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Synthesis, characterization and thermal study of the new Schiff base ligand derived from pyrazole with cobalt, nikel copper, zinc, cadmium and mercury complexes

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ABSTRACT :

In this research, a new series of transition metal complexes 0f cobalt, copper, zinc, cadmium and mercury in their divalent states were prepared using Schiff bases. The new Ligand Schiff base named [(Z)-4-((3-chloro-benzylidene) amino)-1,5-di-methyl-2phenyl-1,2dihydro-3H-pyrazol-3one] Aseries of new metal complexes of common molecular formula $[M(L)_2H_2OCl].H2OCl$ and $[M(L)_2Cl_2]H_2O$ had been synthesized and identified by the infra-red, UV-Visible spectra, elemental analyses, atomic absorption, chloride content, mass spectra, magnetic susceptibility and conductivity measurements in addition to the thermogravimetric analysis (TGA, DSC). In consistence with magnetic spectral researches' results, the proposed geometrical structures for all produced complexes were octa-hedral formulas.

KEY WORDS : pyrazol, acitic acid, benzaldehyde.

تحضير وتشخيص ودراسة حرارية لليكاند قاعده شف الجديد المشتق من البايرازول ومعقداته مع بعض الايونات الفلزية

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مستخلص:

يتضمن هذا العمل تحضير وتشخيص قاعدة شف (L) (Z)-4-((3-chlorobenzylidene)amino)-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one من مفاعلة 3- chlorobenzaldehyde و 4- amino-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one حيث تم تحضير سلسلة جديدة من معقدات المعادن الانتقاليه من الكوبلت والنحاس والزنك والكادميوم والزئبق في حالاتها ثنائية التكافؤ باستخدام قواعد شف تم تحضير سلسلة من معقدات معدنية جديدة ذات صيغة جزيئية مشتركة $M(L)_2H_2OCl].H2OCl$ and $[M(L)_2Cl_2]H_2O$

وتشخيص المعقدات بواسطة الطرائق التطبيقية والتحليلية ، مطيافية الاشعة تحت الحمراء (FTIR)، مطيافيه الاشعة الفوق البنفسجية المرئية (UV-Vis)، مطيافيه الرنين المغناطيسي (HNMR)، طيف الكتلة (GC-mass)، التحليل الدقيق للعناصر (C.H.N.O.Cl)، التحلل الحراري الوزني (TGA-DSC) فضلاعن قياس الذوبانية ، قياس درجه الانصهار .

Introduction

The schiff base composites have been considered with azomethine group(-CH=N-) presence as per the reflux consequences amongst ketone or aldehyde with the primary amin1. Studies had exhibited that azo-methine group(-CH=N-) represents donor-acceptor group and is an acceptor via π- orbital of double bond; and donor through nonacceptor of the electrons to nitrogen atom of this group [2]. Schiff base can be derived from benzaldehyde or its derivative complexes with the aniline or aniline derivatives Schiff base molecule is not even, as benzene ring that is attached to atom of nitrogen is outside the remaining molecule's level, and it had turned out that compensators on molecule of the benzaldehyde are of a higher influence in electronic distribution when compared to compensators on the cycle of aniline [3]. Mainly, the Schiff bases move unlike other zones such as pharmacology as anticancer agents [4]. In addition to that they're applied in the manufacture of things, such as thermal Ignitions in Radical polymerization [5].

Materials and Methods

Preparing metallic complexes [Co(II), Cd(II), cu(II), Hg(II) and Zn(II)] via ligand(L), chelate facilities of the ligand and the metal (1:2) have been arranged through dissolving (0.20g) of Schiff base in 10.0ml of the solvent. Consistent hydrated metal Chloride salt of $CoCl_2 . 6 H_2O$= 0.073g, $CuCl_2.2H_2O$= 0.292g, $HgCl_2$=0.083, and Cd $Cl_2.H_2O$=0.06g has been liquified in the absolute ethanol 10ml varied with ligand solvent and refluxed for a duration of 3hr on the contents cooling. The produce has been filtered, and after that, they had been splashed with the solvent and de-hydrated after that below the vacuity.

All of the composites that were utilized have been of the highest levels of the BDH Fluka purity.

Instrumentation

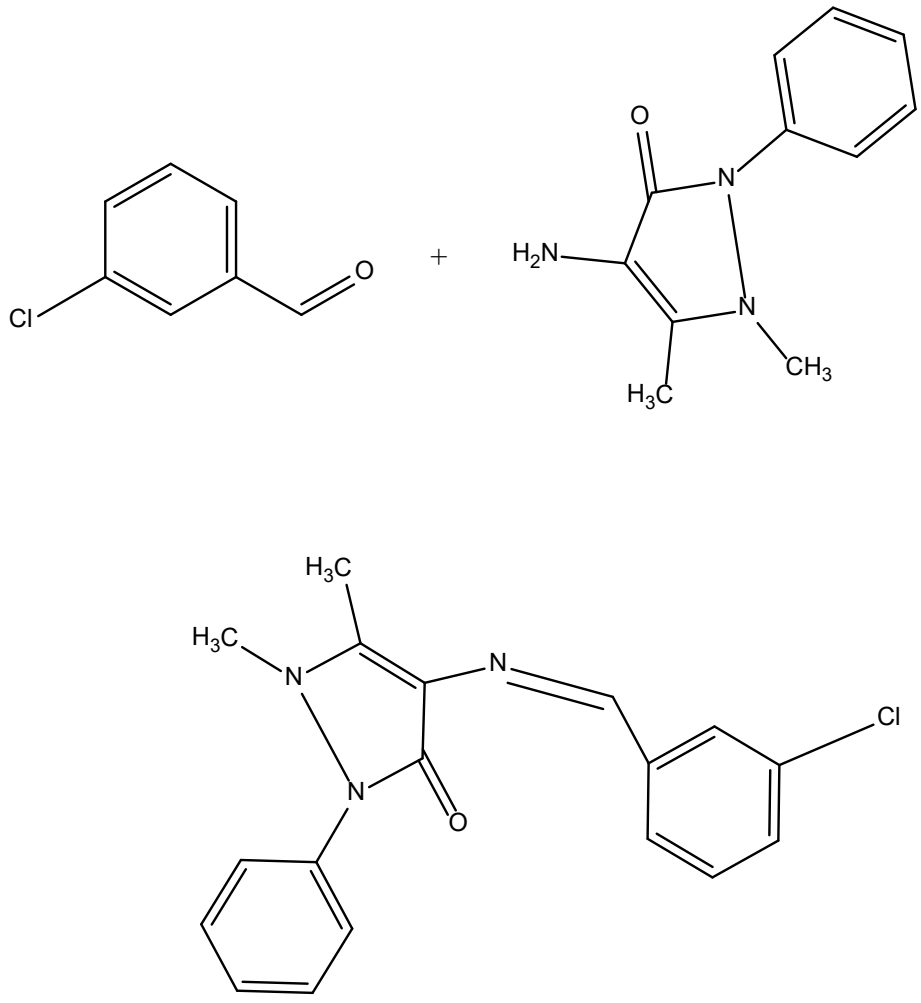
TGA-DSC has been characterized then analyzed, FT-IR-Spectra have been recorded on the shimadzu 8400s in arrange of 400cm-400cm with the use KBrdisk. Analyzed CHN was accomplished on Euro-EA Eiemental and

H-NMR spectra were chara cterized

Facility Preparations

Preparations of New schif base ligand [(Z)-4-((3chlorobenzylidene) amino)-1,5-di-methyl-2phenyl-1,2 dihydro-3H-pyrazol-3one

In a round bottom flask, 3-chloro benzaldehyde(0.344g) in 5 ml acetic acid and 4-amino antipyrin (0.5g)in 10.0ml ethanol has been refluxed for 5h [6]. After that, the reaction flask has been kept in freeze bath for a number of records, followed by pale green precipitate and letting it dry, which has given precipitate that has Golden yellow color. The ground work of the Schiff base can be depicted in scheme1.



Scheme1: Preparation of Schiff base ligands

Results and discussion

Elemental analysis

Some analytical and physical ligand properties in addition to its complexes have been examined, aimed to find chloride content.

Table1: Physical properties and analytical data of ligands in addition to their complexes

NO.	Compound	Colour	M.P. (oC)	M.wt	Calc./Found% M	C	H	N	O	Cl
1	L	Golden yelow	261-263	325.8		10.896	4.911	12.911	4.9119	10.896
						10.711	4.89	12.88	4.87	10.87
2	[Co(L)2H2OCl]. H2O.Cl	Pale olive green	240-242	817.53	7.302	52.876	4.403	10.2748	7.8285	8.6846
					7.300	52.85	4.38	10.25	7.80	8.64
3	[Ni(L)2 Cl2]. H2O	Pale green	200-202	799.50	7.34	54.0317	4.1275	10.5065	6.00375	8.8805
					7.31	54.00	4.10	10.48	6.00	8.85
4	[Cu(L)2Cl2]. H2O	Radish brown	116-118	804.146	7.9022	53.7215	4.22808	10.4458	5.969	8.82924
					7.900	53.70	4.20	10.41	5.94	8.80
5	[Zn(L)2Cl2]. H2O	Pale green	>300	627.18	8.118	53.599	4.2184	1.2930	5.95548	8.8091
					8.002	53.596	4.2	10.27	5.935	8.800
6	[Hg(L)2H2O Cl]. H2O Cl	Broun nutty	235-236	959.192	20.912	45.0379	3.753	8.757	6.667	7.40206
					20.88	45.00	3.73	8.72	6.63	7.39

FTIR of the Ligand and facilities

IR spectral data of the Schiff base ligand as well as their complexes can be listed in table2. Infra-red spectra of complexes were equated with those of free ligand for the purpose of regulating sites coordination, which could be complicated in the chelation. The band in the infrared spectrum of free ligand at 1647 cm was transferrable to stretching shaking carbonyl group of Schiff base ligand which has been lifted to a lower level of the frequency in the Infra-red spectra of the facilities at 1168 cm-1. Band appearance in (462-444)cm-1 range in infrared spectra of all facilities had resulted from validates of υ(M-O) [7]. A band at (1614cm-1) in infrared specta of free ligand might be due to imine group υ(C=N) stretching vibration that has been altered to higher or lower level of the frequency; in infrared spectra of facilities of Nickel(II), Co(II), and Zn(II),Cd(II) and Hg(II) rose in to higher level of frequency, whereas Cu(II) facilities had fallen to a lower level of frequency that had been specified for harmonizing ligand with the metal ion through N atom [8]. Which has later been validated by presence of an original band in (545-516cm-1) range that is transferrable to the υ(M-N) [9,10]. It has been established that the ligand had played a part of the bi-dentate ligand that is harmonized to the metal ions via O atom of carbonyl group of the benzaldehyde and N atom of the imine group for all of the facilities

Table2: Properties of infra-red bands of the absorption of ligand (L) in addition to its complexes in cm^{-1}

Compound	υOH	υ (C=O)	υ(C=N)	(C-N)	(M-N)	(M-O)
L	3192	1647	1614	1067		
$[Co(L)_2 H_2 O Cl].H_2O Cl$	3412	1645	1592	1077	512	444
$[Ni(L)_2 Cl_2].H_2O$	3221	1643	1566	1079	500	433
$[Cu(L)_2 Cl_2].H_2O$	3158	1678	1651	1093	545	462
$[Zn(L)_2 Cl_2].H_2O$	3278	1645	1617	1079	510	444
$[Hg(L)_2H_2 O Cl].H_2O Cl$	3374	1645	1592	1700	516	444
$Cd(L)_2 Cl_2 H_2 O$	3194	1645	1617	1076	509	446

U.V-Vis

UV-vis of ligand and its (co), (Cu), (Zn), (Ni), (cd) and mercury facilities have been measured and spectral data have been registered as can be seen in table3. u.v-vis of chiff base ligands had been described mainly by 3 absorption top at (277nm)consignd to (329nm) that has been allocated have been lifted to lower or higher frequencies in electronic spectra of all set complexes.

Table3: UV-Visible spectra of the ligand in addition to its chelate facilities

Compounds	λnm	ῡ(cm^{-1})	ε_{max} L/mol·cm	Transitions	Proposed geometric shape
[Co(L)$_2$ H$_2$OCl].H$_2$O.Cl	241	414937	1600	Intra-ligand	Octa-hedral
	314	31847	800	Intra-ligand	
	362	27624	880	Intra-ligand	
	487	20533	50	$^4T_1 g_{(F)} \rightarrow {}^4T_1 g_{(p)}$	
	625	16000	220	$^4T_1 g_{(F)} \rightarrow {}^4A_2 g_{(f)}$	
	663	15082	300	$^4T_1 g_{(F)} \rightarrow {}^4A_2 g_{(f)}$	
	690	14492	310	$^4T_1 g_{(F)} \rightarrow {}^4T_2 g_{(F)}$	
[Ni(L)$_2$ Cl$_2$].H$_2$O	371	26954	1120	Intra-ligand	Octahedral
	655	152671	75	$^3A_2 g_{(F)} \rightarrow {}^3T_1 g_{(P)}$	
	689	14513	6500	$^3A_2 g_{(F)} \rightarrow {}^3T_1 g_{(F)}$	
	896	11160	20	$^3A_2 g_{(F)} \rightarrow {}^3T_2 g_{(F)}$	
[Cu(L)$_2$ Cl$_2$].H$_2$O	384	26041	520	Intra-ligand	Distorted Octa-hedral
	776			Intra-ligand	
	857	11668	40	$^2B_{1g} \rightarrow {}^2Eg$	
	980	102040	60	$^2B_{1g} \rightarrow {}^2B_{2g}$	
Zn(L)$_2$ Cl$_2$] H$_2$O [	313	31948	2030	Intra-ligand	
	362	27624	2040	Intra-ligand	
	450			C.T	
[Hg(L)$_2$H$_2$ OCl].H$_2$OCl	359	27855	210	Intra-ligand	Octahedral
	342	29239	180	Intra-ligand	
	455			C.T	
[Cd(L)$_2$ Cl$_2$]H$_2$O	313	31948	2030	Intra-ligand	
	362	27624	2040	Intra-ligand	
	450			C.T	
	978	10224	40		

MAGANETIC MEASUREMENT Conductivityand

For Schiff base metal complexes that have the general formula[$ML_2 Cl_2$] H_2O,[$ML_2 H_2 OCl$]H_2O Cl, The data of molar conductance calculated at room temperature in ethanol changed from 11.6to 57 S cm2/mol that revealing non- electrolytic kind of complexes.

Table (4): molar conductivityand MAGANETIC MEASUREMENT of complexes.

No.	Complex	μ_{eff} (BM)	Conductivity | µS/cm	Ratio
1	$[Co(L)_2H_2OCl].H_2O$ Cl	**3.865**	**57**	1:1
2	$[Ni(L)_2Cl_2].H_2O$		**25.5**	Neutral
3	$[Cu(L)_2Cl_2].H_2O$	**3.0263**	**26**	Neutral
4	$[Zn(L)_2Cl_2].H_2O$	**0.00**	**11.6**	Neutral
5	$[Hg(L)_2H_2OCl].H_2O$ Cl	**0.00**	**43**	1:1
6	[Cd $(L)_2$ Cl_2].H_2 O	**0.00**	**21**	Neutral

GC-mass of the ligand and the complexes

Electro-spray mass spectra of ligand shows parent ion top at the value of (M/Z) = (325) inconsistence with [M+], other rubbles and their similar pattern of disintegration and abundance was proposed. The electrospray mass spectra of Co(II) complexes shows the parent ion top at the value of (M/Z)=(817) that had been in agreement with [M+], other parts and their comparative abundance and disintegration configuration has been exposed. Electrospray mass spectra of Ni(II) complexes had confirmed parent ion top at (M/Z)=(799), which corresponds to [M+], other parts besides their similar patterns of abundance and disintegration had been shown.

Thermal decompositions of the ligands and Zn(II), Cd (II) Complexes

The prepared ligand's thermo-gram (C_{18} H_{16} N_3OCl) has been conducted through the differential calorimetry (DSC) and TGA, in inert atmosphere

utilizing the argon gas at a mean temperature degree of 10°C/min and a (26 mg) sample weight. prepared ligand (L) TGA curve had shown that it had undergone one weight loss phase [1.90 -1.60]. Thermal study of the complex Cd C_{36} H_{32} N_6 O_3 Cl_4 has been conducted in inert atmosphere of argon at a mean temperature degree of 10°C/min with a (21mg) weight. The curve of the TGA had shown that the complex goes through 4 weight loss stages.

The thermal study of $ZnC_{36}H_{32}N_6O_2Cl_4$ complex has been performed in inert argon atmosphere at a mean temperature degree of 10°C/min by 17mg weight [21]. The curve of TGA had shown that this complex had a single weight loss phase.

Table5: **Thermal analyses of ligand in addition to its complexes**

Compound	Stages	Decomposition Temperature Initial-inal(°C)	Total mass loss	Assignments
L	1	900	(1.619)(1.611)	C_8 H_{10} N_2 O
[Cd(L)2Cl2].H2O	1	905	(5.096)(5.097)	Cd C_{36} H_{33} N_6 O_2 Cl_4
[Zn(L)2Cl2].H2O	1	900	(1.012)(1.013)	$C_{19}H_{17}N_3O_2$ Cl

Conclusions

The objective of the present research was creating a new ligand the contains a group of azomethine (-CH=N-) as donor-acceptor group that had been countered with around transition metal ions in Co(II), Ni(II), Cu(II), mercury and Zn(II) to present a series of new metal complexes of common molecular formulations [M(L)2H2O Cl].H2O. Cl and [M(L)$_2$ Cl_2]H_2O metal complexes have been proven to have octa-hedral formula.

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