S U M M A R Y

SUMMARY

Work on the oximes and phenyl hydrazones of N-aryl 2,3-dioxobutyramide 2-oxime indicated that N-ligands obtained from N-aryl acetoacetamides and related systems need further investigations. Hence it was proposed

1. to prepare N-aryl 2,3-dioxobutyramide 2-oxime and its Schiff bases with primary amines ;
2. to prepare derivatives of oxime of 2-cyano-glyoxylic acid ;
3. to prepare the metal complexes of some of these ligands, using the salts of some transition metals ;
4. to investigate the formation of complexes in solution ;
5. to study the ultra-violet and infra-red absorption spectra of these ligands and their metal complexes ;
6. to investigate the magnetic susceptibility and electrical conductivity of these metal complexes.

N-ligands

Acetoacetic acid derivatives (namely anilide, N-methyl anilide, o-toluidide and o-chloranilide) and cyanoacetic acid derivatives (namely ethyl ester, amide, anilide and N-methyl anilide) were the starting substances.

(a) Monoximes derived from acetoacetic acid derivatives :

N-aryl 2,3-dioxobutyramide 2-oxime was prepared by treating N-aryl acetoacetamide with nitrous acid, and its structure and stereoisomeric nature are discussed.

The ultra-violet absorption spectra of N-methyl 2,3-dioxobutyranilide 2-oxime were studied in different solvents and are discussed in terms of conjugation, ionisation, H-bonding and steric effect.

(b) Oximes derived from cyanoacetic acid derivatives :

Derivatives of the oximes of 2-cyanoglyoxylic acid were prepared by the action of nitrous acid or nitrosyl chloride on the corresponding derivatives of cyanoacetic acid. Their ultra-violet absorption spectra were investigated in different solvents and are discussed in terms of conjugation, ionisation and solvent effect. Their reactions with transition metal ions were studied and unsuccessful attempts (not recorded in the thesis) were made to prepare some transition metal complexes of these ligands.

Attempts to synthesise oximes of 2(hydroxyamidino) glyoxylic acid derivatives by the action of hydroxylamine on the oximes of 2-cyanoglyoxylic acid derivatives were also unsuccessful except that of the preparation of the oxime of 2-(hydroxyamidino) glyoxyl amide.

(c) vic-oxime-imines :

vic-Oxime-imines were prepared by the action of primary amines such as aniline, p-toluidine, p-phenetidine and benzylamine on N-aryl 2,3-dioxobutyramide 2-oxime and their structure and stereoisomeric nature are discussed. Their ultra-violet absorption spectra were investigated and are discussed in terms of conjugation, ionisation and substitution. Infra-red spectra of two ligands were studied by potassium bromide pellet technique and discussed in terms of hydrogen-bonding. The reactions of these ligands with transition metal ions were investigated ; products were isolated in many cases and were studied to elucidate their nature.

The Schiff base from 2,3-butane dione oxime and p-phenetidine was prepared for comparative studies. Its ultra-violet absorption spectra in different solvents were investigated. Its complexes with copper (II) and iron (II) were prepared.

Reaction with nickel (II)

vic-oxime-imines (referred to in general as RH) react with nickel salts, forming complexes which are formulated as NiR_2 or $Ni_2R_3(OH)(H_2O)_3$. They are soluble in many organic solvents and are non-conducting in methanol solutions. The ultra-violet absorption spectra of these complexes in methanol were studied and are discussed in terms of metal-ligand bonding in them. Infra-red spectra of two complexes were investigated ; St.frequency for oxime OH group is absent in these spectra. They are green in colour and magnetic susceptibility measurements of some of them indicated that they are paramagnetic in nature. Taking into consideration the weakening of the ligand field strength and steric hindrance to the planarity of the chelate ring, we suggest a tetrahedral structure for NiR_2 complexes.

It is further observed that when vic-oxime-imines react with nickel salts in presence of excess of ammonia, complexes of the formula $NiR(OH)(NH_3)_x(H_2O)_y$ are formed.

Orange yellow
These are in colour, insoluble in organic solvents and diamagnetic. It is suggested that they are inner-orbital square planar complexes.

Reaction with Copper (II)

vic-Oxime-imines react with copper salts to form complexes of the formula $CuR(OH)(H_2O)_x$; $Cu_2R_3(OH)(H_2O)_y$ or $Cu_3R_4(OH)_2(H_2O)_2$. They are greenish brown in colour and soluble in organic solvents. Their ultra-violet absorption spectra in methanol were investigated ; infra-red spectra, electrical conductivity and magnetic susceptibility of some of them were investigated and are discussed in relation to their structure.

Reaction with Palladium (II)

vic-Oxime-imines react with palladium (II) salts to form complexes of the formula $Pd_2R_3(OH)(H_2O)_x$ or $Pd_3R_4(OH)_2(H_2O)_y$. They are yellow in colour and slightly soluble in organic solvents. The ultra-violet absorption spectra, infra-red spectra, electrical conductivity and magnetic susceptibility of some of them were studied and are discussed in relation to their structure.

Reaction with Iron (II)

vic-Oxime-imines react with iron salts to form complexes of the formula $FeR_2(H_2O)_2$, $Fe_2R(SO_4)(OH)$ or $Fe_3R_2(SO_4)(OH)_2$. They are violet-blue in colour and soluble in many organic solvents. The structure of the complexes $FeR_2(H_2O)_2$ is duscussed in relation to the paramagnetic nature of the complexes.

Reaction with Cobalt (III)

vic-Oxime-imines react with hexammine cobalt (III) chloride to form complexes of the formula CoR_3, or $CoR_2(OH)(NH_3)(H_2O)_x$. They are soluble in organic solvents. The ultra-violet absorption spectra, infra-red spectra, electrical conductivity and magnetic susceptibility of some of these complexes were investigated and are discussed in relation to their structure.

Complexes in solution

Since complexes of copper and nickel with vic-oxime-imines prepared in the present investigations were not formulated as MR_2 in many cases, attempts were made to find if complexes of similar compositions existed in solutions. Continuous variation method was adopted and investigations were carried out spectrophotometrically in the ultra-violet region. In case of nickel complexes, vic-oxime-anils appear to form complexes of the type $[NiR]^+$ rather than $[Ni_2R_3]^+$ in solution while the other vic-oxime-imine forms the complex of the type NiR_2 in solution. In case of copper complexes metal-to-ligand ratio of 1 : 1 is found in most of the solutions under investigation, while the complexes prepared have the ratio 1 : 1, 2 : 3 or 3 : 4 in different cases.