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Research Article

SYNTHESIS AND STUDYING OF APPLICATIONS IN (COORDINATION, CHROMATOGRAPHY, CHEMICAL MEASUREMENTS) OF HEXA: DENTATE LIGANDS IN THE COMPLEXES

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ABSTRACT

Objective: Our studying involved, synthesis of new two ligands containing six - chalet in same ligand and six - donor and their complexes with zinc ion Zn (II), all reactions included azotation reaction, imination reaction, coupling reaction.

Methods: The formatted ligands and their complexes were identified by (infrared, ultraviolet-visible [UV-VIS], H.NMR), molar conductance and melting points, chromatographic studying and other physical studying.

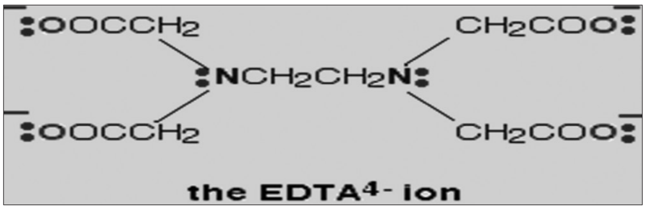
Results: The two ligands appeared good indicators and their complexes through many studies for determination of optimal conditions of complexation with mole ratio (M: L) (1:1) and the ligand (L_1) and ligand (L_2) gave octahedral shape *via* six - atoms donor.

Conclusion: The coordination through nitrogen of imine group (CH=N) and oxygen of hydroxyl group of phenol or hydroxyl group of carboxyl in complexes and the formatted compounds gave good evidences for complexation and good suggestion shape for complexes for ligands.

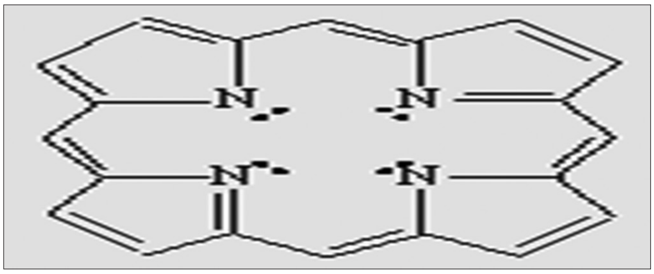
Keywords: Import, Atom, Coord.

INTRODUCTION

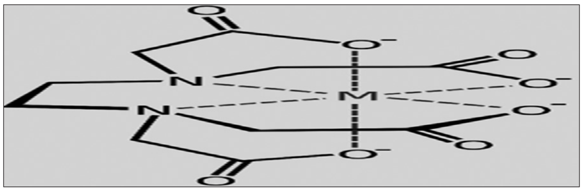
A hexa dentate ligand has 6 lone pairs of electrons - all of which give co-ordinate bonds with the same metal ion [1-3]. The best example of this type is ethylenediamine tetraacetic acid.



Cyclic ligands are those in which the donor atoms form a ring even before complex formation. An example is the porphyrin ring, modified forms of which are complexed with Fe at the O_2 binding site in haemoglobin, and with Mg in chlorophyll [4-8].



Chelating ligands may often bind in more than one arrangement, putting varying degrees of strain into the ring formed. Five or six membered rings are often favored with saturated C and N based ligands [9-13], as in the example:



Experimental

All measurements such as:

1. Melting points were determined in open capillary tube and were uncorrected
2. The infrared (IR)- spectra were recorder in KBr-disc, Shimadzu (8300)
3. Chromatography analysis
4. Ultraviolet-visible (UV-VIS)-spectra photometer
5. Molar conductance (dimethyl sulfoxide [DMSO]-solvent)
6. (H.NMR)-spectra in Canada
7. Optimal conditions
8. Thin-layer chromatography - plate.

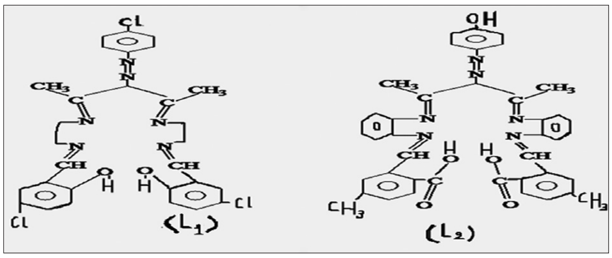
METHODS

Sythesis of first ligand (L_1)

(0.1mole) of p-chloro aniline was dissolved in (3 ml) of concentrated hydro chloric acid and (0.5 g) of sodium nitrite in temperature (0-5)°C then ethanolic solution of acetyl acetone (0.1mole) added, after (36 hrs), the precipitate was filtered and dried, which (0.1mole) refluxed with (0.2mole) of (ethylene di amine), according procedures [14-16], the precipitate were filtered and dried, which (0.01mole) refluxed with (0.02mole) of (4-chloro-formal phenol) to yield (80%) from ligand (L_1).

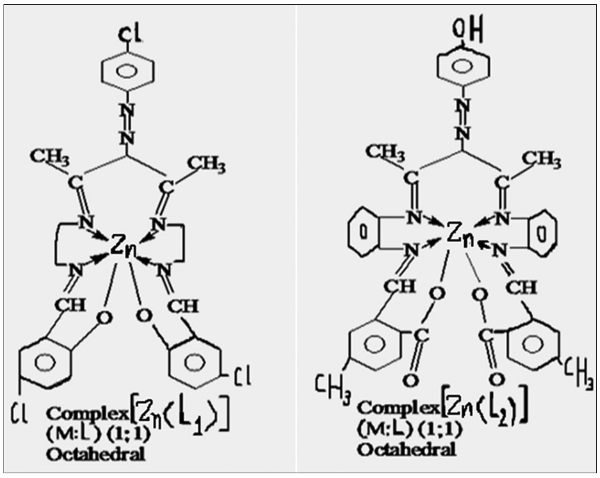
Synthesis of second ligand (L_2)

4-Hydroxy aniline (0.01mole) was dissolved in (3 ml) of hydrochloric acid and (0.7 g) of sodium nitrite at (0-5)°C, then ethanolic solution of acetyl acetone (0.01mole), after (36 hrs), the precipitate was filtered and dried, which (0.01mole) refluxed with (0.02mole) of O-phenylene diamie to produce compound, which (0.01mole) refluxed with (0.02mole) of 4-methyl -2-formal- benzoic acid for (5 hrs) according to studying [14-16], the precipitate was filtered, recrystallized from ethanol to produce 82% of ligand (L_2).



Synthesis of two complexes with ion (Zn^{2+})

According to procedures [17,18], the hot ethanolic solution of ligands ([L_1] or [L_2]) respectively was added to solution of ion salt of chloride ($ZnCl_2$) in mole ratio (metal:ligand) (1:1) respectively after stirring (2 hrs), precipitates formed, dried and recrystallized to give (78%, 84%) respectively from complexes of two ligands respectively.



RESULTS AND DISCUSSION

Hexadentate ligands fron azo - imine compounds are important ligands in coordination chemistry. The imine is basic and exhibits pi-acceptor properties in most of ligands. All ligands and complexes were identified and characterization by several methods.

Determination of condition of complexes formation

For determination of conditions of formation of complexes: The optimal conditions of complexes with ion Zn(II) were studied in this studying such as calibration curves of optimal concentration of Zn^{2+}= (0.70×10^{-4}m), while concentration of ligands (0.5×10^{-3}M of ligand [L_1], 1×10^{-3}M of ligand [L_2]), while optimal (pH=8) for the two complexes of ligand (L_1) and ligand (L_2) in base medium, and chemical identification UV-VIS. Other studies of these complexes in Table 1 and Figs. 1-6.

The formatted compounds gave good evidences for complexation and good suggestion shape for complexes for ligands in (pH=basic medium) which the two ligands able to remove their proton and coordinate with ion.

Mole ratio of complexes

Formation of complexes by job method and mole ratio method (Figs. 7 and 8) through series solutions were prepared having a constant concentration (1×10^{-3}M) of Zn salt ($ZnCl_2$) and ligand, The (M: L) ratio was determined from relationship between the absorption and mole ratio (M:L) found to be (1:1) for all complexes.

Table 1: Physical properties and UV-VIS of ligands with complexes

Ligands and complexes	M.P (C)^0	λ_{max}	Conductance Ω^{-1}.cm^2.mole
Ligand (L_1)	188	265	/
Ligand (L_2)	200	270	/
Complex [Zn (L_1)]	218	350	1.54
Complex [Zn (L_2)]	242	340	0.98

UV-VIS: Ultraviolet-visible

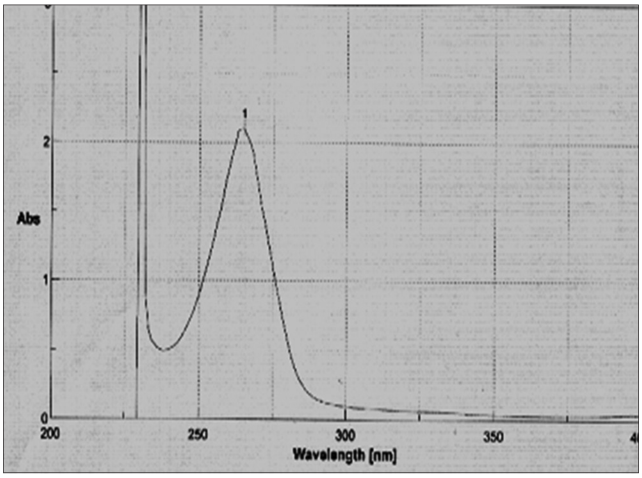


Fig. 1: Ultraviolet-visible spectrum of ligand (L_1)

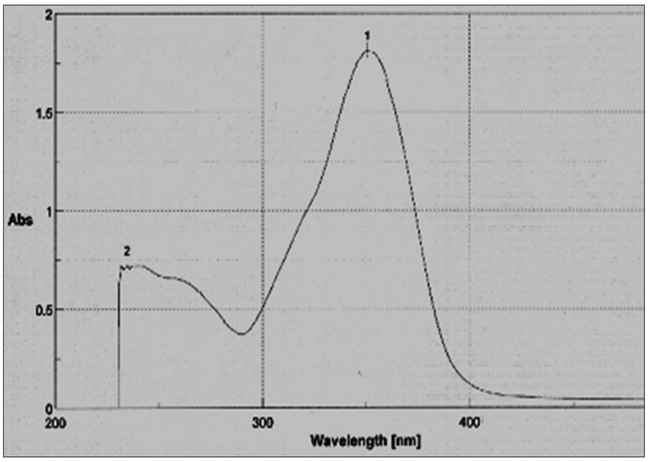


Fig. 2: Ultraviolet-visible spectrum of complex (Zn [L_1])

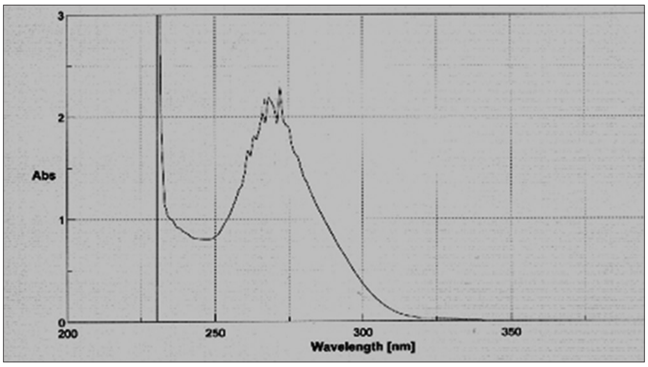


Fig. 3: Ultraviolet-visible spectrum of ligand (L_2)

All results for two complexes gave (mole ratio, calibration curve, stoichiometry, chemical spectra) indicate that the Zn- complexes with the two ligands were stoichiometry (metal:ligand) (1:1).

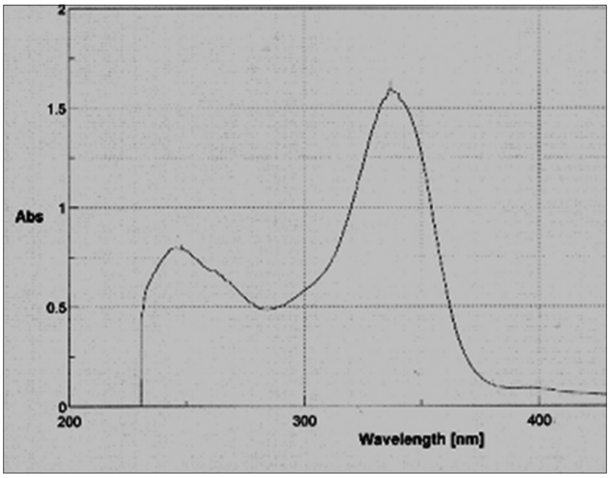


Fig. 4: Ultraviolet-visible spectrum of complex (Zn [L_2])

The conductivity

Table 1 showed all results of some physical properties were measured such as melting point, conductivity measurements which were (0.98, 1.54) ohm^{-1}.mole^{-1}.cm^2 of (1×10^{-3}M) solution in (DMSO) which indicates that the (Zn-complexes) are non-electrolytic in nature, and other property such as melting points, UV-VIS are listed in Table 1.

Spectral characterization

IR-spectra: Shown absorption bands in ligands ([L_1], [L_2]) at (2683-3151, 3406, 3410) cm^{-1} due to hydroxyl groups [15] of phenol in ligand (L_1) and hydroxyl group of carboxylic acid in ligand (L_2) respectively in free ligands which disappeared in spectra of their complexes indicating the coordination through phenolic oxygen moiety and oxygen of carboxyl group at bond (M–O) are (556-541) cm^{-1}. The IR-spectra of (Schiff bases CH=N) [15,16] respectively in ligands exhibit bands at (1629, 1634)cm^{-1} respectively, which have been shifted towards lower frequencies at (1609, 1612) cm^{-1} respectively in complexes to coordination with ion (Zn^{2+}).

The coordination through nitrogen of imine group (CH=N) and oxygen of hydroxyl group of phenol or hydroxyl group of carboxyl in complexes, Table 2 and Figs. 9-12.

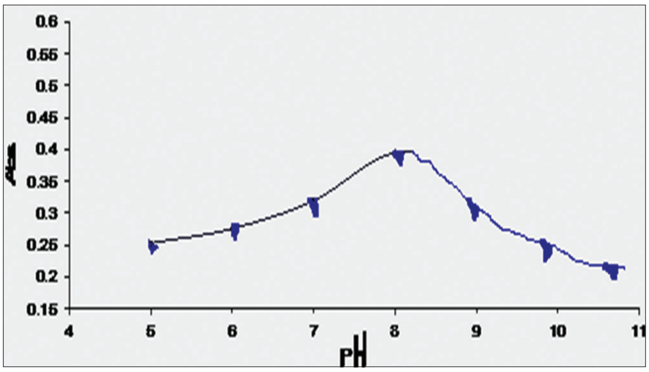


Fig. 5: Optimal pH of complex (Zn [L_1])

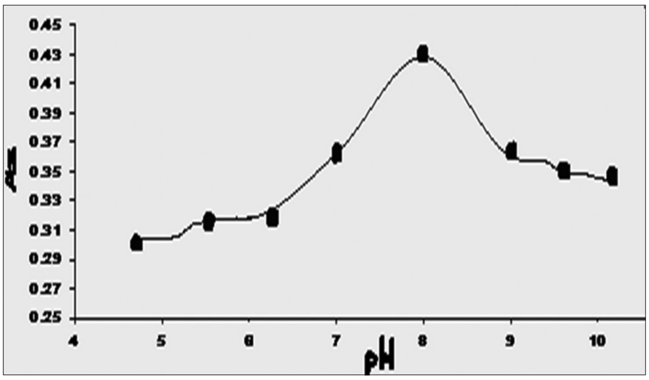


Fig. 6: Optimal pH of complex (Zn [L_2])

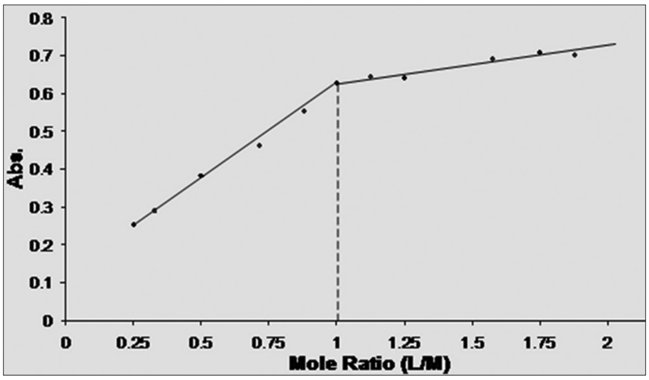


Fig. 7: Mole ratio of complex (Zn [L_1])

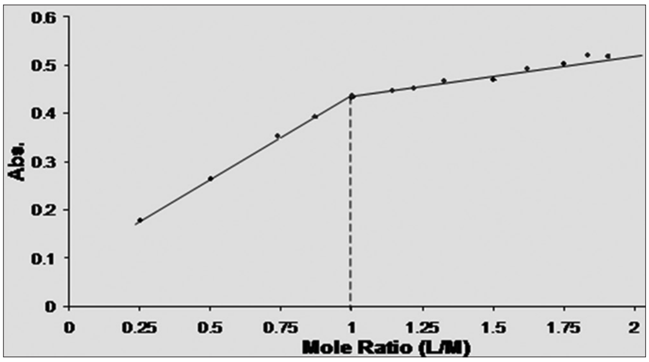


Fig. 8: Mole ratio of complex (Zn [L_2])

Table 2: FTIR data (cm^{-1}) of ligands with complexes

Ligands and complexes	(N=N) Azo group	(-C=N)	(CO-O) carbonyl of carboxyl	(-OH) carboxyl, phenol	(M-N)	(M-O)
(L_1)	1498	1634	/	3406	/	/
(L_2)	1484	1629	1731	2683-3151, 3410	/	/
(Zn [L_1])	1495	1609	/	/	474	556
(Zn [L_2])	1479	1612	1711	/3402	492	541

FTIR: Fourier transform infrared

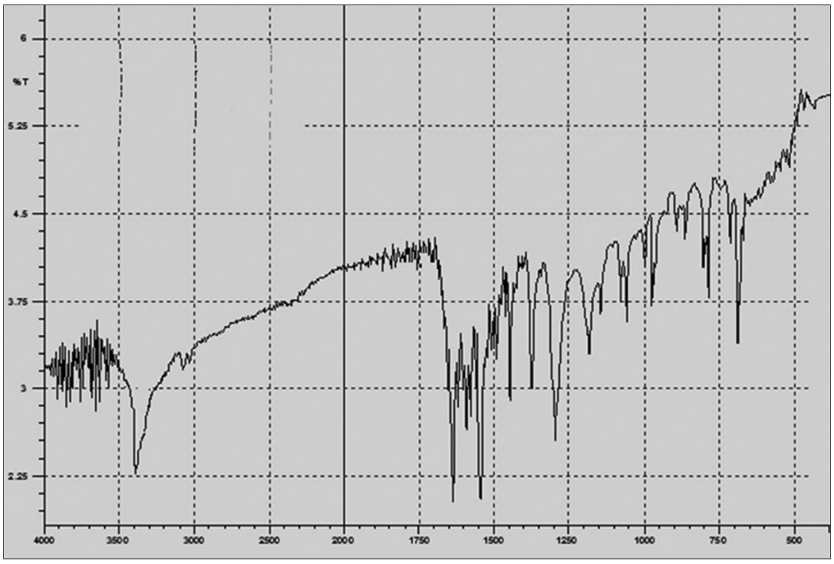


Fig. 9: Fourier transform infrared of ligand (L_1)

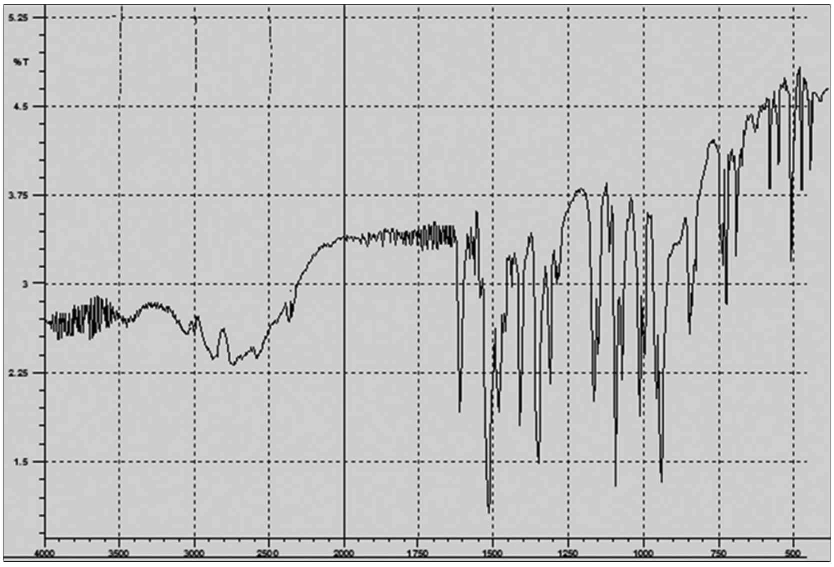


Fig. 10: Fourier transform infrared of complex (Zn [L_1])

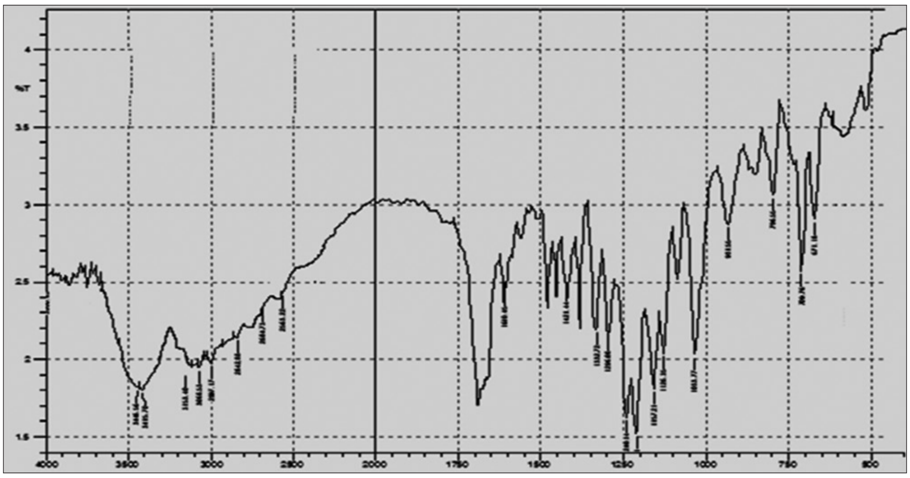


Fig. 11: Fourier transform infrared of ligand (L_2)

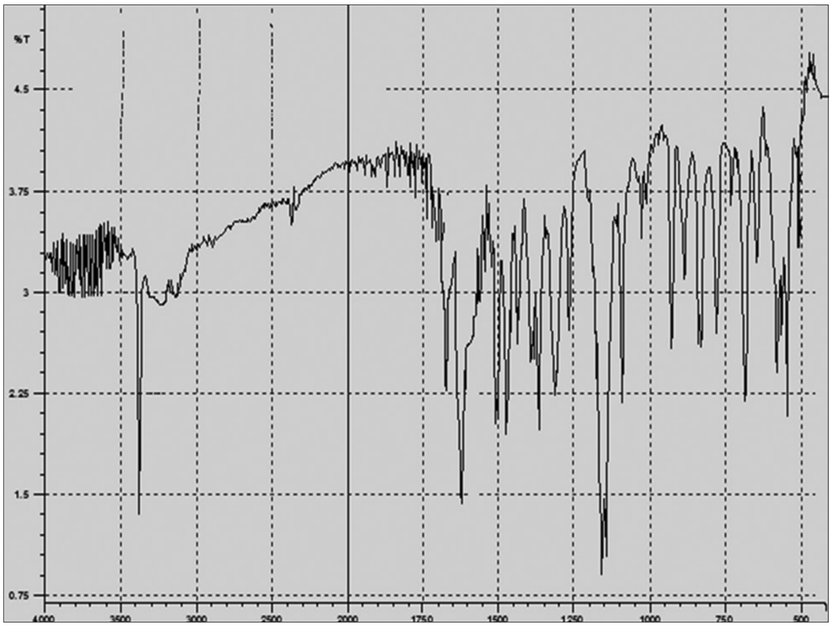


Fig. 12: Fourier transform infrared of complex (Zn [L_2])

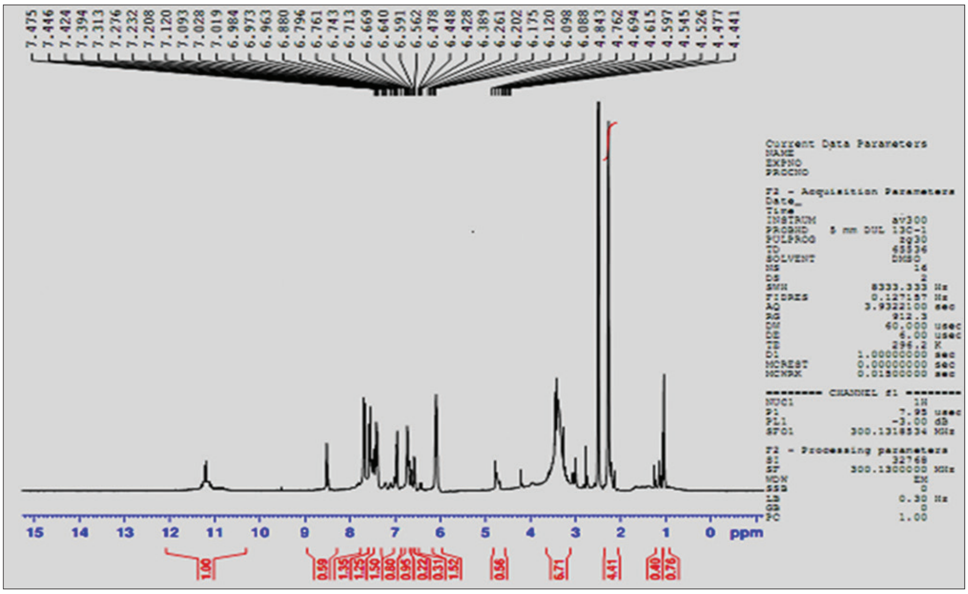


Fig. 13: H.NMR of ligand (L_1)

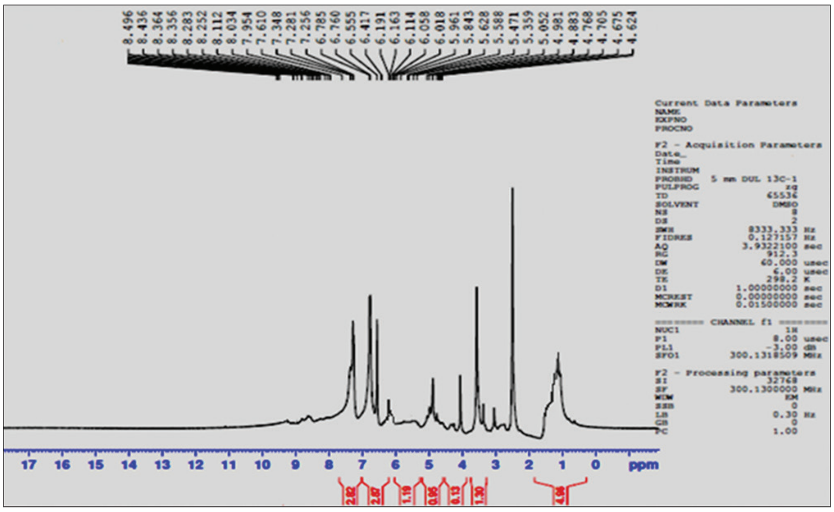


Fig. 14: H.NMR of complex (Zn [L_1])

Table 3: H.NMR data (δ ppm) of ligands with complexes

Ligands and complexes	(OH) phenol	(OH) Carboxyl	Other groups (only functional groups)
Ligand (L_1)	11.31	/	(-pH-) proton of phenyl ring: 6.64-7.47
Ligand (L_2)	11.22	13.10	(-pH-) proton of phenyl ring: 6.71-7.82
Complex (Zn [L_1])	/	/	(-pH-) proton of phenyl ring: 6.88-7.74
Complex (Zn [L_2])	11.19	/	(-pH-) proton of phenyl ring: 6.97-7.86

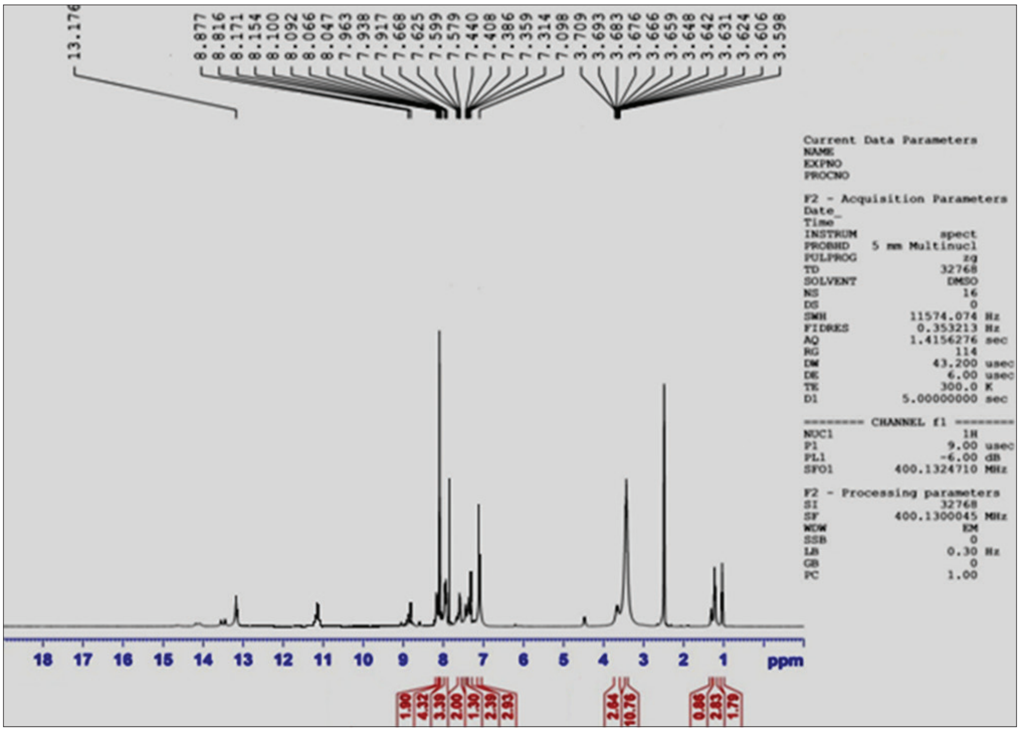


Fig. 15: H.NMR of ligand (L_2)

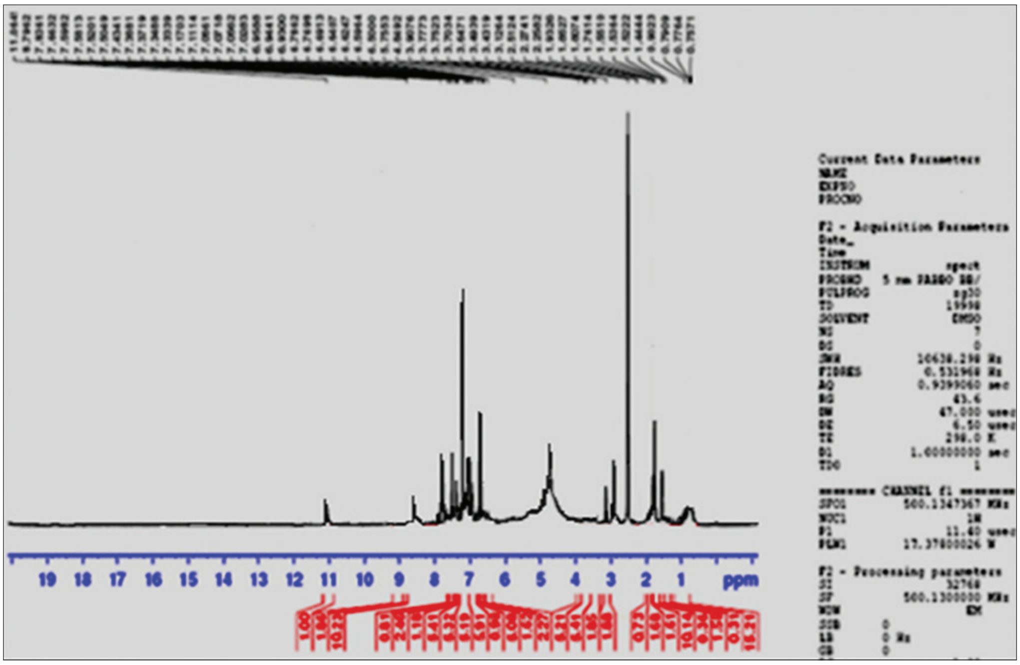


Fig. 16: H.NMR of complex (Zn [L_2])

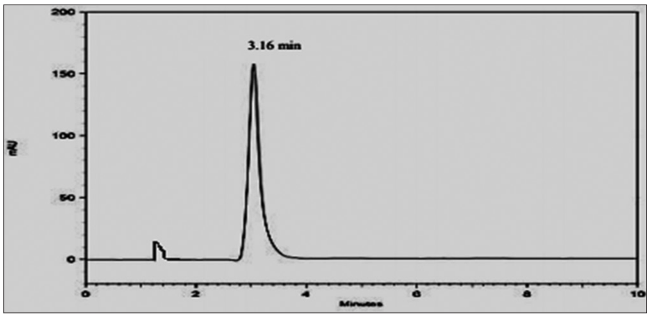


Fig. 17: Chromatogram of ligand (L_1)

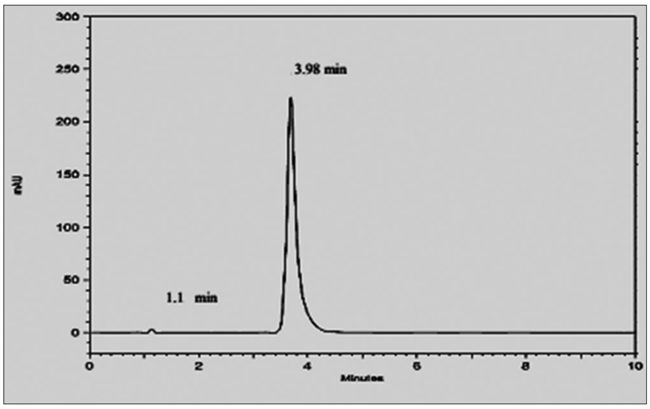


Fig. 18: Chromatogram of ligand (L_2)

All complexes appeared shifting from bands to new band result to formation of complexes with ion and suffered from change in position, intensity, shape of bands as indicators for complexes.

Studying of H.NMR-spectra: Spectra of ligands showed signals at δ (13.10, 11.19-11.31) for hydroxylgroup of phenol and hydroxyl group of carboxyl (OH) in free ligands, which disappeared in their complexes as a result of coordination with (Zn^{2+}), and other signals are shown in Table 3 and Figs. 13-16.

Studying of chromatographic application

From method of studying [19-22] we studied the chromatography behavior of the two ligands (L_1 and L_2), all data are shown in Figs. 17 and 18.

Presence of azo or imine compounds gave a wide area application in and coordination and inorganic chemistry field such as c chromatography, from the results, all compounds separated according to molecular weight and interaction between them in column through separation in chromatography column.

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