Original Article

Synthesis of new Schiff base ligand with spectroscopic identification of the ligand and their metal ion complexes

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Abstract

New Schiff base ligand (N, O) and its complexes were synthesized by using condensation method. The ligand and its complexes C1, C2 and C3 have been identified by using techniques FT-IR spectroscopy, UV. Visible, 1H-NMR,13C-NMR, (CHN) analysis, atomic absorption, Mohr method and molar conductivity. The M(II) complexes had neutral nature and M (III) has been electrolyte behaviour based on molar conductivity. Octahedral structure has been proposed for all of complexes that have the bidentate ligand in metal: ligand mole ratio of (1:2).

Keywords: Schiff base ligand, metal ion complexes, spectroscopic characterization.

1. INTRODUCTION

In 2nd part of the past century, coordination chemistry had taken a widely area in the chemistry, due to the rapid progression in operational aspects of coordination complex preparation. Complexes have been used as important material in many different roles such as industry, Agriculture and Medicine. Formation of metal complexes is a phenomena not limited to transitional element but also for all metal ions too [1, 2]. Schiff base represents a common name of the chemical complexes that contain carbon-nitrogen double bond as functional group. The Schiff base was known since the year of 1864. The reaction has been named after the German chemist H. Schiff who could prepare those complexes from the simple condensations between active carbonyl complexes (i.e. ketones or aldehydes) with the primary amine types [3-6].

2. Apparatus

The spectra of the Fourier transform infra-red (FT-IR) have been recorded through using SHIMADZU 8400, ultra-violet-visible (UVvis) spectra has been recorded on the SHIMADZU 1800. 1H and 13C (NMR) spectra mesurements have been evaluated by using BRUKER AV400 Avance- III (400MHz & 100MHz). metal content has been specified with the use of (GBC Avanta v1.33). atomic absorption analysis has been utilized for the purpose of determining metal contents by Nova350 spectro-photometer. The percentages of the carbon, nitrogen and hydrogen (i.e. CHN elemental analyses) were performed with the use of the CHN that has been recorded on a EuroEA Elemental Analyzer (Euro-EA3000/Italy). Melting point values had been evaluated by the Gallenkamp melting point device. The complexes' molar conductivity has been determined in the DMSO (10^{-3}M) that has been specified in the WTW conduct meter.

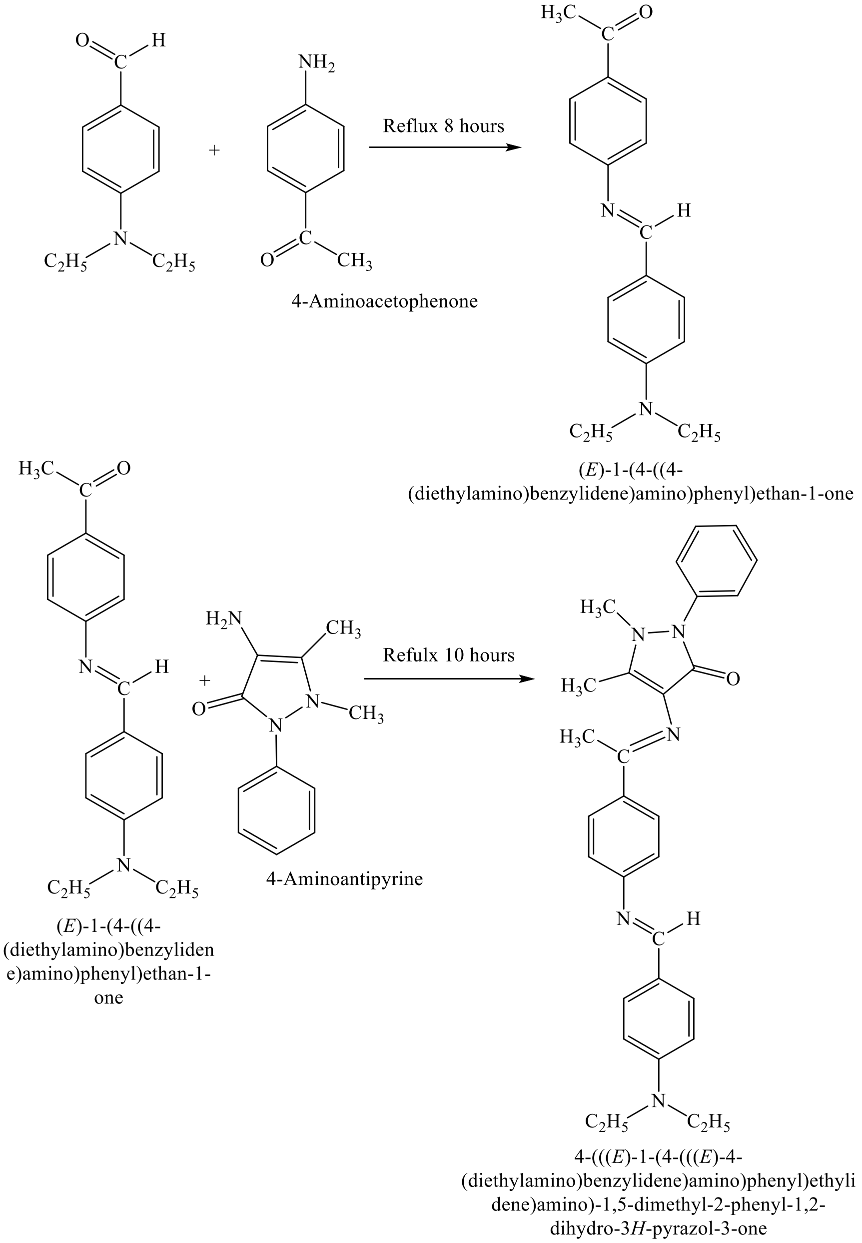
3. The chemicals

Chemical materials that had been used included 4-amino-acetophenone (alpha Acer), 4-Aminoantipyrine (CDH), 4-N,N-Diethyleamino benzaldehyde (merck), $CuCl_2$ (Fluka), $CrCl_3.4H_2O$ (Fluka), $CoCl_2.2H_2O$ (BDH). Organic solvents that have been utilized used included the ethanol 95% (BDH), diethyl ether (Fluka) and glacial acetic acid (BDH).

4. Ligand Synthesis

4-N,N-Di-ethyleaminobenzylidene-4-amino acetophenone preparation has been refluxing in ethanolic solution (25mL) of 4-amino-acetophenone (1mmol) that contains two glacial acetic acid drops with (25 mL) of ethanolic solution of 4N,N-Diethyleamino benzaldehyde (1mmol) for 8hrs and cooled after that at the temperature of the room. Yellow product has been washed thoroughly with the use of the ethanol and air-dried after that. Yield=0.2gm (80%).

An ethanolic solution of 4N,N-Diethyleaminobenzylidene -4-amino aceto-phenone (25mL) of (1mmol) and ethanolic solution (25mL) of 4-Aminoantipyrine (1mmol) have been mixed then refluxed for 10 hr and then cooled overnight at the temperature of the room. This product has been filtered and washed by using Absolute ethanol and then air-dried after that. Yield=0.3gm (70%) Scheme1.



Scheme1: Ligand Synthesis

5. Complex Syntheses

Complexes have been synthesized through the dissolution of (2 mmole) of ligand within (20mL) absolute ethanol then mixed with (10ml, 1 mmole) of the hot solution of the absolute ethanol of the salts of chloride metals of Co(II), Cr(III) and Cu(II) every one of which had been added separately then left under the reflux for a period of 6 hrs, then it was allowed to cool and 10.0mL of the diethyl ether had been added to precipitate solid complexes. Products have been filtered, washed by cold water and ethanol, and then they have been dried, followed by recrystallization with the ethanol.

6. Results and discussion:

6.1. Physical characteristics and elemental analyses:

Atomic absorption data, CHN elements analysis and chloride contents and physical characteristics of synthesized ligand as well as its complexes had been listed in Table1. Molecular formulae of studied complexes have been proposed based upon the CHN, atomic absorption analyses, chloride content, spectral data and conductivity measures.

Table1: Physical characteristics and analytical details for ligand as well as its complexes

Symbols	Colors	mp °C	Yields %	M.Wt g/mol	Micro Elemental Analysis Found (calc.)				Metal contents % Found (calc.)	Chloride contents % Found (calc.)
					C%	H%	N%	O%		
L	**Deep Yellow**	**202-205**	**70**	**479.63**	**75.22 (75.13)**	**6.74 (6.94)**	**15.55 (14.60)**	**3.41 (3.34)**	**----**	**----**
C_1	**Pale yellow**	**145-148**	**68**	**1089.09**	**67.01 (66.17)**	**6.12 (6.11)**	**12.95 (12.86)**	**5.96 (2.94)**	**5.52 (5.41)**	**6.58 (6.51)**
C_2	**Black**	**166-168**	**63**	**1093.70**	**66.09 (65.89)**	**6.10 (6.08)**	**12.66 (12.81)**	**3.05 (2.93)**	**5.95 (5.81)**	**6.54 (6.48)**
C_3	**Yellow-orange**	**115-119**	**71**	**1082.15**	**66.64 (66.60)**	**6.22 (6.15)**	**12.93 (12.94)**	**2.88 (2.96)**	**4.98 (4.80)**	**6.63 (6.55)**

6.2. FTIR spectra of ligand and its complexes:

FTIR spectrum of ligand (L) exhibits broad bands of the absorption at (2,292 – 3,483cm-1) week absorption for OH of water, in some of complexes, water entered in the lattice or that has been coordinated with the metal ions and showed broad band (3,100 to 3,500cm-1) [7]. υ (C=N) imine group has been shown as a sharp band at (1,525 and 1,610cm-1) [8, 9], whereas υ (C-N) had been shown as medium band at (1,369cm-1), υ (C=O) showed a band of absorption at (1,647cm-1), υ (C-O) had shown a band of absorption at (1,230cm-1) [10].. υ (C=O) and υ (C=N) imine, shifts in their position and alter band intensity or shape in comparison to ligand (L), which has been a result of ligand coordination with metal ions and presented indications that complexes have been produced, (1,581cm-1) with sharp strong intensity that result from stretching band of υ (C=C) aromatic and (2,918cm-1) week band of absorption for the H-aliphatic [11]. The (200cm-1 - 600cm-1) range showed band of stretching for υ (M-O), υ (M-N) [12]and υ (M-Cl) [13] in the complexes. FTIR spectral data of synthesized ligand (L) and its metal ions complexes have been exhibited from Figures (1-4).

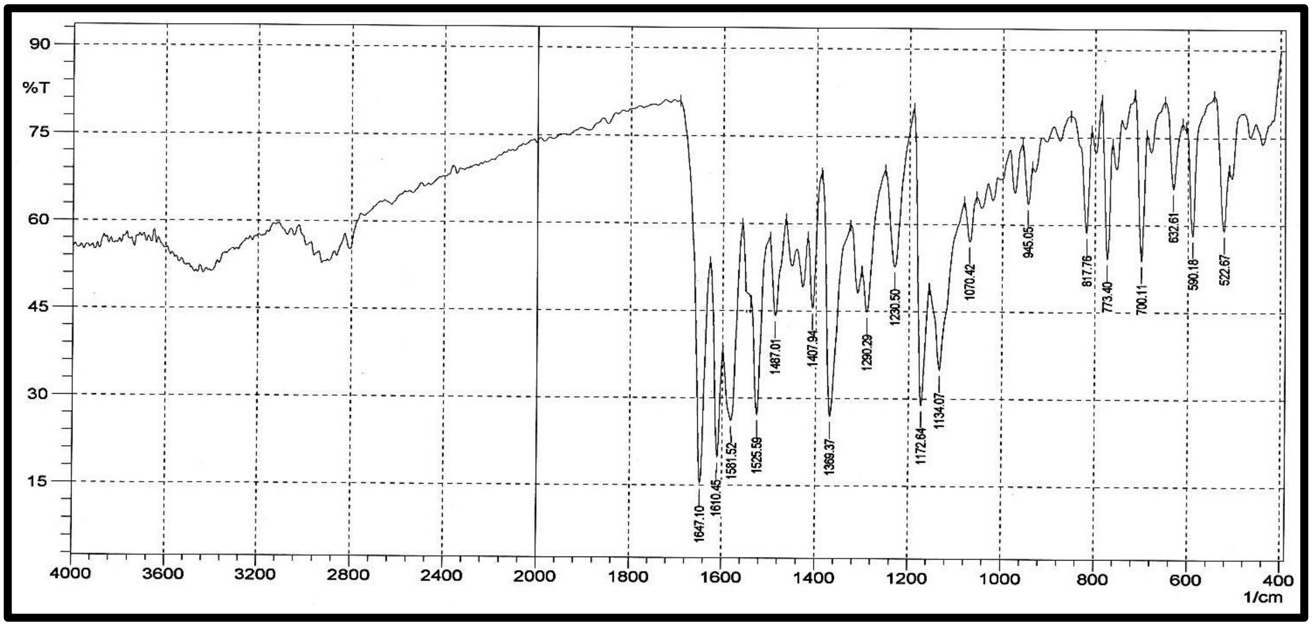


Figure1: Ligand's FT-IR spectrum

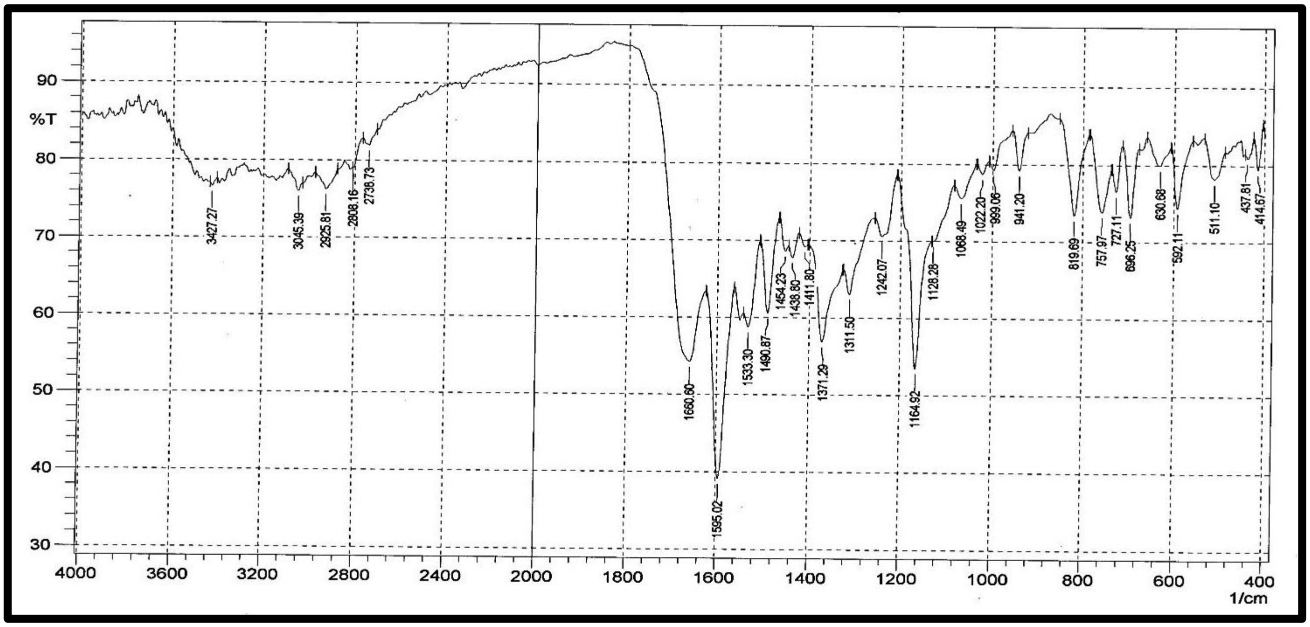


Figure2: C1 FTIR spectrum

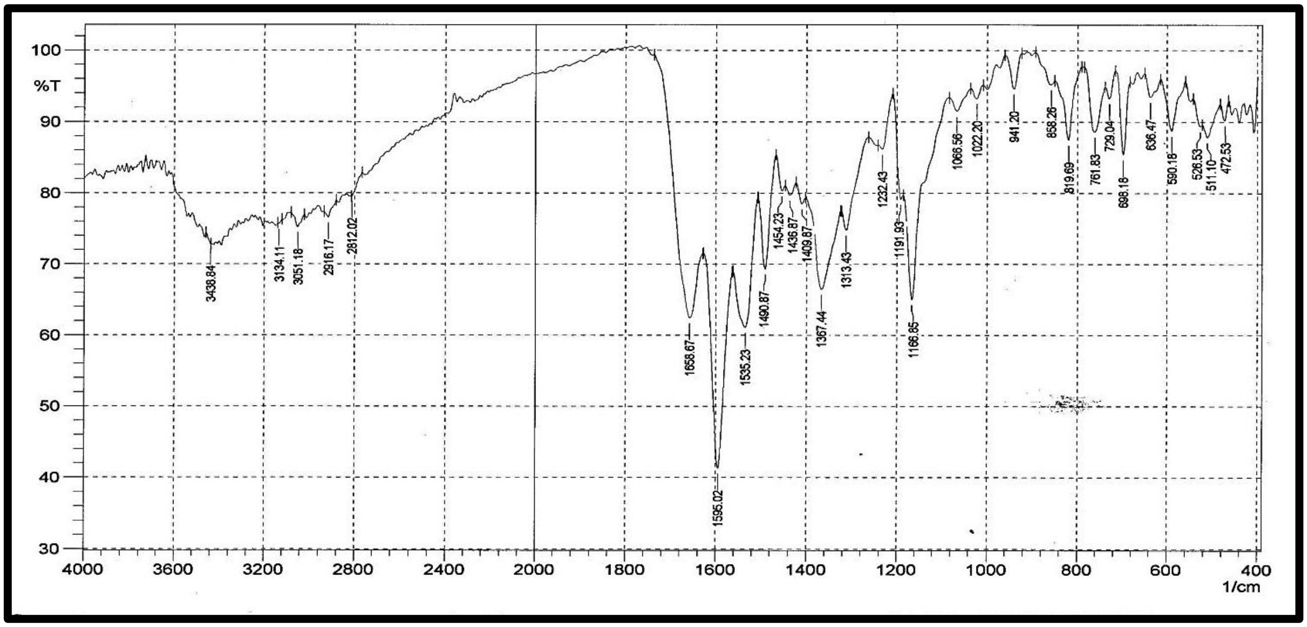


Figure3: C2 FT-IR spectrum

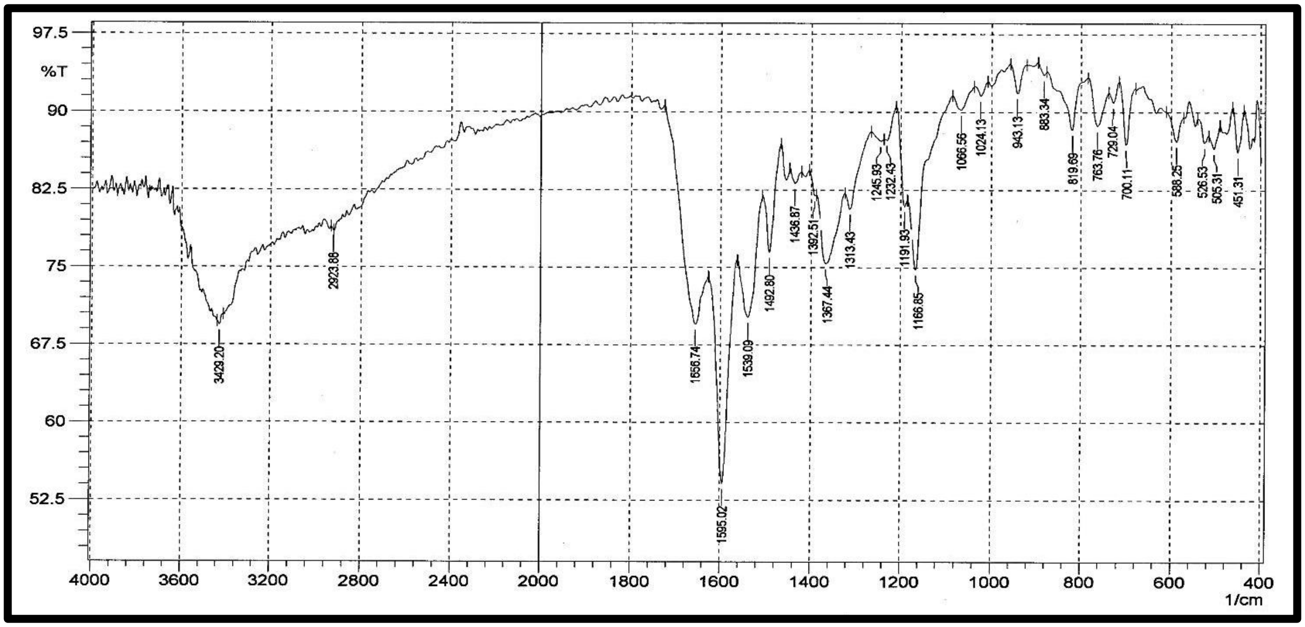
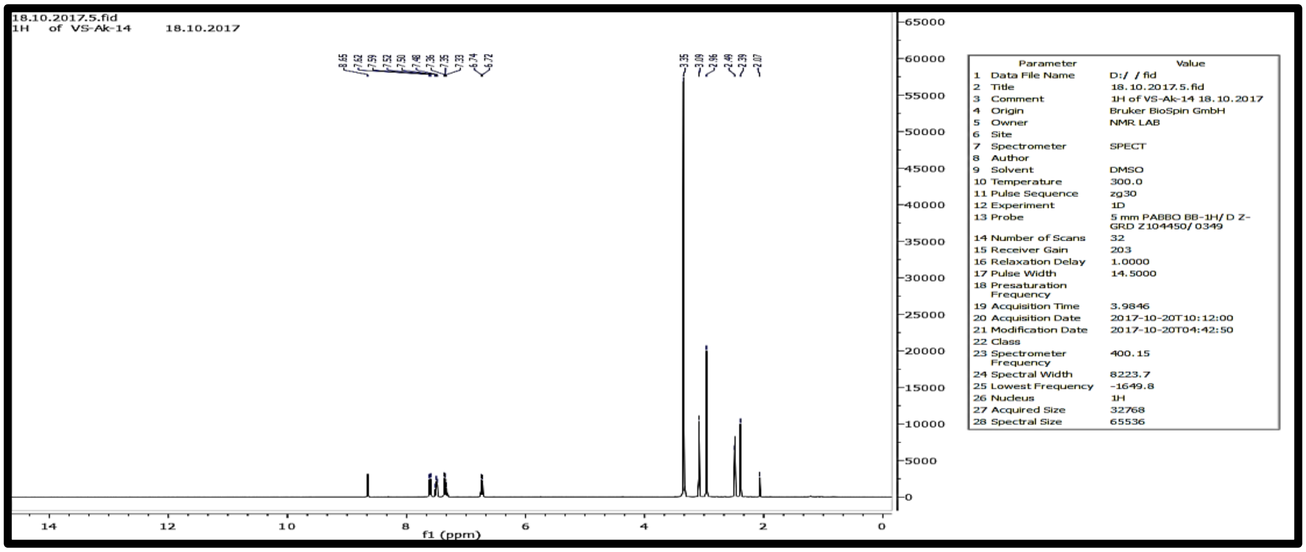


Figure4: C3 FTIR spectrum

6.3. 1H-NMR and 13 C-NMR Spectra of synthesized ligand:

1H-NMR spectrum of synthesized ligand in the DMSO-d6 has been depicted by Fig. (5). The chemical shifting of the methyl protons have been viewed as one peak around □(2.07, 2.39, 2.96ppm). peak near □ (2.5ppm) has been a result of the DMSO [14]. Multiplets peaks have been noticed near □ (6.7-7.6ppm) that had been assigned to the aromatic protons [15, 16]. The chemical shifting of the imine protons have been observed at □ (8.6) [17]. The 13C-NMR spectra of ligand in the DMSO has been illustrated by Fig. (6). The spectrum had shown signal at □ (14.3, 17.9, 36.2) ppm that has been assigned to the group of the methyl. Peaks that have been observed at □ (112.12ppm – 135.29ppm) have been a result of aromatic carbons [18, 19]. Azomethine carbon atom had shown peak at □ (160.58-155.8) ppm[20, 21].



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7 Spectrometer	SPECT
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12 Experiment	1D
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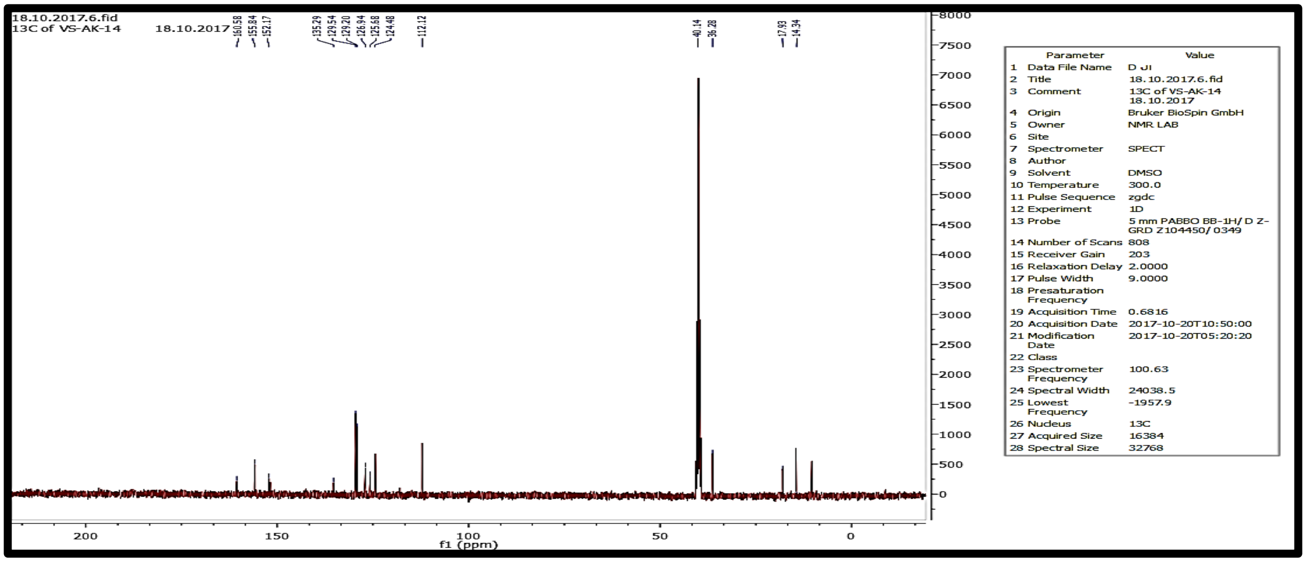
27 Acquired Size	32768
28 Spectral Size	65536

Figure (5): ligand’s 1H-NMR spectra



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28 Spectral Size	32768

Figure 6: ligand’s 13C-NMR spectrum

6.4. Electronic spectra (UV-Vis.):

Electronic spectra of synthesized ligand (L) exhibited three bands have been shown at (353 nm, 28328cm-1) that resulted from (π- π*) transition, the bands at (329nm, 30395 cm-1) for (n-π*) [22]. Electronic spectrum of complex (C1) was exhibited at (409nm, 24449cm-1) for MLCT, (337nm, 29673cm-1) assigned for intra ligand transfer of charge. The electronic spectra of complex (C2) had exhibited 3 bands at (410nm, 24390cm-1) for the MLCT, (332nm, 30120cm-1) and at (250nm, 40000cm-1) that had been assigned for intra ligand transfer of the charge. The spectrum of (C3) complex had exhibited 3 bands at (412nm, 24271cm-1) for MLCT, (330nm, 30303cm-1) and at (275nm, 36363cm-1) assigned for the intra ligand transfer of charge [23-25].

6.5. Molar conductance mesuerment:

The values of molar conductance measures of complexes have been conducted in DMSO as solvent at the temperature of the room [27] and resulting data have been listed in Table2.

Table (2): Molar condactance values of synthesized metal ion complexes

Compounds	Molar Conductance S.cm^2/moL
C_1	45.2
C_2	50.7
C_3	144.2

6.6. Nomenclature and proposed complex structures:

The proposed geometry of metal ions complexes were researched and proved via the use of the FT-IR, UVvis spectroscopy, elemental analyses (CHN), 13C-NMR and 1H-NMR, spectroscopy, molar conductance, mass spectroscopy, atomic absorption in addition to Mohr method. Based on obtained observations, metal ion complex structures have been proposed, which can be seen from Figure (7 - 9):

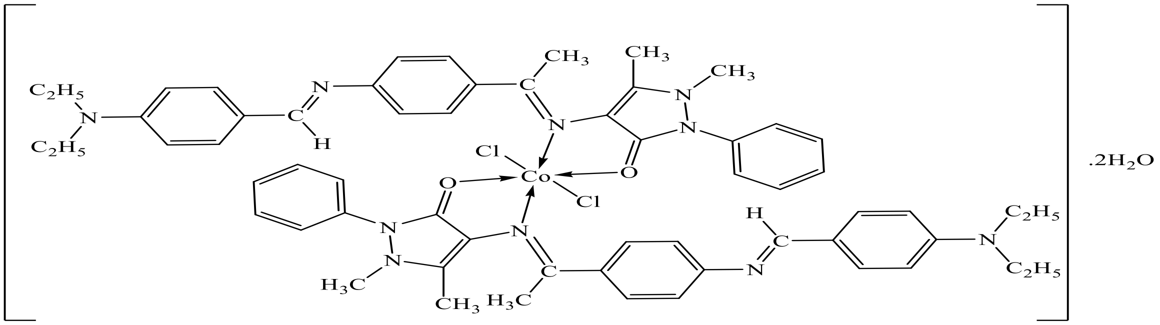

Figure 7: Structures and name of C1: bis (4-(((E)-1-(4-(((E)-4-(diethylamino)benzylidene)amino) phenyl) ethylidene)amino)-1,5- di-methyl-2phenyl-1,2- di-hydro-3H-pyrazol-3one) cobalt(II) dihydrate

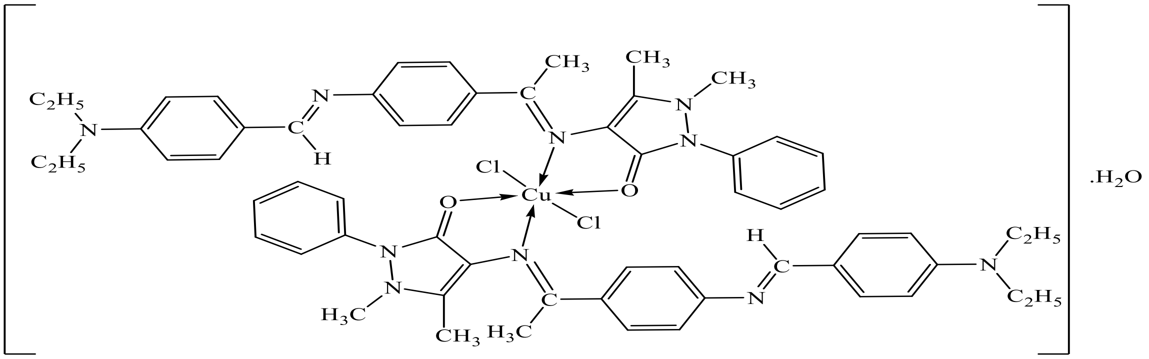

Figure 8: Structures and name of C2: bis (4-(((E)-1-(4-(((E)-4-(diethylamino)benzylidene)amino) phenyl) ethylidene)amino)-1,5- di-methyl-2phenyl-1,2- dihydro-3 H-pyrazol-3one) copper(II) monohydrate

7. Conclusions:

The (N,O) bidentate ligand was synthesized as new ligand that has been obtained from 4-aminoacetophenone, 4N,N- di-methyle amino-benzaldehyde and 4-Aminoantipyrine. All of the comolexes that were synthesized have been taken octa-hedral geometry in (1:2) molar ratio and coordinated to metal ion via O and N atoms. The magnetic suscepitibility had proven paramagntic behavior for complexes of synthesized metal ions. Co(II) and Cu(II) have been were non-electical whereas the Cr(III) had electrical behaviour based on molar conductance.

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