Synthesis, Characterization, Biological Activity and DNA Binding Studies of Metal Complexes with 4-Aminoantipyrine Schiff Base Ligand

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Abstract: A new series of transition metal complexes of Cu(II), Ni(II), Co(II), Zn(II) and VO(IV) have been synthesized from the Schiff base ligand (L) derived from 4-amino antipyrine and 5-bromo salicylaldehyde. The structural features of Schiff base and metal complexes were determined from their elemental analyses, thermogravimetric studies, magnetic susceptibility, molar conductivity, ESI-Mass, IR, UV-VIS, ¹H NMR and ESR spectral studies. The data show that the complexes have composition of ML₂ type. The UV-VIS, magnetic susceptibility and ESR spectral data suggest an octahedral geometry around the central metal ion. Biological screening of the complexes reveals that the Schiff base transition metal complexes show significant activity against microorganisms. Binding of Co(II) complex with calf thymus DNA (CT DNA) was studied by spectral methods.

Keywords: Aminoantipyrine, Schiff base, complex, Antimicrobial studies, DNA binding

Introduction

Antipyrine derivatives are reported to exhibit analgesic and anti-inflammatory effects¹⁻⁴, antiviral⁵, antibacterial⁶ activities and have also been used as hair colour additives⁷ and to potentiate the local anesthetic effect of lidocaine⁸. These compounds have been used in spectrophotometric determination of metal ions. Many of these reagents give intense colours with transition metal ions, providing sensitive probes⁹ and some of them can also coordinate to rare earth ions to form metal complexes with interesting structures¹⁰. Antipyrine Schiff base derivatives can serve as antiparasitic agents and their complexes with platinum(II) and cobalt(II) ions have been shown to act as antitumour substances¹¹. A search through the literature reveals that no work has been done on the transition metal complexes of Schiff base formed by the condensation of 4-aminoantipyrine with 5-bromo salicylaldehyde. In the

present context, we synthesized tridentate ligand system from 4-aminoantipyrine and 5-Br salicylaldehyde. The synthesized compound and its ligation behaviour with metal ions was studied.

Experimental

All the chemicals used were of analar grade. 4-Aminoantipyrine, metal salts and 5-bromo salicylaldehyde were obtained from Sigma Aldrich. Solvents such as ethanol, methanol, petroleum ether were purified by standard procedures.

Instruments

Elemental analysis of the ligands and their metal complexes was carried out using a Perkin-Elmer 240C (USA) elemental analyser. Molar conductances of the metal complexes were measured in a DMSO solution using digisun electronic conductivity meter. Magnetic susceptibilities of the complexes were determined on Guoy balance, model 7550 using Hg [Co(NCS)₄] as standard. The diamagnetic corrections of the complexes were done using Pascal's constants. TGA studies were carried on Shimadzu DTG -60 H system in the temperature range of 0-1000 °C.

IR spectra were recorded in KBr discs on Brucker FTIR spectrophotometer from 400 to 4000 cm⁻¹. Electronic spectra were recorded with an Elico SL 159 UV visible spectrometer from 200 – 1100 nm. ¹H NMR & ¹³C NMR spectra were recorded using CDCl₃, at Brucker 400MHZ spectrometer. The mass spectra were recorded by ESI technique on LCQ ion trap (thermo Finnigan Sanjose CA (USA) mass spectrometer instrument. The ESR spectra of the Cu(II) complexes were recorded on Jeol, JES -A 200 ESR spectrometer at room temperature.

Synthesis of Schiff base(5-Br SALAAP) ligand

The 5-bromo salicylidene-4-aminoantipyrine(5-Br SALAAP) was prepared by using the reported method¹². 4-Aminoantipyrine (2.03 g 0.01 mmol) and 5-bromo salicylaldehyde (2.01 g 0.01 mmol) were dissolved in a methanol solution. The mixture was stirred for 30 min at room temperature to give a yellow precipitate. The mixture was filtered and the solid obtained was recrystallised from methanol solution.

Synthesis of metal complexes

In the preparation of the metal complexes, the metal and the ligands were mixed in 1:2 molar ratio using required quantities of ethanol. Hot ethanolic solution of ligand (0.01 mol) and hot ethanolic solution of corresponding metal salts (0.01/0.005 mol) (MX₂ where M=Cu(II),Ni(II),Co(II),Zn(II) and VO(IV) X=Cl; for VO(IV);X=SO₄) were mixed together, refluxed for 2-3 h and left for evaporation at room temperature for 3 days, coloured solid metal complexes were obtained. The products were filtered, washed with cold ethanol and dried under vacuum over calcium chloride.

DNA binding activity

Absorption spectra were reorded on a UV-Visible spectrophotometer using 1 cm quartz micro cuvettes. Absorption titrations were performed by keeping the concentration of the complex constant (100 µM) and by varying the concentration of CT -DNA from 0-40 µM. The binding constant (K_b) for the binding of the complex with DNA, has been determined from the spectroscopic titration data using the following equation.

$$[\text{DNA}]/(\epsilon_a - \epsilon_f) = [\text{DNA}] / (\epsilon_b - \epsilon_f) + 1/K_b (\epsilon_b - \epsilon_f) \quad (1)$$

Where [DNA] is the concentration per nucleotide, the apparent extinction coefficient ϵ_a , was obtained by calculating $A_{\text{obs}} / [\text{Co(II)}]$, ϵ_f extinction coefficient of the complex in presence of DNA and ϵ_b the extinction coefficients for the fully Co(II) complex in the fully bound form. K_b (binding constant) the ratio of the slope to the intercept, was obtained from a plot of $[\text{DNA}] / (\epsilon_a - \epsilon_f)$ versus [DNA], a slope $1/(\epsilon_b - \epsilon_f)$ and an intercept $1/K_b (\epsilon_b - \epsilon_f)$.

Results and Discussion

Characterization of ligand

Synthesized Schiff base ligand (**L**) (2,3-dimethyl-1-phenyl-4-(5-bromo-2-hydroxy benzylideneamino)-pyrazol-5-one) is yellow coloured solid and is stable at room temperature. It is soluble in ethanol and DMSO.

Infrared spectra

The infrared spectra of the ligand exhibited a broad medium intensity band around 3434 cm^{-1} is due to intramolecular hydrogen bonded OH group. A very strong band occurring at 1637 cm^{-1} is attributed to $\nu_{\text{C=O}}$ of pyrazolone ring. A band at 1595 cm^{-1} in the ligand spectrum is possibly due to the vibrational stretching frequency of azomethine $\nu_{\text{C=N}}$ group.

^1H NMR spectra

The ^1H NMR spectrum of the Ligand (Figure 1) displays the following signals: C_6H_5 as a multiplet at 6-8 ppm. $=\text{C}-\text{CH}_3$ at 2.4 ppm, $-\text{N}-\text{CH}_3$ at 3.2 ppm and azomethine proton at $-\text{CH}=\text{N}-$ at 9.8 ppm, intramolecular hydrogen bonded OH group at 13.4 ppm.

Figure 1. ^1H NMR spectra of 5Br SALAAP

^{13}C NMR spectra

^{13}C Spectrum of Ligand (Figure 2) has 120(C-1), 160.3(C-2), 118.5(C-3), 135.6(C-4), 115 (C-5), 133.7(C-6), 160.7(C-7), 116 (C-8), 134 (C-9), 10.27(C-10), 35.5 (C-11), 160.6 (C-12), 142 (C-13), 112 (C-14), 129(C-15), 118.9 (C-16), 129 (C-17), 112(C-18).

Based on the data of elemental analysis & ESI mass, the composition assigned to the complexes, are formulated and presented in Table 1. The conductance values for all complexes were measured using DMSO solvent, the obtained low values (6-11 Ohm⁻¹ cm² mol⁻¹) suggest the presence of a non-electrolytic nature of complexes in the solvent and that no anions are present outside the co-ordination sphere.

Table 1. Analytical data of complexes

Complex	Formula	M.Wt	C	H	N
Ligand	C ₁₈ H ₁₆ BrN ₃ O ₆	386	55.91% (51.79%)	4.04% (4.14%)	10.90% (10.88%)
[Cu(5BrSALAAP) ₂].H ₂ O	C ₃₆ H ₃₀ N ₆ Br ₂ CuO ₄	834	51.34% (51.79%)	3.62% (3.59%)	10.23% (10.0%)
[Ni(5BrSALAAP) ₂].H ₂ O	C ₃₆ H ₃₀ N ₆ Br ₂ NiO ₄	828	52.11% (52.89%)	3.61% (3.55%)	10.13% (10.41%)
[Co(5BrSALAAP) ₂].H ₂ O	C ₃₆ H ₃₀ N ₆ Br ₂ CoO ₄	830	52.01% (52.04%)	3.62% (3.61%)	10.14% (10.12%)
[Zn(5BrSALAAP) ₂].H ₂ O	C ₃₆ H ₃₀ N ₆ Br ₂ ZnO ₄	835	51.11% (51.73%)	3.61% (3.59%)	10.09% (10.05%)
[VO(5BrSALAAP) ₂].H ₂ O	VOC ₃₆ H ₃₀ N ₆ Br ₂ O ₄	838	51.14% (51.55%)	3.61% (3.57%)	10.03% (10.02%)

Infrared spectra

The IR spectra of the complexes are compared with that of the free ligand to determine the changes that might have taken place during the complexation, all data are listed in Table 2. The band assigned to the azomethine group in the free Schiff base ligand was observed at $\nu_{C=N}$ 1595 cm⁻¹ and shifted to lower or higher wave numbers ranging from 1562-1617 cm⁻¹ in the spectra of all complexes. This indicates the participation of the nitrogen atom of the azomethine group in coordination¹³⁻¹⁶. The band at $\nu_{C=O}$ = 1637 cm⁻¹ is characteristic of the carbonyl group present in the free Schiff base ligand. This group was shifted to lower or higher wave numbers ranging from 1591-1641 cm⁻¹ in all complexes, which indicates the involvement of the carbonyl oxygen in coordination^{13-15,17}. The presence of IR broad bands of metal complexes are in the range of 2931 - 3419 cm⁻¹ indicate the presence of coordinated/lattice water molecules supported from thermal analysis^{13,18}. The ν_{C-O} (phenolic) stretching frequency of ligand is seen at 1342 cm⁻¹, which gets shifted to higher (1355-1384 cm⁻¹) region in the complexes indicating coordination of phenolic oxygen¹⁹. The IR spectra of complexes show new bands at 552-573 cm⁻¹ and 429 -473 cm⁻¹ assigned to $\nu_{(M-O)}$ and $\nu_{(M-N)}$ respectively²⁰. The peak observed at 987 cm⁻¹ complexes of VO are due to $\nu_{(V=O)}$.

Table 2. IR spectral data of ligand and its complexes in cm⁻¹

Complex	ν_{O-H}	$\nu_{C=N}$	$\nu_{C=O}$	ν_{C-O}	ν_{M-O}	ν_{M-N}	$\nu_{V=O}$
Ligand	3434	1595	1637	1342	----	----	----
Cu(II)Complex	2931	1617	1653	1384	556	450	----
Ni(II)Complex	3383	1562	1591	1379	553	499	----
Co(II)Complex	3382	1561	1596	1343	555	448	----
Zn(II)Complex	3347	1575	1609	1355	552	429	----
VO(IV)Complex	3419	1582	1641	1375	573	473	987

Electronic spectra and magnetic susceptibility

The electronic spectral data and magnetic moments (μ_{eff} B.M) of the complexes are presented in Table 3. The electronic absorption spectra of ligand and metal complexes were recorded in DMSO, in the range of 200-1100 nm. The electronic spectrum of free Schiff base showed three bands at 297 nm, 347 nm and 407 nm are due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions¹³.

Cu(II) complex displayed four bands at 302 nm, 357 nm, 427 nm and 580 nm. The first two peaks are most probably due to ligand $\rightarrow$ metal charge -transfer transitions. The last two peaks are due to d -d transitions, which is assigned ${}^2E_g \rightarrow {}^2T_{2g}$ suggesting tetragonal geometry (distorted octahedral geometry)²¹. The magnetic moment of Cu(II) was seen at 1.72 B.M. On the basis of electronic spectra and magnetic susceptibility measurements, a distorted octahedral geometry around Cu(II) is suggested.

The electronic spectra of Ni(II) complex displayed four bands at 302 nm, 347 nm, 457 nm and 705 nm. The first two peaks are most probably due to ligand $\rightarrow$ metal charge -transfer transitions. The last two peaks are due to d-d transitions and are assigned as ${}^3A_{2g} (F) \rightarrow {}^3T_{1g} (P)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g} (F)$ respectively. This suggests an octahedral geometry²¹⁻²⁴ around Ni(II) ion.

The magnetic moment of Ni(II) complex was found to be 2.87 B.M which are in the normal range observed for octahedral Ni(II) complexes. The electronic spectrum of the Co(II) complex exhibited four bands at 297 nm, 347 nm, 437 nm and 634 nm. The first two intense maxima are due to intra-ligand transitions of the organic moiety.

The other two transitions may be assigned to ${}^4T_{1g} \rightarrow {}^4T_{1g} (P)$ and ${}^4T_{1g} (F) \rightarrow {}^4T_{2g} (F)$ respectively, suggesting an octahedral geometry around Co(II) ion²⁵. The magnetic moment of Co(II) complex which was found to be 5.14 B.M. is also an indicative of octahedral geometry²⁶.

The Zn(II) complex has been found to be diamagnetic in nature. On the basis of analytical, conductance and spectral data, the Zn complex, assigned to be an octahedral geometry²⁷. The observed magnetic moment value for VO(IV) complex is 1.91 B.M. which suggests octahedral geometry for this complex²⁸. In the present studies, VO(IV) complex shows four bands at 307 nm, 347 nm, 452 nm and 527 nm. The first two intense maxima are due to intra-ligand transitions of the organic moiety. The other two transitions may be due to ${}^2B_2 \rightarrow {}^2B_1$ and ${}^2B_2 \rightarrow {}^2A_1$. The low frequency band corresponding to ${}^2B_2 \rightarrow {}^2E$ is not clearly resolved in the spectrum. Based on the two bands observed, octahedral geometry is proposed for the above complex²⁹.

Table 3. Electronic spectra and magnetic susceptibility data for ligand and complexes

Complex	Absorption, nm	μ_{eff} (B.M)
Ligand	297, 347, 407	-
Cu(II) complex	302, 352, 427, 580	1.72
Ni(II) complex	302, 347, 457, 705	2.87
Co(II) complex	297, 347, 437, 634	5.14
Zn(II) complex	-	dia
VO(IV) complex	307, 347, 452, 527	1.91

ESR spectra

The ESR spectra of the Cu(II) complex (Figure 4) was recorded on Jeol, JES -FA 200 ESR spectrometer at R.T. The observed data for complex showed that $g_{\parallel} = 2.07-2.543$ and $g_{\perp} = 2.22$. This complex showed $g_{\parallel} > 2.3$ which is characteristic of anion environment. The

trend $g_{\parallel} > g_{\perp} > 2.0023$ observed for the complexes indicates that unpaired electron is localised in $d_{x^2-y^2}$ orbital of the Cu(II) ion. Thus a tetragonal geometry is proposed for the complex. $G = (g_{\parallel} - 2) / (g_{\perp} - 2)$, which measure the exchange interaction between the metal centres in a polycrystalline solid has been calculated. Acc to Hathaway³⁰ if $G > 4$ the exchange interaction is negligible if $G < 4$ indicates considerable exchange interaction in the solid complexes. The above reported complex showed G values < 4 indicating the exchange interaction in complex. Further more, Masa cesi *et al*³¹ reported that $g_{\parallel}$ is 2.4 for copper-oxygen bonds and 2.3 for copper-nitrogen bonds. for the complex reported here, $g_{\parallel}$ values between 2.3 – 2.4 which further confirms ,the presence mixed copper- nitrogen and copper – oxygen bonds in these chelate complex.

Figure 4. ESR spectra of Cu(II) complex

Thermal analysis

In the present investigation heating rates were suitably controlled at $10\text{ }^{\circ}\text{C min}^{-1}$ under nitrogen atmosphere and the weight loss was measured from the ambient temperature up to $1000\text{ }^{\circ}\text{C}$. Water molecules in complexes are generally of two types lattice water and coordinated water³². The lattice water will be lost at low temperature ($60\text{--}120\text{ }^{\circ}\text{C}$) where as the loss of coordinated water molecule is observed at high temperatures ($150\text{--}200\text{ }^{\circ}\text{C}$). In the thermograms of DTA and TGA of complexes $[\text{Co(II)}(5\text{-BrSALAAP})_2]\text{H}_2\text{O}$, $[\text{VO(IV)}(5\text{-Br SALAAP})_2]\text{H}_2\text{O}$, (Figure 5 & 6) a small weight loss in the range of $60\text{--}120\text{ }^{\circ}\text{C}$ is assigned to loss of lattice water, maximum and gradual weight loss in the range of $300\text{--}1000\text{ }^{\circ}\text{C}$ is and attributable to decomposition of ligand moiety. The residue at $1000\text{ }^{\circ}\text{C}$ indicates the non volatile metal component present in the complex.

Figure 5. Thermogram of Cu(II) complex

Figure 6. Thermogram of VO(IV) complex

Mass spectra

Mass spectra of complexes provides a vital clue for elucidating the structure of compounds. The ESI mass of the ligands and its metal complexes recorded at room temperature were used to compare their stoichiometry.

The molecular ion peaks of Cu(II), Ni(II) and Co(II), (Figure 7) Zn(II) and VO(IV) complexes were observed respectively at 834, 828, 830, 835 and 838 and which were in good agreement with the molecular weight of the proposed structures and few unidentified ions were also observed.

Figure 7. Mass spectra of Co(II) complex

Antimicrobial activity

In the present investigation, biological activity of the ligand and their complexes with Cu(II), Ni(II), Co(II), Zn(II) and VO(IV) have been screened for antimicrobial activity against bacteria (*E.coli* and *S.aureus*) by paper disc method. The concentration for these samples maintained as 200 µg/mL, 100 µg/mL and 50 µg/mL in DMSO. In the present study the zones of inhibition of antibacterial activity have been presented in Table 4. The results indicate that copper and cobalt complexes show activity against *E.coli* and *S. aureus* at 200 µg/mL (Figure 8).

Table 4. Antimicrobial activity of complexes (inhibition of growth)

Complex	<i>E.coli</i> 200 µg/mL	<i>S.aureus</i> 200 µg/mL	<i>E.coli</i> 100 µg/mL	<i>S.aureus</i> 100 µg/mL	<i>E.coli</i> 50 µg/mL	<i>S.aureus</i> 50 µg/mL
Ligand	---	---	---	---	---	---
Cu(II)Complex	+ve	+ve	---	---	---	---
Ni(II)Complex	---	---	---	---	---	---
Co(II)Complex	+ve	+ve	---	---	---	---
Zn(II)Complex	---	---	---	---	---	---
VO(IV)Complex	---	---	---	---	---	---
DMSO Control	---	---	---	---	---	---

+ve indicates inhibition of growth around the paper disc --- indicates no inhibition growth

Figure 8. Cu(II) & Co(II) complex inhibition zone of *S.aureus*

DNA binding activity

In general, complexes with aromatic moieties which bind to DNA through intercalation usually results in hypochromism and bathochromism, due to the stacking interaction between aromatic chromophore of the complexes and the base pairs of DNA. The absorption spectra of the complex, Co(II)-5-Br SALAAP in the absence and presence of calf thymus DNA are illustrated in Figure 9. In the presence of DNA, decrease of peak intensities were observed in the absorption spectra of complexes. Hypochromism was suggested to be due to the interaction between the electronic state of the intercalating chromophore and that of the DNA bases³³⁻³⁷.

Figure 9. Absorption spectra of $[\text{Co(II)} (5\text{-Br SALAAP})_2]$ in the absence and presence of increasing amounts of DNA, $[\text{Co}] = 100 \mu\text{M}$, with increasing DNA concentration from 0–40 μM . (Arrow ($\downarrow$) shows the absorbance changes upon increasing DNA concentration. In side: Linear plot for the calculation of the intrinsic DNA binding constant K_b)

Figure 10. Proposed structures of metal complexes ($\text{M} = \text{Cu(II)}, \text{Ni(II)}, \text{Co(II)}, \text{Zn(II)}$ and VO(IV))

In addition to the decrease in intensity, a small red shift (bathochromism) was also observed in the spectra. These spectral changes are consistent with the intercalation of complexes into the DNA base stack. The plot of the absorption titration data according to equation $[\text{DNA}]/(\epsilon_a - \epsilon_f) = [\text{DNA}]/(\epsilon_b - \epsilon_f) + 1/K_b (\epsilon_b - \epsilon_f)$ gave a linear plot and resulted in an intrinsic binding constant (K_b) $1 \times 10^5 \text{ M}^{-1}$ for Co(II) complex.

Molecular modelling studies

The possible geometries of metal complexes were evaluated (Figure 11 & 12) using the molecular calculation with arguslab³⁸ software. Initially the atomic charges of each complex were calculated by a semiempirical method. The structures using the standard force field included in the package, further refinement was done for the complexes. The refined structures were screened on the basis of the lowest strain energy. The energies of the resulting systems were calculated using UFF³⁸⁻⁴⁴.

Molecular modelling structures

Figure 11. Cu(II)complex

Figure 12. Ni(II)complex

Conclusion

The metal chelates of ligand have been structurally characterized. The complexes of the ligand are non electrolytes in DMSO. This ligand act as tridentate, coordinating through nitrogen of azomethine, phenolic oxygen and carbonyl of antipyrine ring respectively. Geometries of the metal complexes are assigned, based on analytical, conductance, magnetic and electronic spectral data. Biological studies of these complexes reveal that they show better activity when compared to that of the ligand.

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