

Stabilization of a Hydrogen Bonded Left-handed Helical Chain in a Co(III) NNN Donor Schiff Base Complex

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Date of Submission: 3rd October, 2015

Date of Acceptance: 10th October, 2015

Abstract

One mononuclear Schiff base complex of Co(III) [CoL(N₃)₃] (**1**) where L = N¹-Pyridin-2-ylmethylene-ethane-1,2-diamine was synthesized. The complex was characterized by elemental analysis, IR and UV spectroscopies, and single crystal X-ray crystallography analysis. In complex **1** Co(III) is in an octahedral environment being bonded to three N atoms from the tridentate NNN Schiff base and a terminal N atom of an azide molecule in the equatorial plane and two other N atoms from two different azide molecules attached to the axial positions. Complex **1** forms a hydrogen bonded left handed helical chain along [010] direction.

Keywords: Co(III) complex, Schiff base, Azido ligand, Helical Chain, H-bonding.

1. Introduction

Over the past decade, the rational design and synthesis of metal–organic coordination polymers has attracted much attention in coordination chemistry, not only because of their intriguing variety of architectures and topologies, but also owing to their potential applications in non-linear optics, enantioselective catalysis, and medicine^{1,2}. The syntheses and properties of metal-azido complexes have attracted great research interest for many years due to their fascinating structural diversities, their importance in understanding magneto-structural correlations, and their promising potential applications in functional materials³. There has been considerable interest in helical supramolecular architectures, particularly helices from coordination compounds⁴. In most of these helical structures, the building units (e.g., coordination compounds) are linked via covalent bonds⁵. Even though supramolecular architecture has largely taken advantage of noncovalent (e.g., hydrogen-bonding)

interactions⁶, hydrogen-bonded assemblies of coordination compounds that lead to helical structures have not been explored much. We report here a supramolecular left-handed helix, formed by N-H••••N hydrogen-bonding interactions, using the Co(III) complex [CoL(N₃)₃] (1) where L = N¹-Pyridin-2-ylmethylene-ethane-1,2-diamine.

2. Experimental

Reagents: The reagents and solvents used were of commercially available reagent quality unless otherwise stated.

Preparations:

Synthesis of the tridentate ligand (L): The ligand L was prepared by refluxing ethylenediamine (0.134 mL, 2 mmol) with 2-pyridinecarboxaldehyde (0.190 mL, 2 mmol) for 1 h. The ligand was not isolated instead, the resulting yellow methanol solution containing the tridentate ligand L was used directly for complex formation.

Synthesis of [CoL(N₃)₃] (1). A clear solution of CoCl₂ (0.260 g, 2 mmol) in methanol (5 cm³) was mixed with the ligand L (2 mmol) in methanol (10 cm³) with constant stirring. After 15 min a methanol–water solution (9 : 1, v/v) of NaN₃ (0.390 g, 6 mmol) was added and stirring was continued for another 30 min. Overnight, single crystals suitable for X-ray diffraction analysis were obtained from the mother liquor. Yield: 74%. Anal. Calcd for C₈H₁₁CoN₁₂: C, 28.75; H, 3.39; N, 50.30 %. Found: C, 28.71; H, 3.41; N, 50.32 %. IR (KBr, cm⁻¹): 2930 (γ_{C-H}), 2095 (γ_{N-N}), 1552 (γ_{C-N}) and 1444 (γ_{C-H}). UV-Vis spectrum, λ_{max}: 421 nm.

3. Physical measurements

Elemental analyses (C, H and N) were performed using a Perkin-Elmer 240C elemental analyzer. IR spectra in KBr (4500–500cm⁻¹) were recorded using a Perkin-Elmer RXI FT- IR spectrophotometer. The electronic absorption spectra (1200–350 nm) of the complexes were recorded in CH₃OH with a Hitachi U-3501 spectro-photometer.

4. Crystal data collection and refinement

Crystal data for the crystal are given in Table 1. 3521 independent data were collected with MoK α radiation using the Oxford Diffraction X Calibur CCD System. The crystals were positioned at 50 mm from the CCD. 321 frames were measured with a counting time of 10s. Data analyses were carried out with the CrysAlis program⁷. The structures were solved using direct methods with the Shelxs97 program⁸. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Absorption corrections were carried out using the ABSPACK program⁹. The structures were refined on F² using Shelxl97⁸ to R1 0.0367; wR2 0.0629 for 2714 reflections with I > 2 σ (I).

Formula	C ₈ H ₁₁ Co N ₁₂
Formula Weight	334.22
Crystal System	Monoclinic
Space group	P21 (No. 4)
a/Å	9.2977(11)
b/Å	7.0820(9)
c/Å	10.3744(12)
Alpha [deg]	90
Beta [deg]	98.428(10)
Gamma [deg]	90
V[Å ³]	675.74(14)
Z	2
D _c [g/cm ⁻³]	1.643
μ/mm ⁻¹	1.286
F(000)	340
I > 2σ(I)	2714
R1, wR2	0.0367, 0.0629
Temp/K	150

Table 1. Crystal Data and Structure Refinement of Complex 1

5. The structure of [CoL(N₃)₃] (1)

The single-crystal X-ray structural analysis shows that complex **1** is a mononuclear Co(III) complex of formula [CoL(N₃)₃]. A perspective view with the atom numbering scheme of the title complex is shown in Fig. 1, and selected bond distances and angles of complex **1** are gathered in Table 2. The structure of **1** is containing a six-coordinate cobalt atom in a distorted octahedral environment bonded to a tridentate chelating NNN donor tridentate Schiff base ligand in a mer configuration together with three nitrogen atoms N(1), N(4) and N(7) of three different terminal azides.

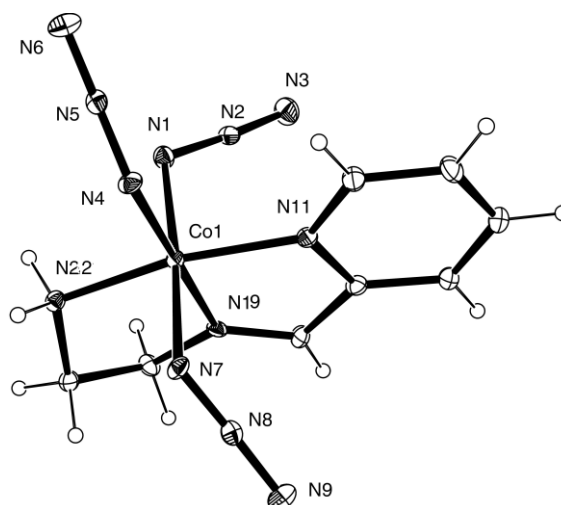


Figure 1: The Ortep view of structure 1 with ellipsoids at 25% probability

Atoms	Distance (Å)	Atoms	Bond angle (°)
Co(1) - N(1)	1.9638	N(1) -Co(1)- N(4)	91.55
Co(1) - N(4)	1.9468	N(1)-Co(1)-N(7)	175.81
Co(1) - N(7)	1.9715	N(1)-Co(1)-N(11)	92.90
Co(1) - N(11)	1.9443	N(1)-Co(1)-N(19)	90.74
Co(1) - N(19)	1.8684	N(1)-Co(1)-N(22)	90.23
Co(1) - N(22)	1.9454	N(4)-Co(1)-N(7)	85.55
		N(4)-Co(1)-N(11)	96.12
		N(4)-Co(1)-N(19)	177.48
		N(4)-Co(1)-N(22)	95.24
		N(7)-Co(1)-N(19)	92.22
		N(7)-Co(1)-N(22)	87.03
		N(11)-Co(1)-N(19)	82.70
		N(11)-Co(1)- N(22)	168.13
		N(19)-Co(1)- N(22)	85.81

Table 2. Bond Lengths (Å) and Angles (deg) in the Co(III) Coordination Sphere in 1

The tridentate NNN donor ligand occupies the equatorial plane with distances Co(1) - N(11) 1.9443, Co(1) - N(19) 1.8684 and Co(1) - N(22) 1.9454 Å together with a terminal azide N(4) at 1.9468 Å. Other two nitrogen atoms N(1) and N(7) of azido ligands being bonded axially to the central Co(1) with distances 1.9638, 1.9715 Å respectively.

In complex **1**, a hydrogen bonded left-handed helical chain along the (010) direction is formed. The hydrogen atoms attached with the primary amine of the tridentate NNN Schiff base plays a significant role in the H-bonding and function as a bridge connecting two neighboring Co(III) monomeric units. Both hydrogen atoms on the amine nitrogen (N22) form hydrogen bonds to N1 and N4 atoms of two azido ligands. Interestingly one of the hydrogen atom H22B forms a bifurcated hydrogen bonds with N1 and N7 atoms resulting a hydrogen bonded left-handed helical chain (Figure 2, Table 3).

D-H...A (Å)	D-H (Å)	D...A (Å)	H...A (Å)	< D-H...A (°)
N22 - H22A...N1	0.9000	2.2100	3.1043	171.00
N22 - H22B...N4	0.9000	2.2300	2.9985	143.00
N22 - H22B...N7	0.9000	2.4100	3.0840	132.00

Table 3: Hydrogen bonding distances (Å) and angles (°) for the complex 1

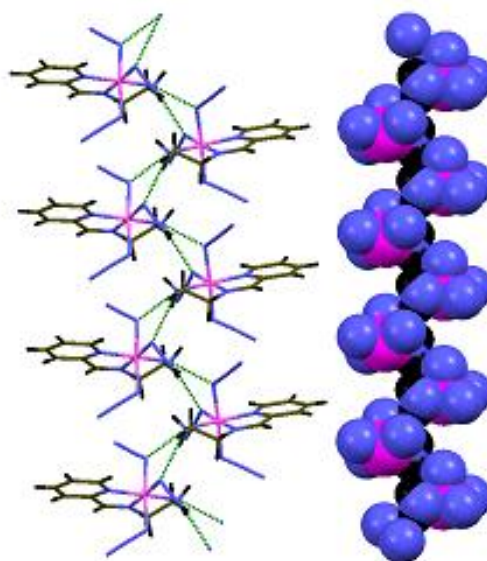


Figure 2: Depiction of the hydrogen bonded left-handed helical chain in complex 1.

5. Conclusion

This report presents a new mononuclear NNN donor tridentate Schiff base complex of Co(III) that forms a hydrogen-bonded left-handed helix along crystallographic *c* axis. The hydrogen atoms attached with the primary amine of the tridentate NNN Schiff base plays a significant role in the H-bonding and function as a bridge connecting two neighboring Co(III) monomeric units. Thus, the present system clearly demonstrates the importance of H-bonding interactions in metal-schiff base complexes

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