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SYNTHESIS AND CRYSTAL STRUCTURE NI(II)-E-3-(HYDROXYIMINO)-4-(((E)-2-(((2E,3Z)-4-HYDROXYPENT-3-EN-2-YLIDENE)AMINO)ETHYLIDENE)AMINO)PENTAN-2-ONE

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Abstract: The title Ni^{II} complex, C16H21NO3Si, is built up by a tridentate dinegative Schiff base ligand bound to a nickelhydroxypent unit. The coordination geometry of the pentacoordinated Ni^{II} atom is a distorted trigonal bipyramid. The presence of the nickelhydroxypent ring in the complex leads to an unusual coordination geometry of the Ni^{II} atom with the N atom from the Schiff base ligand and an amino -N atom in apical positions of the trigonal bipyramid. In the crystal, C-H…O and O-H…O interactions are found within corrugated layers of molecules parallel to the ab plane.

Index Terms: Synthesis; crystal structure;nickel (II) (hydroxyimino); hydroxypent; ethylideneamino; N-H…O; O-H…O; hydrogen bonds; π-stacking; T = 295 K; R factor = 0.0326; wR factor = 0.828; data-to-parameter ratio = 9.05.

I. INTRODUCTION

Transition metal complexes have been extensively studied as anticancer drugs because of their diverse spectral, chemical, and electrochemical properties [1, 2, 3, and 4]. It is well known that DNA is an important cellular receptor. The interaction of metal complexes with DNA has recently gained much attention because it indicates that the complexes may have potential biological activity and their activity depends on the mode and affinity of the binding with DNA. Platinum based drugs have been in clinical use for cancer treatment for more than 30 years [5]. The landmark discovery of the antitumoral properties of cisplatin by Rosenberg in 1965 heralded a new area of anticancer research based on metallopharmaceuticals [6]. Although the mechanism by which cisplatin selectively kills cells is not entirely understood, it is generally believed that the therapeutic effects arise from covalent binding of the drug to DNA [6]. The efficacy of cisplatin, however, is reduced by increasing tumor resistance and high toxicity. These limitations have aroused interest toward the design and evaluation of transition metal complexes other than platinum based

derivatives for therapeutic use [7]. Similarly, protein was also established as one of the main molecular targets in the action of anticancer agents [8]. The interaction between protein and drugs provides useful information on the structural features that determine the therapeutic effectiveness of drugs and also to study the pharmacological response of drugs [9, 10, 11, 12] Therefore interaction of the proteins with the metal complexes become important in the search of new drug molecules.

Dithiocarbazate Schiff base derivatives have emerged as prospective ligands in medicinal chemistry as a result of their various pharmaceutical and biological activities [13, 14, 15]. For some years, we have been undertaking a study of N,S-chelating dithiocarbazato ligands and their corresponding metal complexes, which were observed to crystallize with ligands both in trans and cis configurations [16].

II. Experimental

The title compound Ni(II)-E-3-(hydroxyimino)-4-(((E)-2-(((2E,3Z)-4-hydroxypent-3-en-2-ylidene)amino)ethylidene)amino)pentan-2-one complex was synthesized using reported method[17].

[17] Ref. RSC Adv.,2015,5, 46031–46049.

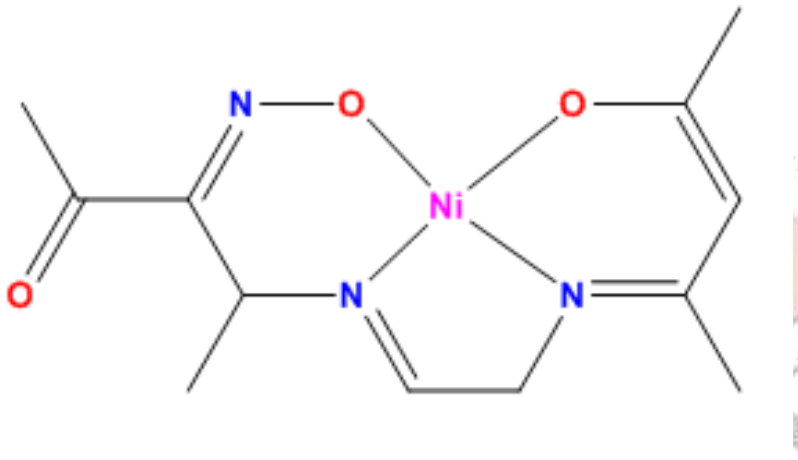

Fig. 1 Scheme diagram of title compound.

III. Data collection

Data collection: APEX3 (Bruker, 2016)[18]; cell refinement: SAINT (Bruker, 2016); data reduction: SAINT (Bruker, 2016); program(s) used to solve structure: SHELXT (Sheldrick, 2015a)[19]; program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015b)[20]; molecular graphics: DIAMOND (Brandenburg & Putz, 2012)[21], PLATON (Spek, 2020)[22]; software used to prepare material for publication: SHELXL2018/3 (Sheldrick, 2015b), PLATON (Spek, 2020) and publCIF (Westrip, 2010)[23].

IV. Refinement

The crystal structure was solved by Direct Methods and refined by full-matrix least-squares methods using the Olex2. All the carbon-bound hydrogen atoms were placed in the calculated positions, with the d(C—H) = 0.93–0.98 Å. The U_{iso}(H) were set to 1.2 U_{eq}(C) and to 1.5 U_{eq}(O).

V. Structural Commentary

The central Ni^{II} atom in the title complex, [C12 H17 N3 Ni O3], is located on an inversion center and adopts a roughly square-planar coordination environment defined by two chelating N, S donor sets of two symmetry-related ligands in a trans configuration. The Ni—N and Ni—O bond lenghts are 1.9193 (14) and 2.1788 (5) Å , respectively, with a chelating N—Ni—O bond angle of 86.05 (4)˚. Nickel (II) crystallized in a centrosymmetric triclinic setting in space group P-1, with crystallographically molecules (Z = 2) (Fig. 2). The structure of Ni confirms its rare secochlorin bisketone connectivity that was previously derived spectroscopically and by means of subsequent reactions (Banerjee et al., 2012; Sharma et al., 2016). Bond lengths and angles are in the expected ranges. Noteworthy, however, are the C—N bonds around the cleavage site at N1, which show a clear asymmetry present in both molecules. The lengths for N1—C3 are 1.3687 (15) and 1.3661 (15) Å. Directional interactions between molecules are scarce, limited to just a few C-H…O contacts, and intermolecular interactions are mostly dispersive in nature.

VI. Superamolecular features

In addition to the intramolecular C-H…O bonds within each molecule, there are also a small number of weak O-H…O hydrogen bond-like interactions present that connect molecules of Nickel (II) with each other (Fig. 3; see Table 3 for numerical values and symmetry operators). Some weak C-H…π interactions are also present (not shown), but these are too weak to be classified as directional and they are unlikely to have any strong structure-determining effects. Instead, intermolecular interactions in the structure of Nickel (II) are dominated by non-directional dispersion interactions (van der Waals interactions).

In the crystal, the dimers are connected into stacks extending along the [101] direction through slipped π-stacking interactions between the six-membered (Cg2: C1–C6 and Cg5: C9– C14) rings (Table 3 and Fig. 4).

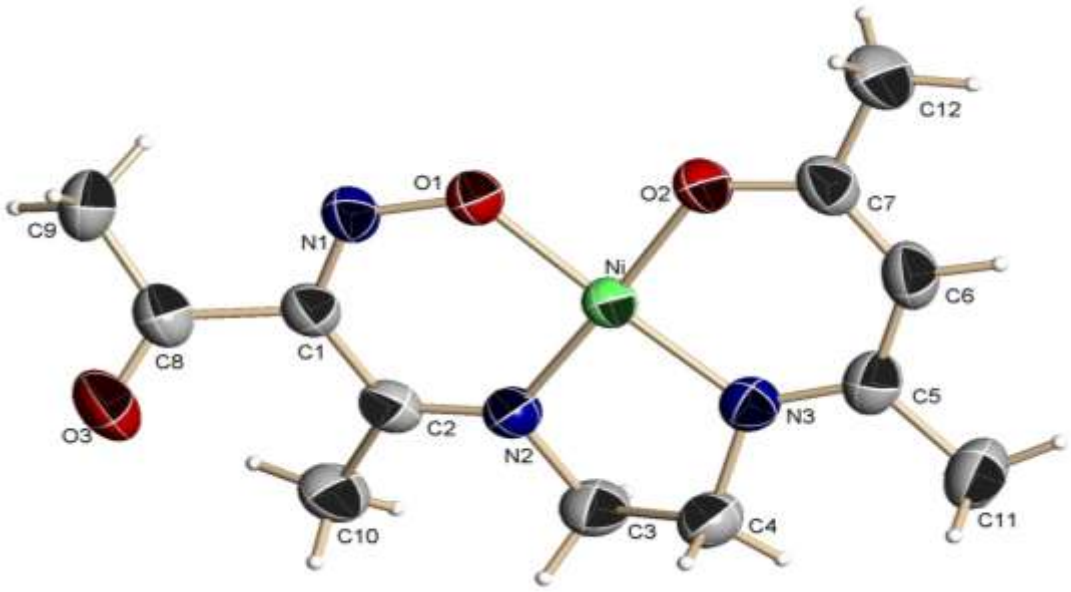

Fig. 2 The molecular structure of title compound with displacement ellipsoids drawn at the 50% probability level

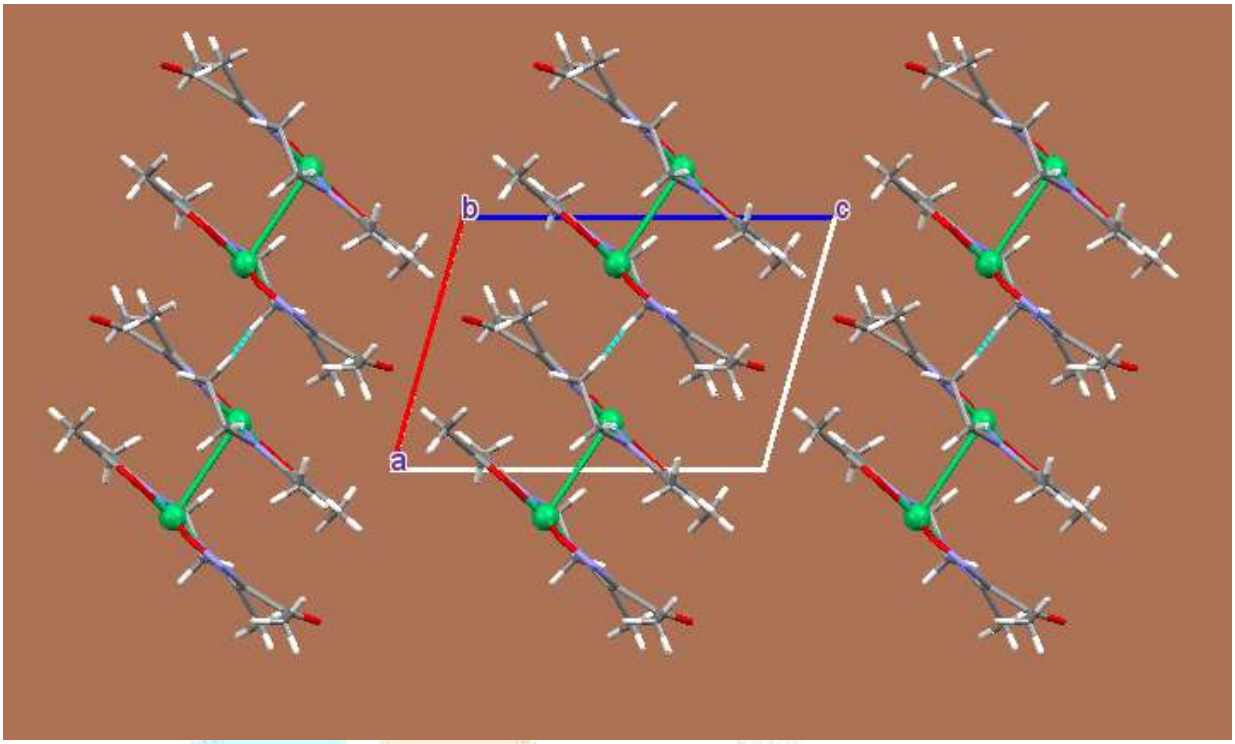

Fig.3 View of the packing seen along the b-axis direction with C-H…O hydrogen bonds interactions depicted,
respectively, by light blue, black and orange dashed lines.

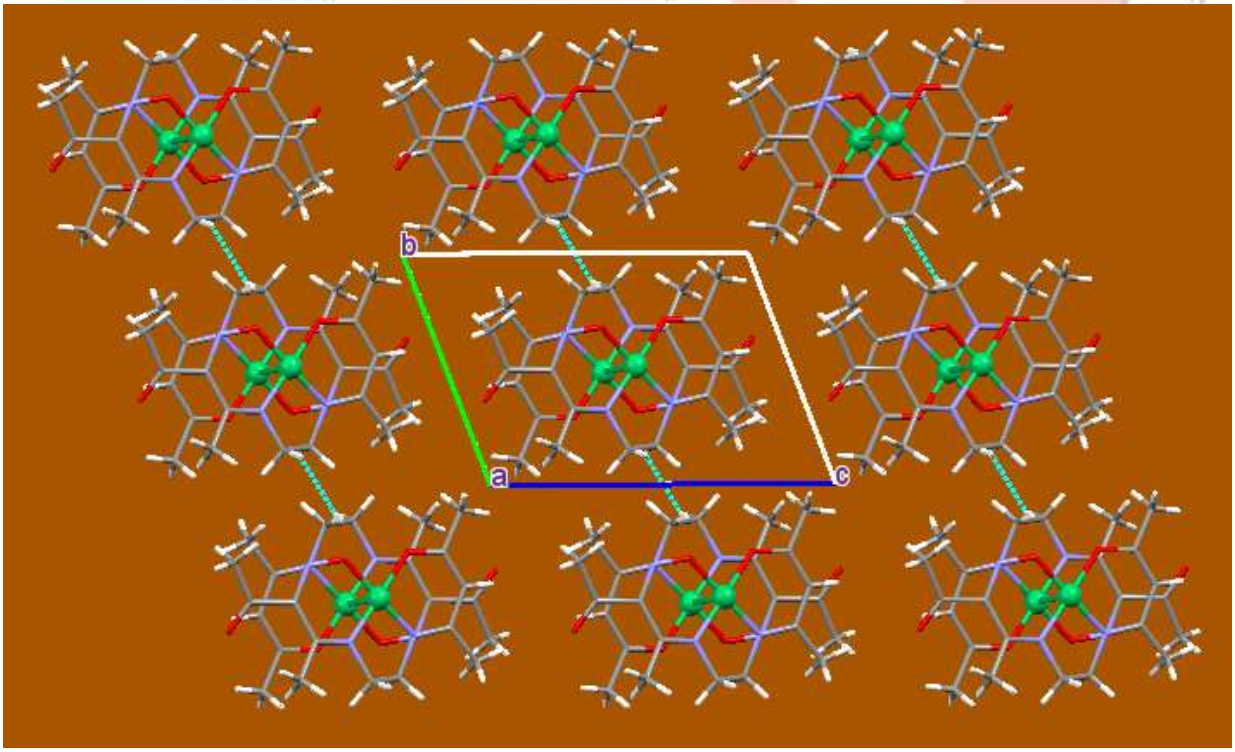

Fig. 4 The crystal structure of title compound with view of a double chain that propagates along the crystallographic b-axis direction: C-H…O and C-H…C contacts are shown with dashed lines.

VII. Table 1

Crystal Data and Details of the Structure Determination

Parameters	**Title of compound**
Empirical formula	C12 H17 N3 Ni O3
Formula weight	309.98
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 7.826(4) Å, α= 107.774(9)°.
	b = 8.149(5) Å, β= 101.539(9)°.
	c = 11.450(6) Å, γ = 100.553(9)°.
Volume	657.6(6) Å3
Z	2
Density (calculated)	1.566 g/cc
Absorption coefficient	1.483 mm-1
F(000)	324
Crystal size	0.16 x 0.08 x 0.04 mm3
Theta range for data collection	1.94 to 24.99°.
Index ranges	-9<=h<=9, -9<=k<=9, -13<=l<=13
Reflections collected	6119
Independent reflections	2288 [R(int) = 0.0216]
Completeness to theta = 24.99°	99.00%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9376 and 0.7930
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	2288 / 0 / 176
Goodness-of-fit on F2	1.095
Final R indices [I>2sigma(I)]	R1 = 0.0326, wR2 = 0.0828
R indices (all data)	R1 = 0.0366, wR2 = 0.0858
Largest diff. peak and hole	0.462 and -0.239 e.Å-3

VIII. Table 2

Selected Bond length and Bond angles (Å, °)

Atom		**Length(Å)**	**Atom**	**Angles(°)**
Ni-O(1)	1.8376(19)	Ni-O(1)	O(1)-Ni-O(2)	83.26(9)
Ni-O(2)	1.8430(18)	Ni-O(2)	O(1)-Ni-N(2)	94.23(9)
Ni-N(2)	1.843(2)	Ni-N(2)	O(2)-Ni-N(2)	176.30(8)
Ni-N(3)	1.858(2)	Ni-N(3)	O(1)-Ni-N(3)	177.92(8)
O(1)-N(1)	1.314(3)	O(1)-N(1)	O(2)-Ni-N(3)	95.12(10)
O(2)-C(7)	1.293(3)	O(2)-C(7)	N(2)-Ni-N(3)	87.32(10)
O(3)-C(8)	1.202(3)	O(3)-C(8)	N(1)-O(1)-Ni	127.95(15)
N(1)-C(1)	1.303(3)	N(1)-C(1)	C(7)-O(2)-Ni	125.82(18)
N(2)-C(2)	1.291(3)	N(2)-C(2)	C(1)-N(1)-O(1)	121.3(2)
N(2)-C(3)	1.475(3)	N(2)-C(3)	C(2)-N(2)-C(3)	119.6(2)
N(3)-C(5)	1.317(3)	N(3)-C(5)	C(2)-N(2)-Ni	127.39(18)

IX. Table

Hydrogen-bond geometry (Å ,°).

D-H…A	D-H	H…A	D…A	D-H…A
C4-H4A…O2^{i}	0.99	2.52	3.332	131
C5-H5A…O1^{ii}	0.93	2.59	3.410	149
C1-H1…O1^{iii}	0.93	2.59	3.410	142

Symmetry codes: (i) 1-x,-1/2+y,1-z
(ii) 1-x,1/2+y,1-z
(iii) 2-x,-1/2+y,-z

X. ACKNOWLEDGMENT

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