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CRYSTAL STRUCTURE DETERMINATION AND ANTIMICROBIAL STUDIES ON DI ((E)-2-(PYRIDINE-2-YLMETHYLENE) HYDRAZINECARBOXAMIDE) NICKEL (II) DICHLORIDE DIHYDRATE

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ABSTRACT

The title compound $[Ni(C_7H_8N_4O)_2]Cl_2.2H_2O$, has been synthesized and characterized by single-crystal X-ray diffraction. The title compound crystallizes in a triclinic, space group P -1 with a = 9.9247 (8) Å, b = 10.3694 (9) Å, c = 12.2201 (10) Å, α=110.765 (6)°, β = 96.948 (7)°, γ = 103.040 (7)°, V = 1117.37 (16) $Å^3$, Z=2, R = 0.061 and wR = 0.181. In the title compound there are two crystallographically independent cations and anions and two water molecules in the asymmetric unit. The Ni^{II} ion has a distorted octahedral coordination environment and is surrounded by four N atoms and two O atoms in a tridentate manner. In the crystal, two N atoms and two O atoms occupying the equatorial plane, and other two N atoms in the axial positions. The crystal structure is stabilized by N—H…Cl, N—H…O, O—H…Cl and O—H…O hydrogen bonds, which link the complex cations, chloride anions and solvent water molecules into a three-dimensional network. One of the chloride anion is disordered over three positions and has a site-occupancy factor of 0.3333. The preliminary antimicrobial activities were studied.

INTRODUCTION

Hydrazones constitute an important class of biologically active drug molecules which has attracted attention of medicinal chemists due to their wide range of pharmacological applications. These compounds are being synthesized as drugs by many researchers in order to combat diseases with minimal toxicity and maximal effects. These predictions has provided therapeutic pathway to develop new effective biologically active hydrazones. A number of hydrazones derivatives have been reported to exert notably antimicrobial, antihypertensive, anticonvulsant, analgesic, anti-inflammatory, antituberculosis, antitumoral, antiproliferative and antimalarial activities (Singh and Raghav, 2011). Hydrazone derivatives containing an azomethine (-CONHN=CH-) group have been shown to exhibit antiproliferative activities and act as cytotoxic agents with the ability to prevent cell progression in cancerous cells through different mechanisms (Patil *et al*., 2011) and which is an important compounds for new drug development (Hai-Yun., 2011). Moreover, hydrazone derivatives have attracted a great deal of interest in synthetic chemistry and considerable research on them in relation to their synthetic utility has been accomplished. Hydrazones are extensively studied as reactants or reaction intermediates since they can readily undergo various ring closure reactions (Özdemir *et al*., 2012). In addition, metal complexes with hydrazones exhibit antimicrobial, DNA-binding and cytotoxic activities. It has also been shown that these metal complexes can be potent inhibitors of cell growth and DNA synthesis (Despaigne *et al*., 2010; Havanur *et al*., 2010; Ambwani *et al*., 2011). Metal complexes with hydrazones also have potential applications as catalysts, luminescent probes and molecular sensors (Seleem *et al*., 2011; Singh and Raghav, 2011). Such a wide range of applications of metal complex with hydrazones promoted us to

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investigate and present a crystal structure of the title compound herein.

MATERIALS AND MTHODS

General

The ligand and complex were prepared by commercially available chemicals of Merck and Sigma Aldrich products and used without further purification. 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 diffract meter (Stoe and Cie, 2002). 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 $F^2>2\sigma(F^2)$.

Experimental

Semicarbazide hydrochloride (2.78 g, 0.025 mol) was dissolved in 20 ml of ethyl alcohol were stirred10 minutes at room temperature and to the solution one pellet of NaOH is added. The reaction mixture was stirred well and then pyridine-2-carboldehyde (2.4 ml, 0.025mol) was added drop wise to the solution with efficient stirring for 45 minutes. As a result, a colourless (white) ligand was obtained. The ligand was filtered, dried and washed with petroleum ether (40-60%). The ligand (1.64g, 0.01 mol) was dissolved in methanol and to the mixture the methanolic solution of nickel 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 allowed to reflux for 8 hrs, yielding black block – shaped single crystals, which was recrystallized using ethanol.

Characterization using X- ray Structure analysis

A single crystal of the title compound 1 with dimensions 0.47 X 0.37 X 0.28 mm was selected for the data collection. The data were collected with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 200 K. For the compound 1 data collection and cell refinement: X- AREA (Stoe and Cie, 2009); data reduction: X-RED32 (Stoe and Cie, 2009); molecular graphics: ORTEP-3 (Farrugia, 1997) and the software used to prepare material for publication: (Spek, 2009). The structure of the compound 1 was solved by direct methods using SHELXS-97 (Sheldrick, 2008) and refined by a full-matrix least-squares procedure using SHELXL-97 (Sheldrick, 2008). 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 = 0.78-0.87 Å, and refined using riding model with $U_{iso}(H) = 1.2U_{eq}$ (CH,NH). In the range 1.71° - 25°, a total of 3883 reflections were collected, of which (R_{int} = 0.110). The largest diffraction peak and holes are 1.86 and -1.94 e/Å^3, respectively. The chemical structure of the title compound 1 is shown in Fig. 1. Molecular structure of the title compound 1 showing the atomic numbering scheme is shown in Fig. 2. 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. Crystallographic data and structure refinement parameters

Empirical formula	$C_{14}H_{20}Cl_2N_8NiO_4$
Formula weight	493.99
Crystal shape, colour	Block, black
Temperature	200 K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 9.9247 (8) Å α = 110.765(6)° b = 10.3694 (9) Å β = 96.948(7)° c = 12.2201 (10) Å γ = 103.040(7)°
Volume	1117.37 (16) Å^3
Z	2
Density (calculated)	1.468 Mg/m^3
Absorption coefficient	1.14 mm^{-1}
F(000)	508
Crystal size	0.47 X 0.37 X 0.28 mm
Theta range for data collection	2.16 to 25°
Index ranges	-11<=h<=11, -12<=k<=12, -14<=l<=14
Reflection collected/Unique	21050
Completeness to theta	98.7%
R_{int}	0.110
Data/restraints/parameters	3883 / 9 / 298
Goodness-of-fit on F^2	1.114
Final R indices [I > 2σ(I)]	R1 = 0.0608, wR2 = 0.1727
R indices (all data)	R1 = 0.0667, wR2 = 0.1796
Largest diff. peak and holes	1.855 and -1.938 e.Å^{-3}

Table 2. Hydrogen bonds geometry [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(3)-H(3B)...Cl(1)	0.78(8)	2.35(8)	3.120(4)	167(7)
N(7)-H(7)...Cl(4)	0.83(8)	2.25(8)	3.053(4)	162(7)
N(7)-H(7)...Cl(3)	0.83(8)	2.35(8)	3.132(6)	157(7)
N(4)-H(4B)...O(4)#2	0.87(2)	1.96(2)	2.822(6)	174(7)
N(4)-H(4C)...O(3)#3	0.87(2)	2.14(2)	3.007(5)	170(7)
N(8)-H(8A)...O(3)#4	0.86(2)	2.15(4)	2.944(5)	153(7)
N(8)-H(8B)...Cl(3)#1	0.87(2)	2.39(4)	3.211(7)	155(7)
N(8)-H(8B)...Cl(4)	0.87(2)	2.70(4)	3.448(4)	144(6)
O(3)-H(3D)...O(2)#5	0.86(7)	2.05(7)	2.842(4)	154(8)
O(3)-H(3C)...Cl(1)#6	0.88(2)	2.25(2)	3.132(4)	175(8)
O(4)-H(4D)...Cl(2)#7	0.88(2)	2.28(4)	3.087(4)	154(7)
O(4)-H(4E)...Cl(1)	0.88(2)	2.32(5)	3.109(4)	148(8)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+2,-z+1 #2 -x+1,-y+1,-z+2 #3 x,y,z+1
#4 x,y+1,z+1 #5 -x+1,-y+1,-z+1 #6 x,y,z-1
#7 x+1,y+1,z+1

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 °C. The synthesized compounds 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 °C for 24 hours. After incubation reading of the results were done by measuring the diameters of inhibition zone generated by the test substance.

RESULTS AND DISCUSSION

X-ray Structure analysis of the title compound

The chemical structure of the title compound as shown in Fig. 1. The title compound crystallizes in a triclinic, space group

P -1, with a = 9.9247 (8) Å, b = 10.3694 (9) Å, c = 12.2201 (10) Å, α=110.765 (6)°, β = 96.948 (7)°, γ = 103.040 (7)°, V = 1117.37 (16) Å^3, Z=2, R = 0.061 and wR = 0.181.

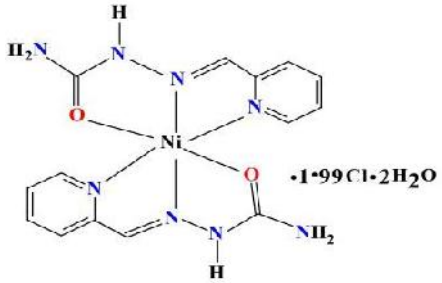

Fig. 1. Chemical structure of the title compound

The title compound consists of a $[Ni(C_7H_8N_4O)_2]^{2+}$ complex cation, chloride anions and two hydrate solvent molecules. As shown in Fig. 2, two tridentate 2-(pyridine-2-ylmethylene) hydrazinecarboxamide ligands are coordinated to the Ni^{II} atom solely *via* four N atoms and two O atoms; an N2 and N6 atoms are in the axial positions, and the other two N atoms (N1, N5) and O atoms (O1, O2) are in the equatorial plane. The coordination of the hydrazones to Ni center results in the formation of four five-membered chelating rings.

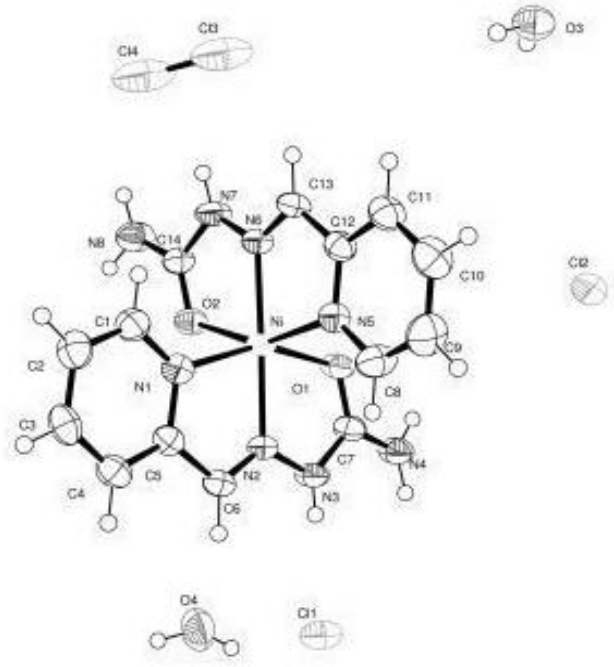

Fig. 2. The molecular structure of the title compound, with an atom labelling. Displacement ellipsoids drawn at the 50% probability level

Bond lengths and Bond angles

In the four rings, Ni—$N_{pyridyl}$ bond lengths of 2.090(3) and 2.081(3) Å are larger than those for Ni—N_{iminol} bonds [1.995(3) and 1.992(3) Å]. The Ni—O1 and Ni—O2 involving the hydazonic oxygen have the metal-ligand distance of 2.090(3) and 2.152(3) Å. The Ni—N and Ni—O bond distances are similar to those observed in other mononuclear Ni^{II} complexes with tridentate ligands (Datta *et al*., 2010; Aiswarya *et al*., 2012). The distortion from regular octahedral symmetry is relatively large considering that the bond angles surrounding nickel ion lie between 75.97(12) and 178.44(13)°.

Crystal packing

Hydrogen-bond geometry is given in Table 2. In the crystal, intermolecular N—H…Cl, N—H…O, O—H…O and O—H…Cl hydrogen bonds (Fig.3 and Table 2) link the molecules into a three-dimensional supramolecular network, in which they may be effective in the stabilization of the structure.

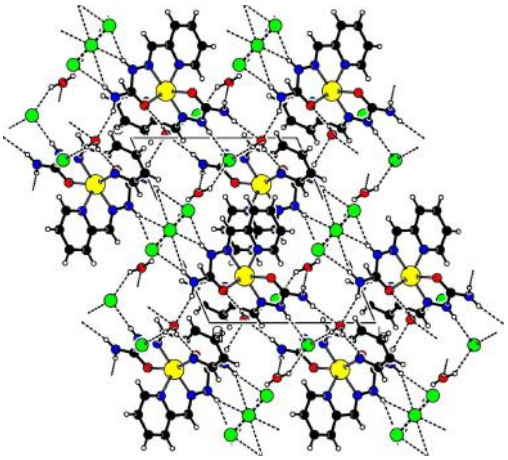

Fig. 3. Crystal packing of the title compound viewed along the *a* axis. Hydrogen bonds are shown as dashed lines

Table 3. Antimicrobial activity of L4 and L4Ni (diameter of the zone of inhibition in mm) at 100µg/mL

	L4	L4Ni	Standard
Staphylococcus aureus	15	20	26
E.coli	09	27	30
Candida albicans	14	24	13
A.niger	15	18	15

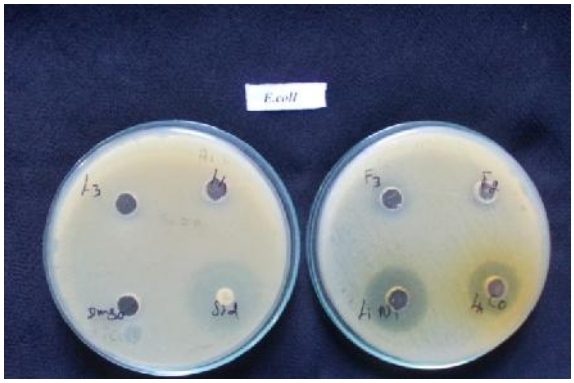

Fig. 4a. Zone of inhibition against *E.coli*

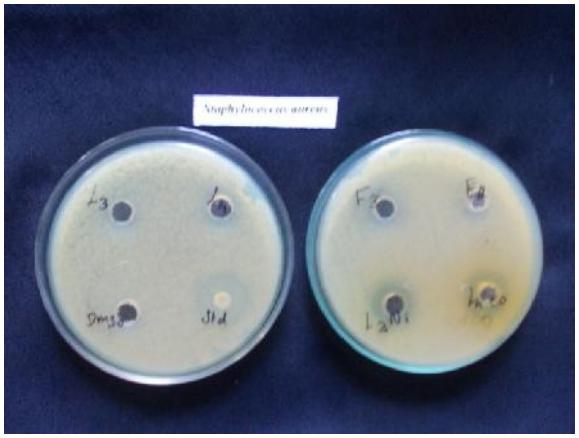

Fig. 4b. Zone of inhibition against *Staphylococcus aureus*

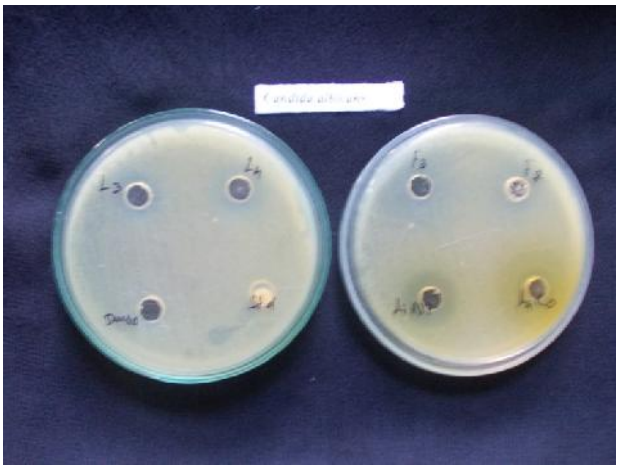

Fig. 4c. Zone of inhibition against *Candida albicans*

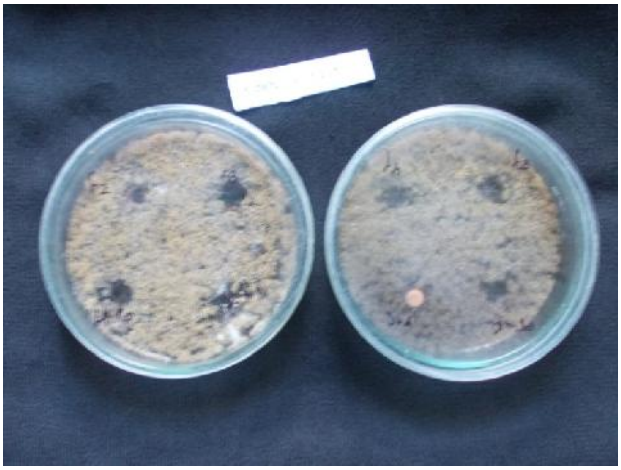

Fig. 4d. Zone of inhibition against *A.niger*

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 *A.niger* and *Candida albicans*. Even though, it is notable that the activities of metal complex (L4Ni) are stronger than those of ligand (L4). The inhibition zone generated by the test substance (see Fig. 4a, 4b, 4c and 4d).

Conclusion

In the above study, the title compound has been prepared, and their structure was confirmed by 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 CCDC 1035090, and is freely available upon request from the following web site: www.ccdc.cam.ac.uk/data_request/cif.

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