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Synthesis, Identification and Calculation of Complex Crystallographic Structure of Cobalt (II) with theLigand Heterocyclic Derived from Pyridine

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ABSTRACT

A novel Pyridine-2,6-dicarboxylic acid mixed ligands complex of formula $[Co(NO_3)_2].6H_2O$ has been obtained by the reaction of Pyridine-2,6-dicarboxylic acid with cobalt nitrate and 1,10-phenanthroline on heating in water. The structures of $[Co(pydc)(Phen)(H_2O)](pydcH_2).4H_2O$ receptors, and their complexes were optimized using DFT method at the B3LYP/3-21G** level. The highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}) energies have been derived at the same level of theory. All the calculations were performed using the GAUSSIAN 03 program. The optimized geometries and frequencies of the stationary point are calculated at the B3LYPlevel of theory. The large HOMO-LUMO energy gap, both in neutral and anionic form, further provide evidence of their stability.Complex structure of the protein withamino acid groups is shown. All chemicals purchased were of reagent grade or better and were used without further purification.

Keywords: Cobalt nitrate; HOMO-LUMO gap; Pyridine; phenanthroline; complex Cobalt (II)

INTRODUCTION

Metal acetylide complexes are of both theoretical and practical interest, in particular, as their potential to form molecular wires [1-3], liquid crystals [4], electrical conductors [5], and other nanoelectronic devices [6]. Ligands containing pyridine ring arewide studied and their p-donor properties are interesting. Their combination with other donor atoms should in principleafford complexes with tunable spectroscopic properties [7-9]. Transition metal complexes containing pyrimidine ligands [10-12] are commonly found inbiological media and play important roles inprocesses such as catalysis of drug interaction with biomolecules [13] eterocyclic systems occupies an important place in the realm of synthetic organic chemistry,due to their therapeutic and pharmacological properties

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[14]. They have emerged as integral back bones of over 7000 existing drugs. The pyridine nucleus is an integral part ofanticancer and anti-inflammatory agents too. On the other hand, cyanopyridone andcyanopyridine derivatives have shown to posses promising antimicrobial and anticanceractivities [15-16]. Their study is of great interest both from the theoretical as well as practicalimportance. Various compounds such as alkaloids, essential amino acids, vitamins, haemoglobin, hormones, large number of synthetic drugs and dyes contain heterocyclic ring systems. There arelarge number of synthetic heterocyclic compounds, like pyrrole, pyrrolidine, furan, thiophene, piperidine, pyridine and thiazole having important application and many are important intermediates in synthesis [17-18]. *N*-heterocyclic compounds are well qualified to play more protection for steel corrosion [19-21].

Many *N*-heterocyclic compounds such as derivatives of pyrazole [22], bipyrazole, triazole, tetrazole, imidazole, pyridine, pyrimidine, pyridazine and imidazopyridine have been reported as effective corrosion inhibitorsfor steel in acidic media. The heterocyclic compound containing nitrogen atoms can easily beprotonated in acidic medium to exhibit good inhibitory action on the corrosion of melats in acidsolutions.

EXPERIMENTAL

Materials and methods

Elemental analyses for H, C, and N were performed at a Flash EA 1112 full automatic trace element analyzer, and cobalt content was carried out at Perkin-Elmer Analyst 700 Model AAS. The structures ofthe investigated compounds and their numbering used are shown in Figure 1.

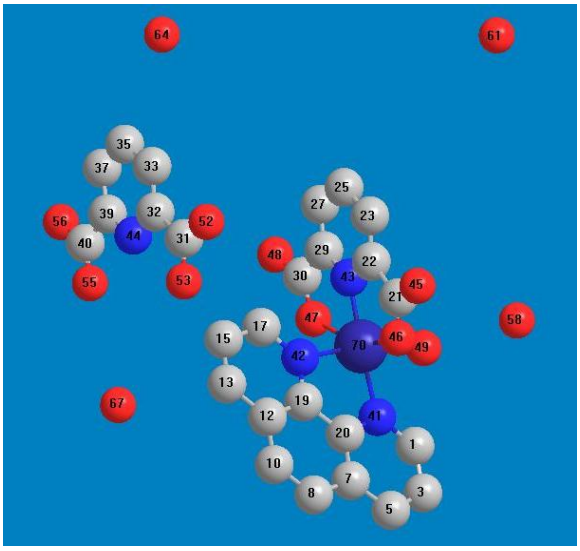


Fig. 1. Numbering system adopted in the study for complex $[Co(pydc)(Phen)(H_2O)](pydcH_2).4H_2O$ using DFT/3-21G**, (hydrogen atoms are omitted).

Synthesis of Ligand $[(PhenH)_2(Pydc)]$

Pyridine-2,6-dicarboxylic acid (2.26 gr, 13.03mmol) and 1,10-phenanthroline (2.25 gr, 11.7 mmol) were mixed and stirred in ethanol (50 ml) at room temperature for 60 min to give anred-orange solution.The resulting precipitate was then filtered, thoroughlywashed with water, and crystallized from ethanol. (Fig. 2)

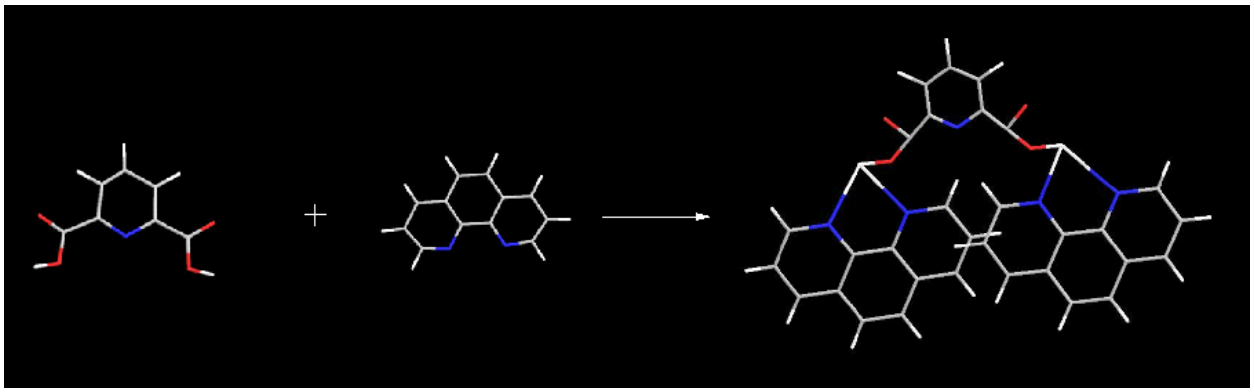
For $[C_{31}H_{21}N_5O_4]$ anal. calcd., %: C, 70.58; H, 4.01; N, 13.28; O, 12.13;

Found, %: C, 70.5; H, 4.1; N, 13.24; O, 12.11;

Mol. Wt.: 527.53, found: MW:527.62

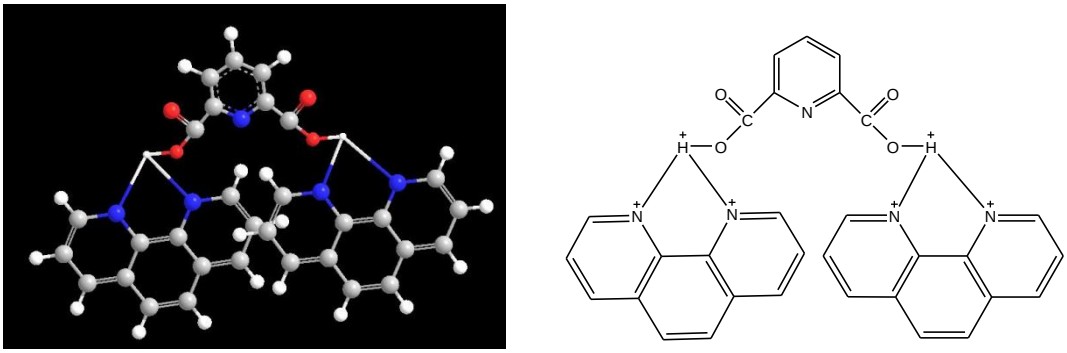
Exact Mass: 527.16

m/e: 527.16 (100.0%), 528.16 (35.5%), 529.17 (5.6%), 529.16 (1.4%)



a)

Synthesis of ligand[$(PhenH)_2$ (Pydc)],(***Stick*** models)



b)

Ball & Stick models

Fig. 2. System adopted in the study for ligand[$(PhenH)_2$ (Pydc)]atDFT/3-21G**level, **a)** (*Stick* models), **b)** *Ball&Stick* models.

Synthesis of Complex [Co(pydc)(Phen)(H_2O)](pydcH_2)·4H_2O

1.612 g (6mmol) [$(PhenH)_2$(Pydc)] was added to a ethanol solution(60 mL) of 0.415 gr

(1.7 mmol) of $Co(NO_3)_2.6H_2O$ in adry 100mL Schlenk flask. The reaction mixture was stirred vigorously while refluxing for 24 h. The solventwas reduced under vacuum.

For [$C_{26}H_{26}CoN_4O_{13}$] anal.calcd., %: C, 47.21; H, 3.96; Co, 8.91; N, 8.47; O, 31.45

Found, %: C,47.29; H, 3.71;Co, 8.89; N, 8.45; O,31.42;

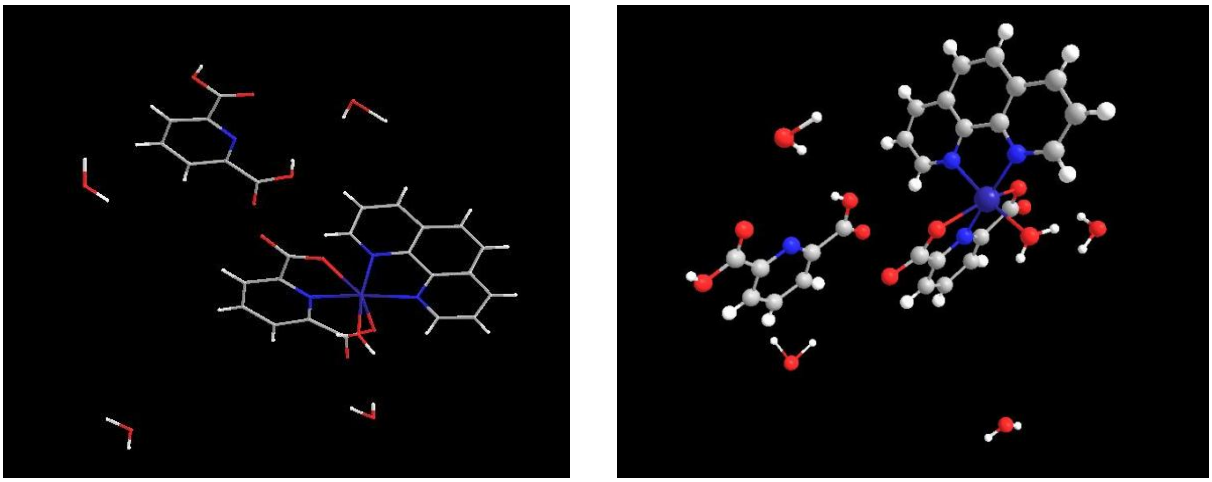
Mol. Wt.: 661.44, found: MW: 661.38

Exact Mass: 661.08

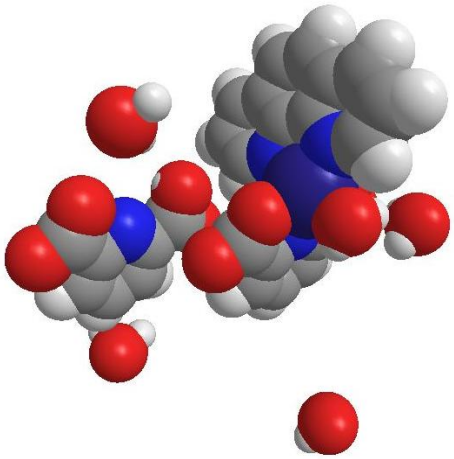
m/e: 661.08 (100.0%), 662.09 (28.9%), 663.09 (6.7%), 662.08 (1.5%), 664.09 (1.2%)

COMPUTATIONAL METHOD

The structures of [Co(pydc)(Phen)(H_2O)](pydcH_2).4H_2O receptors, and their complexes were optimized usingDFT method at the B3LYP/3-21G**level [23].Thehighest occupied molecular orbital (E_{HOMO}) and the lowestunoccupied molecular orbital (E_{LUMO}) energies have beenderived at the same level of theory.All the calculations were performed using theGAUSSIAN 03 program [24]. (Fig. 3)



a) *Stick* models **b)** *Ball & Stick* models



C) ***Space-filling*** model

Fig. 3. Optimized geometry of [Co(pydc)(Phen)(H_2O)](pydcH_2).4H_2O at DFT/3-21G**, **a)** ***Stick*** models, **b)** ***Ball & Stick***models, **C)** ***Space-filling*** model.

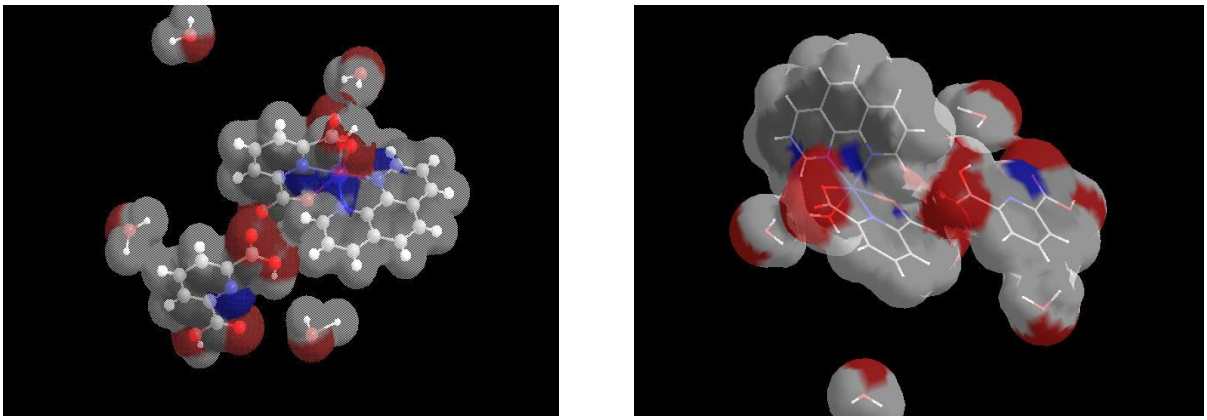
RESULTS AND DISCUSSION

The asymmetric unit consists of one independent cobalt(II) atom, one Pyridine-2,6-dicarboxylic (Pydc) ligand and one 1,10-phenanthroline (Phen) ligand and one (OH) anion and four water molecules, as shown in (Figs. 4, 5). Also contains an uncoordinated pyridine-2,6-dicarboxylic acid molecule.The data and selected intramolecular bonddistances and angles are given in Tables 1 and 2,respectively.The Co(II) atom is six coordinated by three nitrogen atomsfrom two different ligands, and threeoxygen atomsfrom Water molecular and Pyridine-2,6-dicarboxylic ligands.

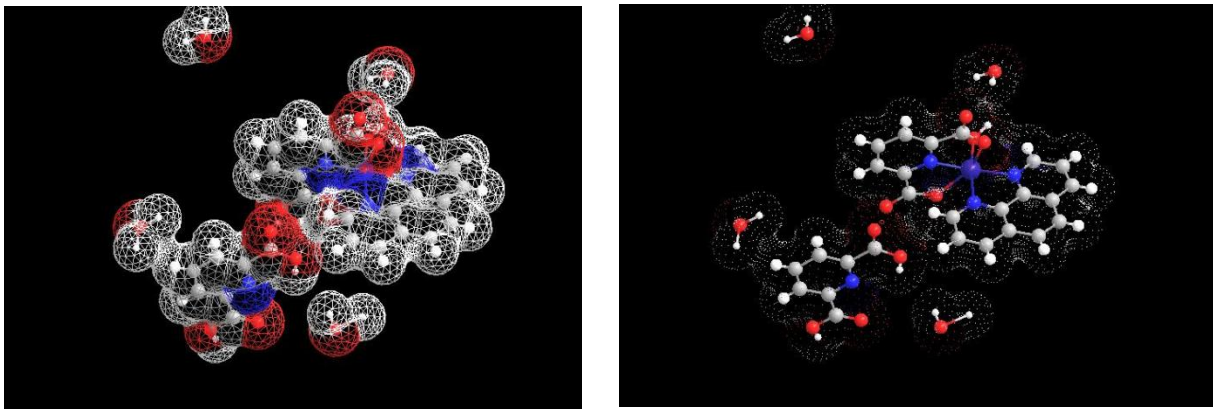
The central Co atom is coordinated by two N atoms of (Phen), with an average Co-N(41) and Co-N(42) bond length of 2.136 Å, 2.244 Åand one N and two O atoms from the tridentate (Pydc) ligand, with anaverage Co-O(46) and Co-O(47) bond length of 2.082 Å,2.323 Å. The shortest Co-N bond is Co-N(43) with 2.027 Å bond length. Atom Co is also

coordinated O atom of water. The shortestCo-O(49) bond is 2.328 Å. The largest and smallest deviations from the ideallinear value of 180° are observed forN(41)-Co(70)-N(43) [173.296°] and N(43)-Co(70)-O(47) [62.219°], angels respectively (Fig. 6). Concerning the molecular structure of the compound, the Co(II) cation($3d^7$) with six sp^3d^2hybrided orbitals can form distorted octahedral complexes with two coordinating atoms N from (Phen), and one N and two O atoms from thetridentate (Pydc) and one aqua molecule. The single crystal structure model suggests structural distortions away from the idealized Oh geometry (Fig. 7).

a) **b)**



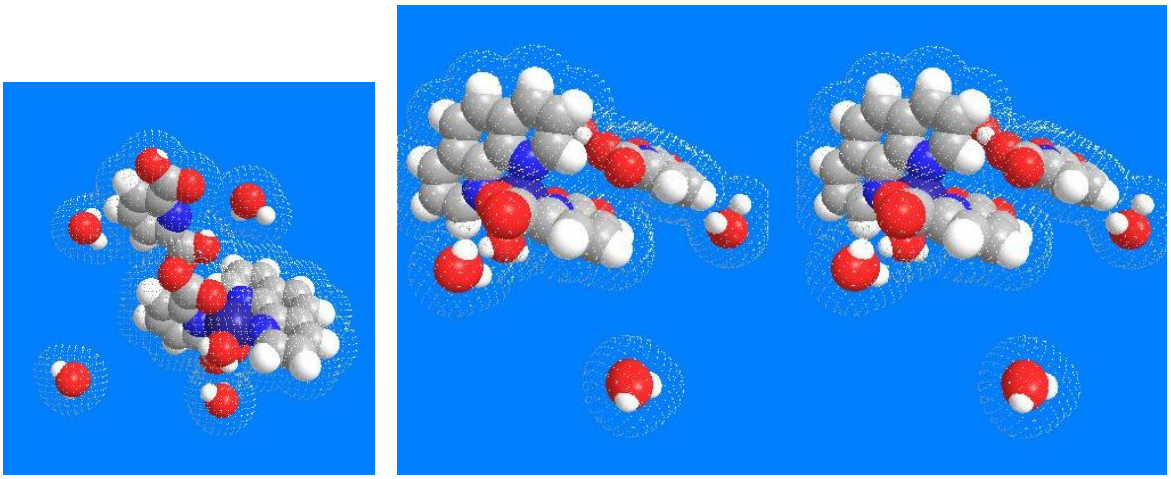
Stick models,*(Solvent Accessible Surface: Translucent) Ball & Stick* models, *(Solvent Accessible Surface: Translucent)*



c) **d)**

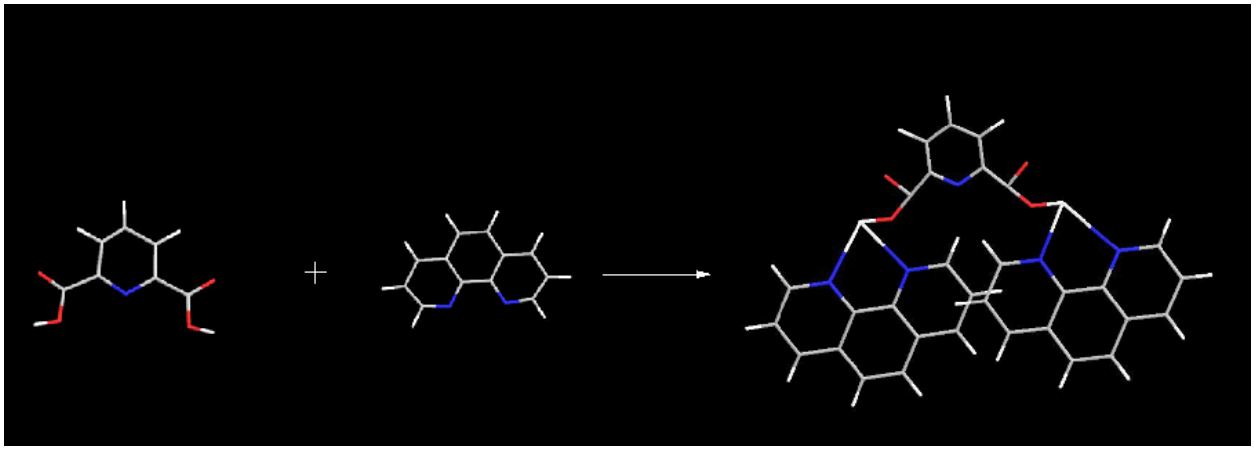
*Ball & Stick*models, *(Solvent Accessible Surface: Wire Mesh)Ball & Stick*models, *(Solvent Accessible Surface: Dots)*

Fig. 4. Optimized geometry of complex [Co(pydc)(Phen)(H_2O)](pydcH_2).4H_2O at DFT/3-21G**.

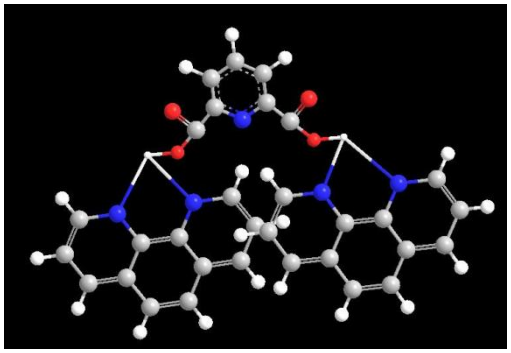


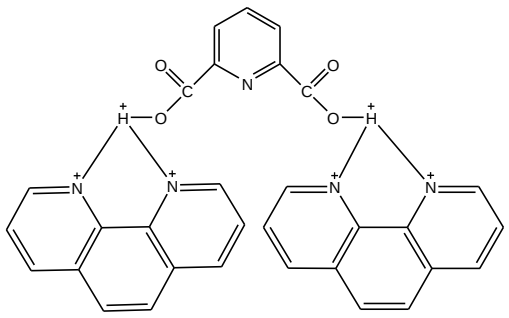
a) **b)**

Fig. 5.*Space-filling* modelandOptimized geometry of complex [Co(pydc)(Phen)(H_2O)]($pydcH_2$).4H_2O at DFT/3-21G**level, ***(Solvent Accessible Surface: Dots)***.



a)





b)

Synthesis of ligand[(PhenH)$_2$ (Pydc)](***Stick***models)
Ball&Stickmodels

Fig. 6. System adopted in the study for ligand[(PhenH)$_2$ (Pydc)]atDFT/3-21G**level,

a) (***Stick*** models), **b)** ***Ball & Stick*** models.

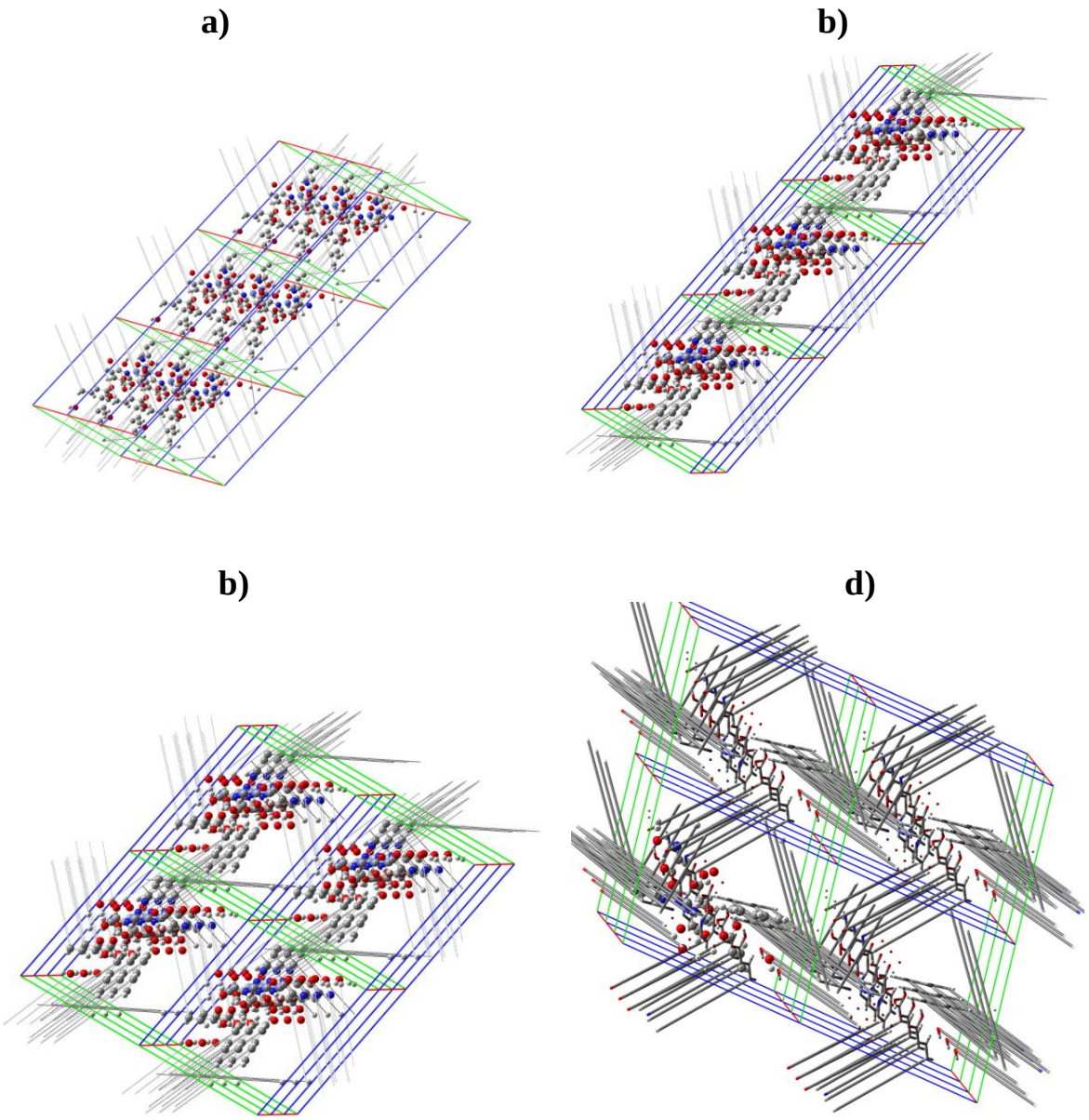


Fig. 7. The unit-cell 3D Crystal packing of the [Co(pydc)(Phen)(H_2O)]($pydcH_2$).4H_2O complex.

MOLECULAR GEOMETRY

The optimized molecular structure for [Co(pydc)(Phen)(H_2O)]($pydcH_2$).4H_2O in the ground state was computed by the DFT and B3LYP calculations computed by the 3-21G**basis set.The calculated geometricalparameters (bond lengths and bond angles) were compared with experimentally obtained x-ray single crystal structure analyses data values (Table 1, 2). As the experimental values for [Co(pydc)(Phen)(H_2O)]($pydcH_2$) 4H_2O are known, the theoretically calculated values may give an idea about the geometry of the molecule changes from the ab initio method of calculation and the DFT method of calculation.

Table 1. Geometric parameters of[Co(pydc)(Phen)(H_2O)]($pydcH_2$) $4H_2O$ complex

a) Bond Lengths (A°)

Bond Lengths (A°)	Actual	Optimal	Bond Lengths (A°)	Actual	Optimal
C(1)-C(3)	1.418	1.523	C(30)-O(47)	1.309	1.402
C(1)-N(41)	1.499	1.438	C(30)-O(48)	1.388	1.402
C(1)-H(2)	0.959	1.113	N(41)-Co(70)	2.136	-
C(3)-C(5)	1.413	1.523	N(42)-Co(70)	2.244	-
C(3)-H(4)	1.049	1.113	N(43)-Co(70)	2.027	-
C(5)-C(7)	1.582	1.523	O(46)-Co(70)	2.082	-
C(5)-H(6)	0.946	1.113	O(47)-Co(70)	2.323	-
C(7)-C(8)	1.491	1.523	O(49)-Co(70)	2.328	-
C(7)-C(20)	1.417	1.523	O(49)-H(50)	0.933	0.992
C(8)-C(10)	1.535	1.523	O(49)-H(51)	0.848	0.992
C(8)-H(9)	0.941	1.113	C(31)-C(32)	1.659	1.505
C(10)-C(12)	1.454	1.523	C(31)-O(52)	1.066	1.402
C(10)-H(11)	0.959	1.113	C(31)-O(53)	1.284	1.421
C(12)-C(13)	1.589	1.523	C(32)-C(33)	1.384	1.523
C(12)-C(19)	1.452	1.523	C(32)-N(44)	1.15	1.438
C(13)-C(15)	1.373	1.523	C(33)-C(35)	1.514	1.523
C(13)-H(14)	0.967	1.113	C(33)-H(34)	0.807	1.113
C(15)-C(17)	1.458	1.523	C(35)-C(37)	1.199	1.523
C(15)-H(16)	1.057	1.113	C(35)-H(36)	0.94	1.113
C(17)-N(42)	1.505	1.438	C(37)-C(39)	1.409	1.523
C(17)-H(18)	0.939	1.113	C(37)-H(38)	1.018	1.113
C(19)-C(20)	1.627	1.523	C(39)-C(40)	1.287	1.505
C(19)-N(42)	1.364	1.438	C(39)-N(44)	1.471	1.438
C(20)-N(41)	1.401	1.438	C(40)-O(55)	1.235	1.402
C(21)-C(22)	1.702	1.505	C(40)-O(56)	1.44	1.421
C(21)-O(45)	1.138	1.402	O(53)-H(54)	0.672	0.942
C(21)-O(46)	1.182	1.402	O(56)-H(57)	0.595	0.942
C(22)-C(23)	1.334	1.523	O(58)-H(59)	1.082	0.942
C(22)-N(43)	1.197	1.438	O(58)-H(60)	0.922	0.942
C(23)-C(25)	1.548	1.523	O(61)-H(62)	0.998	0.942
C(23)-H(24)	0.835	1.113	O(61)-H(63)	0.763	0.942
C(25)-C(27)	1.244	1.523	O(64)-H(65)	1.27	0.942
C(25)-H(26)	0.901	1.113	O(64)-H(66)	1.492	0.942
C(27)-C(29)	1.359	1.523	O(67)-H(68)	0.911	0.942
C(27)-H(28)	1.039	1.113	O(67)-H(69)	1.543	0.942
C(29)-C(30)	1.32	1.505	*	*	*
C(29)-N(43)	1.487	1.438	*	*	*

Table 1. Geometric parameters of[Co(pydc)(Phen)(H_2O)](pydcH_2) 4H_2O complex

b) Bond Angles (º)

Bond Angles (^{0})	Actual	Optimal	Bond Angles (^{0})	Actual	Optimal
C(3)-C(1)-N(41)	125.667	109.500	C(30)-O(47)-Co(70)	129.461	*
C(1)-C(3)-C(5)	112.189	109.500	N(41)-Co(70)-N(42)	87.279	*
C(3)-C(5)-C(7)	123.494	109.500	N(41)-Co(70)-N(43)	173.296	*
C(5)-C(7)-C(8)	128.863	109.510	N(41)-Co(70)-O(46)	83.071	*
C(5)-C(7)-C(20)	120.374	109.510	N(41)-Co(70)-O(47)	124.368	*
C(8)-C(7)-C(20)	110.743	109.510	N(41)-Co(70)-O(49)	83.651	*
C(7)-C(8)-C(10)	126.290	109.500	N(42)-Co(70)-N(43)	91.612	*
C(8)-C(10)-C(12)	124.199	109.500	N(42)-Co(70)-O(46)	85.600	*
C(10)-C(12)-C(13)	127.235	109.510	N(42)-Co(70)-O(47)	90.110	*
C(10)-C(12)-C(19)	110.627	109.510	N(42)-Co(70)-O(49)	170.137	*
C(13)-C(12)-C(19)	122.137	109.510	N(43)-Co(70)-O(46)	90.253	*
C(12)-C(13)-C(15)	122.167	109.500	N(43)-Co(70)-O(47)	62.219	*
C(13)-C(15)-C(17)	111.908	109.500	N(43)-Co(70)-O(49)	97.843	*
C(15)-C(17)-N(42)	127.337	109.500	O(46)-Co(70)-O(47)	152.038	*
C(12)-C(19)-C(20)	125.184	109.510	O(46)-Co(70)-O(49)	97.107	*
C(12)-C(19)-N(42)	115.403	108.800	O(47)-Co(70)-O(49)	91.813	*
C(20)-C(19)-N(42)	119.391	108.800	C(32)-C(31)-O(52)	124.864	107.700
C(7)-C(20)-C(19)	122.934	109.510	C(32)-C(31)-O(53)	127.933	107.700
C(7)-C(20)-N(41)	115.768	108.800	O(52)-C(31)-O(53)	107.204	97.000
C(19)-C(20)-N(41)	121.278	108.800	C(31)-C(32)-C(33)	132.285	109.510
C(22)-C(21)-O(45)	124.175	107.700	C(31)-C(32)-N(44)	115.350	108.800
C(22)-C(21)-O(46)	122.554	107.700	C(33)-C(32)-N(44)	112.365	108.800
O(45)-C(21)-O(46)	113.269	97.000	C(32)-C(33)-C(35)	129.823	109.500
C(21)-C(22)-C(23)	133.978	109.510	C(33)-C(35)-C(37)	118.759	109.500
C(21)-C(22)-N(43)	118.585	108.800	C(35)-C(37)-C(39)	107.768	109.500
C(23)-C(22)-N(43)	107.410	108.800	C(37)-C(39)-C(40)	113.766	109.510
C(22)-C(23)-C(25)	128.080	109.500	C(37)-C(39)-N(44)	133.721	108.800
C(23)-C(25)-C(27)	124.097	109.500	C(40)-C(39)-N(44)	112.512	108.800
C(25)-C(27)-C(29)	104.216	109.500	C(39)-C(40)-O(55)	112.810	107.700
C(27)-C(29)-C(30)	115.365	109.510	C(39)-C(40)-O(56)	111.934	107.700
C(27)-C(29)-N(43)	131.339	108.800	O(55)-C(40)-O(56)	135.255	97.000
C(30)-C(29)-N(43)	113.271	108.800	C(32)-N(44)-C(39)	117.550	107.700
C(29)-C(30)-O(47)	105.495	107.700	*	*	*
C(29)-C(30)-O(48)	117.998	107.700	*	*	*
O(47)-C(30)-O(48)	136.507	97.000	*	*	*
C(1)-N(41)-C(20)	122.500	107.700	*	*	*
C(1)-N(41)-Co(70)	131.185	*	*	*	*
C(20)-N(41)-Co(70)	106.296	.*	*	*	*

Table 1. Geometric parameters of[Co(pydc)(Phen)(H_2O)](pydcH_2) 4H_2O complex

c) Dihedral Angles (º)

Dihedral Angles (^{0})	Actual	Dihedral Angles (^{0})	Actual	Dihedral Angles (^{0})	Actual
N(41)-C(1)-C(3)-C(5)	-0.688	C(21)-C(22)-N(43)-C(29)	179.746	C(29)-N(43)-Co(70)-O(46)	179.206
C(3)-C(1)-N(41)-C(20)	-0.161	C(21)-C(22)-N(43)-Co(70)	-7.411	C(29)-N(43)-Co(70)-O(47)	-5.914
C(3)-C(1)-N(41)-Co(70)	178.011	C(23)-C(22)-N(43)-C(29)	-1.896	C(29)-N(43)-Co(70)-O(49)	81.996
C(1)-C(3)-C(5)-C(7)	1.043	C(23)-C(22)-N(43)-Co(70)	170.946	C(21)-O(46)-Co(70)-N(41)	176.421
C(3)-C(5)-C(7)-C(8)	177.566	C(22)-C(23)-C(25)-C(27)	1.036	C(21)-O(46)-Co(70)-N(42)	-95.791
C(3)-C(5)-C(7)-C(20)	-0.637	C(23)-C(25)-C(27)-C(29)	-1.442	C(21)-O(46)-Co(70)-N(43)	-4.194
C(5)-C(7)-C(8)-C(10)	-177.506	C(25)-C(27)-C(29)-C(30)	-177.566	C(21)-O(46)-Co(70)-O(47)	-13.889
C(20)-C(7)-C(8)-C(10)	0.837	C(25)-C(27)-C(29)-N(43)	0.471	C(21)-O(46)-Co(70)-O(49)	93.742
C(5)-C(7)-C(20)-C(19)	178.124	C(27)-C(29)-C(30)-O(47)	174.31	C(30)-O(47)-Co(70)-N(41)	-178.056
C(5)-C(7)-C(20)-N(41)	-0.266	C(27)-C(29)-C(30)-O(48)	-5.389	C(30)-O(47)-Co(70)-N(42)	95.166
C(8)-C(7)-C(20)-C(19)	-0.379	N(43)-C(29)-C(30)-O(47)	-4.086	C(30)-O(47)-Co(70)-N(43)	3.402
C(8)-C(7)-C(20)-N(41)	-178.77	N(43)-C(29)-C(30)-O(48)	176.215	C(30)-O(47)-Co(70)-O(46)	14.374
C(7)-C(8)-C(10)-C(12)	0.023	C(27)-C(29)-N(43)-C(22)	1.546	C(30)-O(47)-Co(70)-O(49)	-94.509
C(8)-C(10)-C(12)-C(13)	178.32	C(27)-C(29)-N(43)-Co(70)	-169.557	O(52)-C(31)-C(32)-C(33)	-1.845
C(8)-C(10)-C(12)-C(19)	-1.283	C(30)-C(29)-N(43)-C(22)	179.615	O(52)-C(31)-C(32)-N(44)	177.788
C(10)-C(12)-C(13)-C(15)	-179.205	C(30)-C(29)-N(43)-Co(70)	8.513	O(53)-C(31)-C(32)-C(33)	178.247
C(19)-C(12)-C(13)-C(15)	0.356	C(29)-C(30)-O(47)-Co(70)	-0.236	O(53)-C(31)-C(32)-N(44)	-2.119
C(10)-C(12)-C(19)-C(20)	1.734	O(48)-C(30)-O(47)-Co(70)	179.378	C(31)-C(32)-C(33)-C(35)	-179.601
C(10)-C(12)-C(19)-N(42)	-179.969	C(1)-N(41)-Co(70)-N(42)	177.897	N(44)-C(32)-C(33)-C(35)	0.757
C(13)-C(12)-C(19)-C(20)	-177.893	C(1)-N(41)-Co(70)-N(43)	-101.489	C(31)-C(32)-N(44)-C(39)	-179.407
C(13)-C(12)-C(19)-N(42)	0.405	C(1)-N(41)-Co(70)-O(46)	-96.208	C(33)-C(32)-N(44)-C(39)	0.3
C(12)-C(13)-C(15)-C(17)	-0.452	C(1)-N(41)-Co(70)-O(47)	89.627	C(32)-C(33)-C(35)-C(37)	-1.331
C(13)-C(15)-C(17)-N(42)	-0.124	C(1)-N(41)-Co(70)-O(49)	1.777	C(33)-C(35)-C(37)-C(39)	0.53
C(15)-C(17)-N(42)-C(19)	0.914	C(20)-N(41)-Co(70)-N(42)	-3.709	C(35)-C(37)-C(39)-C(40)	-178.946
C(15)-C(17)-N(42)-Co(70)	-179.454	C(20)-N(41)-Co(70)-N(43)	76.905	C(35)-C(37)-C(39)-N(44)	0.533
C(12)-C(19)-C(20)-C(7)	-0.994	C(20)-N(41)-Co(70)-O(46)	82.186	C(37)-C(39)-C(40)-O(55)	-179.137
C(12)-C(19)-C(20)-N(41)	177.31	C(20)-N(41)-Co(70)-O(47)	-91.979	C(37)-C(39)-C(40)-O(56)	1.05
N(42)-C(19)-C(20)-C(7)	-179.23	C(20)-N(41)-Co(70)-O(49)	-179.829	N(44)-C(39)-C(40)-O(55)	1.271
N(42)-C(19)-C(20)-N(41)	-0.926	C(17)-N(42)-Co(70)-N(41)	-176.344	N(44)-C(39)-C(40)-O(56)	-178.542
C(12)-C(19)-N(42)-C(17)	-0.952	C(17)-N(42)-Co(70)-N(43)	10.273	C(37)-C(39)-N(44)-C(32)	-1.098
C(12)-C(19)-N(42)-Co(70)	179.325	C(17)-N(42)-Co(70)-O(46)	100.403	C(40)-C(39)-N(44)-C(32)	178.386
C(20)-C(19)-N(42)-C(17)	177.451	C(17)-N(42)-Co(70)-O(47)	-51.938	*	*
C(20)-C(19)-N(42)-Co(70)	-2.271	C(17)-N(42)-Co(70)-O(49)	-153.227	*	*
C(7)-C(20)-N(41)-C(1)	0.634	C(19)-N(42)-Co(70)-N(41)	3.329	*	*
C(7)-C(20)-N(41)-Co(70)	-177.933	C(19)-N(42)-Co(70)-N(43)	-170.055	*	*
C(19)-C(20)-N(41)-C(1)	-177.785	C(19)-N(42)-Co(70)-O(46)	-79.925	*	*
C(19)-C(20)-N(41)-Co(70)	3.648	C(19)-N(42)-Co(70)-O(47)	127.735	*	*
O(45)-C(21)-C(22)-C(23)	7.247	C(19)-N(42)-Co(70)-O(49)	26.446	*	*
O(45)-C(21)-C(22)-N(43)	-174.931	C(22)-N(43)-Co(70)-N(41)	12.023	*	*

O(46)-C(21)-C(22)-C(23)	-173.166	C(22)-N(43)-Co(70)-N(42)	92.387	*	*
O(46)-C(21)-C(22)-N(43)	4.656	C(22)-N(43)-Co(70)-O(46)	6.782	*	*
C(22)-C(21)-O(46)-Co(70)	1.454	C(22)-N(43)-Co(70)-O(47)	-178.339	*	*
O(45)-C(21)-O(46)-Co(70)	-178.918	C(22)-N(43)-Co(70)-O(49)	-90.428	*	*
C(21)-C(22)-C(23)-C(25)	178.9	C(29)-N(43)-Co(70)-N(41)	-175.553	*	*
N(43)-C(22)-C(23)-C(25)	0.905	C(29)-N(43)-Co(70)-N(42)	-95.189	*	*

Table 2. Geometric parameters of Geometric parameters of [Co(pydc)(Phen)(H_2O)](pydcH_2) 4H_2O complex

a)

Atom	Bond atom	Bond Length	Angle Atom	First Angle	Third atom	Second Angle	Angle type
C(7)	-	-	-	-	-	-	-
C(20)	C(7)	1.417	-	-	-	-	-
C(19)	C(20)	1.627	C(7)	122.934	-	-	-
C(12)	C(19)	1.452	C(20)	125.184	C(7)	-0.994	Dihedral
N(41)	C(20)	1.401	C(7)	115.768	C(19)	121.278	Pro-R
C(5)	C(7)	1.582	C(20)	120.374	N(41)	-0.266	Dihedral
C(10)	C(12)	1.454	C(19)	110.627	C(20)	1.734	Dihedral
N(42)	C(19)	1.364	C(12)	115.403	C(20)	119.391	Pro-S
Co(70)	N(41)	2.136	C(20)	106.296	C(19)	3.648	Dihedral
C(1)	N(41)	1.499	C(20)	122.5	Co(70)	131.185	Pro-S
C(8)	C(7)	1.491	C(20)	110.743	C(5)	128.863	Pro-R
C(13)	C(12)	1.589	C(19)	122.137	C(10)	127.235	Pro-R
C(17)	N(42)	1.505	C(19)	121.039	Co(70)	133.385	Pro-S
N(43)	Co(70)	2.027	N(41)	173.296	N(42)	91.612	Pro-S
O(49)	Co(70)	2.328	N(41)	83.651	N(42)	170.137	Pro-R
C(3)	C(1)	1.418	N(41)	125.667	C(20)	-0.161	Dihedral
C(15)	C(13)	1.373	C(12)	122.167	C(19)	0.356	Dihedral
C(22)	N(43)	1.197	Co(70)	105.608	N(41)	12.023	Dihedral
O(46)	Co(70)	2.082	N(43)	90.253	N(41)	83.071	Pro-R
H(9)	C(8)	0.941	C(7)	111.975	C(10)	121.735	Pro-S
H(11)	C(10)	0.959	C(8)	123.867	C(12)	111.934	Pro-R
H(50)	O(49)	0.933	Co(70)	110.887	N(41)	-53.503	Dihedral
C(21)	C(22)	1.702	N(43)	118.585	Co(70)	-7.411	Dihedral
C(29)	N(43)	1.487	C(22)	124.82	Co(70)	129.116	Pro-R
O(47)	Co(70)	2.323	N(43)	62.219	O(46)	152.038	Pro-S
H(2)	C(1)	0.959	C(3)	111.296	N(41)	123.038	Pro-S
H(4)	C(3)	1.049	C(1)	123.245	C(5)	124.565	Pro-S
H(6)	C(5)	0.946	C(3)	113.331	C(7)	123.175	Pro-R
H(14)	C(13)	0.967	C(12)	124.949	C(15)	112.883	Pro-S
H(16)	C(15)	1.057	C(13)	122.75	C(17)	125.342	Pro-R
H(18)	C(17)	0.939	C(15)	111.306	N(42)	121.357	Pro-R
H(51)	O(49)	0.848	Co(70)	107.728	H(50)	127.899	Pro-R
C(23)	C(22)	1.334	N(43)	107.41	C(21)	133.978	Pro-S
C(27)	C(29)	1.359	N(43)	131.339	C(22)	1.546	Dihedral
O(45)	C(21)	1.138	C(22)	124.175	O(46)	113.269	Pro-R
C(25)	C(23)	1.548	C(22)	128.08	N(43)	0.905	Dihedral

C(30)	C(29)	1.32	N(43)	113.271	C(27)	115.365	Pro-S
O(48)	C(30)	1.388	C(29)	117.998	O(47)	136.507	Pro-R
H(24)	C(23)	0.835	C(22)	107.426	C(25)	124.494	Pro-S
H(26)	C(25)	0.901	C(23)	129.579	C(27)	106.324	Pro-R
H(28)	C(27)	1.039	C(25)	124.466	C(29)	131.317	Pro-S

Table 2. Geometric parameters of Geometric parameters of [Co(pydc)(Phen)(H_2O)](pydcH_2) 4H_2O complex

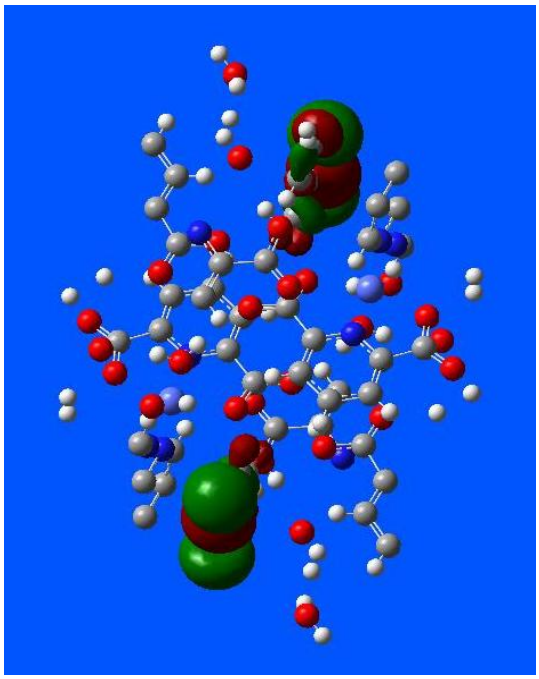
b)

Atom	Bond atom	Bond Length	Angle Atom	First Angle	Third atom	Second Angle	Angle type
C(37)	O(48)	5.762	C(30)	146.305	C(29)	-79.548	Dihedral
C(35)	C(37)	1.199	C(7)	80.885	C(5)	-108.071	Dihedral
C(33)	C(35)	1.514	C(37)	118.759	C(7)	-14.052	Dihedral
C(32)	C(33)	1.384	C(35)	129.823	C(37)	-1.331	Dihedral
C(39)	C(37)	1.409	C(35)	107.768	C(33)	0.53	Dihedral
H(36)	C(35)	0.94	C(33)	132.001	C(37)	109.239	Pro-R
N(44)	C(32)	1.15	C(33)	112.365	C(35)	0.757	Dihedral
H(34)	C(33)	0.807	C(32)	109.228	C(35)	120.949	Pro-R
H(38)	C(37)	1.018	C(35)	119.845	C(39)	132.387	Pro-S
C(31)	C(32)	1.659	C(33)	132.285	N(44)	115.35	Pro-S
C(40)	C(39)	1.287	C(37)	113.766	N(44)	112.512	Pro-R
O(53)	C(31)	1.284	C(32)	127.933	C(33)	178.247	Dihedral
O(56)	C(40)	1.44	C(39)	111.934	C(37)	1.05	Dihedral
O(52)	C(31)	1.066	C(32)	124.864	O(53)	107.204	Pro-S
O(55)	C(40)	1.235	C(39)	112.81	O(56)	135.255	Pro-S
H(54)	O(53)	0.672	C(31)	105.41	C(32)	-13.554	Dihedral
H(57)	O(56)	0.595	C(40)	103.327	C(39)	-176.679	Dihedral
O(58)	O(55)	13.647	C(40)	107.824	C(39)	-32.009	Dihedral
O(61)	O(55)	13.954	C(40)	68.485	C(39)	-38.436	Dihedral
O(64)	O(55)	7.541	C(40)	30.894	C(39)	-10.567	Dihedral
H(59)	O(58)	1.082	C(7)	97.066	C(5)	104.516	Dihedral
H(62)	O(61)	0.998	C(7)	129.689	C(5)	132.909	Dihedral
H(65)	O(64)	1.27	C(7)	39.214	C(5)	-121.752	Dihedral
H(60)	O(58)	0.922	H(59)	104.555	C(7)	-64.098	Dihedral
H(63)	O(61)	0.763	H(62)	109.602	C(7)	-153.672	Dihedral
H(66)	O(64)	1.492	H(65)	84.154	C(7)	110.555	Dihedral
O(67)	O(64)	10.9	H(65)	65.869	H(66)	83.878	Pro-R
H(68)	O(67)	0.911	C(7)	59.328	C(5)	-133.286	Dihedral
H(69)	O(67)	1.543	H(68)	97.335	C(7)	-11.285	Dihedral

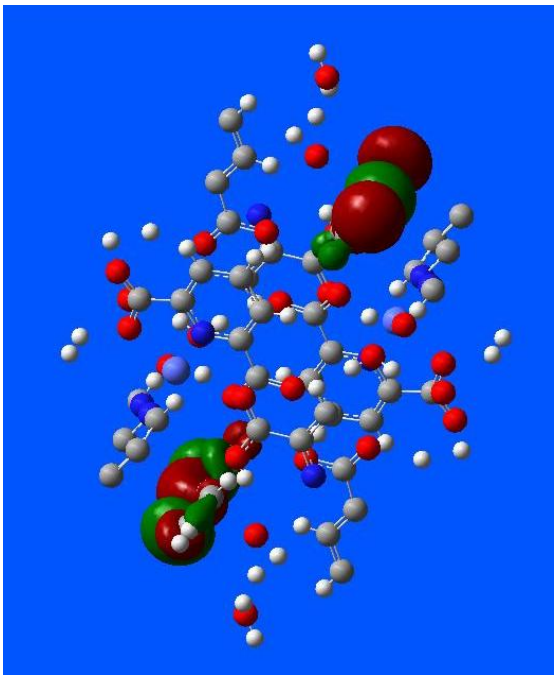
Pro-R: Atoms Positioned by Three Other Atoms
Pro-S: Atoms Positioned by Three Other Atoms
NOTE: The terms Pro-R and Pro-S used in Chem3D to position atoms bear no relation to the Cahn-Ingold-Prelog R/S specification of the absolute stereochemical configuration of a chiral atom. Pro-R and Pro-S refer only to the positioning of D and do not imply any stereochemistry for C. C may be chiral, or achiral.
To position Atom D in Pro-S Orientation (left) and Pro-R Orientation (right)
Dihedral:Showing Dihedral Angles

The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron the HOMO and LUMO energy calculated by DFT levels with the3-21G**basis set(Fig. 8. a, b).Transition from the ground to the first excited state and is mainly described byone-electron excitation from the HOMO to the LUMO. The LUMO of π nature, (i.e., heterocyclic ring) is delocalized over the whole C-C and C-N bond.

a) ***Bal l& Stick*** models

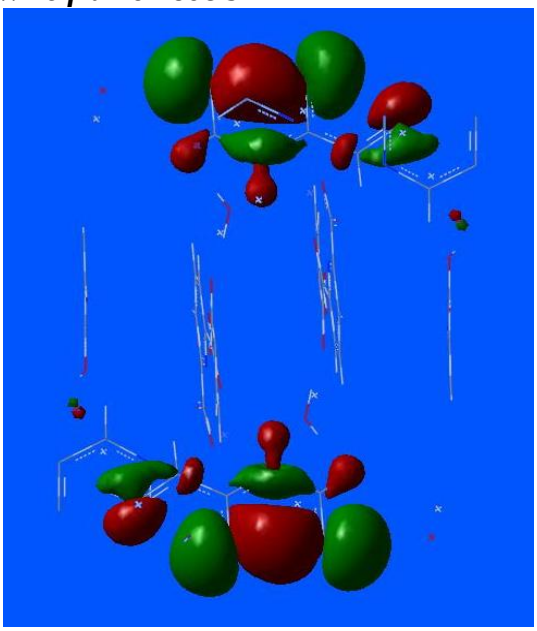


HOMO

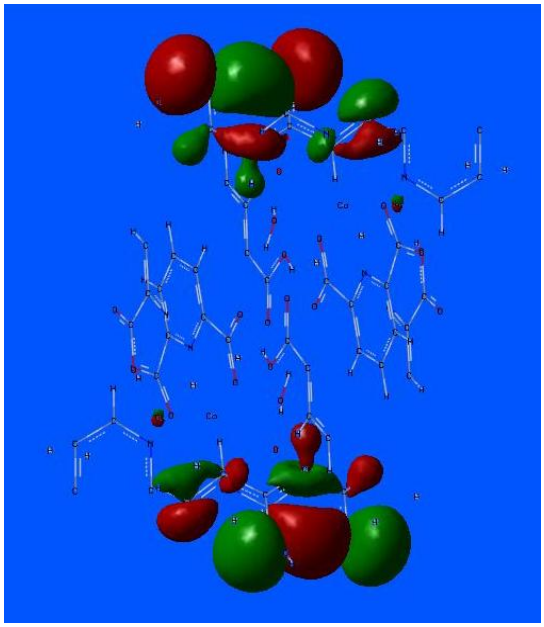


LUMO

b) ***Wire frame***models

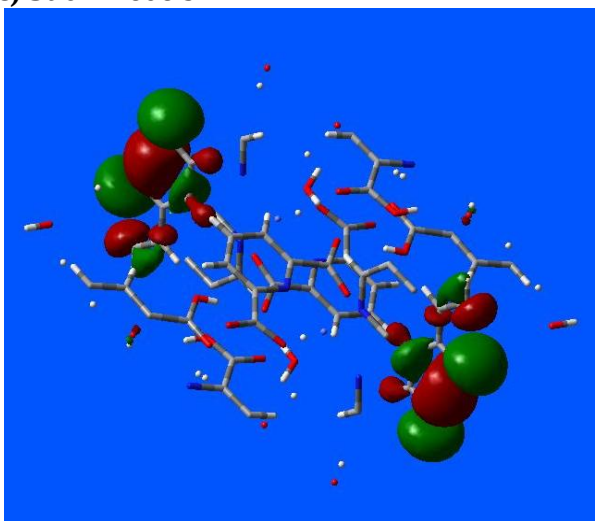


HOMO

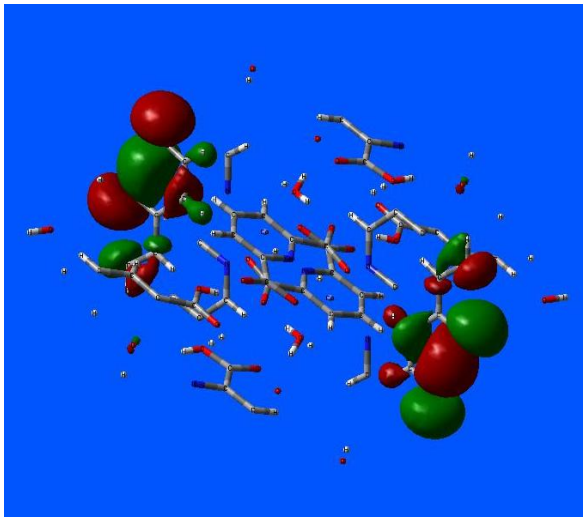


LUMO

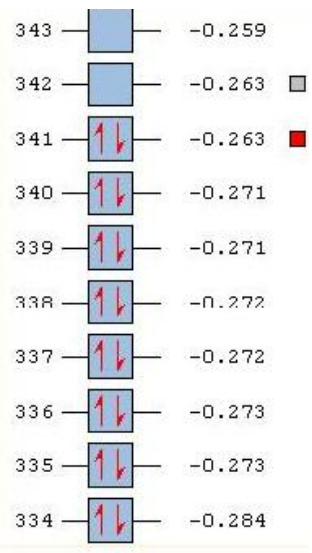
c) *Stick* models



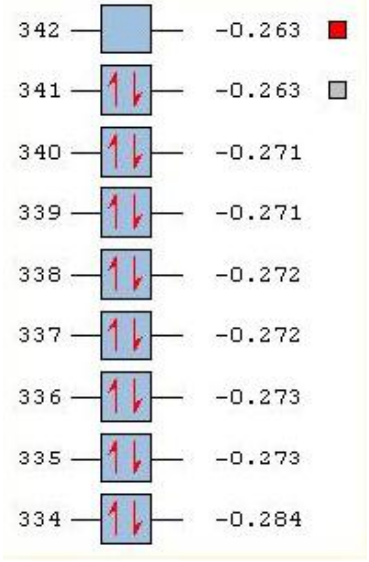
HOMO



LUMO



HOMO (DFT)
E_{HUMO} =-10.15781 a.u.
(Ground State)



LUMO (DFT)
E_{LUMO} =3.18794 a.u.
(Excited State)

ΔE = LOMO - HOMO (Energy gap) = 13.34575 a.u.

Fig. 8. The atomic orbital compositions of the frontier molecular orbital for [Co(pydc)(Phen)(H_2O)](pydcH_2) 4H_2O at the DFT/3-21G**, **a) *Ball & Stick*** models, **b) *Wire frame*** models, **c) *Stick*** models**.**

The HOMO-LUMO energy of the complex cobalt was calculated at the B3LYP/3-21G** leveland are shown in Figure 8-c, which reveals that the energy gap reflect the chemical activity of themolecule. LUMO as an electron

acceptor represents the ability to obtain an electron, HOMOrepresents the ability to donate an electron.

In general, the HOMO becomes less bound while the LUMO becomesmore boundfrom Figure8, it is concluded that the lowest energy gap was found at the DFTmethod. The atomic orbital compositions of the molecular orbitals are sketched in Figure8.

Complexstructureto form aproteinwithamino acidgroupsisshownin Figure 9.

Ribbons models show large protein molecules in a form that highlights secondary and tertiary structure. Ribbon models can be colored by group to help identify the amino acid constituents.

The Cartoon models, like Ribbon models, show large protein molecules in a form that highlights secondary and tertiary structure in Figure10.

CONCLUSIONS

The full geometrical optimization of complexCo(II) wasperformed using density functional theory at B3LYP/3-21G**level, without any symmetry restriction. The most possible packing structure belongs to *P*1 spacegroup. For the packing of complex Co(II), see (Figs. 11, 12).

To obtain an insight in the electronic structures andbonding properties of the complexCo(II), calculations using thedensity functional theory DFT method with the B3LYPfunctional of GAUSSIAN-03 were carried out. Before thecalculations, their geometries were optimized in singletstates using the DFT method B3LYP with the basis set 6-31G**. The lowering of the HOMO-LUMO energy gap value has substantial influence on theintramolecular charge transfer of the molecule.The bond order and atomiccharges of the title molecule have been studied by DFT method.

Fig. 9. ***Ribbons*** models show large protein molecules in a form that highlights secondary and tertiary structure. Ribbon models can be Colored by Group to help identify the amino acid constituents.

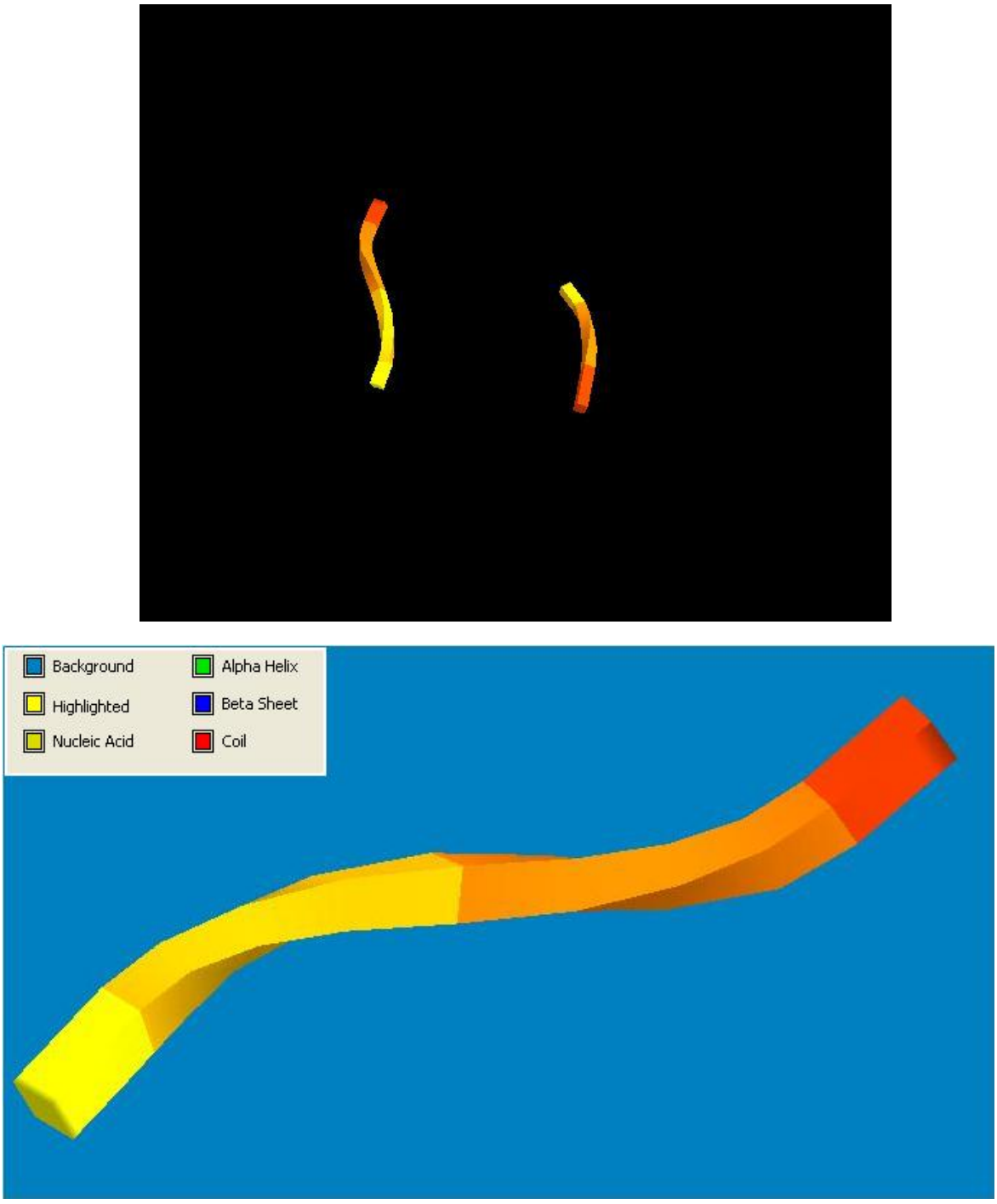


Fig. 10. ***Cartoon*** models, like Ribbon models, show large protein molecules in a form that highlights secondary and tertiary structure.

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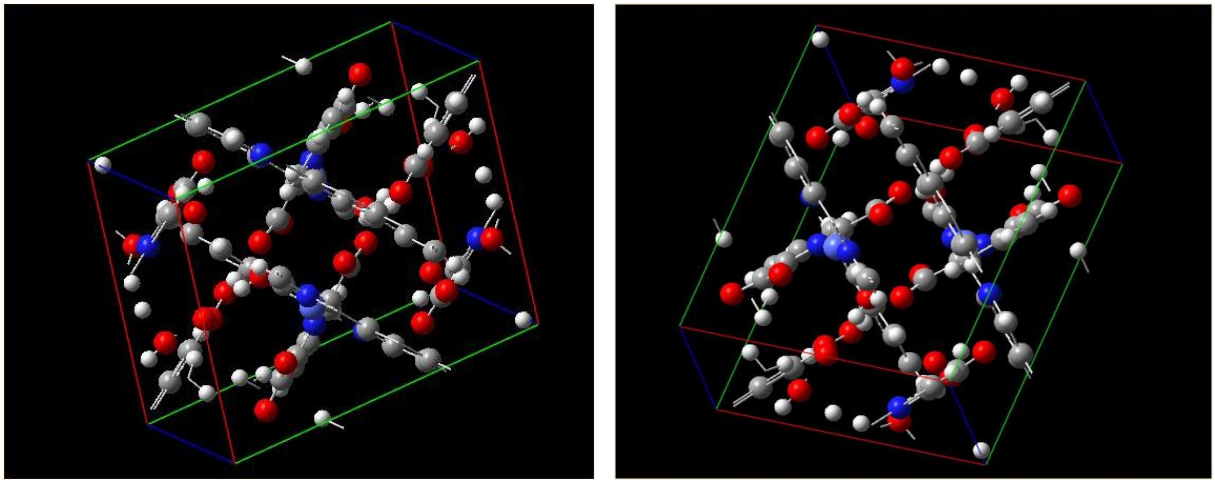

Fig. 11. Packing diagram of complex [Co(pydc)(Phen)(H_2O)](pydcH_2).4H_2O.

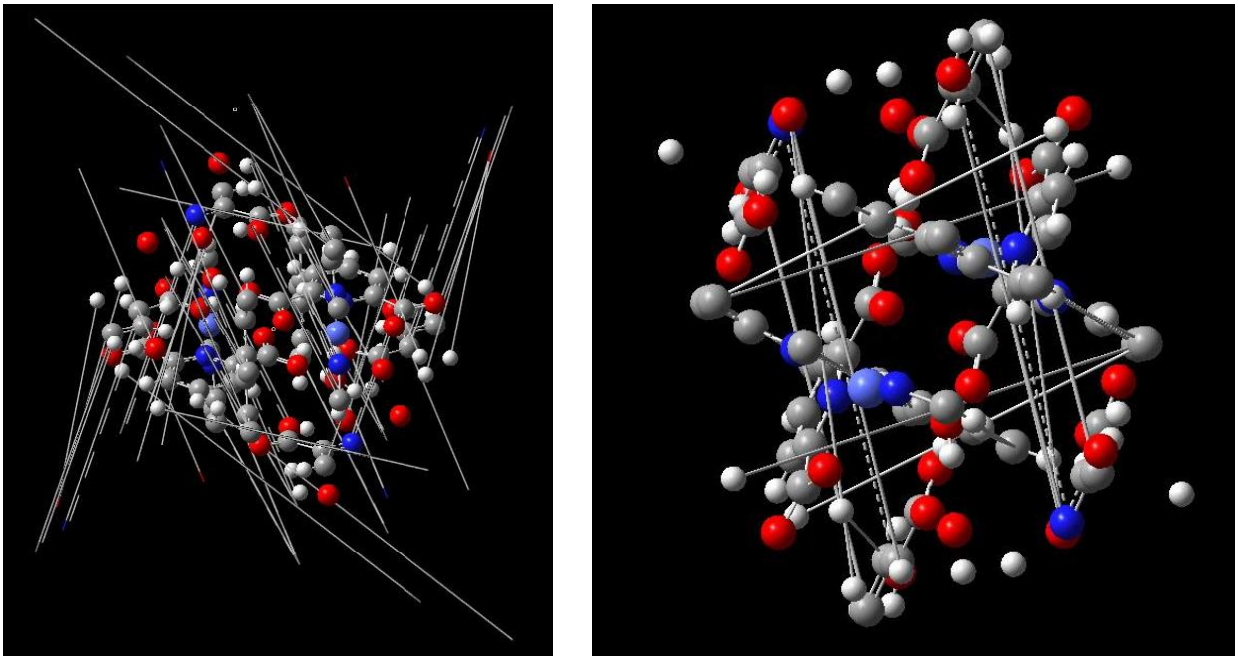

Fig. 12. Molecule structure of complex Co (II).

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