S U M M A R Y

V SUMMARY:

Oximino ligands are well known for their ability to form metal complexes with numerous metal ions. The oxime group usually functions as an acidic group; sometimes it behaves as a donor group.

The investigations on the complexes of dioximes prompted investigations on the complexes of other oximino ligands. Considerable work has been carried out in our laboratories on the N-ligands obtained from 2,3-dioxo-butyranilide-2-oxime and related compounds. Talati (227) prepared 2,3-dioxobutyr(aryl) amide-2-oxime and 2,3-dioxobutyr(aryl)amide dioxime and studied their analytical applications towards the estimations of copper, nickel and palladium. He also prepared the metal complexes of the dioximes and studied their properties. Desai (233) prepared the aryl hydrazones of 2,3-dioxobutyr(aryl)amide-2-oxime and studied their complexes with copper, nickel, cobalt and palladium. Patel (237) prepared aryl imines of 2,3-dioxobutyr(aryl) amide-2-oxime and studied their complexes with copper, nickel, cobalt and iron. Kapadia (238) studied some of the complexes of copper, nickel and cobalt with the products of 2,3-dioxobutyranilide-2-oxime and semicarbazide, thio-semicarbazide, hydrazine and diamines. The present work is the continuation and extension of these studies.

It was planned

(i) to devise a suitable method or methods for the preparation of the metal complexes of 2,3-dioxo-butyranilide-2-oxime with various metals and to study

their magnetic and spectral properties;

(ii) to prepare the iron complex of 2,3-dioxobutyranilide dioxime and to study its magnetic and spectral properties;

(iii) to prepare some complexes of the phenyl hydrazone of 2,3-dioxobutyranilide-2-oxime;

(iv) to prepare the complexes of the methyl imine of 2,3-dioxobutyranilide-2-oxime with some transitional metals and to study their magnetic and spectral properties;

(v) to prepare the complexes of the cyclohexyl imine of 2,3-dioxobutyranilide-2-oxime with some transitional metals and to study their magnetic and spectral properties;

(vi) to prepare the complexes of the bis-bidentate ligand that can be obtained from hexamethylene diamine and 2,3-dioxobutyranilide-2-oxime with some transitional metals and to study their magnetic and spectral properties;

(vii) to prepare the complexes of copper and nickel with tridentate ligand that can be obtained from glycine and 2,3-dioxobutyranilide-2-oxime; and

(viii) to prepare new oximino ligands comparable to 2,3-dioxobutyranilide-2-oxime.

Complexes of 2,3-dioxobutyranilide-2-oxime :

The ligand (OK) is found to have a syn-amide isomeric nature (XXXI-b). Its complexes with copper, nickel and cobalt were prepared by different methods. The two-phase

method of preparation was found better than other methods of preparation and was adopted subsequently for the preparation of other complexes.

(a) Nickel complex:(OKNi)

The electrical conductivity, UV and visible absorption spectra and the magnetic moment of the complexes were studied. The complex is suggested to be non-ionic and to have the octahedral crystal field around nickel. The crystal field parameters for the complex are

D_q = 1080 cm^{-1}

B' = 840 cm^{-1}

β = 0.797 and

h = 1.69.

(b) Copper complex : (OKCu)

The electrical conductivity, the UV and visible absorption spectra and the magnetic moment of the complex were studied. The complex is suggested to be non-ionic and to have a tetragonal crystal field around copper. The crystal field parameters for the complex were evaluated as

Δ = 15890 cm^{-1}

δ = 1270 cm^{-1} and

μ = 690 cm^{-1} .

(c) Cobalt complex : (OKCo)

The electrical conductivity, UV and visible absorption spectra and the magnetic moment of the complex were studied. It was found to be a weak electrolyte. It is considered to be a low-spin octahedral complex. The crystal field parameters for the complex were evaluated as

D_q = 1700 cm^{-1}

B' = 665 cm^{-1}

β = 0.594 and

ν = 12240 cm^{-1}

(d) Iron complex : (OKFe)

The magnetic moment and the UV and visible absorption spectra of the complex were studied. The complex contains two iron atoms per molecule. One is suggested to be spin-paired and diamagnetic and surrounded by a strong octrahedral crystal field. The other atom is suggested to be ionic. A charge-transfer band is observed in its visible absorption spectrum.

(e) Manganese complex : (OKMn)

The magnetic moment and the UV and visible absorption spectra of the complex were studied. It is suggested to have an octrahedral configuration. The crystal field parameters were evaluated as

D_q = 660 cm^{-1}

B' = 550 cm^{-1} and

β = 0.573.

(f) Zinc complex: (OKZn)

Its magnetic moment and the UV absorption spectrum were studied. It was found to be diamagnetic. It is considered to have an octrahedral configuration.

(g) Strontium complex : (OKSr) and Magnesium complex: (OKMg)

The magnetic susceptibility and the UV absorption

spectrum of OKSr and OKMg were studied. They are found to be diamagnetic.

(h) Metal complexes - general : (OKM)

The complexes are divided into two groups. The complexes of copper, nickel, magnesium and strontium fall in ML_2 series and the complexes of cobalt, iron, zinc and manganese fall in ML_3 series.

The metals fall in the increasing order of Δ values as

$$Mn^{2+} < Ni^{2+} < Co^{2+}$$

π-Bonding between cobalt and the ligand and the delocalisation of the t_{2g} electrons of cobalt are suggested from the UV absorption band, the magnetic moment and the crystal field splitting.

2,3-Dioxobutyranilide dioxime and its iron complex :

The ligand (OO) is found to have an antidioxime structure (XLII-b)

(a) Iron complex : (OOFe)

Its magnetic moment, and UV and visible absorption spectra were studied. It contains two iron atoms per molecule. One of the two atoms is suggested to be spin-paired and diamagnetic and to be surrounded by the strong octahedral crystal field. The other iron atom is ionic. It has a charge-transfer band in the visible absorption spectrum.

Complexes of the phenyl hydrazone of 2,3-dioxobutyranilide-2-oxime

The ligand (OZ) is suggested to have an anti-configuration.

(a) Barium, aluminium and zinc complexes (OZBa, OZAl) and OZ-Zn)

The UV absorption spectra of these complexes were studied.

(b) Copper complex : (OXCu)

The ligand is found to undergo oxidation in presence of copper ions and the copper complex of the oxidation product was isolated.

Complexes of the Schiff-base from methyl amine and 2,3-dioxobutyranilide-2-oxime

The ligand (OA) is suggested to have an anti-configuration. Its UV absorption spectrum was studied.

(a) Nickel complex : (OANi)

Its magnetic moment, and the UV and visible absorption spectra were studied. It is paramagnetic and considered to have an octahedral crystal field around nickel. The conjugation of the ligand π-system has undergone extension on complex formation with nickel. The value of Δ/k^2 is suggested as 7800 cm^{-1}.

(b) Copper complex : (OKCu)

The reaction of the ligand with the copper salt resulted in the formation of the complex (OKCu) and not (OACu).

(c) Cobalt complex : (OACo)

Its magnetic moment, and the UV and visible absorption spectra were studied. It is found to be a low-spin, octahedral complex. The value of Δ/k^2 is suggested as 17100 cm^{-1}. The conjugation of the ligand π-system has

undergone extension on complex formation with cobalt.

(d) Iron complex : (OAFe)

Its magnetic moment, and the UV and visible absorption spectra were studied. The ligand is coordinated to the metal ion. It is considered to be a sqaare planar complex and has a charge-transfer band.

(e) Manganese complex : (OAMn)

The magnetic moment of the complex was studied. The ligand is coordinated to the metal acetate in the complex.

(f) Metal complexes-general : (OAM)

Comparison of OA and OK and their complexes shows that (i) the complexes of OA and OK with cobalt and nickel are similar, (ii) their complexes with iron and manganese are different and (iii) their complex with copper is the same.

The π extension of conjugation of the ligand π-system is in order

$$Ni^{2+} < Fe^{2+} < Co^{2+} .$$

Complexes of the Schiff Base from cyclohexyl amine and 2,3-dioxobutyranilide-2-oxime.

The ligand (OC) is suggested to have an anti-configuration. Its UV absorption spectrum was studied. The cyclohexyl group exerts steric hindrance and hence the complexing ability of the ligand is much reduced.

(a) Nickel complex : (OCNi)

A basic complex is obtained. Its magnetic moment and absorption spectra were studied. It is considered to have a distorted octahedral crystal field around nickel.

(b) Cobalt complex : (OKCoC)

The cobalt complex obtained is not of OC but is of OK. Its magnetic moment indicates a tetragonal nature of the complex.

(c) Iron complex : (OCFe)

A basic complex is obtained. Its magnetic moment and absorption spectra were studied. It is considered to have a distorted octahedral crystal field around iron.

Complexes of the Schiff base from 2,3-dioxobutyranilide-2-oxime and 1,6-diamino hexane

The ligand (OD) is considered to have an anti-configuration. Its UV absorption spectrum was studied.

(a) Nickel complex : (ODNi)

Its magnetic moment and UV and visible absorption spectra were studied. It is considered to have a distorted octahedral crystal field around nickel. The conjugation of the ligand π-system has undergone extension on complex-formation.

(b) Copper complex : (ODCu)

Its magnetic moment and UV and visible absorption spectra were studied. It is considered to have a distorted octahedral crystal field around copper. The conjugation of the ligand π-system has undergone extension on complex-formation.

(c) Cobalt complex : (ODCo)

Its magnetic moment and UV and visible absorption spectra were studied. It is considered to be a low-spin, octahedral complex. The value of Δ/k^2 is evaluated as 6780 cm^{-1}.

(d) Iron complex : (ODFe)

Its magnetic moment and UV and visible absorption spectra were studied. It is considered to have a distorted octrahedral crystal field around iron. It has a charge-transfer band. The conjugation of the ligand π-system has undergone extension on complex-formation.

(e) Manganese complex : (ODMn) and Zinc complex : (ODZn)

These complexes are considered to have octrahedral structures.

(f) Metal complexes + general : (OD-M)

It is observed that OD is more stable to metal ions like copper and cobalt ions than OA or OC.

It was suggested that octahedral complexes of OD are formed with cobalt, manganese and zinc.

Complex of di-glycinato-nickel and 2,3-dioxobutyranilide-2-oxime

The magnetic moment and the visible absorption spectrum of the complex were studied. It is a mixed -ligand complex. It is considered to have distorted octahedral crystal field around nickel.

Complex of di-glycinato-copper and 2,3-dioxobutyranilide-2-oxime

The magnetic moment and the visible absorption spectrum of the complex were studied. It is a mixed-ligand complex.

Oximino ligands

3-Phenyl 2,3-dioxopropionanilide-2-oxime and ethyl 3-phenyl 2,3-dioxopropionate-2-oxime were prepared.

Their UV absorption spectra were studied and compared with those of 2,3-dioxobutyranilide-2-oxime, α-benzil monoxime and β-benzil monoxime. Their reaction with iron is also considered.