Inorganica Chimica Acta, 13 (1975) 91–103
© Elsevier Sequoia S. A., Lausanne – Printed in Switzerland

Review Paper

Oxime and Hydroxylamine Derivatives of Metals and Metalloids

R. C. MEHROTRA, A. K. RAI, A. SINGH and R. BOHRA
Chemical Laboratories, Rajasthan University, Jaipur, India
Received October 1, 1974

Contents

1. Introduction

Diacetyl dioxime (commonly known as dimethylglyoxime) was the first organic reagent to be used in analytical chemistry for estimation of nickel[1]. Since then the analytical applications of a number of bidentate chelating ligands like dioximes, acyloinoximes and aromatic *o*-hydroxy-aldoximes have been developed extensively and apart from analytical applications, studies have centered around their stability data with a variety of metal ions in aqueous medium[2].

Due to the highly hydrolysable nature of E–O–N–bond present in derivatives of simple oximes and substituted hydroxylamines with a number of elements like B, Al, Si, Ge, Sn, Pb, Ti, Zr, V, Nb, Ta, P, As, Sb and Bi, synthesis of such derivatives has been achieved in non-aqueous media, mainly during the last decade (out of the 170 references at the end of this article, more than 150 pertain to post-1960 period). This review would deal particularly with the above derivatives. However, as derivatives of these ligands with organometallic moieties have been reviewed recently[3], these have been omitted from the present article except for brief references. Addition compounds of these ligands prepared in non-aqueous (or even pseudo-aqueous) media are also just mentioned mainly in the preparative section.

2. Methods of Preparations

For brevity various preparations will be presented with minimum of discussion.

A. Addition Complexes

Oximes and hydroxylamines possess two potential donor sites, *i.e.,* nitrogen and oxygen atoms and hence, they are capable of forming adducts with a variety of Lewis acids. Derivatives of metals in their higher valency states tend to be susceptible to hydrolysis, hence, their addition complexes are commonly prepared in non-aqueous media. The reactions employed in the non-aqueous media for the synthesis of oxime and hydroxylamine adducts of halides of boron[4–6], silicon, germanium, tin, titanium[7–10] and phosphorus[11] are summarised below:

$$BF_3\cdot Et_2O + R'R''C{:}NOH \xrightarrow{Et_2O} BF_3\cdot R'R''C{:}NOH \quad \text{Ref. 4}$$

($R'R''C{:}NOH$ = acetoxime, furfuraldoxime, acetaldoxime, cyclohexanone oxime, acetophenone oxime and benzophenone oxime)

$$B_2H_6 + 2\,HONR'R'' \xrightarrow{Et_2O} 2\,HONR'R''\cdot BH_3$$

($R' = H, CH_3$ and $R'' = H, CH_3$) Ref. 5, 6

$$MF_4 + 2\,Me_2C{:}NOH \xrightarrow[\text{THF or dimethoxyethane}]{Et_2O,\ C_6H_6,\ CH_3CN} MF_4\cdot 2\,Me_2C{:}NOH \quad \text{Ref. 7, 8}$$

(M = Si, Ge, Sn and Ti)

$$TiCl_4 + n\,DMGH_2 \xrightarrow[20^\circ C]{CHCl_3 \text{ or Pet. ether}} TiCl_4\cdot n\,DMGH_2 \quad \text{Ref. 9}$$

($DMGH_2$ + dimethylglyoxime; $n = 1$ or 2)

$$MX_4 + n\,BMOH \xrightarrow{CHCl_3 \text{ or } C_6H_6} MX_4\cdot n\,BMOH \quad \text{Ref. 9, 10}$$

(M = Sn and Ti; BMOH = α-benzylmonoxime; X = Cl, Br; $n = 1, 2$)

$$PF_5(gas) + R'R''C{:}NOH \xrightarrow{C_6H_6} PF_5\cdot R'R''C{:}NOH$$

Ref. 11

($R'R''C{:}NOH$ = acetoxime and 2-furfuraldoxime)

Apart from the isolation of adducts in non-aqueous media, metal halide addition complexes of bi- and trivalent metals, which are less susceptible to hydrolysis, have been prepared generally by mixing a salt of the metal with the oxime or hydroxylamine in pseudo-aqueous media; the choice of a water miscible organic solvent is generally based on the solubility of the reactants and the insolubility of the product which facilitates isolation. Ethanol has been used in most of these reactions and the following addition compounds have been synthesised.

$CuX\cdot Me_2C{:}NOH$[12] (X = Cl, Br); $CuCl_2\cdot Me_2C{:}NOH$[12]; $CuCl_2\cdot Ph_2C{:}NOH$[12]; $CuCl_2\cdot 4PrCH{:}NOH$[13]; $CuCl_2\cdot (CH_3)_2CHCH{:}NOH$[12]; $CuCl_2\cdot 4C_6H_5CH{:}CHCH{:}NOH$[12]; $CuCl_2\cdot C_6H_5C(NOH)C(NOH)(C_6H_5)$[12]; $CuCl_2\cdot$2-T-Oxime[19] (2-T-Oxime = 2-Thiophenealdoxime); $CuX_2\cdot 2pa$[27] (pa = pyridine-4-carbaldoxime; X = Cl, Br); $CuCl_2\cdot 2HPPK$[29] (HPPK = *Syn*-phenyl-2-pyridyl ketoxime); $CuCl_2\cdot 2FDH$[28] (FDH = β-furfuraldoxime); $ZnCl_2\cdot$2Oxime[13] (Oxime = propanone oxime, butanone oxime, 2-methyl-3-butanone oximes and 4-heptanone oxime); $ZnCl_2\cdot 2FDH$[28]; $ZnCl_2\cdot 2NH_2OH$[14]; $ZnCl_2\cdot 2MeNHOH$; $ZnCl_2\cdot$(2-T-oxime)[19]; $CdX_2\cdot 2MeNHOH$[15] (X = Cl, I); $CdCl_2\cdot$(2-T-Oxime)[19]; $MCl_3\cdot(3\alpha$-benzoinoxime)[24] (M = Y, La, Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho and Er); $CrCl_3\cdot 3FDH$[28]; $MnCl_2\cdot 2MeNHOH$[15]; $MnCl_2\cdot 4PrCH{:}NOH$[13]; $MnCl_2\cdot 2FDH$[28]; $MnCl_2\cdot 2HPPK$[16]; $FeCl_2\cdot 2FDH$[28]; $FeCl_3\cdot 3FDH$[28]; $FeCl_2\cdot 2pa$[27]; $COBr_2\cdot 4MeCH{:}NOH$[12]; $COCl_2\cdot 4PrCH{:}NOH$[13]; $CoI_2\cdot 2Me_2C{:}NOH$[12]; $CoCl_2\cdot(CH_3)_2CHCH{:}NOH$[12]; $CoX_2\cdot 4\beta$-benzaldoxime[12] (X = Cl, Br); $COCl_2\cdot 4C_6H_5CH{:}CHCH{:}NOH$[12]; $COX_2\cdot 2pa$[27] (X = Cl, Br); $CO(NO_3)_2\cdot 2HPPK$[16]; $COCl_2\cdot$(2-T-Oxime)[19]; $NiX_2\cdot 4MeCH{:}NOH$[12,20] (X = Cl, Br); $NiCl_2\cdot 4PrCH{:}NOH$[13]; $NiX_2\cdot 4(CH_3)_2CHCH{:}NOH$[12] (X = Cl, Br); $NiCl_2\underbrace{(CH_2)(CH_2)_3C}{:}NOH$[20]; $NiI_2\cdot 6NH_2OH$[18]; $NiCl_2\cdot 4NH_2OH$[18]; $NiI_2\cdot 3HPOX\cdot 2H_2O$[17] (HPOX = 2-pyridinaldoxime); $NiCl_2\cdot 2HPOX$[17]; $NiAc_2\cdot 2HPOK$[17]; $NiX_2{:}2pa$[27] (X = Cl, Br); $NiCl_2\cdot H_2DMG$[25] (H_2DMG = Dimethylglyoxime); PdX_22L[21] (L = acetoxime unit; X= Cl, Br); $NiCl_2\cdot 2FDH$[28]; $NiCl_2\cdot$(2-T-Oxime)[19]; $PdCl_2\cdot$(2-T-Oxime)[19]; $PdCl_2\cdot(H_2DMG)$[25]; $Pt(OH)_2\cdot 4NH_2OH$[23]; $PtCl_2\cdot 2NH_2OH$[23]; $PtCl_2\cdot 4NH_2OH$[23] and $PtCl_2\cdot(H_2DMG)$.[25]

B. Substitution Derivatives

(i) Metal–Halogen Bond Cleavage Reactions

Metal–oxygen–nitrogen bonds are frequently established by the reaction between an oxime (hydroxylamine) and anhydrous covalent halides. The driving force for these reactions appears to be the energy gain that accompanies the change from M–X to M–O bond, and these reactions appear to be further facilitated by the removal of the liberated hydrogen halide by a proton acceptor. Quite a large number of oxime and hydroxylamine derivatives of various metals and metalloids have been reported to be synthesised in the presence of a base like pyridine (R_3Si[30–32], RSi[33], As(III)[34], R_2As[34], ROAS[34]) and triethylamine (R_3Si[35–37], R_2Si[37], RSi[37], R_3Ge[36,41], R_2Ge[42,43], Ti(IV)[44], R_2As[40], RAS[38,39], As(III)[46], Sb(III)[47], Nb(V)[48], Ta(V)[49]). Typical reactions of non-alkylated species are given below:

$$MCl_n + x\,HON{:}CR'R'' + x\,Et_3N \rightarrow M(ON{:}CR'R'')_n + n\,Et_3NHCl$$

(n = 4, M = Si, Ge, Ti; n = 3, M = As, Sb; n = 5, M = Nb, Ta)

$$AuCl_3 + HPPK \xrightarrow{\text{hot EtOH}} Au(PPK)Cl_2 + HCl$$

(HPPK = *Syn*-phenyl-2-pyridyl ketoxime[29])

$$O{=}Ti(ClO_4)_2 + 2\,C_{13}H_{12}OC{:}NOH \rightarrow O{=}Ti(C_{14}H_{11}NO_2)_2 + 2\,HClO_4$$

($C_{13}H_{12}OC{:}NOH$ = α-benzoinoxime[26])

In view of experimental convenience, ammonia has also been successfully used as hydrogen chloride acceptor for the synthesis of a variety of germanium derivatives[41,42]. Germanium tetra-oximates are synthesised according to the reaction illustrated below:

$$GeCl_4 + 4\,HON{:}CR'R'' + 4\,NH_3 \xrightarrow[\text{reflux}]{C_6H_6} Ge(ON{:}CR'R'')_4 + 4\,NH_4Cl$$

Trimethylsilyl hydroxylamine was first described in 1963, but the di- and tri- substituted species have been obtained only recently[50–56]. The reaction of Me_3SiCl with excess NH_2OH itself gives only mono-substituted product Me_3SiONH_2 and the first amino hydrogen of this derivative is replaced by trimethylsilyl group by the reaction with excess Me_3SiCl in presence of proton acceptor like Et_3N, but the replacement of second amino hydrogen required prior metallation of $Me_3SiONHSiMe_3$ with BuLi.

(ii) Exchange Reactions

The reactions of metallic salts of oximes (hydroxylamines) with organometal halides, *e.g.*, of Si[56,58,59], Sn[57,64], and simple metal halides, *e.g.*, of B, Si, Ge, P, As, Sb, Bi[60–62] have been employed extensively for the preparation of oxime (hydroxylamine) derivatives:

$$MCl_n + n/2\,Hg[ON(CF_3)_2]_2 \rightarrow M[ON(CF_3)_2]_n + n/2\,HgCl_2$$

As might be expected, the net effect is usually to combine chlorine with the more electropositive element and the organic group with the element of greater electronegativity.

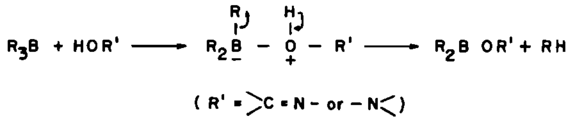
(iii) Metal–Carbon Bond Cleavage Reactions

In these reactions, attempt is made to substitute the organic group in an organometallic compound by an oximate (hydroxylaminate) group. It has been found that the simple metal alkyls, *e.g.*, RM where M = Li[36, 65], R_2M where M = Be[66], Zn[67–69] and R is an alkyl group; Ph_2Zn[69], R_3M (M = Al, Ga, In and Tl)[65, 70], undergo metal–carbon bond cleavage reactions quite readily when the electronegativity difference between the element (*e.g.*, Li, Be, Al, Ga, In and Tl) and carbon is greater than about 0.8 on the Pauling scale. Smaller electronegativity differences correspond to less polar element–carbon bonds and comparatively higher temperatures are needed for completion of the reaction in such case (*e.g.*, R_3B)[65, 70]. Few recent preparations of boron derivatives[71] are shown below:

$$Bu^n_3B + HON{:}\underline{C(CH_2)_4CH_2} \xrightarrow[35^\circ C]{CCl_4} Bu^n_2BON{:}\underline{C(CH_2)_4CH_2} + Bu^nH$$

$$Bu^n_3B + HONEt_2 \xrightarrow[35^\circ C]{CCl_4} Bu^n_2BONEt_2 + Bu^nH$$

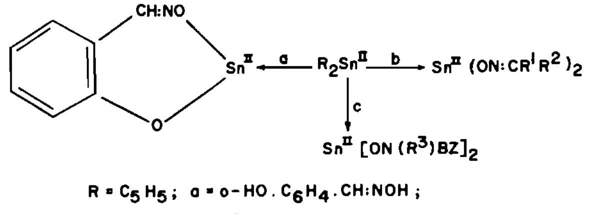
The reactions of oximes and hydroxylamines with trialkylboranes appear to proceed by heterolytic mechanisms[71]. The initial co-ordination between the trialkylborane and the protic reagent labilises the alkyl group attached to boron as a carbanion, at the same time increasing the acidity of the protic hydrogen:



$$R_3B + HOR' \longrightarrow \overset{R}{R_2\underset{-}{B}} - \overset{H}{\underset{+}{O}} - R' \longrightarrow R_2BOR' + RH$$

$$(R' = {>}C{=}N- \text{ or } -N{<})$$

Tin(II) derivatives of oximes and hydroxylamines have been recently prepared[73] in yields greater than 90% by the protolysis of tin(II)–carbon bonds of the cyclopentadienyltin(II) compounds in anhydrous benzene or tetrahydrofuran (THF):



R = C_5H_5; a = o-HO.C_6H_4.CH:NOH;
b = 2(HON:CR^1R^2); c = 2HON(R^3)BZ

(iv) Metal–Hydrogen Bond Cleavage Reactions

In the cases of most of the metals and metalloids the bond with hydrogen is polarised in the sense $^{+\delta}M{-}H^{-\delta}$ and is subsequently likely to break, in the direction $^+M{-}\bar{H}$. This is illustrated in the reaction of metal hydrides with oximes[35, 58, 73] and hydroxylamines[51, 52], where organic group essentially replaces hydride ion.

Interaction of $Hg[ON(CF_3)_2]_2$ with compounds containing M–H bonds[60, 62] afforded compounds of the type $M[ON(CF_3)_2]_n$ (M = Si, Ge and As) along with $(CF_3)_2NOH$ and free mercury:

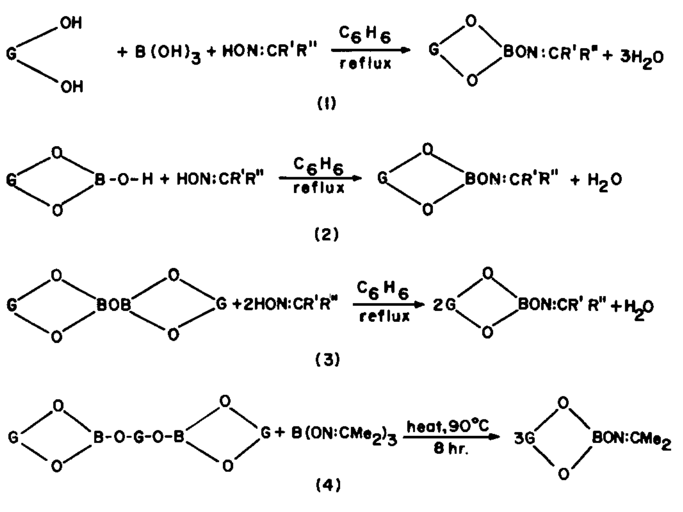
$$M{-}H + Hg[ON(CF_3)_2]_2 \rightarrow M[ON(CF_3)_2] + Hg + (CF_3)_2NOH$$

(v) The reaction of Oximes and Hydroxylamines with Metallic and Organometallic Oxides and Hydroxides

In view of their acidic nature, oximes and hydroxylamines react with basic metallic[59, 74] and organometallic hydroxides or oxides[36, 57, 75–82]. Reaction conditions depend on the basic character of the hydroxide or oxide. For example, silicic acid and alkylsilanols do not appear to react, while less basic derivatives, such as organogermanium oxides[41, 42] require acidic catalysts and continuous fractionation of liberated water azeotropically. Reactions with basic organometallic hydroxides or oxides[36, 57, 75–82] are faster and do not require a catalyst.

Boronic and borinic acids form 1:1 complexes with hydroxylamine[83]. A variety of oximes[84], hydroxylamines[85, 86] and amidoximes[87, 88] have been shown to react with aliphatic and aromatic boronic acids.

Singh and Mehrotra[89] have recently explored different routes for the synthesis of 2-iminoxy-4,4,6-trimethyl-1,3,2-dioxaborinanes. The reactions can be depicted as follows:



(G = -CMe.CH2.CHMe-)

The reactions (1), (2) and (3) proceed slowly to afford the anticipated products in about 40% yields. Reaction (4) yields the product in quantitative yield.

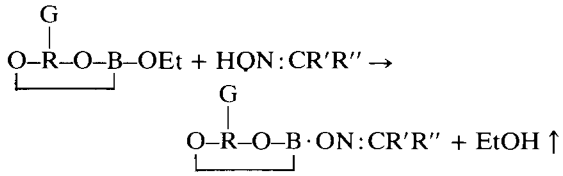
(vi) Alkoxy–iminoxy (or Amino–oxy) Exchange Reactions

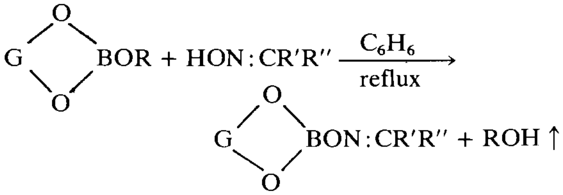
The interchangeability of alkoxy group in an alkoxide with the protic reagents has been found to be facile[90,91]. The reactions are generally carried out in inert solvents like benzene and the liberated alcohol (usually ethanol or isopropanol) is fractionated off azeotropically. Mehrotra and coworkers have employed this technique widely for the preparation of oximates and hydroxylaminates of a number of elements *e.g.*, B[45,92,93], Al[92,94], Si[37], Ge[41,42,45], Sn[36,57,77,82,93], Ti[44,95], Zr[96], As[46], Sb[47,57], V[97], Nb[48], Ta[49]. The reactions are given below:

$$B(OR)_3 + n\,HON{:}CR'R'' \xrightarrow[\text{reflux}]{C_6H_6} B(OR)_{3-n}(ON{:}CR'R'')_n + n\,ROH\uparrow$$

$$B(OR)_3 + n\,HONEt_2 \xrightarrow[\text{reflux}]{C_6H_6} B(OR)_{3-n}(ONEt_2)_n + n\,ROH\uparrow$$

(R = Et or Pr^i)





(G = –CMe$_2$·CH$_2$·CHMe– and –CMe$_2$·CMe$_2$–)

$$M(OR)_n + x\,HON{:}CR'R'' \xrightarrow[\text{reflux}]{C_6H_6} M(OR)_{n-x}(ON{:}CR'R'')_x + x\,ROH\uparrow$$

(n = 3, M = Al, As or Sb; n = 4, M = Si, Ge or Ti; n = 5, M = Nb or Ta; x = 1–4; R = Et or Pr^i)

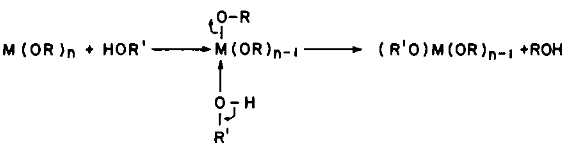
$$M(OR)_n + x\,HONEt_2 \xrightarrow[\text{reflux}]{C_6H_6} M(OR)_{n-x}(ONEt_2)_x + x\,ROH\uparrow$$

(n = 3, M = Al, As or Sb; n = 4, M = Ti; n = 5, M = Nb or Ta; R = Et or Pr^i)

$$Zr(OPr^i)_4Pr^iOH + n\,HON{:}CR'R'' \xrightarrow[\text{reflux}]{C_6H_6} Zr(OPr^i)_{4-n}(ON{:}CR'R'')_n + (n+1)Pr^iOH\uparrow$$

$$O{=}V(OEt)_3 + n\,HON{:}CMe_2 \xrightarrow[\text{reflux}]{PhH} O{=}V(OEt)_{3-n}(ON{:}CMe_2)_n + n\,EtOH\uparrow$$

The reactions may be represented in general, as follows:



$$M(OR)_n + HOR' \longrightarrow \overset{O-R}{\underset{O-H\atop R'}{M(OR)_{n-1}}} \longrightarrow (R'O)M(OR)_{n-1} + ROH$$

(R' = >C:N– , >N–)

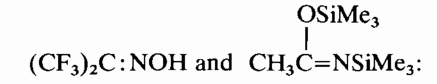
The above transesterification technique in the presence of an azeotrope-forming inert solvent has some unique advantages: a) The possibility of its use in stoichiometric ratios of reactants, leading to substitution products with values of n varying from 1 to x in $M(OR)_{x-n}(ON{:}CR^1R^2)_n$, b) The tendency of cations to catalyse Beckmann rearrangement of the oximes is reduced, *e.g.*, Lewis acids BX_3, SnX_4, TiX_4 are catalysts for the transformation of oximes to amides, whereas their corresponding alkoxides do not possess such activity. Mehrotra and coworkers have noticed the following significant observations during the reactions of metal alkoxides with oximes and hydroxylamines: a) Reactions of ethyl, isopropyl and butyl borates with diethylhydroxylamine are slow in refluxing benzene and only bis- and tris- derivatives could be isolated[92]. b) Reactions of ethyl and isopropyl borates with oximes are sterically controlled[45] and tris- derivatives could be prepared only in cases of acetone oxime and methyl ethyl ketone oxime. The reactions of various oximes with 2-ethoxy-4,4,6-trimethyl-1,3,2-dioxaborinane and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane are controlled[89] by the nature of the solvent, the oxime and the alkoxy group attached to the boron atom. c) Reactions of aluminium isopropoxide with oximes[94] and diethylhydroxylamine[92] are much faster than those of alkyl borates. Two isopropoxy groups are easily replaced; replacement of the third is slower. These observations are in line with those of alcoholysis[98,99] and transesterification reactions[100] of aluminium isopropoxide. d) The reactions of alkoxysilanes with oximes[37] and diethylhydroxylamine[51] are much slower and require a catalyst and an efficient fractionating column for completion of the reaction. Even under these conditions reaction of tetraethoxysilane with acetone oxime yielded only the tri- substituted product[37]. e) In constrast to $Si(OEt)_4$, germanium tetraethoxide reacts readily with acetone oxime[45] giving the tetra-substituted product. f) Reactions of oximes[82] and diethylhydroxylamine[93] with organotin alkoxides are much faster. g) Reactions of transition metal alkoxides, *e.g.*, of Ti[37,95], Zr[96], V[97], Nb[48], Ta[49] with oximes and diethylhydroxylamine are quite facile, so that in case of Ti[95] and V[97] mono- and disubstituted products are isolated even at the room temperature. Ti^{4+} and V^{5+} suffer reduction to lower oxidation states when made to react with aldoximes[43] and acetone oxime[97] respectively in stoichiometric ratios 1:3 or greater. h) Arsenic[46] and antimony ethoxides[47] react quite readily with oximes and diethylhydroxylamine under refluxing conditions.

A number of workers from other laboratories have also employed this method for the synthesis of organotin[36,57] and organoantimony oximates[57].

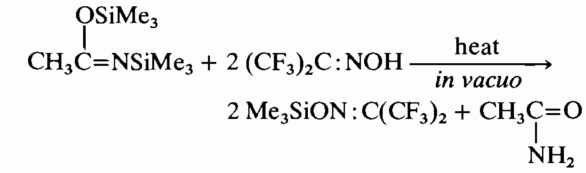
(vii) Metal–Nitrogen Bond Cleavage Reactions

Most of the metal dialkylamides are more reactive towards compounds containing active hydrogen[101]. Aminoboranes[102], aminosilanes[37,58,73,103,104] and aminotin compounds[36] react with oximes and hydroxylamines to yield corresponding oximate (hydroxylaminate) derivatives along with ammonia or amine.

Derivatives of hexafluoroacetone oxime[105] have been recently prepared by heating *in vacuo* a mixture of



$(CF_3)_2C{:}NOH$ and $CH_3\overset{OSiMe_3}{\overset{|}{C}}{=}NSiMe_3$:



$$CH_3\overset{OSiMe_3}{\overset{|}{C}}{=}NSiMe_3 + 2\,(CF_3)_2C{:}NOH \xrightarrow[in\ vacuo]{heat} 2\,Me_3SiON{:}C(CF_3)_2 + CH_3\underset{NH_2}{\underset{|}{C}}{=}O$$

(viii) Miscellaneous Reactions

The highly electronegative free radical bis(trifluoromethyl)nitroxide is capable of abstracting hydrogen from compounds containing metal–hydrogen bonds, and this nitroxide appears to be more reactive than unfluorinated dialkylnitroxides[106,107].

The bis(trifluoromethyl)nitroxide radical displaces[59,63,107] halogen from a number of non-metallic halides *e.g.*, BCl_3, BBr_3, $SiBr_4$, SiI_4, $GeBr_4$, GeI_4, $AsCl_3$, $AsBr_3$, BX_3 (X = Cl, Br), SiX_4 (X = Br, I); GeX_4 (X = Br, I); AsX_3 (X = Cl, Br and I). The reaction with BCl_3 and $AsCl_3$ is assisted by the presence of iodine. PBr_3 and $POBr_3$ are converted to $PO[ON(CF_3)_2]_3$.

$$MX_n + n\,(CF_3)_2NO\cdot \rightarrow M[ON(CF_3)_2]_n + n/2\ X_2$$

With GeH_3Br and GeH_3I only hydrogen is replaced by the radical while with SiH_3Br and SiH_2I_2 both hydrogen and halogen are replaced[63]. CsI and SeO adds trifluoromethylnitroxide radical to form the polyhalide like salt $CsI[ON(CF_3)_2]_2$ and $SeO[ON(CF_3)_2]$ while CoI_2 forms $Co[ON(CF_3)_2]_2$ type of compounds[63].

The reactions of bis(trifluoromethyl)nitroxide with tribromoborane to give bromine and $[(CF_3)_2NO]_3B$ may be an example of S_N2 reaction at boron[107].

$$(CF_3)_2NO\cdot + BBr_3 \rightarrow (CF_3)_2NOBBr_2 + Br\cdot$$

Displacement also occurs when bis(trifluoromethyl)nitroxide reacts with tris(trifluoromethyl)arsine[108–110]

$$(CF_3)_2NO\cdot + As(CF_3)_3 \rightarrow (CF_3)_2NOAs(CF_3)_2 + CF_3\cdot$$

Tris(trifluoromethyl)phosphine and bis(trifluoromethyl)chlorophosphine[108] are converted into P(V) derivatives:

$$2\,(CF_3)_2NO\cdot + P(CF_3)_3 \rightarrow [(CF_3)_2NO]_2P(CF_3)_3$$

$$2\,(CF_3)_2NO\cdot + (CF_3)_2PCl \rightarrow (CF_3)_2PCl[ON(CF_3)_2]_2$$

Bis(trifluoromethyl)nitroxide reacts slowly at room temperature with various metals and metalloids to afford crystalline products[111–113]:

$$M + n\,(CF_3)_2NO\cdot \rightarrow M[ON(CF_3)]_n$$

(M = Pb, Sn, n = 2; M = As, n = 3; M = Se and Te, n = 4).

Tin nitrosodicyanomethanides[114] have been obtained by the interaction of organotin chloride with silver nitrosodicyanomethanide.

The reaction of triethylphosphite with several representative halonitroparaffins has been studied[118] and the reaction is shown to proceed according to the following equation:

$$R'R''XCNO_2 + 2\,(R''O)_3P \rightarrow RR'C{:}NOP(O)(OR'')_2(R''O)_3PO + R''X$$

(Ia, R = R′ = Cl; R″ = Et
Ib, R = R″ = Me; R″ = Et; X = Cl or Br)

(ix) Ortho-Metalation Reactions

Aromatic oximes have been reported to react with lithium tetrachloropalladate(II) to form di-μ-chloro-bis(2,N-*dihapto*-aromatic oxime)dipalladium(II)[115].

Treatment of $RhCl_3 \cdot 3H_2O$ with aromatic oximes and excess sodium chloride or bromide afforded five membered chelate rings[116].

3. Properties

A. Volatility

Oximates and hydroxylaminates of Be, Zn, B, Al, Si, Ge, Sn, Pb, Ti, Zr, P, As, Sb, Bi, Nb and Ta, described in this review, are generally white solids or colourless liquids, highly susceptible to hydrolysis even by atmospheric moisture and are soluble (except some of the aldoximates which are reported to be sparingly soluble) in all common organic solvents.

Oximates of a number of metals (*e.g., Be, Zn, B, Al, Ti, Zr, Nb and Ta) are reported to be non-volatile even under reduced pressure, whereas similar derivatives of a number of less electropositive elements (e.g.,* Si, Ge, As and Sb) are volatile. Compared to oximates, hydroxylaminates generally show greater volatility and derivatives of B, Si, Ge, As and Sb as well as of Ti, Nb and Ta can be distilled under reduced pressure.

B. Molecular Complexity

Ketoximates have been shown to be generally monomeric in boiling benzene with some tendency of dimerisation whereas aldoximate derivatives show tendency of higher association depending upon the nature of ligand. With the same oxime ligand, the molecular complexity appears to be governed by the atomic size of the central metal atom. For example, a comparison of molecular complexity of zirconium and titanium oximates shows the following three prominent features: a) Molecular complexity of zirconium oximates is greater than that of titanium oximates. b) The molecular complexity is affected by the chain length and ramification in zirconium series whereas no such effect was observed in titanium series, in which case even the least remified oxime gives only a monomeric derivative due to the smaller size of titanium. c) Same alkyl groups when attached to the imino carbon atom offer more shielding effect than when attached to the carbinol carbon atom.

Molecular complexities of hydroxylaminates and alkoxide hydroxylaminates of B, Al and Ti are reported to be of the order of 1.0, 2.0–2.5 and 1.0 to 1.5 respectively. Similar derivatives of As, Sb, Nb and Ta are monomeric in boiling benzene.

The addition complexes like MX_nL (where M = Cu, Ni, Co, Fe, Pt, Pd and Au; X = halogen and L = oxime) are found to be polymeric in nature.

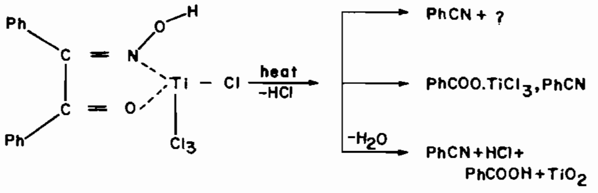
C. Thermal Stability

The majority of oxime derivatives are thermally stable and some of these can be distilled under reduced pressure. Compared to these, the addition complexes[70] obtained by the interaction of metal halides like $TiCl_4$ and $PtCl_2$ with oximes are thermally unstable and undergo decomposition with the formation of substituted derivatives. For example:

$$TiCl_4 \cdot 2BMOH \cdot 0 \cdot 5CHCl_3 \xrightarrow{\text{slow heat}} TiCl_3 \cdot BMO \cdot BMOH + HCl + 0.5\ CHCl_3$$

(BMOH = α-Benzylmonoxime)

On heating to a higher temperature, the above oxime derivative decomposes with the formation of phenyl cyanide; the following mechanism was suggested by Charalambous and Frager[9] for this decomposition:



The formation of phenyl cyanide during decomposition of titanium oximates has been observed by Mehrotra and coworkers[44] also.

Raluca *et al.*[117] studied the thermal decomposition of *cis* and *trans* forms of $[Pt(AOX)_2Cl_2]$ (where, AOX = $Ac_2C{:}NOH$) by DTA and TGA. These workers observed that the *trans* form is more stable than the *cis* form. Further $[Pt(AOX)_3Cl]Cl$ was converted by heating into the more stable *trans* form $[Pt(AOX)_3Cl_2]$.

Oxime esters of pentavalent phosphorous acids[118], $RR'C{:}NOP(O)(OR'')_2$ (where R = R' = Cl, Me, H and R'' = Et) on heating undergo Beckmann rearrangement accompanied by decomposition giving some tarry matter from which no pure product could be isolated. The presence of hydrogen at the α-carbon atom[119] lends thermal instability to the oxime derivatives. For example, acetaldoximate[94] derivatives have been found to undergo violent decomposition even when heated under continuous vacuum suction with the formation of corresponding hydrated metal oxide and cyanides:

$$Al(ON{:}CHR)_3 \xrightarrow{200°\,C} Al(OH)_3 + 3\,RC{\equiv}N$$
$$\downarrow$$
$$1/2\ Al_2O_3 \cdot xH_2O$$

$B(OPr^i)(ON{:}CMe_2)_2$ undergoes disproportionation on heating even under reduced pressure[45]:

$$3\,(Pr^iO)B(ON{:}CMe_2)_2 \rightarrow B(OPr^i)_3 + 2\,B(ON{:}CMe_2)_3$$

Emeleus and coworkers[120] reported a quantitative recovery of bis(bis-trifluoromethyl)nitroxide radical without dimer formation on heating $Hg[ON(CF_3)_3]$ at 100° C under vacuum.

Parry and coworkers[5,6] reported the thermal decomposition of the compounds, $CH_3ONH_2BH_3$, $(CH_3O)NHCH_3BH_3$ and $(CH_3O)N(CH_3)_2BH_3$, by heating under controlled conditions:

$$3\,(CH_3O)NH_2BH_3 \xrightarrow[\text{several hr}]{55°} H_3NB(OCH_3)_3 + 2/x\,(C_{1.5-x}NBH_{1.5-x})_x + (3+2x)\,H_2$$

$$3\,(CH_3O)NCH_3H \cdot BH_3 \xrightarrow[\text{several hr}]{65°} (CH_3)_2HNB(OCH_3)_3 + 1/x\,(HNBH)_n + 1/3\,(HCH_3NBH_2)_3 + 3\,H_2$$

$$3\,(CH_3O)N(CH_3)_2BH_3 \rightarrow (CH_3)_2HNB(OCH_3)_3 + 2/x\,[(CH_3)_2NBH_2]_x + 2\,H_2$$

Although all the products mentioned in above equations are generally volatile, but only hydrogen and trimethoxyborane could be isolated in quantitative yields.

D. Reactions with Protic Reagents

(i) Reaction with water

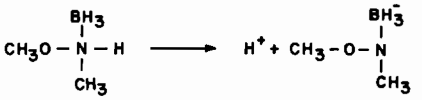
Oxime derivatives of weakly electropositive elements like boron, silicon and arsenic are highly susceptible to hydrolysis in general. On slight exposure, they regenerate the parent ligand[45,70,121]:

$$M(ON{:}CMe_2)_n + n\,H_2O \rightarrow M(OH)_3 + n\,Me_2C{:}NOH$$

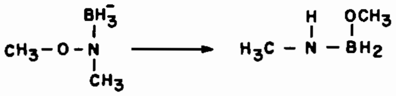
$$(n = 3, M = B \text{ or } As;\ n = 4, M = Si)$$

The hydrolysis tendency appears to decrease with increasing chain length and ramification of the alkyl groups in the parent oxime. The aromatic bidentate oxime derivatives are comparatively more stable to hydrolysis due to their chelated character[45]. On drastic hydrolysis some acetoximate derivatives yield acetone[70] instead of acetoxime.

Hydrolysis of the derivatives $(CH_3O)NH_2BH_3$, $(CH_3O)NCH_3HBH_3$ and $(CH_3O)N(CH_3)_2BH_3$ by 50% KOH[5,6] show that the hydrogen attached to the nitrogen plays a dominant role in group transfer. In case of the first two derivatives, the methoxy group attached to nitrogen is replaced by the hydrogen attached to boron, *e.g.*:



The anion rearranges as :



However, in case of $(CH_3O)N(CH_3)_2BH_3$, free base is liberated on hydrolysis; BH_3 formed simultaneously gives free hydrogen and borates.

(ii) Reactions with Alcohols and Glycols

The mixed alkoxide oximate or diethylhydroxylaminate derivatives (generally ethoxide or isopropoxide[44–49,92,93] on treatment with primary, secondary and tertiary butanols yield corresponding butoxide oximate or diethylhydroxylaminate derivatives with the liberation of ethanol or isopropanol:

$$M(OEt)_{n-x}(ON{:}CR'R'')_x + R'OH\ (\text{excess}) \rightarrow M(OR)_{n-x}(ON{:}CR'R'')_x + (n-x)\ EtOH\uparrow$$

$$M(OPr^i)_{n-x}(ONEt_2)_x + R'OH\ (\text{excess}) \rightarrow M(OR')_{n-x}(ONEt_2)_x + (n-x)\ Pr^iOH\uparrow$$

(M = B, Al, Ti, Zr, Si, Ge, Nb, Ta, As and Sb
R'OH = Primary, secondary and tertiary butanol
n = 3, 4 and 5, x = 2, 3 and 4 respectively)

Similar reactions have been reported with $R_xM(OEt)_y(ON{:}CR'R'')_{4-(x+y)}$ derivatives[3,45] also, where M = Si, Ge and Sn and R = alkyl or aryl.

Mixed alkoxide acetoximates[45] have been shown to react with glycols as shown below:

$$Ti(OPr^i)_2(ON{:}CMe_2)_2 + HO(CH_2)_2OH \xrightarrow[\text{reflux}]{\text{Benzene}} \underline{O(CH_2)_2O{-}T}i(ON{:}CMe_2)_2 + 2\,Pr^iOH$$

The derivative was reported to be dimeric in boiling benzene and undergoes decomposition on heating even under vacuum.

(iii) Reactions with Acetylacetone and Hydrogen chloride

$Ti(OPr^i)_2(ON{:}CMe_2)_2$ on treatment with acetylacetone[44] reacts as follows:

$$Ti(OPr^i)_2(ON{:}CMe_2)_2 + n\,acacH \rightarrow Ti(OPr^i)_{2-n}(acac)_n(ON{:}CMe_2) + n\,Pr^iOH$$

$$(n = 1, 2)$$

These derivatives are reported to be monomeric in nature and undergo decomposition on attempted distillation[44].

Emeleus and coworkers[62] reported the formation of $AsCl_3$ by the reaction:

$$As[ON(CF_3)_2]_3 + 3\,HCl \rightarrow AsCl_3 + 3\,(CF_3)_2NOH$$

Organometallic oxime derivatives also behave similarly on treatment with anhydrous hydrogen chloride[36] and form corresponding organometallic chloride and parent oxime.

(iv) Reactions with Acetyl chloride

Titanium tetraacetoximate on treatment with acetyl chloride gives corresponding chloride oximates[45]:

$$Ti(ON{:}CMe_2)_4 + CH_3COCl \xrightarrow{\text{Room temp.}} ClTi(ON{:}CMe_2)_3 + Me_2C{:}NOCOCH_3$$

$$Ti(ON{:}CMe_2)_4 + 2\,CH_3COCl \xrightarrow{80^\circ C} Cl_2Ti(ON{:}CMe_2)_2\cdot 2Me_2C{:}NOCOCH_3$$

$$Ti(ON{:}CMe_2)_4 + 3\,CH_3COCl \xrightarrow{\text{reflux}} Cl_3Ti(ON{:}CMe_2)\cdot 2Me_2C{:}NOCOCH_3 + Me_2C{:}NOCOCH_3$$

Similarly, $Sb(ON{:}CMe_2)_3$ gives $ClSb(ON{:}CMe_2)_2$ and $Cl_2Sb(ON{:}CMe_2)\cdot Me_2C{:}NOCOCH_3$ on reacting with acetyl chloride[47].

These chloro-derivatives are reported to be coloured in nature and undergo decomposition on heating.

Mercuric bis(trifluoromethyl)nitroxide reacts with acetyl chloride[120] giving mercuric chloride:

$$Hg[ON(CF_3)_2]_2 + 2\,CH_2COCl \rightarrow HgCl_2 + 2\,(CF_3)_2NOCOCH_3$$

Organometallic oximate derivatives react similarly when treated with acetyl[3,38,41,58] and benzoyl chlorides[122].

(v) Reactions with Acetic Anhydride

Acetic anhydride reacts with $Bu_3GeON:CR'R''$ ($R'R''$ = Me, Me; Me, Et) giving the corresponding acetates[41]:

$$Bu_3GeON:CR'R'' + (CH_3CO)_2O \rightarrow Bu_3GeOOCCH_3 + R'R''C:NOCOCH_3$$

The *o*-acyl oxime ester produced in the reaction was fractionated out and a pure acetate derivative was extracted. No such reaction was reported with any other oxime derivative.

(vi) Oximolysis of lower Oxime Derivatives

The replacement of lower oximes with higher oximes similar to that of alcohol interchange reactions described in case of many metal alkoxides[91] are reported with $Bu_3GeON:CR'R''$[41]:

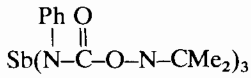
$$Bu_3GeON:CR'R'' + Me(n\text{-}C_5H_{11})C:NOH \xrightarrow{200°C} Bu_3GeON:CMe(n\text{-}C_5H_{11}) + R'R''C:NOH$$

No such reaction has been reported with oxime or diethylhydroxylamine derivatives of other metals and metalloids.

(vii) Insertion Reactions

$Sb(ON:CMe_2)_3$ undergoes insertion reactions when mixed with PhNCO in 1:3 molar ratios[47]:

$$Sb(ON:CMe_2) + 3\,PhN{=}C{=}O \rightarrow$$



$$Sb(\overset{\overset{Ph}{|}}{N}-\overset{\overset{O}{\|}}{C}-O-N{-}CMe_2)_3$$

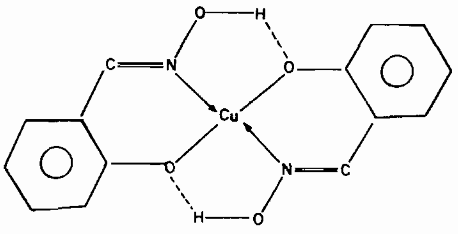
Similar insertion reactions of organometallic tin oximates[36,123] have also been studied in detail with CCl_3CHO, CBr_3CHO, PhNCO, MeNCO, EtNCO and PhNCS.

E. Structures

Structural aspects of oximates and hydroxylaminates of the elements described in this review have received little attention and have been studied mainly by their i.r. spectra. Structures of a few oxime chelates have been elucidated by i.r., n.m.r., X-ray and magnetic measurements and these are included below being of relevant interest for future investigations. Structure of hydroxylaminate derivatives have received even lesser attention and a brief account of these is presented at the end of this section.

The bis(dimethylglyoximate) chelates of a few divalent latter transition metals, *e.g.*, Ni(II), CO(II), Cu(II), Pt(II) and Pd(II) had been shown to be square planar by X-ray diffraction[124–129], i.r. spectrometry[130–134] and magnetic measurements[135–139]. The presence of stable hydrogen bridges and metal *dπ–pπ* (oxime) bonding in these complexes has been postulated[140–143].

Cox[144] proposed a square planar structure of nickel salicyldoximate in solid state by X-ray measurements. A similar structure was confirmed by Lingafelter and coworkers[145,146] for the copper salicyldoximate derivative[147], in which the square planar units are, linked through two longer Cu–O bonds:

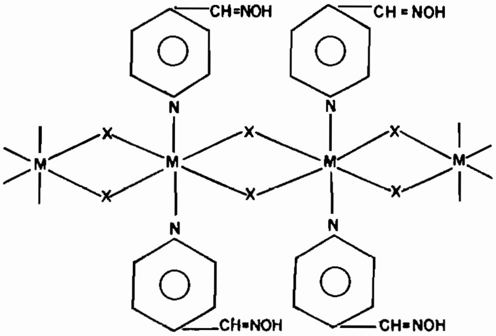


Coakley and Casey[19] synthesised the metal chelates of 2-thiophene aldoxime with metal (*e.g.*, Zn, Cd, Co, Ni, Cu and Pd) halides and had reported the formation of 2:1 chelates, $MCl_2(2\text{-oxime})$. Magnetic, i.r. and physico-chemical studies reveal an octahedral configuration for Zn, Cd, Ni and Co chelates and a tetragonal configuration for the Cu chelate.

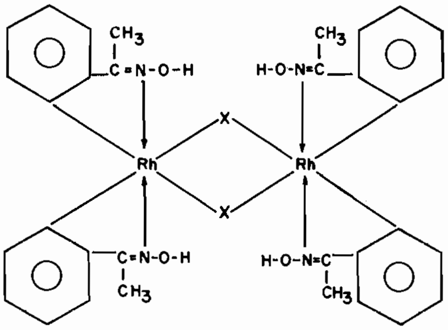
Ward and coworkers[148] reported the synthesis of complexes of nickel halides and nitrate with *Syn*-phenyl-2-pyridyl ketoxime whereas Sen and Malone[16,29] synthesised various complexes with metals (*e.g.*, Ni, Co, Mn, Pd, Pt, Cu, Ag and As *etc.*) using the above ligand. Spectral and magnetic studies lead to octahedral geometry for Co(II), Co(III), Ni(II) and Mn(II) complexes, linear for $[Ag(HPPK)_2]NO_3$ and square planar for $Pd(PPK)_2$ and $Au(PPK)Cl_2$ complexes. The electronic spectrum of [Pd(HPPK)(PPK)] Cl bears striking resemblance to the spectrum of square planar $[PdCl_4]^{-2}$ ion. All the addition complexes show strong hydrogen bonding tendency via the oxime proton and the benzene π-electron cloud.

Electronic spectra, i.r. spectra, magnetic measurements, conductivity and molecular weight studies of some furfuraldoxime complexes[28] with metals such as Cr(III), Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) show their octahedral geometry. The ligand functions as a bidentate ligand in all above complexes except in $[Cr(FDH)_3Cl_3]$ and $[Fe(FDH)_3Cl_3]$ where it functions as a monodentate ligand.

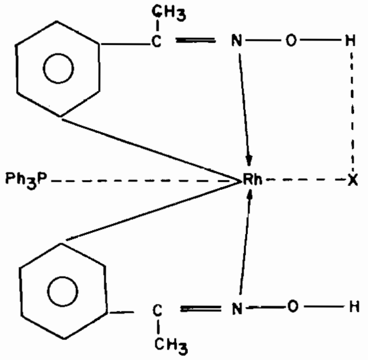
Pyridine-4-carbaldehyde oxime complexes[27], MPa_2X_2 [where M = Co(II), Ni(II) or Cu(II), Pa = oxime and X = Cl, Br] and $[FePa_2Cl_2]$ are shown to be polymeric in nature and possess a pseudo-octahedral geometry on the basis of i.r., diffuse reflectance spectra and magnetic moment studies. The ligand coordinates through the pyridine N-atom and shows no coordination *via* the oxime group N. The far i.r. spectral studies indicate the presence of only bridging halogen atoms:



Acetophenone oxime undergoes *o*-metalation reaction and forms complexes with rhodium(I) and (III)[116]. The dimeric nature and absorption in the region 3340–3300 cm^{-1} corresponding to νOH in solid as well as in solution indicate intramolecular hydrogen bonding and bridging through the atoms:



The halobridged complexes give addition compounds on treatment with triphenylphosphine. The i.r. studies in solid state reveal the presence of free as well as intramolecular bonded –OH groups in the molecule:



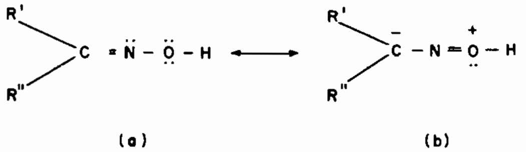
In solution, however, the complex appears to be partially dissociated into triphenylphosphine and the original halo-bridged dimer[116].

Spectroscopic and analytical studies of metal complexes[149–152] formed by the interaction of metals (*e.g.*, rare earths, Cu, Ni, Co, Pd and Pt *etc.*) and benzoin-α-oxime reveal the attachment of two molecules of the ligand by one principal valency and one coordinate link or by two coordinate links depending upon the nature of metal ions.

The reaction of benzoin-α-oxime with titanyl perchlorate in pseudo non-aqueous media reveals not only the loss of two perchlorate ions but also of π bonded oxygen atom[26]. The molecular weight, i.r. and p.m.r. studies show the involvement of the two hydroxy groups in the complex formation and not the C=N group. The presence of only Ti–O absorption bands in the complex and its dimeric nature confirm the bonding of oxygen atoms of the ligand to two titanium moieties.

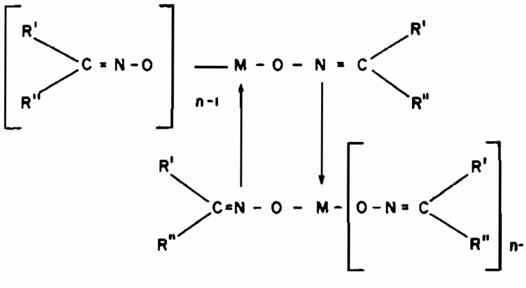
The i.r. studies of metal complexes[153–156] formed by interaction with hydroxyketoximes show the replacement of phenolic hydrogen by the metal ion and a lowering of C=N stretching frequency. The lowering in the C=N frequency leads to the inference that the metal is coordinated to the nitrogen of the oxime group. The observation of a band near 3260 cm^{-1} was attributed to intramolecular hydrogen bonding[155].

It might be mentioned that studies on oximes themselves have revealed the stabilisation of C=N bond by resonance[74, 157, 158] with the non-bonding electron pair on the oxygen atom of the hydroxy imino group:



The removal of hydrogen by some more electropositive elements like Al, As, Sb, Ti, Zr, Nb and Ta *etc.* may favour structure (b) resulting in the decrease of C=N stretching frequency due to partial attainment of single bond character. Alternatively, this type of lowering may also be ascribed to the mass effect[36].

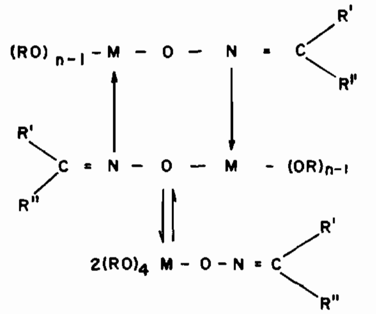
The appearance of two C=N stretching bands, one in the 1660–1630 cm^{-1} region and the other in the 1630–1600 cm^{-1} region in the case of oxime derivatives of B, Al, As, Sb, Ti, Si, Ge, Nb and Ta in comparison to the one observed near 1668 cm^{-1} in parent oximes is attributed to the probable association through MON–MON type bonding:



Where n = 3, 4 and 5

The monomeric nature of such derivatives in boiling organic solvents indicates the weak nature of these bridges. The appearance of these two bands for C=N stretching vibration may also be due to stereochemistry of the complex molecule in which the ligand exists in two different environments[121].

The appearance of two C=N stretching bands even in $(RO)_{n-1}$ M(ON:CR'R'') derivatives was explained on the assumption of a dynamic equilibrium between a bridged and a non-bridged species[121]:



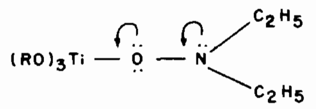
These derivatives are reported to be monomeric in nature in boiling organic solvents.

I.r. spectra (4000–400 cm^{-1}) of hydroxylamine complexes of Co, Ni and Pt having formula $[Co(NH_2OH)_6]Cl$, $[Co(en)_2(NH_2OH)Cl]Cl_2$, $[Ni(NH_2OH)_4]Cl_2$, $[Ni(NH_2OD)_4]Cl_2$, $[Ni(NH_2OH)_4]I_2$, $Pt(NH_2OH)_2Cl_2$ and $Pt(NH_2OD)_2Cl_2$ have been studied by Khoritonov and coworkers[159]. The spectra of cobalt and nickel are found to be similar to that of *trans* platinum complexes indicating bonding through nitrogen atom. The difference in the spectra of chlorine and iodine complexes was attributed to the difference in the crystal structure and nature of hydrogen bonding. Mitkinova and coworkers[160] assigned the important absorption bands of $[Pt(NH_2OH)_4]Cl_2$, $[Pt(NH_2OMe)_4]Cl_2$, $[Pt(ND_2OD)_4]Cl_2$ and $[Pt(ND_2OMe)_4]Cl_2$ complexes.

Kharitonov and coworkers[161] have attempted to interpret the i.r. spectra of *trans*-dihydroxylamine dichloride, *trans*-$[Pt(NH_2OH)_2Cl_2]$, by assuming the coordination of NH_2OH molecule by the nitrogen atom. Attempts have been made to calculate the possible absorption frequencies for the *trans*, *gauche* and *cis* forms of $Pt(NH_2OH)_2Cl_2$ and $Pt(ND_2OD)_2Cl_2$ models but no definite conclusions could be achieved.

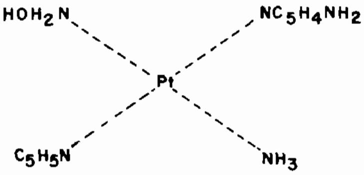
The structures of various organotin hydroxylamine derivatives are discussed and postulated on the basis of i.r., n.m.r., mass spectra and Moessbauer studies[162].

I.r. study of $Ti[ON(C_2H_5)_2]_4$ and $Ti(OR)_{4-n}[ON(C_2H_5)_2]_n$ derivatives[93] show a shifting of Ti–O and N–O stretching frequencies towards the higher side. This shifting was explained on the assumption of interaction between oxygen and titanium which may drift the electron density from nitrogen to oxygen. The possible electronic change was depicted as follows:



Similar shifts[92] observed in B and Al analogs were explained by considering the probability of delocalisation of π electrons over three atoms, *i.e.*, metal, nitrogen and oxygen.

Goremykin reported[163] a platinum complex with all four coordinating groups different, and out of three possible isomers of the complex only the one depicted below could be isolated;



A series of other platinum complexes[163] of the type *cis*-$[Pt(NH_2OH)(NH_3)_2]Cl_2$, $[Pt(NH_2OH)(NH_3)Cl_2]$, $[Pt(NH_2OH)(NH_3)(Py)Cl]$, $[Pt(NH_2OH)(NH_3)(Py)(NH_2Py)]PtCl_4$ and *trans*-$[Pt(NH_2OH)_2I_2]$ were also synthesised. Their probable structures have been assigned qualitatively on the basis of their physicochemical properties.

The observance of the shift of C=O stretching frequency to the lower side and of NO frequency in NOH to higher side by Shevchenko and coworkers[164] in the complexes of the type $TiOFn_2$, $TiOBn_2$, $NbOFn_2Cl$ and WO_2FnCl (where Fn and Bn are furoyl and benzoylphenylhydroxylamine ions), indicate the replacement of H from NOH group and the coordination of C=O to the metal. The existence of M–O–M type chain structure in these derivatives has also been indicated.

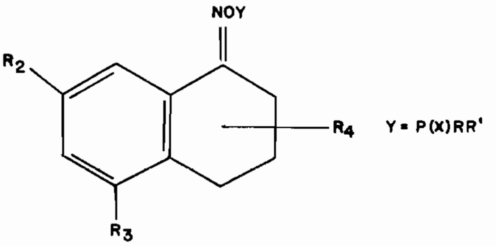
4. Uses

Compounds having general formula $R_nSn(ON{:}CR'R'')_{4-n}$, where R is an organic group, R' an organic group or hydrogen and R'' a tertiary amine substituted aromatic and aliphatic group or pyridine are reported to be active[77,80] against a variety of parasitic and saprophytic fungi, yeast and bacteria. These are reported to be non toxic and may be used as seed dressing agents, for protection of banana fruit stems, leather and synthetic resins against fungi and bacteria. These may be combined with any plant protecting agents, preservatives and fertilizers *etc.* Some of the organotin oximes[78–79] are shown to be useful as insecticides, disinfectants and postemergent herbicides. Pande[165] has reported the use of some metal oximes, $(OPr^i)_nM(ON{:}CMe_2)_n$ (where M = Al or Ti) as polymer catalysts and as end blockers in silicone chemistry. Oxime complexes of palladium have been employed as catalysts, in the manufacture of vinyl acetate[166].

Lead tetraacetate oxime intermediate complexes[167] have been extensively employed for the conversion of keto- and aldooximes to the respective nitro-derivatives.

The addition complexes of PF_5 with certain substituted oximes[168] are reported to be effective herbicides and can be used in a variety of ways at various concentrations as pre- or post-emergence herbicides.

Phosphorous acid derivatives[169] having the general composition



(where X = O or S; R = OMe, OEt or Me; R′ = OMe, OEt, or NMe_2; R_2 = H, F, Me or Me_3C; R_3 = H or Cl; R_4 = H, 2- or 3-Me) are reported to be active as insecticides, acoricides and nemotocides. Oximatosilanes[170] have been found to be useful as vulcanizing agents for silicon rubber.

5. References

1 L. Tschugaeft, *Z. Anorg. Allgem. Chem., 46,* 144 (1905); *Ber., 41,* 2219 (1908).

2 H. Diehl, "The Application of the Dioximes to Analytical Chemistry", The G. Fredrick Smith Chemical Co., Columbus, Ohio (1940); Van Nostrand, New York (1947); C.V. Banks, "Analytical Chemistry", Elsevier, Amsterdam (1963).

3 A. Singh, V.D. Gupta, G. Srivastava and R.C. Mehrotra, *J. Organometal. Chem. Rev., 64,* 145 (1974).

4 H.J. Beck, K. Schmidt and G. Weigel, *German Patent,* 1, 169, 922 (1964); *C.A., 61,* 4274 (1964).

5 T.C. Bissot, D.H. Campbell and R.W. Parry, *J. Am. Chem. Soc., 80,* 1868 (1958).

6 D.H. Campbell, T.C. Bissot and R.W. Parry, *J. Am. Chem. Soc., 80,* 1549 (1958).

7 E.L. Muetterties, *J. Am. Chem. Soc., 82,* 1082 (1960).

8 R. Feld, Unpublished work [*cf.* R. Feld and P.L. Cowe, "The Organotin Chemistry of Titanium", Butterworths, London, 125 (1965)].

9 J. Charalambous and M.J. Frazer, *J. Chem. Soc. A,* 2361 (1968).

10 K.M. Ali, J. Charalambous and M.J. Frazer, *J. Chem. Soc. Dalton,* 206 (1972).

11 M.E. Brokke and G.E. Lukes, *U.S. Patent,* 3, 375, 278 (1968); *C.A., 68,* 113551C (1968).

12 W. Hieber and F. Lentert, *Ber., 60B,* 2296 (1927); *60B,* 2310 (1927).

13 P. Billon, *Compt. Rend., 182,* 584 (1926); *Ann. Chim., 7,* 314 (1927); M. Masni and K. Hotta, *Chem. Pharm. Bull. (Tokyo), 12,* 564 (1964); *C.A., 61,* 39010 (1964).

14 J.E. Walker and D.M. Howell, *Inorg. Syn., 9,* 2 (1967).

15 M.A. Sarukhanov, S.S. Val'dman, N.A. Parpiev, *Zh. Neorg. Khim., 18,* 838 (1973); *C.A., 78,* 131508e (1973).

16 B. Sen and D. Malone, *J. Inorg. Nucl. Chem., 34,* 3509 (1972).

17 R.A. Krause and D.H. Busch, *J. Am. Chem. Soc., 82,* 4830 (1960).

18 A.V. Babaeva and I.E. Buklov, *Obshchei i Neorg. Khim. Akad. Nauk. SSSR, 31,* 67 (1955); *C.A., 50,* 15319d (1956).

19 M.P. Coakley and M.E. Casey, *J. Inorg. Nucl. Chem., 34,* 1937 (1972).

20 M.E. Stone and K.E. Johnson, *Can. J. Chem., 51,* 1260 (1973).

21 A.V. Babaeva, M.A. Mosyagina and S.S. Dyndina, *Dokl. Akad. Nauk. SSSR, 89,* 467 (1953).

22 A.V. Babaeva, M.A. Mosyagina and M.A. Shinkina, *Inst. Obshcheii Neorg. Khim., 26,* 48 (1951); *C.A., 49,* 10790e (1955).

23 A.I. Stetsenko, *Zhur. Neorg. Khim., 6,* 1769 (1961); *C.A., 56,* 4354g (1962).

24 R. Pastorek, *Monatsh. Chem., 103,* 831 (1972); *C.A., 77,* 83090t (1972).

25 R.A. Krause, D.C. Jicha and D.H. Busch, *J. Am. Chem. Soc., 83,* 528 (1961).

26 N.S. Biradar, V.B. Mahale and V.H. Kulkarni, *J. Inorg. Nucl. Chem., 35,* 2565 (1973).

27 P.S. Gomm, G.I.L. Jones and A.E. Underhill, *J. Inorg. Nucl. Chem., 35,* 3745 (1973).

28 B. Sen and M.E. Pickerell, *J. Inorg. Nucl. Chem., 35,* 2573 (1973).

29 D. Malone and B. Sen, *J. Inorg. Nucl. Chem., 35,* 2114 (1973).

30 B.N. Dolgov, Z.I. Sergeeva, N.A. Zubkova, Z.M. Matveeva and M.G. Voronkov, *Izv. Akad. Nauk. SSSR., Otd. Khim. Nauk.,* 951 (1960).

31 B.N. Dolgov, Z.I. Sergeeva, N.A. Zubkova and M.G. Voronkov, *Zh. Obshch. Khim., 30,* 3347 (1960).

32 Z.I. Sergeeva, Z.M. Matveeva and M.G. Voronkov, *Zh. Obshch. Khim., 31,* 2017 (1961).

33 I. Hashishiro and S. Horii, *Japan Patent,* 711, 272 (1971); *C.A., 76,* 73498x (1972).

34 G. Kamai and R.G. Miftakhova, *Zh. Obsch. Khim., 35,* 2001 (1965); *C.A., 64,* 66859 (1966).

35 F. Lukevics and M.G. Voronkov, *Khim. Geterotsikl. Soldin, Akad. Nauk. Latv. SSSR,* 36 (1965).

36 P.G. Harrison and J.J. Zuckerman, *Inorg. Chem., 9,* 175 (1970).

37 A. Singh, A.K. Rai and R.C. Mehrotra, *J. Chem. Soc. Dalton,* 1911 (1972).

38 G. Kamai, R.G. Miftakhova and N.G. Gazetdinova, *Zh. Obshch. Khim., 39,* 1798 (1969).

39 R.G. Miftakhova, S.G. Maksimenko and Yu.I. Kusov, *Zh. Obshch. Khim., 42,* 1969 (1972); *C.A., 78,* 43635 (1973).

40 G. Kamai, R.G. Miftakhova and L.M. Frenkel, *Izv. Vyssh. Ucheb. Zaved, Khim. Khim. Tekhnol., 12,* 522 (1969); *C.A., 71,* 50142j (1969).

41 A. Singh, A.K. Rai and R.C. Mehrotra, *J. Organometal. Chem., 57,* 301 (1973).
42 A. Singh and R.C. Mehrotra, *Syn. React. Inorg. and Metal–org. Chem.* (1974).
43 A. Singh and R.C. Mehrotra, Unpublished results.
44 A. Singh, (Miss) C.K. Sharma, A.K. Rai, V.D. Gupta and R.C. Mehrotra, *J. Chem. Soc. A,* 2440 (1971).
45 A. Singh, *Ph. D. Thesis,* University of Rajasthan, Jaipur (India), 1972.
46 R.C. Mehrotra, A.K. Rai and R. Bohra, *Syn. React. Inorg. and Metal–org. Chem., 4,* 167 (1974).
47 R.C. Mehrotra, A.K. Rai and R. Bohra, *J. Ind. Chem. Soc., 51,* 304 (1973).
48 R. Bohra, A.K. Rai and R.C. Mehrotra, *Indian J. Chem.,* in press (1974).
49 R.C. Mehrotra, A.K. Rai and R. Bohra, *Z. Anorg. Allgem. Chem., 399,* 338 (1973).
50 K.C. Pande and R.E. Ridenour, *French Patent,* 1, 506, 185 (1967); *C.A., 69,* 106868 (1968).
51 K.C. Pande and R.E. Ridenour, *Chem. Ind.,* 56 (1970).
52 R.A. Murphy, *French Patent,* 1, 462, 725 (1966); *C.A., 67,* 54258 (1967).
53 O. Smrakar and U. Wannagat, *Monatsh. Chem., 100,* 760 (1969).
54 U. Wannagat and J. Pump, *Monatsh. Chem., 94,* 141 (1963).
55 U. Wannagat in H.J. Emeleus and A.G. Sharpe (Eds), "Advances in Inorganic and Radiochemistry", Academic Press, Vol. VI, 251 (1964).
56 U. Wannagat and O. Smrekar, *Monatsh. Chem., 100,* 750 (1969).
57 P.G. Harrison and J.J. Zuckerman, *Inorg. Nucl. Chem. Lett., 6,* 5 (1970).
58 E. Frainnet and F. Dubondin, *C.R. Acad. Sci. Ser. C, 262C,* 1693 (1966).
59 R.E. Banks, R.N. Hazeldine and D.L. Hyde, *Chem. Commun.,* 413 (1967).
60 H.J. Emeleus, J.M. Shreeva and P.M. Spaziante, *Chem. Commun.,* 1252 (1968).
61 H.J. Emeleus, J.M. Shreeve and P.M. Spaziante, *J. Chem. Soc. A,* 431 (1969).
62 H.J. Emeleus, J.M. Shreeve and P.M. Spaziante, *J. Inorg. Nucl. Chem., 31,* 3417 (1969).
63 H.J. Emeleus, P.M. Spaziante and S.M. Williamson, *J. Inorg. Nucl. Chem., 32,* 3219 (1970).
64 K.C. Pande, *French Patent,* 1, 506, 186 (1967); *C.A., 69,* 106878 (1968).
65 J.R. Jennings and K. Wade, *J. Chem. Soc. A,* 1333 (1967).
66 G.E. Coates and A.H. Fishwick, *J. Chem. Soc. A,* 640 (1968).
67 D.F. Menard and J.G. Aston, *J. Am. Chem. Soc., 56,* 1601 (1934).
68 G.E. Coates and R. Ridley, *J. Chem. Soc. A,* 1064 (1966).
69 J.G. Noltes and J. Boersama, *J. Organometal. Chem., 12,* 425 (1968).
70 I. Pattison and K. Wade, *J. Chem. Soc. A,* 2618 (1968).
71 F.G. Foot and B.P. Roberts, *J. Chem. Soc. C,* 3475 (1971).
72 P.G. Harrison and S.R. Stobart, *J. Chem. Soc. Dalton,* 940 (1973).
73 E. Frainnet and F. Duboudin, *Int. Sepn. Organosilicon Chem. Sci. Commun. Prague,* 342 (1965).
74 R.A. Krause, N.B. Colthup and D.H. Busch, *J. Phys. Chem., 65,* 2216 (1961).
75 P.G. Harrison, *J. Organometal. Chem., 38,* C 5 (1972).
76 G. Weissenberger, *U.S. Patent,* 3, 282, 672 (1966); *C.A., 66,* 28891 (1967).
77 A.G. Farbenfabriken Bayer, *British Patent,* 945,068 (1963); *C.A., 60,* 12051 (1964).
78 G. Weissenberger, *U.S. Patent,* 3,275,659 (1966); *C.A., 65,* 20164 (1966).
79 R.C. Poller, "The Chemistry of Organotin Compounds", Logs–Press, London, 72 (1970).
80 M. Nakanishi and S. Inamasn, *Japan Patent,* 6,724,573 (1967); *C.A., 69,* 44022 (1968).
81 M. Nakanishi and S. Inamasu, *Japan Patent,* 6,726,296 (1967); *C.A., 69,* 52304 (1968).
82 A. Singh and R.C. Mehrotra, *Indian J. Chem.,* in press (1973).
83 B. Serafin and M. Makosza, *Tetrahedron, 19,* 821 (1963).
84 H. Mohrle, B. Gusowski and R. Feil, *Tetrahedron, 27,* 221 (1971).
85 L.P. Kuhu and M. Inatome, *J. Am. Chem. Soc., 85,* 1206 (1963).
86 H.J. Roth and B. Miller, *Arch. Pharm., 297,* 744 (1964).
87 E.J. Pribyl, H.L. Yale and J. Bernstein, *U.S. Patent,* 3,137,723 (1964); *C.A., 61,* 9526 (1964).
88 A. Dornow and K. Fischer, *Chem. Ber., 99,* 68 (1966).
89 A. Singh and R.C. Mehrotra, *Synthesis in Inorg. and Metal–organic Chemistry,* (1974).
90 D.C. Bradley, *Progr. Inorg. Chem., 2,* 303 (1961).
91 R.C. Mehrotra, *Inorg. Chim. Acta, Rev., 1,* 99 (1967).
92 (Miss) C.K. Sharma, V.D. Gupta and R.C. Mehrotra, *Indian J. Chem.,* in press (1974).
93 (Miss) C.K. Sharma, *Ph. D. Thesis,* University of Rajasthan, Jaipur, India (1970).
94 A. Singh, A.K. Rai and R.C. Mehrotra, *Indian J. Chem., 11,* 478 (1973).
95 A. Singh, A.K. Rai and R.C. Mehrotra, *Indian J. Chem.,* in press (1973).
96 A. Singh, A.K. Rai and R.C. Mehrotra, *Inorg. Chim. Acta,* in press (1973).
97 R. Bohra, A.K. Rai and R.C. Mehrotra, Unpublished results.
98 R.C. Mehrotra, *J. Ind. Chem. Soc., 30,* 585 (1953).
99 R.C. Mehrotra, *J. Ind. Chem. Soc., 31,* 85 (1954).
100 R.H. Baker, *J. Am. Chem. Soc., 60,* 2673 (1938).
101 D.C. Bradley, "Advances in Inorganic and Radiochemistry", Academic Press, New York, *15,* 259 (1972).
102 H. Noth, Unpublished results in R.J. Brotherton and H. Steinberg (Eds.), "Progress in Boron Chemistry", Vol. III, Pergamon Press (1970).
103 E. Frainnet, F. Duboudin, C. Jarry and F. Dabescate, *C.R. Acad. Sci., Ser. C, 270,* 240 (1970).
104 K. Witke, P. Reich and H. Kriegamann, *J. Organometal. Chem., 15,* 37 (1968).
105 Yu.V. Zeifman, E.G. Abduganiev, E.M. Rokhlin and I.L. Kunyants, *Izv. Akad. Nauk. SSSR, Khim., 12,* 2737 (1972); *78,* 97752f (1973).
106 A.R. Forrester, J.M. Hay and R.H. Thomson, "Organic Chemistry of Stable Free Radicals", Ch. 5, Academic Press, London (1968).

107 H.J. Emeleus, P.M. Spaziante and S.M. Williamson, *Chem. Commun.*, 768 (1969).
108 H.G. Ang and K.F. Ho, *J. Organometal. Chem.*, *18*, 19 (1969).
109 H.G. Ang and K.F. Ho, *J. Organometal. Chem.*, *27*, 349 (1971).
110 K.U. Ingold and B.P. Roberts, "Free-Radical Substitution Reactions", Wiley–Interscience, New York (1971).
111 S.P. Makarov, M.A. Englin, A.E. Videiko, V.A. Tobolin and S.S. Dubov, *Dokl. Akad. Nauk. SSSR*, *168*, 344 (1966).
112 H.G. Aug, *Chem. Commun.*, 1320 (1968).
113 H.G. Aug, J.S. Coombes and V. Sukhoverkhov, *J. Inorg. Nucl. Chem.*, *31*, 877 (1969).
114 H. Koehler, U. Lange and B. Eichler, *J. Organometal. Chem.*, *35*, C17 (1972).
115 H. Onoue, K. Minami and K. Nakagawa, *Bull. Chem. Soc. Japan*, *43*, 3480 (1970).
116 H. Onoue and I. Moritani, *J. Organometal. Chem.*, *44*, 189 (1972).
117 R. Raluca, K. Imrah and G. Szekely, *Z. Monatsh. Chem.*, *100(S)*, 1761 (1969).
118 J. Forrest Allen, *J. Am. Chem. Soc.*, *79*, 3071 (1957).
119 A.E. Arbuzov, B.A. Arbuzov and B.P. Lugovkin, *Bull. Acad. Sci. URSS Classe Sci. Chim.*, 538 (1947).
120 H.J. Emeleus and P.M. Spaziante, *Chem. Commun.*, 770 (1968).
121 Rakesh Bohra, *Ph. D. Thesis*, University of Rajasthan, Jaipur, India (1974).
122 E. Frainnet and F. Duboudiu, *Intern. Symp. Organosilicon Chem. Sci., Commun.*, 342 (1965); *C.A.*, *65*, 12225 (1966).
123 A.J. Bloodworth and A.G. Davies in A.K. Sawyer (Ed.), "Organotin Compounds", Marcel Dekker, New York (1971).
124 L.E. Godycki and R. Rundle, *Acta Crystallogr.*, *6*, 487 (1953).
125 D.E. Williams, G. Wohlaner and R.E. Rundle, *J. Am. Chem. Soc.*, *81*, 755 (1959).
126 E. Frasson, C. Panattoni and R. Zammetti, *Acta Crystallogr.*, *12*, 1027 (1959).
127 E. Frasson, R. Bardi and S. Bezzi, *Acta Crystallogr.*, *12*, 201 (1959).
128 E. Frasson and C. Panattoni, *Acta Crystallogr.*, *13*, 893 (1960).
129 K.S. Viswanathan and N.R. Kundur, *Acta Crystallogr.*, *14*, 675 (1961).
130 C.B. Singh and B. Sahoo, *J. Inorg. Nucl. Chem.*, *36*, 1259 (1974).
131 J. Fujita, A. Nakahara and R. Tsuchida, *J. Chem. Phys.*, *23*, 1541 (1955).
132 R. Blinc and D. Hadzi, *J. Chem. Soc.*, 4536 (1958).
133 R. Blinc and D. Hadzi, *Spectrochim. Acta*, *16*, 852 (1960).
134 R.D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 6041 (1963).
135 L. Cambi and L. Szeo, *Ber. Chem. Dtsch. Ger.*, *2591* (1931).
136 S. Sugden, *J. Chem. Soc.*, 246 (1932).
137 R. Fereday, *Proc. Phys. Soc. (London)*, *44*, 274 (1932).
138 J.B. Willis and D.F. Mellor, *J. Am. Chem. Soc.*, *69*, 1237 (1937).
139 C.V. Banks, R.W.V. Harr and R.P. Vanerwal, *J. Am. Chem. Soc.*, *77*, 324 (1955).
140 T. Matsumoto, T. Kato and K. Shinra, *J. Chem. Soc. Japan*, *86*, 1266 (1965).
141 T. Matsumoto, I. Masuda and K. Shinra, *J. Chem. Soc. Japan*, *88*, 46 (1967).
142 K. Burger, I. Ruff and F. Ruff, *J. Inorg. Nucl. Chem.*, *27*, 179 (1965).
143 K. Burger and I. Ruff, *Talanta*, *10*, 329 (1963).
144 P. Cox, *J. Chem. Soc.*, 459 (1935).
145 M.A. Jarski and E.C. Lingafelter, *Acta Crystallogr.*, *17*, 1109 (1964).
146 P.L. Orioli, E.C. Lingafelter and B.W. Brown, *Acta Crystallogr.*, *17*, 1113 (1964).
147 F. Ephraim, *Ber.* *63B*, 1928 (1930).
148 L.G. Ward, T.L. Meck and G.E. Cheney, *Inorg. Chim. Acta*, *4*, 43 (1970).
149 V.R. Rao and R.P. Murty, *Ind. J. Chem.*, *6*, 465 (1968).
150 R.P. Murty and V.R. Rao, *Curr. Sci.*, *36*, 233 (1967).
151 F. Fiegel, *Ber. Dt. Chem. Ger.*, *56*, 2083 (1923).
152 I.S. Jennings, E. Sherrat and W. Warlow, *J. Chem. Soc.*, 818 (1935).
153 S.N. Poddar, *Z. Anal. Chem.*, *154*, 254 (1957).
154 H. Singh and K.C. Sharma, *Ind. J. Appl. Chem.*, *28*, 43 (1965).
155 R.E. Rundle and M. Parsole, *J. Chem. Phys.*, *20*, 1487 (1952).
156 B.D. Gupta and W.U. Malik, *J. Ind. Chem. Soc.*, *48*, 59 (1971).
157 F.G. Bordwell, "Organic Chemistry", McMillan, New York (1963).
158 R.C. Fuson, "Reactions of Organic Compounds", Wiley, New York (1962).
159 Yu.Ya. Kharitonov, M.A. Sarukhanov and I.B. Boranooskii, *Zh. Neorg. Khim.*, *12*, 163 (1967).
160 N.D. Mitkinova, N.V. Ivannikova, Yu.S. Varshavskii and A.I. Stetsenko, *Zh. Neorg. Khim.*, *15*, 572 (1970).
161 Yu.Ya. Kharitonov and M.A. Sarukhanov, *Zh. Neorg. Khim.*, *11*, 2532 (1966).
162 P.G. Harrison, *Inorg. Chem.*, *12*, 1545 (1973).
163 V.I. Goremykin, *Bull. Acad. Sci. URSS, Classe Sci. Chim.*, 241 (1947); *C.A.*, *42*, 44814 (1948).
164 A. Pilipenko, E.A. Shpok and L.L. Shevehenko, *Zh. Neorg. Khim.*, *12*, 463 (1967).
165 K.C. Pande, *U.S. Patent*, 3,252,672 (1966); *C.A.*, *66*, 28891c (1967).
166 H. Saburo, M. Hiroaki and N. Yoshihiro, *Japan Patent*, 7,024,125 (1970); *C.A.*, *74*, 23213p (1971).
167 R.N. Butler, *Chem. and Ind.*, 523 (1972).
168 M.E. Brokke, G.E. Luker and D.R. Arneklue, *U.S. Patent, 3,375,277 (1965); C.A.*, *68*, 113551C (1968).
169 G. Hoerlein, G. Salbeck and L. Emmel, *Ger. Often.*, 2,214,297 (1973); *C.A.*, *80*, 14848w (1974).
170 J. Boissieras and L. Ceyzeriat, *Ger. Often.*, 2,065,407 (1973); *C.A.*, 4671u (1974).