I N T R O D U C T I O N

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1. N-ligands.

By the term ligand we understand any ion or molecule which is directly attached to a metal ion and which we regard as bonded to it. The most common types of ligands are negative ions and neutral polar molecules. The latter are usually those which have one pair of unshared electrons available for bonding and hence are suitably directed at the metal ion. Among the more novel types of ligands are unsaturated hydrocarbons and their radicals.

N-ligands are ones which contain nitrogen functional groups and are bonded to the metal ion through nitrogen. The common N-ligands are primary, secondary and tertiary amines, hydrazines, imines (Schiff bases-anils), oximes, nitroso compounds, nitrosoamines, hydrazones , semicarbazones, thiosemicarbazones, azines, azo, diazo and polyazo compounds, N-heterocyclics (pyridine, quinoline, isoquinoline etc.) and nitric oxide.

N-functional groups under investigation are oxime and imine (Schiff base). Hence a discussion of these groups follows.

2. Oximes.

2(a) Preparation of oximes :

Oximes are prepared by (i) the action of hydroxylamine on aldehydes, ketones or nitriles ; (ii) the

action of nitrous acid, ester of nitrous acid or nitrosyl chloride on compounds containing reactive methylene group ; (iii) oxidation of primary amine with Caro's acid (1) ; (iv) reduction of nitro-olefin with zinc and acetic acid (2) ; (v) reduction of pseudonitrile with hydroxylamine (3) ; etc.

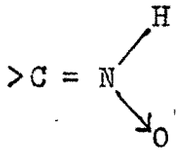
2.(b) Isomerism of oximes :

Oximes exhibit stereoisomerism (4). Cis-trans isomers possible in the case of unsymmetrical oximes may be represented as

Syn - R anti - R

Atack and Whinyates (5) proposed structural isomerism for the oximes which may be represented by two structures

>C = N - OH (hydroxyimine)



(imine oxide)

It is suggested that in solution an oxime may be a tautomeric mixture of these two forms.

2.(c) Alkylation and acylation of oximes :

Oximes may be alkylated to O-alkyl or N-alkyl

ethers. The structures of oximes, their sodium salts and their O-methyl and N-methyl ethers were studied in relation to their chemical properties and absorption spectra by Brady and his co-workers (6 to 9). Oximes have been acetylated by Brady and Grayson (10), Wohl (11), Exaner (12), etc. They investigated their absorption spectra and suggested O-acetyl nature of the acetylated product.

2.(d) Ultraviolet absorption spectra of oximes :

Bielecki and Henri (13) found no selective absorption in the oximes. Ramart-Lucas and co-workers (14 ; 15) observed that oximes and their derivatives exist in two (structurally different) forms : absorbent and transparent. They also observed that the oximes of $PhCOCH_2R$ and $PhCOCR_3$ differ in their spectra and attributed it to the difference in the structures of oximes in the two cases. This type of observation was also made by Guilmart (16) from the study of oximes of similar compounds.

Grammaticakis (17) found from the study of the absorption spectra of oximes and their derivatives that N-substituted oximes are more absorbing than oximes or their O-substituted derivatives. Meisenheimer and Dorner (18) related absorption spectra of oximes to their structure and stability. Watts (19) and Körtum (20) investigated the spectra of aromatic and aliphatic oximes respectively.

2.(e) Infra-red and Raman spectra of oximes :

Freymann and Freymann (21) observed the presence of the characteristic frequencies for both - OH and - NH groups in $PhCOCR_3$. They also suggested that oximes are

associated at ordinary temperature. Duyckaerts (22) investigated the spectra of oximes and their complexes and discussed the effect of H-bonding. Palm and Werbin (23) found that the "solid spectra" have different frequencies for associated OH group in case of 'α' and 'β' oximes, but in solution 'α' and 'β' isomers have the same absorption band. Buswell et al. (24) suggested association of the oximes through H-bonding. Sadler (25) suggested intramolecular H-bonding from the observation that the frequency for -OH group in the solid state remained unchanged in chloroform solution.

Milone (26) investigated the Raman spectra of oximes and suggested the absence of nitronic structure and functional tautomerism. Bonino and Manzoni-Ansidei (27) studied the Raman spectra of oximes and their salts and suggested nitronic formula for oximes in their sodium salts. Bernstein and Martin (28) and Biquard (29) discussed the structure of oximes in relation to their Raman spectra. Kahovec and Kohlrausch (30) discussed molecular association from the study of the Raman spectra of oximes.

2.(f) Dipole moment of oximes :

Sutton and Taylor (31) found appreciable differences in the values of dipole moment of 'α'- and 'β'-isomers of N-methyl ethers of oximes. Parsons and Porter (32), however, suggested that the results of dipole moment investigations did not give unambiguous answer to the question of oxime structure. Low values of dipole moment for oximes in solutions have been attributed to

association. Hassel and Naeshagen (33) Calderbank and Le Fevre (34) and Reiser et al. (35) also investigated the dipole moment of oximes and discussed the structure of oximes.

2.(g) Transition metal complexes of oximes:

Transition metal complexes of some ketoximes and aldoximes (monodentate ligands) are as follows : Babaeva and Mosyagina (36) prepared cobalt, copper and platinum complexes of acetone oxime and determined the crystal nature and magnetic susceptibility of the platinum complex. Babaeva and Karepina (37) prepared platinum complexes of acetone oxime and studied the electrical conductivity and absorption spectra of their cis and trans isomers.

Hofmann and Ehrhardt (38) and Sacco and Freni (39) prepared the complexes of nickel with formaldoxime and discussed their structures. Marquez (40) investigated the action of a polymer of formaldoxime on cobalt. Baudisch (41) prepared iron compounds of formaldoxime and studied their oxidation-reduction properties. Okac and Bartusek (42) investigated the formation of nickel and manganese complexes of formaldoxime photometrically and polarographically and their analytical application. They (43) also investigated the formation of complexes of nickel,cobalt and manganese with formaldoxime in solution photometrically, polarographically, by paper electrophoresis, by ion exchange, and by potentiometric and conductometric titrations and discussed their structures. Marczenko and Minczewski(44)

studied the coloured complexes formed by formaldoxime with nickel, manganese, iron and cerium by spectral and gasometric analysis and by means of ion-exchange.

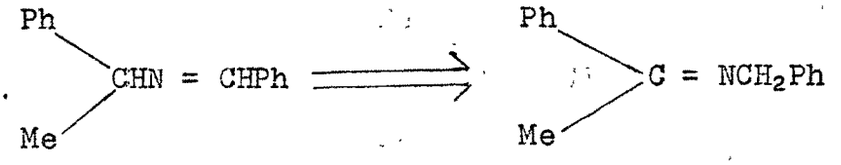
Peshkova (45) studied the absorption spectra of the complexes of acetaldoxime with cobalt and nickel. Heiber and Leutert (46) investigated the reactions of cobalt, nickel and copper salts with aldoximes. Korenman (47) and Plodiv(48) studied the formation of complexes by metal ions with oximes.

3. Schiff bases :

3.(a) Preparation and structure of Schiff bases :

Schiff bases are usually prepared by the action of primary amine on aldehyde or ketone. They are also obtained by the condensation of a keto-dichloride with aromatic amine or of a nitroso compound with a substance containing reactive methylene group.

They are considered to exist in tautomeric equilibria (49,50). Herrera and Hidalgo (51) have shown that the prototropic change



is a trimolecular reaction. Hires and Balog (52) could not observe cis⟶trans conversion from the study of "dark" and "illuminated" spectra, and suggested the existence of trans form. Trans form is also proposed for Me - N = CHR by Kahovec (53).

3.(b) Ultra-violet absorption spectra of Schiff bases :

Varga (50) observed a band at 440 mμ in the absorption spectra of Schiff bases and related it to the tautomerism involving quinonoid transformation of the molecule. Kiss and Aver (54) found that absorption bands due to the parent molecules were absent in the spectra of Schiff bases. They also observed that the band underwent a bathochromic and hyperchromic shift on extending the conjugation in the molecule of the Schiff base.

Ferguson and co-workers (55 to 57) investigated the absorption spectra of Schiff bases and related compounds. They discussed their relative chromophoric power and the effect of substitution, association and chelation in the molecule on the spectra.

Izmail and Smirnov (58) do not regard azomethine group as a main chromophore. They also discussed theoretically the compound PhCH = NPh regarded as a single conjugated chromophoric system. Grammaticakis (59) compared the spectra of aryl imines with those of oximes and hydrazones. Itano (60),Grammaticakis (61), Krohnke and Gross (62) and Gore and Wheeler (63) discussed the substitutent, solvent and steric effects on the absorption spectra of Schiff bases. Mc Casland and Horswell (64) attributed the band at 247 mμ to the chromophore PhCH = N -. Menkin, Osipov and Kogam (65) suggested that the band at 260 mμ was due to the electron transfer between aldehyde and aromatic amine moieties.

3.(c) Infra-red and Raman spectra of Schiff bases :

Hidalgo (66) investigated the infra-red spectra of a series of azomethines and made assignments for most of the bands. Cloughetry et al. (67) attributed a band at 1621-1631 cm^{-1} in the infra-red spectra of Schiff bases to the azomethine group. Bergmann and Kaluszyner (68) similarly assigned a band at 1650 cm^{-1} to the C = N group. Goulden (69) discussed the effect of conjugation on the changes in the frequency and the intensity of the band. Kahovec (53) investigated the Raman spectra of MeN = CHR and discussed the stereoisomerism of Schiff bases.

3.(d) Metal complexes of Schiff bases :

Bahr (70) prepared copper, nickel and iron complexes of α-diimines from benzil and 2,3-butane dione and studied their structures and reactivity. Busch and Bailar (71) prepared iron complexes of α-diimines and discussed their structures.

Wolter (72) studied the complex formation between Plutonium and Schiff bases with a view to utilise it for extraction, decontamination and purification of plutonium.

Sweetening of petroleum fractions in presence of cobalt complexes of Schiff bases has been patented (73 to 75).

Marvel and co-workers (76,77) prepared metal complexes of Schiff bases and studied their heat stabilities.

Holm (78) prepared nickel complexes of Schiff bases and related their absorption spectra to the ligand field strength.

Kaneniwa et al. (79) studied the colour reaction of 28 metal ions with Schiff bases.

Savich and co-workers (80,81) studied the uranyl complexes of polymeric Schiff bases and also the catalytic activity of metal complexes of Schiff bases.

4. N-ligands (α-diketone derivatives) :

In the present investigations are studied vic-oxime ketones, vic-dioximes and vic-oxime-imines. A discussion of these groups follows. (Compounds containing these groups and obtained from cyano-and acetoacetic acid derivatives are not included as they are discussed separately. Further, cyclic vic-oxime-ketones such as o-quinone monoximes, 4,5-pyrazoledione monoximes, 4,5-isoxazoledione monoximes, etc. are also excluded from the discussion.)

4.(a) vic-Oxime ketones :

Compounds containing - CO - C(=NOH) - are prepared by the action of nitrous acid or its ester or nitrosyl chloride on compounds containing - CO - CH_2 -.

Taylor and Ewbank (82) studied the volatility, solubility and carbonyl reactivity of the isomeric monoximes of α-diketones and suggested that the existence of H-bond could explain the physical and chemical differences of the compounds.

Acly and French (83), Baly (84) and Purvis (85) studied the ultra-violet absorption spectra of 2,3-butane dione monoxime and found them to be continuous.

Okac and Simek (86) studied the preparation and chemical behaviour of nickel and cobalt complexes of 2,3-butane dione monoxime, α-benzil monoxime, etc.

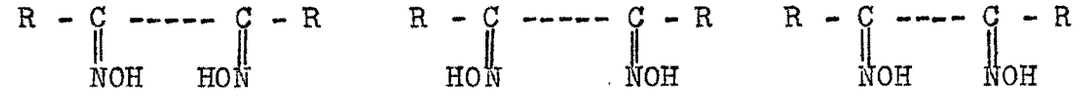
Malatesta (87) prepared nickel complexes of oxime-ketones and studied their magnetic behaviour.

vic-Oxime ketones form yellow alkali salts and give characteristic iron-blue reaction which was first observed by Whiteley (88). Feigl (89) discussed the effect of structure and geometry of the oxime-ketones on iron-blue reaction. Sargent (90) patented iron (II) complexes of oxime-ketones for use on photo-image. Masuda (91) prepared iron (II) complexes of oxime-ketones and studied their absorption spectra. Cambi (92) prepared iron (II) complexes of oxime-ketones, oxime-amides, etc. and investigated their magnetic properties.

4.(b) <u>vic-Dioximes</u> :

They are prepared by the action of hydroxylamine on α-diketone, its monoxime or α-(dichloro) ketone.

In the case of symmetrical vic-dioxime, three geometrical isomers can exist, thus



Syn anti amphi

Ultra-violet absorption spectra of vic-dioximes : Chugaev and Glebko (93), Baly and Stewart (94) and Purvis (85) observed absence of selective absorption in the spectrum

of 2,3-butanedione dioxime. Barany et al. (95) observed absorption bands for glyoximes and discussed the effect of methyl substituents. Borello and Catino (96) studied the absorption spectra of aliphatic and aromatic vic-dioximes, their syn,anti and amphi isomers, sodium salts, etc. Banks and his colleagues (97,98) investigated the absorption spectra of 1,2-cyclohexane dione dioxime and its alkyl derivatives and discussed the effect of alkyl substituents. Bambaneck and Pflaum (99) discussed the absorption spectra of glyoximes in neutral and anionic forms in aqueous solutions.

Infra-red spectra of glyoximes were investigated by Duyckaerts (22), Borello and Henri (100),etc. They assigned frequencies for C = N and OH groups and made correlations with the corresponding frequencies observed in other oximes.

Dipole moment of vic-dioximes was investigated by Durio (101), Milone and Muller (102), etc. They correlated the differences in values with steroisomeric nature of sym.and unsym.glyoximes.

Chugaev (103) prepared the metal chelates of bivalent nickel with dimethylglyoxime. He also prepared and studied the complexes formed by iron,cobalt,palladium, etc. with dimethyl glyoxime in presence of ammonia,pyridine, etc. Sugden (104) and Dwyer and Mellor (105) separated the isomers of the complexes of nickel and palladium with benzyl methyl glyoxime. Atack (106) and Heiber and Leutert (107) prepared the complexes of nickel with isomeric

glyoximes. The complexes of nickel with many other dioximes such as α-diphenylglyoxime (103) γ-diphenyl-glyoxime (108), α-furildioxime (109), diaminoglyoxime (110), 1,2-cyclohexane dione dioxime (111,112), 1,2-cycloheptanedionedioxime (112), etc. were also investigated. Similarly, the reactions of vic-dioximes with bismuth,rhenium,rhodium etc. (113 to 117) and reactions of copper and nickel with glyoximes in presence of oxidising agents were also investigated (118 to 126).

It has been shown that (i) anti-dioximes exhibit the characteristic reactions with metal ions, wherein the glyoxime molecule would act as monobasic acid, (ii) syn-dioximes are incapable of forming metallic complexes (127) and (iii) amphi-dioximes form complexes with nickel where the glyoxime molecule appears to be dibasic (106, 107, 127).

Magnetic moments of nickel glyoximates were determined by Cambi and Szego (128), Klemm et al. (129), Cavell and Sugden (130), Banks et al. (131), etc. Without exception they are dimagnetic and have square planar structure. Magnetic studies of the complexes of palladium, cobalt and iron (II) with glyoximes also suggested planar distribution of glyoxime molecules in the complex (131 to 134).

X-ray diffraction and infra-red spectroscopic studies of metal glyoximates showed H-bonding leading to the formation of additional rings in the complex (135 to 138).

Metal-metal bonding in metal complexes of glyoximes was also investigated (139,140).

4.(c) vic-Oxime-imines :

Pfeiffer (141) prepared the nickel complex of the condensation product of 2,3-butane dione oxime with methyl amine and compared it with nickel dimethyl glyoximate.

Recently Masuda (142) prepared the iron (II) complex of the above ligand and studied its absorption spectrum ; and Mathur and Narang (143) investigated the products obtained by the condensation of 2,3-butane dione oxime with ethylene diamine and o-phenylene diamine as gravimetric reagents for nickel and palladium.

A related investigation has been carried out by Murmann (144). He investigated the complexes of copper, nickel,cobalt,palladium and platinum with 2-methyl 2-amino 3-butanone oxime.

5. N-ligands obtained from cyanoacetic acid derivatives :

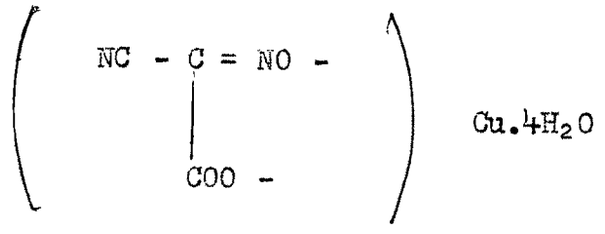
N-ligands of the types considered so far and obtained from the derivatives of cyanoacetic acid are now discussed.

5.(a) Monoximes : Derivatives of the oxime of 2-cyano-glyoxylic acid :

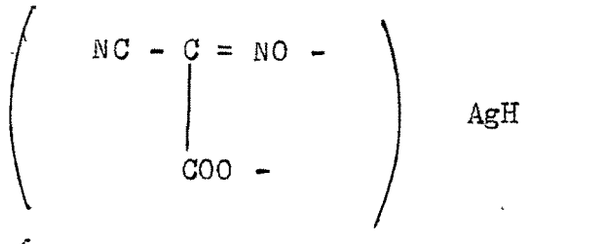
The oxime of 2-cyanoglyoxylic acid could not be prepared by the action of nitrous acid on cyanoacetic acid. Wolff and Gans (145) prepared it by treating furazan-carboxylic acid with sodium hydroxide. Wolff (146) also prepared it by boiling furazan dicarboxylic acid with water. Muller (147) obtained it by treating the oxime of ethyl 2-cyano glyoxylate with alkali. Hantzsch and Urbahn (148) prepared it by the action of nitrous acid

on the ammonium salt of 5-isoxazolone 3-carbohydroxamic acid. It was also prepared from the dioxime of dioxo-succinic acid by Soderbaum (149), the oxime of 2-cyano-glyoxylo-hydroxamic acid by Ulpiani (150), the oxime of 2(hydroxyamidino) glyoxylic acid by De Paolini and Imberti (151), etc.

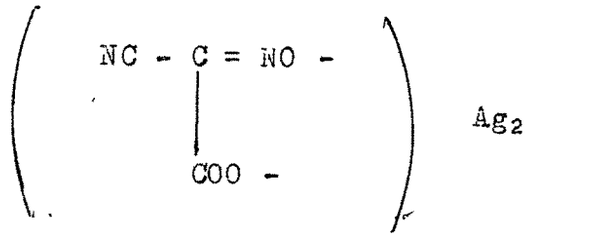
It gives yellow colour with alkali. It forms salts with copper and silver, which may be represented as



$Cu.4H_2O$



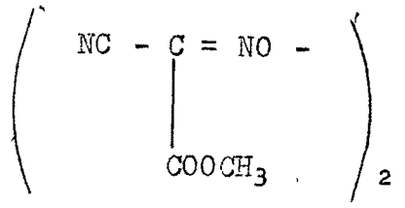
AgH



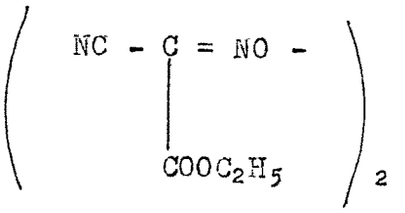
Ag_2

The oximes of methyl, ethyl and benzyl esters of 2-cyanoglyoxylic acid were prepared by the action of nitrous acid or amyl nitrite on the corresponding esters of cyanoacetic acid by Muller (147), De Paolini and Imberti (151), Conrad and Schulze (152), Sprung (153), Cook et al. (154), etc.

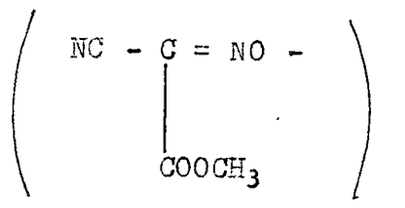
They form salts with copper, silver, lead, etc. which may be formulated as



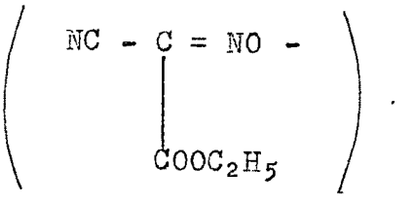
Cu



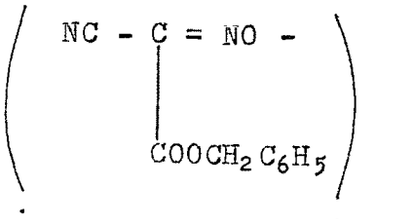
Cu.2 1/2 H_2O



Ag



Ag



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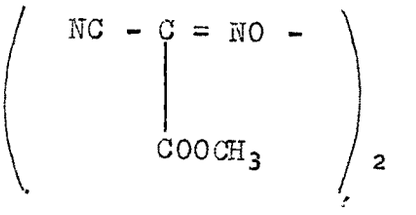
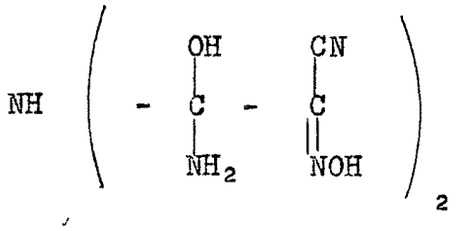


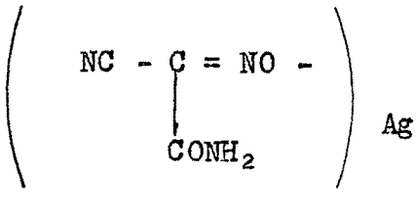
Pb. PbO.H_2O

Conrad and Schulze (152) prepared the oxime of 2-cyanoglyoxylamide by the action of nitrous acid on cyanoacetamide. They (152) and Nef (155) prepared it by the action of ammonia on the oxime of ethyl 2-cyano glyoxylate. It was also prepared from ethyl fulminurate by Seidel (156) and from

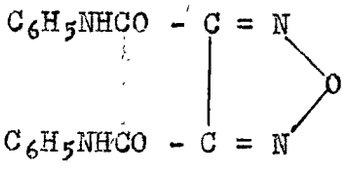


by Diels and Borgwardt (157). Miller et al. (158) prepared the oxime of 2-cyano-C^{14}-glyoxylamide by the action of nitrous acid on cyano-C^{14}-acetamide.

Its sodium salt gives red colour with iron (II) chloride. Its silver salt may be formulated as



Dimroth (159) prepared the oxime of 2-cyano-glyoxylanilide by the action of silver cyanide on the oxime of 2-chloroglyoxyl anilide, and by the action of alkali on

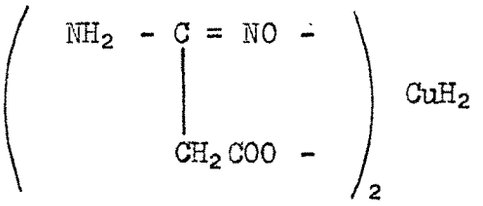


Darapsky and Hillers (160) obtained it by the action of aniline on the oxime of 2-cyano glyoxyl azide.

5.(b) Monoximes : Derivatives of 2-(hydroxyamidino) acetic acid :

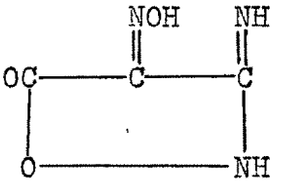
Modeen (161) prepared 2-(hydroxyamidino) acetic acid by the action of hydroxylamine on cyanoacetic acid and also by the action of mineral acid on 2-(hydroxyamidino) acetohydroxamic acid.

It forms copper salt formulated as



5.(c) Dioximes : Derivatives of the oxime of 2-(hydroxyamidino) glyoxylic acid :

Wieland and Hess (162) prepared the oxime of 2-(hydroxyamidino) glyoxylic acid by treating



with baryta water. De Paolini and Imberti (151) prepared it by the action of hydroxylamine on the oxime of 2-cyano-glyoxylic acid.

It gave red colouration with iron (III) chloride,

reddish precipitates with nickel acetate and silver salt with silver nitrate.

Ulpiani (150) prepared the oxime of 2-(hydroxy-amidino) glyoxylamide by the action of ammonia on syn or amphi isomer of the oxime of 2-cyano-glyoxylo-hydroxamic acid. Wieland and Baumann (163) prepared it by the action of ammonia on chloro formaldehyde oxime. The dioxime group is shown to have anti-configuration. It gave golden yellow colouration with alkali and deep brown-red colouration with iron (III) chloride.

6. N-ligands obtained from acetoacetic acid derivatives :

N-ligands of the types considered so far and obtained from the derivatives of acetoacetic acid are now discussed.

6.(a) vic-Oxime-ketones : Derivatives of 2,3-dioxobutyric acid 2-oxime :

Acetoacetic acid and its derivatives can be converted into 2,3-dioxobutyric acid 2-oxime and its derivatives by the action of nitrous acid, its ester or nitrosyl chloride.

Acetoacetic acid reacts with nitrous acid to form 2,3-dioxobutyric acid 2-oxime ; it is so unstable that it instantaneously decomposes into pyruvaldehyde aldoxime, carbon dioxide and water.

Ethylacetoacetate was converted into ethyl 2,3-dioxo butyrate 2-oxime by the action of nitrous acid by Meyer (164,165), Jowitschitsch (166), Ceresole (167),

Wieugel (168), Rodionov et al. (169), Nussberger (170), Adkins and Reeve (171), Pannizzi (172), etc.

Euler and Euler (173) prepared it by the action of nitrous acid on the ammonium salt of ethyl 2-(hydroxy-imino) 3-(nitrosoimino)butyrate.

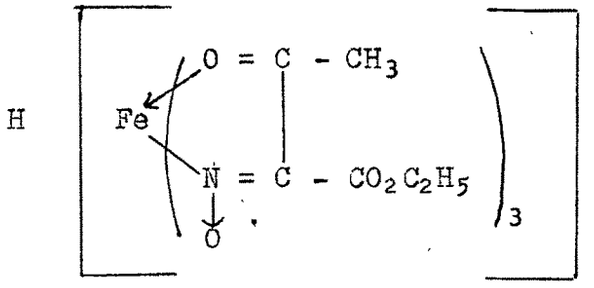
It was also obtained from ethyl acetoacetate by the action of (i) methyl nitrite by Bouveault and Wahl (174), Wolf (175) and Slater (176), (ii) amyl nitrite by Ajello and Siggilo (177) and (iii) nitrosyl chloride by Dorabialska (178).

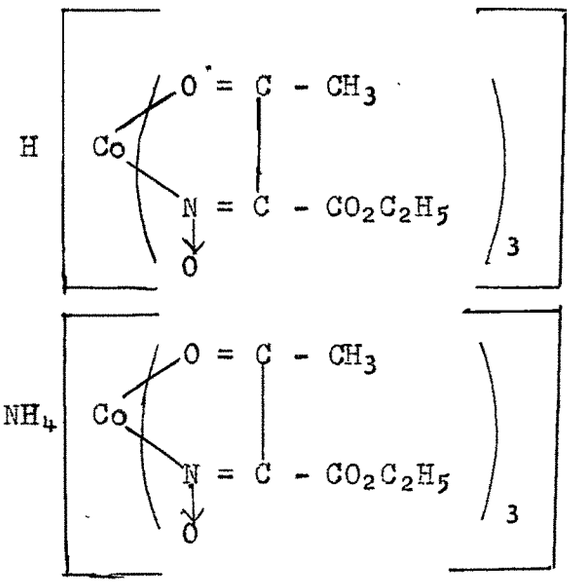
Since earlier attempts to acetylate it failed, it was assumed to contain the nitroso group rather than hydroxyimino group (Meyer) ; it has been acetylated, however, by Wahl (179) and Cerchez and Colesiu (180).

Its ultraviolet absorption spectrum has been studied by Baly (84) and its infra-red spectrum by Ungnade and Kissinger (181). The latter investigators suggested that the oxime group is more or less H-bonded.

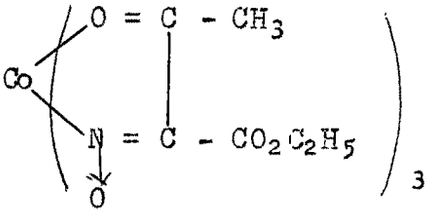
It gives characteristic blue colouration with iron (II) salts. Boucherle (182) has suggested that the reaction can be utilised for the colorimetric determination of iron (II) at pH 7 to 8.

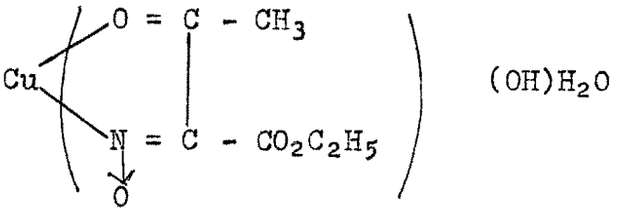
Kuster (183) found that it forms metal complexes. The products which he isolated are

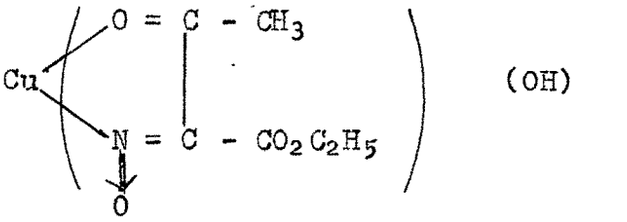


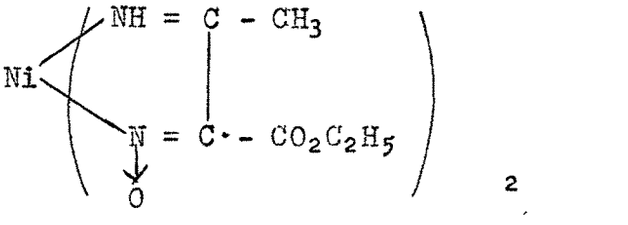


Taylor and Ewbank (82) prepared the complexes which may be represented as









Cambi (92) prepared its complex with iron (II) in the hydrated form and determined its magnetic moment.

2,3-dioxobutyranilide 2-oxime was prepared by Knorr (184) by the action of nitrous acid on acetoacetanilide ; 2-Oximes of N-aryl 2,3-dioxobutyramides (where aryl amide may be anilide, o-toluidide,p-toluidide, 3,4-xylidide, α-naphthylamide or β-naphthylamide) were prepared by Naik et al. (185) by the action of nitrosyl chloride on the corresponding N-aryl acetoacetamides. Dave and Talati (186) prepared 2-oximes of N-aryl 2,3-dioxobutyramides (where aryl amide may be anilide, o-toluidide, o-chloranilide, p-chloranilide, p-phenetidide or 2:4-xylidide) by the action of nitrous acid on the corresponding N-aryl acetoacetamides.

Their ultra-violet absorption spectra were investigated by Naik et al. (185) in aqueous solution and by Talati (187) in aqueous, alcoholic and chloroform solutions.

They gave characteristic yellow colouration with alkali and intense blue colouration with iron (II) salts. Their iron (II) complexes are studied by Desai (188).

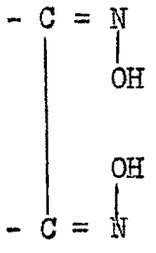
6.(b) vic-Dioximes : Derivatives of 2,3-dioxobutyric acid dioxime :

The dioxime of ethyl 2,3-dioxobutyrate was prepared by the action of hydroxylamine on 2-oxime of ethyl 2,3-dioxobutyrate by Ceresole and KDeckert (189) Rodionov et al. (169), Nussberger (170),etc. Ceresole

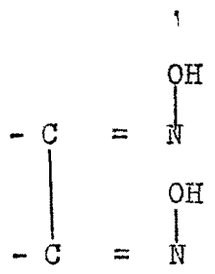
and Koeckert converted it by saponification followed by acidification into the dioxime of 2,3-dioxobutyric acid. It gave barium and silver salts.

While studying the reaction of hydroxylamine on 2-oxime of ethyl 2,3-dioxobutyrate, they also isolated another product, and called it external anhydride of 2,3-dioxobutyric acid dioxime ($C_8H_{10}N_4O_7$). It formed deep red barium salt ($C_8H_8N_4O_7$) Ba 1/2 H_2O and reddish brown silver salt ($C_8H_8N_4O_7$) Ag_2. They suggested that the anhydride was a dibasic acid, formed by the union of two molecules through two of the oxime groups.

Nussburger (170) showed that the dioxime of 2,3-dioxobutyric acid and its ethyl ester prepared by Ceresole and Koeckert (189) were syn-glyoximes.



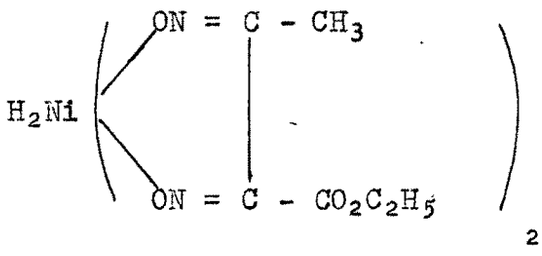
The ester gave green precipitates with neutral copper sulphate and the acid gave white precipitates with silver and mercurous nitrates, yellowish brown precipitates with copper acetate and brown colouration with iron (III) chloride. He converted the syn-isomer of the ester into amphi isomer.



by heating its ethereal solution with hydrochloric acid. He also prepared diacetyl derivatives of both syn and amphi isomers of the dioximes.

Bouveault and Wahl (190) prepared the dioxime of ethyl 2,3-dioxobutyrate by the action of hydroxylamine on ethyl 2,3-dioxobutyrate and found that it was converted into isoxazolone derivative by the action of hydrochloric acid. They obtained mono and diacetyl derivatives of the dioxime and concluded from their studies that there is only one dioxime of ethyl 2,3-dioxobutyrate.

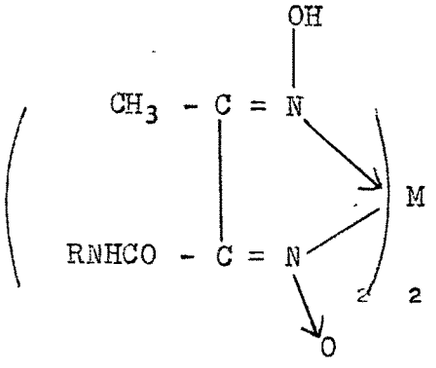
It gave bluish-violet precipitates with ferrous salt in presence of little ammonia, red colouration with ferric chloride, olive green precipitates with copper sulphate and dirty green precipitates with nickel nitrate. The nickel compound is formulated by Kuster (183) as



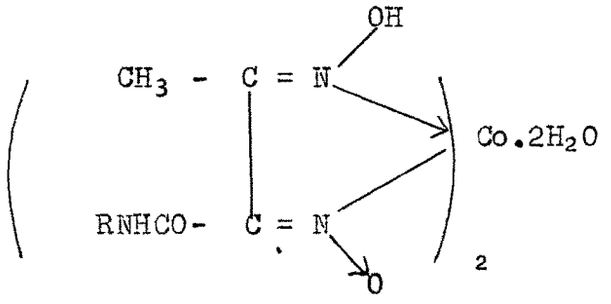
Erbstein (191) prepared the dioxime of 2,3-dioxo-butyramide by the action of ammonia under pressure on

the dioxime of ethyl 2,3-dioxobutyrate at 100°.

Knorr and Reuter (192) prepared the dioxime of 2,3-dioxobutyranilide by the action of hydroxylamine hydrochloride on 2-oxime of 2,3-dioxobutyranilide. Dave and Talati (186) prepared the dioximes of N-aryl 2,3-dioxobutyramides (where arylamide may be anilide, o-toluidide, o-chloranilide, o-anisidide, p-chloranilide, p-phenetidide or 2,4-xylidide) by the action of hydroxylamine hydrochloride on the corresponding 2-oximes of N-aryl 2,3-dioxobutyramides. They investigated the ultra-violet absorption spectra of these compounds in water and alcohol. They (193) prepared their nickel, palladium, copper and cobalt complexes which are formulated as



(M : Cu, Ni or Pd)



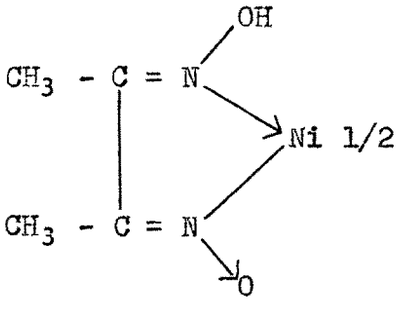
and investigated their magnetic properties. They also studied some of these dioximes as analytical reagents for the gravimetric estimation of copper,nickel and palladium. Desai (188) prepared iron (II) complex of the dioxime of 2,3-dioxobutyranilide and determined its magnetic moment.

6.(c) vic-Oxime-imines: Schiff bases from the derivatives of 2,3-dioxobutryic acid 2-oxime :

Although phenyl hydrazones of ethyl 2,3-dioxobutyrate 2-oxime and 2,3-dioxobutyranilide 2-oxime (179, 192) were prepared,the Schiff bases from the derivatives of 2,3-dioxobutyric acid 2-oxime are not reported in literature.

7. Aim of present work :

Pfeiffer (141) suggested five membered ring structure for nickel dimethyl glyoximate prepared by Chugaev (103).



-OH of the second oxime group is not involved in bond formation with the metal in the complex. This was demonstrated by the fact that mono-O-methyl ethers of the

glyoxime form exactly similar compounds with nickel (141,194,195). It was also shown that when one of the oxime group is replaced by an imino or methylimino group, the resulting compounds form complexes with metal ions in the same manner as vic-dioximes. It was considered that when one of the oxime groups is replaced by the aryl imine group, the metal complexes formed by these reagents would be similar to those of glyoximes. A literature survey showed only a few attempts where vic-oxime-imines were investigated for their reactions with metal ions. Hence it was thought interesting to study vic-oxime-imines and their reactions with transition metal ions.

Studies on the dioximes of N-aryl 2,3-dioxo-butyramides have shown that they form insoluble complexes not only with nickel and palladium but also with copper (193). It was believed that the oximes of 2(hydroxy-amidino) glyoxylamides would behave similarly and would form stable complexes with transition metal ions. It was further believed that Schiff bases from N-aryl 2,3-dioxo-butyramide 2-oxime would form complexes with transition metal ions, which would be similar to those of mono-ethers of vic-dioximes.

With this view, it was proposed:

(i) to prepare N-aryl 2,3-dioxobutyramide 2-oxime and its Schiff bases with primary amines ;

(ii) to prepare derivatives of the oxime of 2-cyano-

glyoxylic acid ;

(iii) to prepare the metal complexes of some of these ligands using the salts of some transition metals ;

(iv) to investigate the formation of complexes in solution ;

(v) to study the ultra-violet and infra-red absorption spectra of some of these ligands and their metal complexes.

(vi) to investigate the magnetic susceptibility and electrical conductivity of the metal complexes.

Investigations carried out with the above considerations in view, and discussions of the results obtained are presented in the following pages.