Organocobaloximes: Cobalt–Carbon Bond Stability and Synthesis*

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Abstract

Following the discovery that the naturally occurring vitamin B_{12} coenzyme contained a stable Co–C sigma bond and the further realization that porphyrin-like corrin was an important factor in the stabilization of the Co–C bond, has led to the synthesis of a large number of organocobalt complexes. Inspite of the many known examples of such complexes in the literature, the synthesis of the Co–C bond with new or modified structural features continues to be a fascinating field of study. Many synthetic routes have been reported and many new ones are frequently emerging. In this article, a complete analysis of the synthetic aspects of organocobalt compounds and organocobaloximes, in particular, is undertaken. The stability of the Co–C bond, general methods of synthesis and experimental procedures are discussed.

1. Introduction—Historical Sketch

The sigma bonded organometallic compounds of main group elements and transition metals have been fairly well known for many years and contribute a diverse and rich field of research. However, the chemistry of the Co–C bond could not be enlightened to a similar degree until 1960 [1]. However, the synthetic impetus gained momentum following the X-ray crystallographic investigation of vitamin B_{12} coenzyme by Lenhert and Hodgkin [2, 3]. For the first time a naturally occurring transition metal organometallic complex was recognized and was one of the most stable sigma bonded organocobalt compounds ever reported. The unusual stability of vitamin B_{12} and its derivatives was, for quite sometime, attributed to the presence of a porphyrin-like corrin ring. This led to the synthesis of a large number of sigma bonded organocobalt complexes having analogous quadridentate ligands [4]. The year 1964 may be designated as a landmark in this field with the name of G. N. Schrauzer, who reported [5] a number of organobis(dimethylglyoximato)cobalt complexes, trivially known as cobaloximes. It was soon established that the stability of the cobalt–carbon bond virtually depended upon a sufficiently strong, essentially planar, ligand field. Today a wide variety of such equatorial ligand systems are known that range from aromatic porphyrins to the completely saturated [14]-ane N_4 systems with more than 2500 complexes in the literature [6–11]. A few representative examples of equatorial ligands are shown in Fig. 1. However, it must be emphasized that, because of their biochemical relevance to vitamin B_{12} coenzyme, cobaloximes are the most studied ones [12, 13].

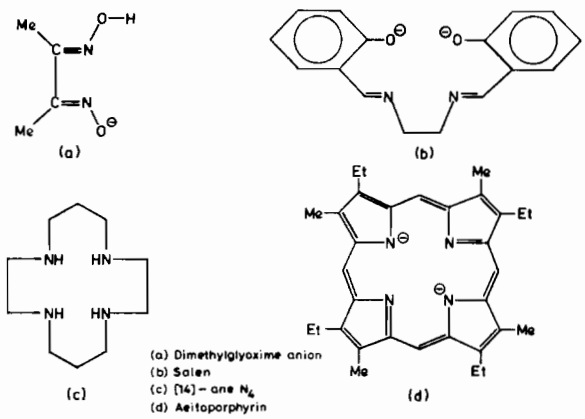

Fig. 1. Equatorial ligands.

2. Scope of the Review

Inspite of many known examples of organocobaloximes in the literature, synthesis of the cobalt–carbon bond with new or modified structural features continues to be a fascinating area in cobaloxime chemistry, mainly because of the yet-incomplete understanding of structure *versus* the Co–C bond reactivity relationship in coenzyme-B_{12} and its model compounds [14–21]. Following recent reports [22, 23] that cobaloximes and cobalamins mediate many interesting and useful chemical transformations, a gain in momentum in the synthesis of these complexes is envisaged. Many synthetic routes have been accrued in the literature and new or modified methods are frequently emerging. Though

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many reviews on various aspects of organocobalt chemistry have appeared [9–21], no comprehensive account on the synthetic aspects of organocobaloximes has been published since 1973 [8]. The principal aim of the present article, therefore, is to provide a complete analysis of the synthetic aspects of organocobaloxime chemistry*. The discussion is broadly classified into the following sections:

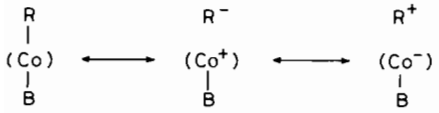
—the stability of the Co–C bond

—general methods of organobaloxime synthesis and experimental procedures.

3. Stability of the Cobalt–Carbon Bond

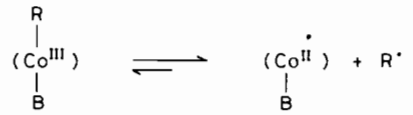
The success of any organocobaloxime synthesis invariably depends upon the stability of the Co–C bond it has. Hence, prior to an attempted synthesis, it is necessary that the factors leading to a stable Co–C bond be clearly understood. The essential structural, chemical and electrochemical parameters that govern the stability of the Co–C bond in organocobalt complexes in general and cobaloximes in particular, are highlighted below.

Alkyl cobalamins and cobaloximes have been found to be thermally stable organocobalt complexes [25]. One possible way of expressing this axial Co–C bond stability may be through the resonating structures as follows



It is noteworthy that in the bis(bidentate) and tetradentate cobalt complexes the number of axial ligands depends crucially on the oxidation state of the central cobalt atom. In general (Co^{III}) is bound by two axial ligands (R, B), (Co^{II}) by one (B) and (Co^{I}) by one (B) or none [26]. This trend of decreasing coordination number has been qualitatively described by the R–Co–B three centre 4–5–6 electron bonding model, which combines axial ligand sigma orbitals with metal orbitals of substantial d_{z^2} character [27]. Molecular orbital calculations [28–30] further indicate that the interaction of the (metal bound) carbon sp^3 orbital with the $3d_{z^2}$, $4p_z$ and 4s orbitals of cobalt are mainly responsible for Co–C bond stabilization. If the organic residue (R) is an sp^2 or sp hybridized carbon, then additional interaction of the π-carbon orbital with the $3d_{xz}$ and $3d_{yz}$ orbitals of cobalt lead to further stabilization of the axial bond. Thus, for a similar axial base ligand (B), the Co–C bond length in organocobaloximes is about 2.00, 1.96 and 1.90 Å for sp^3, sp^2 and sp hybridized carbon, respectively. This trend is however, violated if the carbon atom is appended with bulky substituents.

The electronic influence of either the equatorial ligand (electronic *cis* influence) or the axial base ligand (electronic *trans* influence) towards the stability of the Co–C bond in organocobaloximes is rather less pronounced [20, 21]. This is attributed to (i) the lesser π-electron delocalization in dimethylglyoxime ligand and (ii) the strong *trans*-influence of the axial organic group (R) over the base ligand (B). However, the σ-donating ability of the base ligand has considerable effect on the Co–C bond stability. Thus, more basic ligands have been shown to stabilize the parent organocobalt(III) complex relative to the cobalt(II) dissociation product and hence increase the Co–C bond dissociation energy [15].



Unlike the electronic effects, the steric factors play a significant role in the Co–C bond stability [31]. The importance of such an influence comes mainly from the X-ray crystal structure determination of a number of organocobalt complexes [20]. These measurements reveal significant lengthening, hence weakening of the Co–C bond with increasing steric bulk of the axial ligands (R and/or B). There appears to be a linear relationship between the Co–C bond length and the number of substituents on the α-carbon to metal. Besides, a significant sterically induced conformational distortion of the equatorial ligand from planarity is observed. In general the displacement of the cobalt atom is towards and the bending of the dimethylglyoxime plane is away from the bulkiest of the two axial ligands. Furthermore, with bulky substituents on the α-carbon to cobalt the $Co–C_\alpha–C_\beta$ angle is found to be much higher than expected for a tetrahedral carbon (C_α) atom, for example, in B_{12} coenzyme this angle is 125°. This large bond angle is explained in terms of a rehybridization at the α-carbon atom which is necessary in order to increase the overlap with the cobalt sigma metal orbitals and to reduce repulsions between the non-bonded electron pairs on the cobalt and the electron pairs in the $C_\alpha–C_\beta$ and C_α–H bonds. The *cis* steric interaction between the R group and the dimethylglyoxime ligand further influences,

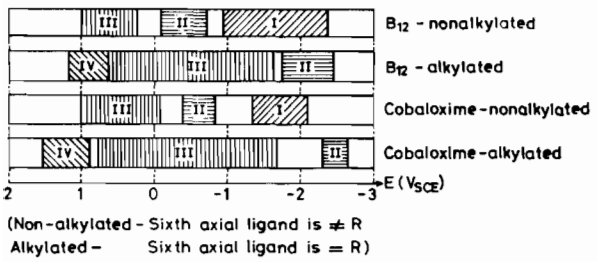
(i) the Co–C bond to bend in the plane defined by Co, N_a, N_b (N_a, N_b are the dimethylglyoxime nitrogen atoms, *trans* to each other) and

(ii) the axial base ligand (B) to bond towards N_a (or N_b) away from the R group.

*Complexes having the general formula $XCo^{III}(dmgH)_2B$, where X is a neutral or anionic non-organo group are not included in the discussion [24].

The Co–C bond dissociation energy of several organocobalt complexes and B_{12} coenzyme has recently been estimated by Halpern *et al.* [15, 32]. It ranges from 17–30 kcal mol^{-1}, while in B_{12} coenzyme it is estimated to be 26 kcal mol^{-1}. The low value of the Co–C bond energy and its high valent nature suggest that it is much weaker compared to other metal–carbon bonds and is susceptible to homolytic cleavage which may even be effected by visible radiation.

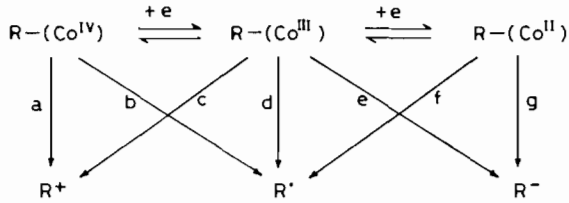
All the organocobalt complexes isolated in the +3 oxidation state are the most stable ones. Synthesis of these complexes has been achieved from (Co^{I}), (Co^{II}), (Co^{III}) substrates and a variety of methods are available in the literature. In order to choose the right pathway, one has to know the exact nature of the reduction potential of cobalt in the various oxidation states. One and/or two electron reduction/oxidation potentials of a large number of cobalt(III) chelates are known and the values depend on the axial and equatorial ligands and also on the nature of the solvent [20, 23, 33–40]. Since metal reduction from $+3 \rightarrow +2 \rightarrow +1$ is coupled with axial ligand expulsion, $E^{\circ}_{3/2}$ and $E^{\circ}_{2/1}$ depend on the complex formation constant of axial ligands with cobalt in different oxidation states. The thermodynamic stability of different cobalt chelates at variable electrode potentials, therefore, can be tabulated. Scheme 1 shows the general



Scheme 1. Ranges of thermodynamic stability of cobalamins and cobaloximes at various electrode potentials.

behaviour of cobaloximes and B_{12} derivatives. In Scheme 1 the E° values are represented by white zones, their width being due to the variation of E° caused by different axial ligands and solvents. The white zones separate stability zones of the different oxidation states (dark areas) as a function of electrode potential. Reported E° values for different axial bases and various solvents/electrolytes (all adapted to the SCE reference systems) lie within the white zones.

It may be further noted that if one axial ligand is an alkyl residue, reversible coordination is excluded. In most cases the lifetime of the six coordinate organocobalt(II) or cobalt(IV) complexes has been found to be very small and they irreversibly expel the alkyl residue. The relative stability of the Co–C bond with respect to the oxidation state of the metal may be best understood from Scheme 2; in which the possible mode of cleavage of the Co–C bond is depicted.



Scheme 2. Relative stability of the (Co–C) bond.

The group R may react as an electrophile in R–(Co^{IV}) (path a), as radical in R–(Co^{III}) (path d) or as nucleophile in R–(Co^{II}) (path g). However, reduction or oxidation of R–(Co) may allow decay routes b, c, e and f. As stated earlier, only organocobalt(III) complexes are stable enough to be isolated. However, during synthesis the organocobalt(III) should be protected from any reagent which may affect a bimolecular radical reaction, moreover, the work-up should be carried out in diffused light.

From the foregoing discussion it seems certain that in all the organocobalt compounds synthesized so far a delicate balance of electronic and steric factors (arising from the axial and equatorial ligands) as well as the oxidation state of the metal has been maintained.

4. General Methods of Synthesis of Organocobaloximes

The preparative methods of organocobaloximes can be broadly classified into the following main categories (Table I).

A. Reaction of (Co^{I}) or cobalt hydride species with electrophilic reagent;

B. Reaction of (Co^{II}) reagents with free radicals;

C. Reaction of (Co^{III}) complexes with nucleophiles;

D. Modification of a organocobalt complex.

A.1. From (Co^{I}) Species

This is by far the most useful method which employs the nucleophilic attack of (Co^{I}) anionic species at the electrophilic centre of an alkylating reagent (RX).

$$(Co^{I})^{-} + RX \longrightarrow R\text{–}Co^{III} + X^{-} \qquad (1)$$

The success of this method lies in the high nucleophilic reactivity of (Co^{I}) species. Pearson nucleophilicity of (Co^{I}) derived from cobalamin and its model compounds lies within the range of 14 ± 0.5, which is manyfold higher than those of conventional

TABLE I. Summary of Methods of Preparation of Organocobalt(III) Complexes

Section	Inorganic reagent	Organic substrate	Products
A.1	(Co^{I})	RX; X = halide, tosylate etc.	$R(Co^{III}) + X^{-}$
	(Co^{I})	$RCHCH_2X$; X = O, NH etc.	$RCHOHCH_2(Co^{III})$
	(Co^{I})	XCH=CHPh; X = Br, Cl	$PhCH=CH(Co^{III}) + X^{-}$
	(Co^{I})	$XCH=CH_2$; X = CN etc.	$XCH_2CH_2(Co^{III})$
	(Co^{I})	XC≡CH; X = Ph etc.	$XCH=CH(Co^{III})$
A.2	$H(Co^{III})$	$RCH=CH_2$	$MeCHR(Co^{III})$
	$H(Co^{III})$	RC≡CH	$CH_2=CR(Co^{III})$
	$H(Co^{III})$	$PhNH_2/HCHO$	$PhNHCH_2(Co^{III}) + H_2O$
B	(Co^{II})	RX; X = halide	$R(Co^{III}) + X(Co^{III})$
	(Co^{II})	$RNHNH_2/O_2$	$R(Co^{III}) + N_2 + H_2O$
	(Co^{II})	$RCMe_2OOH$	$R(Co^{III}) + OH(Co^{III}) + Me_2CO$
C	$X(Co^{III})$; X = halide	RM; M = metal	$R(Co^{III}) + MX$
	$X(Co^{III})$; X = halide	$CH_2=CHOR/ROH$	$(RO)_2CHCH_2(Co^{III})$
	$RO(Co^{III})$	R^1CH_3; R^1 = CN etc.	$R^1CH_2(Co^{III}) + ROH$
D	$RO_2CCH_2(Co^{III}) + OH^{-}/H^{+}$		$HO_2CCH_2(Co^{III})$
	$HOCH_2CH_2(Co^{III}) + Ac_2O/ROH/RCO_2H$		$XOCH_2CH_2(Co^{III})$; X = Ac, R, CO_2R

nucleophiles [CN^{-} (6.70); I^{-} (7.40)], therefore, (Co^{I}) species are termed as supernucleophiles [12, 41].

Several alkylating agents (RX) have been employed for the syntheses of organocobaloximes according to eqn. (1); for example, R may be alkyl, allyl, acyl, allenyl, alkenyl, alkynyl, benzyl, heteroaromaticmethyl etc., while X^{-} may be Cl^{-}, Br^{-}, I^{-}, tosylate and less commonly carboxylate, sulphate, phosphate, anhydride, trialkylamine and even mercury metal or nitrogen of diazomethane [8, 11, 42, 43]. The attack of (Co^{I}) species at a saturated carbon centre of a ring system, for example, cyclopropane, epoxide, ethyleneamine, tetrahydrofuran and β-lactones, effects ring opening (eqn. (2)) [44–46].

$$(Co^{I}) + R-\overline{CH-CH_2-X} \longrightarrow RCH(XH)CH_2(Co^{III}) \quad (2)$$

(X = O, NH)

Organocobaloximes having an activated methylene group next to a heteroatom (O, S, NH) have also been synthesized [47]. In an interesting variation, the alkenyl cobaloxime $[(p\text{-}ClC_6H_4)_4C=(Cl)C](Co^{III})$ has been synthesized by the reaction of (Co^{I}) with (*p,p'*-DDT), a fully saturated molecule [48]. Also a sugar derivative (R = 1,2,3,4-diisopropylidene-6-deoxy-6-yl-α-D-galactopyranose) has been prepared from (Co^{I}) and the iododerivative of the sugar [49]. Recently, Brown *et al.* [50] reported the syntheses of carboxyalkyl, 2-alkoxyethyl, 2-aryl-2-hydroxyethyl cobaloximes and carboxyalkyl cobalamins by the reductive alkylation route [50–53].

Unlike reductive alkylation, reductive arylation of (Co^{I}) with aryl halides has achieved little success so far [54–56]. Syntheses of complexes having equatorial ligands such as BAE, SALEN, DMGH, etc., are reported albeit in low yield. For cobaloxime synthesis the method works better only when aromatic halides contain electron withdrawing substituents in the ring. It must, however, be noted that the Grignard route (Section 4.C) is always preferred since it proceeds with high yields.

The reaction of vicinal dihalides with (Co^{I}) yields acetylenes but no organocobalt complex [11]. Cobalt(I) species is generated by

(i) reduction of (Co^{II}) or (Co^{III}) reagents by sodium borohydride in alkaline medium,

(ii) disproportionation of (Co^{II}) to (Co^{III}) and (Co^{I}) in highly alkaline medium,

(iii) reduction of (Co^{II}) by hydrogen in acidic, neutral or in alkaline medium.

Reduction of cobalt(II) chelates other than cobaloximes is done by sodium and potassium metals or their amalgams. For cobaloximes, methods (i) and (ii) above are employed most. However, for base sensitive alkylating agents, method (iii) is found to be most effective. The reduction is generally carried out at temperature below 0 °C under an inert atmosphere and is visibly sharp—a brown (Co^{II}) complex changing over to green to blue (Co^{I}) species (experimental details of each method is given in Section 6.4).

The reaction of (Co^{I}) with substrate RX may occur either via S_N2 or electron-transfer mechanism depending on the substrate, conditions and reagents used. For example, several kinetic studies on the

S_N2 $(Co^I) + R{-}X \longrightarrow R{-}(Co^{III}) + X^-$

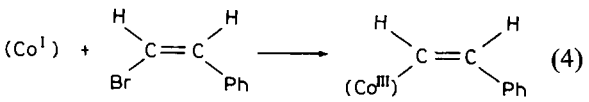
Electron-transfer $(Co^I) + R{-}X \longrightarrow (Co^{II}) + RX^{\cdot -}$

$RX^{\cdot -} \longrightarrow R^{\cdot} + X^-$

$(Co^{II}) + R^{\cdot} \longrightarrow R{-}(Co^{III})$

alkylation of (Co^I) by alkyl and allyl halides point to the bimolecular nucleophilic mechanism [41, 57] which is also supported by the observed inversion of configuration at the displacement centre in a number of alkyl halides (eqn. (3)) [58–60]. On the other hand, kinetic studies on the alkylation of (Co^I) by substituted vinyl halides indicate that the reaction proceeds via concerted displacement at the sp^2 carbon with retention of configuration about the double bond (eqn. (4)) [61].

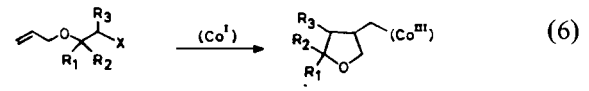
(3)



(4)

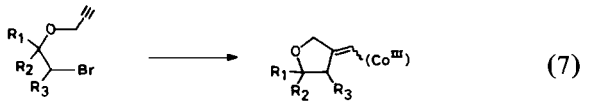
A recent semiquantitative analysis of the kinetic studies on the alkylation of cobalamin(I) points to an oxidative addition mechanism [62].

(5)



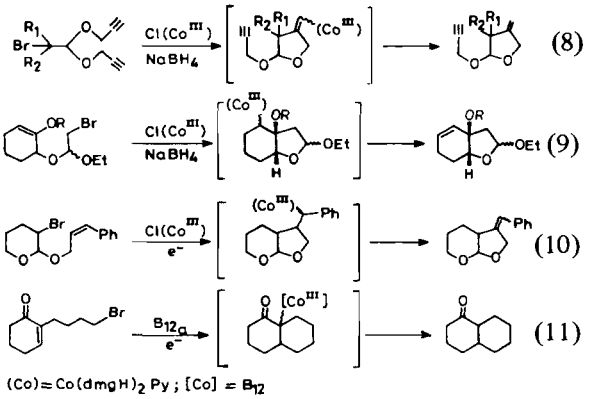
(6)

[R_1 = Ph; R_2 = R_3 = H, R_1 = H; R_2, R_3 = $-(CH_2)_4-$, X = Br, I]



(7)

[R_1 = R_2 = Ph; R_3 = H, R_1 = Ph; R_2 = R_3 = H, R_1 = H; R_2, R_3 = $-(CH_2)_4-$]



(8)

(9)

(10)

(11)

(Co) = Co(dmgH)$_2$Py; [Co] = B_{12}

Scheme 3.

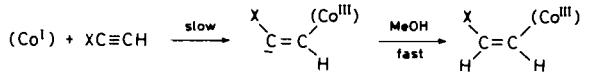
An electron transfer mechanism has recently been proposed in the reductive alkylation of (Co^I) by sterically hindered halides where the product organocobaloxime shows retention of configuration with respect to the halide (eqn. (5)) [63–66]. However, conclusive evidence for such a mechanism has been given by Tada *et al.* (eqns. (6) and (7)) [67, 68]. Similarly in many of the recently reported organic transformations, the intermediate formation of the cyclized cobaloximes may involve such an electron transfer mechanism (eqns. (8)–(10)) [69–71]. Scheffold has used vitamin B_{12s} in analogous studies (eqn. (11)) [23, 72]. Interestingly, the alkylation of (Co^I) by 2,2-dimethyl-but-3-enyl halides does not form any organocobaloxime, instead, reduction of the halide takes place for which an electron transfer mechanism has been proposed [73].

Beside the substitution reactions, cobalt(I) reagents add to unsaturated electrophiles, for example, they rapidly react with acrylonitrile and other such activated olefins to give π complexes which then slowly rearrange to the β-substituted cobaloxime (eqn. (12)) [74].

$$(Co^I) + XCH{=}CH_2 \xrightarrow{\text{fast}} \underset{CH_2}{\overset{CHX}{\|}} \longrightarrow (Co^I) \xrightarrow{\text{slow}} XCH_2CH_2(Co^{III}) \qquad (12)$$

(X = CN, CO_2R)

Similar addition reactions have also been demonstrated with alkynes [61, 75, 76]. The mechanism involves nucleophilic attack by Co^I on the β-carbon atom of the alkyne, via a π complex, followed by a rapid *trans*-addition of a solvent proton (eqn. (13)).



(13)

(X = Ph, CO_2R, CH_2OH, CF_3, CH_2CO_2Me)

However, with propargyl alcohol (X = CH_2OH) a mixture of α- and β-substituted products is obtained while propylene (X = CH_3) gives only the α-substituted product.

A.2. From Cobalt Hydride Reagent

The cobalt(I) species in less basic medium picks up a proton reversibly to give the corresponding cobalt(III) complex with a coordinated hydride.

$$(Co^I) + H^+ \rightleftharpoons H{-}(Co^{III})$$

Being the conjugate acid of (Co^I), the hydride complex decomposes in alkaline medium to the former, thereby undergoing most of the substitution reactions [12, 46] described for (Co^I) in Section A.1. This reagent, however, has been exploited mostly

for the synthesis of pentacyanocobalt(III) and cobalamin derivatives.

Interestingly the addition of hydride species across the double and triple bond produces the α-substituted derivatives, unlike that of (Co^{I}) discussed earlier. Kinetic and stereochemical studies indicate the possibility of two different mechanisms with a four centre and biradical transition state, respectively, the former being the more favourable one [57, 61, 74, 75, 77]. The following example [78] provides another interesting case of the addition reaction of cobalt hydride, the mechanism may involve the attack of the hydride species on the carbinoalamine formed *in situ* from aniline and formaldehyde.

$$H\text{–}(Co^{III}) + PhNH_2 + HCHO \longrightarrow PhNHCH_2(Co^{III}) + H_2O$$

Many new cobaloximes have been synthesized by the addition of cobalt hydride to *N,N*-disubstituted monothiocarbamic acid *S*-vinyl esters [79].

$$H\text{–}(Co^{III}) + R^1R^2NC(O)S\text{–}CH{=}CH_2 \longrightarrow R^1R^2NC(O)S\text{–}CH(CH_3)(Co^{III})$$

($R^1 = R^2 = nPr$, $R^1 = Et$; $R_2 = nBu$, $R^1 = Et$; $R^2 =$ cyclohexyl)

B. Preparation from Cobalt(II) Complexes

Cobalt(II) complexes react with a number of organic and organometallic free radicals to form the corresponding organocobalt(III) complexes [80]. The atom transfer reactions of alkyl halides (RX) with cobalt(II) complexes in several equatorial ligand systems have been studied [81–86].

$$2(Co^{II}) + R\text{–}X \longrightarrow R(Co^{III}) + X(Co^{III})$$

The method has been proved to be particularly useful over the reductive alkylation route (Section A.1) where (i) the generation of (Co^{I}) is difficult, for example $[Co\,Me_6(14)ane\,N_4]^+$, and (ii) the alkylating reagent either is very susceptible to decomposition under reaction condition or reacts very slowly with (Co^{I}) giving rise to a poor yield of $R(Co^{III})$. Cobalt(II) reagents can be used either directly or generated *in situ* by reducing a cobalt(III) chelate, $L(Co^{III})$ ($L = H_2O$, Cl, Br, CN etc.). While a clean one electron reduction of cobalt(III) corrins with chemical reducing agents is rather difficult [8, 87, 88], cobaloximes can be conveniently reduced with activated zinc wool, as observed in the synthesis of many alkyl cobaloximes from reactive halides like α-halogeno esters [89] (for preparative follow-up, see Section 6.4.IV). Halpern *et al.* have proposed the following mechanism for the atom transfer reaction [81, 90, 91].

$$(Co^{II}) + R\text{–}X \xrightarrow{slow} X(Co^{III}) + R^{\bullet}$$

$$R^{\bullet} + (Co^{II}) \xrightarrow{fast} R(Co^{III})$$

The reactivity of alkyl halide (RX) depends on both the stability of $\dot{R}$ and the nature of the halogen, for example, the reactivity increases along the sequences, $CH_2ClCOOR < CHCl_2COOR < CCl_3COOR$ and $R\text{–}Cl < R\text{–}Br < R\text{–}I$.

The generation of the radical $\dot{R}$ has also been achieved from substrates [92–94] other than alkyl halide and even by pulse radiolysis [95]. Thus, photolysis of an acidic solution of carboxylatopentaaminecobalt(III) complexes in the presence of $[Co^{II}(N_4)(OH_2)_2]^{2+}$ affords moderate to good yields of $[RCo^{III}(N_4)OH_2]^{+2}$.

$$Co(NH_3)_5OOCR^{+2} \xrightarrow{h\nu/H^+} Co^{+2} + 5NH_4^+ + CO_2 + \dot{R}$$

$$\dot{R} + Co^{II}(N_4)(OH_2)_2 \longrightarrow RCo^{III}(N_4)OH_2^{+2} + H_2O$$

[R = Me, Et, $PhCH_2$, CF_3, $CH{=}CH_2$; (N_4) = (Me_6[14]-diene-N_4), (Me_6[14]ane-N_4), ([14]ane-N_4), (Me_6[14]diene-N_4)].

Espenson and Martin have synthesized many organocobalt(III) complexes by the reaction of tertiary alkyl hydroperoxide ($RCMe_2OOH$, R = Et, Ph etc.) with (Co^{II}) chelates [94]. The following mechanism has been proposed for these reactions.

$$RCMe_2OOH + (Co^{II}) \xrightarrow{slow} RCMe_2\dot{O} + OH(Co^{III})$$

$$RCMe_2\dot{O} \xrightarrow{fast} \dot{R} + Me_2CO$$

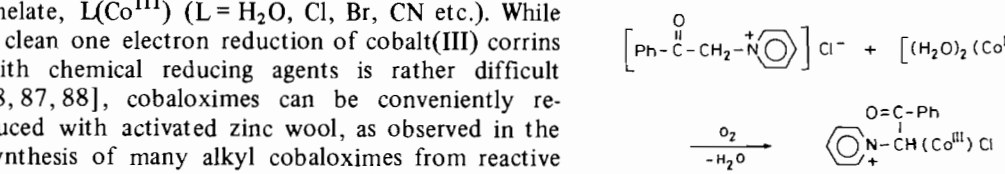
$$\dot{R} + (Co^{II}) \longrightarrow R(Co^{III})$$

Organic hydrazines have also been shown to react with (Co^{II}) in the presence of molecular oxygen to form corresponding organocobaloxime [96].

$$(Co^{II}) + RNHNH_2 \xrightarrow[CH_3CN]{O_2} R(Co^{III}) + N_2$$

(R = H, Me, Ph)

An interesting example showing the use of (Co^{II}) reagents in the synthesis of $R(Co^{III})$ derivatives has recently been reported [97].



C. Preparation from Cobalt(III) Complexes

A number of stable halocobalt(III) complexes react smoothly with alkyl and aryl magnesium

halides and with alkali metal alkyls to give corresponding organocobalt(III) complexes [11, 98–104]. Though the reductive alkylation method (Section A.1) is normally preferred over this route for the synthesis of alkyl cobaloximes, for Grignard compatible aryl groups this method gives better yields of aryl cobaloximes [101–104].

$$Cl(Co^{III}) + PhC{\equiv}CMgCl \xrightarrow{THF} PhC{\equiv}C\text{–}(Co^{III}) + MgCl_2$$

Poor solubility of halocobalt(III) complexes in ethereal solvents and the use of manyfold excess of Grignard reagents are the two main drawbacks of this method.

Because of their sufficient electrophilic character, some hydroxy- or alkoxycobalt(III) complexes also react with compounds containing an active or enolizable hydrogen [105–108].

$$RO\text{–}(Co^{III}) + R^1R^2CH_2 \xrightarrow{EtOH} R^1R^2CH(Co^{III}) + ROH$$

(R = H, Me; R^1 = CN, H; R^2 = CN, $CONH_2$, CO_2Et, NO_2)

Hydroxycobalamin has recently been methylated with a new methylating agent $(CH_3SiF_6)(NHCl)_3$ [109].

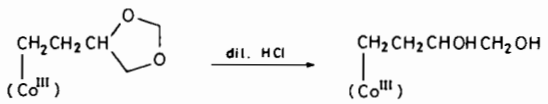
The reactions of cobaloximes and cobalamins with vinyl ethers in the presence of alcohols provide another route to cobalt–carbon bond formation [110]. Complex formation is believed to take place via an intermediate olefin π complex.

$$Br(Co^{III}) + H_2C{=}CHOEt \xrightarrow[Et_3N]{EtOH} (EtO)_2CHCH_2(Co^{III})$$

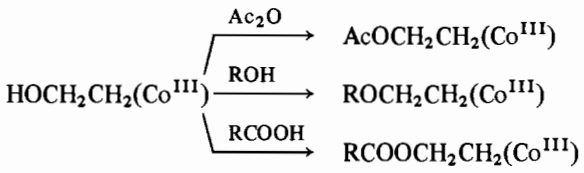
Diazoalkanes also react with halocobalt(III) porphyrin complexes to form substituted vinylcobalt(III) porphyrins [111].

D. Modification of Organic Ligands

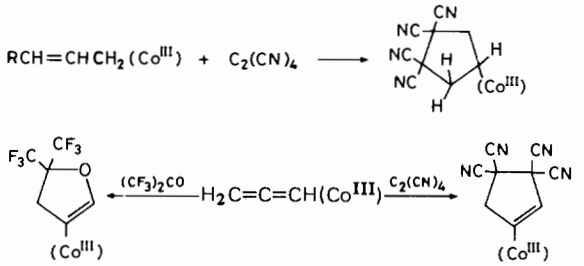
Many organocobalt complexes that are difficult to prepare by the above conventional routes (A, B and C) have recently been synthesized by initially preparing a suitable chelate on which the axial or equatorial group functionalities are then modified, for example, solvolysis for ester functionality in axial organic ligand provides the simplest route to new cobaloximes. Thus, *meta*- and *para*-substituted carboxyphenylcobaloximes are synthesized in good yields by hydrolysis of corresponding methyl esters in 0.5 M KOH in aqueous methanol [54]. Acetyl hydrolysis of many cobaloximes and cobalamins also proceeds smoothly in acidic medium [112].



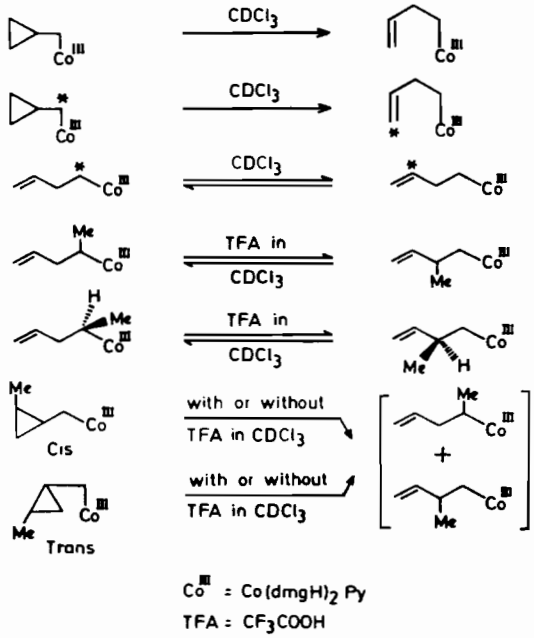
Hydroxy alkylcobaloximes have been used as precursors for many interesting transformations as illustrated below [113].



Cycloaddition reactions have also been carried out in a number of cobaloximes with tetracyanoethylene and hexafluoroacetone [114, 115].



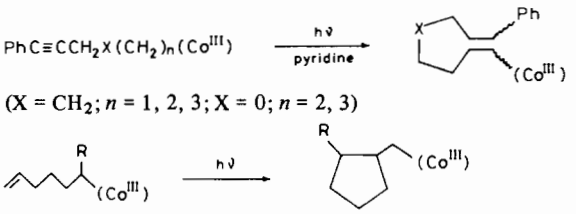
Many reactions have been reported by Johnson and Golding in which the axial organic ligands in cobaloximes undergo σ–π migration to give new cobaloximes as illustrated in Scheme 4 [116–119].



Scheme 4. σ–π migration.

These reactions are of considerable synthetic utility and have played important role in the model studies of B_{12}-dependent diol dehydrase and α-methyleneglutarate mutase reactions.

Recently, Johnson has reported a number of reactions in which substituted alkyl cobaloximes, on photolysis, undergo rearrangement to more stable substituted alkyl or alkenyl cobaloximes [120]. The rearrangements have been rationalized in terms of a reversible homolysis of the cobalt–carbon bond, rearrangement of the organic radical and recapture by the (Co^{II}) fragment.



(X = CH_2; n = 1, 2, 3; X = 0; n = 2, 3)

A similar mechanism is proposed by Ohgo and Takeuchi in the rearrangement of $XCH_2CH_2(Co^{III})$ to [XCH(Me)(Co^{III})] (X = CN, COOMe) [121].

Like the axial organo group (R) the equatorial dimethylglyoximate ligand can also be modified in organocobaloximes. Such modifications include, (i) protonation [122, 123] of equatorial ligand to generate RCo(dmgH)($dmgH_2$)B or RCo($dmgH_2$)$_2$B and (ii) reaction with boron trifluoride [124] to form RCo($dmgBF_2$)$_2$B (see Section 6.4 for details).

5. Novel Organocobaloximes

Among a wide variety of organocobaloximes discussed so far, examples of the following kind of complexes seem very few in the literature

(i) cobaloximes with tertiary α-carbon atom,
(ii) optically active cobaloximes,
(iii) intramolecularly bridged cobaloximes.

Cobaloximes with tertiary carbon bound cobalt are difficult to synthesize probably because of considerable weakening of the Co–C bond in such complexes and their susceptibility to eliminate cobalt hydride under reaction conditions. The known examples of such cobaloximes are listed in Table II.

Since organocobaloximes have been used as catalysts in many reactions, optically active cobaloximes have been synthesized with an aim that they will provide precise information about the elementary processes of such catalytic reaction [133–135]. Representative examples are illustrated in Fig. 2 (**1** and **2**). Besides, Gaudemer *et al.* have reported the first example of chiral atropisomeric cobaloxime (Fig. 2; **3**) in which the rotation of the atropisomeric ligand is inhibited by the cobaloxime substituent [136]. A few novel intramolecularly bridged cobaloximes (Fig. 2; **4**) have also been

TABLE II. The Known Examples of Organocobaloximes with Tertiary α-Carbon Atom

R	Method of synthesis	Reference
Me_2CCN	A.1, A.2	82, 125
1-Methyl-2,2-diphenylcyclopropyl	A.1	126
t-Adamantyl	A.1	64
t-Norbornyl	A.1	64
$MeC(Me)CH=CH_2$	A.1	127
$MeC(Et)C\equiv CH$	A.1	127
Me(OAc)(MeCOO)C	A.2	128
$Cl_2CC(=O)OMe$	B	129
Cl_2CCN	B	129
Cl_3C	B	129, 130
Br_2CPh	a	131
CMe_2COOMe	a	132

[a]Suggested intermediate in the reaction of organocobaloximes.

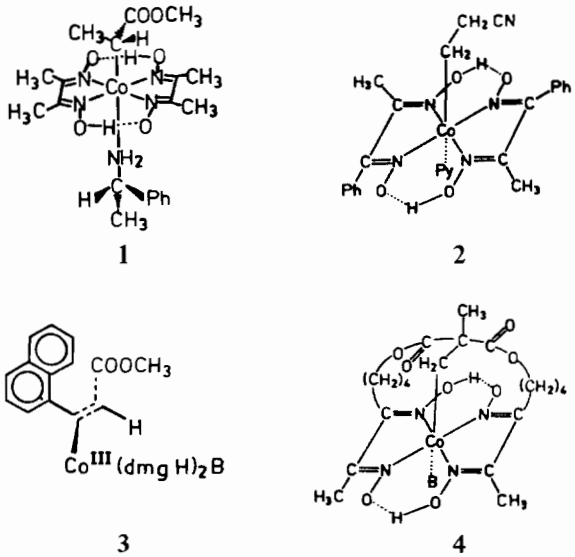


Fig. 2. Novel organocobaloximes.

synthesized to model the B_{12}-dependent enzymatic methyl malonyl–CoA mutase reaction [137].

6. Organocobaloxime Synthesis: Preparative Methods

6.1. Qualitative analysis of reaction mixture

Since it is frequently desirable to monitor the progress of an organocobalt preparation prior to work-up, thin layer chromatography on silica gel affords an easy and rapid qualitative analysis of reaction mixtures*. Most of the organocobaloximes are of intermediate polarity, and migrate to R_f = 0.6–0.8 when eluted with ethyl acetate, acetone or

*^{1}H NMR spectroscopy can also be used effectively to monitor the reaction (for more details see Section 6.3).

methanol. They produce bright yellow or orange spots which gradually turn brown on exposure to visible light due to the photo lability of the Co–C bond. Non-alkylated cobaloximes, like halocobaloximes, are, in general, more polar and remain at the origin in both ethyl acetate and acetone and migrate significantly only in methanol. Most of the alkylating agents used in the synthesis of organocobaloximes are colourless and relatively non-polar so that they do not migrate in these polar solvents. Thin layer chromatography, therefore, provides a rapid and reliable method to assess the success of a synthetic procedure prior work-up.

6.2. Work-up of reaction mixture

In most cases products are isolated in moderate to good yields simply by pouring a concentrated alcoholic reaction mixture to water (*ca.* 1–3 *v/v*). Repeated washings with water followed by ether gives sufficiently pure sample for most practical purposes. However, recrystallization when required, is achieved by diluting a concentrated methanolic solution with water or dichloromethane solution with cyclohexane. Use of other solvents in specific cases is also reported, for example, benzyl cobaloximes crystallizes out well from 2-butanone.

When yields are poorer or the above work-up procedures prove unworthy due to lability of the complexes in water medium, column chromatography on silica gel has proved convenient for isolation and purification of organocobaloximes. Generally, elution with dichloromethane or chloroform removes the alkylating agent and other organic products formed as side products. Subsequently, the desired cobaloxime may be eluted with acetone or ethyl acetate–methanol mixture. Non-alkylated cobaloximes, if present in the reaction mixture, remain on the column and may be eluted with some difficulty with methanol.

It is often desirable to change the axial base ligand *trans* to the organic group. This is best done by initially preparing the organo(aquo)cobaloxime and subsequently treating it with excess of base ligand in methanol or dichloromethane. Overnight stirring at room temperature followed by the usual work-up affords the desired product. Aquo cobaloximes have been prepared by many methods as shown below [46, 54, 122, 123, 137].

$$RCo(dmgH)_2Py + Dowex\text{–}SO_3H \xrightarrow{MeOH/HCl} RCo(dmgH)_2OH_2 + Dowex\text{–}SO_3^-PyH^+$$

$$RCo(dmgH)_2Py + HCl \xrightarrow{MeOH/H_2O} [RCo(dmgH)(dmgH_2)Cl]\cdot H_2O + PyH^+Cl^-$$

$$[RCo(dmgH)(dmgH_2)Cl]\cdot H_2O + HPO_4^{-2} \xrightarrow{MeOH/H_2O} RCo(dmgH)_2OH_2 + H_2PO_4^-$$

6.3. Characterization of organocobaloximes

Organocobaloximes are generally characterized by their spectral analysis, as discussed below.

Electronic spectra [11, 32, 138]. The cobaloximes exhibit very ill-defined electronic spectra between 250–400 nm and attempts to correlate them have had little success so far. But the important low energy absorption between 400–500 nm ($\epsilon = 10^3$) has been assigned to a charge transfer band (Co–C, MLCT) which is sensitive to the axial base ligand and also to the 2s character of the axial carbon attached to the cobalt atom. In addition, the π–π^* transition due to the equatorial dimethylglyoximato ligand appears at *ca.* 240 nm.

Vibrational spectra [139, 140]. The infrared spectral features of cobaloximes reflect very broad generalities. Thus, for alkyl cobaloximes, the band at around 1560 cm^{-1} is attributed to C=N stretching frequency of the dimethylglyoxime ligand and is dependent on the axial base ligand. The bands which may be used for partial characterization are ν(O–H···O) (1720–1760 cm^{-1}), ν(N–O) (1230–1240 and 1080–1100 cm^{-1}) and ν(Co–N)(dmgH) (510–520 cm^{-1}).

^{1}H NMR spectra [20]. By virtue of the +3 oxidation state of the metal, organocobaloximes are diamagnetic and have low spin ground state. Therefore, much information about their structure, intramolecular interactions and reactions can be derived from the study of their ^{1}H NMR spectral behaviour. Indeed, up to the present, the use of NMR spectroscopy in research in this field has been extensive.

The ^{1}H NMR spectra of organocobaloximes are generally very simple, the four methyl groups on the equatorial bis(dimethylglyoximato) ligand appear as a sharp 12 H singlet around 2.00–2.40 δ. This, therefore, becomes a very useful tool for identifying the product even in the crude sample. Also, in the reactions of cobaloximes, the appearance or disappearance of the 12 H singlet can be taken as a diagnostic feature for monitoring the reaction.

6.4. Organocobaloxime synthesis: various experimental procedures

A brief experimental outline for the preparation of organocobaloximes by various methods is given below (method I–VI). These methods vary depending upon the substrate cobalt complex used, method of reduction of (Co^{III})/(Co^{II}) to (Co^{I}), sensitivity/reactivity of the alkylating agent and the mode of addition of various substrates. The procedure for the syntheses of two important substrate cobalt complexes is also included (methods VII and VIII).

Caution: Due care must be taken to maintain a near-absolute oxygen free atmosphere in reactions, for which an inert atmosphere is indicated. In addition, the reaction vessel should be kept away from intense light source.

I. From $CoCl_2 \cdot 6H_2O$ by borohydride reduction/ by disproportionation. Cobalt(II) chloride hexahydrate (9.52 g, 40 mmol) and dimethyl glyoxime (9.38 g, 80 mmol) are stirred in methanol (200 ml) for 0.2 h under an inert atmosphere. An aqueous solution of NaOH (80 mmol, *ca.* 5 ml) is added, followed by pyridine* (2.2 ml, 40 mmol). After cooling the mixture to 0–5 °C, a few drops of aqueous NaOH solution (*ca.* 10 mmol) are added followed by solid sodium borohydride (1.51 g, 40 mmol)**. The colour of the solution changes sharply from dark brown to deep blue. An appropriate organic halide (40 mmol) in methanol or ether (10 ml) is added dropwise to the reaction mixture when the colour changes from blue to red or orange–red. The reaction mixture is stirred at room temperature till completion (TLC inference). For most of the preparations the reaction time ranges between 3 and 5 h. However, cases have been reported where the time varies from as low as 5 min to as high as 25 h. Usual work-up by concentrating the solution and pouring it into water (200 ml) containing a few drops of pyridine, affords the cobaloxime. If this proves to be difficult, other work-up procedures as described earlier (Section 6.2) may be tried.

II. From $ClCo^{III}(dmgH)_2Py$ by borohydride reduction. Chloro(pyridine)cobaloxime (7.36 g, 20 mmol) is suspended in methanol (0.50 ml) under an inert atmosphere. After cooling to 0 °C, a few drops of aqueous NaOH solution are added followed by sodium borohydride (1.51 g, 40 mmol) to generate blue (Co^{I}) solution. The rest of the procedure is the same as given under method I above.

Note: (1) Tetrahydrofuran can be employed in place of methanol for base and water sensitive alkylating agents. The reduction is done by adding borohydride only. The reaction time is longer due to non-homogeneity of the reaction medium. (2) For reactive alkylating agents like 3,3,3-triphenyl-1-iodopropane, an alternate addition of a borohydride solution in ethanol and a solution of the halide in benzene affords the desired cobaloxime [141].

III. From cobalt hydride $[H–(Co^{III})]$ and olefin. To a stirred mixture of dimethylglyoxime (5.8 g, 50 mmol), finely powdered NaOH (2.0 g, 50 mmol) and pyridine (2.5 ml, 30 mmol) in methanol (130 ml) is added $Co(ClO_4)_2 \cdot 6H_2O$ (19.5 g, 25 mmol) under a hydrogen atmosphere. After stirring for 5 min, an appropriate olefin (30 mmol) is added and the reaction mixture is stirred till H_2 uptake ceases. The mixture is cooled in ice, diluted with water and stirred for 0.5 h. Filtration and washing with water affords the crude product which is subjected to further purification as described in Section 6.2.

IV. From (Co^{II}) and reactive halide. Cobalt(II) acetate tetrahydrate (0.49 g, 2 mmol), dimethylglyoxime (0.47 g, 4 mmol) and pyridine (0.012 g, 6 mmol) in degassed benzene (10 ml) at 60 °C under an inert atmosphere are mixed with the halide (4 mmol) and an excess of zinc wool (*ca.* 6 mmol). After completion of reaction (1 to 6 h), work-up via column chromatography gives moderate to good yields of the desired cobaloxime.

Note: (1) Normal halides afford a moderate yield of cobaloximes, when stirred with (Co^{II}) in methanol or dichloromethane at room temperature and under inert atmosphere. (2) Instead of generating (Co^{II}) *in situ* as above, one can use $[Co^{II}(dmgH)_2\text{-}Py]_2$ directly.

V. From $ClCo^{III}(dmgH)_2Py$ and Grignard reagent. Appropriate organomagnesium reagent (30 mmol) in tetrahydrofuran (15 ml) is added dropwise to a cooled (<0 °C) suspension of chlorocobaloxime (4.0 g, 10 mmol) in tetrahydrofuran (25 ml) under an inert atmosphere. During addition, the reaction mixture becomes green while on further stirring it turns red–brown (heating is sometimes required to facilitate the reaction). After completion of the reaction, the cooled solution is hydrolyzed with 10% HCl containing ice. The crude product is filtered and purified by Soxhlet extraction with dichloromethane. The concentrated dichloromethane solution is subjected to column chromatography for further purification.

Note: As mentioned earlier, this method is particularly useful for the syntheses of arylcobaloximes.

VI. Modification of equatorial ligand to BF_2 bridge complex. Pyridine (6 ml) is added dropwise to a stirred suspension of cobaloxime (20 mmol) and boron trifluoride etherate (10 ml) in ether (50 ml) under an inert atmosphere. After 48 h of additional stirring, the suspended solids are collected by filtration and recrystallized from acetone. The yields are moderate.

VII. Preparation of chlorobis(dimethylglyoximato)(pyridine)cobalt(III). To a hot solution of

*Pyridine is generally used as the axial base ligand in cobaloxime preparations. However, other bases in the same molar-equivalent can be added.

**In the disproportionation method, an excess of aqueous NaOH solution (100 ml, *ca.* 10 ml) is added to the cooled reaction mixture, instead of sodium borohydride. This results in the disproportionation of (Co^{II}) to (Co^{III}) and (Co^{I}) under such high pH (≏12) conditions.

cobalt(II) chloride hexahydrate (5 g, 21 mmol) and dimethylglyoxime (5.5 g, 47 mmol) in 95% ethanol (200 ml), pyridine (3.5 g, 43 mmol) is added dropwise. After cooling to 20 °C, air is blown through the solution for 0.5 h, and the mixture is then allowed to stand for 1 h. The brown crystals are collected, washed with water, ethanol, ether and dried at ambient temperature *in vacuo* (yield 65%).

Chlorocobaloxime with different base ligands can be prepared by the same method except that the time for air blowing should be varied (*ca.* 1–3 h).

VIII. Preparation of bis(dimethylglyoximato)-(pyridine)cobalt(II) dimer. Cobalt(II) acetate tetrahydrate (4.9 g, 20 mmol), dimethylglyoxime (4.65 g, 40 mmol) and pyridine (0.4 g, 20 mmol) are added to methanol (50 ml) under an inert atmosphere. After stirring for 3 h the dark brown precipitate is filtered under an inert atmosphere, washed with methanol, ether, dried *in vacuo* and then stored under an inert atmosphere in dark coloured bottles (yield 70–85%).

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