Ten novel transition metal complexes of N,O donor ligands have been synthesized by the reaction of ligands with metal acetates in 2:1 molar ratio. These reactions were carried out under reflux in methanol for 3-6 hours. The ligands and their transition metal complexes were characterized on the basis of physical properties, elemental analysis, Infrared spectroscopy, Magnetic susceptibility, Ultraviolet and Atomic absorption spectroscopy and \(^1\)H-\(^{13}\)C NMR spectroscopy. The FT-IR spectra of the complexes indicated that ligands behaved in bidentate manner coordinating via the nitrogen and oxygen. \(^1\)H-NMR and \(^{13}\)C-NMR data of the ligands in pure and complex form confirmed the formation of the complexes. Other analytical techniques demonstrated that transition metal complexes of Cu, Ni, Co and Zn are four coordinated and those of Mn are six coordinated. Furthermore, antibacterial activities have been discussed.

Keywords: Transition metal complexes; NO donor Schiff bases; Spectral characterization and biological activity

Introduction

The preparation and study of inorganic compounds containing biologically important ligands is made easier, because certain metal ions are active in many biological processes; species of low molecular weight are, hence, sought that reproduce, as far as possible, the structural properties and the reactivity of naturally occurring complexes of these ions in such processes. The fact that copper together with magnesium, calcium, iron, zinc, chromium, vanadium, and manganese are essential metallic elements and display great biological activity when associated with certain metal–protein complexes, participating in oxygen transport, electronic transfer reactions, or the storage of ions [1] has produced enormous curiosity in the study of systems containing these metals [2].

Schiff bases have a vital position in metal coordination chemistry even almost a century since their discovery. Due to their simplicity in preparation, diverse properties, medicinal, biochemical and industrial applications, the keen interest in the study of these compounds arose in the recent years. A number of metal coordination complexes of Schiff bases have been suggested as antibacterial, antifungal, cytotoxic, anti-inflammatory and Cytostatic agents. [3-6] In order to widen the scope of investigations on the coordination behavior of various donor ligands including Schiff base towards organo metallics, we carried out the investigations and established their bioactivities.[3,4,7-10] As an extension of this research, herein, we report the synthesis, characterization and bactericidal activity of some Schiff base metal complexes.

Materials and Instrumentation

All the chemical reagents used were of analytical grade. 2,3-Dihydroxybenzaldehyde, 3-Chloroaniline, 3-Trifluoromethylaniline and metal salts were obtained from Aldrich (U.S.A) chemicals and E.Merck (Germany). All the solvents which were used were of spectroscopic grade and were obtained from E.Merck (Germany) and Fluka Ltd. Melting points were determined in a capillary tube using electrothermal melting point apparatus Mitamura Riken Kogyo (Japan) model MPD. Infrared spectra were measured as KBr pellets on a FT-IR spectrometer Bio-Rad Excalibur (USA) model FTs 300 MX in a frequency range of 4000-400 cm\(^{-1}\). The electronic absorption spectra of the ligands and complexes were recorded using DMSO as solvent on a UV-visible Spectrophotometer M/s Shimadzu 1600. The elemental analysis was performed on an Elemental analyzer LECO Corporation (USA) CHNS-932. \(^1\)H- NMR and \(^{13}\)C-NMR spectrum of ligands and their metal complexes were recorded using a FT-NMR spectrometer Bruker (Germany) 300 MHz.

Synthesis

Synthesis of ligands

The ligands were synthesized by the reported methods [11].

General procedure for synthesis of transition metal complexes

Transition metal complexes were prepared by mixing the corresponding ligands with transition metals Cu(CH\(_3\)COO)\(_2\)2H\(_2\)O, Co(CH\(_3\)COO)\(_2\).4H\(_2\)O, Ni(CH\(_3\)COO)\(_2\).4H\(_2\)O, Mn (CH\(_3\)COO)\(_2\).4H\(_2\)O and Zn (CH\(_3\)COO)\(_2\).2H\(_2\)O.

Synthesis

To a solution of HL\(_1\) or HL\(_2\) in methanol (20 ml) a solution of metal salts in 15 ml methanol in 2:1 molar ratio was added drop wise. The reaction mixture was refluxed for 3-6 hours at 60°C. The precipitates were filtered and washed with commercial...
methanol. The resulting product was air dried. Solids products obtained were recrystallized in suitable solvents.

**Results and Discussion**

The reactions of Schiff bases with transition metal salts were quite facile and were completed in 3 to 8 hours, the water form during the reaction as byproduct was removed using Dean Stark funnel (Scheme 1 and 2).

The complexes are air-stable, hygroscopic, with higher melting points, soluble in organic solvents. The results of the elemental analysis were in good agreement with the composition of the compounds. In both intensity pattern and integration. The integration of spectra showed that all metals were in +2 oxidation state (Table 4). So it was taken as evidence that all metals were in +2 oxidation state [14].

**Irradiated spectroscopy**

The common region for infrared analysis in organo transition chemistry is 4000-200 cm⁻¹. IR spectra of all the compounds have been recorded using KBr pellets in the range 4000-400 cm⁻¹. The characteristic absorption bands are listed in Table 2. The important absorption frequencies are ν (OH), ν(M-O), ν(M-N) and ν (C=N).

Assignment of different vibration bands have been made by the comparison of ligand spectra with that of transition metal complexes. In the spectra of the ligands a strong band at 3300 and 3450 cm⁻¹ was assigned to −OH stretching vibration. After complex formation this band was still observed in case of Mn complexes only, supporting the fact that water molecule is present as water of coordination.

A strong band appeared in the range of 1600-1625 cm⁻¹ in the free ligand, was attributed to the −C=N stretching vibration. In complexes the −C=N stretching vibration shifted to lower frequencies as compared to the free ligand. This shift indicated donation of the nitrogen lone pair of electron of the azomethine group to the metal atom [3,12].

In the low frequency region, the band observed in the complexes in the region of 500-550 cm⁻¹ and 400-470 cm⁻¹ is attributed to (M-N) and ν(M-O) respectively [7]. The IR data suggested that the metal was bonded to the Schiff base (Table 2).

**UV-Visible spectroscopy**

UV-Visible studies were made in DMSO. From the values of λ\text{max} obtained it was found that n→π* and π→π* transitions are observed which are due to chromophoric groups (imine and aromatic ring) in the ligands. The spectra of the complexes showed red shift. All solutions were of 10⁻⁴ molar concentration; due to this dilute concentration no d→d transitions were observed [13]. The obtained values were compared to literature values and it was found that values for copper, nickel and cobalt were close to the values for four coordinated systems compared to literature values and it was found that values for copper, nickel and cobalt were close to the literature values. For manganese the values were in the range of six coordinated system (Table 3).

**Magnetic susceptibility**

Magnetic susceptibility is quite useful technique for determining unpaired electrons in paramagnetic complexes which in turns help in suggesting structure of the complexes and the nature of ligand. Ligands were strong field ligands and this fact was supported by magnetic moment values for metals. The values indicated that ligand was strong field ligand as all electrons in nickel have been paired up. Value of magnetic moment for nickel is 0.72 B.M which indicated that there be higher if the electrons were unpaired. For other metals like copper, cobalt and manganese the values were in the range of 1.59-1.72 which was close to literature value for one unpaired electron [14]. So it was taken as evidence that all metals were in +2 oxidation state (Table 4).

**Multinuclear NMR**

H-NMR Data: ¹H-NMR spectra of all compounds had been recorded on 300 MHz NMR spectrometer. The characteristic resonance peaks in the ¹H NMR spectra of ligand were recorded in CDCl₃ and its metal complexes in DMSO. The expected resonance was assigned by intensity pattern and integration. The integration of spectra showed good agreement with the composition of the compounds. In both ligand (HL¹, HL²) hydroxyl proton showed signal at 13.23 ppm and 12.31 ppm respectively. These signals disappeared in all complexes due to the deprotonation of OH [15,16]. Both ligands HL¹, HL² showed a simple pattern for aromatic protons which is due to presence of only...
Table 1: Physical data of the ligands and their metal complexes.

| Comp. No | Empirical formula (formula weight) | M.P. °C | Yield (%) | Colour | %C Calc. (Found) | %H Calc. (Found) | %N Calc. (Found) | %M Calc. (Found) |
|----------|-----------------------------------|---------|-----------|--------|-----------------|-----------------|-----------------|-----------------|
| 1        | C₂₀H₂₈N₂O₅F₄ (281)                | 134     | 87        | Orange | 57.78 (58.86)   | 2.95 (3.03)     | 4.48 (4.59)     | —               |
| 2        | C₁₉H₁₈N₄O₆F₄Cu (623)              | >300    | 78        | Green  | 53.51 (53.88)   | 2.75 (2.98)     | 4.38 (4.49)     | 9.77 (10.02)    |
| 3        | C₁₉H₁₈N₄O₆F₄Co (618)              | >310    | 81        | Dark brown | 53.30 (54.30) | 2.35 (2.93)     | 4.27 (4.54) | 8.91 (9.14)    |
| 4        | C₁₉H₁₈N₄O₆F₄Ni (618)              | >300    | 76        | Dark brown | 53.83 (54.20) | 2.32 (2.90)     | 4.44 (4.52) | 8.86 (9.03)    |
| 5        | C₁₉H₁₈N₄O₆F₄Zn (625)              | >320    | 65        | Dark Mahron | 52.91 (53.72) | 2.77 (2.87)     | 4.23 (4.47) | 8.67 (9.96)    |
| 6        | C₁₉H₁₈N₄O₆F₄Mn₂H₂O (653)          | >300    | 70        | Light Mahron | 51.42 (51.62) | 3.23 (3.37)     | 4.08 (4.30) | 7.56 (7.99)    |
| 7        | C₉H₁₈ClNO₂ (247)                  | 145     | 85        | Pinkish red | 63.03 (62.56) | 3.82 (3.91)     | 4.90 (5.03) | —               |
| 8        | C₉H₂₀N₂O₄Cl₂Cu (556)              | >300    | 78        | Brown   | 55.06 (55.66)   | 2.93 (3.04)     | 4.83 (4.94) | 10.80 (11.02)  |
| 9        | C₉H₂₀N₂O₄Cl₂Co (551)              | >310    | 81        | Dark red | 53.30 (54.30) | 2.35 (2.93)     | 4.27 (4.54) | 10.67 (10.88)  |
| 10       | C₉H₂₀N₂O₄Cl₂Ni (551)              | >300    | 76        | Reddish | 54.57 (55.03)   | 3.29 (3.44)     | 4.55 (4.60) | 9.63 (10.03)   |
| 11       | C₉H₂₀N₂O₄Cl₂Zn (556)              | >330    | 65        | Red     | 56.05 (56.39)   | 3.04 (3.13)     | 4.86 (4.93) | 10.70 (10.96)  |
| 12       | C₉H₂₀N₂O₄Cl₂Mn₂H₂O (587)          | >330    | 70        | Brick red | 52.42 (52.62) | 3.29 (3.37)     | 4.22 (4.30) | 9.40 (9.89)    |

Table 2: Infrared spectra of the ligands and metal complexes.

| Compound | Wavelength (A) | Absorption (A) | Type of transitions |
|----------|----------------|----------------|---------------------|
| 1        | 354, 230       | 1.50, 0.50     | n-π and π- π         |
| 2        | 440.234        | 1.67, 0.55     | n-π- π and - π        |
| 3        | 477.236        | 1.75, 0.751    | n-π- π and - π        |
| 4        | 412.265        | 1.65, 0.67     | n-π- π and - π        |
| 5        | 383.245        | 1.57, 0.852    | n-π- π and - π        |
| 6        | 404.247        | 1.64, 0.573    | n-π- π and - π        |
| 7        | 365.276        | 1.571, 0.541   | n-π- π and - π        |
| 8        | 450.260        | 1.75, 0.511    | n-π- π and - π        |
| 9        | 414.287        | 1.62, 0.43     | n-π- π and - π        |
| 10       | 386.290        | 1.58, 0.47     | n-π- π and - π        |
| 11       | 411.278        | 1.60, 0.852    | n-π- π and - π        |
| 12       | 432.268        | 1.73, 0.573    | n-π- π and - π        |

Table 3: UV spectral data of ligands and its Synthesized Transition Metal Complexes.
seven protons in this region. These protons do not show any significant change. As ligand to metal ratio was 2:1, therefore, signals for 14 protons were observed after complex formation. The azomethinic protons of the ligands gave signal at 8.63 and 8.86 for HL₁ and HL₂ respectively. The downfield shift of both the signals to 8.99 and 8.94 suggests the bonding of N to the metal (Table 5).

**C NMR Data:** The ¹³C NMR spectral data of ligand and its metal complexes were recorded in DMSO. The C₁ attached to OH group shifted to a lower field region in complexes, indicating participation of the C-O group in coordination to transition metal to form C-O-M bonds. The resonances due to the aromatic C-atoms did not shift significantly on bonding to transition metals. The azomethinic C-7 showed a downfield shift due to shifting of electron density from nitrogen to metal supporting the formation of N-M bond (Table 6).

**Biological activity**

The antibacterial activity of Schiff base and metal complexes against *Staphylococcus aureus* strain was screened using agar well...
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