Journal of Natural Sciences Research www.iiste.org
ISSN 2224-3186 (Paper) ISSN 2225-0921 (Online)
Vol.5, No.11, 2015

Synthesis and Spectral Identification of Various New Ligands and Complexes with (Pb^{2+})

Dr. Aeed Salih Mohammed
Chemistry Dept .,Education College of Women., Al-anbar Univ., Iraq

Abstract
This paper involved ,synthesis of new four ligands & their complexes with lead ion (Pb^{2+}) have been synthesized via coupling reaction of azo compound & condensation reaction of imine compounds , the resulting compound containing azo group ($ligand_1$) linked with imine compound will react with (maleic anhydride , sodium azide , chloro acetyl chloride) to give other three ligands containing azo –heterocycles from (azo–oxazepine , azo –tetrazole , azo –azetidine), All four ligands & their complexes were confirmed by spectral studies such as{FT.IR–spectra , ^{1}H.NMR-spectra , UV.Vis –spectra , Atomic Absorption } , and physical studies such as { molar conductance ., solubility in different solvents ., measurement of melting point } , with analytical studies such as stoichiometric of complexes ., determination of optimal conditions of complexes . It has been found that the four ligands behave as tridentate donor ligands forming chelates with (1:2) (Pb**:** ligand) stoichiometry .
Keywords : optimal , conductance , coordination , donor .

Introduction :
The chemistry of hetero cyclic compounds is studied extensively because of its high synthesis and are used to design medicinal compounds [1-3] ., the chemical attempts to design & synthesize analytical reagents as a ligands which will benefit in coordination with transition metals . Heterocyclic compounds are very widely distributed in nature & are essential to life in many applications .Metal complexes of azo ligands have been studied extensively in recent years due to the sensitivity of these ligands towards various metals[4-7] . It is well known from the literature that azo compounds containing heterocycles have biological activity as antibacterial , antifungal , anticancer , anti oxidative , analgesic , anti–inflammatory ,and it gaves broad spectrum as antibacterial activity against (staphylococcus aurous , proteus vulgaris , E–coli) ., on the other hand , azo–heterocyclic compounds have applications as an effective corrosion inhibitor , applications in synthesis of polymers[5,8] & in other fields[9,10] .

This work involved synthesis of azo compounds containing heterocycles such as (oxazepine , tetrazole , azetidine) in their structures , which act as tridentate ligands with cadmium ion ., most of ligands used in coordination chemistry as chelating ligands from (-N=N-) bond & other donors .

Experimental :
All measurements were carried out by : **(UV-Vis)** –spectrophotometer., **FT.IR**-spectra , Infrared shimadzu 8300 , KBr–disc ., **^{1}H.NMR**–spectra in DMSO–solvent were carried out in **Canada** , and physical properties such as : **Molar conductance** in DMSO–solvent and **melting point** in electro thermal 9300 , LTD,U.K.

Synthesis of $Ligand_1$ [IA] :
The $ligand_1$ was synthesized according to procedures[5,11] .,2-amino imidazole (0.01mole) was dissolved in (2ml) of hydrochloric acid with solution of (0.55gm) sodium nitrite at temperature (0-5)C^o ,after this step, ethanolic solution of p-hydroxy benzaldehyde (0.01mole) was added ,after (24hrs) ,the precipitate was filtered and dried to give (84%) of azo compound which refluxed with 4-methoxy aniline for (2hrs) to yield azo-schiff compound [$ligand_1$] .,which was used in synthesis of other three ligands in this work .

Synthesis of $Ligand_2$ [IAO] :
(0.01mole) refluxed with (0.01mole) of maleic anhydride in presence of dry benzene (50ml) for (4 hrs) according to procedure[5,11] ., the precipitate was filtered and dried , re crystallized to give (88%) of $ligand_2$ [IAO] .

Synthesis of $Ligand_3$ [IAT] :
The $ligand_3$ was synthesized according to procedures[4,11] ., (0.01mole) from compound [As] which was prepared previously in first step ,reacted with sodium azide (0.01mole) in presence of (50ml) of tetrahydrofuran with reflux for (4hrs) ,the precipitate was filtered and dried , re crystallized from dioxan to give (86)% of $ligand_3$ [IAT] .

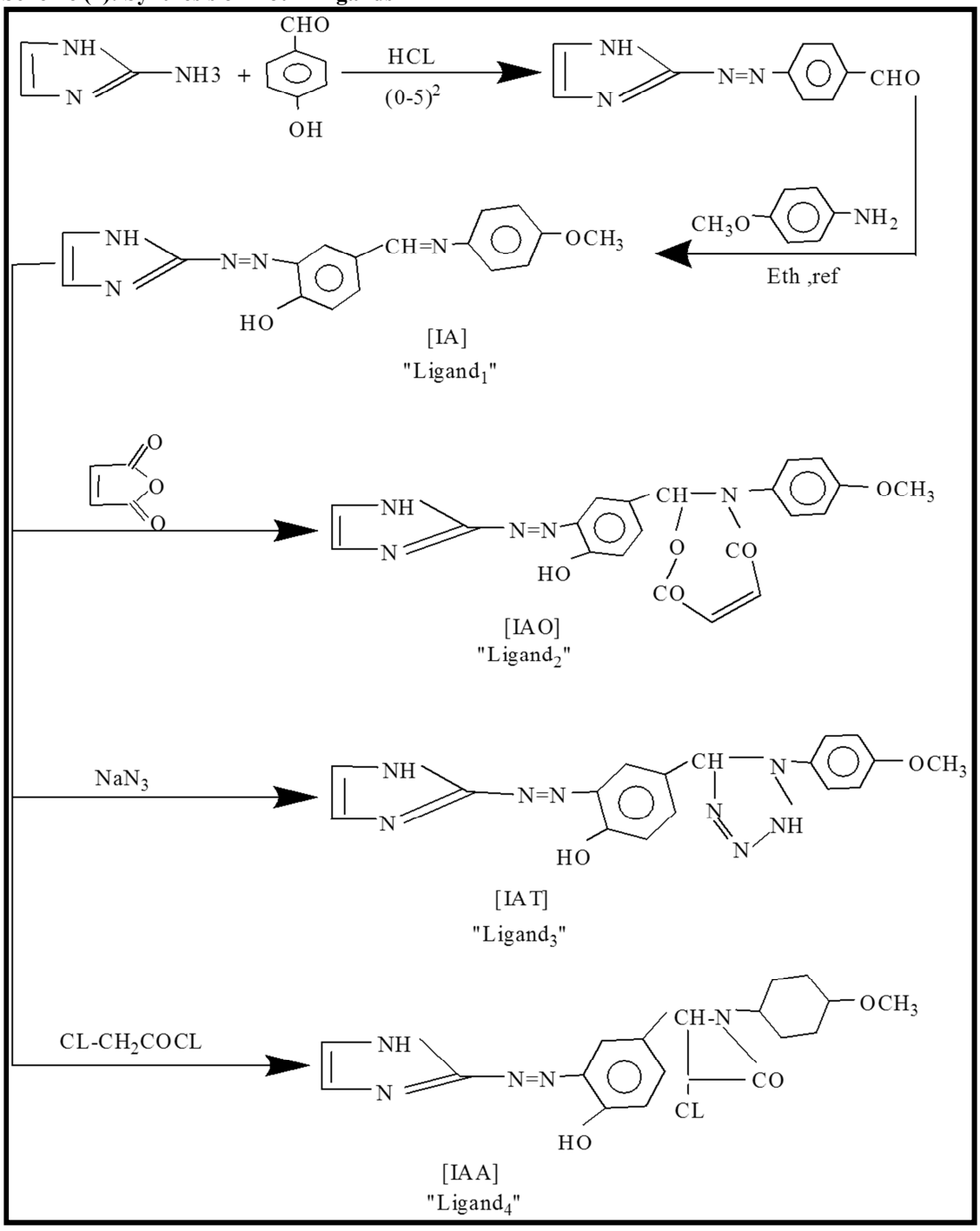
Synthesis of Ligand$_4$ [I AA] :

This ligand$_4$ was synthesized according to procedures[4,11] .,a mixture of compound [IA] (0.01mole) with (0.01mole) of chloro acetyl chloride was reacted in presence of (50ml) dioxane with trimethyl amine at (5-10)C^o ,the mixture was stirred for (4hrs) ,after that ,the precipitate was filtered and dried to yield (84%) of ligand$_4$ [I AA] .

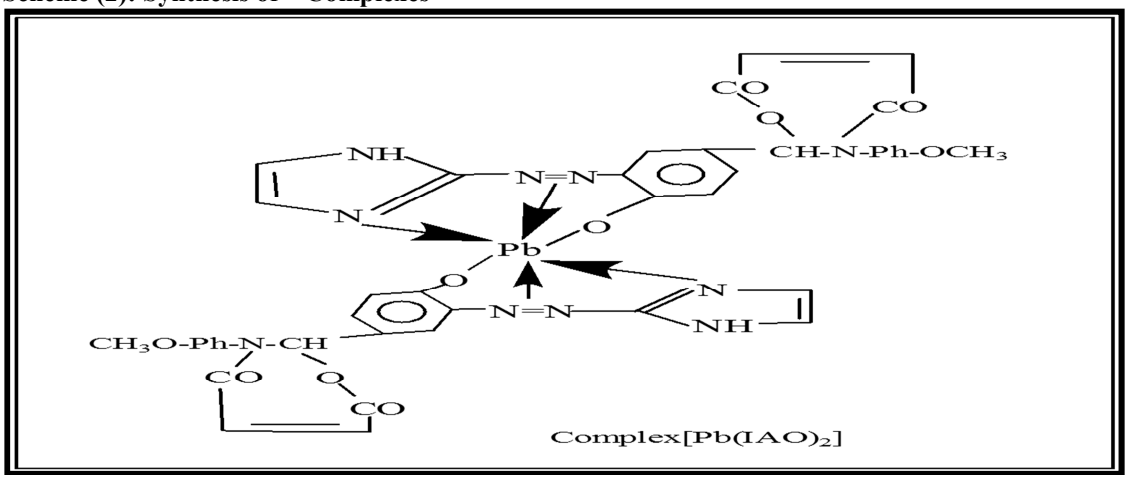
Synthesis of Complexes with (Pb^{2+}):

The complexes were prepared according to procedure[4,5] ., the hot solution of three ligands [(IAO), (IAT), (IAA)] respectively were added to solution of cadmium salt ($PbCl_2$. $2H_2O$) in mole ratio (metal: ligand) (1:2) for all complexes ., after stirring (1hrs) ,the precipitates were formed ,dried and recrystallized to give (86, 84, 84)% respectively from complexes .

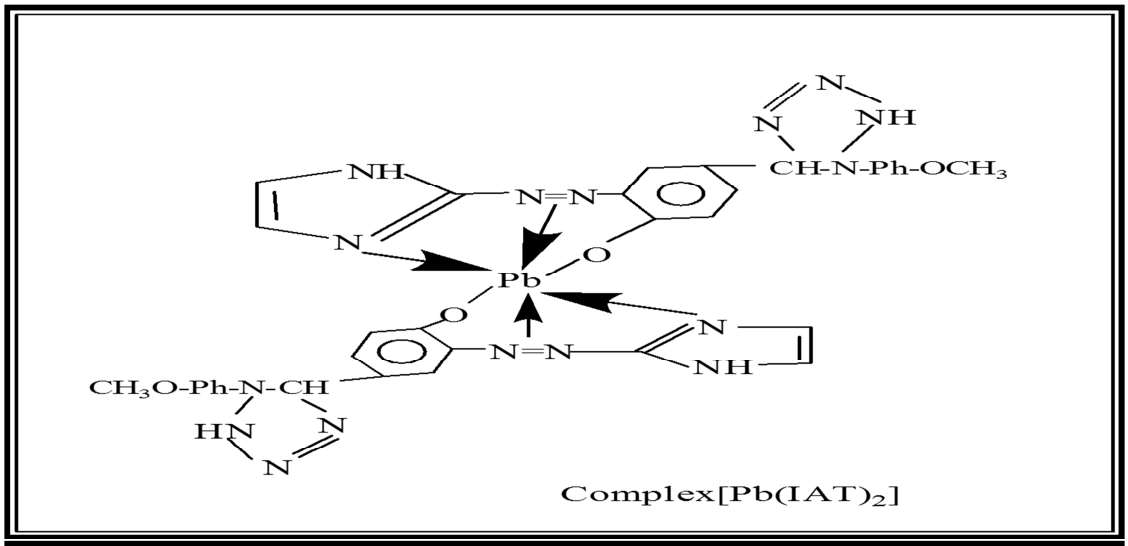
Scheme (1): Synthesis of Four Ligands



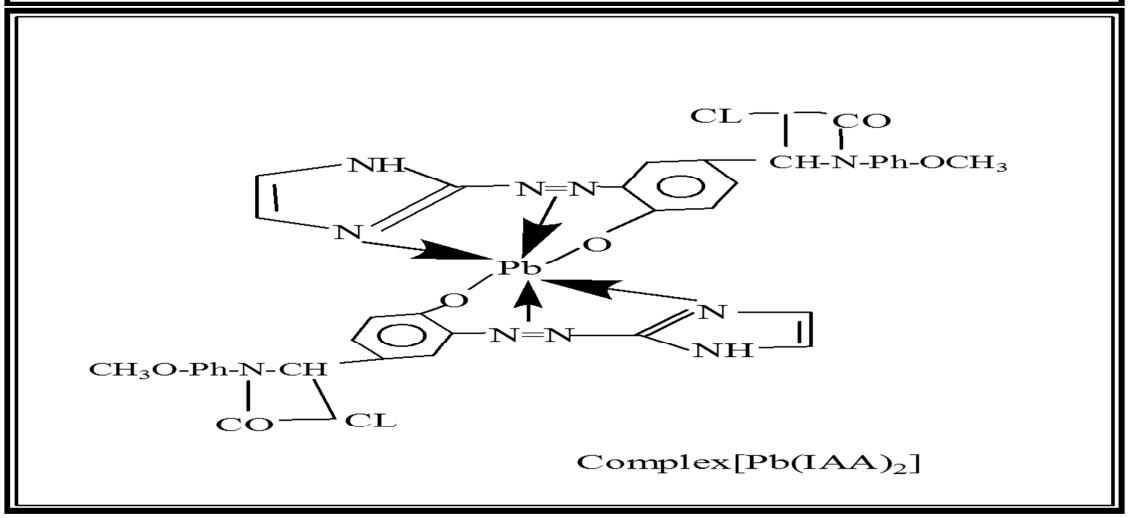
Scheme (2): Synthesis of Complexes



Complex[Pb(IAO)$_2$]



Complex[Pb(IAT)$_2$]



Complex[Pb(IAA)$_2$]

Results and Discussion :

In this work we synthesized four ligands and three complexes with (Pb^{+2}), Identification by several methods and determination of optimal conditions :

Study of optimal conditions of complexes :

This paper involved ,study of the optimal conditions of complexes with Lead ion (II) such as calibration curves of optimal concentration of (Pb^{+2} =0.7 x10^{-4}M), while concentration of ligands [0.35x10^{-3}M of ligand (IAO).,

$0.5x10^{-3}$M of ligand (IAT) .,$0.8x10^{-3}$M of ligand (IAA)] ., the optimal pH of complexes with Pb^{+2} [pH=8.0 for ligands [(IAO) ,(IAT) and (IAA)] ., mole ratio method[4,5] gave (M:L) ratio (1:2) stoichiometry for all complexes., and other studies of these complexes with their physical properties in table (1) and figures (1-4).

Important physical measurements :

From results of optimal conditions study like mole ratio method which indicate that the Pb- complexes with ligands [(IAO) ,(IAT) and (IAA)]] have stoichiometry
(metal **:** ligand) (1:2) .

The molar conductance data :

Result of conductivity gave (0.90 -1.62) $ohm^{-1}.mole^{-1}.cm^2$ of ($1x10^{-3}$M) solution in (DMSO) which indicates that the (Pb - complexes) are non-electrolytic in nature .

Table (1) : physical properties of Ligands with Complexes.

Ligands & Complexes	M.P (C^o)	λmax	Ω$ohm^{-1}.Cm^2.mole^{-1}$ conductance
(IA) $C_{17}H_{15}N_5O_2$ **Ligand$_1$**	170	352	/
(IAO) $C_{21}H_{17}N_5O_5$ **Ligand$_2$**	204	360	/
(IAT) $C_{17}H_{16}N_8O_2$ **Ligand$_3$**	180	380	/
(IAA) $C_{19}H_{16}N_5O_3Cl$ **Ligand$_4$**	194	388	/
[Pb(IAO)$_2$]	226	410	0.90
[Pb(IAT)$_2$]	240	428	1.40
[Pb(IAA)$_2$]	248	436	1.62

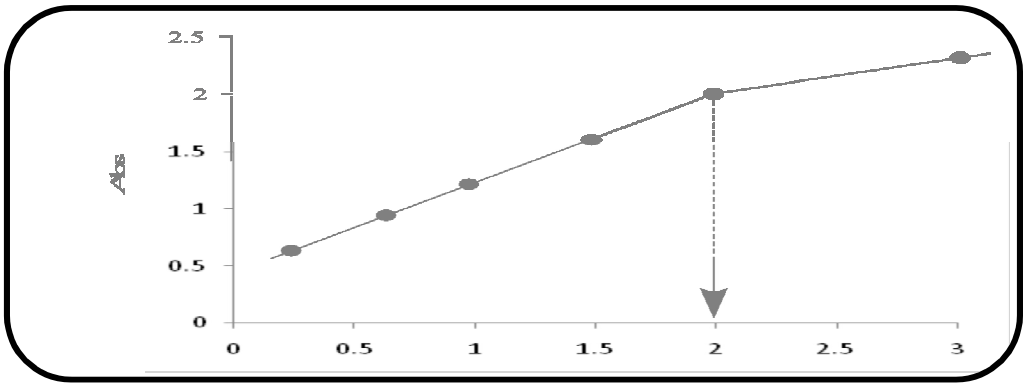


Fig. (1) : Mole ratio of Complex [Pb(IAO)$_2$]

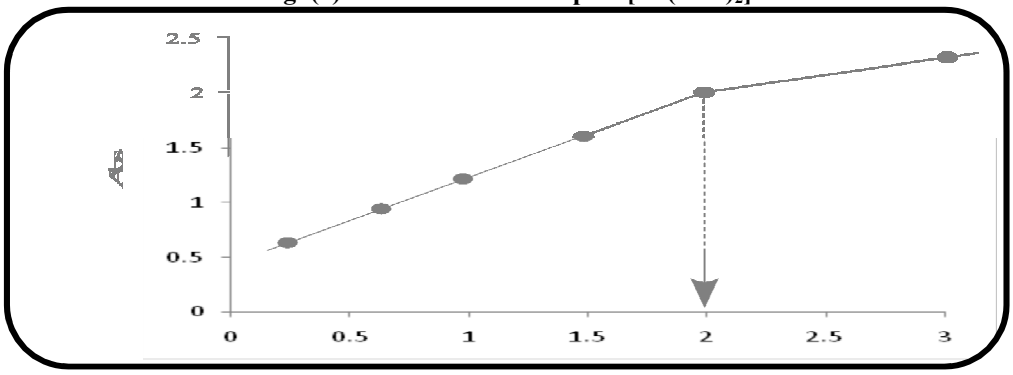


Fig. (2) : Mole ratio of Complex [Pb(IAT)$_2$]

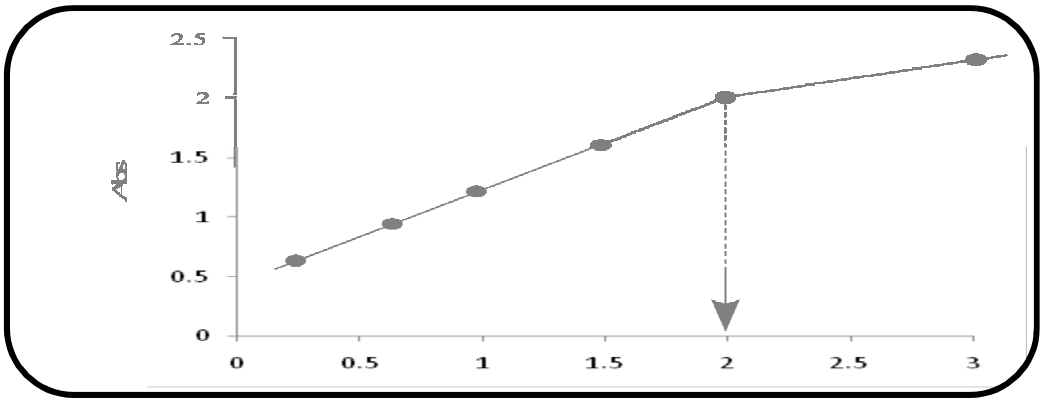
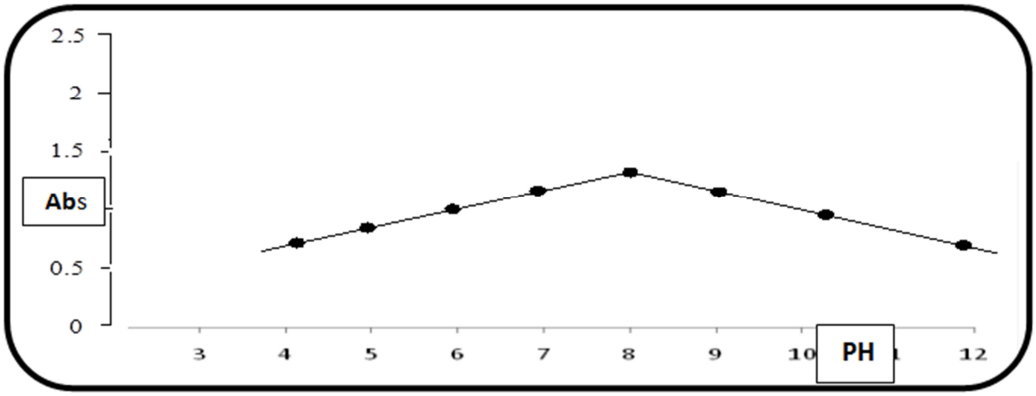


Fig. (3) : Mole ratio of Complex $[Pb(IAA)_2]$



Fig(4): Variation of PH of Complexes

FT.IR- spectra :shown absorption bands in all ligands at (3434-3412)cm^{-1} due to hydroxyl[4,12,13] group (OH) of phenol ring in free ligands which disappeared in spectra of their complexes and other bands appeared such as [(476-482) cm^{-1} and (522-566)cm^{-1}] due to [(M-N) and (M-O)] respectively in complexes as a result of coordination with lead ion (II) .,other bands at (1456-1480) cm^{-1} due to azo group[14-16] (-N=N-) in all ligands which shifted towards lower frequency at (1432-1469) cm^{-1} respectively in their complexes .,other bands in table (2) and figures (5-7) .

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

Ligands & Complexes	(-N=N-) Azo	(OH)	(M-N)	(M-O)	Other groups
(IA) $C_{17}H_{15}N_5O_2$ $Ligand_1$	1458	3412	/	/	(CH=N) :1615 ,(NH) :3250
(IAO) $C_{21}H_{17}N_5O_5$ $Ligand_2$	1464	3430	/	/	(CO-O-)Lactone:1722, (CO-N-)lactam:1696 ,(=CH) alkene : 3074
(IAT) $C_{17}H_{16}N_8O_2$ $Ligand_3$	1456	3413	/	/	(NH): 3277, (N=N-N):1289
(IAA) $C_{19}H_{16}N_5O_3Cl$ $Ligand_4$	1480	3434	/	/	(CO-N) :1692 ,(C-Cl) :790.
$[Pb(IAO)_2]$	1469	/	482	536	(CO-O-)Lactone:1717, (CO-N-)lactam:1691, (=CH) alkene :3087
$[Pb(IAT)_2]$	1447	/	480	522	(NH) :3204 ,(N=N-N): 1300
$[Pb(IAA)_2]$	1432	/	476	566	(CO-N) :1690 ,(C-Cl) :782

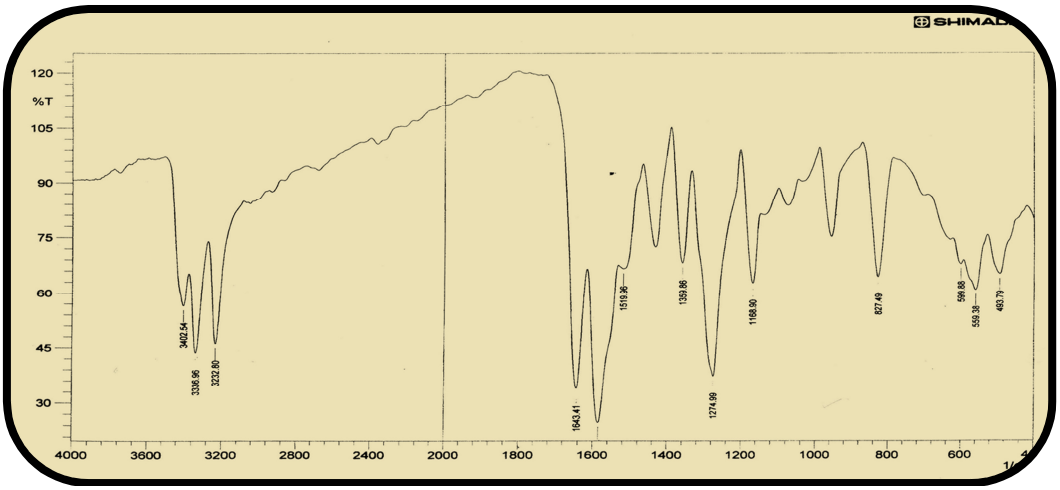


Fig (5): FT.IR of Ligand$_1$ [IA]

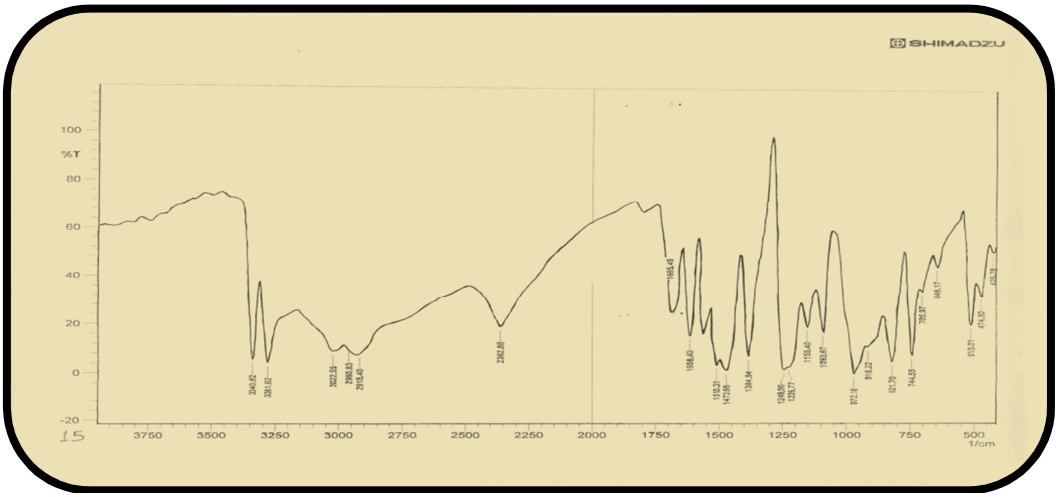


Fig (6): FT.IR of Ligand$_2$ (IAO)

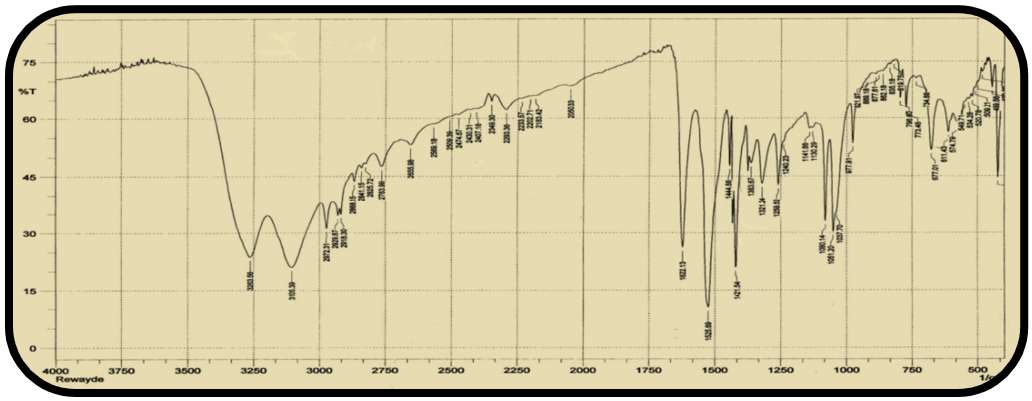


Fig (7): FT.IR of Ligand$_3$ (IAT)

H.NMR- spectra of four ligands shows peaks at δ (11.04-11.74) due to hydroxyl[4,5] group (OH) in free ligands [(IAO), (IAT), (IAA)] respectively ., which disappeared in their complexes as a result of coordination with (Pb^{2+})., and other peaks are shown in table (3) and some of figures (8 ,9) .

Table (3) : H.NMR data (δ ppm) of Ligands with Complexes .

Ligands & Complexes	(OH) phenol	Other groups ((only functional groups))
(IA) $C_{17}H_{15}N_5O_2$ Ligand$_1$	11.74	9.02(NH)imidazole **.,** 8.55(CH=N)imine group.
(IAO) $C_{21}H_{17}N_5O_5$ Ligand$_2$	11.33	2.76(O-CH-N) **.,** 4.12, 4.33(CO-CH=CH-CO)**.,** 9.11(NH)imidazole **.,**
(IAT) $C_{17}H_{16}N_8O_2$ Ligand$_3$	11.12	2.86 (N-CH-N) ., 9.75 (NH) .
(IAA) $C_{19}H_{16}N_5O_3Cl$ Ligand$_4$	11.04	3.75 , 3.51 (N-CH-CH-Cl) . 9.02(NH)imidazole **.,**
[Pb(IAO)$_2$]	/	2.65(O-CH-N) **.,** 4.0 , 4.26(CO-CH=CH-CO) ,9.21(NH)imidazole **.**
[Pb(IAT)$_2$]	/	2.71 (N-CH-N) **.,** 9.30(NH)imidazole **.,**
[Pb(IAA)$_2$]	/	3.00 , 3.19 (N-CH-CH-Cl) **.,** 9.36(NH)imidazole **.,**

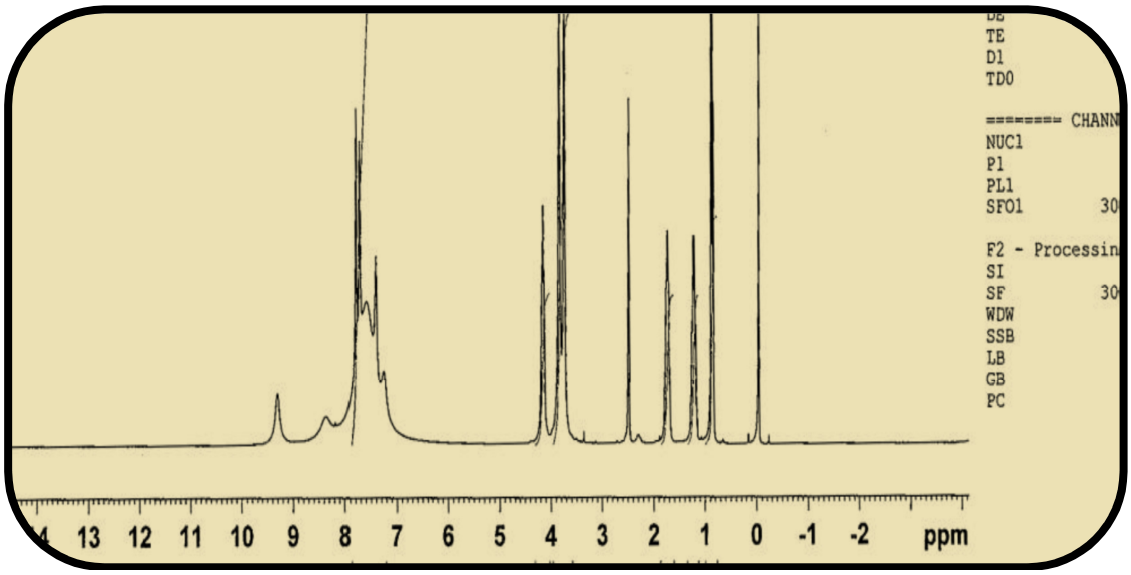


Fig (8): H.NMR of Complex [Pb (IAO)$_2$]

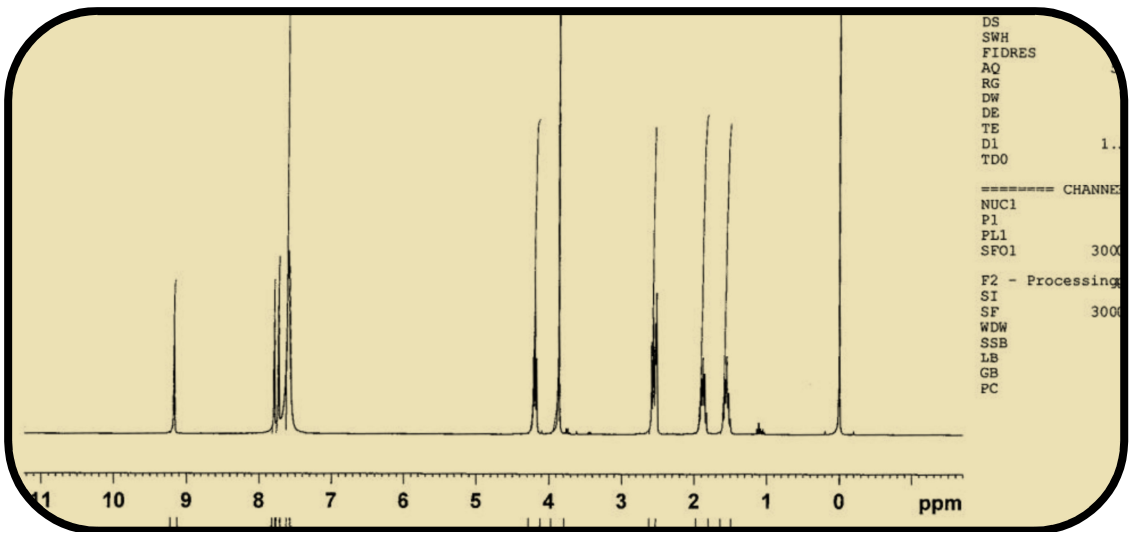


Fig (9): H.NMR of Complex [Pb (IAA)$_2$]

The suggestion figures of complexes:
The results of studies indicate that the ligands [(IAO), (IAT), (IAA)] are tri dentate ,the coordination through nitrogen of azo group (-N=N-) and oxygen of hydroxyl group[4,17] with nitrogen atom of imidazole ring to give octahedral geometry (6-coordination[4,5,10] complexes) in form (ML_2) .

Solubility of ligands in different solvents :
The solubility of all ligands was studied in different solvents according to polarity of solvents , the results are shown in table (4).

Table (4) : Solubility of ligands in Various Solvents.

Ligands	Solvents					
	Ethanol	Methanol	DMSO	Benzene	Dioxane	THF
(IA)	+	+	+	-	-	-
(IAO)	+	+	+	+	+	+
(IAT)	+	+	+	+	+	+
(IAA)	+	+	+	+	+	+

Reference

1. Anitha, K.R.Venugopala Reddy and VittalaRao K.S. ., J.Chem.Pharm.Res.,3(3):511-519,(2011).
2. Atmaram .K and KIiran .V., Int .J. J. chem. Tech .Res., 3,2, 636-641 (2011).
3. Fabio .B, Reda. M , Zahra .M, Angle .T and Barsella. A., J. Dyes. Pigm., 96, 45-51 (2013)., Cited by IVSL of Iraq* .
4. Nagham. M. Aljamali., Asi .J. Resch., 7,2, 225-231 (2014) .
5. Nagham. M. Aljamali , Miead.M and Hanaa .K and Athraa .A., PharmaBitika. ,1,1, 102-114, (2014) .
6. Abd. T and Abadi .A. ,As .J. Resch., 7,5, 530-537 (2014) .
7. Mehdi. H., world .J. Medc. Medl . Scires., 2,2, 26-34, (2014) .
8. Huda .S., Global .J. Org and Inorg ., 2,1, 1-10 (2014) .
9. Abed .T, Jawad. G and Mohammed .F ., Int .J. Multi Res. Devp., 1,1, 41-45 (2014) .
10. Miad .H., Merit. Res. J. EnvSci .Tox., 2,1,1-8 (2014) .
11. Nagham. M. Aljamali., World .J. Pharm and Pharml. Sci.,3,6,338-351,(2014).
12. Narjis .N and Muhamed .Z., Sci. Int. Lahore., 23,1, 27-31 ,(2011) .
13. Suueed .K, vamsi. A, Tatendra .K., Omprakash. G., J. Chem. Pharm. Res., 3,5, 234-252 (2011) .
14. Noaimi .M, Sunjuk .M , Khateeb .M, Salim .F., Haniyeh .A and Murad .D., Polyhedron ., 42, 66-73 , (2012) .
15. Varadaraj .D , Suban .S., Kubaran .K, Kasi.R., Ramas .V., Palusa .S., Nalilu .K and Hari .N ., J . Serb.Chem. Soc., 76, 2, 165-175 ,(2011) .
16. Adnan .S , Kasim.H, Thamer .H., As. J. Resch., 7,3,251-255 (2014).
17. Miad . H ., J.,INNO. J .Sci., 2,1 , 1-5 , (2014) .

The IISTE is a pioneer in the Open-Access hosting service and academic event management. The aim of the firm is Accelerating Global Knowledge Sharing.

More information about the firm can be found on the homepage:
http://www.iiste.org

CALL FOR JOURNAL PAPERS

There are more than 30 peer-reviewed academic journals hosted under the hosting platform.

Prospective authors of journals can find the submission instruction on the following page: http://www.iiste.org/journals/ All the journals articles are available online to the readers all over the world without financial, legal, or technical barriers other than those inseparable from gaining access to the internet itself. Paper version of the journals is also available upon request of readers and authors.

MORE RESOURCES

Book publication information: http://www.iiste.org/book/

Academic conference: http://www.iiste.org/conference/upcoming-conferences-call-for-paper/

IISTE Knowledge Sharing Partners

EBSCO, Index Copernicus, Ulrich's Periodicals Directory, JournalTOCS, PKP Open Archives Harvester, Bielefeld Academic Search Engine, Elektronische Zeitschriftenbibliothek EZB, Open J-Gate, OCLC WorldCat, Universe Digtial Library , NewJour, Google Scholar