A New Cobalt Complex Derived From Pyrazole Based Heterocyclic Schiff Base: Synthesis, Characterization And Bond Valence Sum (BVS) Computation

Kinsuk Das*

*Assistant Professor
Department of Chemistry,
Chandernagore College, Hooghly, West Bengal 712136, India

Abstract:

A new cobalt(II) complex [Co(**L**)Cl$_2$] (**1**) involving a pyrazole based tetradentate Schiff base ligand [5-methyl-1-(pyridin-2-yl)-*N'*-[pyridin-2-ylmethylidene] pyrazole-3-carbohydrazide] (**L**) was successfully synthesized and structurally characterized by elemental analysis, mass spectroscopy (MS), Fourier-transform infrared (FT-IR) spectroscopy, nuclear magnetic resonance (NMR), ultraviolet-visible (UV-vis) spectrum, molar conductance, room temperature magnetic moment and X-ray crystallographic studies accordingly. Complex **1** is pseudo-octahedral in geometry spanning the tetradentate Schiff base ligand (N$_4$ chromophore) equatorially and two additional chloride anions span are in trans orientation. Bond Valence Sum (BVS) calculation has been carried out to elucidate the oxidation state of central cobalt ion and it reveals that in the title complex **1** the formal oxidation state of cobalt is +2 instead of +3.

Keywords: Schiff base ligand, Single crystal X-ray crystallography, Bond Valence Sum calculation.

Introduction:

For last few decades Schiff base and their metal complexes arrest significant interest of the chemists not only due to their greater stability and chelating properties [1, 2] but also for their potential use in catalytic and medicinal field [3]. With the rapid development of heterocyclic chemistry pyrazole, pyridine, pyrimidine, imidazole based polydentate ligands and their transition metal complexes have aroused wide concern from structural and functional point of view [4]. The well characterized bio functionality of pyrazole (isomeric with imidazole) derivatives is often related to the chelation phenomena with trace metal ions. Cobalt (II) is a potent candidate for the creation of metal-organic framework by executing its ability to adapt diverse coordination geometry with nitrogen containing Schiff base ligand [5-7]. Transition metals are able to form coordination complexes in different oxidation states. Sometimes during the course of the synthetic reactions either aerial oxygen (may be responsible for oxidation) or the nature of the ligand (either oxidizing or reducing) may play a significant role in adjustment of the oxidation state of the central metal ion compared to the precursor salts of the metal ion. Hence the formal oxidation state evaluation is essential. The Bond Valence Sum (BVS) model, based solely on structural data information, relates the bond length

around a metal centre to its oxidation state. Hence, this model acts as a bridge between experimental results and theoretical calculations that may aid an additional support for accuracy of the crystal structure determination [8].

The title Schiff base ligand [5-methyl-1-(pyridin-2-yl)-*N'*-[pyridin-2-ylmethylidene] pyrazole-3-carbohydrazide] (**L**) is a promising contender from coordination perspective by using pyrazole, two pyridine, azomethine nitrogen and carbohydrazide carbonyl oxygen towards central metal ion. Here this ligand (**L**) acts as a tetradentate ligand towards cobalt (II) centre leaving carbohydrazide carbonyl oxygen atom silent in the coordination game. From X-ray crystallographic study it is evident that the cobalt complex adopts a pseudo-octahedral geometry (tetradentate Schiff base N_4 donor spans in basal plane and two axial positions were occupied by two chloride ions). In comparison to starting hexaaqua cobalt chloride the title complex (**1**) has gained more stability due to extensive chelate effect (two five and one six membered chelate ring is there around central cobalt ion). Here in this present case BVS calculation has been carried out to evaluate the formal oxidation state of cobalt in complex **1** it is found to be +2 and excludes the presence of +3 oxidation state through oxidation.

2. Experimental methods:

2.1. Materials and Methods

All chemicals were of reagent grade, purchased from commercial sources and used without further purification. Pyridine-2-carbaldehyde was purchased from Aldrich Chemical Company, USA and used without further purification. All reactions were carried out in aerobic condition and in aqueous-methanol solvent. During the whole experiment freshly boiled, doubly distilled water was used. Fourier transform infrared (FT-IR) spectra were recorded from a PerkinElmer LX-1 FT-IR spectrophotometer (KBr disk, $4000-400$ cm^{-1}) and an Elemental analysis (carbon, hydrogen and nitrogen) of the metal complex was determined with a Perkin–Elmer CHN analyzer 2400. ^{1}H-NMR spectrum was recorded in d$_6$-DMSO with TMS as the internal standard on a Bruker, AV 300 Supercon Digital NMR system. The mass spectrum of the ligand was with a JEOLJMS-AX 500 mass spectrophotometer and UV-vis absorption spectra was obtained using UV-1700 Pharma Spec UV-vis spectrophotometer (SHIMADZU). The molar conductance value of the complex was measured in purified DMF with a Systronic model 304 digital conductivity meter. The room temperature magnetic moment of the complex was obtained from a magnetic susceptibility balance MK1 Sherwood.

2.2. Synthesis of the ligand (L):

The title Schiff base ligand [5-methyl-1-(pyridin-2-yl)-*N'*-[pyridin-2-ylmethylidene] pyrazole-3-carbohydrazide] (**L**) [9] was synthesized by refluxing a methanolic solution (30 cm^3) of ethyl-5-methyl-1-(2-pyridyl) pyrazole-3-carbohydrazide [10] (2.17g, 10 mmol) with pyridine-2-carbaldehyde (1.06g, 10 mmol) also taken in methanol (10 cm^3) (scheme 1).
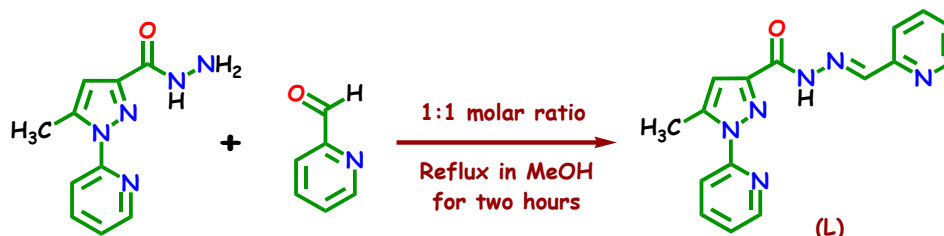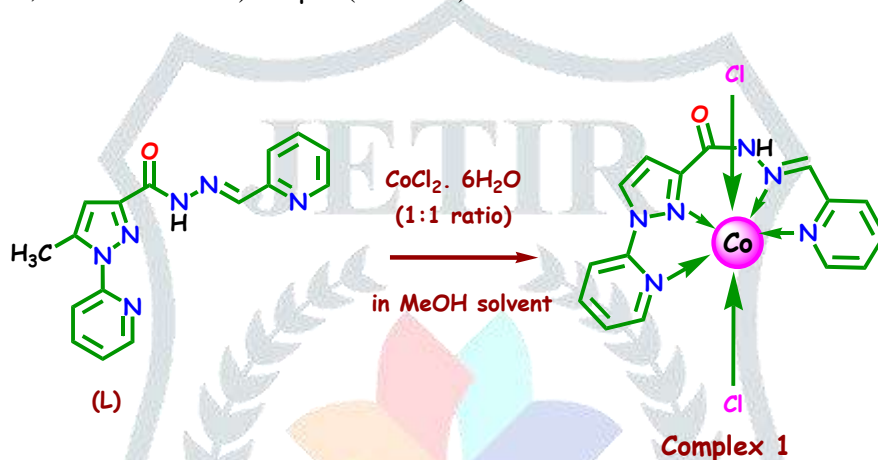

Scheme 1. Schematic representation of synthesis of the ligand (**L**)

Reflux was continued for about 30 minutes at water bath temperature. A yellow microcrystalline solid compound separated out after slow evaporation of the mixture. The solid was filtered off, washed several times with cold methanol and dried in vacuo over fused calcium chloride. (Yield: 77.4%); M.p.(ºC) 178; Anal. Calc. for $C_{16}H_{14}N_6O$: C, 62.74; H, 4.57; N, 27.45. Found: C, 62.33; H, 4.43;N, 27.0. IR (KBr,

cm^{-1}): 1582 (py $\nu_{C=N}$), 1466 (pz $\nu_{C=N}$), 1687 ($\nu_{C=O}$), 1539 ($\nu_{C=C}$), 1042 (pz ν_{N-N}), m/z 306 (M^+, 100%).
^{1}HNMR (in d_6-DMSO, δ): 8.4 (s, 1H, –CH=N–), 7.1–8.7(m, 8H, Py), 6.8(s, 1H, ring Pz), 2.67(s, 3H, -CH$_3$). UV-Vis (DMF): $\lambda_{max/nm}$ = 287 and 347.

2.3. Synthesis of complex [Co(L)Cl₂] (1)

A methanolic solution (20 ml) of CoCl$_2$.6H$_2$O (0.237g, 1mmol) was added dropwise to a solution of **L** (0.3g, 1mmol) in the same solvent (15 ml) taken in a 1:1 molar (scheme 2) ratio with constant stirring and it was continued for additional three hours. The solution turns pinkish red. Then it was filtered and kept undisturbed for crystallization by slow evaporation at room temperature. After two weeks X-ray quality crystals of **1** were separated out and were collected by usual techniques. (Yield: 69%). Anal. Calc. for C$_{16}$H$_{14}$CoN$_6$OCl$_2$: C, 44.04; H, 3.21; N, 19.27. Found: C, 43.93; H, 3.13;N, 19.23. IR (KBr, cm^{-1}): 1599 (py $\nu_{C=N}$), 1438 (pz $\nu_{C=N}$), 1032 (pz ν_{N-N}), 1680 ($\nu_{C=O}$), 1512 ($\nu_{C=C}$) (figure 1). $\lambda_{max/nm}$ = 267, 308 and 489 (figure 2). λ_M (DMF, $ohm^{-1}cm^2mol^{-1}$): 9. μ_{eff} (at 298K) = 3.77 B.M.

Scheme 2. Schematic representation of synthesis of complex **1**
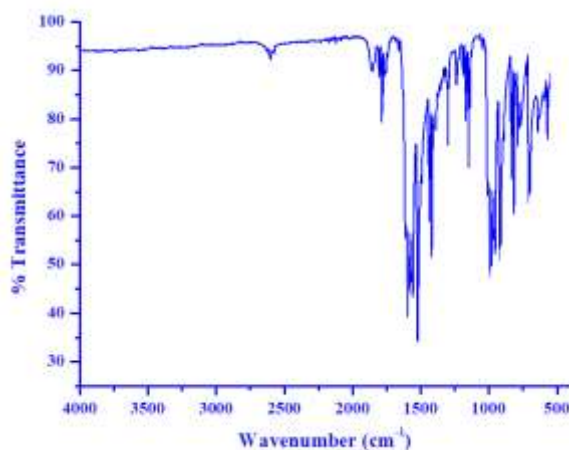

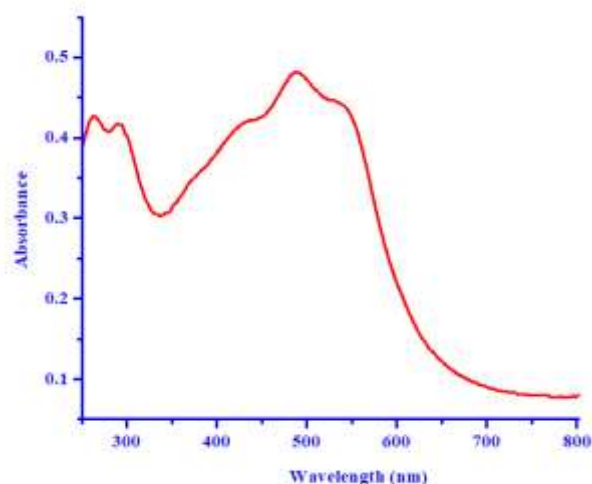**Fig. 1**: IR spectrum of Complex **1**

Fig. 2: UV-Visible spectrum of Complex **1**

2.4. Single crystal X-ray crystallography

Selected crystal data for **1** has given in table 1 and selected metrical parameters of the complex is listed in table 2. For complex **1**, data collections were made using Bruker SMART APEX II CCD area detector equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) source in ω scan mode at 208(2) K. The structure of complex **1** was solved by conventional direct methods and refined by full-matrix least square methods using F^2 data. SHELXS-97 and SHELXL-97 programs [11] were used for structure solution and refinement of the complex respectively.

3. Structural description of complex 1:

The perspective view of complex **1** with suitable atom numbering scheme is shown in figure 3 and selected bond length and bond angle parameters of **1** is given in table 2.

Table: 1. Crystallographic data for of **1**

Compound	**1**
Empirical formula	$C_{16}H_{14}CoN_6OCl_2$
Formula weight	435.93
Temperature (K)	208(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	Cc
Unit cell dimensions	
a (Å)	12.4120 (13)
b (Å)	11.6701 (13)
c (Å)	13.2536 (12)
α (º)	90
β (º)	97.9310(10)
γ (º)	90
Volume ($Å^3$)	1954.8(3)
z	4
Density$_{cal}$ (Mg m^{-3})	1.776
Absorption coefficient (mm^{-1})	1.210
F(000)	1066
Crystal size (mm^3)	0.40 x 0.15 x 0.15

| θ Range (°) for data collection	2.41 - 27.94
Index ranges	$-16 \leq h \leq 16$
	$-15 \leq k \leq 15$
	$-17 \leq l \leq 17$
Goodness-of-fit on F^2	1.015
Completeness to theta =25.00˚ (%)	99.9
Independent reflections [R_{int}]	3493 [0.0556]
Absorption correction	multi-scan
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	3493 / 5 / 308
Reflections collected	13377
Final R indices [$I > 2\sigma (I)$]	R1 = 0.0345, wR_2 = 0.0867
Largest difference peak and hole (eÅ^{-3})	0.429 and -0.364
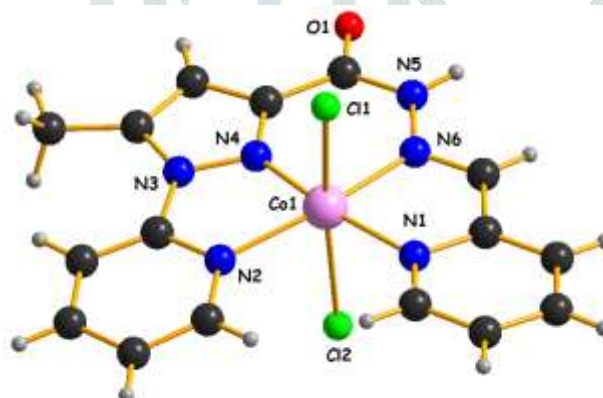
Fig. 3: Perspective view of molecular structure of complex **1** with selective atom numbering scheme

Complex **1** crystallizes in Cc space group (under monoclinic crystal system) and the unit cell of **1** is comprised of four molecules. Single crystal X-ray diffraction study reveals that complex **1** is neutral, mononuclear and assembled by the coordination of a Schiff base ligand [5-methyl-1-(pyridin-2-yl)-*N'*-[pyridin-2-ylmethylidene] pyrazole-3-carbohydrazide] (**L**) and two chloride ions. The structural geometry around cobalt (II) is best described as a distorted octahedron with N_4Cl_2 chromophore. In the title complex, the Schiff base ligand '**L**' acts as a tetradentate one exploiting two pyridine nitrogen (N1 and N2), one pyrazole nitrogen (N3) and one azomethine nitrogen (N6) encapsulating the metal ion and spanning itself in basal plane.

Table: 2. Selected bond distances (Å) and angles (º) in **1**

Selected Bonds	Value(Å)	Selected Angles	(º)
Co(1)-N(1)	2.118	N(1)-Co(1)-N(2)	111.35 (10)
Co(1)-N(2)	2.137	N(2)-Co(1)-N(4)	82.28 (10)
Co(1)-N(4)	2.263	N(4)-Co(1)-N(6)	78.68 (10)
Co(1)-N(6)	2.249	N(6)-Co(1)-N(1)	86.65 (10)
Co(1)-Cl(1)	2.397	N(1)-Co(1)-N(4)	168.44 (10)
Co(1)-Cl(2)	2.389	N(2)-Co(1)-N(6)	163.30 (10)
		Cl(1)-Co(1)-Cl(2)	174.08 (9)

The equatorial distances Co1–N1 (2.118 Å), Co1–N2 (2.137 Å), Co1–N4 (2.263 Å) and Co1–N6 (2.249 Å) along with two trans axial distances Co1–Cl1 (2.397 Å) and Co1–Cl2 (2.389 Å) are in accordance with the similar compounds reported earlier [4-6] The dipositive charge of the central cobalt ion is satisfied by two coordinated chloride anion and molar conductance (9 ohm^{-1}cm^{2}mol^{-1}) data supports this. The sum of three chelate angle namely N1–Co1–N6 [86.65 (10)], N6–Co1–N4 [78.68 (10)] and N4–Co1–N2 [82.28 (10)] (two five and one six membered ring) and one non chelated [N1–Co1–N2= 111.35 (10)] of the equatorial plane (table 2) is 358.96º close to ideal planar structure. The non-chelated angle is comparatively open due to absence of any spacer. The apical chloride atoms including the central cobalt ion shows a little deviation (174.78º) from ideal linear arrangement. One pyridyl nitrogen ((N1) is trans to the pyrazole nitrogen (N4) and another pyridyl nitrogen (N2) is trans to the azomethine nitrogen (N6) atom. The cobalt ion sits almost in an equatorial plane constituted by N1N2N4N6 atoms with almost negligible deviation (0.012Å towards the apical Cl1 atom). Room temperature magnetic moment data (3.77 B.M.) reveals the existence of three unpaired electrons and the electronic configuration of central cobalt ion is $t_{2g}^5 e_g^2$.

4. Bond Valence Sum (BVS) Calculation

Bond Valence Sum calculation is a significant approach to assess the chemical plausibility of inorganic crystal structure [12]. This is based on the sum of the bond valences 'S$_{ij}$', around any ion 'i', is equal to its valence, 'V$_i$' (the formal oxidation state)

$$Vi = \sum_j Sij$$

(where the sum goes overall neighbouring atoms 'j' from the atom; I')
 'S$_{ij}$' can be calculated by using the formula

$$Sij = e^{\frac{R0-Rij}{B}}$$

(where 'R$_0$' and 'B' are constant parameters and 'R$_{ij}$' is the interatomic distance between central 'i' to terminal 'j' atoms. 'R$_0$' and 'B' parameters were taken from a list compiled by I. D. Brown from several references and stored in a CIF file, *bvparm 2016.cif*) [13, 14]

Table 3. Bond Valence Sum calculation and related parameters for Complex 1

i – j (reported)	R_0	i – j (complex 1)	R_{ij}	S_{ij}	V_i
Co^{2+} - N^{3-}	1.72	Co(1) – N(1)	2.118	0.341	
Co^{2+} - N^{3-}	1.72	Co(1) – N(2)	2.137	0.324	
Co^{2+} - N^{3-}	1.72	Co(1) – N(4)	2.263	0.250	**1.926**
Co^{2+} - N^{3-}	1.72	Co(1) – N(6)	2.249	0.239	
Co^{2+} - Cl^{-1}	2.033	Co(1) – Cl(1)	2.397	0.374	
Co^{2+} - Cl^{-1}	2.033	Co(1) – Cl(2)	2.389	0.398	
i – j (reported)	R_0	i – j (complex 1)	R_{ij}	S_{ij}	V_i
Co^{3+} - N^{3-}	1.69	Co(1) – N(1)	2.118	0.314	
Co^{3+} - N^{3-}	1.69	Co(1) – N(2)	2.137	0.299	
Co^{3+} - N^{3-}	1.69	Co(1) – N(4)	2.263	0.212	**1.836**
Co^{3+} - N^{3-}	1.69	Co(1) – N(6)	2.249	0.220	
Co^{3+} - Cl^{-1}	2.05	Co(1) – Cl(1)	2.397	0.391	
Co^{3+} - Cl^{-1}	2.05	Co(1) – Cl(2)	2.389	0.400	

As there is a general tendency for cobalt (II) to be oxidized to Co(III) in aerobic condition due of high gain in crystal field stabilization, it is very significant to assure the formal oxidation state of the central cobalt atom. Though Co(II) salt has been taken for the synthesis, it may happen that during the course of synthesis it is to be oxidised to Co(III) and hence to assign the formal oxidation state the BVS calculations have been carried out. I have taken the standard values for both Co(II) and Co(III) from the available structural database and check where the deviation is minimum. From the BVS calculation, it is confirmed that the central cobalt atom exits in '+2' oxidation state as the 'V_i' value is very close to '2' [V_i =1.926] (table 3). The slight deviation of the BVS from an ideal integer value commonly comes from possible steric constrains executed by the crystals [15].

Conclusion:

A new Co(II) complex (**1**) using the ligand [5-methyl-1-(pyridin-2-yl)-*N'*-[pyridin-2-ylmethylidene] pyrazole-3-carbohydrazide] (**L**) was synthesized and characterized both structurally and spectroscopically. Single crystal X-ray diffraction study reveals that complex **1** is pseudo-octahedral and Co(II) ion placed itself into the equatorial pocket constructed by the N_4 moiety of the ligand (**L**) and the trans positions were occupied by two chloride ions. Due to high gain in crystal field stabilization energy (CFSE) generally Co(II) shows an inherent tendency towards aerial oxidation. Hence assignment of formal oxidation state on cobalt is essential. In this regard I have performed the Bond Valence Sum (BVS) calculation. BVS is a significant and well appreciated theoretical approach to assess the oxidation state for a metal ion present in a complex and the bond valence is calculated for each bonded atom for each of the presumed oxidation state. Here in this present case BVS calculation tells unambiguously that the formal oxidation state of cobalt in title complex **1** is +2.

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