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Synthesis and Characterization of Schiff Base Complexes with Ni(II), Zn(II) and Pt(IV) Ions

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Summary: The transition metal ions Ni(II), Zn(II) and Pt(IV) complexes with Schiff base derived from a reaction of salicylaldehyde with glutamine have been prepared and investigated by using different physicochemical techniques as; elemental analysis, molar conductance, infrared, electronic and electron paramagnetic resonance spectroscopy. The elemental analysis exhibited the formation of 1:2 [M:L] ratio. The molar conductance measurements of the complexes indicated the presence of an electrolytic and non-electrolytic nature. The infrared spectral data displayed coordination sites of the Schiff base toward the metal ions under investigation. The electronic spectral results of Schiff base and its complexes revealed the existence of π-π^*, n-π^* (H-C=N) transitions, and these results suggest that all the complexes are octahedral. The electron paramagnetic resonance spectra were recorded and reported.

Introduction

The literature survey reveals that large number of Schiff base complexes have been synthesized and investigated, but no work has been done on the applications of the complexes on the effect of root and shoot lengths of cucumber seeds. Salicylaldehyde and glutamine amino acid are bidentate ligands and have a good ability to form many complexes with transition and non transition metal ions.(1) Complexes of chlorosalicylalideneaniline with Co(II) and Cu(II) ions were synthesized and screened for antibacterial activity against several bacterial strains.(2) A ligand (HL) obtained from the Schiff base condensation of 4-(diethylamino)salicylaldehyde with 4-nitroaniline is reported with its Ni(II), Cu(II), and Co(II) complexes.[3] The complexes of Mn(III) with Schiff bases obtained by condensation of 2-hydroxyl-1-naphthaledehyde with glycine, L-alanine, L-phenylalanine, L-histidine, L-tryptophan and L-therionine have been synthesized and characterized by elemental analyses, UV-VIS, IR, magnetic susceptibility, thermogravimetry and nonaqueous titration.[4] It is well known that 6-methoxy-2-benzoxazolinone (MBOA) and its related compounds inhibit the germination and growth of several plant species. However, the physiological mechanism of MBOA on germinate inhibition is not fully understood. MBOA inhibited the germination of cress and lettuce seeds at concentrations greater than 0.03 mM. Both inhibitions increased with increasing concentrations of MBOA, and the extent of the germination was positively correlated with the activity of alpha-amylase in the seeds. Alpha-Amylase is considered essential for seed germination because this enzyme principally triggered starch degradation in endosperm that MBOA may inhibit the germination of cress and lettuce seeds by inhibiting the induction of alpha-amylases activity. It may be one of the possible action mechanisms of MBOA on inhibition of plant germination.[5]

The present paper aims to synthesize some transition metal complexes with a Schiff base derived from salicylaldehyde and glutamine and to elucidate their geometrical structures.

Experimental

Chemicals

All chemicals used in this investigation were reagent pure BDH or Aldrich. All organic solvents were obtained as pure grade materials.

Synthesis of Schiff Base

The amino acid Schiff base was synthesized as follows: NaOH (10 mmol; 0.4 g) was dissolved in methanol (20 cm^3) and the L-glutamine (10 mmol; 1.17 g) was added to the solution, the mixture was stirred magnetically at room temperature. When the mixture becomes homogenous, a solution of salicylaldehyde (10 mmol; 1.22 g) in ethanol (20 cm^3) was added. After two minutes, the solution was evaporated to 20% of its original volume and 1cm^3 of CH_3COOH was added immediately. After 2 hours, yellow crystals appeared. The crystals were filtered and washed with ethanol. They were recrystallized form hot methanol to give yellow crystals.

Synthesis of Schiff Base Complexes

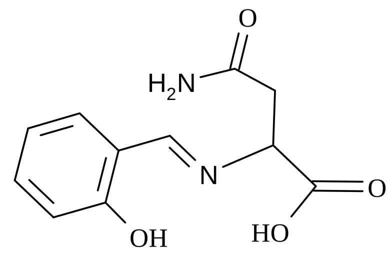
The amino acid (glutamine) (10 mmol; 1.17g) was dissolved in (50 cm^3) of methanol containing NaOH (20 mmol; 0.8 g) and stirred at room temperature. A solution of salicylaldehyde (2.44 g) in 50 cm^3 of ethanol was added to the solution. After 2 minutes, the metal salt (10 mmol); ($Ni(CH_3COO)_2.4H_2O$, $ZnCl_2$ or $PtCl_4$) was stirred magnetically for 3 hours. The solution volumes were reduced to 75% by evaporation and the residue was left to stand overnight, crystals were obtained, and the solids were recrystallized from methanol\ ethanol (50%) mixture.

Apparatus

The synthesized Schiff base and its metal complexes were subjected to CHN elemental analyses using 2400 elemental analyzer. The molar conductance measurements were carried out in DMF solvent using conductivity meter model CMD650 digital. The infrared spectra were obtained by using KBr disk technique on IFS DPUS/IR spectrometer(Bruker) in the range of 4000-400 cm^{-1}. The electronic spectra were measured in DMF solvent using UV-VIS, NIR 3101PC. The electron paramagnetic resonance spectra were recorded by using EMX ESR spectrometer (Bruker) 1998Y. Schimadzu of 10 ^oC/min.

Results and Discussion

The reaction of salicylaldehyde with glutamine in methanol yields the amino acid Schiff base, represented by the following formula:



Glutamine Schiff Base

Microanalysis

The elemental analyses (C, H, N and M) of the amino acid Schiff base and its complexes are listed in Table-1. The empirical formulae of the complexes indicated the formation of 1:2 [M:L] complex.

Table-1: Elemental analysis and some physical properties of the Schiff base and its complexes

Schiff base \complexes	C%	H%	N%	M.P ^{o}C	M.Wt	Λm**	M%
L ($C_{11}H_{12}O_4$ N_{2}.$3H_2O$)	44.75 (45.51)	4.43 (4.13)	8.80 (9.65)	268-270	290	–	-
$Na_2[Ni(L)_2]$ $3.5H_2O$	35.51 (35.62)	3.61 (3.13)	7.49 (7.98)	233-234	747.71	78.40	7.85 (7.36)
$Na_2[Zn(L)_2]$ $2H_2O$	36.29 (36.74)	3.30 (3.87)	7.70 (8.21)	>350	727.38	75.08	8.99 (8.59)
$[Pt(L_1)_2]$ $2H_2O$	33.54 (32.54)	4.70 (4.93)	6.80 (6.90)	>350	811.09	09.10	24.04 (23.97)

( ) Experimrntal values , Λm – Molar conductance ohm^{-1}.cm^{2}. mol^{-1}

Molar conductance measurements

The molar conductance values of the prepared complexes in 10^{-3}M DMSO solvent were 78.40, 75.08 and 9.10 Ohm^{-1} cm^{2} mol^{-1} of Ni(II), Zn(II) and Pt(IV) complexes respectively. The results indicate that Ni(II) and Zn(II) complexes are having electrolytic nature and Pt(IV) complex is a non-electrolytic complex.[6] The presence of sodium ions out side of the first two complexes confirmed the appearance of electrolytic phenomenon, meanwhile, the absence of this ion supported the existence of a non- electrolytic character as in platinum(IV) complex.

Infrared spectra

The infrared spectra of the complexes exhibit three bands at 1586, 1610 and 1612 cm^{-1} due to ν(C=N) of azomethine. A slight change is observed for ν(C=N; 1602 cm^{-1}) band a after complexation, indicates the involvement of the azomethine nitrogen atom in coordination.[7] The spectrum of the prepared Schiff base displays another band at 1540 cm^{-1} which may due to the existing of $\nu(COO)^-$ group. The Schiff base complexes exhibit the bands of $\nu(COO)^-$ group of the carboxyl group in the range of 1536-1546 cm^{-1} region, indicating the participation carboxyl group in complexation with metal ions [8,9] The observed bands at 533-682 cm^{-1} and 446-457 cm^{-1} are due to ν(M-O) and ν(M-N) vibrations, which are not present in the free Schiff base.[10] The infrared spectra of the complexes show ν (OH) bands in the range of 3250-3407 cm^{-1} region, which indicates the presence of water molecules in complexes.[11], (Table -2) .

Electronic spectra

The electronic spectral data of the synthesized Schiff base show two bands (Table-2) indicating the existence of intraligand transitions.[12] The electronic spectrum of Ni(II) Schiff base complex, exhibits two bands at 369 nm (27100 cm^{-1}) and 324 nm (30864 cm^{-1}) attributed to charge transfer transitions, suggesting the existence of an octahedral geometry.[13] For Zn(II)-L complex, the electronic spectrum exhibits a band at 369 nm (27100 cm^{-1}) resulting from the overlap of energy $\pi\rightarrow\pi^*$ transition mainly localized within the imine chromophore, supported the existence of an octahedral geometry.[14] The electronic spectrum of Pt(IV)-L complex reveals three bands at 536 nm (18656 cm^{-1}), 625 nm (16000 cm^{-1}), 360 nm (27777 cm^{-1}) due to the presence of $^1A_1g(I)\rightarrow{}^1T_2g(I)$,

$^{1}A_{1}g(I)\rightarrow{}^{1}T_{1}g(I)$ and $A^{1}g(I)\rightarrow{}_{1}Eg(I)$ transitions and an octahedral geometry was suggested.[(15)]

Electron paramagnetic resonance spectrum of Ni(II) Complex

The electron paramagnetic resonance spectrum of Ni(II)-L complex exhibit g_{eff} value (2.04). The large deviation of the g_{eff} value than the ideal value (2.0023) results from the partial ionic character of the covalent bond between the metal ion and the ligand under investigation. This value supports the existence of an octahedral geometry,[(16)] and confirmed the obtained result from the electronic absorption spectra.

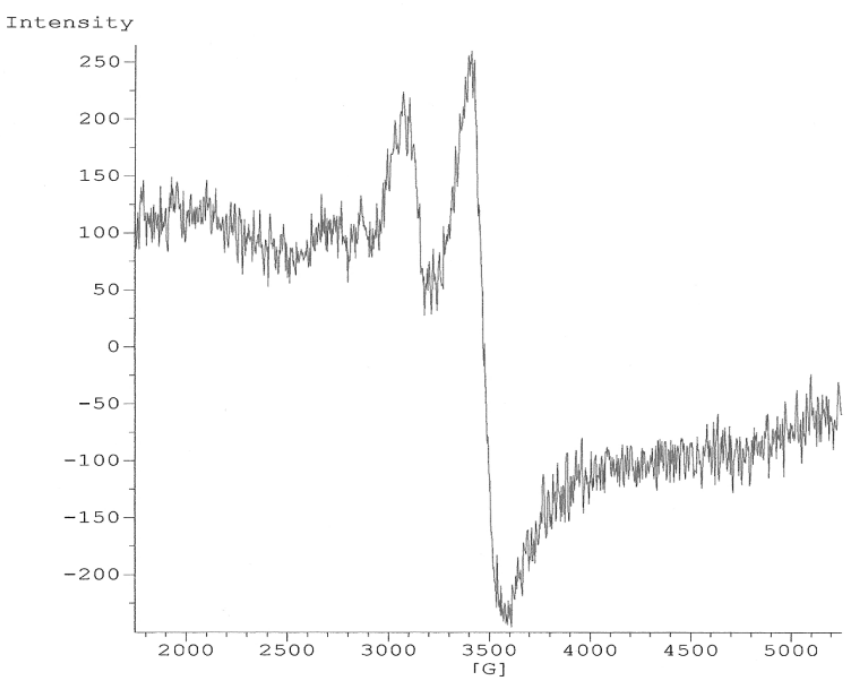


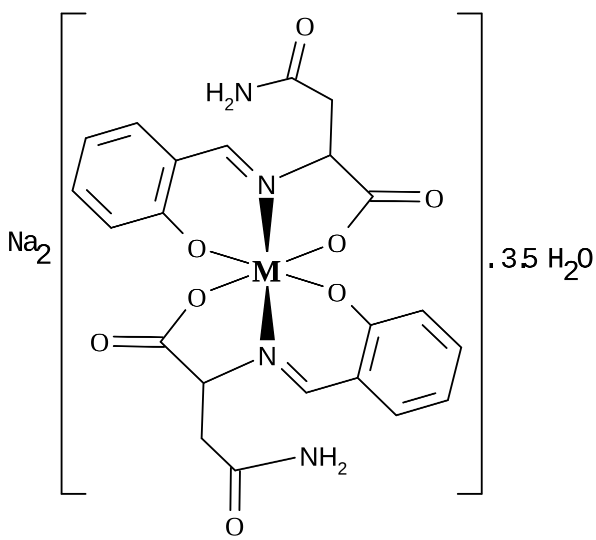
Fig-1: Electron paramagnetic resonance spectrum of Ni(II)-L complex

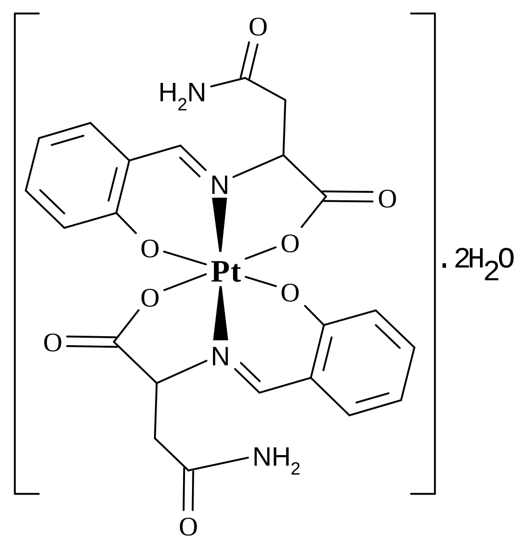
Table-2: Infrared and electronic spectral data of Schiff base and its complexes

Schiff base/Complexes	$\nu_{(OH)}$ H_2O	νC=N)	ν(COO)	ν(M-O)	ν(M-N)	nm (cm^{-1})
$C_{11}H_{12}O_4N_{2}.3H_2O$ (L)	3500	1602	1540	-	-	336 (29761) 273 (36630)
$Na_2[Ni(L)_2].3.5H_2O$	3382	1612	1644	682	446	396 (27100) 324 (30864)
$Na_2[Zn(L)_2].2H_2O$	3407	1586	1636	620	455	369 (27100)
$[Pt(L)_2].2H_2O$	3250	1610	1649	533	457	536(18656), 625 (16000) 360 (27778)

Conclusion

Form the previous results; one can suggest the following chemical structures.





M = Ni (II) or Zn(II)

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