

Preparation and Characterization of Some Transition Metal Complexes with Schiff base ligand (DBAB)

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Abstract

Cu(II), Zn(II) and Cd(II) metal complexes of Schiff base(DBAB)derived from 2-amino benzoic acid and 4-(N,N-dimethyl amino) benzaldehyde have been synthesized and characterized by elemental analysis, IR and electronic spectra, in addition of molar conductance and magnetic moment measurements. It has been found that the Schiff base ligand behaves as mono basic bidentate (N,O) ligand forming chelates with 1:2 (metal:ligand) stoichiometry. The conductivity data for all complexes are consistent with those expected for an electrolyte.

Key Words: Schiff base, Metal chelat complexes, Characterization.

الخلاصة

تضمن البحث تحضير معقدات فلزية لايونات النحاس(II)، الخارصين(II) والكاديوم(II) مع ليكاند قاعدة شف(DBAB) المشتقة من 2-أمينو حامض البنزويك و4-(N,N-ثنائي مثيل أمينو) بنزالديهايد. شخّصت الليكاند المحضرة ومعقداتها بوساطة التحليل الدقيق للعناصر والاشعة تحت الحمراء والاطياف الالكترونية كما درست التوصيلية المولارية والحساسية المغناطيسية لهذه المعقدات. بينت نتائج الدراسة ان الليكاند تسلك كليكاند أحادية الشحنة السالبة ثنائية المخلب (N,O) ترتبط مع الايونات الفلزية بنسبة مولية 2:1 (فلز:ليكاند) لجميع المعقدات.

Introduction

Schiff bases are characterized by the (-N=CH-) azomethine group which is important in elucidating the mechanism of transamination and racemisation reaction in biological systems^(1,2).

Many Schiff bases are known to be medicinally important and are used to design medicinal compounds^(3,4). They have been prepared from a variety of amino and aldehyde or ketone compounds, such as Isthain, 3,3'-diamino Benzedine, Systeine, amino thiazoles, amino acid, *o*-phenylene diamine, and aromatic aldehyde or ketons⁽⁵⁻¹⁰⁾.

A large number of Schiff bases complexes have been prepared and characterized by several physical tools in particular; elemental analysis, molar conductance, magnetic moment, infrared and electronic spectra were used to investigate the chemical structure of these prepared complexes⁽¹¹⁻¹⁵⁾.

The present paper aims to prepare and characterize of Schiff base derived from 2-amino benzoic acid and 4-(N,N-dimethyl amino) benzaldehyde and its complexes with Cu(II), Zn(II) and Cd(II) metal ions by available techniques.

Experimental

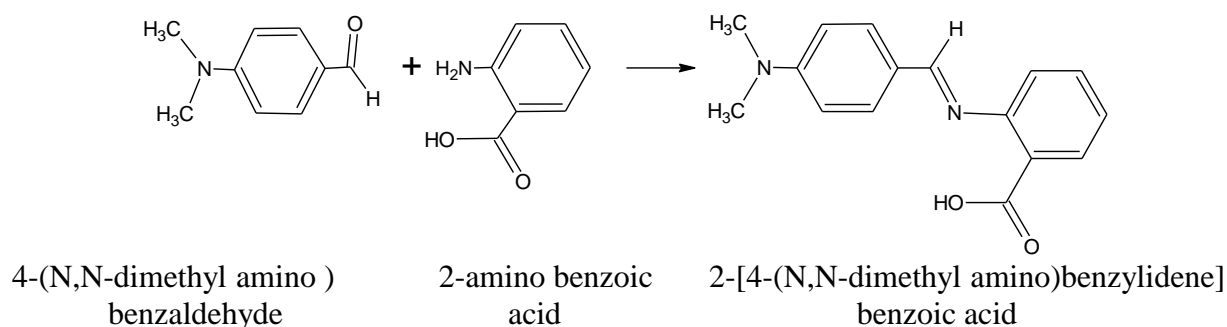
Materials and measurements

All Chemicals used in this work were reagent grade (BDH / Aldrich) and used with out further purification. The elemental analyses were carried out in Al-Albat university / Jordan by means of Micro analytical unit of EA 300 A C.H.N Elemental analyzer. IR spectra were recorded using KBr discs 4000-400 cm⁻¹ on FT-IR Testscan Shimadzu model 8000. Uv-Vis spectra were recorded in ethanol on Shimadzu model 1700 Uv-Vis spectrophotometer. Magnetic susceptibilities were measured as powder samples using Faraday method, Balance Magnetic MSB-MKI was employed for this purpose. The diamagnetic corrections were made by Pascal's constant⁽¹⁶⁾. Molar conductance measurements were determine in DMF by using Alpha Digital conductivity meter model 800. Electro thermal melting point model 9300 was used to measure the melting points of the ligand and its complexes.

Preparation of Schiff base (DBAB)

The Schiff base (DBAB) was prepared by adding (25mL) of 2-amino benzoic acid ethanolic solution (1.37 g , 0.01 mol) to the same volume of ethanolic solution of 4-(N,N-dimethyl amino) benzaldehyde (1.49 g , 0.01 mol). The mixture was refluxed with stirring for 3hrs. The resulting solution was evaporated to half volum and the precipitated product was collected by filtration, washed twice with (5mL) hot ethanol and dried over anhydrous CaCl₂.

The condensation of 4-(N,N-dimethyl amino) benzaldehyde and 2-amino benzoic acid in ethanol gives single product according to the following reaction.



Preparation of the complexes

A general method has been used for the preparation of all Chelate complexes. A solution (1.34 g, 0.005 mol) of ligand dissolved in (25 mL) of hot ethanol was added with stirring a stoichiometric amount (2:1) (ligand:metal) ratio for Cu(II), Zn(II) and Cd(II) chloride salts and the mixture were refluxed for 30 min. On cooling at room temperature, the coloured complexes precipitated out in each case. They were filtered, washed with (5mL) ethanol and dried over anhydrous CaCl₂.

Results and Discussion

General

The ligand is orange crystal, which is soluble in common organic solvents. The reaction of the ligand with the metal ions mentioned above gives vary in colour crystals, depending on the nature of metal ions. All complexes are quiet air- stable, insoluble in water, but its soluble in most organic solvents.

Some physical and chemical properties for (DBAB) ligand and its chelate complexes with Cu(II), Zn(II) and Cd(II) metal ions are listed in table1. The result of the elemental analysis of the prepared compounds which are recorded in table1, are in a good agreement with those required by the proposed formula. In all cases (1:2) metal : ligand solid complexes are isolated, that is agreement with the stoichiometric ratio found using molar ratio method.

Infrared spectra of the ligand and its complexes :

Selected infrared absorption of the ligand and complexes are shown in table2. The spectrum of free ligand shows two weak bands 3120 cm^{-1} and 2850 cm^{-1} which due to $\nu(\text{C-H})$ aromatic and aliphatic respectively. These bands are in stable in positions in both ligand and chelat complexes. The spectrum of ligand shows strong band at 1660 cm^{-1} assigned to $\nu\text{C=O}$ this band was shifting to lower region $1625\text{-}1616\text{ cm}^{-1}$ indicates the involvement of deprotonated hydroxyl group of (COOH) in bonding with metal ions⁽¹⁷⁾. Another band appeared 1585 cm^{-1} in the spectrum of Schiff base ligand due to $\nu(\text{C=N})$ vibration this band was shifting to lower frequency $1560\text{-}1550\text{ cm}^{-1}$ in the spectra of the chelat complexes, suggesting acooordination of Cu(II), Zn(II) and Cd(II) ions through nitrogen atom of azo methane group^(18,19).

New bands are attributed to $\nu(\text{M-N})$ and $\nu(\text{M-O})$ vibrations, respectively. The appearance of these new bands vibrations supports the involment of nitrogen and oxygen atoms in complexation with metal ions under investigation^(20,21).

Thus the above IR spectra data lead to suggest that the ligand behaves as a bidentate chelating agent, and the coordination sites are, the nitrogen atom of azo methane group, and oxygen atoms of the carboxy group to give six- membered chelat ring.

Magnetic measurement and electronic spectra

The spectral data and the magnetic moment of prepared complexes are listed in table 3. The magnetic moment value of the copper (II) complexes (1.79 BM) which may suggest an square planar structure. Its electronic spectrum shows a band centered at 17513cm^{-1} which may assigned to ${}^2\text{B}_{2g} \rightarrow {}^2\text{B}_{1g}$ transition in square planar environment⁽²²⁾.

The Uv-Vis spectra of Zinc(II) and Cadmium(II) complexes are diamagnetic moments for d^{10} ions and the electronic spectra of there complexes do not show any d-d band⁽²³⁾.

Conductivity measurement

All chelate complexes prepared in this work showed conductivity values ranged between ($7.76\text{-}9.92$) $\text{S}\cdot\text{mol}^{-1}\cdot\text{cm}^2$, in DMF at room temperature these values indicating that no conductivity species exist⁽²⁴⁾. The conductivity measurements data are listed in Table3. According to these results the structural formula of prepared complexes may be proposed in figs. 1, and 2.

Table 1:Physical properties and analytical data of the ligand (L) and its complexes

No	Compound	Colour	M.P °C	Formula	Found (calc) %			
					C	H	N	M
1	HL	Orange	178	$[\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2]$	71.48 (71.64)	5.71 (5.97)	10.12 (10.44)	(---) ---
2	$[\text{CuL}_2]$	Green	215	$[\text{C}_{32}\text{H}_{30}\text{N}_4\text{O}_4\text{Cu}]$	63.00 (64.26)	5.13 (5.02)	9.08 (9.37)	10.33 (10.62)
3	$[\text{ZnL}_2]$	Orange	220	$[\text{C}_{32}\text{H}_{30}\text{N}_4\text{O}_4\text{Zn}]$	63.89 (64.06)	5.12 (5.00)	9.12 (9.34)	11.24 (10.90)
4	$[\text{CdL}_2]$	Orange	227	$[\text{C}_{32}\text{H}_{30}\text{N}_4\text{O}_4\text{Cd}]$	59.07 (59.40)	4.54 (4.64)	8.47 (8.66)	17.51 (17.38)

HL = Ligand

Table 2: Characteristic IR absorption bonds of the ligand and its complexes in cm^{-1} units.

Compd.	$\nu(\text{CH})_{\text{arom}}$	$\nu(\text{CH})_{\text{aliph}}$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
HL	3120 w	2850 w	1660 s	1585 s	----	----
[CuL ₂]	3120 w	2850 w	1618 m	1560m.sh	750 w	450 w
[ZnL ₂]	3115 wbr	2845 wbr	1625 m	1553 m	755 w	445 w
[CdL ₂]	3120 w	2850 w	1616 m	1550m.sh	745 w	450 w

HL = Ligand , s = strong , br =broad , sh = shoulder , m = medium , w= weak

Table 3: Electronic spectra, Molar conductance and magnetic moment data of the complexes

Complex	AbsorptionBands (cm^{-1})	Transition	Conductivity $\text{S.mol}^{-1}.\text{cm}^2$	$\mu_{\text{eff}}(\text{B.M})$
[CuL ₂]	17513	${}^2\text{B}_{2g} \rightarrow {}^2\text{B}_{1g}$	7.76	1.79
[ZnL ₂]	----	----	6.36	dia
[CdL ₂]	----	----	5.92	dia

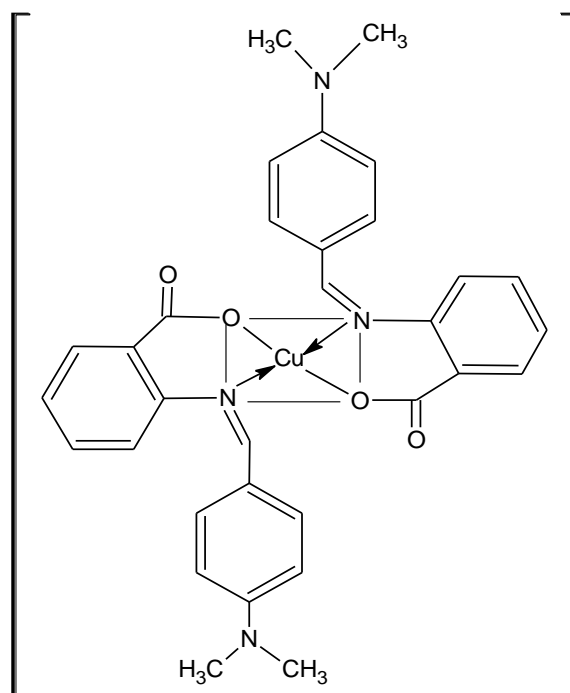


Fig .1: The proposed structural formula of Cu(II) complex

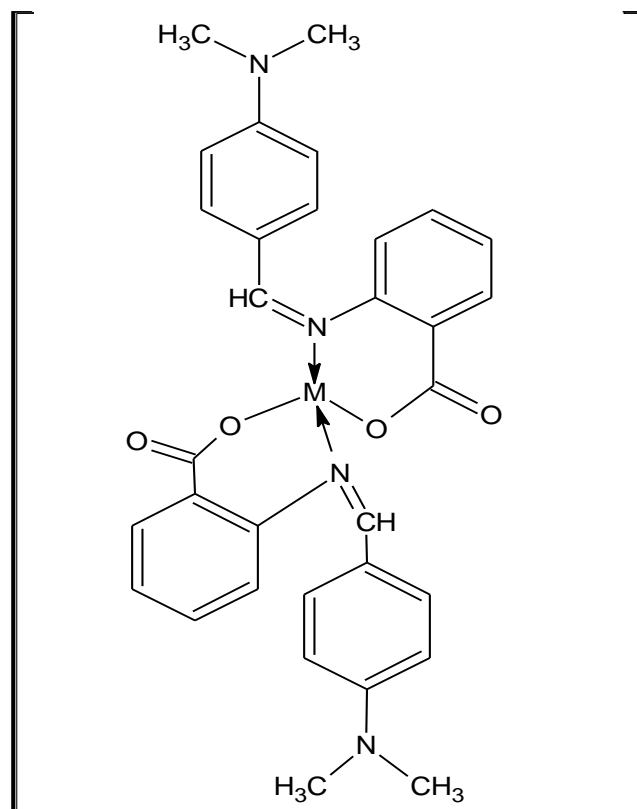


Fig.2: The proposed structural formula of Zn(II) and Cd(II) metal chelat complexes.

Conclusion

Schiff base ligand 2- [4-(N,N-dimethyl amino)benzylidene] benzoic acid (DBAB) and its chelat complexes have been synthesized. All the complexes are stable and nonionic. An square planar geometry is proposed for Cu(II) complex and tetrahedral stereochemistry for Zn(II) and Cd(II) chelat complexes.

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