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

METAL COMPLEXES

OF

OXIMINO LIGANDS

INTRODUCTION

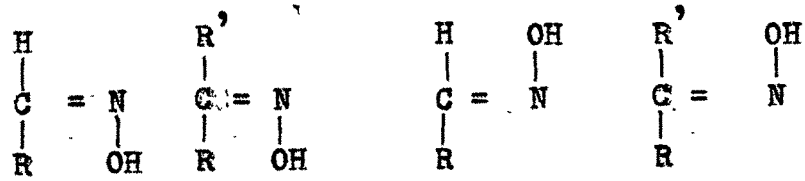
1. General :

Oximino ligands are well known for their ability to form metal complexes with numerous metal ions. The oxime group (> C = N H) is considered to possess acidic property and to form salts with various metal ions. The oxime group-represented in another form (> C = N -OH) is known mainly for its ability to function as a donor group and in a few cases for its weakly acidic behaviour. Besides the mono dentate oximino ligands, various bidentate, tridentate and polydentate ligands containing one or more oximino groups are known. A brief survey of such ligands and their metal complexes is presented here.

2. Oximes :

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

Oximes exhibit stereoisomerism, first interpreted successfully by Hantzsch and Werner (4). Cis-trans isomers possible in the case of aldoximes and unsymetrical ketoximes, may be represented as (I)

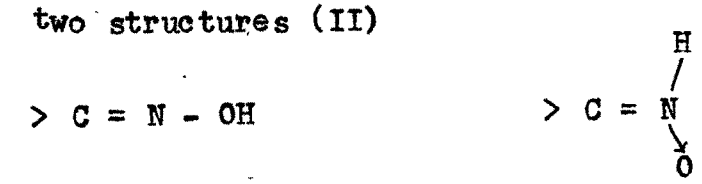


Syn - R anti - R

(a) (b)

(I)

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



(Hydroxyimine) (imine oxide)

(a) (II) (b)

It is suggested that in solution, an oxime is a tautomeric mixture of these two forms. If this is so, the equilibrium would be very much on the side of the hydroxy form in many cases.

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 were acetylated by Brady and Grayson (10), Wohl (11), Exaner (12) etc. O-acetyl products were obtained.

Ultraviolet absorption spectra of the oximes and their derivatives were studied by Bielecki and Henri (13), Ramart-Lucas and coworkers (14,15),Grammaticakis (16), Watts (17), Meisenheimer and Dorner (18), Kortum (19), Guilmart (20),etc.

Infra-red spectra of the oximes were investigated by Freymann and Freymann (21), Buswell et al. (22), Duyckaerts (23), Palm and Werbin (24), Califano and Luttke (25), Sadler (26),etc.

Raman spectra of the oximes were investigated by Bonino and Manzoni-Ansidei (27), Milone (28), Bernstein and Martin (29), Biquard (30), Kahovec and Kohlrausch (31), etc.

Electric dipole moments of the oximes were studied by Sutton and Taylor (32), Parsons and Porter (33), Hassel and Naeshagen (34), Calderbank and le-Fe'vre (35), Reiser and co-workers (36),etc.

Gilbert, Norman and Price (37) studied the hyperfine splitting in the electron spin resonance spectra of iminoxy radicals obtained from oxime. Kleinspehn, Jung and Studniarz (38) investigated the deshielding of OH proton in the NMR spectrum of benzil monoxime.

3. Monodentate oximino ligands and their metal complexes :

Hofmann and Ehrhardt (39) and Sacco and Freni (40) prepared the complexes of nickel with formaldoxime (IIIa) and discussed their structures. Marquez (41) investigated the reaction of polymeric formaldoxime

with cobalt. Baudisch (42) prepared iron complexes of formaldoxime and studied their oxidation reduction properties. Okac and Bartusek (43,44) investigated the formation of nickel,cobalt and manganese complexes of formaldoxime photometrically, polarographically, by ion exchange,by paper electrophoresis and by potentiometric and conductometric titrations and discussed their structures and analytical use. Marczenko and Minczewski (45) studied the complexes formed by formaldoxime with nickel,manganese,iron and cerium by spectral and gasometric analysis and by means of ion-exchange.

R =

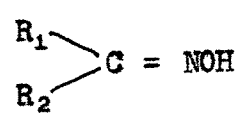
(a) H RCH = NOH

(b) CH_3

(III)

Peshkova (46) studied the absorption spectra of the complexes of acetaldoxime (IIIb) with cobalt and nickel. Heiber and Leutert (47) investigated the reactions of cobalt,nickel and copper salts with aldoximes.

Babaeva and coworkers (48,49) prepared cobalt, copper and platinum complexes of acetone oxime (IV) and studied the crystal structure,magnetic susceptibility, electrical conductivity and absorption spectra of platinum complexes.



$R_1 = R_2 = CH_3$

(IV)

Korenman (50) and Plodiv (51) studied the formation of complexes by metal ions with various oximes.

Aldoximes and Ketoximes were investigated as reagents for the analysis of copper, nickel, cobalt, manganese, zinc, iron (II), mercury (II), lead, etc. by Meyer and Fannin (52), Beckmann (53), Bach (54), Pfeiffer (55), Krohnke (56), Brady and Goldstein (57), Deniges (58), Sen (59), Cunningham (60), Sideris (61), Hayes and Chandlee (62), Waldbauer and Ward (63) etc.

R - CO -NHOH

(V)

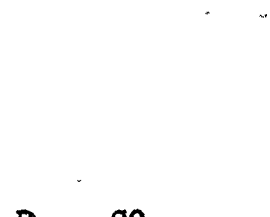
Hydroxamic acids (V) have been widely investigated. Their metal complexes were prepared and studied by Aksnes (64), Ley and Mannchen (65), Jones and Werner (66), Weinland and Baier (67), Cambi, et al. (68), Musante (69), etc. These acids were studied as analytical reagents for the estimation of various metals by Gupta and Sogani (70), Mosmier and Schwarberg (71), Majmudar and Mukherjee (72), Ryan and coworkers (73), West (74), Wolter (75), Shome (76), Singh and Das Gupta (77), Dutta (78), etc.

4. Ridentate ligands containing oximino groups and their metal complexes :

The bidentate ligands containing oximino groups are (i) Oxime-ketone,(ii) hydroxy-oxime,(iii) oxime-Phenol,(iv) oxime-imine,(v) oxime-hydrazone,(vi) oxime-semicarbazone and (vii) dioxime. (Studies on the ligands obtained from 2,3-dioxobutyranilide are discussed separately).

(i) Oxime ketone :

vic-Oxime ketones (VI) form yellow alkali salts and give characteristic iron-blue reaction which was first observed by Whiteley (79). Feigl (80) discussed the effect of structure and geometry of the oxime-ketones on iron-blue reaction. Sargent (81) patented iron (II) complexes of oxime-ketones for use of photo-image. Masuda (82) prepared iron (II) complexes of oxime ketones and studied their absorption spectra. Cambi (83) prepared iron (II) complexes of hydroxyimino acetone,hydroxyimino malonamide etc. and investigated their magnetic properties.



(VI)

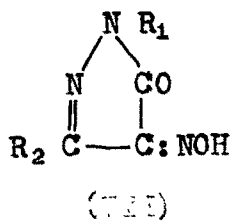
	R_1 =	R_2 =
(a)	CH_3	CH_3
(b)	CH_3	H
(c)	C_6H_5	C_6H_5
(d)	C_6H_5	H
(e)	CH_3	$COCH_3$
(f)	NH_2	$CONH_2$

Okac and Simek (84) studied the preparation and chemical behaviour of nickel and cobalt complexes of oxime-ketones.

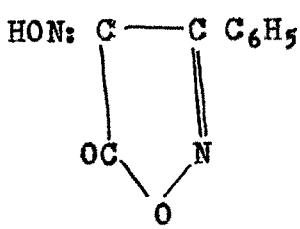
Malatesta (85) prepared nickel and cobalt complexes of oxime-ketones and studied their magnetic behaviour. Rao (86) prepared and studied the complexes of oxime-ketones with rare earth metals.

The oxime ketones were investigated as analytical reagents for iron,cobalt,nickel,copper, manganese,zinc,cadmium,mercury,tin,lead,antimony, bismuth etc. by Meyer and Zublin (87), Ceresole (88) , Wolff (89),Diels and Jost (90), Kuster (91), Mironoff (92), Hovorka and Sykora (93), Pallard (94), Calzolari and Donda (95) etc.

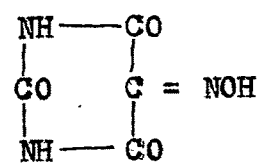
Hovorka and Sucha (96) prepared nickel and manganese complexes of 4-isonitroso-5-pyrazolone and its derivatives (VII) and studied the magnetic properties and thermal stability.



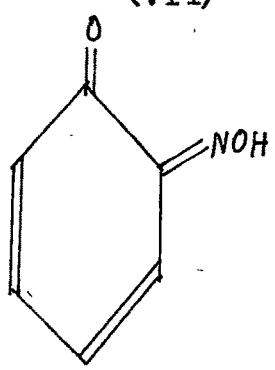
(VII)



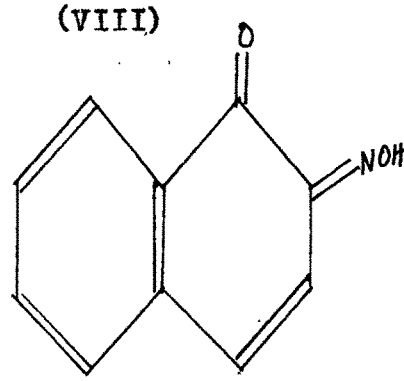
(VIII)



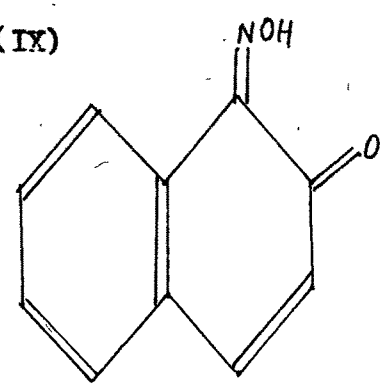
(IX)



(a)



(b)



(c)

(X)

Hantzsch and Coworkers (97.98) studied the complexes of lithium, sodium, potassium, rubidium, cesium, silver, barium, clacium and zinc with the three substituted derivatives of the oxime of 4,5-dioxo isoxazoline (VIII).

Giller (99) and Riche (100) investigated the structure of potassium, rubidium and barium violurate. Violuric acid (IX) was studied as an analytical reagent for various metal ions by Ligten and Velthuyzen (101), Cernj (102), Bockwerthmann (103) etc.

Callahan, Fernelius and Block (104) and Astakhova and Savostina (105) studied the solution stability of Zinc, cadmium, magnesium, lead, cobalt, nickel, copper and silver complexes of nitroso phenols and naphthols (X). Complexes of cobalt, nickel, uranium, vanadium, zirconium, magnesium, ruthenium, rhodium etc. of nitroso phenols and naphthols (x) were prepared by Watanabe (106), Kolthoff and Jacobsen(107), Zolotov and Alimarin (108), Astakhova, Savotina and Peshkova (109), Federkiel, Pfilzer and Baumann (110), Jonassen and De Monsabert (111), Bochm, Fressler and Rittmayer (112), Benzon and Cajan (113), Dutta, Syamal and Ghosh (114), etc.

Spectroscopic studies of the chelates of nitroso-naphthols have been made by Takahashi (115), Gall (116), Sterk and Ziegler (117) etc. Matsunage (118) carried out magneto chemical studies of the complexes and Stukan and Coldanskil (119) investigated the NMR spectrum of the iron chelate.

Nitroso-β-naphthols have been investigated as reagents for the analyses of Cobalt (120), palladium (12), copper (122), chromium (123), ruthenium (124), tungsten (125), neptunium (126), vanadium (127), iridium (128), beryllium (129), iron (130) etc.

(ii) Hydroxy-oximes :

Sauter and West (131) prepared copper complexes of α-acyloin oxime (XI) and studied their structures ; and Schoffa, Ristace and Wahler (132) investigated the electron spin resonance spectra of these chelates. Palladium and platinium complexes were prepared by Pshenitsyn and Nekrasova (133) and lead complexes by Ishibashi and Shimidzu (134).

$$R_1 - CHOH$$
$$\quad\quad\quad |$$
$$R_2 - C = NOH$$

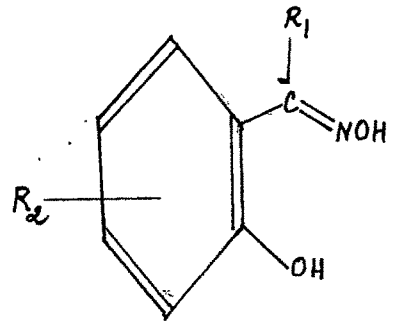
(XI)

Acyloin oximes have been used as analytical reagents for the estimation of copper, nickel, chromium, molybedenum, tungsten, etc. by Dunleavy, Wiberley and Harley (135), Lavender (136), Jensen and Weaver (137), Carpenter, Gardner, Ashley and Henicksman (138), Pfeifer and Hecht (139), Oka, Yamasaki, Matsuo and Muloko (140), Sverak (141), Leonwish (142), Peng and Sandell (143).

(iii) Phenol-oximes :

Salicyaldoxime (XII a) is used for the estimation

of copper (144, 145), lead (146), palladium (147), iron (148), nickel (149), bismuth (150), vanadium (150) etc.



(XII)

	R_1 =	R_2 =
(a)	H	H
(b)	CH_3	H
(c)	H	OH
(d)	CH_3	OH

Nakamura, Shimura and Tsuchida (151) prepared vanadium complexes of salicylaldoxime. Poddar (152) prepared copper, nickel and palladium complexes of 2-hydroxy acetophenone oxime, studied their magnetic properties and used the ligand as a reagent for the estimations of palladium (153), iron (154), vanadium (155), titanium (156) etc. Kabadi and Venkatachalam (157) studied the solution stability of copper, nickel, cobalt, manganese, zinc, cadmium and magnesium chelates of the above ligand.

(iv) Oxime-imines :

Masuda (158) prepared the iron complex of the Schiff base (XIII) prepared from diacetylmonoxime and methylamine and studied its absorption spectrum.

$$\begin{array}{l} R_1 - C = NR_3 \\ \quad\quad | \\ R_2 - C = NOH \end{array}$$

(XIII)

(v) Oxime hydrazones :

Cimusa (159) studied the complexes of nickel and

cobalt with oxime (phenyl) hydrazones of biacetyl and benzil (XIV). Edelman (160) investigated the action of bromine on the nickel complexes of biacetyl oxime phenyl hydrazone.

$$R_1 - C = NNHR_3$$
$$R_2 - C = NOH$$

(XIV)

(vi) Oxime semicarbazone :

Hovorka and Holzbecher (161) prepared the complexes of nickel, copper, iron with diacetyl oxime thiosemicarbazone (XVb) and discussed their structures. Hovorka, Holzbecher, Moravek, Valcil and Jatka (162) prepared the complexes of nickel, palladium with thianaphthenquinone-2-oxime-3-thiosemicarbazone and discussed their structures. Ablov and Belichuk (163) prepared the complexes of nickel, copper, cobalt with diacetyl oxime semicarbazone (XVa) and studied their debyegrams.

$$R_1 - C = NNHC\ X\ NH_2$$
$$R_2 - C = NOH$$

(XV)

X =

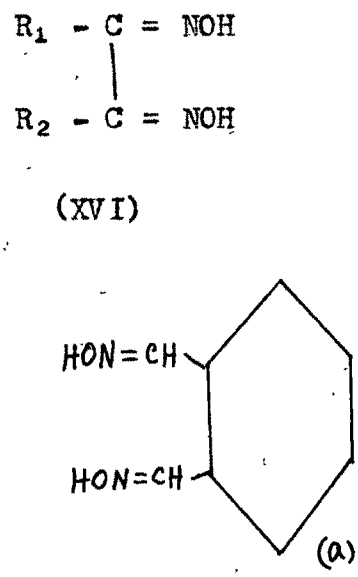
(a) O

(b) S

(vii) Dioximes :

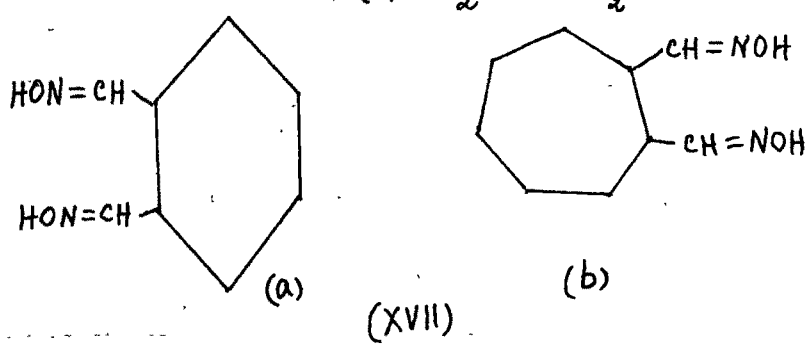
In 1905 Chugaev (164) first prepared the metal chelate of bivalent nickel with dimethylglyoxime. He also prepared and studied the complexes formed by iron, cobalt palladium etc. with dimethylglyoxime in presence of ammonia,

pyridine,etc. Sugden (165) and Dwyer and Mellor (166) separated the isomers of the complexes of nickel and palladium with benzyl methyl glyoxime. The complexes of nickel with many other dioximes (XVI and XVII) such as α-benzilglyoxime (164), γ-benzilglyoxime (167), α-furildioxime (168), oxalene diamidoxime(169),1,2-cyclohexane-dionedionemdioxime (170),1,2-cycloheptane-dionedioxime (171) etc. were also investigated.



(XVI)

	R_1 =	R_2 =
(a)	CH_3	CH_3
(b)	C_6H_5	C_6H_5
(c)	CH_3	$C_6H_5CH_2$
(d)	NH_2	NH_2



(XVII)

Dioximes have been widely investigated as analytical reagents for nickel,palladium,iron,rhenium etc. (172 to 182). Reactions of copper and nickel with dioximes in presence of oxidising agents were investigated and studied for their analytical applications (183 to 191)

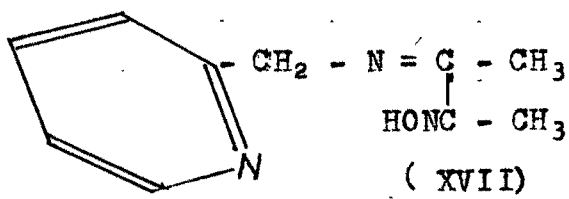
Magnetic moments of nickel dioximates have been determined by Cambi and Szego (192), Klemm et al. (193) Cavell and Sugden (194), Banks et al. (195) etc. Without exception they are diamagnetic and have square

planar structure. Magnetic studies of the complexes of palladium,cobalt and iron (II) with dioximes also suggested planar distribution of dioxime molecules in the complex (195 to 198).

X-ray diffraction and infra-red spectroscopic studies of metal dioximates showed H-bonding leading to the formation of additional rings in the complex (199 to 202). Metal-metal bonding in metal complexes of dioximes was also investigated (203,204).

5. Tridentate ligands containing oximino groups and their metal complexes :

Lions and Martin (205) prepared the complexes of iron and cobalt with 2-oximino-3-methyl-4-aza-5-α-pyridyl- Δ^3- pentene (XVII) and investigated their magnetic properties and discussed their structure.

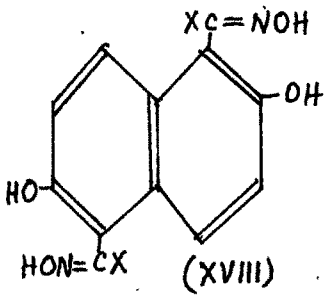


(XVII)

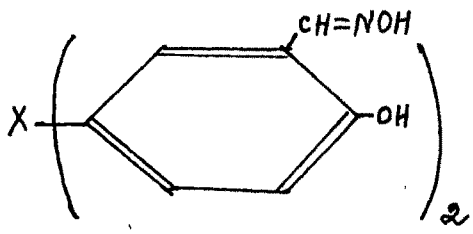
6. Tetradentate ligands containing oximino group (s) and their metal complexes :

Dewar and Talati (206) prepared the complexes of copper,nickel and palladium with the dioxime of 1,5-diacetyl-2,6-dihydroxynaphthalene (XVIII) and studied their conductivity. Mistry (207) prepared and investigated the cobalt chelate polymer of the above ligand.

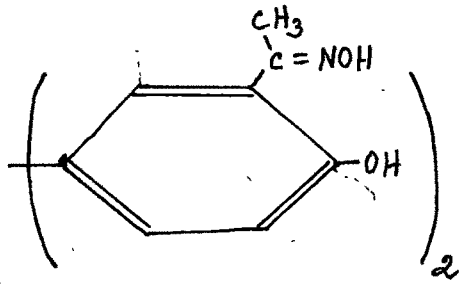
Kapadia (208) studied the chelate polymers of bis (salicylaldoxime) (XIX) . Bhat (209) has investigated the polymeric complexes formed by the dioxime of diacetyl dihydroxy dipheryl (XX)



(XVIII)



(XIX)



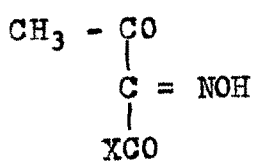
(XX)

7. N-ligands derived from acetoacetic acid derivatives :

(i) vic-oxime ketone: Derivatives of 2,3-dioxobutyric acid-2-oxime :

The derivatives of acetoacetic acid(ester, anilide etc.) were converted into the corresponding derivatives of 2,3-dioxobutyric acid-2-oxime (XXIV) by the action of nitrous acid, its ester or nitrosyl chloride by Meyer (87, 210).

Jowitschitsch (211), Ceresole (88), Wleugel (212), Rodionov et al. (213), Nussberger (214), Adkins and Reeve (215), Pannizzi (216), Euler and Euler (217), Bouvesult and Wahl (218), Wolff (219) and Slater (220), Ajello and Sigille (221), Dorabialska (222).

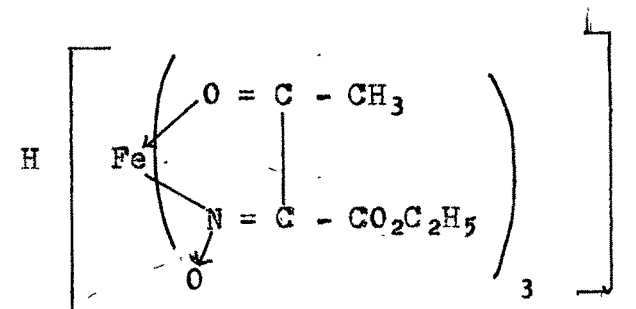


(XXIII)

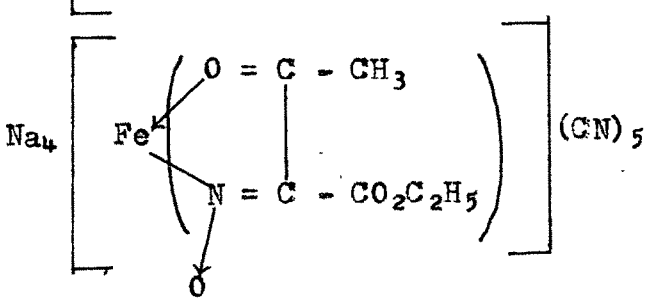
Their ultra-violet absorption spectra were investigated by Naik,Trivedi and Mankad (223) in

aqueous solution and by Talati (224) in aqueous, alcoholic and chloroform solutions. They give characteristic yellow colouration with alkali and intense blue colouration with iron. Boucherle (225) suggested that the reaction can be ultilised for the colorimetric determination of iron (II) at pH 7 to 8. Kuster (226), Taylor and Ewbank (227) and Cambi (228) prepared its complexes with various metals and studied their properties.

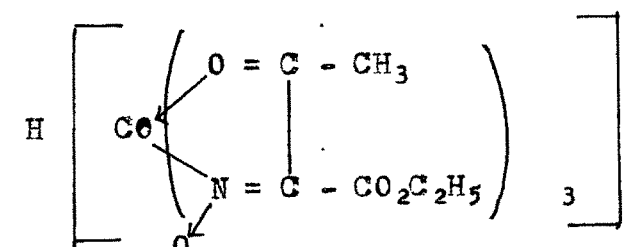
The products isolated by Kuster were (91) formulated as



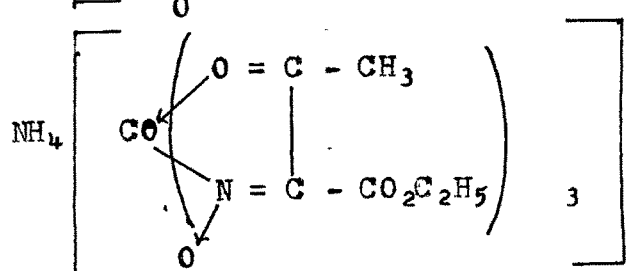
(a)



(b)



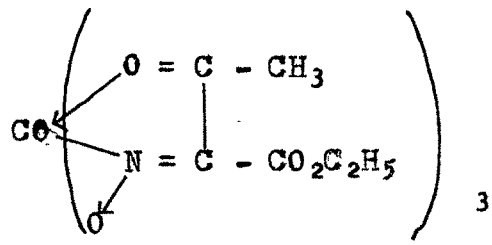
(c)

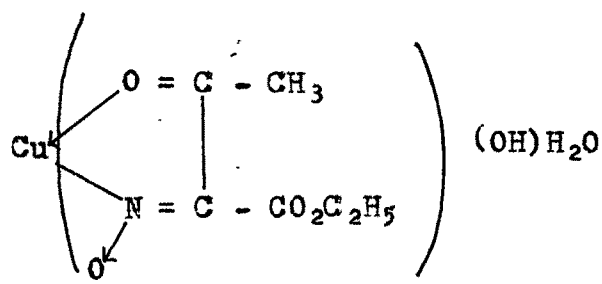


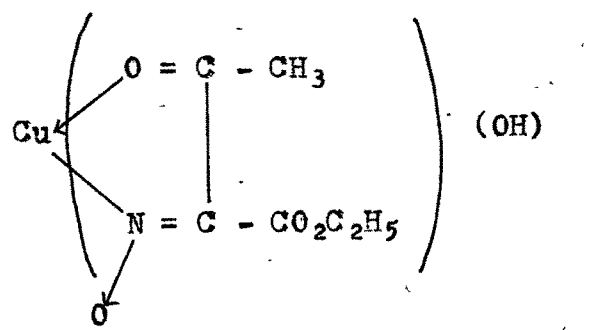
(d)

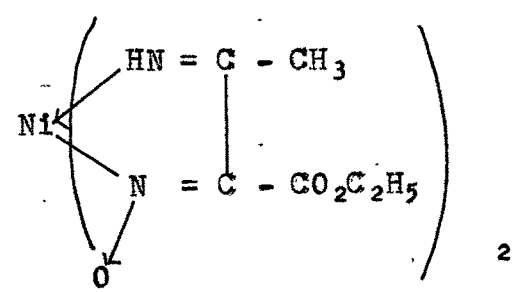
(XXI)

The complexes prepared by Taylor and Ewbank (227) were represented as

(a) 

(b) 

(c) 

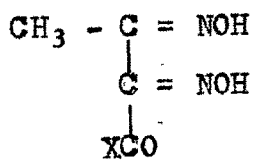
(d) 

(XXII)

(ii) Dioxime : Derivative of 2,3-dioxobutyric acid dioxime :

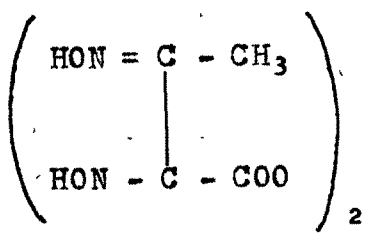
Dioximes of ethyl 2,3-dioxobutyrate and 2,3-dioxobutyranilide were prepared by the action of hydrolxylamine

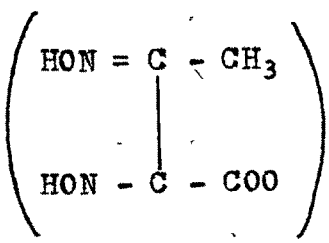
on ethyl 2,3-dioxobutyrate-2-oxime or 2,3-dioxobutyramide-2-oxime by Ceresole and Koeckert (229), Nussberger (214) Rodionov et al. (213), Knorr and Reuter (230) and Talati (231). Their ultra-violet absorption spectra were investigated by Naik, Trivedi and Mankad in aqueous solution (223) and by Talati (214) in aqueous, alcoholic and chloroform solutions.



(XXIV)

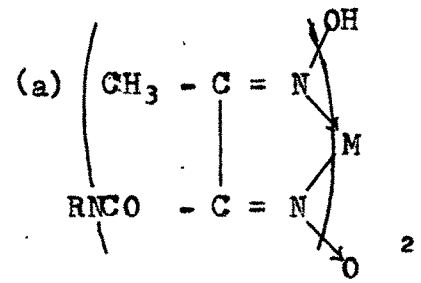
Ceresole and Koeckert (229) prepared barium and silver salts of the dioxime of 2,3-dioxobutyric acid.

(a) 

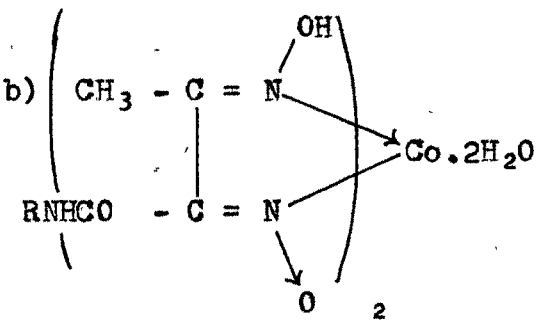
(b) 

(XXX)

Dave and Talati (231) prepared the nickel, Palladium,copper and cobalt complexes which are formulated as



M = Cu, Ni or Pd

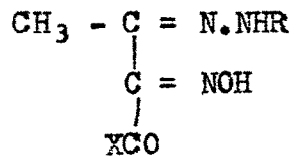


(XXVI)

and investigated their magnetic properties. They (232) also studied some of these dioximes as analytical reagents for the gravimetric estimation of copper,nickel and palladium.

(iii) vic-Oxime hydrazones Derivatives of the hydrazone of 2,3-dioxobutyric acid-2-oxime :

The derivatives of 2,3-dioxobutyric acid-2-oxime (XXIII) were converted into the corresponding hydrazone derivatives of 2,3-dioxobutyric acid-2-oxime by treatment with hydrazine and its derivatives (XXVII) (230).

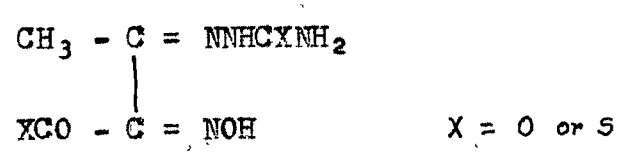


(XXVII)

Desai (233) studied their ultra-violet and infra-red absorption spectra and prepared their complexes with cobalt, nickel and palladium.

(iv) vic-Oxime-semicarbazone :

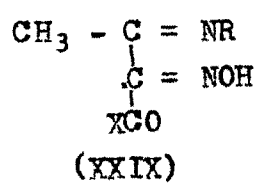
Patel and Mankad (234) prepared semicarbazone and thio semicarbazone derivatives of 2,3-dioxobutyranilide-2-oxime (XXVIII) by treatment with semicarbazide or thiosemicarbazide and their nickel and palladium complexes.



(XXVIII)

(v) vic-Oxime-imines :

Patel and Mankad (235) and Talati and Patel (236) prepared a number of Schiff bases of 2,3-dioxobutyranilide 2-oxime (XXIX). Patel (237) studied their ultraviolet and infra-red absorption spectra and prepared their copper, nickel and iron complexes. Patel and Mankad (235) prepared their palladium complexes.

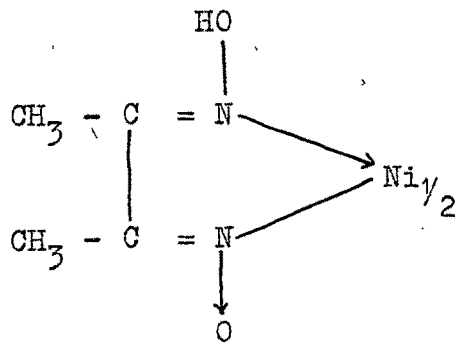


(XXIX)

Kapadia (238) prepared the iron, cobalt, nickel and copper complexes of the 2,3-dioxobutyranilide-2-oxime in presence of various mono-and di-amines.

8. Present work :

Pfeiffer (239) suggested a five membered ring structure for nickel dimethyl glyoximate prepared by Chugaev (164)



-OH of the second oxime group is not involved in the formation of the metal complex. This was demonstrated by the fact that mono O-methyl ether of the Dioxime forms exactly similar compound with nickel (239,240). It was also shown that when one of the oxime groups 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 hydrazone or aryl imine group the metal complexes formed by these reagents would be comparable to those of dioximes.

Considerable work has been carried out in our laboratories on the N-ligands obtained from 2,3-dioxobutyr (aryl) amides. 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 with copper, nickel, cobalt and palladium and studied their properties. Desai (233) prepared the aryl hydrazones of 2,3-dioxobutyr(aryl) amide-2-oxime and prepared their complexes with copper, nickel, cobalt and palladium. Patel (237) prepared aryl imines (Schiff bases) of 2,3-dioxobutyr(aryl)amide-2-oxime and their complexes with copper , nickel, cobalt and iron. Kapadia (238) prepared the semicarbazone and thiosemicarbezone of 2,3-dioxobutyranilide-2-oxime and studied their complexing ability with copper, nickel and cobalt. He also prepared the complexes of copper, nickel and cobalt with 2,3-dioxobutyranilide-2-oxime in presence of p-toluidine, semicarbazide or thio-semicarbazide. All these studies have provided interesting results. The present work is the continuation and extension of these studies.

Early attempt to prepare the transition metal complexes of 2,3-dioxobutyranilide-2-oxime had failed to yield reproducible products. Hence it was considered interesting to find out a suitable method whereby such complexes can be prepared and to extend its applicability to the preparation of complexes of other transitional and non-transitional metals.

Similarly it was believed that complexes of the hydrazone of 2,3-dioxobutyranilide-2-oxime can be prepared with other transitional and non-transitional metals.

Further, the studies on the aryl imines of 2,3-dioxobutyranilide-2-oxime indicated that alkyl or cycloalkyl

imine of 2,3-dioxobutyranilide-2-oxime be prepared and studied. More interesting would it be if bis-bidentate ligands or tridentate ligands of the imine-oxime type could be obtained and studied.

With the above considerations in view, it was proposed

(1) to devise a suitable method or methods for the preparation of the metal complexes of 2,3-dioxobutyranilide-2-oxime with various transitional and non-transitional metals such as copper, nickel, cobalt, iron, manganese, zinc, magnesium, strontium , etc. and to study their magnetic and spectral properties ;

(ii) to prepare the complex of 2,3-dioxobutyranilide-1-[redacted] dioxime with iron and to study its magnetic and spectral properties ;

(iii) to prepare the complexes of the phenyl hydrazone of 2,3-dioxobutyranilide-2-oxime with the metals like barium, aluminium, zinc, etc. ;

(iv) to prepare the complexes of the methyl imine of 2,3-dioxobutyranilide-2-oxime with the metals such as copper, nickel, cobalt, iron, manganese, etc. and to study their magnetic and spectral properties. ;

(v) to prepare the complexes of the cyclohexyl imine of 2,3-dioxobutyranilide-2-oxime with the metals such as copper, nickel, cobalt, iron, etc. 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 the metals such as copper, nickel, cobalt, iron, manganese, zinc, etc. and to study their spectral and magnetic properties. ;

(vii) to prepare the complexes of the tridentate ligand that can be obtained from glycine and 2,3-dioxobutyranilide-2-oxime with copper, nickel, etc. and to study their magnetic and spectral properties and

(viii) to prepare new ligands [redacted] comparable to 2,3-dioxobutyramide-2-oxime.

Investigations carried out as suggested above and results obtained are presented and discussed in the following pages.