Mansoura University
Faculty of Science

PREPARATION, CHARACTERIZATION AND ANTIBACTERIAL ACTIVITY OF SOME SCHIFF BASES COMPLEXES

Abdsalam M. Ali hamil[1], Marie M. El-Ajaily[2], Mohamed Abdelkrim[3] Mohamed Himmett[4] and Hammed Ali bogdadi[5]

[1]Chemistry Department, Faculty of Science, Sebha University, Sebha, Libya **(e-mail:abdsalam_1956@yahoo.com)**

[2]Chemistry Department, Faculty of Science, Benghazi University, Benghazi, Libya **(e-mail:melajaily@yahoo.com**

[3]Chemistry Department, Faculty of Science, Sudan University of Science and Technology, Sudan

[4]Chemistry Department, Faculty of Science, Omdorman Islamic University, Sudan

[5]Botany Department, Faculty of Science, Sebha University, Sebha, Libya

Reprint from the Mansoura Journal of Chemistry, Mansoura University, vol. 40 (1), Supl.,June, 2013.

2013

Mansoura Journal of Chemistry V. 40 (1) June, 2013.

PREPARATION, CHARACTERIZATION AND ANTIBACTERIAL ACTIVITY OF SOME SCHIFF BASES COMPLEXES

Abdsalam M. Ali hamil[1], Marie M. El-Ajaily[2], Mohamed Abdelkrim[3] Mohamed Himmett[4] and Hammed Ali bogdadi[5]

[1]Chemistry Department, Faculty of Science, Sebha University, Sebha, Libya (e-mail:abdsalam_1956@yahoo.com)

[2]Chemistry Department, Faculty of Science, Benghazi University, Benghazi, Libya (e-mail:melajaily@yahoo.com

[3]Chemistry Department, Faculty of Science, Sudan University of Science and Technology, Sudan

[4]Chemistry Department, Faculty of Science, Omdorman Islamic University, Sudan

[5]Botany Department, Faculty of Science, Sebha University, Sebha, Libya

ABSTRACT

The Schiff bases derived from 1,4-phenylenediamine and 2-hydroxyacetophenone were synthesized and investigated by using several physical techniques, in particular; CHN elemental analysis, infrared, ultraviolet and mass spectra. Only one product was formed from the reaction of the carbonyl and primary amine. The purity of the isolated Schiff base was confirmed by its melting points and by TLC technique. The Schiff base under investigation forms complexes with Co(II), Ni(II), Cu(II), Cr(III) and La(III). The synthesized complexes were confirmed by elemental analysis, molar conductivity, TGA analysis, magnetic moment and spectral (IR, Uv.-vis., and ESR) measurements.

The data show the formation of Schiff base complexes with ratio 1:2 (M:L). The molar conductance measurements of the complexes reveal a non-electrolytic nature. The magnetic moment values exhibit that the La(III) complex is diamagnetic while the other complexes are paramagnetic. The TGA data of some complexes show the presence of water molecules in the isolated complexes. The IR data display the coordination behavior of the Schiff base toward the metal ions. The UV-Vis spectral results of the Schiff bases and their complexes show $\pi \rightarrow \pi^*$

Presented at the 11 th "ICCRD"2013.

(phenyl ring), n→π* (HC=N) and the expected geometrical structures for the synthesized complexes.

Basis on the ESR spectral data, an octahedral structure was suggested for all the complexes. The synthesized Schiff base and its complexes were tested against some pathogenic bacteria [*Escherichia coli, Proteus* Sp, *Pseudomonas aeruginosa* and *Staphylococcus aureus*].

INTRODUCTION

Although there are wide applications of Schiff bases and their metal complexes in biological systems **(Calvin, 1974 and Maurer, et al., 2002)**, catalysis **(Selbin, 1966 and Vasin, et al., 1990)**, dying processes **(Maki & Hashimato 1954 and papie, et al., 1994)** and analytical applications **(khader et al., 2005)**. The spectral studies of the Schiff bases containing heterocyclic ring are comparatively minor **(khader et al., 2005; Cimerman & Miljanic 1999; Issa, et al., 2005 and El-ajaily et al., 2006)** have synthesized and investigated some complexes derived from salicylaldehyde and histidine and they found to have antibacterial activity on some pathogenic bacteria. This study aims to synthesis, characterize Schiff base and its complexes with Co(II), Ni(II), Cr(III), Cu(II) and La(III) ions and screen their antibacterial activity on some pathogenic bacteria.

EXPERIMENTAL

All the chemicals used in this study were analytical grade reagents (BDH). The molar conductance measurements were performed on a BC 3020 Professional Benchtop Conductivity Meter. Magnetic susceptibility was determined using a Johnson Matthey instrument at room temperature (25 °C) with $Hg[Co(SCN)_4]$ as calibrate. Diamagnetic corrections for the ligands and metal atoms were reduced using Pascal's constant. The IR spectra were recorded as KBr disc on a Perkin – Elmer 1430 IR Spectrophotometer. The UV spectra were recorded on a Unicam Model UV-2 Spectrophotometer. The ESR spectra were recorded by using EMX ESR spectrometer **(Bruker, 1998)** Y. All analyses were done at Microanalytical center, Cairo University, Giza, Egypt.

Synthesis of Schiff base

The compound under investigation was synthesized by adding (6.02 cm^3, 0.05 mmole) of 2-hydroxyacetophenone dropwise to 1,4-phenylenediamine (5.40g, 0.05 mmole) in 50 cm^3 of absolute ethanol. The reaction mixture was refluxed for three hours. The obtained compound was allowed to cool at ambient temperature, filtered and recrystallized from ethanol, and dried under vacuum to get is light brown precipitate (m.p > 250°C ; yield 68%).

Synthesis of complexes

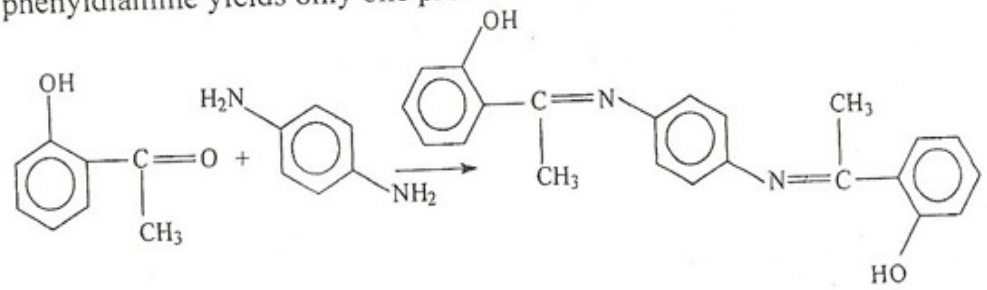
The present complexes were synthesized by adding (3.53 gm; 0.01 mole) of the ligand in 50 cm^3 EtOH to $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuSO_4.5H_2O$, $CrCl_3.6H_2O$ and $LaCl_3.7H_2O$ (2.3793 gm), (2.3769 gm), (2.4968 gm) , (2.6650 gm) and (3.7137 gm) in 50 cm^3 in EtOH. The reaction mixtures were refluxed for three hours. The colored complexes were filtered, recrystallized and finally kept in a desiccator over silica gel.

Bacteria assay

The Schiff base complexes [Co(II), Ni(II), Cu(II) and Cr(III) ions] were added separately to the mixtures of DMF and H_2O solvent (1:1). The obtained mixtures were further purified and filtered by using Whatman filter paper No 1. The stock solutions of the extracts were sterilized by filtration using a Millipore membrane filter of 0.2 μm pore-size. The sterile mixtures resulted from each compounds were stored at 4°C for further uses,[5,6] and the stock mixtures of the compounds were tested against four pathogenic bacteria species (*Escherichia coli , Proteus Sp, Pseudomonas aeruginosa and Staphylococcus aureus*). Antibacterial activity was determined by the well (6 mm diameter) diffusion method. Petri dishes containing Mueller Hinton agar medium were seeded with a 24 hrs culture of the bacterial species were growth on nutrient agar. Each well was filed with 50μl of the compound. Solvents were used as a negative control. Inoculated plates were Incubated at 37 °C for 24 hr.[7] The assessment of antibacterial activity was based on measurement of the diameter of inhibition formed around the well.

RESULTS AND DISCUSSION

The reaction between the 2-hydroxyacetophenone and 1,4-phenyldiamine yields only one product which is as follow:



Microanalysis and molar conductance measurements

The obtained results of the Co(II), Ni(II), Cu(II) and La(III) complexes showed the formation of 1:1 (M:L) ratio complexes. Meanwhile, the Cr complex is formed in 2:1 [M:L] stoichiometry (Table 1). The obtained data are consistent with the calculated values indicating that the complexes are formed in the mentioned ratios. The elemental analysis data exhibited that most of the complexes have more than one water molecule associated with the complex formation. The molar conductance measurements of all complexes were carried out in DMF solvent (10^{-3} M) using conductivity meter model BC 3020 Professional Benchtop Conductivity meter, Sebha university, Libya. The molar conductance values (Table.1) revealed that all the complexes are non electrolytes.**(Geary, 1971).** These data confirm that no inorganic anions are present outside the complexes.

Table (1): CHN and some physical characters of the Schiff base and its complexes

Complexes	Color	M.wt.	M.P., ^{0}C	Found (calc.) %				Λ
				C%	H%	N%	Cl%	
$[Co_2L4Cl_4(H_2O)_4]\ 2H_2O$	black	675.29	299.9	39.98(39.13)	4.92(5.07))	4.21(4.15)	10.62(10.50)	6.30
$[Ni_2L4Cl_2(H2O)_6]\ H_2O$	black	656.79	299.5	40.58(40.23)	4.23(4.91)	4.39(4.27)	10.41(10.80)	980
$[Cr_2L4Cl_4(H2O)_4]\ 2H_2O$	green	696.29	280.6	36.35(37.95)	4.35(4.34)	3.54(4.02)	19.09(20.37)	9.50
$[Cu_2L4Cl_2(H2O)_6]\ H_2O$	brawn	666.5	274.9	39.77(39.65)	4.62(4.84)	4.44(4.20)	10.54(10.64)	5.85
$[La_2L4Cl_4(H_2O)_4]\ 2H_2O$	black	870.11	281.1	29.70(30.37)	4.14(3.48)	3.26(3.22)	15.90(16.30)	14.30

Infrared spectra

The IR spectra of the complexes exhibit broad bands in the range of 3520–3590 cm^{-1} which are attributed to νOH vibration of water molecules associated with complex formation**(Nakamoto, et al., 1998)**. The change of phenolic OH groups positions in the spectra of the complexes supports the participation of OH groups in chelation with metal ion, this confirmed by the existence of new bands at 572 –498 cm^{-1} in the spectra of the complexes, these new bands can be referred to νM-O vibration which is absent in the IR spectrum of free Schiff base **(Raman & Ravichhandran 2004).** The νC=N band observed at 1609 cm^{-1} is shifted to lower frequency in the IR spectra of all complexes confirming the complexation of the nitrogen atom of azomethine group to the metal ions. This can be supported by the existence of new bands in the range of 459 – 415 cm^{-1} assigned to νM-N bands **(Belaid, et al., 2008)**.

Table (2): Infrared, electronic and paramagnetic resonance spectral data of some complexes.

Complexes	νOH (H_2O)	ν C=N	νM-O	νM-N	λmax nm (cm^{-1})	g- values
$[Co_2L4Cl_2(H_2O)_6]\ 2H_2O$	3377	1506	608	431	**560** (17857), **575** (17391)	2.09328,
$[Ni_2L4Cl_2(H_2O)_6]\ H_2O$	3396	1509	527	415	**580** (17241), **595** (16806)	1.98167
$[Cr_2L4Cl_4(H_2O)_4]\ 2H_2O$	3357	1577	492	443	**570** (17543), **590**(16949)	1.97781
$[Cu_2L4Cl_4(H_2O)_4]\ H_2O$	3284	1591	498	456	**560** (17857), 590 (16949)	1.99766
$[La_2L4Cl_4(H_2O)_4]\ 2H_2O$	3407	1628	507	459	570 (17543)	0.00

Thermogravimetric analysis

The Thermogravimetric analysis data (Table 3) show the weight-losses for complexes in the range of 3.11 - 6.01% which are in a good agreement with the theoretical values, indicating the existence of one or two hydrated water molecules at 34 - 133^{0}C. Meanwhile, at the temperatures of 133 – 188^{0}C, the values in the range of 8.74 - 17.36% which are closed to the theoretical values corresponding to the presence of 4 or 6 coordinated water molecules in the complexes. At temperatures of 297 – 630 ^{0}C, the Schiff base (free ligand) decomposes as carbonate or oxalate ion **(Mishra & Khare 2000)**. The metal oxides (CoO, Cr_2O_3, NiO, CuO and La_2O_3) appeared at the end of the curves as stable states >630 ^{o}C.

Electronic spectra

The $[Co_2LCl_2(H_2O)_6].2H_2O$ complex has one shoulder band situated in the range of 560 – 575 nm which are assigned to $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ (F) transition within an octahedral structure**(Kaya, 2004).** $[Ni_2LCl_2(H_2O)_6].H_2O$ displays two bands at 580 and 595 nm in which can be assigned to $^3A_2g(F) \rightarrow {}^3T_{2g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ transitions including octahedral geometry around Ni(II) ion. The electronic spectra of Cr(III) complex exhibit two bands at 570 and 590 nm assigned $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ and $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ transitions. The intensity of the bands suggests the existence of an octahedral geometry around Cr(III) ion.

Whereas, the electronic spectral data of $[Cu_2LCl_2(H_2O)_6]$ show one band situated at 590 nm which can be attributed to $^2T_{2g} \rightarrow {}^2E_g$ transition, and an octahedral geometry was proposed for the complex.

For La(III) complex, the electronic spectrum shows charge transfer band situated at 570 nm suggesting an octahedral geometry around the La(III) complex **(Taha, et al., 2011)**.

Electron paramagnetic resonance spectra

The observed e p r values of the complexes (Table. 2) are deviated from the ideal value (2.0023), this difference is in agreement with the covalent character of the metal- ligand bond **(Wilkinson, et al., 1987)** . The present deviation of these values compared to the ideal value supports the existence of an octahedral geometry around the metal ions.

Table (3): Thermogravimetric analysis data of some complexes

Complexes	Hydrated water weight loss%	No. of water molecules	Temp °C	Coordinated water weight loss%	No. of water molecules	Temp °C	Temp. °C of Schiff base decomposition	Metal oxide weight loss%	Temp °C
$[Co_2L4Cl_2(H_2O)_6].2H_2O$	6.01 (5.33)	2	28-169	16.63 (15.99)	6	170-315	316-656	10.99)11.09)	>656
$[Ni_2L4Cl_2(H_2O)_6]\ H_2O$	3.14 (2.74)	1	34-121	16.05(16.44)	6	122-310	311-584	12.22 (11.37)	>584
$[Cr_2L4Cl_4(H_2O)_4]\ 2H_2O$	4.77 (5.17)	2	39-133	9.88 (10.34)	4	134-293	294-584	21.02(21.83)	>584
$[Cu_2L4Cl_2(H_2O)_6].H_2O$	-	-	-	17.36 (16.65)	6	188-257	257-606	13.22(12.27)	>606
$[La_2L4Cl_4(H_2O)_4]\ 2H_2O$	4.95 (4.14)	2	35-105	8.74 (8.27)	4	106-170	171-597	37.82 (37.44)	>597

Antibacterial activity

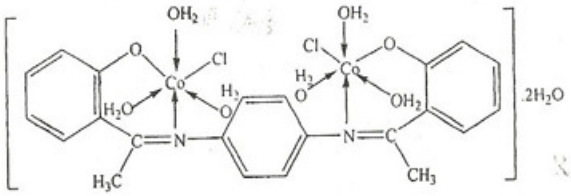
The free Schiff base shows inhibitory activity on *Proteus Sp* bacteria, and the synthesized complexes were screened for antibacterial activity on some pathogenic bacteria. The $[Cu_2LCl_2(H_2O)_2].3H_2O$ complex showed inhibitory activity against all bacteria specie (9 mm).Whereas, the Co(II), Ni(II) and Cr(III) did not show any inhibitory activity against *Escherichia coli* and *Proteus Sp* (Table 4).

Table (4): Antibacterial activity results (mm) of the Schiff base and its complexes Inactive

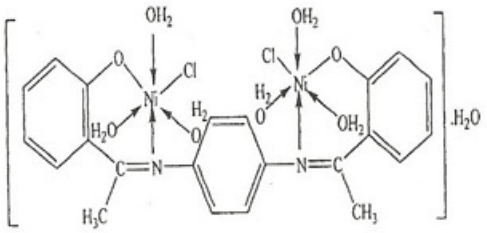
L and its complexes	bacteria species			
	Escherichia coli	*Proteus Sp*	*Pseudomonas aeruginosa*	*Staphylococcus aureus*
$(C_{22}H_{20}N_2O_2)$	-	13	-	-
$[Co_2LCl_2(H_2O)_6].2H_2O$	-	-	9	9
$[Ni_2LCl_2(H_2O)_6].H_2O$	-	-	-	9
$[Cr_2LCl_4(H_2O)_4].2H_2O$	-	-	10	9
$[Cu_2LCl_2(H_2O)_6].H_2O$	9	9	9	9

CONCLUSION

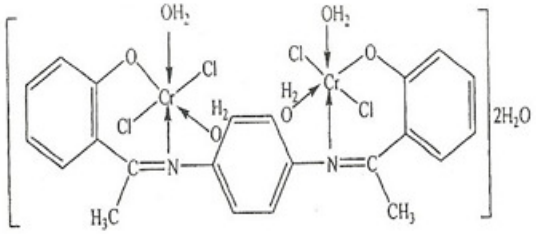
From the above results, we can suggest the following geometrical structures:



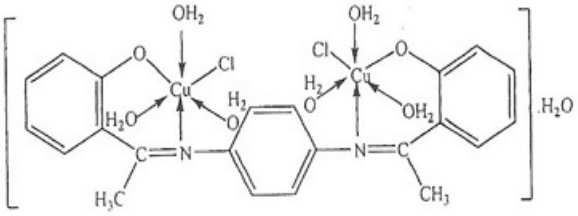
$[Co_2LCl_2(H_2O)_6]\ 2H_2O$



$[Ni_2LCl_2(H_2O)_6].H_2O$



$[Cr_2LCl_4(H_2O)_4]\ 2H_2O$



REFERENCE

Belaid, S., Landreau, B.O., Khan, M. A. and Bouet, G.,Trans. Met. Chem., **33**, 54 **(2008).**

Calvin, M., Science, **184**, 375 **(1974).**

Cimerman, Z. and Miljanic, S.A., J. Spectro. Letter, **33**, 181 **(1999).**

El-ajaily, M.M., Maihub, A.A., Ben-Gweirif, S.F. and El-tajoury, A.N., journal of Science and its applications, **1** (1), 196-210 **(2006)**.

Geary, J. D., Coord. Chem. Rev., 7, 81 (1971).

Issa, R.M., Khader, A.M., Rizk, H. F., Spectrochimica Acta A, **62**,621 **(2005).**

Kaya ,C. M., J. Coord. Chem. **57**, 1217 **(2004).**

Khader, A.M., Gaber, M., Issa, R.M. and Erten, H., Dyes Pigments, **67**, 116 **(2005)**.

Maki, M. and Hashimato, H., Bull. Chem. Soc. (Japan), **27**, 602 **(1954).**

Maurer, R. I., Blover, P.I., Dilworth, J.R. and Reynoh, C.A., J. Med.. Chem.,**46**, 1420 **(2002).**

Mishra, A. P. and Khare, M., Journal of the Indian Chemical Society, 77 (8), 367 **(2000)**.

Nakamoto, K., " Infrared and Raman Spectra of Inorganic and Coordination Compounds, Parts A &B, John Wiley, New York, USA **(1998)**.

Papie, S., Kaprivanae, N., Grabarie , Z. and Paracosterman, D., Dyes Pigments, **25**, 229 **(1994).**

Raman, N., Ravichhandran, S. and Thangaraja, C., Journal of Chemical Sciences India, **116** (4), 215 **(2004)**.

Selbin, J. Coord. Chem., Rev., 293 **(1966).**

Taha, Z. A., Ajlouni, A. M., Al Momani, W. and Al-Ghzawi, A. A., Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, **81**(1), 570 **(2011).**

Vasin, S.V., Cetralla, J. and Bernal, R.A., Inorg. Chem., **29**, 885 **(1990).**

Wilkinson, G., " Comprehensive Coordination Chemistry Vol 3: Main Group and Early Transition Elements", Pergamon Press, Oxford, UK **(1987).**

الملخص العربى

تم تحضير بعض مرتبطات قواعد شيف المشتقة من 1,4- فينيلين ثنائى الامين و ٢-هيدروكسى اسيتوفينون وقد تمت دراستها بإستخدام التقنيات الفيزيائية مثل التحليل العنصرى ، الاشعة تحت الحمراء ، الاشعة فوق البنفسجية ومطياف الكتلة . وقد تم التأكد من النقاوة بواسطة درجات الانصهار والكروماتوجرافى . وقد تم تحضير متراكبات هذه المرتبطات مع الكوبلت ، النيكل والنحاس الثنائى والكروم واللانثانوم الثلاثى وقد تحديد الاشكال الفراغية بواسطة الطرق الطيفية والمغناطيسية والتحليل الحرارى .

مجلة المنصورة للكيمياء

العدد الأربعون (١)
يونيو ٢٠١٣

إصدار :
كلية العلوم - جامعة المنصورة
المنصورة - ج . م . ع

ISSN:1687-5060

كلية العلوم
جامعة المنصورة

MANSOURA JOURNAL OF CHEMISTRY

MANSOURA UNIVERSITY
جامعة المنصورة

VOL. 40 (1) MJC
June 2013

Published By:
FACULTY OF SCIENCE MANSOURA UNIVERSITY
MANSOURA, EGYPT

ISSN : 1687-5060
Fax : 002050-346254 , 002050 - 346781
E- Mail : scimag@mans.edu.eg