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SYNTHESIS AND CHARACTERIZATION OF COMPOUND PMPA USING NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY AND OPTIMIZED MOLECULAR STRUCTURES CALCULATED USING THE DFT/B3LYP METHOD WITH THE 3-21G** BASIS SET COMBINED WITH THE Co^{II} COMPLEX

^{1,4}Mohammad Mahdi Akbarzadeh, ²Khirollah Mehrani,
³Shahriar Ghammamy, ⁴Vahideh Hadigheh Rezvan

1Building Chemical Engineering, Tehran – Iran

2Islamic Azad University – Iran

3Imam Khomainsi International University – Iran

4Ardabil Branch, Islamic Azad University – Iran

Abstract. In this study, the Schiff base complex of Co^{II} derived from reaction between Benzene-1,2-diamine, Acetophenone, and 1*H*-Pyrrole-2-carbaldehyde have been synthesized. All the complexes have been characterized on the basis of elemental analysis and spectral studies. All the complexes are light in color and stable to atmosphere. Elemental analysis shows ML₂ stoichiometry for the complex. IR spectral data indicates coordination through NH pyrrole and azomethine nitrogen groups. Electronic spectral data suggests a polymeric octahedral structure for the Co^{II} complex. The structural characterization of Schiff base and cobalt complexes were carried out on the basis of their melting point, solubility, elemental analyses, conductivity measurements, FT-IR, ¹H NMR, ¹³C NMR, DEPT 90, and HETCOR spectroscopy studies. Molecular geometries, vibrational frequencies, and NMR frequencies of the title compounds in the ground state are calculated using the Hartree-Fock (HF) and density functional theories (DFT/B3LYP), and GIAO methods with the 3-21G** basis set and compared with the experimental data. The calculated results show that the optimized geometries can reproduce the crystal structural parameters, and the theoretical vibrational frequencies show good agreement with the experimental values. The calculated Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) energies show that charge transfer occurs within the molecule. The geometries and normal modes of vibrations obtained from DFT/3-21G** calculations are in good agreement with the experimentally observed data.

Keywords: 1*H*-Pyrrole-2-carbaldehyde, HETCOR, DEPT 90, DFT/B3LYP, ¹³C-¹³C COSY

Introduction

The compounds containing azomethine ($-C=N-$) group are known as Schiff bases, are formed by condensation of primary amines with carbonyl compounds such as aldehydes or ketones (Royer et al., 2005). Schiff bases are characterized by the $-N=CH-$ (imine) group, which is important in elucidating the mechanism of transamination and racemization reactions in biological systems (Jaeger et al., 1979). Literature review shows that Schiff bases show bacteriostatic and bactericidal activities (Tarafder et al., 2000; Sakiyan et al., 2004). Antibacterial, antifungal, antitumor, and anticancer activities have been reported in a number of studies, and are active against a wide range of organisms (*e.g.*, *C. albicans*, *E. coli*, *S. aureus*, *B. polymyxa*, and *P. viticola* etc.) (Aiad & Negm, 2009a; 2009b; Chohan et al., 2010). Schiff based reagents are becoming increasingly important in the pharmaceutical, dye (Aksuner et al., 2009) and plastic industries (Gupta et al., 2006), as well as for Liquid Crystal Display technology and mechanistic investigations of drugs used in pharmacology, biochemistry, and physiology (Pardridge, 2009; Fricker, 2006; Chen & Rhodes, 1996). However, despite extensive scientific reports on synthesis, characterization, and crystalline structure of the transition metal-salen complexes, few reports have been published on the use of salen molecules as ionophores in ion-selective studies (Sadeghi et al., 2006; Fatibello-Filho et al., 2007).

A series of transition metal ions form complexes with schiff bases (Gupta & Sutar, 2008; Cozzi, 2004; Chohan et al., 2001), aromatic hydrazones (Sridhar et al., 2001; 2002; Pouralimardan et al., 2007) like *o*-hydroxy 5-methyl salicylidinehydrazone, 2-hydroxy-4-methylacetophenone phenyl hydrazine, *o*-hydroxy 5-methyl acetophenone phenyl hydrazone, *o*-hydroxy 4-methoxysalicylidine phenyl hydrazone, *o*-hydroxy 5-methyl salicylidine phenyl hydrazine (Karabatsos & Taller, 1963; Garcia-Herbosa et al., 1994; Metwally et al., 2012; Sacconi, 1954) hydroxamic acid (Gibson & Magrath, 1969) and α -mercapto-2-amino phenyl acetohydroxamic acid (Rudzka et al., 2005; Gould et al., 1978; Puerta & Cohen, 2002).

In this paper, we have synthesized (N^1Z, N^2Z)- N^1 -((1H-Pyrrol-2-yl)methyl-en)- N^2 -(1-phenylethylidene)ethane-1,2-diamine (PMPA) chelating agent and used to synthesize metal chelates with Co^{II} transition metal (Fig. 1). These metal chelates were characterized by analytical, thermal, infrared and 1H NMR, ^{13}C NMR, DEPT 90, and HETCOR spectroscopy.

Herein, we report the synthesis and molecular structure of LM type of $[Co(C_{19}H_{17}N_3)_2]Cl_2$.

To the best of our knowledge, no theoretical Hartree-Fock (HF) or Density Functional Theory (DFT) calculations or detailed Vibrational infrared (IR) and NMR analyses have been performed on the molecule structure.

DFT calculations are known to provide excellent vibrational wave numbers scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies and anharmonicity effects (Scott & Radom, 1996;

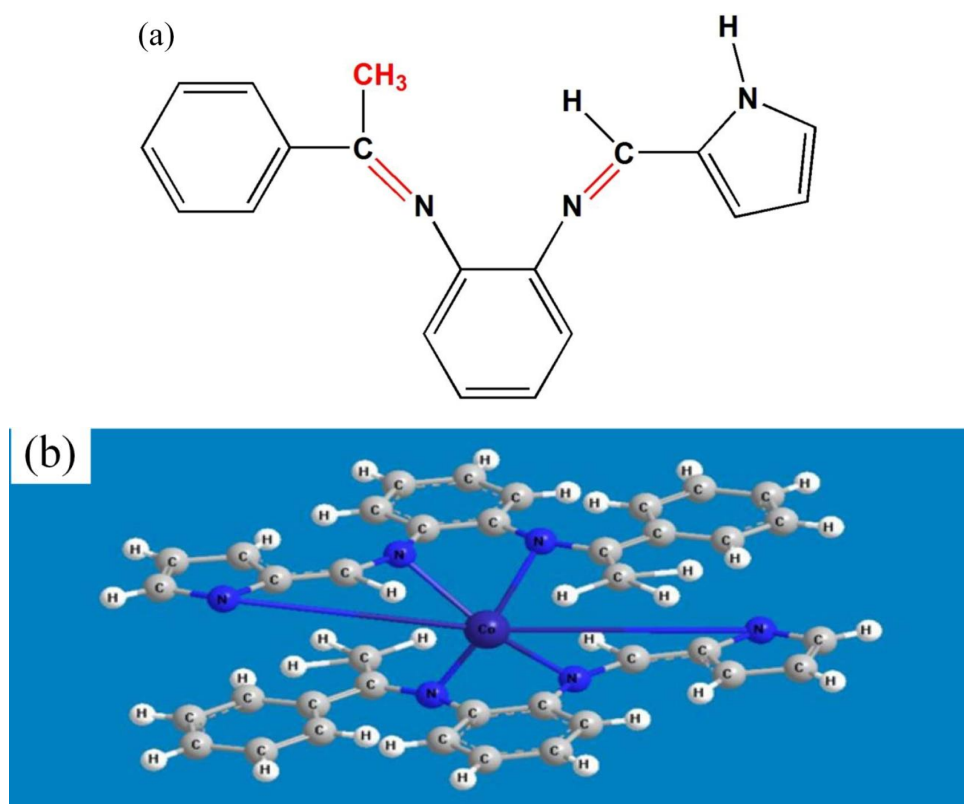


Fig. 1. Chemical structure of compound: (a) (N1Z, N2Z)-N1-((1H-Pyrrol-2-yl)methylen)-N2-(1-phenylethylidene)ethane-1,2-diamine; (b) Ball & Stick models and system adopted in the theoretical study (Nakano et al., 1983; Masonjones et al., 2014) for complex $[\text{Co}(\text{C}_{19}\text{H}_{17}\text{N}_3)_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ at DFT/3-21G** level.

Stephens et al., 1994; Sinha et al., 2004; Halls et al., 2001; Kim & Jordan, 1994). DFT is the best method compared to the ab initio method for computation of molecular structure, vibrational wave number, and energies of molecules (Mole et al., 1996; Eichkorn et al., 1997). In this work, by using the DFT/B3LYP and GIAO methods (Aliev et al., 2009; Cimino et al., 2004; Dybiec & Gryff-Keller, 2009), we calculated the vibrational and ^1H , ^{13}C , ^{15}N NMR wave numbers of (N¹Z, N²Z)-N¹-((1H-Pyrrol-2-yl)methylen)-N²-(1-phenylethylidene)ethane-1,2-diamine and molecular geometric parameters. These calculations are available for providing insight into vibrational spectra and molecular parameters.

Calculations were carried out using the GAMESS program (Bode & Gordon, 1998). The images of the structures and Molecular Orbitals (MOs) were obtained using the MOLDEN program (Schaftenaar & Noordik, 2000).

HOMO represents the ability to donate an electron. On the other hand, LUMO as an electron acceptor, represents the ability to obtain an electron. The HOMO and LUMO energies are calculated by the DFT at 3-21G** method (Scuseria, 1999; Zandler & D'Souza, 2006; Zhang & Musgrave, 2007).

Experimental

Materials and methods

All reagents and solvents employed were commercially available and used as received without further purification. The FT-IR spectra were recorded from KBr pellets in the range of 4000 - 400 cm^{-1} on a NEXUS 670 spectrometer. The ^1H and ^{13}C NMR, DEPT 90 and HETCOR spectra were measured on an Avance-300 Bruker instrument (300 MHz) in CDCl_3/TMS . The C and H microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer.

Computational method

A careful examination of the structures, computed using different ab initio and DFT methods pointed out that the B3LYP method in conjunction with the 3-21G** basis set, was an efficient level for performing geometry optimization. Therefore, all the molecular structures were optimized with the DFT (B3LYP) levels at the 3-21G** basis set (Fig. 2; Table 1). Vibrational frequencies for the optimized molecular structures of the title compounds were calculated using the DFT/B3LYP method with the 3-21G** basis set and compared with experimental data (Fig. 3; Table 2).

Table 1. Spectra ^{13}C NMR compound PMPA

Entry	Calculated (ppm)				Experimental (ppm)			
¹³ C NMR	CH ₃	CH ₂	CH	C	CH ₃	CH ₂	CH	C
C _{2B}	22	-	-	-	42.187	-	-	-
C _{3D}	-	-	108	-	-	-	110.089	-
C _{2D}	-	-	111.8	-	-	-	110.49	-
C _{4D}	-	-	118.3	-	-	-	114.214	-
C _{2C}	-	-	123.6	-	-	-	115.48	-

C _{5C}	-	-	123.6	-	-	-	116.527	-
C _{3C}	-	-	128.6s	-	-	-	116.795	-
C _{4C}	-	-	128.6	-	-	-	117.584	-
C _{3A}	-	-	128.9	-	-	-	118.79	-
C _{5A}	-	-	128.9	-	-	-	120.307	-
C _{2A}	-	-	129.2	-	-	-	123.281	-
C _{6A}	-	-	129.2	-	-	-	126.885	-
C _{4A}	-	-	131	-	-	-	128.354	-
C _{1D}	-	-	-	132.7	-	-	-	131.06
C _{1A}	-	-	-	134	-	-	-	134.708
C _{1C}	-	-	-	140	-	-	-	137.523
C _{6C}	-	-	-	144	-	-	-	141.432
C _{1B}	-	-	-	165	-	-	-	146
C _{5D}	-	-	151	-	-	-	148.323	-

Table 2. Theoretically computed energies (a.u.), zero-point vibrational energies (kcal mol⁻¹), rotational constants (GHz), entropies (cal mol⁻¹ K⁻¹) (Boyer, 1970) for compound PMPA at the B3LYP/3-21G**

Entry	Ea (Thermal)	CVb	Sc
	kcal mol ⁻¹	cal mol ⁻¹ K ⁻¹	cal mol ⁻¹ K ⁻¹
Total	205.053	73.327	137.718
Translational	0.889	2.981	42.862
Rotational	0.889	2.981	34.722

Zero-point correction	0.308687 (Hartree/Particle)
Thermal correction to Energy	0.326772
Thermal correction to Enthalpy	0.327717
Thermal correction to Gibbs Free Energy	0.262283
Sum of electronic and zero-point Energies	0.609596
Sum of electronic and thermal Energies	0.627681
Sum of electronic and thermal Enthalpies	0.628625
Sum of electronic and thermal Free Energies	0.563191

^aEnergy; ^bConstant Vibration; ^cStandard.

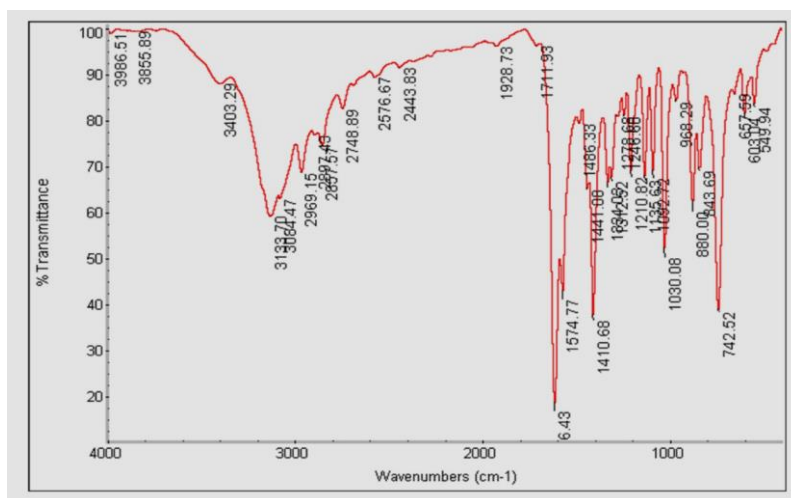


Fig. 2. FT-IR spectrum in (KBr) disk of compound PMPA in the range of 4000-400 cm^{-1} on a NEXUS 670 spectrometer

In addition, NMR frequencies for the optimized molecular structures of the title compounds were calculated using the DFT/B3LYP methods with the 3-21G**(6D, 7F) standard basis set, and compared with the experimental data (Xing et al., 2008; Han et al., 2009). All calculations were performed using the Gaussian 03 program package on a Windows 7 Ultimate Operating system.

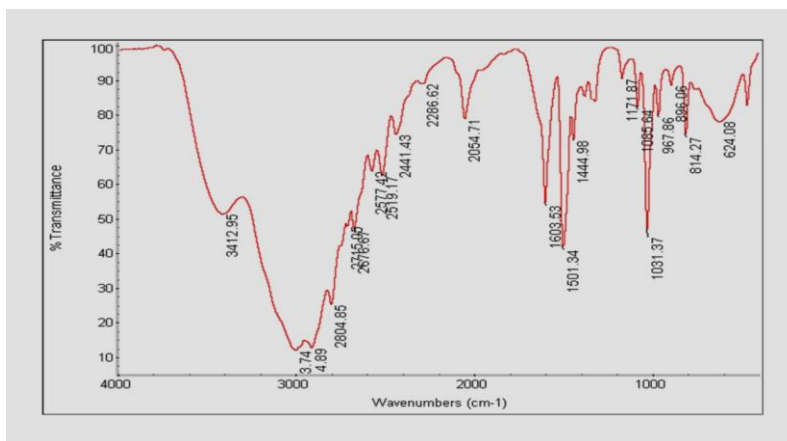


Fig. 3. FT-IR spectrum in (KBr) disk of complex $[\text{Co}(\text{C}_{19}\text{H}_{17}\text{N}_3)_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ in the range of 4000-400 cm^{-1} .

Synthesis of ligand ($\text{N}^1\text{Z}, \text{N}^2\text{Z}$)- N^1 -((1H-pyrrol-2-yl)methylen)- N^2 -(1-phenylethylidene)ethane-1,2-diamine

($\text{N}^1\text{Z}, \text{N}^2\text{Z}$)- N^1 -((1H-Pyrrol-2-yl)methylen)- N^2 -(1-phenylethylidene)ethane-1,2-diamine was synthesized from benzene-1,2-diamine 11.2 g, acetophenone 5 g, and 1H-Pyrrole-2-carbaldehyde 5.1 g. The reaction mixture was stirred in ethanol (120 ml) at 90 °C for 24 h and then cooled to room temperature, followed by concentrating the resulting mixture to a yellow solid product. Boiling point of the solution was measured 79 °C.

$[\text{C}_{19}\text{H}_{17}\text{N}_3]$; **IR** (KBr, cm^{-1}):

Calcd., 3136.78 (N-H), 2906.63, 2914.98 (=C-H), 1647.32 (C=N), 881.709, 961.619, 794.219, 801.525 (C-H, OPP), 3346.43 (C-H, SP^2), 3176.74, 3158.23 (C-H, SP^3), 1458.21 (C=C), 1548.02, 1647.32, 1755.62 (N-H, C-N);

IR (KBr, cm^{-1}):

Found: 3133.70 m (N-H), 2857.57 w, 2748.89 w (=C-H), 1616.4 s (C=N), 1030.08 m, 880.0 w, 742.52 m (C-H, OPP), 3084.47 w (C-H, SP^2), 2969.15 w, 2997.43 w (C-H, SP^3), 168 m (C=C), 1574.77 m (N-H, C-N);

^1H NMR (300MHz, CDCl_3): δ 9-10 ppm (s, 1 H, NH), 8-9 (s, 1 H, =C-H), 6-8 (m, 12 H, Ar-H) phenyl group and hetroaromatic groups (Fig. 4);

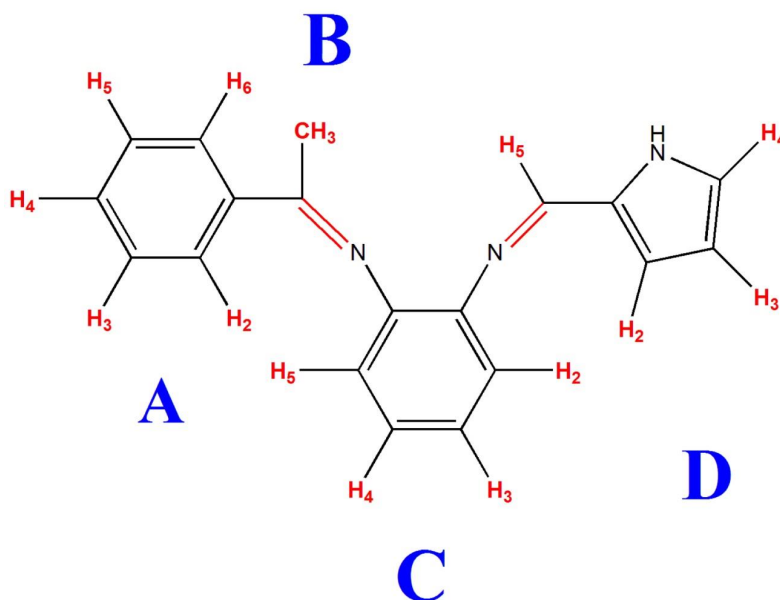


Fig. 4. Chemical structure of compound PMPA with bonds numbered hydrogen atoms

^{13}C NMR (300 MHz CDCl_3): δ 42 ppm ($-\text{CH}_3$), 70-80 (CDCl_3), 100-145 (Phenyl group and heteroaromatic group), 146 ($\text{Ph}-\text{C}=\text{N}$), 148 ($=\text{C}-\text{H}$);

For $\text{C}_{19}\text{H}_{17}\text{N}_3$

anal. Calcd: C, 79.41; H, 5.96; N, 14.62 %

Found: C, 79.56; H, 5.84; N, 14.64 %

Mol. Wt.: 287.36, found: 287.41 MW

Exact Mass: 287.14 m/e: 287.14 (100.0 %), 288.15 (20.7 %), 289.15 (2.0 %), 288.14 (1.1 %).

Synthesis of Complex $[\text{Co}(\text{C}_{19}\text{H}_{17}\text{N}_3)_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$

The Schiff base PMPA 4.3 g was dissolved in acetonitrile (20 ml) to which an acetonitrile solution (120 ml) of $[\text{CoCl}_2]6\text{H}_2\text{O}$ 1.2 g was added by stirring. The mixture was stirred for 3 h and then cooled to room temperature followed by concentrating the resulting mixture to an orange solid product.

$[\text{C}_{38}\text{H}_{32}\text{CoN}_6]$; **IR** (KBr, cm^{-1}):

Found: 3412 m (N-H), 2804.85 s, 2715.05 m ($=\text{C}-\text{H}$), 1603.53 m, 1031.37 m, 967.86 w ($\text{C}=\text{N}$), 1085.64 w (C-H, OPP), 3000.74 s (C-H, SP^2), 2914.89 s (C-H, SP^3), 1444.98 w, 1501.34 m (N-H, C-N);

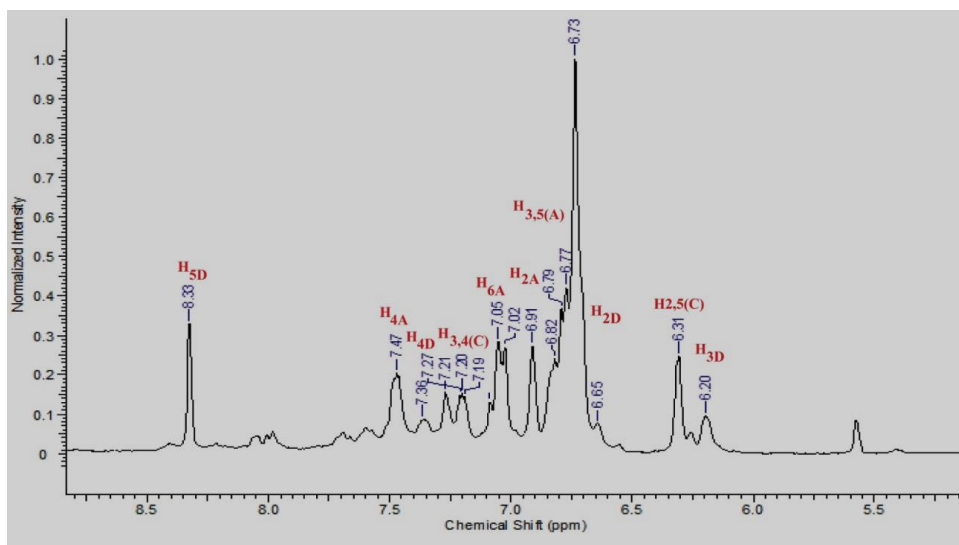


Fig. 5. ^1H NMR spectrum (in the magnetic field 300 MHz, solvent CDCl_3) of the synthesized ligands PMPA in the range δ 6-8 ppm with hydrogen atoms positions

For $\text{C}_{38}\text{H}_{32}\text{CoN}_6$

anal. Calcd: C, 72.26; H, 5.11; Co, 9.33; N, 13.31 %

Found: C, 72.24; H, 5.18; Co, 9.31; N, 13.28 %

Mol. Wt.: 631.63, found: 631.59 MW

Exact Mass: 631.2 m/e: 631.20 (100.0 %), 632.21 (41.5 %), 633.21 (8.4 %), 632.20 (2.2 %), 634.21 (1.3 %)

Structure elucidation

The structures of both compounds were determined using FT-IR, ^1H NMR, and ^{13}C NMR spectroscopy (including DEPT 90 and HETCOR).

$2\text{D}[^{13}\text{C}], [^1\text{H}]$ HETCOR experiments: $2\text{D}[^{13}\text{C}], [^1\text{H}]$ HETCOR spectra were measured according to the Van Rossum et al. (1997) method. The pulse sequence for the $2\text{D}[^{13}\text{C}], [^1\text{H}]$ HETCOR experiment is shown in Fig. 5.

Results and discussion

IR Spectral Studies

All spectral data were consistent with the assigned structure of the compounds. The IR spectra of the ligand give a broad band at 3133.70 cm^{-1} assignable to $\nu(\text{NH})$ stretching vibration.

The ligands show strong band in the 1616.43 cm^{-1} region due to $\text{C}=\text{N}$, which is assignable to the Schiff bases appearing in both synthesized ligands Fig. 6.

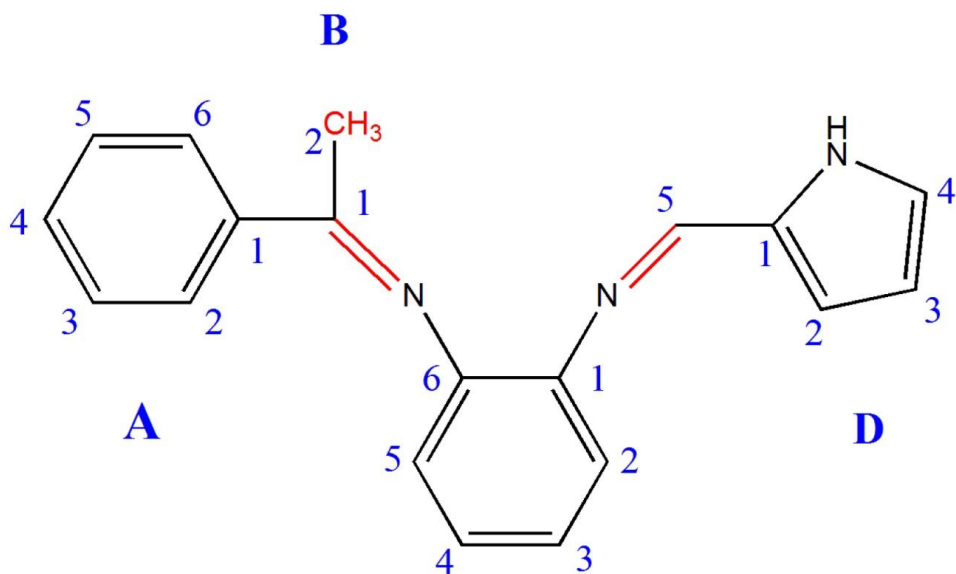


Fig. 6. Chemical structure of compound PMPA with bonds numbered carbon atoms

Vibrations due to $\nu(\text{C}=\text{N})$ and $\nu(\text{N}-\text{H})$ were found in range of 1616.43 and 3133.70 cm^{-1} for ligands, and from 1603.53 and 3412.95 cm^{-1} for complexes, respectively. This decrease in the frequency of $\text{C}=\text{N}$ and increase in frequency of $\text{N}-\text{H}$ for the complex indicates complication. From the infrared spectra of complexes, it is clear that there is no doublet peak in the region of $700\text{--}950\text{ cm}^{-1}$, which indicates the connected nature of the ligand.

As seen in Fig. 7, this band is shifted to a lower frequency in the complex, indicating the coordination through azomethine nitrogen. It is found from the IR spectra of the complexes that there is a wide and strong band at $620\text{--}800\text{ cm}^{-1}$ for $(\text{M}-\text{N})$ bonding Fig. 7.

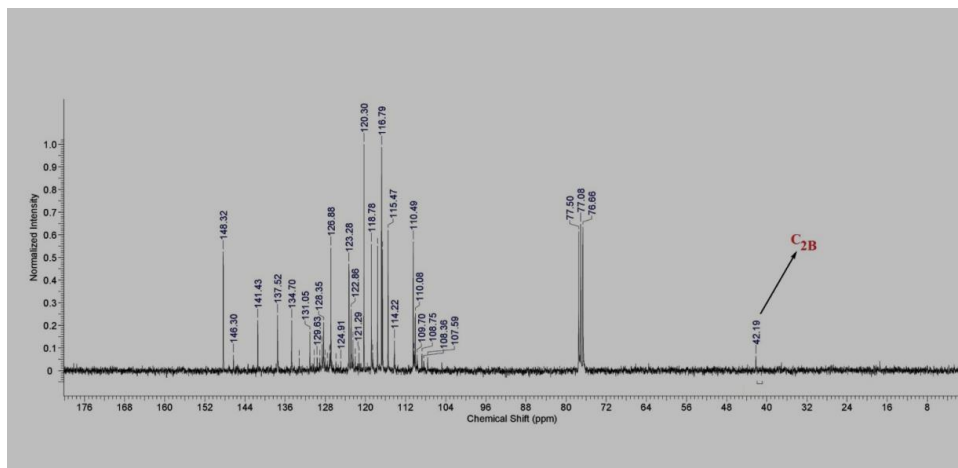


Fig. 7. ^{13}C NMR spectra (in the magnetic field 300 MHz, solvent chloroform-*d*) related to the structure of the synthesized PMPA

Metal ligand vibrations are generally observed in the far-IR region and usually provide valuable information regarding the bonding of ligand to the metal-ions.

These bands will give valuable information regarding bonding modes of ligand to metal ions in the complexes.

NMR spectral studies

Further evidence for the formation of target compounds was obtained from the ^1H NMR spectra, which proved to be a diagnostic tool for positional elucidation of the proton. Assignments of the signals are based on the chemical shift and intensity pattern Fig. 8.

A single peak in the range δ 8.6-8.75 ppm indicated the proton of the $\text{CH}=\text{N}$ group. All the Schiff bases showed negative test for aldehyde, ^1H NMR spectra exhibited a single peak at near δ 8.4 ppm due to the proton of azomethine (Fig. 9).

The NH peak, which appears as a singlet at δ 10.136 ppm in the ligand is absent in all the complexes, which shows the deprotonation of the ligand. The signal at δ 10.136 ppm is assigned to proton NH of the ligand.

The aromatic protons at δ 6-8 (m, Ar-H) shift down field in the complexes. The signal at δ 2.642 (s, 3H) is assigned to the protons of the methyl group of acetophenone. Thus, ^1H NMR spectral observation supplements the assigned geometry.

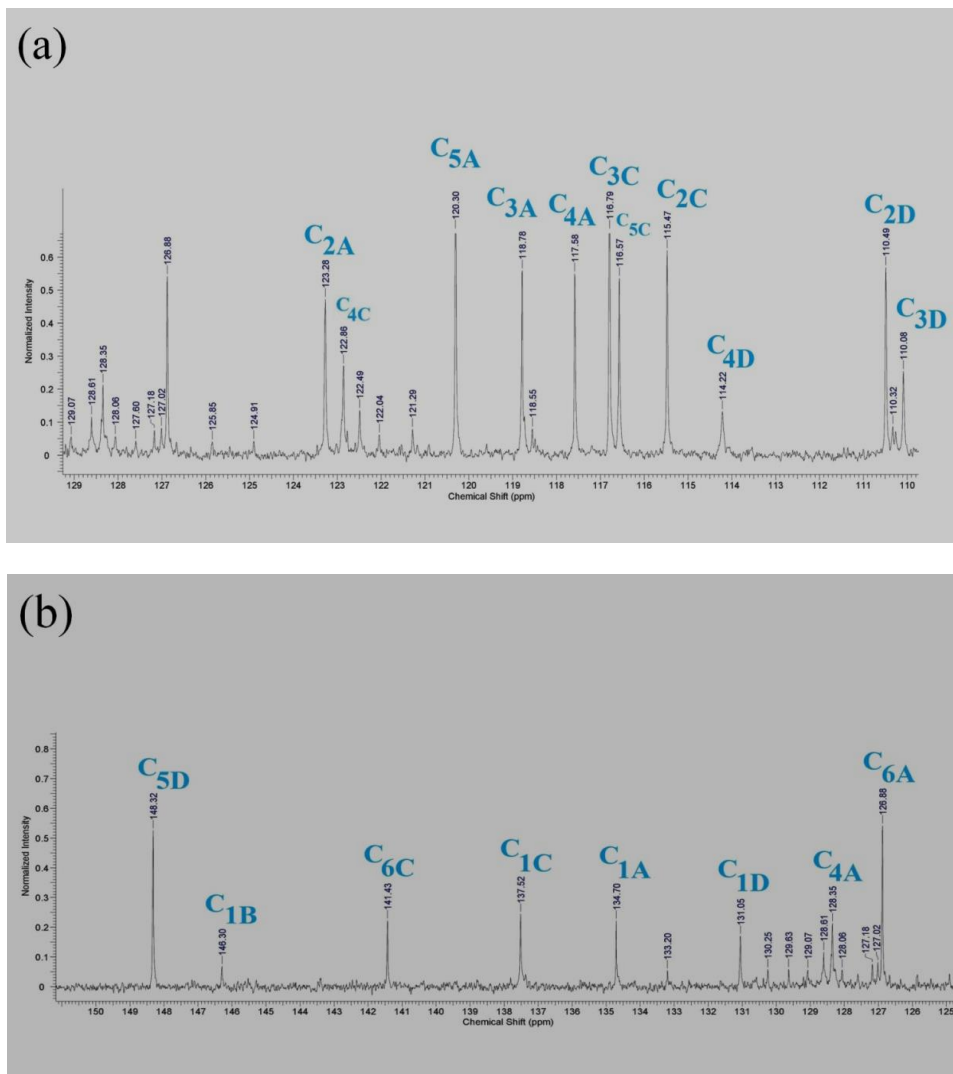


Fig. 8. ^{13}C NMR spectra PMPA (in the magnetic field 300 MHz, solvent CDCl_3) related to the structure of the synthesized ligand (a) Positions of the carbon atoms in the range δ 110 – 125 ppm; (b) Positions of the carbon atoms in the range δ 125 – 150 ppm

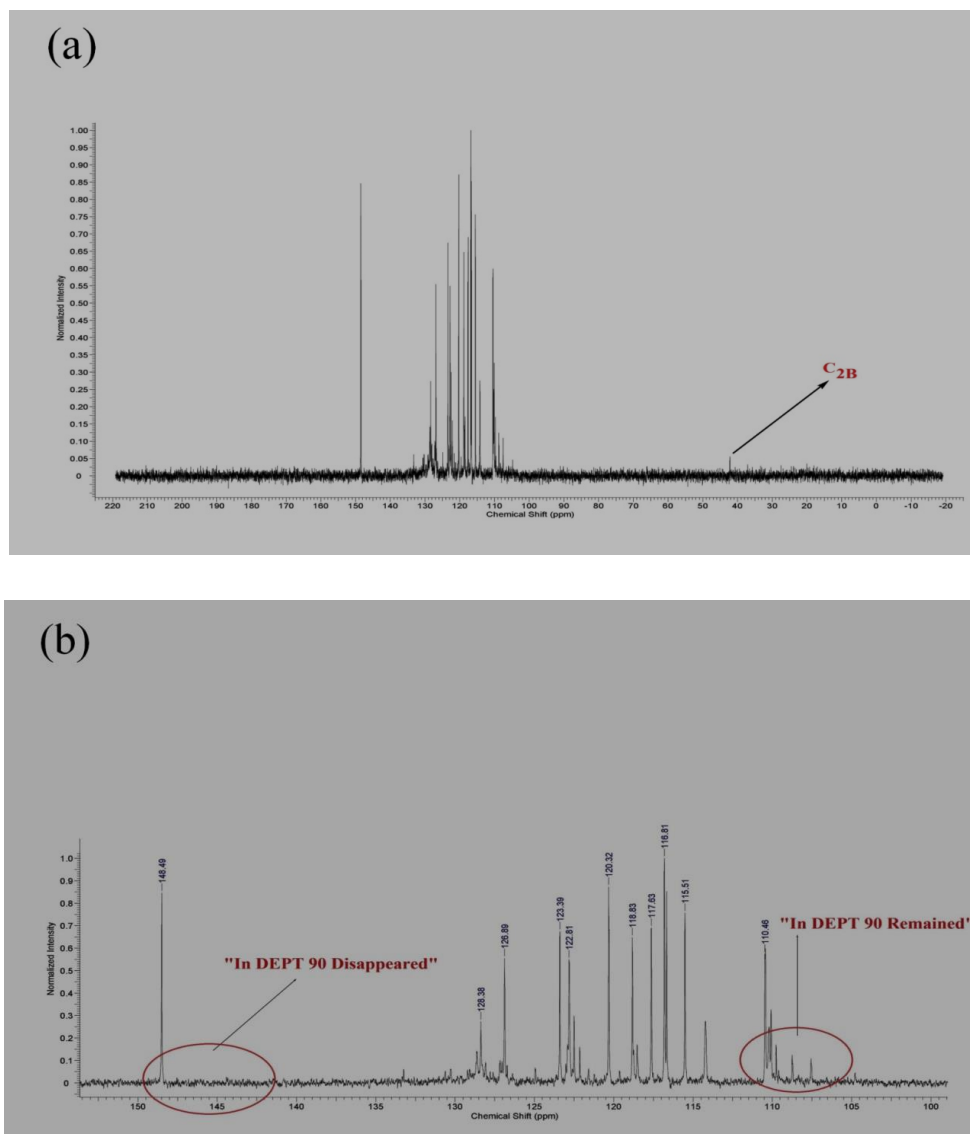


Fig. 9. DEPT 90 spectra (in the magnetic field 300 MHz, solvent $CDCl_3$) related to the structure (Blinka et al., 1984) of the synthesized logand PMPA: (a) position carbon atom C_{2B} ; (b) The position disappearance of carbon atoms in Spectra DEPT 90

The characteristic resonance peaks in the ^{13}C NMR spectra of the ligand PMPA, are given in the experimental section (Table 3) (Fig. 10). The carbon atoms of the phenyl group and hetroaromatic groups appear in the expected aromatic region ranging from δ 105-145 ppm.

A peak signal appearing at δ 42.187 ppm is the characteristic of the carbons ($\text{C}_{2\text{B}}$) of $-\text{CH}_3$ (Fig. 11).

Table 3. Theoretical frequencies in cm^{-1} calculated by DFT/3-21G** method for compound PMPA

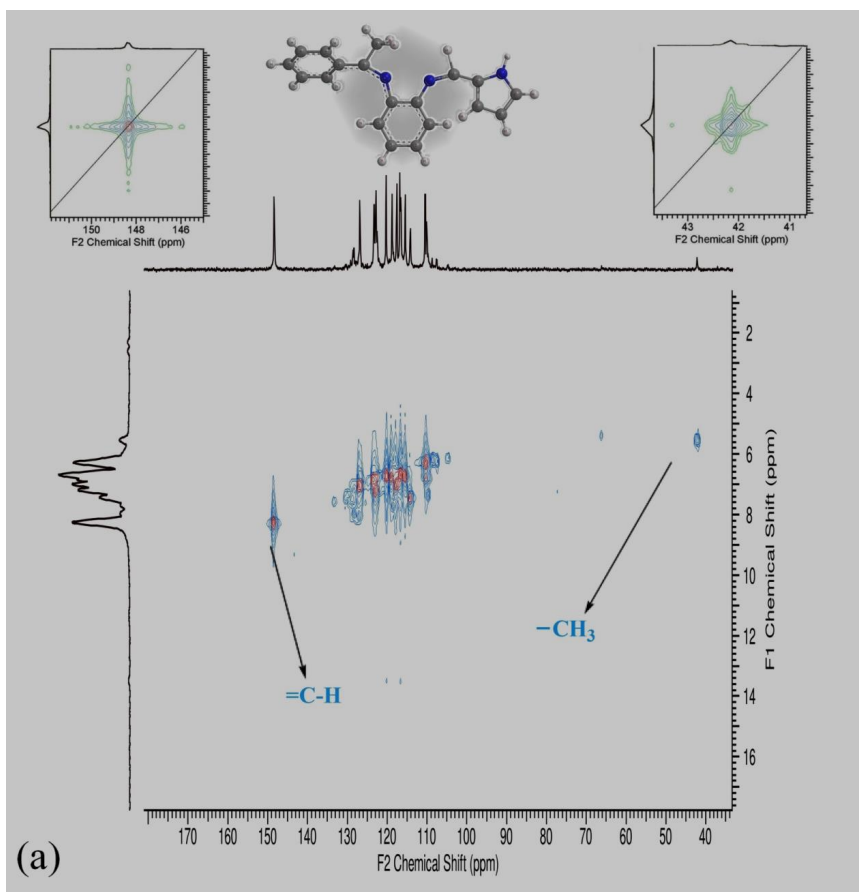
Observed values	DFT/3-21G**	Approximate assignments
3133.70 w	3136.78	N-H symmetric stretching
2857.57 w	2906.63	-C=H stretching (aldehyde)
2748.89 w	2914.98	
1616.40 m	1647.32	C=N stretching
-	1054.34	(C-H In plane) stretching
1030.08m	881.709	(C-H OPP) stretching
880.0w	961.619	
742.52m	794.219	
-	801.525	
3084.47 w	3346.43	(C-H SP^2) stretching
2969.15 w	3176.74	(C-H SP^3) stretching
2997.43 w	3158.23	
1410.68 w	1458.21	C=C bending
-	1548.02	(C-N , N-H)
1574.77m	1647.32	
-	1755.62	

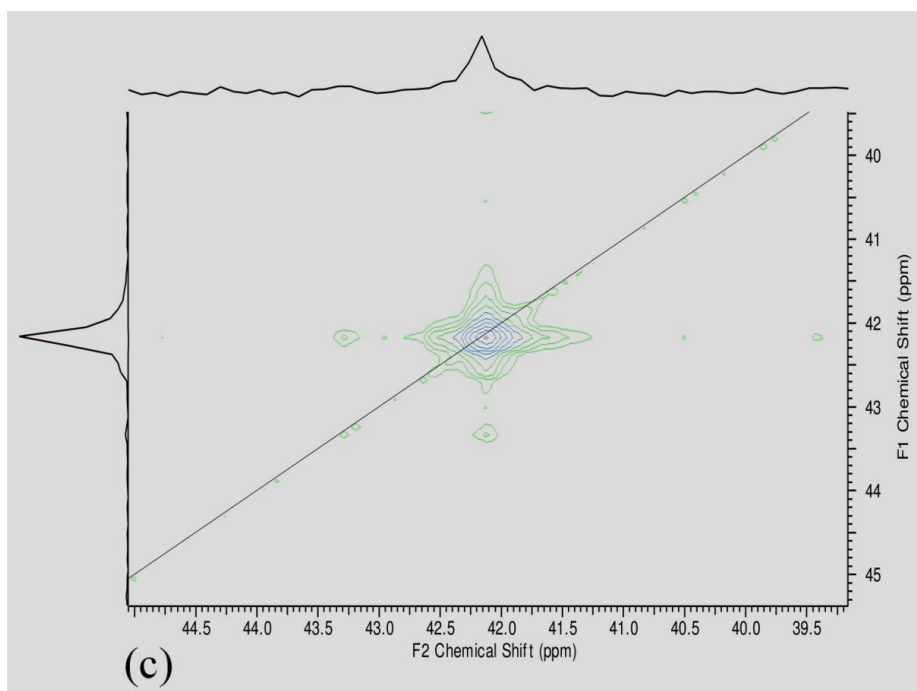
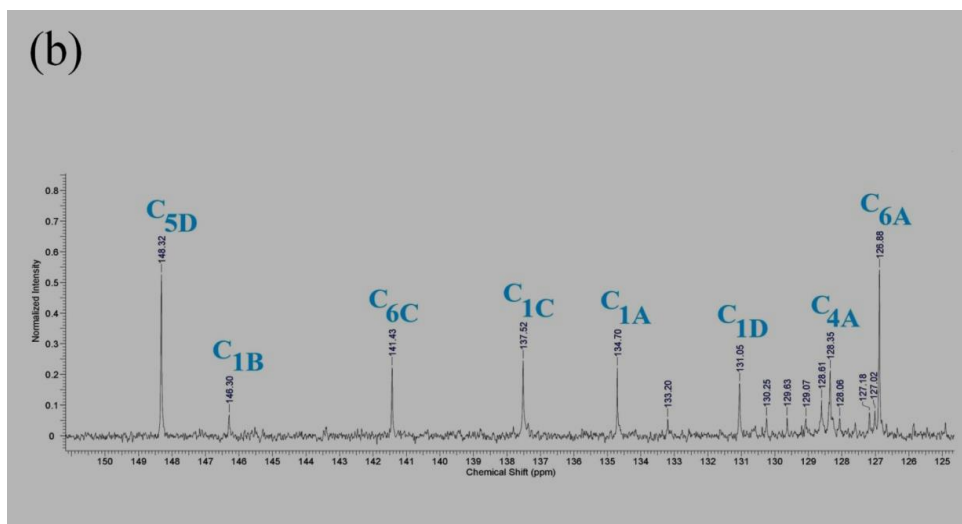
A sharp signal at δ 148.323 ppm due to the characteristics of $=C-H$ (C_{5D}) carbon was in accordance with all the proposed structure (Fig. 12).

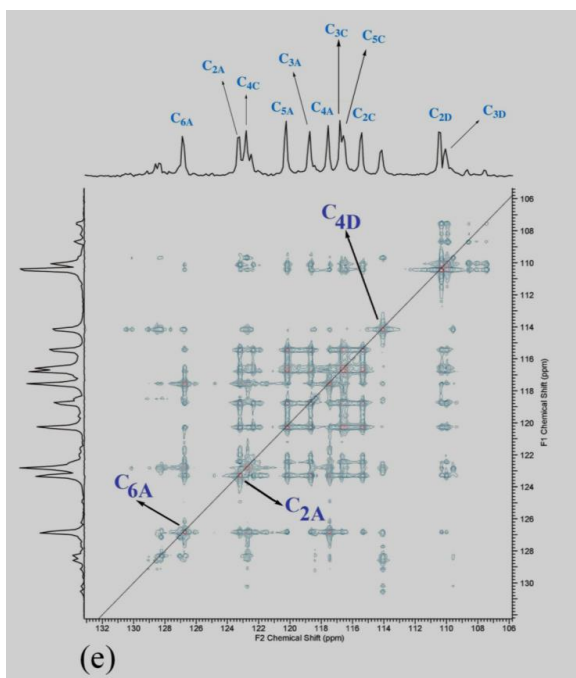
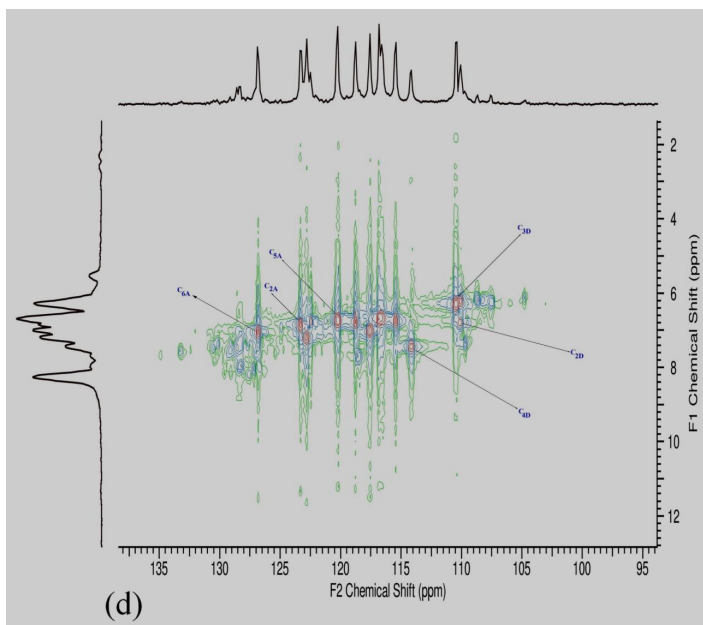
In the spectrum of DEPT 90, disappearance of the peak area (C_{1B}) 146 ppm, (C_{6C}) 141.432 ppm, (C_{1C}) 137.523 ppm, (C_{1A}) 134.708 ppm, (C_{1D}) 131.060 ppm proton is not related to the fourth type of carbon.

In addition, taking the spectrum DEPT 90 of the composition PMPA, the absence of ethanol solvent was approved (Fig. 13).

An additional confirmation of signal assignments in principal PMPA structures was done based on the HETCOR spectrum (Fig. 14a). 1H - ^{13}C COSY is the hetero nuclear correlation spectroscopy. This spectrum was interpreted using established carbon-proton correlations (Kilpeläinen, 1994). The cross peaks mean correlation between a proton and a carbon (Fig. 14b-d).







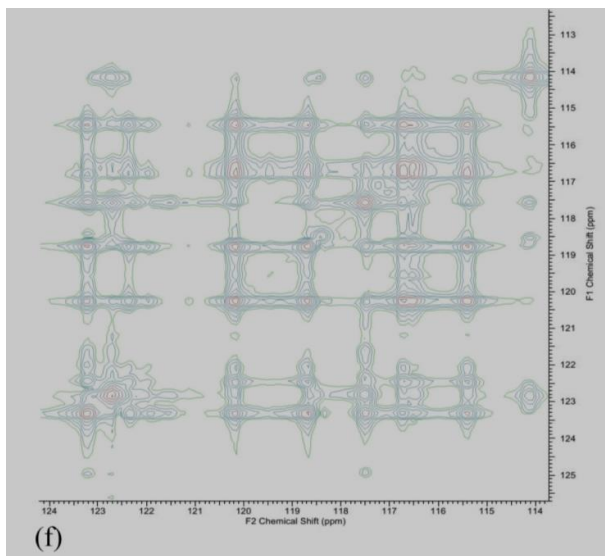


Fig. 10. HETCOR spectra (in the magnetic field 300 MHz, solvent CDCl_3) compound: (a) PMPA; (b) Position $=\text{C}-\text{H}$ in the range δ 146-150 ppm; (c) Position $-\text{CH}_3$ in the range δ 41-43 ppm; (d) In the range δ 95-135 ppm; (e) $^{13}\text{C}-^{13}\text{C}$ COSY (Correlation Spectroscopy) (Zhang & Brüscheiler, 2004) of compound PMPA in the range δ 106-132 ppm; (f) In the range δ 114-124 ppm

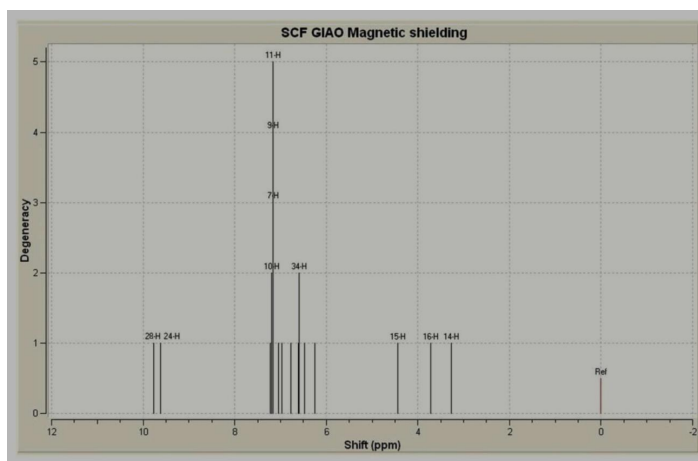


Fig. 11. Calculated ^1H NMR of (N1Z,N2Z)-N1-((1H-Pyrrol-2-yl)methyl-en)-N2-(1-phenylethylidene)ethane-1,2-diamine PMPA, at the DFT/3-21G**

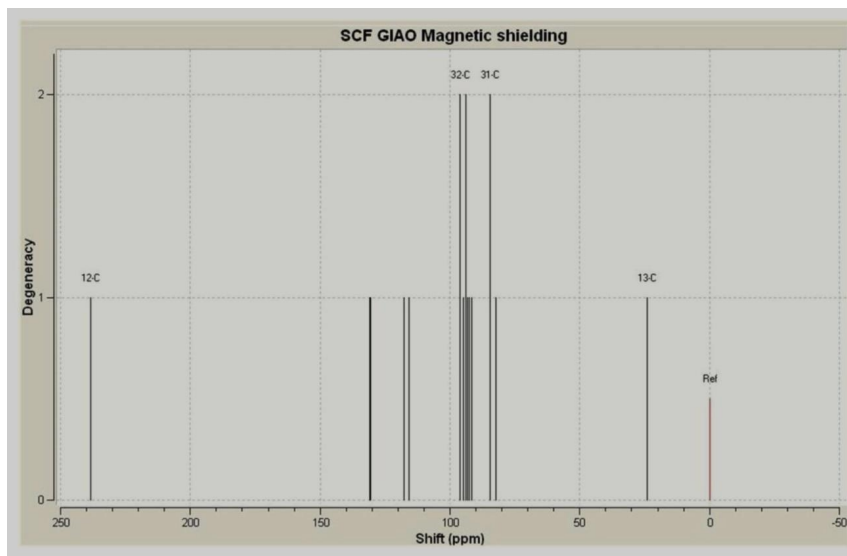


Fig. 12. Calculated ^{13}C NMR of (N1Z,N2Z)-N1-((1H-Pyrrol-2-yl)methyl-en)-N2-(1-phenylethylidene) ethane-1,2-diamine PMPA, at the DFT/3-21G**.

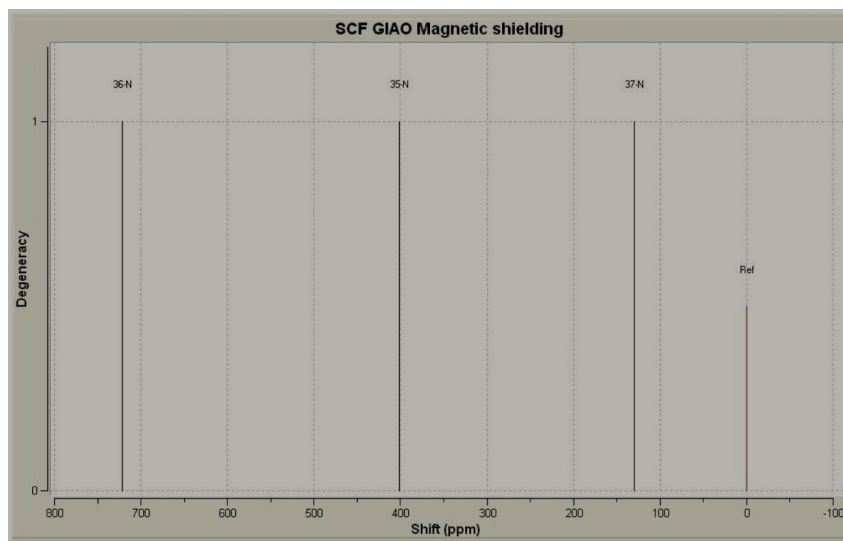


Fig. 13. Calculated ^{15}N NMR of (N1Z,N2Z)-N1-((1H-Pyrrol-2-yl)methyl-en)-N2-(1-phenylethylidene)ethane-1,2-diamine at the DFT/3-21G**

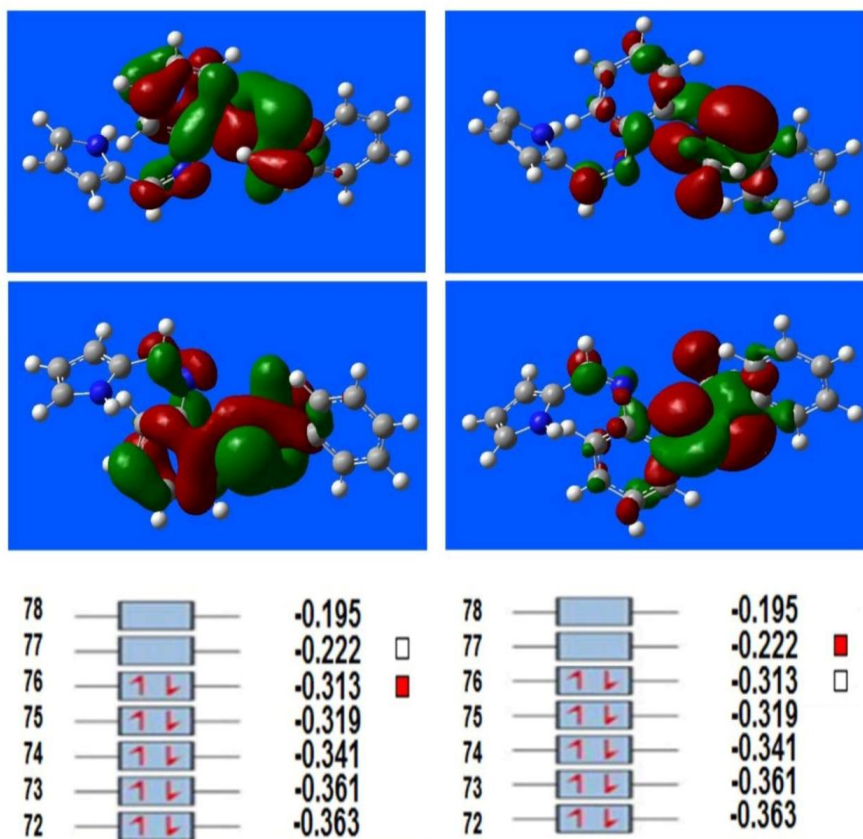


Fig. 14. The atomic orbital compositions of the frontier molecular orbital for compound PMPA, [C19H17N3] at the DFT/3-21G*

¹³C-¹³C COSY (Correlation spectroscopy)

¹³C-¹³C COSY is used for clearly indicate correlation with coupled carbons. A point of entry into a COSY spectrum is one of the keys to predict information from it successfully. Relation of Coupling carbons is determined by cross peaks (correlation peaks) and in the COSY spectrum. In other words, Diagonal peaks by lines are coupled to each other.

Figure 14c indicates that there are correlation peaks between carbon C_{2C} and C_{3,5C} as well as between C_{3,5C} and C_{3,5,2A}. This means the C_{3,5C} coupled to C_{2C} and C_{3,5,2A}. In Figure 14c indicates that there are correlation peaks between carbon C_{4A} and C_{2A} as well as between C_{2A} and C_{6A}. This means the C_{2A} coupled to C_{4A} and C_{6A}.

Figure 14e,f indicates that there are correlation peaks between carbon C_{3,5A} and C_{2A}. Also there are correlation peaks between carbon C_{4A} and C_{4C} as well as between C_{4C} and C_{6A}. This means the C_{4C} coupled to C_{4A} and C_{6A} (Simpson, 2012; Rienstra et al., 1998; Olsen et al., 2003; Omichinski et al., 1991).

Molecular geometry

The ONIOM (B3LYP/3-21G**) optimized structure of the ligand PMPA and the binding energies obtained at the B3LYP/3-21G** level are shown in Table 4.

Table 4. Theoretical and experimental IR spectral data (cm⁻¹) of compound PMPA at the DFT/3-21G**

Bond lengths	DFTa/3-21G**	Bond angles	DFT/3-21G**
C1-C2	1.39516	C1-C2-C3	120.00865
C2-C3	1.39471	C2-C3-C4	119.99413
C3-C4	1.39543	C3-C4-C5	119.99402
C4-C5	1.39482	C4-C5-C6	120.00471
C5-C6	1.39514	C5-C6-C1	120.00002
C6-C1	1.39483	C6-C1-C2	119.99843
C6-C12	1.54	C6-C12-C13	109.47238
C12-C13	1.50715	C6-C12-N36	109.4767
C12-N36	1.50713	C13-C12-N36	111.80195
N36-C17	1.54	C12-N36-C17	110.62903
C17-C18	1.39516	N36-C17-C18	119.99721
C18-C20	1.39471	C17-C18-C20	120.00863
C20-C23	1.39543	C18-C20-C23	119.99416
C23-C21	1.39483	C20-C23-C21	119.99394
C21-C19	1.39514	C23-C21-C19	120.00475

C19-C17	1.39483	C21-C19-C17	120.00001
C18-N35	1.54	C19-C17-N36	120.00431
N35-C27	1.32591	C19-C17-C18	119.99848
C27-C39	1.47	C17-C18-N35	119.98082
C39-C29	1.3918	C20-C18-N35	120.01051
C29-C31	1.40185	C18-N35-C27	122.71598
C31-C30	1.43487	N35-C27-C39	122.72008
C30-N37	1.40175	C27-C39-C29	125.60775
N37-C39	1.3918	C39-C29-C31	108.41367
-	-	C29-C31-C30	107.18577
-	-	C31-C30-N37	107.18724
-	-	C30-N37-C39	108.41766
-	-	N37-C39-C27	125.59659

^a Density Functional Theory

The values of the total energy for PMPA from the DFT and B3LYP calculation by employing the 3-21G** basis set are found to be 0.30090845 a.u and 0.262283 a.u, respectively.

Figures 15 - 17 show comparative representations of theoretical ¹H, ¹³C, and ¹⁵N NMR spectra, respectively (Mäki et al., 2005).

Vibrational spectroscopy is extensively used in organic chemistry for the identification of functional groups of organic compounds, the study of molecular conformations, and reaction kinetics *etc.* The observed and calculated data of the vibrational spectrum of PMPA are given in Table 2. The comparative graph of calculated vibrational frequencies by DFT method at 3-21G** basis sets for the PMPA are given in Table 2.

Prominent peaks around 3346.43 and 1647.32 cm⁻¹ in the FT-IR spectra are attributed to ν N-H and ν C=N modes, respectively. The in plane bending vibration and out of plane bending vibrations of the aromatic C-H group are characterized by bands in the ranges 1196.43, 1169.39, 1162.86, 1158.73, 1157.39, and 1139.7 cm⁻¹, respectively.

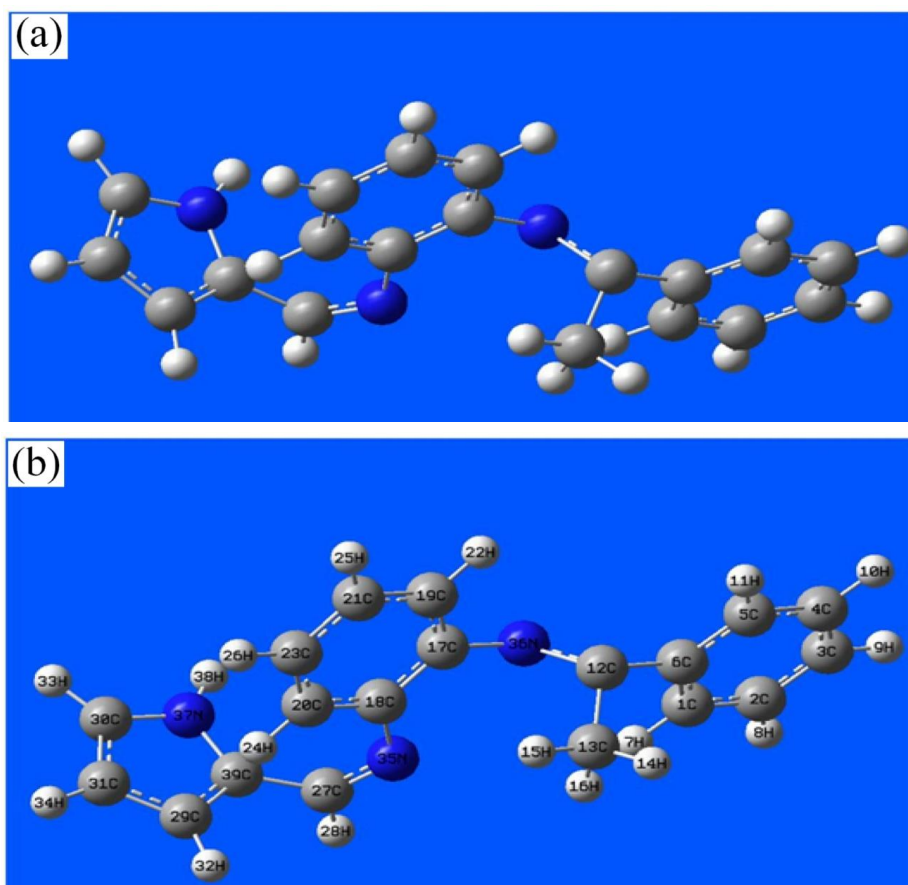


Fig. 15. System adopted in the theoretical study: (a) compound PMPA; (b) Num-bering compound PMPA using DFT/3-21G** level.

The HOMO-LUMO energy of the PMPA was calculated at the B3LYP/3-21G** level and is shown in Fig. 18.

$$\begin{aligned} &\text{HOMO (DFT)} \\ &E_{\text{HOMO}} = -14.31737 \text{ a.u} \\ &(\text{First excited state}) \end{aligned}$$

$$\begin{aligned} &\text{LUMO (DFT)} \\ &E_{\text{LUMO}} = -0.20621 \text{ a.u} \\ &(\text{First excited state}) \end{aligned}$$

$$\begin{aligned} \Delta E = \text{LUMO-HOMO} &= 14.11116 \text{ a.u} \\ &(\text{Ground state}) \end{aligned}$$

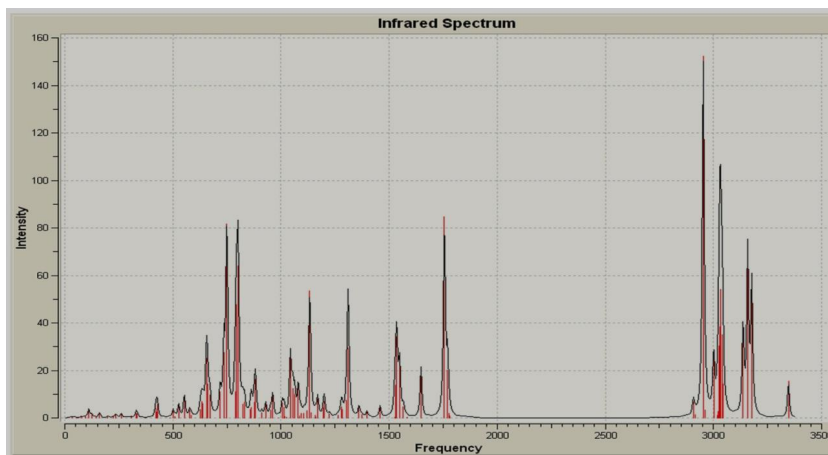


Fig. 16. Theoretical calculated infrared spectra (Klähn et al., 2005; Langhoff, 1996) of compound PMPA, [C₁₉H₁₇N₃] (top to bottom, frequencies in cm⁻¹, intensities in arbitrary units)

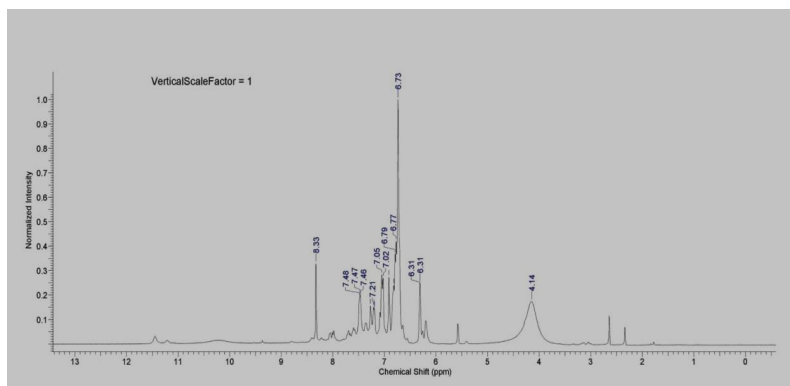


Fig. 17. ¹H NMR Spectrum (in the magnetic field 300 MHz, solvent chloroform-*d*) of the synthesized compound (Huynh et al., 2005) PMPA

It reveals that the energy gaps reflect the chemical activity of the molecule. LUMO as an electron acceptor represents the ability to obtain an electron, while HOMO represents the ability to donate an electron.

The LUMO of nature, (i.e.m heterocyclic ring) is delocalized over the whole C-C and C-N bond. This electronic absorption corresponds to the transition from the ground to the first excited state, and is mainly described by one electron excitation from the highest occupied molecular or orbital LUMO.

Conclusions

A series of novel porphyrin hetero-aromatic were synthesized and structurally characterized by ^1H NMR, ^{13}C NMR, DEPT 90, HETCOR, and IR spectroscopy. The hetero-aromatic are coordinated with Co^{II} ion through N-H and azomethine nitrogen.

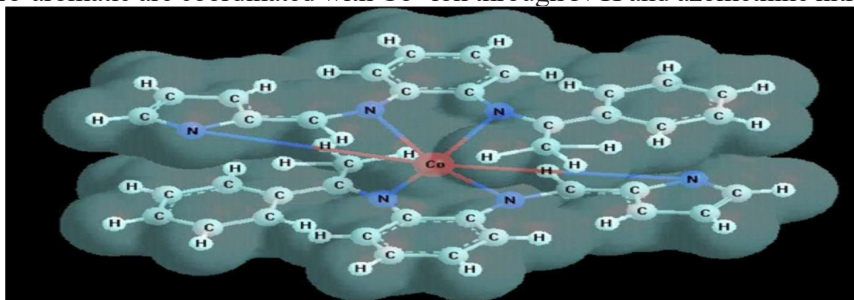


Fig. 19. Ball & Stick models and system adopted in the study (Nakano et al., 1983; Masonjones et al., 2014; Merritt & Murphy 1994) for complex $[\text{Co}(\text{C}_{19}\text{H}_{17}\text{N}_3)_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ at DFT/3-21G** level, (Solvent Accessible Surface: Translucent)

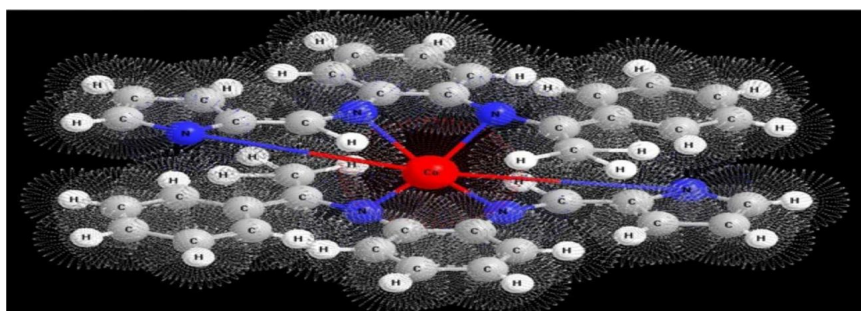


Fig. 20. Ball & Stick models and system adopted in the study for complex $[\text{Co}(\text{C}_{19}\text{H}_{17}\text{N}_3)_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ at DFT/3-21G** level, (Solvent Accessible Surface: Translucent)(Connolly Molecular Surface: Dots) (Connolly, 1993).

The HETCOR spectrum is correlated ^{13}C nuclei with directly attached protons. ^1H - ^{13}C coupling is one bond. If a line does not have cross peak, this means that the carbon atom has no attached proton. The structure of $(\text{N}^1\text{Z}, \text{N}^2\text{Z})\text{-N}^1\text{-}((1\text{H-Pyrrol-2-yl})\text{methylene})\text{-N}^2\text{-(1-phenylethylidene)ethane-1,2-diamine}$ geometry was compared with optimized parameters obtained by means of ab initio calculations with the 3-21G** basis set (Figs. 19, 20).

The geometries and normal modes of vibration obtained from DFT/3-21G** calculations are in good agreement with the experimentally observed data. The HOMO and LUMO levels of PMPA have been studied with DFT/3-21G** level. Moreover, NMR frequencies for the optimized molecular structures of the title compounds were calculated

using these DFT/B3LYP methods with the 3-21G**(6D,7F) standard basis set, and where then compared with experimental data.

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✉ **Mr. Mohammad Mahdi Akbarzadeh (corresponding author)**

Faculty of Sciences
Islamic Azad University
Science and Research Branch P.O. Box 14778-93855
Tehran, Iran
E-mail: mehdiakbarzadeh10@yahoo.com