR spectrum (KBr pellet) of 1 · H₂O showed a broad band at 3529 cm⁻¹ belonging to the frequency of H₂O. Characteristic peaks of bipy appeared at 3079 cm⁻¹ (ν_{CH}), 1601 cm⁻¹ and 771 cm⁻¹ ($\nu_{\text{C=N}}$), and 1442 cm⁻¹ ($\nu_{\text{C=C}}$) [12]. Functional groups of 2 · 2 H₂O were in the same regions of those of 1 · H₂O.

The room temperature effective magnetic moment of 1 · H₂O of 3.69 μ_{B} was consistent with three unpaired electrons. 2 was also paramagnetic. Its magnetic susceptibility was measured at 293 K and gave μ_{eff} = 3.78 μ_{B} which fell in the normal range of magnetic moment of chromium(III) system. This value had no significant difference from compound previously synthesized [11].

The cations of both complexes were determined by single-crystal X-ray diffraction analysis. They are monomers with six-coordinated octahedral geometry with one chloride as an counter anion. The molecular structure of 1 · H₂O is depicted in Figure 1. Selected interatomic distances and bond angles are shown in Table 1 and 2, respectively. 1 crystallized in the orthorhombic space group. The complex had two molecules of water coordinated and cocrystallized with one molecule of H₂O. The metal atom of the cation is coordinated to two nitrogen atoms of bipy that sit cis to each other, and two oxygen atoms of water. These four atoms are the basal plane and measured planarity (0.8710(2)) does not differ from the normal range of octahedral one. In addition, 1 is located on a C₂ axis through two chloride atoms in the axial position. The bond lengths of Cr-N and Cr-N(a) are the same which has the distance of 2.044(2) Å indicating the characteristic of Cr-N distance for chromium bipyridine complexes (2.08 Å). Bond distances in bipyridine rings reveal no alternating long and short bond lengths, suggesting that electrons delocalized through the rings.

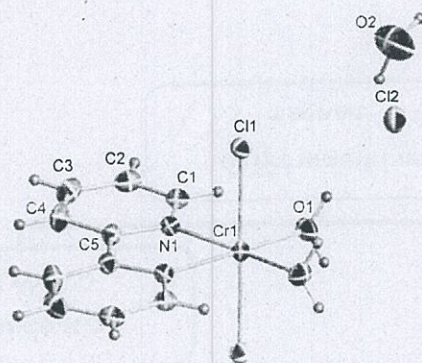


Figure 1 Molecular Structure of $[\text{Cr}(\text{bipy})(\text{H}_2\text{O})\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$ ($1 \cdot \text{H}_2\text{O}$)

Molecular structure of $2 \cdot 2\text{H}_2\text{O}$ is demonstrated in Figure 2. Selected interatomic distances and bond angles are listed in Table 1 and 2, respectively. Although the structure information of **2** was investigated by X-ray powder diffraction [13], the revealment of molecular structure of **2** offered us much more structural details. **2** crystallized in the triclinic space group and had no water coordinated in the coordination sphere. **2** cocrystallized with two molecules of water as reported before [10]. Since H_2O in **1** is substituted for bipy, unlike **1**, the basal plane of **2** is occupied by three nitrogen atoms of pyridine rings and one chloride atom. The plane of **2** possesses of slightly more octahedral planarity (0.9730(4)) than that of **1**. The axial position composes of one nitrogen atom of a pyridine ring and another chloride atom. All bond distances in bipyridine rings were almost the same and shorter than C-N and C-C single bonds indicating to the aromatic character. The bonds in heterocycle show a pattern of bond distances that is typical for bipyridine.

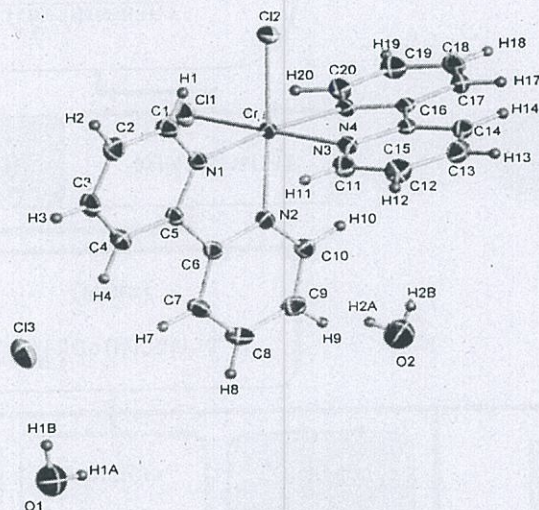


Figure 2 Molecular Structure of $[\text{Cr}(\text{bipy})_2\text{Cl}_2]\text{Cl} \cdot 2 \text{H}_2\text{O}$ ($2 \cdot 2 \text{H}_2\text{O}$)

Table 1 Selected Interatomic Distance (Å)

$[\text{Cr}(\text{bipy})(\text{H}_2\text{O})\text{Cl}_2]\text{Cl}$ (1)	$[\text{Cr}(\text{bipy})_2\text{Cl}_2]\text{Cl}$ (2)
Cr(1)-O(1) 1.979(2)	Cr(1)-N(1) 2.0551(18)
Cr(1)-O(1a) 1.979(2)	Cr(1)-N(4) 2.0618(18)
Cr(1)-N(1) 2.044(2)	Cr(1)-N(3) 2.0618(19)
Cr(1)-N(1a) 2.044(2)	Cr(1)-N(2) 2.0656(19)
Cr(1)-Cl(1) 2.3096(8)	Cr(1)-Cl(2) 2.2869(7)
Cr(1)-Cl(1a) 2.3096(8)	Cr(1)-Cl(1) 2.2917(7)

Table 2 Selected Bond Angles (deg)

[Cr(bipy)(H ₂ O)Cl ₂]Cl (1)		[Cr(bipy) ₂ Cl ₂]Cl (2)	
O(1)-Cr(1)-O(1a)	94.36(14)	N(1)-Cr(1)-N(4)	173.37(8)
O(1a)-Cr(1)-N(1 ^a)	93.37(9)	N(1)-Cr(1)-N(3)	96.12(7)
O(1)-Cr(1)-N(1)	93.37(9)	N(4)-Cr(1)-N(3)	78.84(7)
O(1)-Cr(1)-N(1a)	171.85(10)	N(1)-Cr(1)-N(2)	78.65(7)
O(1a)-Cr(1)-N(1)	171.85(10)	N(4)-Cr(1)-N(2)	96.88(7)
N(1a)-Cr(1)-N(1)	79.04(13)	N(3)-Cr(1)-N(2)	89.48(7)
O(1)-Cr(1)-Cl(1a)	88.98(8)	N(1)-Cr(1)-Cl(2)	95.60(6)
O(1a)-Cr(1)-Cl(1)	88.98(8)	N(4)-Cr(1)-Cl(2)	88.58(6)
O(1)-Cr(1)-Cl(1)	90.72(8)	N(3)-Cr(1)-Cl(2)	88.01(6)
O(1a)-Cr(1)-Cl(1a)	90.72(8)	N(2)-Cr(1)-Cl(2)	173.44(5)
N(1)-Cr(1)-Cl(1)	88.34(7)	N(1)-Cr(1)-Cl(1)	88.10(6)
N(1a)-Cr(1)-Cl(1a)	88.34(7)	N(4)-Cr(1)-Cl(1)	96.80(6)
N(1)-Cr(1)-Cl(1a)	92.00(7)	N(3)-Cr(1)-Cl(1)	175.32(6)
N(1a)-Cr(1)-Cl(1)	92.00(7)	N(2)-Cr(1)-Cl(1)	89.34(5)
Cl(1a)-Cr(1)-Cl(1)	179.56(5)	Cl(2)-Cr(1)-Cl(1)	93.63(3)

4. CONCLUSIONS

Cationic 2,2'-bipyridine complexes of chromium(III) have been synthesized and characterized spectroscopically and structurally. Stoichiometry synthesis in the mole ratio of 1:1 and 1:2 between chromium and bipy yielded bipy coordinated to the metal center one and two molecules as the formula of [Cr(bipy)(H₂O)₂Cl₂]Cl · H₂O and [Cr(bipy)₂Cl₂]Cl · 2 H₂O, respectively. Both compounds cocrystallized with water molecule(s). These compounds can be used as starting materials for many synthetic routes to earn other compounds.

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