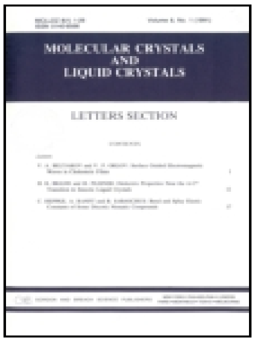

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Crystal structure and DFT computational studies on diaquabis(pyridine) cobalt(II) dichloride

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ABSTRACT
Single-crystal diffraction experiment was carried out using the high-resolution home diffractometer equipped with an area detector. Data sets were collected at room temperature (293 K) Mo K_α radiation ($\lambda = 0.71073$ Å). The molecule structure of Diaquabis(pyridine) cobalt(II) dichloride crystallizes in a space group *P-1* of triclinic system with cell parameters a = 6.1718(3) Å, b = 6.5395(3) Å, c = 8.5379(4) Å, á = 109.199(3)°, â = 102.822(3)°, $\gamma = 97.484(3)°$ and V = 309.49(3) $Å^3$. The molecular geometry were calculated using the density functional method (B3LYP) with 3-21G basis set. The calculated results show that the optimized geometry can well reproduce the crystal structure. The electric dipole moment (μ), the polarizability (α) and the first hyperpolarizability (β) were calculated using the density functional B3LYP method with the lanl2dz basis set. For the results, the title compound shows nonzero (β) value revealing second order NLO behavior.

KEYWORDS
X-ray; single crystal; organometallic; DFT; hyperpolarizability (β); NLO

1. Introduction

In the recent years many researches were established on the physical and chemical properties of the complexes organics witch present a great potential for photonic and the nonlinear optical (NLO) properties due to their high molecular transfer charge [1,2].

Considerable number of organometallic compounds have been studied for their potential applications in nonlinear optics, ferroelectric, superconductivity, magnetic and electrical properties [3–6]. Pyridine ligands have received considerable attention in the fields of coordination chemistry and molecular materials. This ligand is of interest due to his capacity to act towards metal atoms with various coordination modes and for their high degree of electronic [7–10].

In this paper, we present the results of the X-ray single-crystal diffraction and the molecular geometry calculation of the diaquabis(pyridine) cobalt(II) dichloride [$C_{10}H_{14}Cl_2Co_1N_2O_2$] compound. This compound crystallizes in a space group *P-1* of triclinic system with cell

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CCDC 951979 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk

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parameters a = 6.1718(3) Å, b = 6.5395(3) Å, c = 8.5379(4) Å, á = 109.199(3)°, â = 102.822(3)°, γ = 97.484(3)° and V = 309.49(3) Å^3. Using the density functional method (B3LYP) with 3-21G basis set the molecular geometry is calculated. The calculated results were a good agreement with the results obtained from crystal structure.

2. Experiments

2.1. Preparation

The title compound [$CoCl_2(C_5H_7NO)_2$, $2H_2O$] was obtained from an acetonitrile solution of the $CoCl_2$ (0.23793g,1mmol) and the pyridine ligand (160μl ; 2mmol) was refluxed for 1h at room temperature. The blue crystals suitable for X-ray analysis were precipitated and washed in water.

X-ray

Single-crystal diffraction experiment was carried out using the high-resolution home diffractometer equipped with an area detector. Data sets were collected at room temperature (293 K) Mo K_α radiation (λ = 0.71073 Å). The compound crystallizes in a space group *P-1* of triclinic system with cell parameters respectively: a = 6.1718(3) Å, b = 6.5395(3) Å, c = 8.5379(4) Å, á = 109.199(3)°, â = 102.822(3)°, γ = 97.484(3)° and V = 309.49(3) Å^3,. The crystal structure was solved by direct methods using SIR92 (WINGX) [11] and refined by a full matrix least-square method using SHELXL97 [12]. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located by Fourier difference map and refined with isotropic thermal parameters. Details of the collected parameters, crystallographic data and final agreement factors are presented in the Table 1. All hydrogen bonds are listed in Tables 1.

2.2. Computational methods

Theoretical calculations were performed with the Gaussian 09 program [13]. The complex was optimized using the hybrid density functional B3LYP method (Becke's three-parameter nonlocal exchange functional [14] and the correlation functional of Lee et al [15] with the lanl2dz basis set. Stationary points have been positively identified for local minima (with the number imaginary frequencies NIMAG = 0). Vibrational band assignments were made using the Gauss-View molecular visualization program [16]. The optimized geometric parameters (bond lengths and angles) of the title compound have been calculated using B3LYP/lanl2dz method. Theoretical and experimental geometric parameters are listed in Table 2.

3. Results and discussion

3.1. Structures and crystal packing

The asymmetric unit of Diaquabis(pyridine) cobalt(II) chloride compound (see Figure 1) consists one Co metal located on inversion center, bonded at two pyridine ligands and coordinated by two water molecules and two chloride atoms.

Table 1. Crystal data and structure refinement for Diaquabis(pyridine) cobalt(II) chloride.

$C_5H_7ClCoNO$
$M_r = 162.03$
Triclinic, P-1
$a = 6.1718$ (3) Å
$b = 6.5395$ (3) Å
$c = 8.5379$ (4) Å
$\alpha = 109.199$ (3)°
$\beta = 102.822$ (3)°
$\gamma = 97.484$ (3)°
$V = 309.49$ (3) Å^3

$Z = 2$
$F(000) = 165$
$D_x = 1.739$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1741 reflections
$\theta = 2.6$–$25.0°$
$\mu = 1.81$ mm^{-1}
$T = 293$ K
Prism, white
0.1 × 0.1 × 0.1 mm

Data collection
APEXII, Bruker-AXS diffractometer
Radiation source: Enraf Nonius FR590
Graphite monochromator
CCD rotation images, thick slices scans
2758 measured reflections
1093 independent reflections

1038 reflections with $I > 2\sigma(I)$
$R_{int} = 0.015$
$\theta_{max} = 25.0°, \theta_{min} = 2.6°$
$h = -7 \rightarrow 7$
$k = -7 \rightarrow 7$
$l = -10 \rightarrow 10$

Refinement
Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.043$
$S = 1.10$
1093 reflections
87 parameters
0 restraints

Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.P)^2 + 0.3101P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

The projection of the structure on the plan (a,c) (see Fig. 2)shows that this one is formed by chains along the direction b. These chains are constituted by the pyridine ligands. The cohesion and the stability of the structure are insured by a three-dimensional network of hydrogen bonding interactions O–H …Cl.

Table 2. Selected molecular structure parameters.

Parameters	Experimental	B3LYP/ lanl2dz
Bond lengths (A°)		
C1-C2	1.380	1.402
C2-C3	1.377	1.406
C3-C4	1.383	1.406
C4-C5	1.383	1.402
Cl1-Co1	2.508	2.454
N1-Co1	2.126	1.998
O1W-Co1	2.108	2.239
Bond angles (°)		
C-C-C	118,9°	119.11°
C-Cl-O	91.26°	81.00°
Cl-Co-N	90.29°	91.29°
N-Co-O	92.62°	91.78°
C3-C4-C5	119.0°	119.26°
C2-C3-C4	118.5°	118.55°
C1-C2-C3	119.2°	119.26°

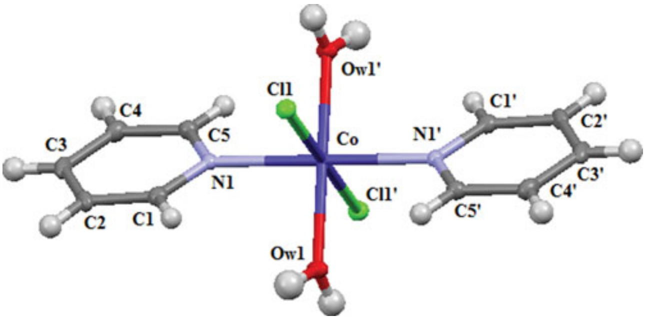

Figure 1. Molecule structure of Diaquabis(pyridine) cobalt(II) chloride compound.

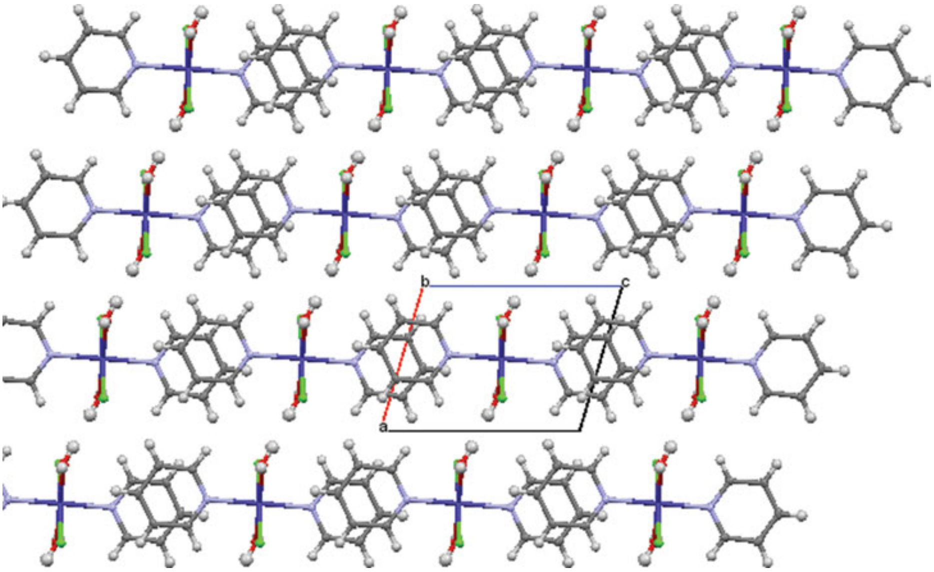

Figure 2. Packing diagram of the structure along the b axis.

The environment of the atom of cobalt is a octahedral defined by two N donor atoms of the pyridine ligand with the length of Co–N bond of 2.126 Å, O atoms of two water molecules with the length of Co–Ow bond of 2.108 Å and two Cl atoms on length bond of 2.508 Å.

The environment octahedral of the atom of Co ($CoN_2O_2Cl_2$) develops in chain following a and c at ½ of a and ½ of c (see Fig. 3).

The both pyridine ligands possesses a plane geometry situated in the same plane are substituted in N1. The lengths of C–C and C-N bonds of the pyridine ligands is comparable to the results found in the literature [17–20] with an average distance respectively of C–C and C-N bonds of 1.381 Å and 1.341 Å.

The crystal packing of studied compound is stabilized by a complex hydrogen bonding network involving the coordinating water molecules as donors to the Cl acceptors atoms of the chloride atoms forming four medium-strength interactions (Table 3). These hydrogen bonds arrange the complex molecules into layers parallel to the c axis (fig 4).

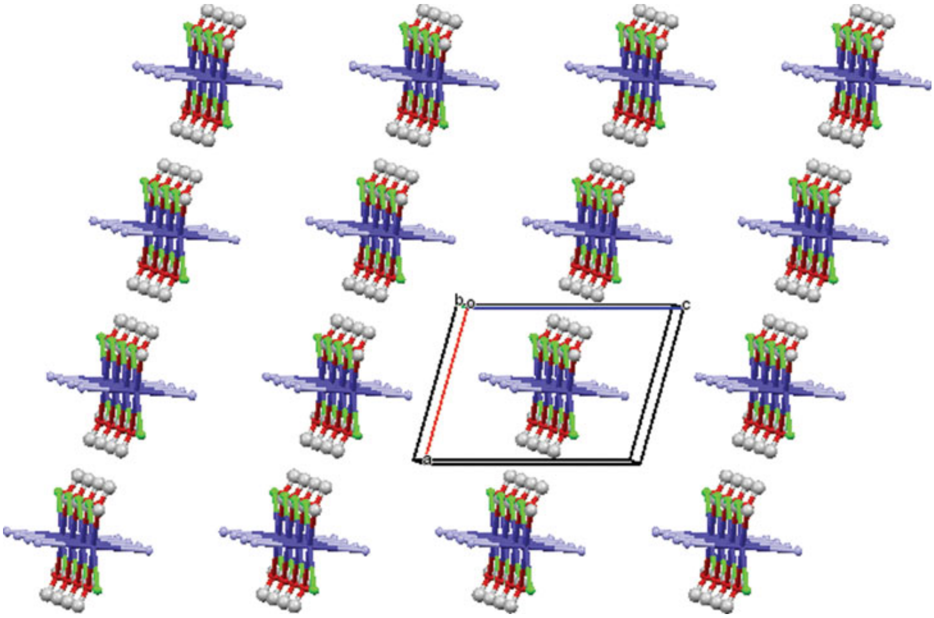

Figure 3. Packing diagram the environment of the atom of cobalt.

Table 3. The calculated average polarizability $\propto_{tot}$ $(A^{\circ 3})$.

Molecule	$\propto_{xx}$(ua)	$\propto_{yy}$(ua)	$\propto_{zz}$ (ua)	$\langle \propto \rangle$ $(A^{\circ 3})$
$[(C_5H_7NO)_2\ CoCl_2,\ H_2O]$	155.580	114.985	234.920	24,937

3.2. *Optimized structure*

From Table 2, we can see that the optimized bond lengths are slightly longer than the experimental values and the bond angles are slightly different from the experimental ones. In general, all the calculated parameters are in good agreement with the reported experimental data. The biggest difference of bond lengths between the experimental and the calculated values is found at O1W-Co1 bond, with the different value being 0.131A° for lanl2dz. For the bond angles, the biggest difference occur at C–Cl–O bond angle, with the different value being 10.26 °. It can be noted that the experimental results are for the solid phase and the theoretical calculations are for the gas phase.

3.3. *Polarizability and hyperpolarizability*

Dipole polarizabilities calculated at the B3LYP/3-21G level of theory are shown in Table 3.

In this work, molecular polarizability (α) is calculated using DFT at B3LYP/3-21G.

The calculated total dipole moments and polarizability are equal to 3,065 Debye and 24,937$A^{\circ 3}$ respectively. The electric dipole moment μ_e of a molecule is a quantity of fundamental importance in structural chemistry. When a molecule is subject to an external electric field E, the molecular charge density may rearrange and hence the dipole moment may change. This change can be described by the tensor Eq. (1)

$$\mu_{tot} = \mu_0 + \propto_{ij} E_j + \beta_{ijk} E_j E_k \tag{1}$$

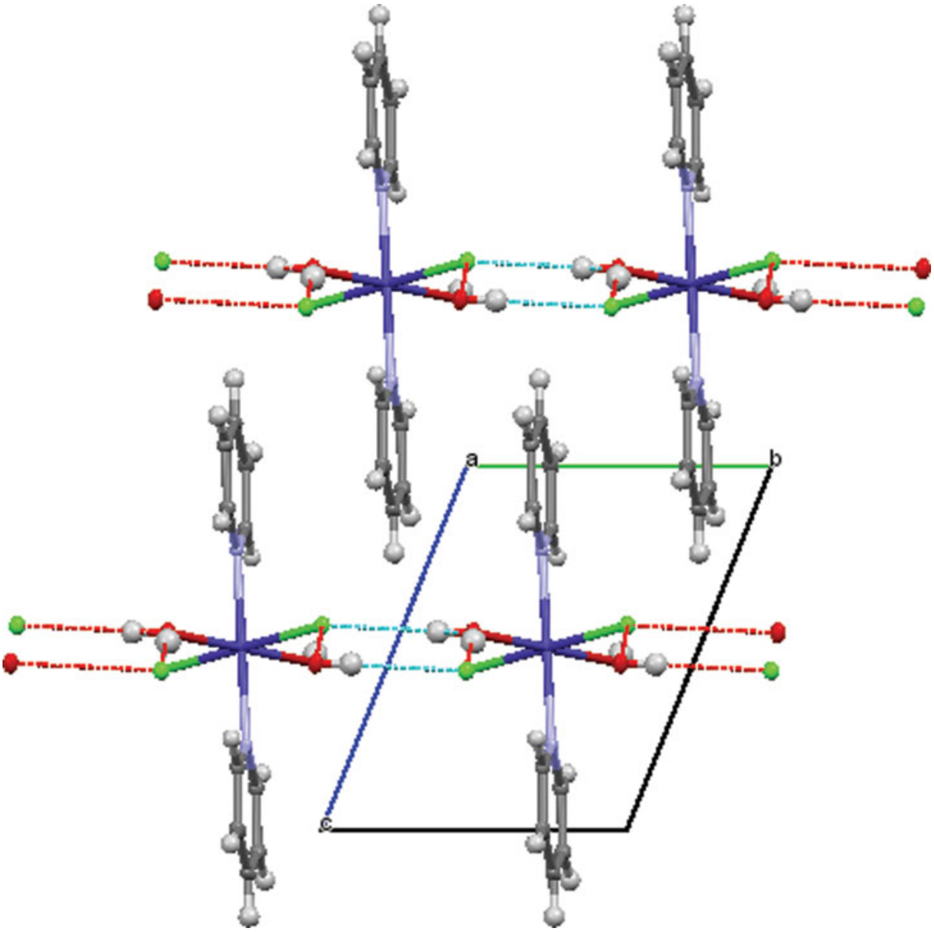

Figure 4. The three-dimensional packing of Diaquabis(pyridine) cobalt(II) chloride viewed down the a axis.

Where $\boldsymbol{\mu}_0$ is the dipole in the absence of a field and $\boldsymbol{\mu}_{tot}$ is the dipole moment in the presence of the field. $\propto_{\mathbf{ij}}$ is the dipole polarizability tensor, $\boldsymbol{\beta}_{\mathbf{ijk}}$ define the first hyperpolarizability tensor components.

The average static polarizability $<\propto_{\mathbf{ij}}>$ tensor is defined, in terms of cartesian components as:

$$\propto_{\mathrm{ij}} = \frac{\propto_{\mathrm{xx}} + \propto_{\mathrm{yy}} + \propto_{zz}}{3} \tag{2}$$

First hyperpolarizability is a third rank tensor that can be described by a 3 × 3 × 3 matrix. The 27 Components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry. ($\beta_{xyy=}\beta_{yxy=}\beta_{yyx,}\ \beta_{yyz} = \beta_{yzy} = \beta_{zyy}, \ldots$.ikewise other permutations also take same value).

The output from Gaussian 09 provides 10 components of this matrix as β_{xxx}, β_{xxy}, β_{xyy}, β_{yyy}, β_{xxz}, β_{xyz}, $\beta_{yyz}\beta_{xzz}$, β_{yzz}, β_{zzz}, respectively.

The components of β can be calculated using the following equation:

$$\beta_i = \beta_{iii} + \frac{1}{3}\sum_{i \neq j}(\beta_{ijj} + \beta_{jij} + \beta_{jji}).$$

Table 4. All β components and β_{tot} calculated using B3LYP for [(C5H7NO)$_2$ CoCl$_2$,H$_2$O].

Complex	Hyperpolarizability	
[(C$_5$H$_7$NO)$_2$ CoCl$_2$]	β_{xxx}	0.7173742
	β_{xxy}	− 0.0183112
	β_{xyy}	11.872
	β_{yyy}	2308
	β_{xxz}	0.0286649
	β_{xyz}	0.010822
	β_{yyz}	− 2.7984977
	β_{xzz}	− 0.0040349
	β_{yzz}	− 79.4962344
	β_{zzz}	− 0.0642012
	$\beta_{tot} \times 10^{30}$(esu)	193,59

Using the x, y and z components of β, the magnitude of the first hyperpolarizability tensor can be calculated.

$$\beta = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

The complete equation for calculating the magnitude of b from GAUSSIAN09 output is given as follows.

$$\beta_{tot} = \left[\left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz}\right)^2 + \left(\beta_{yyy} + \beta_{yzz} + \beta_{yxx}\right)^2 + \left(\beta_{zzz} + \beta_{zxx} + \beta_{zyy}\right)^2\right]^{1/2}.$$

The values of the first hyperpolarizability tensors of the output file of Gaussian09 are reported in atomic units (a.u.), the calculated values were converted into electrostatic units (1 a.u. = 8.6393×10^{-33} esu).

All the β components and the final β_{tot} values calculated using GAUSSIAN09, for the molecules under investigation are given in Table 4.

3.4. *Effect of HOMO–LUMO energies*

The DFT calculated HOMO–LUMO gaps at B3LYP/ lanl2dz level of theory for Diaquabis (pyridine) cobalt (II) dichloride is show in Table 5.

The electronic absorption corresponds to the transition from the ground to the first excited state and is mainly described by one electron excitation from HOMO to LUMO. The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron. Both HOMO and LUMO are the main orbitals that take part in chemical stability [21]. The eigenvalues of LUMO and HOMO and their energy gap reflect the chemical activity of the molecule. To understand this phenomenon in the context of molecular orbital theory, we examined the molecular HOMOs and molecular LUMOs of the title compound and showed in Fig. 5

The HOMO–LUMO energy gaps were calculated as 4,161 eV.

Table 5. B3LYP/ 3-21G energy gap calculated for [(C5H7NO)$_2$ CoCl$_2$,H$_2$O].

Molecule	HOMO (au)	LUMO (au)	E_{gap} *(eV)*
[(C$_5$H$_7$NO)$_2$CoCl$_2$,H$_2$O]	−0,21869	−0,06577	4,161

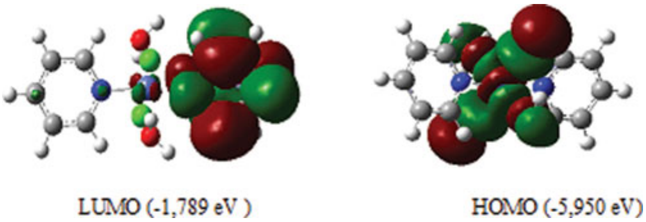

Figure. 5 HOMO and LUMO of the complex.

4. Conclusions

In this work, we presented the results on the calculation and single crystal of a new complexes organomettallic compound. The crystals of studied compound were obtained from reflux of solution aqueous and characterised by single crystal X-ray diffraction at 298 K. This compound crystallizes in *P-1* space group of triclinic system. The structure is formed by chains formed by the ligands pyridine. The cohesion and the stability of the structure are insured by a three-dimensional network of two different kinds of hydrogen bonding interactions O−H …Cl.

The molecular geometry were calculated using the density functional method (B3LYP) with 3-21G basis set. The calculated results show that the optimized geometry can well reproduce the crystal structure. The electric dipole moment (μ), the polarizability (α) and the first hyperpolarizability (β) were calculated using the density functional B3LYP method with the lanl2dz basis set

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