Review Article

Synthesis, Crystal structure, and Antimicrobial Activities of Di ((E)-2-(pyridine-2-ylmethylene)hydrazinecarboxamide)cobalt(II) dichloride trihydrate

ABSTRACT

The title compound $[Co(C_7H_8N_4O)_2]Cl_2.3H_2O$, has been synthesized and characterized by elemental analysis, IR apectra and single-crystal X-ray diffraction. The title compound crystallizes in a triclinic, space group P-1 with a = 9.3547(5) Å, b = 9.8985(5) Å, c = 12.8840(7) Å, α=106.033(4)°, β = 103.916(4)°, γ = 95.717(4)°, V = 1095.20(10) $Å^3$, Z=2, R = 0.0255 and wR = 0.0687. In the title compound there are two crystallographically independent cations and anions and three water molecules in the asymmetric unit. The Co^{II} ion has a distorted octahedral coordination environment and is surrounded by four N atoms and two O atoms in a tridenate manner. In the crystal, N—H…Cl, N—H…O, O—H…Cl and O—H…O hydrogen bonds link the complex cations, chloride anions and solvent water molecules into a three-dimensional network. The preliminary antimicrobial activities were studied.

Keywords: X-ray diffraction, octahedral coordination, tridenate, hydrogen bonds, antimicrobial activity.

1. INTRODUCTION

Cobalt is an element of biological interest due to its presence in the active center of cobalamine, which regulates indirectly the synthesis of DNA, and the involvement in the co-enzyme of vitamin B12 used as a supplement of the vitamin and in other cobalt-dependent proteins [1]. Numerous

cobalt complexes showing antitumor, antiproliferative, antimicrobial, antifungal, antiviral and antioxidant activity [2-4]. Metal complex with hydrazides have found wide application as pharmaceutical agents and in industry. The biological activity of the compounds is mainly dependent on their molecular structure[5].

The construction of coordination compounds of cobalt(II) of different nuclearities is the centre of attraction due to interesting structural and physico-chemical properties [6]. Fascinating chemistry of transition metal complexes incorporating ligands that are capable of binding the metal centre in facial manner, enhanced the interest on the synthesis of new tridentate ligands that are suitable for obtaining facially coordinated complexes [7]. To ascertain the molecular conformation, the structure determination of the title compound has been carried out.

2. MATERIAL AND METHODS

2.1 General

The ligand and complex were prepared by commercially available chemicals of Merck and Sigma Aldrich products and used without further purification. The elemental analysis was performed using CHNO analyzer. The IR spectra were measured with Shimadzu FT-IR spectrometer in the 4000-400 cm^{-1} region. The ^{1}H and ^{13}C NMR spectra were recorded with a Bruker spectrometer at 300 MHz and 100 MHz respectively, spectra were recorded in DMSO as the solvent and TMS as a internal standard, the chemical shifts were expressed in ppm. Single crystal X-ray diffraction analysis was carried out to confirm the crystalline quality and also to identify the universal lattice parameters using STOE IPDS 2 diffractometer [8]. The MoKα radiation of wavelength, (λ = 0.71073 Å) and integration technique for absorption were used for data collection. The lattice parameters were determined by the least-squares method on the basis of all reflections with $F^2>2\sigma(F^2)$.

2.2 Synthesis

2.2.1 Synthesis of Di ((E)-2-(pyridine-2-ylmethylene)hydrazinecarboxamide)cobalt(II) dichloride trihydrate

2.2.1.1 Preparation of ligand (L3)

semicarbazide hydrochloride (2.78 g, 0.025 mol) was dissolved in ethyl alcohol (20 ml), the solution was stirred using magnetic stirrer for 10 minutes and one pellet of NaOH is added and Stirred well. Then pyridine-2-carboldehyde (2.4 ml, 0.025 mol) is slowly added to the solution and stirred well for 45 minutes. As a result, a colourless (white) ligand is obtained. This ligand was filtered, dried and washed with petroleum ether (40-60%). Recrystallised using ethanol . Yield: 83%; Anal. Calcd. (%): C, 51.18; H, 4.90; N, 34.10; O, 9.70; Found (%): C, 51.21; H, 4.91; N, 34.13; O, 9.75; IR data (cm^{-1}): 3386 (N-H), 2929 (C-H), 1692 (C=O), 1146 (C=N); 1H NMR data (300MHz, DMSO in ppm): 10.5(s, 1H, OH (enolic)), 8.5(d, 1H, pyridine(6)), 8.1(d, 1H, pyridine(3)), 7.8(s, 1H, azomethine(C=N)), 7.7(t, 1H, pyridine(4)), 7.3(t, 1H, pyridine(5)), 6.6(s, 1H, NH_2); ^{13}C NMR data(100MHz, DMSO in ppm): 156, 154, 149, 140, 136, 123, 120.

2.2.1.2 Preparation of cobalt complex (L3Co)

L3 (1.64g, 0.01 mol) is dissolved in methanol and then methanolic solution of cobaltus chloride hexahydrate (1.19g ,0.005 mol) is taken in the ratio of 2:1. A small amount of chloroform (5 ml) is added and then reflux for 8 hrs a orange colour solid is obtained. Then recrystallised using ethanol . Yield: 87%; Anal. Calcd. (%): C, 32.83; H, 4.33; N, 21.88; O, 15.62; Found (%): C, 32.92; H, 4.54; N, 21.24; O, 15.42; IR data (cm^{-1}): 3374 (N-H), 2924 (C-H), 1667 (C=O), 1175 (C=N), 528 (Co-N), 426 (Co-O).

2.2 X- ray Structure analysis

A single crystal of the title compound 1 with dimensions 0.36 X 0.29 X 0.17 mm was selected for the data collection. The data were collected with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 200(2) K. For the compound 1 data collection and cell refinement: X- AREA [9] ; data reduction: X-RED32 [10]; molecular graphics: ORTEP-3 [11] and the software used to prepare material for publication: PLATON [12]. The structure of the compound 1 was solved by direct methods using SHELXS-97 [13] and refined by a full-matrix least-squares procedure using SHELXL-97 [13]. All non-hydrogen, atoms were assigned anisotropic displacement parameters in the refinement. All hydrogen atoms were positioned geometrically and refined as riding atoms, with C-H = 0.95 Å (aromatic) and N-H = 0.84 Å (NH), 0.79-0.90 Å (NH_2), and refined using riding model with $U_{iso}(H) = 1.2U_{eq}(C,N)$. In the range 1.71° - 25°, a total of 20903 reflections were collected, of which (R_{int} = 0.0515). The largest diffraction peak and holes are 0.395 and -0.330 e/$Å^3$, respectively. The chemical structure of the title compound 1 is shown in scheme 1**.** Molecular structure of the title compound 1 showing the atomic numbering scheme is shown in Fig. 1. The crystallography details for the structures determination of the compound are displayed in Table 1 and Hydrogen bond geometry are listed in Table 2 respectively.

Table 1. Crystal data, data collection and structure refinement parameters

Formula weight	512.23
Crystal shape, colour	block, dark orange
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 9.3547(5) Å α= 106.033(4)°. b = 9.8985(5) Å β= 103.916(4)°. c = 12.8840(7) Å γ= 95.717(4)°.
Volume	1095.20(10)$Å^3$
Z	2
Density (calculated)	1.553 Mg/m^3
Absorption coefficient	1.070 mm^{-1}
F(000)	526
Crystal size	0.36 X 0.29 X 0.17 mm^3
Theta range for data collection	1.71 to 25.00°
Index ranges	-11<=h<=11 -11<=k<=11 -15<=l<=15
Reflection collected	20903
Completeness to theta	98.7 %
Max. and min transmission	0.8390 and 0.6993
Refinement method	Full-matrix least-squares method F^2
Data/restraints/parameters	3806/ 0 / 307
Goodness-of-fit on F^2	1.064
Final R indices I >2sigma(I)]	R1 = 0.0255, wR2 = 0.0677

R indices (all data)	R1 = 0.0272, wR2 = 0.0686
Largest diff. peak and holes	0.395 and -0.330 e.Å^{-3}

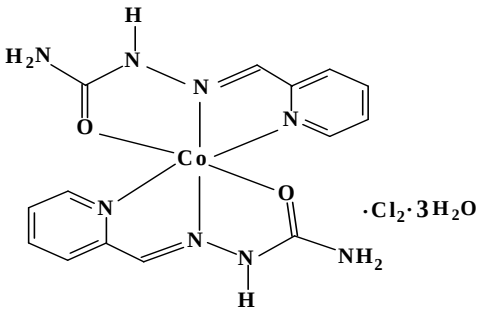
2.3 Antimicrobial Test

Qualitative determination of antimicrobial activity was done using Kirby-Bauer Agar well diffusion method. Bacterial strains were maintained on nutrient agar slants at 4 ℃. The synthesized compounds (L3 and L3Co) were dissolved in DMSO at a concentration of 100 µg/mL. The respective microbial culture was swabbed into the nutrient agar plates for uniform distribution of colonies. The synthesized compounds were poured into each well using a sterile micro pipette and streptomycin was used as a standard. The plates were incubated at 37 ℃ for 24 hours. After incubation reading of the results were done by measuring the diameters of inhibition zone generated by the test substance.

3. RESULTS AND DISCUSSION

3.1 Structure Description of Title Compound

The chemical structure of the title compound as shown in scheme- 1.



Scheme 1. Chemical structure of the title compound.

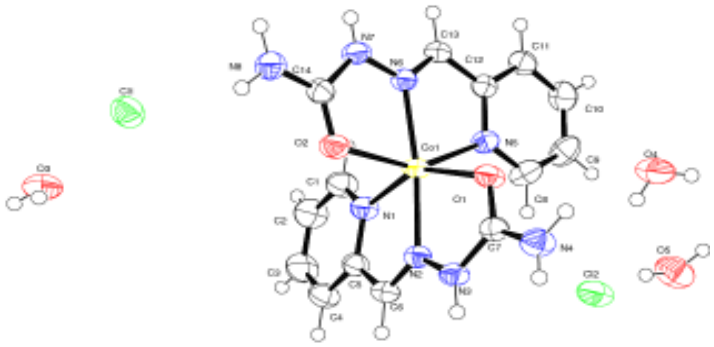


Fig. 1. The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level

Table 2. Hydrogen bonds geometry (Å, º)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(3)-H(3B)...O(3)#1	0.84(3)	1.89(3)	2.726(2)	171(3)
N(4)-H(4C)...Cl(1)#1	0.79(3)	2.74(3)	3.3629(16)	137(3)
N(4)-H(4B)...Cl(1)#2	0.90(3)	2.42(3)	3.3157(18)	173(2)
N(8)-H(8A)...Cl(1)	0.85(3)	2.46(3)	3.2489(17)	156(3)
N(8)-H(8B)...Cl(1)#3	0.89(3)	2.56(3)	3.4168(18)	161(2)
O(3)-H(3D)...Cl(2)#4	0.84(4)	2.30(4)	3.1227(18)	167(3)
O(5)-H(5A)...Cl(2)	0.98(4)	2.20(4)	3.156(2)	166(3)
O(3)-H(3C)...O(5)#5	0.72(4)	1.99(4)	2.709(2)	173(4)
O(5)-H(5B)...Cl(1)#6	0.84(4)	2.39(4)	3.2150(19)	167(3)
O(4)-H(4D)...Cl(2)	0.76(4)	2.36(4)	3.1152(18)	170(4)
O(4)-H(4E)...Cl(1)#6	0.79(4)	2.66(4)	3.339(2)	146(3)

Symmetry transformations used to generate equivalent atoms:

#1 x,y-1,z #2 -x+1,-y+1,-z+2 #3 -x+1,-y+2,-z+2

#4 -x+1,-y+1,-z+1 #5 x-1,y+1,z #6 x+1,y-1,z

The title compound crystallizes in a triclinic space group P-1, with a = 9.3547(5) Å, b = 9.8985(5) Å, c = 12.8840(7) Å, α=106.033(4)°, β = 103.916(4)°, γ = 95.717(4)°, V = 1095.20(10) $Å^3$, Z=2, D_c = 1.553mg/m^3, F(000) = 526, R = 0.0255 and wR = 0.0687. The title compound consists of a $[Co(C_7H_8N_4O)_2]^{2+}$ complex cation, chloride anions and three hydrate solvent molecules. As shown in Fig. 1, two tridenate 2-(pyridine-2-ylmethylene)hydrazinecarboxamide ligands are coordinated to the Co^{II} atom solely *via* four N atoms and two O atoms. The coordinated bond angles are in the range of 74.57(5) – 168.95(5)°, suggesting a significant deviation fr om a perfect octahedral coordination. The Co-N distances are varying from 2.0484(13) – 2.1641(14) Å. The Co-O distances are 2.1215(11) and 2.1670(12) Å, respectively. Such distances are similar to those found in other related structures [14-17].

The crystal packing of the title compound 1 is viewed along b-axis as shown in Fig. 2. In the crystal, intermolecular N—H…O, N—H…Cl, O—H…Cl and O—H…O hydrogen bonds (Fig. 3 & Fig. 4 and Table2) link the molecules into a three- dimensional supramolecular network, in which they may be effective in the stabilization of the structure.

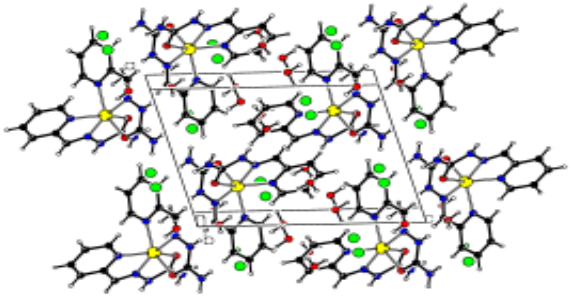


Fig. 2. Crystal packing of the title compound viewed down the b-axis

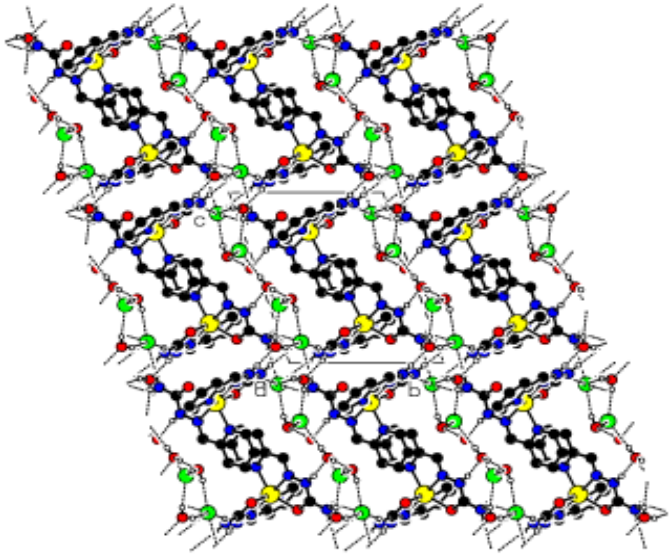


Fig. 3. Crystal packing of the title compound viewed down the a-axis showing hydrogen bond interactions with dashed lines

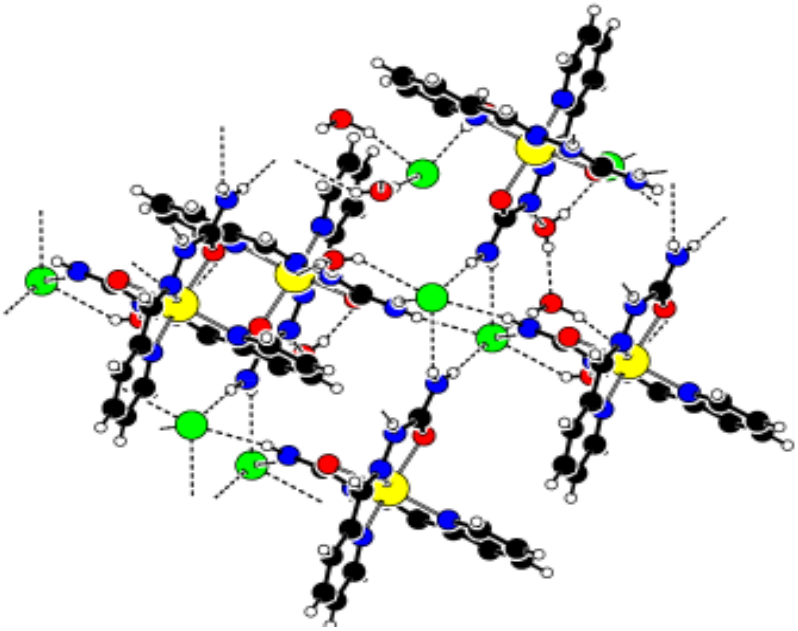


Fig. 4. Crystal packing of the title compound viewed down the c-axis showing N—H…Cl, N—H…O, O—H…Cl and O—H…O interactions with dashed lines

3.2 Antimicrobial Activity

In the present investigation, biological activity of the ligand and its metal complex have been screened for antimicrobial activity against *Staphylococcus aureus, E.coli, Candida albicans and A.niger* by well diffusion method and the results are summarized in Table 3. The results show that the synthesized compounds have moderate to good antimicrobial efficiency against different strains. The title compound exhibited strong activity against E.coli ,Candida albicans and Staphylococcus aureus. Even though, it is notable that the activities of metal complex (L3Co) are stronger than those of ligand (L3).

Table 3. Antimicrobial activity of L3 and L3Co (diameter of the zone of inhibition in mm) at 100µg/mL

	L3	L3Co	standard
Staphylococcus aureus	13	24	26
E.coli	08	30	30
Candida albicans	12	26	13
A.niger	14	20	15

4. CONCLUSION

In the above study, the title compound has been prepared, and their structure was confirmed by elemental analysis, IR spectra and single-crystal X-ray determination. The antimicrobial test shows that title compound exhibit better activity than the corresponding ligand. The title compound is a good choice in search for antimicrobial materials.

SUPPLEMENTARY DATA

"CIF file containing complete information on the studied structure was deposited with CCDC, deposition number 968266, and is freely available upon request from the following web site: www.ccdc.cam.ac.uk/data_request/cif".

.COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Sadler PJ. Inorganic chemistry and drug design. Adv Inorg Chem. 1991;36:1-48.
2. Tsiliou S, kefala L-A, Perdih F, Turel I, Kessissoglou DP, Psomas G. Cobalt(II) complexes with non-steroidal anti-inflammatory drug tolfenamic acid: structure and biological evaluation. Eur J Med Chem. 2012;48:132-142.
3. Dimiza F, Papadopoulos AN, Tangoulis V, Psycharis V, Raptopoulou CP, Kessissoglou DP, Psomas G. Biological evaluation of cobalt(II) complexes with non-steroidal anti-inflammatory drug naproxen. J Inorg Biochem. 2012;107:54-64.
4. Dimiza F, Papadopoulos AN, Tangoulis V, Psycharis V, Raptopoulou CP, Kessissoglou DP, Psomas G. Biological evaluation of non-steroidal anti-inflammatory drugs- cobalt(II)complexes. Dalton Trans 2010:39:4517-4528.
5. Gaber M, Al-Shihry SS. Cobalt (II), Nickel (II) and Copper (II) complexes of carbohydrazide and its Aryidene derivatives. Scienntific Journal of King Faisal University (Basic and Applied Sciences). 2004;5:1425.
6. Kundu S, Roy S, Bhar K, Ghosh R, Lin C-H, Ribas J, Ghosh BK. Synthesis, molecular and crystalline architectures, and properties of a mononuclear complex [co^{II} $(benzidine)_2$($NCS)_2$ $(OH_2)_2$]. J Chem Sci. 2013;125:723-730.
7. Pattanayak P, Patra D, Prathihar JL, Burrows A, Mahon MF, Chattopadhyay S. Osmium and cobalt complexes incorporating facially coordinated N,N,O donor azo-imine ligands: Redox and catalytic properties. J Chem Sci. 2013;125:51-62.
8. Stoe, Cie X-SHAPE. Stoe and Cie. Darmstadt. Germany. 2002.
9. Stoe, Cie. X-AREA. Stoe and Cie. Darmstadt. Germany. 2009.
10. Stoe, Cie X-RED32. Stoe and Cie. Darmstadt. Germany. 2009.
11. Farrugia LJ, ORTEP-3 for Windows- A version of ORTEP- III with a graphical User Interface (GUI), Journal of Applied Crystallography. 1997;30:565.
12. Spek AL, Structure Validation in Chemical Crystallography, Acta Crystallography, 2009;D65:148-155.
13. Sheldrick GM. SHELXS-97 and SHELXL-97, Program for Crystal structure solution and refinement. University of Gottingen; 1997.
14. Xu D-J, Zhang B-Y, Yang Q, Nie J-J. Diaquabis(pyrimidine-2-carboxylic acid – κ^2 N,O)cobalt(II) dichloride. Acta Crystallographica. 2008;E64:m77.
15. Zhao P-Z, Xuan X-P, Tang Q-H. Bis(benzoate-κ^2O,O')(2,9-dimethyl-1,10-phenanthroline-κ^2N,N')cobalt(II). Acta Crystallographica. 2008;E64:m327.
16. Li B. Diaquabis{5-(pyrindin-2-yl-κN)-3-[4-(pyridine-4-yl)phenyl]-1H-1,2,4-triazol-1-ido-κN^1}cobalt(II). Acta Crystallographica. 2013;E69:m141.
17. Zhong K-L. Bis(1,10-phenanthroline-κ^2N,N')(sulfato-κ^2O,O')cobalt(II)propane-1,2diol monosolvate. Acta Crystallographica. 2013;E69:m26.