

Schiff Bases Derived From Isonitrosoacetophenone and 2,4 Dithiobiurets: Application In Environment

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ABSTRACT

Applications of Schiff bases chelating compounds in wider quantitative analysis and sample preparations for chemical analysis have been reviewed. The synthesis and stability of Schiff bases chelates have been discussed in this paper. The wider applications in analytical field and latest applications of Schiff bases in green technology are found in progress.

The metal complexes have been screened for their antibacterial activity. Escherichia Coli, Staphylococcus, Bacillus Cereus, Bacillus Subtilis were studied on laboratory grown cultures, these yield several kinds of information which are of value in guiding and understanding their therapeutic use. The work reported here deals with the synthesis and spectroscopic studies of some transition metal complexes with poly dentate Schiff bases. These Schiff bases were derived by condensing carbonyl oximes-like isonitrosoacetophenone, α -benzyl monoxime, isonitroso acetyl acetone with amines like 2,4 dithiobiurets. The characterization of the complexes was done on the basis of elemental analysis, molar conductivity, spectral IR, electronic thermal analysis spectra. The metal complexes have been screened for their antimicrobial activity. The concentration required to inhibit various organisms and the effects of environmental conditions on their activity are of paramount importance. The complexes show moderate activity against (10-22 mm) the above mentioned bacteria. This shows that besides the complex formation, the nature of the metal ion has important role in the inhibition of the pathogenic activity of the bacteria. The conductivity measurement indicates that they are non-electrolyte in nature. The complexes are thermally stable, insoluble in water but soluble in organic solvent to varying extent. The room temperature magnetic susceptibility measurements indicate their octahedral geometry which is further supported by electronic absorption /diffuse reflectance spectra.

The development of Schiff base was a major step forward in the area of coordination chemistry. Schiff bases, a class of organic compounds, carry the imine or azomethine ($>C=N-$) functional group. Schiff bases played an influencing role in the development of coordination chemistry and were a key point in the development of inorganic, bioinorganic chemistry and optical materials. Schiff bases, widely used in inorganic, organic, and analytical chemistry, account for a significant portion of the more commonly employed classes of organic molecules. The ability of Schiff base ligands to form stable metal complexes with a wide range of transition and other metal ions makes them extremely useful. Condensation of a primary amine with an aldehyde or ketone yields a Schiff bases. In this chapter, we focused on introducing Schiff bases, classified them and their metal complexes, and discussed several synthesis methods, including conventional and green approaches. This chapter also elaborated on the industries' applications, such as the

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food industry, agrochemical industry, dye industry, analytical chemistry, catalysis, energy storage, environmental, chemo-sensing, bio-sensing, and biomedical applications of novel Schiff bases and their metal complexes.

Applications of Schiff bases chelating compounds in wider quantitative analysis and sample preparations for chemical analysis have been reviewed. The synthesis and stability of Schiff bases chelates have been discussed in this paper. The wider applications in analytical field and latest applications of Schiff bases in green technology are found in progress.

The metal complexes have been screened for their antibacterial activity. *Escherichia Coli*, *Staphylococcus*, *Bacillus Cereus*, *Bacillus Subtilis* were studied on laboratory grown cultures, these yield several kinds of information which are of value in guiding and understanding their therapeutic use.

The title ligands have been reported for the first time in the present work. They are obtained as fine powdered solids by the reaction of phenyl/tolyl 2,4-dithiobiuret with isonitroso-acetophenone (HINAP). They are abbreviated as HPEPDTB and HPETDTB respectively. The ligands are insoluble in water but soluble in common organic solvents like chloroform, methanol, carbon tetrachloride etc. With varying solubility. The elemental analysis is in agreement with the empirical formulae of the compounds. Table 5.21 gives colour, m.p. and analytical data of the ligands. The melting point of HPETDTB is greater than that of HPEPDTB, which also reflects the order of thermal stability of the ligands and the strength of the inter-molecular forces.

The elemental analysis of the metal complexes of HPEPDTB and HPETDTB corresponds to 1:1 metal: ligand stoichiometry and suggests that the complexes may be represented by the general formula $M_2L_2Cl_2 \cdot xH_2O$ where $M = Co(II)$, and $x = 4$.

The complexes are coloured and non-hygroscopic in nature. They are insoluble in water and sparingly soluble in common organic solvents though somewhat more soluble in dimethyl formamide (DMF) at room temperature. They give intense colour with dil. NaOH solution suggesting the presence of a free oxime group in the complexes.

All the complexes are thermally stable at least up to 120°C (Table 5.25, 5.26) indicating fairly high thermal stability and hence a strong metal-ligand bond.

The values of molar conductance of the metal complexes in DMF solution at 10^{-3} M concentration are $< 1.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ (Table 5.25, 5.26) and are suggestive of the non-electrolytic nature of these complexes ($>C=N$) group. The aromatic protons of the ligands resonate as multiples between 7.2 and 7.5 δ while a singlet due to C-H proton is observed in both ligands at 7.8 δ . The oxyimino proton ($=NOH$) is observed in the region $\sim 12.4 \delta$ in both the spectra. The -NH and -SH proton signals are observed near 8.8 and 10.6 δ respectively⁵². The PMR spectrum of HPETDTB also additionally shows a signal at 2.4 δ for methyl ($-CH_3$) protons. The PMR spectral data on the ligands are summarized in Table 5.23.

The FT infrared spectra of the ligands in KBr discs in the region $4000-400 \text{ cm}^{-1}$ are shown in Figs. 5.60 and 5.61. The spectra are quite complex due to the presence of a large number of bands with varying intensities. It is therefore not possible to assign all the bands without ambiguity. An attempt has however been made to assign some of the structurally important bands on the basis of some infrared spectral bands reported for 2,4-dithiobiuret (HDTB)⁵³, HINAP²⁷ and similar compounds.

A significant and common feature of the IR spectra of both the ligands is that they do not show a band due to free or hydrogen bonded carbonyl group, observed in the region around 1660 cm^{-1} in HINAP. This indicates successful replacement of the carbonyl oxygen in HINAP by azomethine nitrogen in the Schiff base formation during the preparation of ligands. This is further supported by the appearance of an additional strong band in the region $1660-1640 \text{ cm}^{-1}$ due to $\nu_{C=N}$ of azomethine group in addition to the band around $1580-1600 \text{ cm}^{-1}$ attribute to the $\nu_{C=N}$ stretching mode of the oxyimino group. In general, $C=N$ vibrations in isonitrosoketones³¹ are known to occur around 1600 cm^{-1} . In formaldehyde dimethyl hydrazone, the $\nu_{C=N}$ stretching vibrations are reported to occur at 1584 cm^{-1} . In the infrared spectra of bis-(1,2-diphenyl-1-hydroxyimino 2-ethylidene) 1,3-diamino propane, Rai et al⁵⁵ have assigned bands at 1630 cm^{-1} and 1475 cm^{-1} to $C=N$ stretching vibrations of azomethine and oxyimino group respectively. Recently, the two $\nu_{C=N}$ modes observed in the regions around 1598 cm^{-1} and 1560 cm^{-1} in the infrared spectra of complexes of alkylamino derivatives of isonitroso propiophenone (HINPP), assigned respectively to azomethine and

oxyimino groups, have been reported. The assignment of the higher energy band around 1610-1613 cm^{-1} to $\nu_{\text{C=N}}$ (azomethine) and the lower one in the range 1566-1568 cm^{-1} to $\nu_{\text{C=N}}$ (oxyimino) in the present case is therefore justified.

The spectra of the ligands reveal a broad band near 3420-3424 cm^{-1} which is assigned to hydrogen bonded $\nu_{\text{O-H}}$ mode of the >NOH group. The N-H stretching vibrations are observed near 3235 cm^{-1} in the ligands.

In several isonitrosoketones^{8-11,58}, the band due to N-O stretching vibrations is known to occur around 900-1000 cm^{-1} , presumably due to the existence of only one isomer which exists in the oxime form. In hydrazone derivatives of isonitrosoacetophenone (HINAP), this band is seen in the range⁵⁶ 985-900 cm^{-1} . The medium-to-strong intensity band observed around 995-100 cm^{-1} in the spectra of HPEPDTB and HPETDTB may therefore be attributed to $\nu_{\text{(N-O)}}$ stretching frequency, while a fairly strong band in the ligands at 1246 cm^{-1} is assigned to C=S stretching vibrations⁵⁹. In addition, a medium to strong intensity band observed in the ligands around 1440-1435 cm^{-1} can tentatively be assigned to $(\delta_{\text{N-H}} + \nu_{\text{C-N}} + \nu_{\text{C-S}})$ ⁵⁸

Electron Spectra

The electronic absorption spectral data of the metal complexes, recorded in the range 200-350 nm in methanol, are summarised Table 5.27

All the metal complexes in solution exhibit two intra-ligand transitions in the ultra violet region around 36,360-38,460 cm^{-1} and 47,160-48,076 cm^{-1} respectively, which may be ascribed to $\pi - \pi^*$ and $n - \sigma^*$ transitions which are observed at 34,960 and 37,630 cm^{-1}

The two Co(II) complexes show a broad band around 7,407-7,692 cm^{-1} and a weak shoulder at 15,625-16,120 cm^{-1} which can be ascribed to the transitions ν_1 and ν_2 respectively in an octahedral geometry. The ratio of the two band energies¹⁶, ν_2/ν_1 , has diagnostic importance of octahedral Co(II) complexes and is usually found to be much lower than the theoretical value of 2.2. For many octahedral Co(II) complexes the ratio is found to be even lower than 2.0. In the present cases, the values for the ratio ν_2/ν_1 are found to be 2.11 and 2.09 for the octahedral Co(II) complexes of HPEPDTB and HPETDTB respectively, and are well within the range expected and hence are in conformity with the band assignments.

The calculated values of the various spectral parameters like 10Dq, B' and β have been calculated using various equations described by Koing¹⁸ and are presented in the table; these are within the range normally observed. An attempt has also been made to calculate the transition energies by using the equation¹⁸:

$$\nu_2, \nu_3 = 1/2 [15B' + 30 Dq] \pm 1/2 [15B' - 10 Dq]^2 + [15B' \times 10Dq]^{1/2}$$

The values of the calculated transition energies are given in the parentheses and are in fair agreement with the values experimentally observed.

Infrared Spectra :

The FT-infrared spectra of the metal chelates contain large number of bands of varying intensities and are quite complex. However, several structurally important bands, such as those due to $\nu_{\text{(O-H)}}$, $\nu_{\text{(C=N)}}$, $\nu_{\text{(N-OH)}}$, $\nu_{\text{(C-S)}}$ etc modes have been identified to derive information regarding the structural features of the ligands and their manner of bonding with the metal ions.

All the metal complexes, except those of Cu(II), show a broad band around 3400-3430 cm^{-1} in their FT-IR spectra. This band may be attributed to O-H stretching mode of water molecules. The centre of gravity of this band near 3420 cm^{-1} implies coordinated nature of these water molecules.

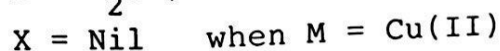
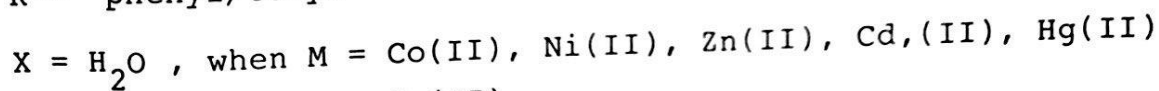
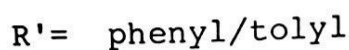
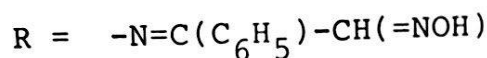
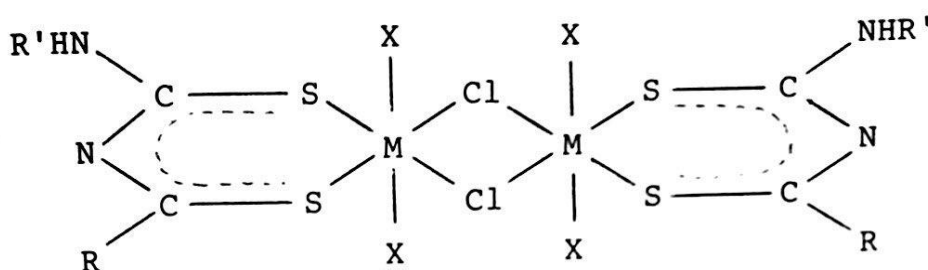
A careful comparison of the spectra of the metal complexes with those of the ligands also reveals that bands due to $\nu_{\text{N-OH}}$, and $\nu_{\text{N-H}}$ in the region around 3200-3300 cm^{-1} are observed for the complexes, which overlap in several cases making their distinction difficult. The -N-H bending vibrations are observed near 1620-1600 cm^{-1} , around the same

position as in ligands, indicating that -NH group is not involved in coordination. The presence of free -NOH function in the complexes is also revealed by their solubility in dilute alkali solution.

The azomethine and oxyimino C=N stretching vibrations are relatively unaffected and are observed at ~ 1610 -14 and 1563 - 1567 cm^{-1} respectively indicating that the azomethine or oxime nitrogen donors are not involved in bonding.

The C=S stretching frequency of the ligands are found to undergo a negative shift on complexation suggesting that the ligands coordinate to the metal ions through sulphur donors. The C=S stretching bands are observed around 1220 - 1240 cm^{-1} in the spectra of the complexes.

Another fairly strong band around 725 - 759 cm^{-1} due to C=S vibrations in ligands is also found to be shifted to lower frequencies between 686 - 692 cm^{-1} in complexes with medium intensity.



The study indicates that the complex decomposes in three steps in the temperature range studied. The first step of decomposition is observed in the temperature 160 - 150°C which corresponds to the loss of four coordinated water molecules.

The loss of $2(C_6H_5-NH) + (C_6H_5)_2$ is observed during the 2nd stage of decomposition observed near 530°C .

The below table shows result of agar cup method for the antibacterial activity of the Co(II) complexes in (DMF).

COMPOUND	B.subtilis(mm)	B.cereus(mm)	S.aureus(mm)	E.coli(mm)
$Co_2(HPEIBSA)_2Cl_2$	16	14	18	12
$Co_2(HBEIBSA)_2Cl_2$	18	10	11.5	17

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