Synthesis, characterization and spectroscopic studies on Schiff base complexes of 1-phenyl-2, 3-dimethyl-4-amino-5-oxo-pyrazole with salicylaldehyde with some divalent transition metals

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Abstract:

In this research, the preparation of bidentate Schiff base was carried out via the condensation reaction of both the salicylaldehyde with 1-phenyl-2,3-dimethyl-4-amino-5-oxo-pyrazole to form the ligand (L). The mentioned ligand was used to prepare complexes with transition metal ions Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). The resulting complexes were separated and characterized by FTIR and UV-Vis spectroscopic technique. Elemental analysis for Carbon, Hydrogen and Nitrogen elements, electronic spectra of the ligand and complexes were obtained, and the magnetic susceptibility tests were also achieved to measure the dipole moments. The molar conductivities were also measured and determination of chlorine content in the complexes and the metal ratio. The complexes have shown the octahydral shapes in the general formula [ML_2Cl_2], whereas M=Mn, Co, Ni, Cu and Zn, ligand which coordinated as bidentate behavior with nitrogen and oxygen as donor atoms.

Key words: Manganese, Cobalt, Nickel, Copper and Zinc Complexes.

Introduction:

Schiff bases have often used as chelating ligands in the field of coordination chemistry and their metal complexes are of great interest for many years[1]. Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer and herbicidal applications[2,3].

Chelating ligands containing N and O donor atoms show broad biological activity and of special interest because of the variety of ways in which they are bonded to metal ions[3]. Schiff base derivatives have been studied with metal as Nickel (II) complex, the mentioned complex played a major role in both synthesis and structural research[4]. Schiff base ligands with nitrogen donor atoms of the azomethane group and oxygen donor atoms of the carbonyl group afforded stable complexes with various transition metals[5]. Schiff bases ligands and their biological complexes have been studied extensively over the past decades. The importance of the coordination compounds has been appeared in the biological structures, the increasing proportion of the application and utilization of these compounds as agents have given rise to an intensification into the investigations of the complexes[6]. The bidentate ligand Schiff base has been prepared via 1-phenyl-2,3-dimethyl-4-amino-5-oxo-pyrazole with salicylaldehyde to prepare the complexes with Mn, Co, Ni, Cu and Zn, divalent transition metals. The complexes were separated and characterized by FTIR, UV-Vis spectra

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and elemental analysis for Carbon, Hydrogen, and Nitrogen elements, electronic spectra of the ligand and complexes were obtained, conductivity measurements, magnetic susceptibility and determination of chlorine.

Materials and Methods:

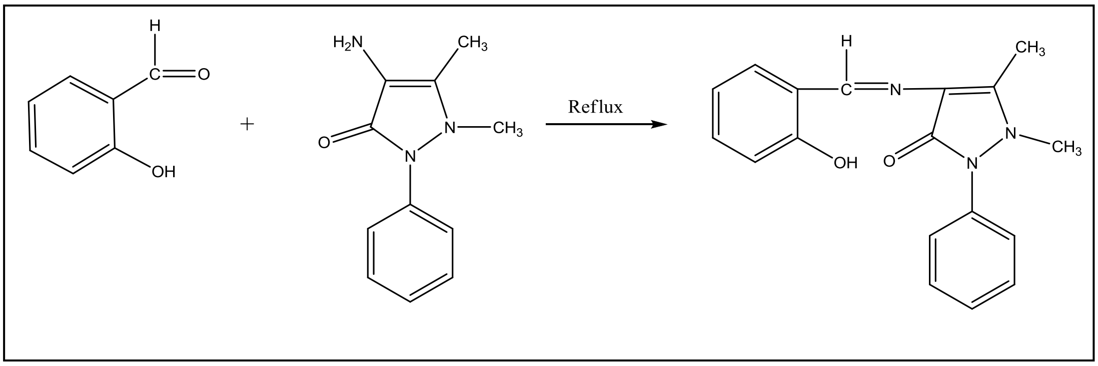
The materials were used as follows, salicylaldehyde, absolute ethanol, methanol, glacial acetic acid, dimethyl-formamide (DMF), phosphorus pentaoxide (P_2O_5) and 1-phenyl-2,3-dimethyl-4-amino-5-oxo-pyrazole were obtained from Fluka. $MnCl_2.4H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$ and $ZnCl_2$ were obtained from British Drug House (BDH). Fourier Transfer Infrared Rays (FTIR) spectra were recorded in range (200-4000) cm^{-1} with a Shimadzu (8300), FTIR Spectrophotometer, using CsI pellets. Electronic Absorption Spectra were recorded in the range (200-1100) nm on a Shimadzu (160) Spectrophotometer in freshly prepared 10^{-3} M solutions in (DMF) at room temperature using quartz cell (1.00) cm. Atomic Absorption Technique was used to determine the metal contents of the complexes using a Shimadzu (A.A680 G) Atomic Absorption Spectrophotometer. Molar conductivity was used to measure the conductivity of the complexes at room temperature in freshly prepared 10^{-3} M solutions in (DMF) using a (PW9526) digital Conductivity Meter. Elemental analysis for Carbon, Hydrogen and Nitrogen elements were carried out at the microanalytical Center Cairo University, Giza, Egypt. Gallen kamp apparatus was used to determine the melting points of the prepared ligand and complexes. Also the chlorine content determined gravimetrically[7].

Preparation of 1-phenyl-2,3-dimethyl-4-salicylaldene-5-oxo-pyrazole ligand

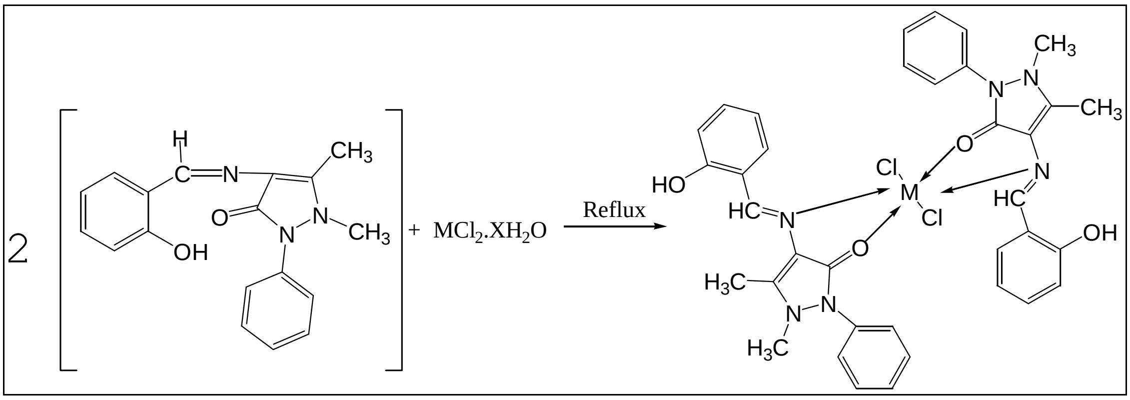
A solution of salicylaldehyde (0.30 g, 2.47 mmole) was added to (10) ml of methanol, this solution was added to another solution which was consisted of (1-phenyl-2,3-dimethyl-4-amino-5-oxo-pyrazole) (0.516 g., 2.47 mmole) was dissolved in 10 ml of methanol. Then, 3 drops of glacial acetic acid were added to the reaction mixture. A reflux was carried out via water bath in temperature range (50-60) ^{o}C for 6 hours. Then the solution was filtered and left 3 days at room temperature in the desiccators to dry. The product was yellow crystals and the yield was 86.32%. and the melting point was (298)^{o}C. The reaction was clarified in scheme (1).

Preparation Method of [ML_2Cl_2] Complexes

A solution of the ligand 1-phenyl-2,3-dimethyl-4-salicylaldene-5-oxo-pyrazole (L) (0.614 g 2mmole) was dissolved in 10 ml absolute ethanol, was added to another solution consisted of $MCl_2.XH_2O$ salts (0.198 $MnCl_2.4H_2O$, 0.238g $CoCl_2.6H_2O$, 0.234g $NiCl_2.6H_2O$, 0.171g $CuCl_2.2H_2O$ and 0.136g $ZnCl_2$) dissolved in 10 ml absolute ethanol, pH of the solution was (6.7). The mixture of each of the above solutions was stirred for 6 hours under nitrogen atmosphere by using water bath at temperature range (50-60 ^{o}C). The complexes were filtered off and washed with cold absolute ethanol. Then, they were dried via P_2O_5 in vacuum. The yields which obtained are shown in table (2). The general reaction was clarified in scheme (2).



Scheme (1)



Scheme (2)

Results and Discussion:

All the complexes have been prepared according to the general equation:

$$2L + MCl_2 \longrightarrow [ML_2Cl_2]$$

Whereas:

M= Mn(II), Co(II), Ni(II), Cu(II), and Zn(II). The synthesized Schiff base ligand and the complexes are very stable at room temperature in the solid state. The complexes composed at higher temperature (221-278)^{o}C, and are insoluble in most common organic solvents. Elemental analysis data suggested that the complexes had (1:2) (ML_2) molar ratio based on the elemental analysis has been suggested the general formula [ML_2Cl_2] for all of the complexes. The elemental analysis results of the ligand and the complexes were clarified in table (1).

The conductivity values for the complexes in DMF 10^{-3}M at room temperature were recorded in the rage (8.0-23.8 $\Omega^{-1}.cm^{2}.mole^{-1}$) which indicate that the non-electrolytic nature of the complexes. This suggests that the non-electrolytic are covalently bonded[8]. The physical properties of the ligand and complexes were clarified in table (2).

The most important appeared and assigned FTIR bands are shown in table (3). Three bands appeared at 3298, 1672 and 1600 cm^{-1} in the free ligand (L) spectrum were assigned to the stretching vibration modes υ O-H, υ C=O and υ C=N respectively[9,10].

The spectrum revealed to υC=O band has the value at 1672 cm^{-1} in the free ligand (L) which has shifted to lower wave number. This shift indicates to the implication of carbonyl oxygen in the coordination at the metallic center[11]. Another band was appeared at 1600 cm^{-1} in the free ligand was assignable to the υ C=N vibration mode, which was shifted to lower wave number, as shown in table (3). In the complexes spectra, this indicates to the participation of nitrogen atom of azomethine group in the coordination[12]. The stretching O-

H bands in salicylaldehyde compounds have a maximum peak at 3298 cm^{-1} in the free ligand (L) and its all complexes which remained largely an effected in the complexes[13]. The most important conclusion drawn from discussion is that the Schiff base ligand (L) was coordinated to the central metal ion as nitrogen and oxygen atoms as bidentate ligand. The formation of M-O, M-N and M-Cl bonds are further supported by appearance of υM-O, υM-N and υM-Cl in the region 578-602, 470-515 and 358-391 cm^{-1} respectively in the spectra of complexes[14].

FTIR complexes spectra showed a band at 3298 cm^{-1} ascribed to OH band of the phenol which is referred that the hydroxyl group does not involve in the coordination. In the other hand this band does not belong to the water because the band of the water always appears in the range between (3350-3550) cm^{-1} which is broad band[10].

Electronic spectra of the free ligand (L) and all its metal complexes were taken in (DMF) 10^{-3} M solutions. The ($\varepsilon_{max}/dm^3cm^{-1}.mole^{-1}$) together with the suggested structures are listed in table (4).

The UV-Vis spectra of the ligand showed three bands at 238nm, 336nm and 362nm, assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition with the molecular, these bands were slightly shifted to blue or red regions in the visible region for the complexes due to coordination with metal ions.

The electronic spectrum of Manganese (II) complex showed one main band at 500nm, this band is assigned to metal (d-d) transition as clarified in table (4). Another band at 371nm ascribed to charge transition (L→M)[15,16]. [CoL_2Cl_2] complex has magnetic moments value 4.9 B.M which agreed with the expected value for the high spin Cobalt(II) ion in octahedral environment. The electrolytic spectrum of Cobalt(II) complex showed two main bands at 410nm and 517nm. These two bands are assigned to $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (υ_2) and $^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$ (υ_3) transitions respectively. The (υ_1) transition is expected to appear at large wave length. Therefore it could not be observed, while the observe transitions are consistent with an octahedral geometry[17,18].

The electronic spectrum of Nickel (II) complex showed two (d-d) transition bands at 505nm and 680nm corresponding to $^3A_{2g}(F)$ ground state, $^3T_{2g}(F)$ and $^3T_{1g}(P)$ in the excited state respectively which suggested mostly octahydral geometry. The magnetic moment value for the Nickel(II) complex of the Schiff base ligand at 25°C was found to be (3.02B.M)[19,20]. A peak of [NiL_2Cl_2] complex spectrum appeared at wave length above 382nm represented to the (L→M) charge transition band.

The electronic spectrum of Copper(II) complex showed two bands. These two bands appeared at 678nm and 590nm ascribed to the (d→d) transitions. A band of [CuL_2Cl_2] complex spectrum appeared above 382nm represented to the (L→M) charge transition band.

The electronic spectrum of Zinc (II) complex showed only the charge transfer transition of 388nm which can be assigned to charge transfer from the ligand to the metal and vice versa (M↔L) no (d→d) transition are expected for d^{10} Zinc(II) complex[21].

Table (1) Elemental analysis of the (L) and its Complexes

Formula M.wt. (gm/mole)	Elemental Analysis Calculated (Found)				
	M%	Cl%	C%	H%	N%
$C_{18}H_{17}N_3O_2$ 307			70.36 (71.02)	5.54 (5.38)	13.68 (13.59)
$MnC_{36}H_{34}N_6O_4Cl_2$ 739.94	7.42 (7.33)	9.60 (9.44)	58.38 (58.93)	4.59 (4.68)	11.35 (11.06)
$CoC_{36}H_{34}N_6O_4Cl_2$ 743.93	7.92 (7.84)	9.54 (9.39)	58.07 (58.87)	4.57 (4.61)	11.29 (11.38)
$NiC_{36}H_{34}N6O_4Cl_2$ 743.71	7.89 (8.01)	9.55 (9.42)	58.09 (58.95)	4.57 (4.64)	11.29 (11.32)
$CuC_{36}H_{34}N_6O_4Cl_2$ 748.54	8.49 (8.27)	9.49 (9.38)	57.71 (58.56)	4.54 (4.83)	11.22 (11.28)
$ZnC_{36}H_{34}N_6O_4Cl_2$ 750.36	8.71 (8.67)	9.46 (9.37)	57.57 (58.37)	4.53 (4.75)	11.19 (11.26)

Table (2) The physical properties of (L) and its metal complexes.

Compound	Color	M.P. °C	Wt.(g) Yield %
L	Yellow	298	(0.53) 86.32
[MnL_2Cl_2]	Green Yellow	278	(0.61) 84.47
[CoL_2Cl_2]	Pink	262	(0.63) 84.68
[NiL_2Cl_2]	Yellow	221	(0.55) 73.95
[CuL_2Cl_2]	Greenish	235	(0.65) 88.12
[ZnL_2Cl_2]	Light Yellow	265	(0.64) 85.29

Table (3) The characteristic bands of FTIR spectra of the (L) and its complexes (cm^{-1})

Compound	O-H	C=O	C=N	M-O	M-N	M-Cl
L	3298	1672	1600	…	…	…
[MnL_2Cl_2]	3301	1660	1572	590	508	388
[CoL_2Cl_2]	3297	1638	1575	602	515	371
[NiL_2Cl_2]	3295	1630	1557	585	470	391
[CuL_2Cl_2]	3302	1622	1565	592	485	358
[ZnL_2Cl_2]	3297	1628	1563	587	473	368

Table (4) Electronic spectra in (DMF) for the (L) and its metal complexes with their conductivity values

Compound	λ nm	υ cm^{-1}	Transition	Ω^{-1}.cm^2.mole^{-1}	Suggested structure
L	238 336 362	42016 29761 27624	$\pi\rightarrow^{*}\pi$ $n\rightarrow^{*}\pi$ $n\rightarrow^{*}\pi$	…..	
[MnL_2Cl_2]	282 350 371 500	35461 28571 26954 20000	Ligand Field Ligand Field C.T $^6A_{1g}\rightarrow{}^4T_{2g}(D)$	14.9	O.h
[CoL_2Cl_2]	275 344 397 410 522	36363 29069 25188 24390 19157	Ligand Field Ligand Field C.T $^4T_{1g}(F)\rightarrow{}^4A_{2g}(F)$ $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$	23.8	O.h
[NiL_2Cl_2]	279 330 382 505 680	35842 30303 26178 19801 14706	Ligand Field Ligand Field C.T $^3A_{2g}(F)\rightarrow{}^3T_{2g}(F)$ $^3A_{2g}(F)\rightarrow{}^3T_{1g}(P)$	11.3	O.h
[CuL_2Cl_2]	297 350 382 588 678	33670 28571 26178 17006 14749	Ligand Field Ligand Field C.T $^2B_{1g}\rightarrow{}^2B_{2g}$ $^2B_{1g}\rightarrow{}^2E_g$	9.2	O.h
[ZnL_2Cl_2]	260 330 388	38461 30303 25775	Ligand Field Ligand Field C.T	8.0	O.h

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تشخيص ودراسة طيفية لمعقدات قاعدة شف المشتقة من 1-فنيل-3,2- ثنائي مثيل-4- أمينو-5- أوكسو- بايرازول مع السليسلديهايد مع بعض الفلزات الانتقالية ثنائية التكافؤ

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الخلاصة:

في هذا البحث حضرت قاعدة شف ثنائية السن من التفاعل التكثيفي للسليسلديهايد مع 1-فنيل-3,2-ثنائي مثيل-4-امينو-5-اوكسو-بايرازول لتكوين الليكاند (L)، استخدم هذا الليكاند بعد تشخيصه لتحضير معقدات مع كل من المنغنيز و الكوبلت و النيكل و النحاس والخارصين ثنائية التكافؤ، وعزلت المعقدات وتم تشخيصها بواسطة مطيافية الاشعة تحت الحمراء وفوق البنفسجية والمرئية والتحليل الكمي الدقيق لعناصر الكاربون، الهيدروجين والنتروجين وتعيين محتوى الكلور في المعقدات ونسبة الفلز والحساسية المغناطيسية والتوصيلية المولارية، حيث اعطت المعقدات الصيغة العامة $[M(L)_2Cl_2]$ حيث ان
M=Mn ,Co ,Ni ,Cu ,Zn اشكالا ثمانية السطوح، حيث اظهر الليكاند (L) سلوكا ثنائي السن عن طريق ذرات النتروجين والأوكسجين الواهبة.