COMPARATIVE STUDIES OF SOLVATOCHROMISM BEHAVIOUR OF COPPER(II) AND NICKEL(II) SCHIFF BASE COMPLEXES

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Abstract

A series of Schiff Bases of Ni(II) and Cu(II) using acetylacetone (acac), salicylaldehyde (sal), ethylenediamine (en), and o-phenylendiamine (dabe) were prepared and characterized. The electronic spectra of some copper chelates in various organic solvents depend strongly on the solvent used and the d-d band of Cu(II) shifts to red with the increase of the Donor Number (DN) of solvent. The color changes from blue to green are observed. The mechanism for solvatochromism is discussed in terms of conformational changes and solvent coordination. Among the nickel complexes, Ni (saloph) is brownish red in chloroform and green in pyridine, probably due to the coordination of two pyridine molecules.

Introduction

Chromotropic phenomena are changes in color caused by external influences. One type of this phenomenon is solvatochromism, i.e, the colors of their solutions change remarkably according to the nature of the solvent used. In most cases, such changes are the reflection of the conformation and electronic changes in them which are brought about by various kinds of solvation, ionization and complexation phenomena. In addition to the spectroscopic studies, factors such as DN, CP (Coordination Power), and SP (Softness Parameter) which indicate the extent of solute-solvent interaction are also reported [1, 2]. The present study shows that their electronic spectra, which are composed of readily explicable d-d bands, change systematically with the donor-acceptor properties of the

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solvent. In many cases they change parallel with the DN of the solvent but, in some rare cases, with the Acceptor Number (AN) of Gutmann and Mayer.

Sone and Fukuda, in their studies on mixed ligand chelates of Cu (II) and Ni (II), found that the chelates of type M (dike) (diam) x (M= Cu, Ni; dike= diketone; diam= diamine; x= Clo4-No3-, B (ph)4- etc) are notably soluble in many kinds of organic solvents and most of them are strongly solvatochromic [3-7].

Based on these findings, Sone and Fukuda proposed that these chelates can serve as "color indicators" for the solvent donor or acceptor properties [8]. For a different application of these phenomena, it might be possible to design and synthesize compounds with certain chromotropic properties. Such compounds may find many practical uses in technology, education, and as models in bio-scientfic researches. Solvatochromic compounds can also be used as sensors in the design of electrodes [9].

These important and interesting phenomena for Schiff Bases were not studied vastly and systematically.

Experimental Section

Preparation

Complexes of 1, 2 (Figure I) were synthesized using template and nontemplate methods as reported in literature [10]. Compound 3 was synthesized with a modified method [11] Compounds 4 and 5 were synthesized with techniques developed in this lab which differ from those reported previously. The chemicals were used without further purification.

Apparatus and Procedures

The ^{1}HNMR spectra were recorded on a Bruker Ac 80 spectrometer and FT-IR spectra. (400-4000 cm-1) of compounds were pressed into KBr pellets and measured with a Philips 9800 spectrophotometer. The electronic spectra of solutions were measured with a Philips 8800 recording spectrophotometer at room temperature.

Preparation of the Ligands

For the synthesis of HL^1, acetylacetone (25.5 mL; 0.25 mol) was added to the solution of ethylenediamine (16.69 mL; 0.25 mol) in chloroform and allowed to stand for 10 hours at room temperature. The solution of HL^1 (7.11g; 0.05 mol) in chloroform (30 mL) and a warm solution of the salicylaldehyde (0.05 mol) in chloroform (200 mL) were mixed and then reflected for 30 minutes.

To synthesis HL^1, acetylacetone (25.5 mL; 0.25 mol) was added to the solution of ophenylenediamine (27 g; 0.25 mol) in chloroform and allowed to stand for 24 hours. The temperature of reaction was 40°C. The solution of HL^1 (11.4 g; 0.06 mol) in chloroform (50 mL) and a warm solution of salicyladehyde (7.32 mL; 0.06 mol) in chloroform (240 mL) were mixed and then refluxed for 60 minutes. H$_2$L^2 was precipitated accordingly.

Preparation of the Complexes

Complex 4 was prepared by the addition of the stoichiometric amount of H$_2$L^2 to metal acetate in methanol. The precipitated solid was filtered off and passed from the chromatography column and dried under vacuum at 80°C.

Complex 5 was prepared by the addition of the stoichiometric amount of HL^1 and metal acetate in methanol. A violet solid was recrystallized and passed from the chromatography column.

Results

FT-IR Spectra

A strong band for H$_2$L$_2$ at~1200 cm^{-1} is assigned to hydrogen bonded OH in plane bending vibration. Peaks of 400-700 cm^{-1} are assigned to a metal chelate ring. In complex 4, three bands of very strong intensity at 1608, 1576, 1481 cm^{-1} are assigned to the c=c stretching vibration

Figure 1. Structure of compounds
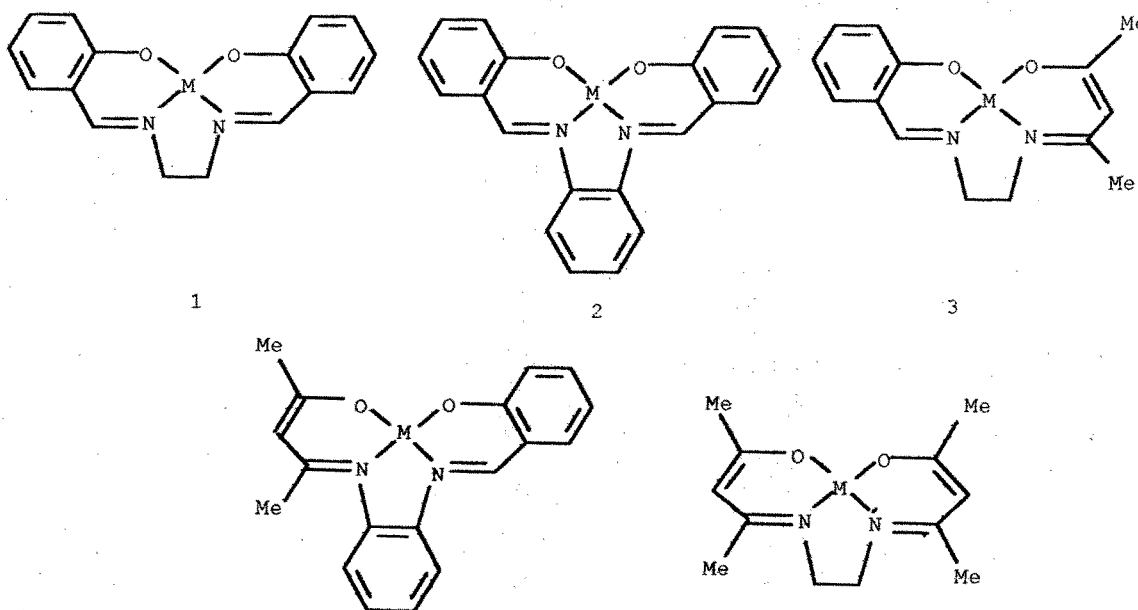
1.M (salen); salen=N, N'-ethylene bis (salicyidenaminato) and M- Ni, Cu 2. M (saloph); salo Ph- N, N'- o-phenylene bis (salicylidenaminato)3.M (sal)(acac)en; (sal)(acacc)en =N,N'-ethylene (ecetylacetonato) (salicylidenaminato)4. M(sal)(acac)dabe; = N, N'-o-phenylene (acetylacetonato) (salicyldienaminato) 5.M(acae)$_2$en; (acac)$_2$en= N, N'-ethylene bis (acetylacetonato)

of the phenyl ring and stretching vibration c=N is observed in~1500 cm⁻¹ and peak of ~750 cm⁻¹ is assigned to the out of plane deformation C-H.

¹HNMR Spectra

The ¹HNMR spectra of ligands recorded in $CDCl_3$. Spectrum of HL^1 shows signals of two methyl, two methylene, vinyl and primary amino groups, and enamine in 1.95s, 2.1s/3.5t/5.5s/8.12/10.8 (br) ppm.

In Hl^1 spectrum, signals of 2.2s/2.35s, 2.85s/6.75s/ 7.35m/10.1s (br) were assigned to proton of OH, two methyl, alyl, aromatic, and hydrogen bond respectively. Protons of amins of aromatic frequently appeared in 3 ppm, (but in this case the absorption peak is broadened because the hydrogen bond between OH and amine moieties and quadrupole relaxation with nitrogen. Broadening is observed in 3.4 ppm.

In spectrum of H_2L^2, signals of 1.9db, 2.2db/3.1 db/5.3 s/6-8 m/8.7 s/9.9 (br)/12.5 s were assigned to two methyl, proton of OH, vinyl, two phenyl ring, azomethine, enamine, and phenol hydroxy. These peaks are doubled because of alyl coupling.

Mass Spectra

Mass spectrum of $Cu(acac)_2$ en are given in Table 1.

Electronic Spectra

Copper complexes 1=3 and 5 show solvatochromic behaviour. 1 and 3 compounds are deep violet in $CHCL_3$, greenish-blue in acetonitril (AN), blue in dimethylformamide (DMF), brownish green in tetrahydrofuran (THF), green in pyridine (py), and piperidine (Pip). The change of color in the case of copper complex 5 is from pink in $CHCL_3$ to blue in piperidine.

The above three compounds also dissolve in a poorly coordinating inert solvent such as $CHCL_3$ without any noticeable color change, which indicates that this solvent has weak interaction with the central metal. Therefore, it completely retains its original planar structure. On the contrary, strong solvents like DMF and Py coordinate effectively, forming the complex of pentacoordinate. Intermediate behaviours are found in acetone, the coordination ability of which lies between these two extremes. From Table 2, it can be seen that for every chelate studied, the order of the λ max values observed in this study agrees with the DN of the solvents. This suggests that some kind of correlation exists between DN and λmas which means that DN increases with the increase λ max (Figure 2). This result coincides with the expectation from simple ligand field theory; since the d_z^2, d_{xz} and d_{yz} orbitals of Cu (II) ion in chelate will all be lifted up by its interaction with polar solvent molecules approaching the chelate plane, the broad d-d transition band will be shifted to lower energy (λmax of d-d transition band of complexes in tetrahydrofuran (DN= 20) is larger ithan DMF (DN= 26.6); as tetrahydrofuran has a ring form. Therefore it

Table 1. Mass Spectrum of $Cu(acac)_2$en

Assignment	M(abundance percent)	Assignment	M(abundance percent)
Mother peak	285(62)	$[C_4H_5NO]^+$	83(34)
$[CuC_6H_9NO]^+$	174(100)	$[C_3H_5NO]^+$	71(45)
$[C_6H_8NO]^+$	110(42)	$[C_3H_5O]^+$	57(75)
$[C_5H_7NO]^+$	97(32)	$[C_2H_4O]^+$	44(68)

Table 2. λmax of Complexes (relation to d-d transition) in different Solvents

Solvent	$CHCl_3$	Ac	DmF	THF	Py	Pip
DN	0	17	26.6	20	33.1	51
Cusalen	564.8	570	571.2	575.2	593.6	620.8
Cu(acac)(sal)en	560.8	567.2	570.4	583.2	602	626.4
$Cu(acac)_2$en	546.4	548.8	550	552	552.8	575.9

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HL1

H2L2

HL1'

H2L2'
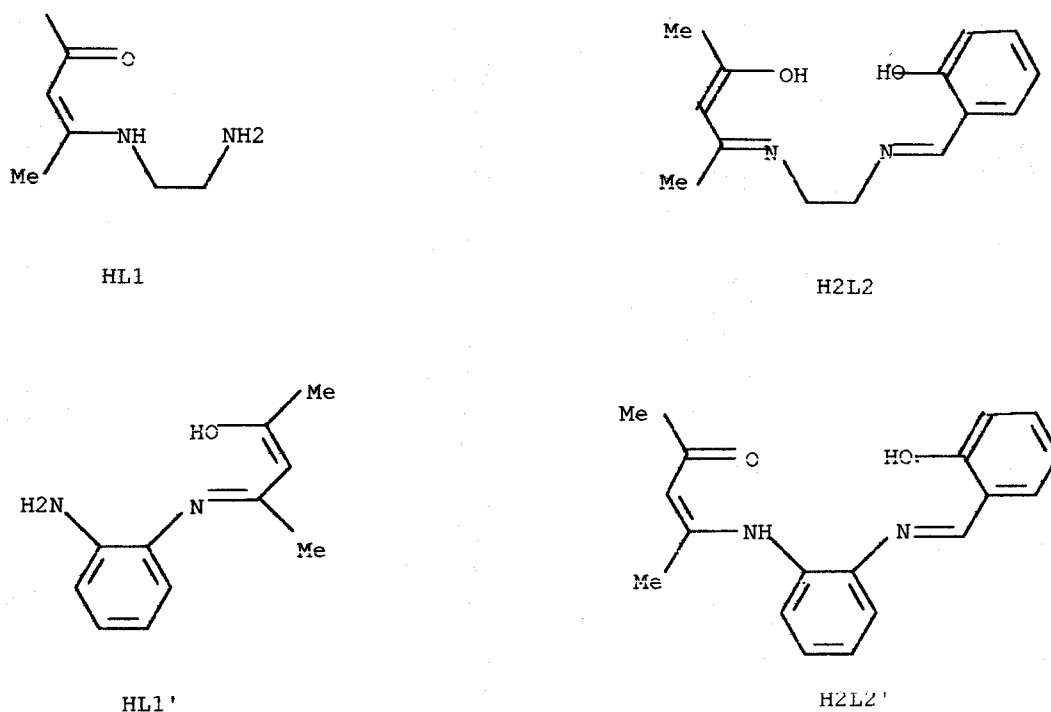
Scheme 1

appears that it has less steric hindrance in the axial position compared to the N,N dimethylformamide. Futhermore, steric hindrance in DMF will cause poor interaction with the central metal acting contrary to DN characteristics.

Discussion

Flexibility of the ligands is a factor governing the reactivity of the central metal. Conformational flexibility of the ligand might also be responsible for changes in the ligand field strength, thereby influencing the color. Thus color isomerism/solvatochromism, exhibited by complexes, can be understood in terms of not only the fifth coordination of the solvent molecule, but also changes in the ethylenediamine conformation.

The electronic spectra of a Cu (II) complex shows one broad d-d band in the visible region, corresponding to the excitation of an electron to the "hole" in $d_{x^2-y^2}$ from the remaining four orbitals. In general, the position of this band (ν max) is shifted to the blue with an increase in the ligand field strength of the equatorial ligands and fixed set of axial ligands. On the other hand, this band is shifted to the red with an increase in the ligand field strength of the axial ligands and a fixed set of equatorial ligands. The repulsion between the equatorial ligands and the electron in $d_{x^2-y^2}$ increase so that this electron will become more and more energy rich. Unlike in Ni (II), it cannot escape into

the d_z^2 orbital which is now fully occupied, so it must hold its position. It is easy to see that no other electron will tend to fill the hole in the same orbital where the ligand repulsion is very strong. Thus, more energy is required for the excitation shifting the ν max to the blue in the order of increasing ligand field strength of the equatorial ligands. On the other hand, in the latter case, the electron pair in $dz2$ (and to a lesser extent, those in d_{xz} and d_{yz}) is repelled and destabilized more strongly by the axial ligands of higher ligand field strength. As a result, less energy is needed to excite electrons to the hole in $d_{x^2-y^2}$ which shifts ν max to the red.

Waters and Hall [12, 13, 14,] have attributed the green color to pentacoordination and brown or violet to tetracoordination of these copper complexes and bands below 400 nm have a very high extinction coefficient and almost certainly associtated with the intra-ligand or charge transfer transition.

Copper complexes 1 and 3 show solvatochromic behaviour in comparison to 2 and 4 Cu(II) complexes. In the case of 1 and 3, one of the reasons for the incidence of phenomena is changes in the ethylenediamine conformation, but in 2 and 4, the phenyl ring is in the bridge. Also in latter compounds, there are resonance in total and electrons are completely distributed. The probability of approaching the fifth ligand is less.
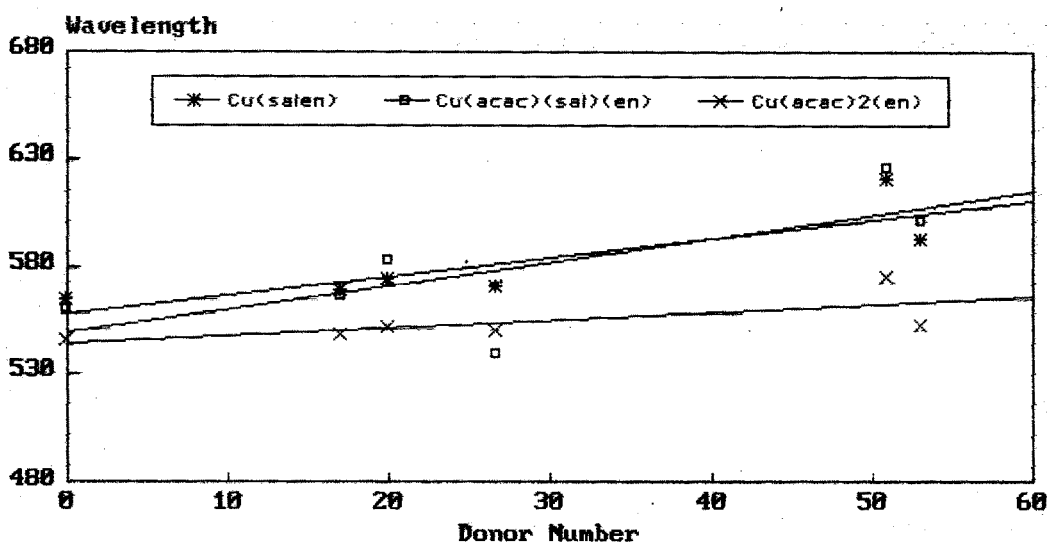
Figure 2. Correlation diagram of the wavelength versus Donor Number

The ability of the Ni(II) ion to take a coordination number exceeding four is governed mainly by the following factors:

1. electronic factor (nature of M-L bond, electronegativity of M and L ligand field strength (LFS)

2. steric factor (shape of ligands, crystal-packing effect). Depending upon these factors, for example, the four coordinated nickel (II) complex, when dissolved in pyridine, may or may not take up pyridine.

There are square-planar nickel (II) complexes which show little or no tendency to combine with a pyridine molecule in spite of the absence of steric hindrance. When there is no steric hindrance, a strong ligand field will favour a four coordinate square-planer configuration over five and six-coordination. The difference between the β-ketoamine and the salicylideneimine complexes may be due to the stronger ligand field produced by the β-ketoamins since the stronger ligand field will increase the energy gap between the $d_{x^2-y^2}$ orbital and the next highest orbital of the Ni(II) ion, making the highest $d_{x^2-y^2}^2$ orbital less readily inclined towards bond formation.

From a comparison of experimental results, the following order is obtained for the strength of the ligand field: saloph<salen<acac$_2$en.

The electronic spectra clearly indicate that Ni(salen) and Ni(acac)$_2$ en do not combine with pyridine, while Ni(saloph) does combine with two molecules of pyridine to form a hexa-coordinate compound. This result is different from what one expects on the basis of the steric factor. The ligand-field strength seems to play a more important part in this phenomena. Considering the steric

factor alone, the hindrance against hexa-coordination would be expected to be larger for saloph than for salen and (acac)$_2$ en.

Although detailed analysis of absorption spectra of complex compounds is not yet possible, several attempts have been made to relate these spectra to their stereochemistry. In this respect Mckenzie, Mellor, Mills and Short [15] found that many paramagnetic nickel complexes show the same absorption bands as the free ligands while for diamagnetic complexes, a new band appears at 410 nm for octahedral complexes, a broad peak in 800-1000 nm is seen also.

The axial Cu-L (L= ligand) bond, strengthened by the removal of the interfering electron pair, pulls the Cu^{2+} ion out of the plane of the chelate to yield a square pyramidal structure. The coordination of another ligand L below the plane is now difficult because of the strong repulsion between it and the displaced electron pair. The chelate rings, now bent downward, also hinder such an approach. The solvated complex formed in such a case assumes a 5-coordinate structure, but nickel complexes can be combined with two solvent molecules.

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