SYNTHESIS AND CHARACTERIZATION OF SCHIFF BASE TRANSITION METAL COMPLEXES

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Abstract

New metal complexes of cu(II); Ni(II); Co(II); Mn(II); Zn(II); VO(IV) and Cd (II) have been synthesized from the Sciff base (L) derived from 4-amino antipyrine,salicyaldehyde and O-phenylene diamine. The prepared complexes where characterized by magnetic susceptibility, Molar conductance,FTIR,Uv-vis. The data show that these complexes have composition of ML type. The uv-vis,magnetic susceptibility data of the complexas suggest asquare-planar geometry around the central metal ion except VO(IV)complex which has square-pyramidal geometry.

Keywords: 4-amino antipyrine,Schiff base, antimicrobial activity.

Introduction

Schiff bases play an important role in inorganic chemistry, as they easily form stable complexes with most transition metal ions. The development of the field of bioinorganic chemistry has increased the interest in Schiff base complexes since it has been recognized that many of these complexes may serve as models for biologically important species (1-4).

Schiff base of 4-amino antipyrine and its complexes have avariety of applications in biological, clinical, analytical and pharmacological areas (5, 6).

On the industrial scale they have awide range of applications such as dyes and pigments (7). Studies of a new kind of chemotherapeutic Schiff bases are now attracting the attention of biochemists (8). Earlier work reported at some drugs showed increased activity ,when administered as metal complexes rather than as organic compounds (5).

Experimental

General

All chemical used were of reagent grade (supplied by either Merck or Fluka) and used as supplied. The FTIR spectra in the range (4000-200)cm^{-1} were recorded as cesiume iodide disc on FTIR 8300 shimadzu spectrophotometer. The uv-visible spectra were measured in DMF using shimadzu uv.vis.160 a-ultra-violet spectrophotometer in the range (200-1000) nm. Magnetic susceptibility measurement for complexes were obtained at room temperature using (Magnetic susceptibility measurement for complexes were obtained at room temperature using (Magnetic susceptibility Balance) Jhonson Maltery catalytic System division.

Synthesis of Sciff base (L)

4-amino antipyrine (1.010 g, 0.005 M) in 20 ml of ethanol was stirred with salicyaldehyde (0.53 ml, 0.005 M) for 2 h. The yellow solid (I) formed was filtered and recrystallized from ethanol. Compound (1) (3 g, 0.01 M) in 20 ml of ethanol was refluxed with (O-phenylenediamine) (0.54 g, 0.005 M) for 36 h after adding anhydrous potassium carbonate. The potassium carbonate was filtered off from the reaction mixture and the solvent was evaporated. The red solid separated was filtered and recrystallized from ethanol Fig.(1).

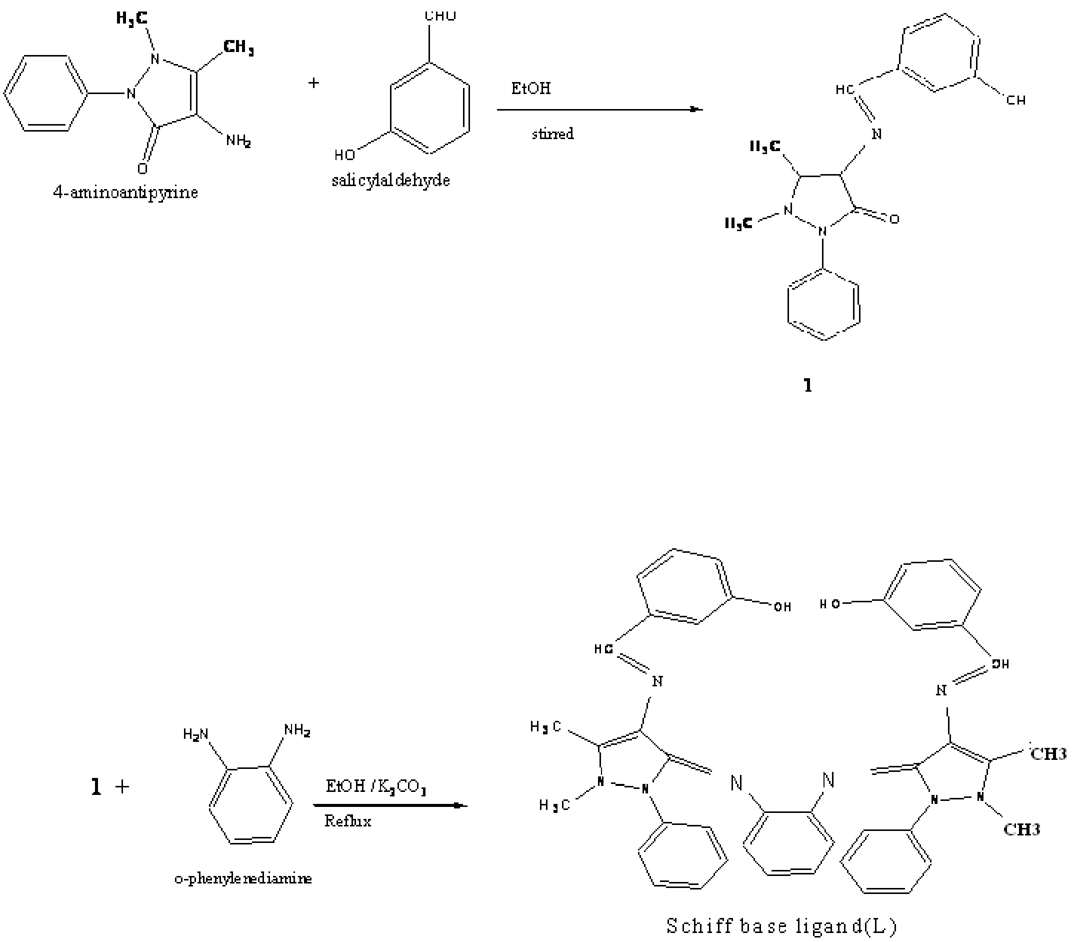

Fig.(1) : Formation of Schiff base ligand (L).

Syntheses of complexes

Asolution of metal (II) chloride in ethanol (2mM) was refluxed with an ethanolic solution of the Sciff base (2mM) for 6 h. The solution was then reduced to one-third on awater bath. The solid complex precipitated was filtered, washed thoroughly with ethanol and dried in vacuo. The oxovanadium (IV) complex was synthesized from the sulphate salt by the same procedure but in the presence of 5 ml of 5% aqueous sodium acetate solution.

Antibacterial and Antifungal studies

All newly synthesized compounds were tested for their in vitro growth inhibitory activity against a standard strain of pathogenic microorganism including Gram-positive bacteria (***Staphyiococcus aureus***), Grame-negative bacteria (***Escherichia coli***) and ayeast like pathogenic fungus. The primary screening was carried out using the agar disc-diffusion methodusing Muller-Hinton agar medium. Bacteria including staphy lococcus aureus and Escherichia coli were grown in nutrient broth at 37c for 24 h .

Result and Discussion

The physical properties for the ligand and complexes are summarized in Table (1) Physical characterization, Molal conductance and magnetic susceptibility data of the ligand and the complexes. The data from complexes correspond well with the general formula ML, where M=Cu(II), Ni(II), Co(II), Mn(II), Zn(II), Cd(II) and VO(IV) L=$C_{42}H_{36}N_{10}O_6$. The magnetic susceptibilities of the complexes at room temperature were consistent with square-planar geometry around the central metal ion, except for the VO(IV) complex which shows a square–pyramidal geometry. The higher conductance values of chelates support their electrolytic nature of Metal complexes.

Table (1)
Physical characterization, Molal conductance and magnetic susceptibility data of the ligand and the complexes.

Compound	**Molar formula**	**Colour**	**Yield%**	**Molar conductance $\wedge_m(\Omega^- cm^2 mol^-)$**	**Meff (BM)**
L	$C_{42}H_{36}N_{10}O_6Cl_2$	Red	70	-	-
[CuL] Cl_2	$CuC_{42}H_{36}N_{10}O_6Cl_2$	Brown	51	40	1.76
[NiL] Cl_2	$NiC_{42}H_{36}N_{10}O_6Cl_2$	Brown	50	44	-
[CoL] Cl_2	$CoC_{42}H_{36}N_{10}O_6Cl_2$	Red	53	50	3.60
[MnL] Cl_2	$MnC_{42}H_{36}N_{10}O_6Cl_2$	Pale brown	58	40	5.30
[ZnL] Cl_2	$ZnC_{42}H_{36}N_{10}O_6Cl_2$	Pale brown	60	52	-
[CdL] Cl_2	$CdC_{42}H_{36}N_{10}O_6Cl_2$	Yellow	57	43	-
[VOL] Cl_2	$VC_{42}H_{36}N_{10}O_{11}S$	Green	55	32	1.63

Infrared spectra

The IR spectra provide valuable information regarding the nature of functional group attached to the metal atom. The IR spectra of the ligand showed a broad band in the region 3200-3600 cm^{-1}, assignable to interamolecular hydrogen bonded–OH groups. The appearance of this peak in all the spectra of the complexes indicates that the–OH group is free from complexation. The spectrum of the ligand shows two different–C=N bands in the region 1590-1550 cm^{-1}, which is shifted to lower frequencies in the spectra of all complexes(1570-1520cm^{-1}) indicating the involvement of –C=N nitrogen in coordination to the metal ion (9,10). Accordingly the ligand acts as a tetradentate chelating agent ,bonded to the metal ion via the four nitrogen (-C=N) atoms of the Schiff base Fig.(2). Assignment of the proposed coordination sites in further supported by the appearance of medium bands at 450-400cm^{-1} which could be attributed to r_{M_N} respectively(11). In addition the vanadyl complex shows a band at 940 cm^{-1} attributed to V=O frequency (12).

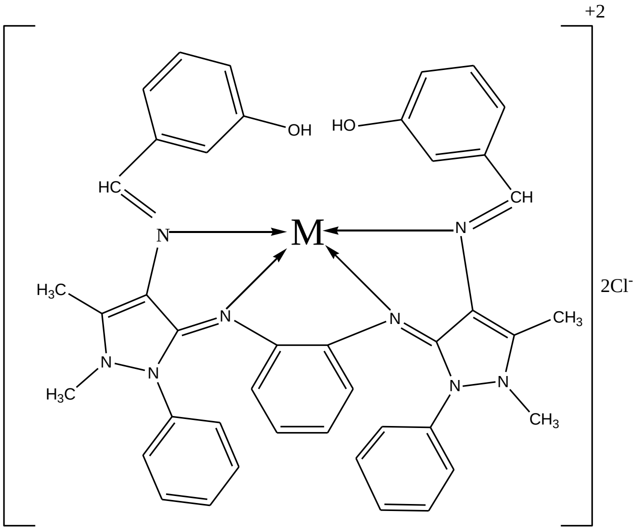

Fig.(2) : The proposed structures of the Schiff base complexes, M= cu(II); Ni(II); Co(II); Mn(II); Zn(II); Cd(II) and VO(IV).

Electronic absorption spectra

The electronic absorption spectra of the Schiff base, cu(II), Ni(II), Co(II), and VO(IV) complexes where recorded at 300K. The absorption region, band assignment and the proposed geometry of the complexes are given in Table (2). Based on these data, asquare planar geometry has been assigned to the complexes except VO(IV)complex which has square-pyramidal geometry Fig. (2). These values are comparable with other reported complexes (13-14).

Table (2)
Electronic absorption spectral data of the compounds.

Compound	**Solvent**	**Absorption (cm^{-1})**	**Geometry**
L	EtOH	40816	-
		25445	
[CuL] Cl_2	DMF	41493	Square planar
		26455	
		20533	
[NiL] Cl_2	DMF	42016	Square planar
		26954	
		19531	
		15797	
[CoL]Cl_2	DMF	41493	Square planar
		26455	
		19607	
[VOL]Cl_2	DMF	41841	Square Pyramidal
		26109	
		19920	
		12315	

Antimicrobial activity

All new synthesized compounds were evaluated for Antimicrobial activity against one strain of Gram +ve bacteria (***Staphyiococcus aureus***), Grame–ve bacteria(***Escherichia coli***) and a fungus (***candida albicans***) Table (3).

Table (3)
Antimicrobial activity of the Schiff base ligand and its metal complexes.

Compound	**Micro-organism**		
	Staphylococcus aureus	**Escherichia coli**	**Candida albicans**
L	+	+	+
[CuL] Cl_2	+ +	+ +	+ +
[NiL] Cl_2	+ +	+ +	+ +
[CoL]Cl_2	+ +	+ +	+ +
[MnL] Cl_2	+ + +	+ + +	+ + +
[ZnL] Cl_2	+ +	+	+ +
[VOL] SO_4	+ + +	+ + +	+ + +
[CdL] Cl_2	+ + +	+ + +	+ + +

+ = (5-10) mm=Slightly active, + + =(11-20) =Moderately active,
+ + + = more than 20 mm= highly active.

The values indicate the most complexes have higher antimicrobial activity than the free ligand. Such increased activity of the metal chelates can be explained on the basis of chelating theory (15).

References

[1] Z.chohan, H.,Sheazi, S. K.A.Synthesis and characterization of some co(II), cu(II) and Ni (II) complexes with nicolinylhydrazine derivatives and their biological role of metals and anions(SO_4^{-2} ,NO_3^- ,$C_2O_4^{-2}$ and $CH_3CO_2^-$) on the antibacterial properties. Synth. React. Inorg. Met.-Org.Chem. 29, 1999, 105-118.

[2] C. Jayabalakrishan, K. Natarajan, Synthesis, Characterization and biological activities of ruthenium (II) carhonyl complexes containing bifunctional tridentate Schiff bases. Synth. React. Inorg.Met.-Org. Chem. 31, 2001, 983-995.

[3] Jee worth ,T.,Wah, H.L.K., Bhowon,M. G., Ghoorhoo. D., Babooraw, K.Synthesis and antibacterial,catalytic properties of Schiff bases and Schiff base metal complexes derived from 2,3-diaminopyridine. Synth. React. Inorg. Met.–Org. Chem. 2000, 30, 1023-1038.

[4] J., N. Dharmora, P. Viswanalhamurthi, K. Natarajan Ruthenium (II) complexes containgbidentate Schiff bases and their antifungal activity. Transit. Metal Chem.26 2001 105-109.

[5] T.Hitoshi, N.Tamao, A.Hideyuki, F. Manabu and M.Takayuki, 1997Polyhedron 16 -3787.

[6] G. S. Trivedi and N. C. Desai 1992 Indian J.Chem. B 31 366.

[7] A.E.Taggi, M.Hafez, H.Wack, B.Young and Dlectka.The development of the first catalyzed reaction of ketones and imines:catalytic asymmetric synthesis of lactams .Am. Chem. Soc.124 2002 6626-6635.

[8] B .Katia, L .Simon, R. Anne, C .General, D. Francoise and M .Bernard Inorg. Chem. 35, 1996, 387.

[9] M.F .Iskander, L. Ei-syed and K.Z. Ismail Trans. Met. chem. 4 1979 225.

[10] Thankamony M and Mohanan K 2007 Indian J.Chem.A46 249.

[11] K.Nakamoto, Inffrared and Raman Spectra Of Inorganic And Coordination Compounds , Wiley, New York, 19973, rd edu.

[12] R.B. Xiu, F.L. Mintz , X. Z. You, R. X. Wang , Q. Yue, Q. J. Meng, Y. J Lu and D. V. Derveer 1996 Polyhedron 15 4585.

[13] A. B. P. Lever Inorganic electronic spectroscopy (Elsevier ,New York) 1968, 2 nd edu.

[14] L.N. sharada and M.C. Ganorkar, indian J. Chem. A27 1988 617.

[15] N .Dharmaraj, P.Viswanathamurthi and K. Natharajan Trans Met. Chem .26 2001 105.