

Crystal Structure of a Bis[1-(benzothiazole-2yl-2κN)(2-Pyridylmethyliden-1κN)(hydrazino-2κN)] Cobalt(II) Complex

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Abstract: The Schiff base 1-(benzothiazol-2-yl)(2-pyridylmethylidene)hydrazine (HL) was synthesis via a condensation of 1-(benzo[d]thiazol-2-yl)hydrazine and 2-pyridine carboxaldehyde in methanol in 1:1 molar ratio reaction. The crystal structure of a mononuclear complex Bis[1-(benzothiazole-2yl-2κN)(2-pyridylmethyliden-1κN)(hydrazino-2κN)] cobalt(II) complex (1) (CoC₂₆H₂₀N₈S₂) was obtained by the reaction of HL with Co(CH₃COO)₂·4H₂O, in 2:1 ratio, in methanol at room temperature. The ligand and the complex are characterized by IR, and physical measurement. The spectroscopic study shows that the Schiff base possesses five potential donor sites. Upon coordination the results show that the ligand acts in tridentate mode. Suitable crystals of the compound 1 were grown by slow evaporation of methanol solution for one week. The structure of 1 was elucidated by X-ray diffraction analysis. The compound crystallizes in the monoclinic crystal system with a space group of P2₁/c. The asymmetric unit of compound 1 contains a mononuclear complex in which the cobalt ion is coordinated to two monodeprotonated molecules of the Schiff base. Each of the ligand molecule acts through three nitrogen atoms. The Co(II) center is hexacoordinated and the environment is best described as a distorted octahedral geometry. The two ligand molecules occupy mean planes which are quasi-perpendicular with a dihedral angle of 89.77(2)°. Each molecule of complex is connected to its neighbor via hydrogen bond of type C–H···S resulting in chains along *b* axis.

Keywords: Crystal Structure, Benzothiazole, Cobalt

1. Introduction

Benzothiazole is a heterocycle which contains five or six membered rings with heteroatoms such as nitrogen, oxygen, or sulfur. Benzothiazole derivatives show a high degree of structural diversity that has proved beneficial in the search for new therapeutic agents [1]. This subject is extremely attractive because of the high number of compounds containing a benzothiazole motif used as drugs to treat various types of diseases [2]. Benzothiazole-based

compounds are reported in numerous studies with biological activities as antimicrobial [3], anti tumour [4], antiparkinsonian [5], anticancer [6] and antidiabetic [7]. Owing to the large spectrum of biologic activities of benzothiazole-based derivatives, great attention is still given for this chemistry [8, 9]. On the other hand, benzothiazole derivatives are used in the synthesis of heterocyclic dyes with high performance, via a coupling reaction with dicarbonyl

compound such as pyridine-2,6-dione [10, 11]. Several bi-heterocyclic benzothiazole/pyridine-based dyes show the same configuration in solid state as well as in non-polar solvent [12, 13]. Benzothiazole derivatives are widely used in coordination chemistry. Complexes obtained from Schiff bases synthesized with amino or hydrazino Benzothiazole present interesting properties. These Schiff bases possessed several binding sites which can coordinate metal ions. Complexes with biological activities [14], photophysical [15, 16], antimicrobial [17, 18], anticancer [19], antitubercular [20] or antiviral [21] properties have been reported. Benzothiazole ligand derivatives can act in diverse modes according to the number of binding sites. The coordination mode also depends on the adopted synthetic procedures. It was found a deprotonated form of a benzothiazole/pyridone ligand acting in two tridentate fashions according to ligand/metal ratio: in 2/1 ratio yielding a mononuclear nickel (II) complex and in 1/1 ratio yielding a tetranuclear copper (II) complex in which the ligand act as bridge [10]. In this context, for synthesis of the cobalt (II) complex, the monodeprotonated Schiff base 1-(benzothiazol-2-yl)(2-pyridylmethylidene)hydrazine (HL), which provides four potentially soft-donating atoms from one pyridine ring, one imino function, one benzothiazole nitrogen atom and one sulfur benzothiazole atom was used together. In the present study, we describe the crystal structure of a cobalt(II) complex constructed with the tridentate monodeprotonated ligand 1-(benzothiazol-2-yl)(2-pyridylmethylidene)hydrazine which acts through three soft donating nitrogen atoms provided by the pyridine ring, the imino function and the benzothiazole heterocycle.

2. Experimental Section

2.1. General Information

1-(benzo[d]thiazol-2-yl)hydrazine, 2-pyridine carboxaldehyde and cobalt acetate tetrahydrate, were purchased from Sigma-Aldrich and used as received without further purification. All solvents used were of reagent grade. Melting points were determined with a Büchi 570 melting-point apparatus and were uncorrected. Elemental analyses of C, H and N were recorded on a VxRio EL Instrument. Infrared spectra were obtained on an FTIR Spectrum Two of Perkin Elmer spectrometer in the 4000-400 cm^{-1} region. The UV-Visible spectra were recorded on a Perkin Elmer Lambda UV-Vis spectrophotometer. The ^1H and ^{13}C NMR spectra were recorded in DMSO- d_6 on a Bruker 500 MHz spectrometer at room temperature using TMS as an internal reference. The molar conductance of 1×10^{-3} M in DMSO solutions of the metal complexes was measured at 25 °C using a WTW LF-330 conductivity meter with a WTW conductivity cell. Room temperature magnetic susceptibilities of the powdered samples were measured using a Johnson Matthey scientific magnetic susceptibility balance (Calibrant: $\text{Hg}[\text{Co}(\text{SCN})_4]$).

2.2. Synthesis of 1-(benzothiazol-2-yl)(2-pyridylmethylidene)hydrazine (HL)

The Schiff base ligand HL was synthesized using standard method related in the literature [22]. 1-(benzo[d]thiazol-2-yl)hydrazine (1 g, 6 mmol) and 2-pyridine carboxaldehyde (0.64 g, 6 mmol) were mixed in methanol and two drops of acetic acid were added. The resulting mixture was refluxed for two hours. The yellow solid yielded was collected by filtration before washed with methanol and ether. $[\text{C}_{13}\text{H}_{10}\text{N}_4\text{S}]$. Yield was 87%. Analysis calculated C, 61.40; H, 3.96; N, 22.03; S, 12.61. Found: C, 61.13; H, 3.98; N, 22.11; S, 12.68%. ^1H NMR (DMSO, δ , ppm) 12.51 (1H, s, broad NH), 8.15 (1H, s, N=CH), 7.13–7.91 (8H, m, H_{Ar}). ^{13}C NMR (DMSO, δ , ppm) 153.09 (C–C=N), 149.5 (S–C=N), 119.36–136.77 (C_{Ar}).

2.3. Synthesis of Complex (I)

To a solution of HL (0.127 g; 0.5 mmol) in 20 mL of methanol was added solid $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.04875 g, 0.25 mmol) under stirring. Immediately the creamy yellow solution turned pinkish red. The mixture was refluxed for 2 h and filtered hot. The filtrate was kept at 298 K. After one-week, wine-red crystalline compound was collected by filtration and washed thoroughly with chilled diethyl ether. Subsequently it was dried in a vacuum desiccator under P_4O_{10} . $[\text{C}_{26}\text{H}_{18}\text{CoN}_8\text{S}_2]$. Yield 84%. Analysis calculated. C, 53.22; H, 3.21; N, 19.81; S, 11.34. Found: C, 53.20; H, 3.23; N, 19.78; S, 11.31%.

2.4. X-ray Data Collection, Structure Determination and Refinement

Details of the X-rays crystal structure solution and refinement are given in Table 1. Diffraction data were collected using an Rigaku AFC11 007-HFENRAF NONIUS Kappa CCD diffractometer with graphite monochromatized $\text{CuK}\alpha$ radiation ($\lambda = 1.54187 \text{ \AA}$). All data were corrected for Lorentz and polarization effects. No absorption correction was applied. Complex scattering factors were taken from the program package SHELXTL [23]. Structure solution and refinement were performed using SHELXT [24] and SHELXL-2014/7 [25]. All hydrogen atoms were added in calculated positions and refined in riding mode on the parent atom. Molecular graphics were generated using ORTEP-3 [26].

3. Results and Discussion

3.1. General Study

The Schiff base 1-(benzo[d]thiazol-2-yl)(2-pyridylmethylidene)hydrazine (HL) was prepared by the condensation of equimolar amounts of 2-pyridine carboxaldehyde with 1-(benzo[d]thiazol-2-yl)hydrazine in methanol under reflux for two hours as illustrated in Figure 1. The solid compound is air-stable and soluble in common organic solvent such as DMSO or DMF. The $\text{C}_{13}\text{H}_{10}\text{N}_4\text{S}$ formulation of the compound agrees with the results of the elemental analysis.

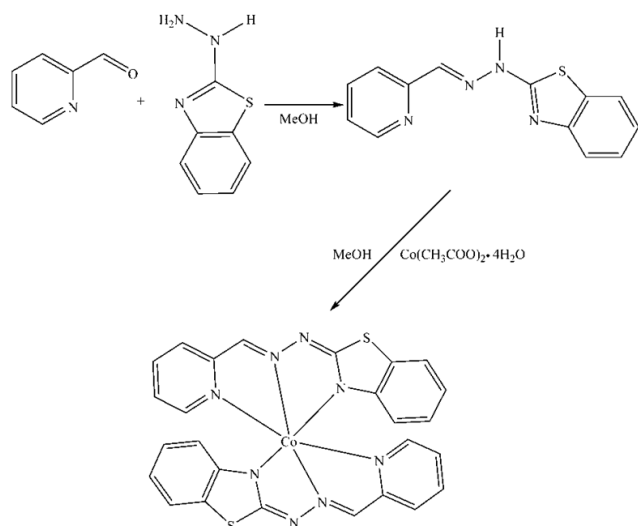


Figure 1. Synthesis of 1-(benzo[d]thiazol-2-yl)(2-pyridylmethylidene)hydrazine (HL).

The infrared spectrum of the compound shows intense absorption band at *ca.* 1635 cm^{-1} is assigned to the azomethine moiety $\nu_{\text{C=N}}$, which is indicative of the occurring of the condensation. The band at 1615 cm^{-1} is assigned to the $\nu_{\text{C=N}}$ of the benzothiazole ring. Additional bands appearing in the range 1600–1450 cm^{-1} are attributed to the vibrations of the aromatic rings. A band of medium intensity pointed at 3325 cm^{-1} is assigned to the N–H stretching vibration. The

proton NMR spectrum of the compound shows a broad signal at 12.51 ppm due to the N–H. The signal due to the azomethine proton H–C=N is pointed at 8.15 ppm. The signals in the range 7.13–7.91 ppm represent the proton of the aromatic rings. The ^{13}C NMR spectrum confirms the condensation with the signal at 153.09 ppm assigned to carbon atom H–C=N. The signal at 149.5 ppm is assigned to the carbon atom of C=N of five membered ring. The signals in the range 136.77–119.36 ppm are attributed to the carbon atoms of the aromatic rings. Upon coordination with cobalt (II), the band due to the azomethine groups in the free ligand disappears and new bands shifted to low frequencies at 1595 cm^{-1} and 1580 cm^{-1} . This fact is indicative of the involvement of the azomethine nitrogen atom in the coordination to the metal center. The molar conductivity Λ of the complex is determined in DMF solution. The value of 7 $\text{S}\cdot\text{mol}^{-1}\cdot\text{cm}^2$ is indicative of a neutral electrolyte [27]. The values of the magnetic moment at room temperature for the diamagnetic complex are indicative of the presence of one metal atom per molecule. In fact, the magnetic moment values of 4.39 μ_{B} is in accordance with one unpaired electron as reported in the literature [28]. The magnetic moment value is supported to the distorted octahedral geometry. The electronic spectrum of the cobalt complex shows one broad band at 625 nm with a weak shoulder at 875 nm. These bands are assigned to $^4\text{T}_{1\text{g}} \rightarrow ^4\text{T}_{2\text{g}}$ and $^4\text{T}_{1\text{g}} \rightarrow ^4\text{T}_{2\text{g}}$ (P) respectively. These peaks belongs to d \rightarrow d transitions in Co (II) complex are indicative of an octahedral coordination around the Co (II) ions [29].

Table 1. Crystal data, X-ray data collection, data reduction and structure refinement for (I).

Crystal data	
Chemical formula	$\text{C}_{26}\text{H}_{18}\text{CoN}_8\text{S}_2$
M_r	565.54
Crystal system, Space group	Monoclinic, $\text{P2}_1/\text{c}$
Temperature (K)	293
a, b, c (\AA)	13.2187 (5), 9.5804 (4), 24.8884 (17)
β ($^\circ$)	92.779 (7)
V (\AA^3)	3148.2 (3)
Z	4
Calculated density (g cm^{-3})	1.505
$F(000)$	1463
Radiation type	$\text{Cu K}\alpha$
μ (mm^{-1})	7.17
Crystal size (mm)	$0.20 \times 0.20 \times 0.20$
Data collection	
Diffractionmeter	Rigaku AFC11 007-HF
Absorption correction	Multi-scan
$T_{\text{min}}, T_{\text{max}}$	0.735, 1.000
Limiting indices	
h	$-9 \rightarrow 9$
k	$-6 \rightarrow 6$
l	$-17 \rightarrow 17$
No. of measured, independent, and Observed [$I > 2\sigma(I)$] reflections	6942, 1184, 1050
R_{int}	0.062
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.057, 0.157, 1.16
No. of reflections	1184
No. of parameters/restraints	335/0
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e \AA^{-3})	0.37 & -0.18

3.2. Crystal Structure of the Complex

The X-ray crystal structure (Figure 2) of complex reveals a 2:1 ratio of L[−]/Co. in the neutral complex. The asymmetric unit contains one Co²⁺ ion coordinated by two monodeprotonated ligand yielding a hexacoordinated cobalt center. Each of the two anions L[−] acts as a tridentate chelating ligand through soft-donating nitrogen atoms of one pyridine ring, one imino function and one benzothiazole heterocycle, resulting in five-membered rings CoNCNN and CoNCCN. The environment of the hexacoordinated Co²⁺ is best described as a severely distorted square bipyramidal geometry in which the basal plane is occupied by N1, N3, N4, and N6 while the apical positions are occupied by N5 and N8. The *cisoid* bond angle between the Co(II) center and the atoms in the basal plane are in the range 76.7(5)–105.9(5)° while the *transoid* angle values are respectively 154.8(5)° and 176.5(5)° (Table 1). The angle subtended by the atoms in apical positions is 153.4(5)°. These values are comparable to those reported for the complex [Co(HL)(L)] (HL is 3-(hydroxyimino)-2-butanone-2-(1H-benzothiazol-2-yl)hydrazone) [30]. The Co–N bond length values of the atoms in basal plane (Co1–N1, Co1–N3, Co1–N4 and Co1–N6) are respectively 2.055(13) Å, 2.014(12) Å, 2.130(13) Å, and 2.025(12) Å (Table 1). The apical position bond length values are longer than those in the base plane (Co1–N5 and Co1–N8): 2.136(12) Å and 2.111(12) Å respectively. The bond lengths N3–C8 and his related homologue N6–C19 are essentially double bond character with distance of 1.287(15) Å and 1.270(4) Å respectively. The sulfur atom of each ligand remains uncoordinated [31]. In each L[−] the two heterocycles show a dihedral angle of 4.09(7)° resulting in quasi-coplanarity of non-hydrogen atoms of the ligand. In the complex the two ligand molecules occupy mean-planes which are nearly perpendicular to each other with angle value of 89.77(2)°.

The crystal structure of 1 reveals only one type of intermolecular bond. Each molecule of complex is associated to neighbor by C–H⋯S hydrogen bond (Table 3). This association result in the formation of chains parallel to *b* axis (Figure 3).

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Benzothiazole derivatives has been widely used as Schiff bases for the preparation of coordination compounds. The current release of the Cambridge Structural Database [32] (CSD version 5.41 updates Mars 2020; Groom *et al.*, 2016) gave 58 hits. Mononuclear complexes of transition metal such as Mn or Fe with refcodes GOGBAF [33] and IXEXAL [34] are similar to the complex reported herein. A trinuclear complex of pyrazole-benzothiazole is reported with refcode TOSYUY01V [35]. Benzothiazole copper(II) complex as inhibitor of ribonucleotide reductase with high antiproliferative activity is synthesized [36]. A benzothiazole derivative binuclear copper complex with a bromo bridged atom is used in DNA and RNA binding studies NULWOJ [37]. Three interesting heteropolynuclear complex, involving Ni and lanthanide ion such as Tb, Dy or

Gd were reported with refcodes OTEYAO [38], OTEXOB [38] and OTEXUH [38]. In all the benzothiazole derivatives complexes found in CSD, the soft-donating sulfur atom remains uncoordinated.

Table 2. Selected geometric parameters (Å, °).

Bond	bond lengths (Å)	Bond	bond angles (°)
Co1—N3	2.014 (12)	N3—Co1—N1	76.7 (5)
Co1—N1	2.055 (13)	N3—Co1—N4	78.2 (5)
Co1—N4	2.130 (13)	N3—Co1—N6	176.5 (5)
Co1—N6	2.025 (12)	N3—Co1—N8	105.8 (4)
Co1—N8	2.111 (12)	N1—Co1—N4	154.8 (5)
Co1—N5	2.136 (12)	N1—Co1—N8	95.0 (4)
		N1—Co1—N5	91.6 (4)
		N4—Co1—N5	91.3 (4)
		N6—Co1—N1	105.9 (5)
		N6—Co1—N4	99.1 (4)
		N8—Co1—N4	93.5 (4)
		N8—Co1—N5	153.4 (5)

Table 3. Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C14—H14⋯S2 ⁱ	0.93	2.93	3.794(18)	156.0

Symmetry code: (i) x, y+1, z.

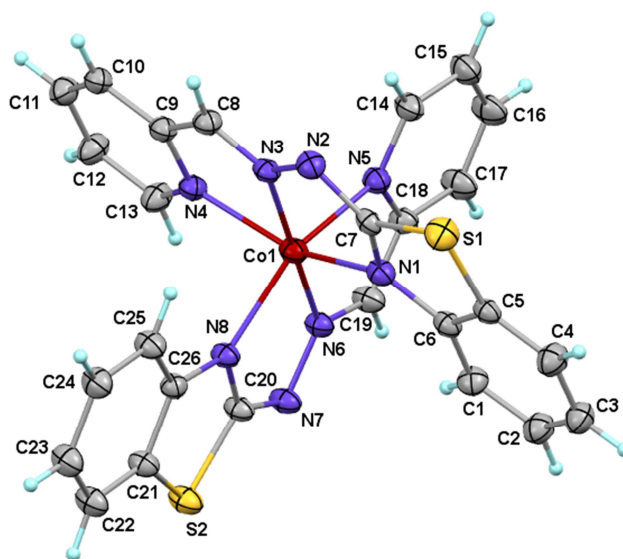


Figure 2. A view of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are plotted at the 30% probability level.

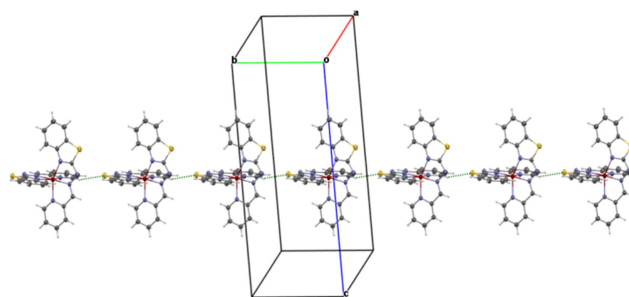


Figure 3. Chains formed by C–H⋯S hydrogen bonds along *b* axis.

4. Conclusion

The benzothiazole derivative namely 1-(benzo[d]thiazol-2-yl)(2-pyridylmethylidene)hydrazine (HL) was successfully synthesized by the condensation of 2-pyridine carboxaldehyde and 1-(benzo[d]thiazol-2-yl)hydrazine and used for preparing the complex of cobalt (II) reported here. The structure of the two compounds were confirmed by element analysis, spectroscopic techniques (FT-IR, UV-visible, ^1H and ^{13}C NMR). The structure of the complex was determined by and X-ray crystallography technique which reveal an octahedral environment around the Co(II) ion. Intermolecular hydrogen bond type of $\text{C}-\text{H}\cdots\text{S}$ connect the molecules in chains along the *b* axis.

Supporting Information

CCDC-2067839 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Conflicts of Interest

The authors declare that they have no competing interests.

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