OXIME-THIOSEMICARBAZONE DERIVATIVES

Oxime-thiosemicarbazones may be considered as novel reagents because they contain two different functional groups (two-in-one) viz. oxime and thiosemicarbazone. This class of derivative may be called as imine-oximes. These are generally synthesized using carbonyl oximes.

Oxime-thiosemicarbazone ligands have not received as much attention as other sulphur containing ligands viz. dithiophosphates, dithiocarbamates, dithiolates, dithio-β-diketones and xanthates.

The present attention has been to investigate the structural features and bonding characteristics of transition metal complexes of oxime-thiosemicarbazones. The elucidation of the structural features in greater detail by chemists becomes essential in their effort to synthesize more efficient and active species. The real driving force towards developing the coordination chemistry of these potential S-ligands is probably provided by their remarkable antitumor, antiviral and antimalarial activities related to their metal-complexing ability.

Most of the work on imine-oximes is centred around two types of ligands $H_{2}TiO$ and $H_{2}Zio$. 
In HTio, T is a coordination site such as pyridyl nitrogen (or) a hydroxyl oxygen. The latter type of ligands (Z = O, S or Se) include semicarbazone, thiosemicarbazone and seleno semicarbazones.

In thiosemicarbazone chelates, bonding to metal occurs as usual at the nitrogen atoms of the oxime and imine functions, the third coordination position is most probably the chalogen atom\(^{17}\)

In complex formation, the oxime protons of I and II may or may not dissociate. In several cases two protons dissociate from II (Z = S or Se). In such instances the ligand may be thought to react in the tautomeric form (III) (Z = S, Se).

\[\text{(I) HTio} \quad \text{(II) H}_2\text{Zio}\]

\[(\text{III})\]
Important stereochemical types among the complexes of II are again the octahedral and the square planar. Octahedral geometry is present in \([M(H_2Zio)_2]X_2\); \(Z = S, M = Fe, Co, Ni\).\(^{18-21}\) Spectral and magnetic data of these complexes suggest that the iron(II) and iron(III) species are low-spin whereas cobalt(II) is high-spin. Generally planar stereochemistry is present in diamagnetic \(Ni(Zio).1/2 H_2O\); \(Cu(Zio).1/2 H_2O\) (probably dimeric with \(H_2O\) bridge) where \(Z = S\). Octahedral complex of \(Ni(Zio)(D)\) is diamagnetic where \(D = \text{imine, e.g. Py, } Z = S\).\(^{22,23}\)

Nickel(II) complexes of two tridentate \(N.N.S\)-chelating oxime-thiosemicarbazone derivative ligands viz. 3-hydroxy iminobutanone thiosemicarbazone (LiH\(_2\)) and 3-hydroxy iminobutanone (4-phenyl thiosemicarbazone) (LH\(_2\)) have been synthesized and characterized by elemental analysis, IR, UV-Vis spectroscopy and cyclic voltammetric studies recently. The structure of \(Ni(LH_2)(NO_3)_2.H_2O\) has been determined by single crystal X-ray diffraction studies. Nickel(II) is in a distorted octahedral \(N_4S_2\) donor environment. In this structure, one of the nitrate groups exhibit partial disorder\(^{24}\).

Crystal structure of diacetylmonoxime thiosemicarbazone is determined by Biyushkin\(^{25}\) \(Ni(II), Co(II)\) and \(Cu(II)\) complexes of diacetylmonoxime thiosemicarbazones are prepared and characterized by elemental analysis: IR and electronic spectral studies. Normal coordinate analysis and CNDO/II (complete neglect of differential overlap) calculations for diacetylmonoxime, its semicarbazones and thiosemicarbazone derivatives are reported\(^{26}\) IR spectra of complexes suggest that the ligand coordinates to the metal ion through its azomethine \(N\), oxime \(O\) and \(S\) atoms. Reflection spectra of the complexes indicate octahedral geometry around the
metal ions\textsuperscript{27} The complexation behaviour of diacetylmonoxime thiosemicarbazone and diacetylmonoxime-4-phenyl thiosemicarbazone with Cu(II), Co(II), Ni(II), Zn(II) and Mn(II) were determined in 50\% (V/V) aq. EtOH at 30, 40 and 50° and at ionic strength of 0.1 M by using Calvin-Bjerrum pH-titration techniques. Stability constants and thermodynamic of coordination values of these complexes are calculated by Hankare \textit{et al.}\textsuperscript{28}

Survey of literature reveals that diacetylmonoxime thiosemicarbazone\textsuperscript{29-34} and diacetylmonoxime-4-phenyl-3-thiosemicarbazone\textsuperscript{35,36} have been used for spectrophotometric determination of Cu(II), Ni(II), Pd(II), Fe(II), Bi(II), Mn(III). Spectrophotometric determination of Fe\textsuperscript{2+} using biacetyl oxime thiosemicarbazone is reported\textsuperscript{34} The detection limit and Sandell’s sensitivity are 0.12 \(\mu\)g of Fe/ml and 43 ng Fe/cm\textsuperscript{2} respectively. It has been shown that Mg\textsuperscript{2+}, Ca\textsuperscript{2+}, Sr\textsuperscript{2+}, Ba\textsuperscript{2+}, Mn\textsuperscript{2+}, Zn\textsuperscript{2+} and Th\textsuperscript{4+} (500:1), Cd\textsuperscript{2+} and Se\textsuperscript{3+} (5:1) interfere.

Analytical properties of 1-phenyl-1,2-propanedione-2-oxime-thiosemicarbazone (PPDOT) and simultaneous spectrophotometric determination of copper(II) and nickel(II) are reported\textsuperscript{37}. The method is applied for the determination of metal ions in edible oils and seeds.

Diacetylmonoxime thiosemicarbazone is also potentially used in the photometric determination of metal complexes. Cu(II) 0.5-5 ppm, or Bi(III) 8-22 ppm can be determined photometrically using diacetylmonoxime thiosemicarbazone\textsuperscript{38} This reagent is also employed in colorimetric determination of manganese\textsuperscript{39}. 
REFERENCES


