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The Structure and Reactivity of Octadehydrocorrins and Corroles

T.A.Melent'eva

The review surveys the chemical properties of corroles, their metal complexes, and the metal complexes of octadehydrocorrins. The reactions of the metal complexes of octadehydrocorrins with electrophiles and nucleophiles, the interconversions of corrinoid compounds, the reactions involving the β,β-double bonds, and the acid-base properties and redox reactions of corrinoid compounds are considered. Problems of the structure of corroles, their metal complexes, and the metal complexes of octadehydrocorrins are discussed.
The bibliography includes 87 references.

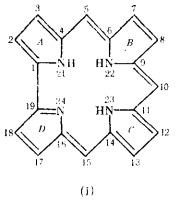
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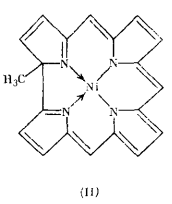
I. INTRODUCTION

Compounds containing the macrocyclic tetrapyrrole systems, which play an important role in biological processes, are presently arousing much interest. Such compounds include the metal complexes of porphyrins and corrins, which constitute the basis of many natural products involved in biocatalytic processes, for example haemin, chlorophyll, vitamin B_{12}, cytochrome *c*, and also the metal complexes of octadehydrocorrins.

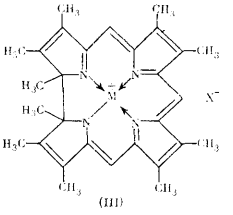
Corroles (I), the nickel complexes of 1-methyloctadehydrocorrins (II), and the metal complexes of 1,19-disubstituted octadehydrocorrins (III) have the steric structure of corrins and the degree of unsaturation of porphyrins, so that the study of their chemical and physicochemical properties makes a significant contribution to the development of the chemistry of tetrapyrrole macrocyclic compounds.



(I)



(II)



(III)

There are no reviews in the literature devoted directly to the chemical and physicochemical properties of octadehydrocorrins and corroles, but some problems have been considered in a review[1] and in a monograph[2] devoted to porphyrins. The present review deals with the available literature data on the chemical and physicochemical properties of corroles, their metal complexes, and the metal complexes of octadehydrocorrins.

II. THE STRUCTURE AND PHYSICAL PROPERTIES OF CORRINOIDS AND THEIR METAL COMPLEXES

1. Corroles

Corroles are crystalline red substances. They contain an aromatic 18π-electron cyclic system, indicated by the intense Soret band (~400 nm) in their absorption spectra, which contain in addition bands in the region of 540, 550, and 600 nm.[3] The mass spectrum of diethylhexamethylcorrole is very close to that of porphyrin and reflects the aromaticity and stability of corrole[4]. The aromatic properties of corroles are also indicated by their ^{1}H NMR spectra, in which the signals of the *meso*-protons are at 8.8–9.4 p.p.m. and those of the imino-protons are at ~–3.5 p.p.m.

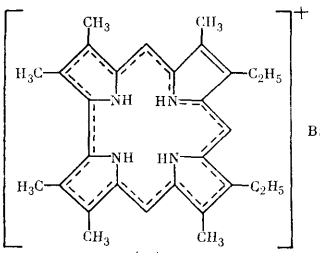
Quantum-chemical calculation of the distribution of π-electron density by the Pariser–Parr–Pople (PPP) method with the parameters of Nishimoto and Forster showed that the highest charge density is at the N atoms, while the π-electron density at the C atoms is enhanced in the 2-, 3-, and 10-positions[5].

The crystal and molecular structures of corrole[6], its hydrobromide (IV),[7] the copper complex of *N*-methylcorrole (Va),[8] the nickel complex of *N*-ethylcorrole (Vb),[9] the triphenylphosphinecobalt(III) complex of corrole (VI),[10] and the rhodium complexes of *N*-methylcorroles, (VII) and (VIII),[11] have not been determined.

8,12-Diethyl-2,3,7,13,17,18-hexamethylcorrole is not exactly planar[6]. Each of the four pyrrole rings is planar, the *A*, *B*, and *C* rings deviate from one another by only 1–3 degrees, while the *D* ring is inclined to the plane of the other rings at an angle of 8–10 degrees. The distances between the N atoms (2.89–2.53 Å) are shorter than in porphyrin (2.90 Å), but the length of three of these (2.89 to 2.66 Å) corresponds to the absence of strain. The N(21)–N(24) distance is 2.53 Å and the steric hindrance between these atoms affects the geometry of the *A* and *D* rings, in which the α,β-bonds are longer than the β,β-bonds. The three inner H atoms lie outside the plane of the macroring and are statistically distributed between the four N atoms[6].

However, quantum-chemical calculation by the PPP method of the bond length and the total π-electron energy of corrole for different dispositions of the inner H atoms shows that the fixation of these atoms in the 21-, 23-, and 24-positions is more probable[12]. The corrole model is asymmetric and has two forms [(+)- and (−)-] in the crystal, where the molecules are arranged in "parallel blocks"[6].

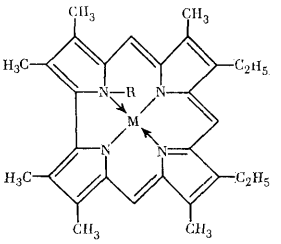
The bromine atom in corrole hydrobromide (IV) [7] is located above the centre of the corrole nucleus at the apex of a pyramid 2.58 Å high with a distorted square base made up of four N atoms. Three H atoms are involved in the formation of hydrogen bonds between the N and Br atoms.



(IV)

(a) R = CH_3, M = Cu

(b) R = C_2H_5, M = Ni



(V, a and b)

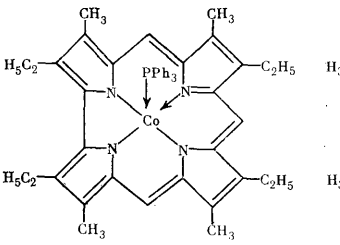
These bonds are non-linear and can bend. Two of them, involving the N(21) and N(23) atoms, are strong, the bond with the N(22) atom is weak, and the N(24)–H bond is directed towards the side away from the Br atom. The corrole system does not have a planar conformation.

The *B* and *D* rings are planar, while the *A* and *C* rings form a dihedral angle of 1–5 degrees along the line passing through the two α-carbon atoms. The N atoms of the *A* and *C* rings are inclined towards the Br atom, while the N atom of the *D* ring is inclined away from the Br atom. This is a result of two opposed effects—the opposite charges on the Br and N atoms and the overloading of the central part of the molecule by the N and H atoms. The *A* and *D* rings deviate in opposite directions, executing a twist around the C(1)–C(19) bond[7].

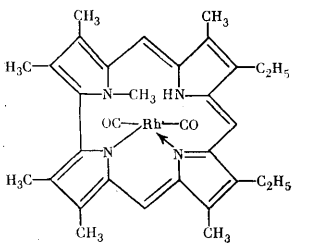
In the copper complex of N(21)-methylcorrole (Va) the *N*-alkylated *A* ring makes an angle of 23° relative to the molecular plane and the ring itself is bent along the line of the α-atoms by 10°, the β,β-bonds in this ring are longer than the α,β-bonds, and the N–CH_3 bond is longer than usual, its length amounting to 1.54 Å.[8]

In the nickel complex of N(21)-ethylcorrole (Vb) the *A* ring is also appreciably displaced from the molecular plane and the N atoms to which the C_2H_5 group is attached is to a large extent sp^3-hybridised[9].

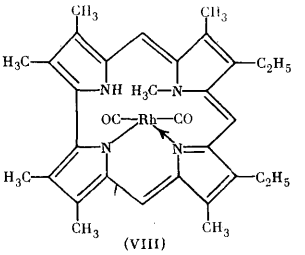
The triphenylphosphinecobalt(III) complex of corrole (VI) is formally a pentacoordinate square-pyramidal complex[10]. The corrole ligand is approximately planar, the N atoms projecting above the molecular plane by ~0.1 Å and the Co atom by 0.38 Å. The average Co–N distance (1.87 Å) is analogous to the corresponding distance in the cobalt complexes of corrins and is somewhat shorter than in porphyrins (1.98 Å). The molecules of complex (VI) have a distorted arrangement in the crystal[10].



(VI)



(VII)



(VIII)

An example of a non-planar complex is provided by the rhodium complexes of corrole (VII) and (VIII) [11] in which the N–CH_3 groups and the bis(dicarbonylrhodium) species are in the *trans*-positions. The pyrrole rings are approximately planar. The rings linked to rhodium are inclined towards it, while the other two rings are displaced in the oppsite direction. The average length of the Rh–N bond is 2.059 Å, being shorter than that of the similar bond in porphyrins (2.084 Å). The Rh...N distance in the *N*-methylated ring is greater by ~0.2 Å. The nitrogen atoms to which the CH_3 substituents are attached are sp^3-hybridised as in the *N*-alkylated copper[8] and nickel[9] complexes.

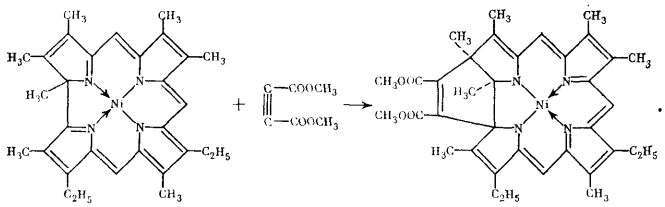
2. Metal Complexes of 1,19-Disubstituted Octadehydrocorrins

The metal complexes of 1,19-disubstituted octadehydrocorrins are high-melting crystalline substances with a violet or dark cherry-red colour. These are salts with a tetragonal-pyramidal structure where the tetradentate heterocyclic octadehydrocorrin system is the equatorial ligand, while the axial ligand (the anion) is at the apex of the pyramid. The cobalt(II) complexes of octadehydrocorrins are low-spin complexes with an unpaired electron in the d_{z^2} orbital of the cobalt atom oriented at right angles to the plane of the macroring[13,14]. The electronic spectra of the metal complexes of octadehydrocorrins contain three main absorption bands in the regions 280–300, 350–365, and 500–580 nm, but do not have a Soret band. The ^{1}H NMR spectra lead to the conclusion that the metal complexes of octadehydrocorrins occupy an intermediate position between those of the aromatic metal complexes of porphyrins and the non-aromatic corrin complexes. The signals of the *meso*-protons of the nickel complexes of octa-alkyl-1,19-dimethyloctadehydrocorrins are at ~7.5 p.p.m.[15], while the signals of the *meso*-protons of the nickel complexes of porphyrins are at ~11 p.p.m.[16] and those of the nickel complexes of corrins are at 5.9–6.4 p.p.m.[17]

3. Nickel Complexes of 1-Alkyloctadehydrocorrins

1-Alkyloctadehydrocorrins are neutral metal complexes. Only the nickel(II) complexes are known. The signals of the *meso*-protons of these complexes are at 6.0–7.0 p.p.m.[18]

1-Alkyloctadehydrocorrins exhibit the properties of unsaturated compounds; they enter into the Diels–Alder reaction with dimethylacetylenedicarboxylate to form the adduct (IX):[2]



(II) (IX)

III. THE ACID–BASE PROPERTIES OF CORRINOIDS AND THEIR METAL COMPLEXES

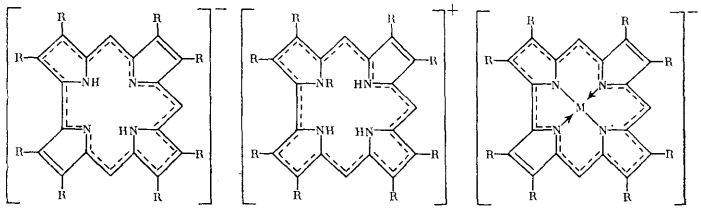
Tetrapyrrole macrocyclic compounds of all kinds react with both acids and bases.

1. The Acid–Base Properties of Corroles and Their Metal Complexes

On treatment with dilute alkali, corroles are converted into the stable aromatic anions (X).[3,19,20] The enhanced acidity of corrole may be explained by the steric hindrance between the imino-hydrogen atoms.

Corroles readily undergo monoprotonation[3,19,20] on treatment with dilute HBr in acetone; the crystalline monobromides formed are aromatic ambident cations (IV) whose charge is delocalised over the macroring[19]. On treatment with concentrated H_2SO_4, CF_3COOH,[3] or FSO_3H,[19,21] corrole is converted into a non-aromatic dication, from which the non-protonated corrole is reformed on treatment with alkali[19]. The ability of corrole to both give up a proton and to combine with one indicates the delocalisation of the free electron pair over all four nitrogen atoms.

N-Alkylcorroles are more basic than the initial corrole. Protonation of the N(21)- and N(22)-methylcorroles takes place when they are merely dissolved in acetic acid with formation of the aromatic monocations (XI).[22] In a 1 M solution of H_2SO_4 in acetic acid, *N*-methylcorroles are converted into dications whose spectra contain the Soret band, which rules out the breakdown of conjugation in the chromophore, but the site of addition of the second proton could not be established.

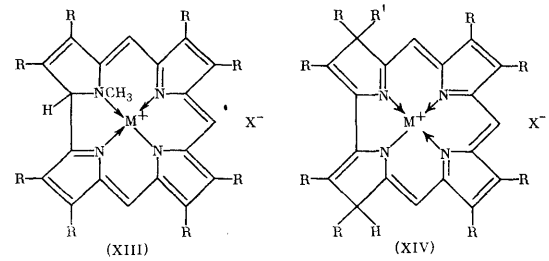


(X) (XI) (XII, a and b), (a) M = Ni; (b) M = Cu

With increasing H_2SO_4 concentration, a third proton adds to the *N*-methylcorrole, apparently at the C(5) atom[22]. The same substance is formed on dissolution of *N*-alkylcorroles in CF_3COOH.[19]

The nickel and copper complexes of corroles are relatively stable[3]. On treatment with alkalies, they are converted into the stable aromatic ambident anions (XII, a and b), whose electronic spectra contain the Soret band[20,23–25].

The nickel complexes of *N*-methylcorroles are protonated in the angular position on dissolution of CF_3COOH with formation of the non-aromatic compound (XIII) whose electronic spectrum is similar to that of the nickel complex of 1-methyloctadehydrocorrin[9,26]. The protonation of the palladium complexes of N(21)-alkylcorroles takes place analogously[27].



(XIII) (XIV)

M = Ni, Pd

Angular protonation of the nickel and palladium complexes of 3,3-dialkylcorroles, which causes the breakdown of the conjugation chain, is less favourable than the *N*-protonation[26–29] and on dissolution of the nickel complexes of 3,3-dialkylcorroles in CF_3COOH, the proton adds to the 17-position with formation of the complex (XIV).[26,29] The protonation of the palladium complexes of 3,3-dialkylcorroles takes place analogously[27,28].

The pyridinium salt of the palladium complex of corrole is diprotonated in CF_3COOH in the 3- and 17-positions, which results in the formation of the complex (XIV), where R′ = H.[27]

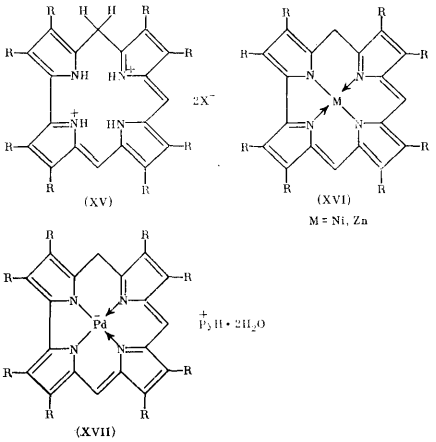
Treatment of a solution of the square-planar cobalt(III) complex of corrole or any other pentacoordinate derivative with HBr in acetone leads to the formation of a green crystalline paramagnetic hydrobromide in which the protonation site has not been established[30]. When $HClO_4$ is added to a solution of Co-corrole in tetrahydrofuran (THF), the monoprotonated Co-corrole is formed, whose electronic spectrum resembles that of Ni-corrole[13]. The protonation of Co-corrole is reversible and the addition of pyridine results in the formation of the non-protonated pyridinecobalt(III) complex of corrole[30].

2. The Interaction of Corroles with Metals

The free bases of corroles readily react with metal cations to form metal complexes. Corrole is a tetradentate ligand, where three out of the four N atoms are linked to hydrogen atoms capable of being substituted. In the formation of metal complexes of corroles, all three, two, or one hydrogen atoms are substituted by the metal depending on the nature of the latter.

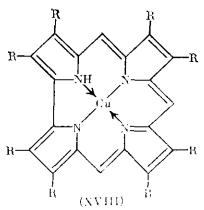
When corrole is treated with solutions of nickel, copper, zinc, and palladium salts[3,27] in the presence of bases, only two hydrogen atoms are substituted by the metal and the products are metal complexes of corroles derived from the non-aromatic base corresponding to the dication (XV),[3,9,26,27] the third hydrogen atom passing to one of the carbon atoms of the macroring and disrupting the aromatic conjugation system of corrole[21]. Its location at C(10) [27,31] or C(5) [21]

has not been finally established. Structure (XVI) is more probable. The palladium complex has been isolated as the dihydrate of the pyridinium salt (XVII), which is formed when corrole is treated with $(CH_3COO)_2Pd$ in pyridine[27].



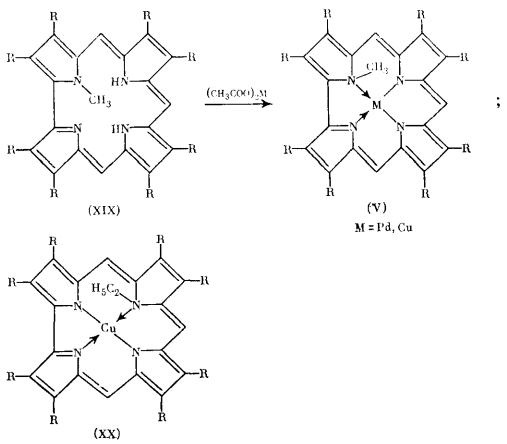
(XV) (XVI) (XVII)

The visible spectra of the copper complexes differ from those of the nickel and palladium complexes and are analogous to the spectra of the copper complexes of N(21)-methylcorroles, indicating at the same time the retention of the conjugated system of the macroring. Structure (XVIII), where the "extra" hydrogen is located at the N(21) atom, was therefore proposed for the copper complexes of corroles[21].



(XVIII)

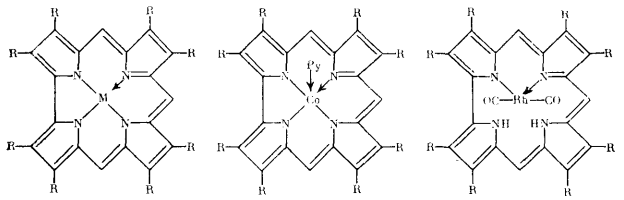
N-Alkylcorroles readily react with metal salts. Treatment of N(21)-methylcorrole (XIX) with $(CH_3COO)_2Pd$ or $(CH_3COO)_2Cu$ yielded the palladium and copper complexes of N(21)-methylcorrole [compounds (V)].[21,27,28] The copper complex of N(22)-ethylcorrole (XX) was obtained analogously by the reaction of $(CH_3COO)_2Cu$ with N(22)-ethylcorrole[21,27,28]:



(XIX) (V) (XX)

The reaction of zinc salts with *N*-alkylcorroles leads to the formation of unstable products[28], while nickel salts do not react with *N*-alkylcorroles[9,28]. The interaction of N(21)-alkylcorroles (XIX) with the perchlorate of the hexamethylnickel cyanide complex leads to the formation of the corresponding nickel complex (V, M = Ni).[9] The metal complexes of *N*-alkylcorroles are aromatic: the signals of their *meso*-protons in the ^1H NMR spectra are at 9.0–9.3 p.p.m.[9,27]

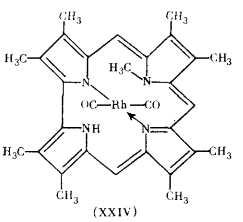
When an attempt is made to insert bivalent cobalt into N(21)-methylcorrole (XIX), the methyl group is split off and all three imino-protons are substituted by the metal with formation of the cobalt(III) complex of the *N*-unsubstituted corrole (XXI).[21,30] The complexes (XXI) are square-planar paramagnetic compounds. When corrole is treated with $(CH_3COO)_2Co$ in the presence of pyridine, purple prismatic crystals of the pentacoordinate pyridinecobalt(III) complex of corrole (VIa) are formed[30]; the latter readily splits off pyridine on treatment with hot methanol[3] and is converted into the planar tetracoordinate complex (XXI).[30] The pentacoordinate complexes (VI) are also formed in the presence of $(C_6H_5)_3P$ and p-$CH_3C_6H_4NC$.[30]



(XXI), (XXII), M = Co, Fe (VIa) (XXIII)

A crystalline paramagnetic iron(III) complex of corrole (XXII) has been synthesised by treating the corrole anion (X) with $FeCl_3$.[30]

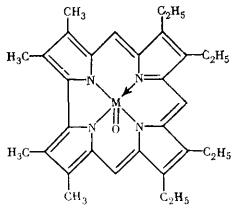
Rhodium complexes of corroles have been obtained quite recently[11,32,33]. The interaction of corrole with $RH_2(CO)_4Cl_2$ leads to the formation of the monorhodium complex of corrole (XXIII). The reaction of N(21)-methylcorrole (XIX) with $Rh_2(CO)_4 \cdot Cl_2$ in chloroform containing CH_3COONa leads to the formation of the complex (VII).[11]



(XXIV)

On interaction with an excess of $Rh_2(CO)_4Cl_2$ at room temperature, N(22)-methylcorrole gives rise to a mixture of the complex (VIII) and (XXIV), the complex (VIII) being converted into the complex (XXIV) on standing. The molybdenum and chromium complexes of corrole have been synthesised after the discovery of superconducting materials[34] in an attempt to obtain an electrical conductor in the form of metal complex species with a metal–metal bond stacked one on top of the other. When corrole was allowed to interact with $MoCl_5$ or $Mo(CO)_6$ at 170–180 °C in nitrogen, the complex (XXV) was obtained. It is a monomeric pentacoordinate oxomolybdenum complex with an axial disposition of the oxygen atom[35]. Its symmetry is close to that of a tetragonal pyramid. In the electronic spectrum there is a Soret band. The EPR spectra indicate a π-bonding interaction between the Mo and O atoms.

There is a considerable contribution of the π-interaction in the plane of the macroring between the Mo atom and the electron-donating N atom; the coordinate bonds have a high degree of covalence[34].

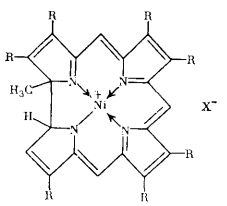


(XXV), (XXVI), M = Mo, Cr

The oxochromium complex (XXVI) has been synthesised by treating corrole with $CrCl_2$ in dimethylformamide (DMF) in the presence of sodium acetate[36]. This is an N_4O-pentacoordinate complex with a symmetry close to that of a tetragonal pyramid[37]. The unpaired electron is in the $3d_{xy}$ orbital of chromium and there is a strong interaction between this orbital and the σ and/or π orbitals of the macroring[36].

3. Protonation of the Metal Complexes of Octadehydrocorrins

The nickel(II) complexes of 1-methyloctadehydrocorrins are effective electron donors and, on treatment with strong acids ($HClO_4$, CF_3COOH, FSO_3H), they are protonated in the 19-position with formation of salts of the nickel complexes of 1-methyloctadehydrocorrins (XXVII);[18,21,38–41] the corresponding perchlorate has been isolated in a crystalline form[39]. The protonation of 1-methyloctadehydrocorrins is reversible and treatment of the salts (XXVII) with alkali results in the reformation of the initial complexes of 1-methyloctadehydrocorrins.



(XXVII)

The metal complexes of 1,19-dimethyloctadehydrocorrins are capable of being protonated in a strongly acid medium[42]. When nickel and cobalt complexes of octadehydrocorrins are dissolved in concentrated sulphuric acid, a proton apparently adds to N(21) or N(24) with formation of an intramolecular hydrogen bond. In addition, the protonated form is probably a radical-cation, which is indicated by the intense absorption at 690 nm, characteristic of the free radicals of cyanonickel complexes of octadehydrocorrins[43]. The protonation of metal complexes of octadehydrocorrins is reversible and dilution of their sulphuric acid solutions with water leads to the reformation of the initial complexes[42].

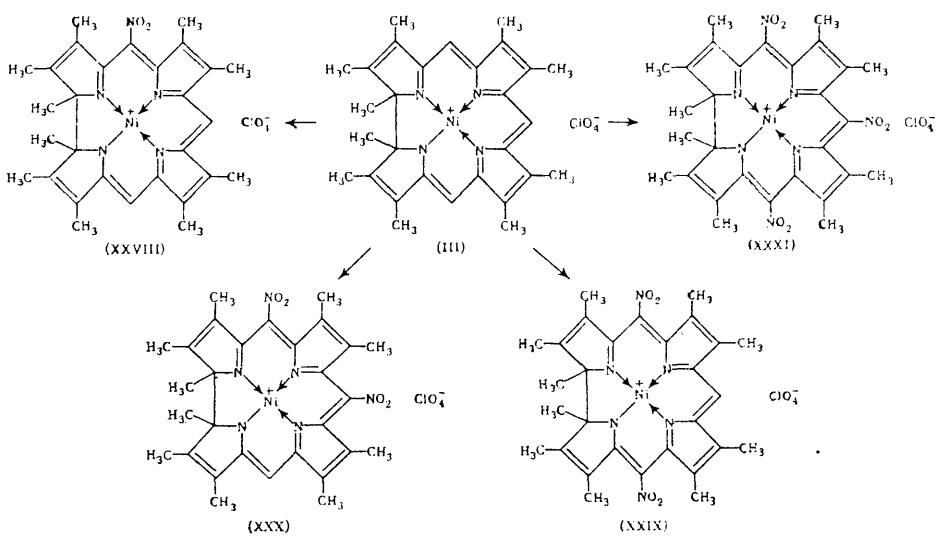
4. Deuterium Exchange

Corrinoid systems of all types are capable of deuterium exchange. Corroles exchange rapidly all three *meso*-hydrogen atoms for deuterium in CD_3COOD.[3] The exchange of all the *meso*-hydrogen atoms of 3,17-diethoxycarbonyl-8,12-diethyl-2,7,13,18-tetramethylcorrole in a mixture of CF_3COOD and $CDCl_3$ at room temperature takes place over a period shorter than 10 min.[19,44,45] The half-exchange period for the proton in the 10-position in the nickel complex of octa-alkyl-1-methyloctadehydrocorrins in CF_3COOD at 35 °C is 15 min, while that for the proton in the 5-position is 11–15 min.[40] In the presence of free β-positions in the octadehydrocorrin macroring, the β-proton exchanges for deuterium[29]. The nickel complex of hexa-alkyl-1,19-dimethyloctadehydrocorrin in CF_3COOD apparently exchanges the *meso*-hydrogen atoms as well as the β-hydrogen atoms.

IV. REACTIONS WITH ELECTROPHILES AND NUCLEOPHILES

1. Electrophilic Substitution Reactions

In the metal complexes of octadehydrocorrins the equatorial ligand is the tetrapyrrole macroring containing an extensive system of conjugated C=C and C=N bonds. The presence of this system is responsible for the ability of these compounds to react with electrophiles.

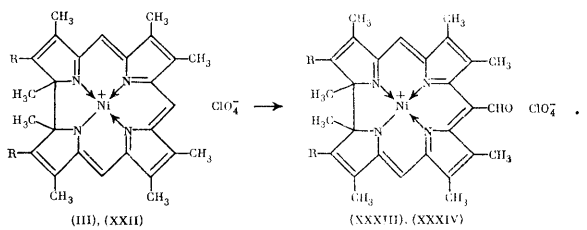


(XXVIII) (III) (XXXI)

(XXX) (XXIX)

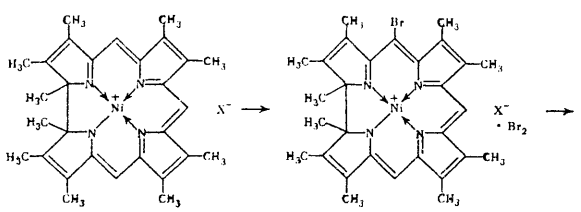
The nickel complexes of octadehydrocorrins are readily nitrated. Treatment of the nickel complex of decamethyl-octadehydrocorrin (III) with fuming HNO_3 and urea at 0 °C yielded the perchlorate of the nickel complex of 5-nitro-octadehydrocorrin (XXVIII).[46] The 5-nitro-derivative is also formed on treatment of the nitrate of the nickel complex of 8,12-diethyl-1,2,3,7,13,17,18,19-octamethyloctadehydro-corrin with $Cu(NO_3)_2$ in acetic anhydride[43,47]. Treatment of the complex (III) with the 1 : 1 mixture of fuming HNO_3 and concentrated H_2SO_4 at 0 °C leads to the formation of a mixture of the perchlorates of the nickel complexes of the 5,10-dinitro derivative (XXIX) and the 5,15-dinitro derivative (XXX). Under more severe conditions, in the 1 : 1 mixture of HNO_3 and oleum, the nickel complex of 5,10,15-trinitro-octadehydrocorrin (XXXI) was isolated[46].

The nickel complexes of octadehydrocorrins readily undergo the Vilsmeier reaction, which takes place more readily with aromatic compounds having an enhanced activity with respect to electrophilic substitution. When the perchlorates of the nickel complexes of decamethyloctadehydrocorrin and octa-methyloctadehydrocorrin (XXXII) in boiling $CHCl_3$ are treated with $POCl_3$ and DMF, the nickel complexes of the corresponding 10-formyloctadehydrocorrins (XXXIII) and (XXXIV) are formed[48], their formyl groups readily forming bisulphite derivatives.



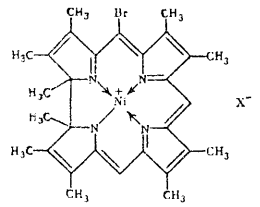
(III), (XXII) (XXXIII), (XXXIV)

Depending on the reaction conditions, the halogenation of the salts of the nickel complexes of octadehydrocorrins leads to the formation of mono- or di-halogeno-derivatives. When the perchlorate and nitrate of the nickel complex of deca-methyloctadehydrocorrin (III, a and b) are treated with bromine in acetic acid, the perchlorate and bromide of the nickel complexes of 5-bromo-octadehydrocorrin (XXXV, a and b) are formed[49], i.e. the substitution reaction is accompanied by the replacement of the NO_3^- anion by the Br^- anion. The two compounds (XXXV, a and b) contain two additional Br atoms, which are not substituents in the macro-ring and are readily removed on treatment with acids or bases with formation of the complexes (XXXVI, a and b):



(III, a and b)
X = ClO_4, NO_3

(XXXV, a and b)
X = ClO_4, Br

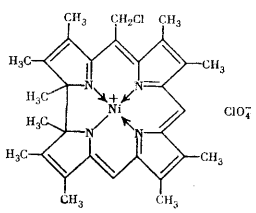

(XXXVI, a and b)

The bromination of the nickel complexes of octadehydro-corrins with bromine in $CHCl_3$ [49] or $C_2H_4Cl_2$ [43] yielded the nickel complexes of 5,10-dibromo-octadehydrocorrins; when hydroquinone was added, 5-bromo-octadehydrocorrin was isolated. The chlorination of the nickel complex of deca-alkyloctadehydrocorrin with chlorosuccinimide leads to the formation of the *meso*-dichloro-derivative[43]. Bromination with Br_2 in acetic acid is an electrophilic substitution reaction, while bromination with Br_2 in $CHCl_3$ and $C_2H_4Cl_2$ and chlorination with chlorosuccinimide takes place via a radical mechanism, i.e. electrophilic halogenation leads to the formation of 5-halogeno-derivatives, while radical halogenation results in the formation of 5,10-dihalogeno-derivatives.

The halogens in the *meso*-positions in octadehydrocorrins are readily substituted by hydrogen in the presence of traces of acid[43]. The debromination of the nickel complex of 5-bromo-octadehydrocorrin (XXXV) takes place when it is dissolved in nitromethane, apparently via the following reaction[49]:

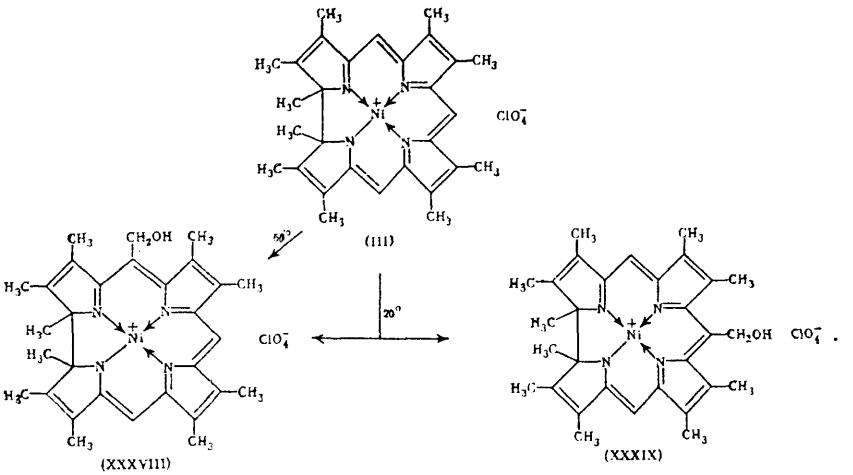
$$\text{C}{-}\text{Br} + CH_3NO_2 \rightarrow \text{C}{-}\text{H} + CH_2BrNO_2 \ .$$

The nickel complexes of octadehydrocorrins readily undergo the chloromethylation reaction, which consists in the direct substitution of hydrogen by the CH_2Cl group on treatment with paraformaldehyde and concentrated HCl in glacial acetic acid. The chloromethylation of the nickel complex of decamethyloctadehydrocorrin led to the isolation of the nickel complex of 5-chloromethyloctadehydrocorrin (XXXVII), i.e. the product of the introduction of one CH_2Cl group into the octadehydrocorrin macroring[50].

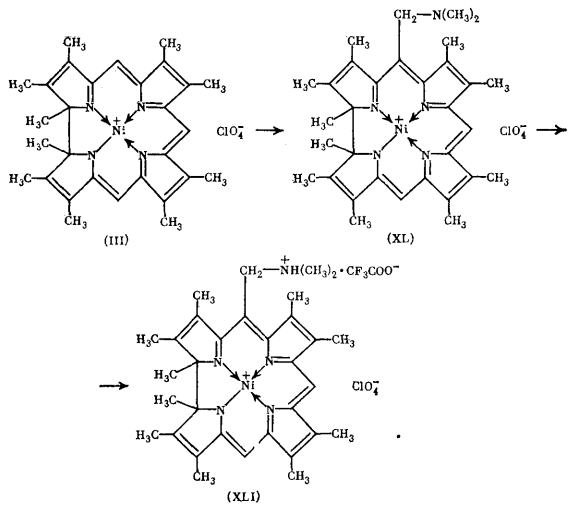


(XXXVII)

Treatment of the nickel complex of decamethyloctadehydro-corrin with paraformaldehyde in glacial acetic acid leads to the formation of the mono-*meso*-hydroxymethyl derivatives (XXXVIII) and (XXXIX).[50] The mode of reaction depends on temperature: the 5-hydroxymethyl derivative (XXXVIII) is formed at 50 °C, while at room temperature there are two products: 5-hydroxymethyloctadehydrocorrin (XXXVIII) and 10-hydroxymethyloctadehydrocorrin (XXXIX):



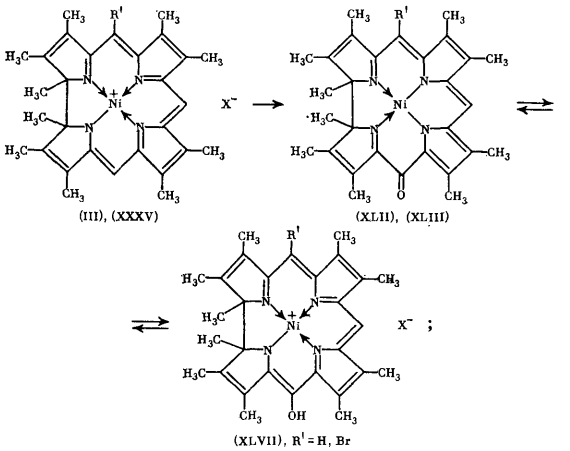
The reaction of the perchlorate of the nickel complex of decamethyloctadehydrocorrin with formaldehyde and dimethylamine in alcohol yielded the nickel complex of 5-dimethylaminomethyloctadehydrocorrin (XL), which is protonated in CF_3COOH and converted into the perchlorate of the nickel complex of decamethyloctadehydrocorrin (XLI) containing the $CH_2^+NH(CH_3)_2.CF_3COO^-$ substituent:[51]



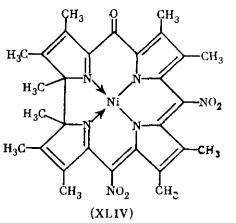
2. Reactions with Nucleophiles

The positive charge in salts of the metal complexes of octadehydrocorrins is not fixed at the central metal atom but is delocalised over the octadehydrocorrin macroring[21]. The delocalisation has a major influence on the chemical behaviour of octadehydrocorrins. In particular, the cationic forms of the nickel complexes of octadehydrocorrins are very sensitive to attack by nucleophiles.

The salts of the nickel complexes of octadehydrocorrins are converted into neutral oxo-complexes on treatment with bases in air[21,43,49,52]. When the nickel complex of decaalkyloctadehydrocorrin, for example, compound (III), was treated with an aqueous solution of NaOH, an excess of $(C_2H_5)_3N$, or CH_3Li in moist THF,[43] the nickel complex of 5-oxo-octadehydrocorrin (XLII) was obtained.

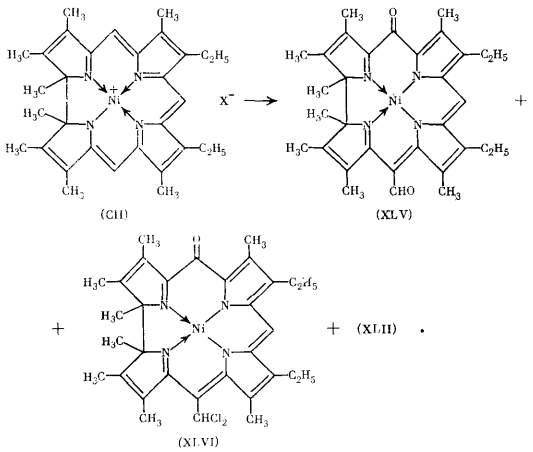


The reaction of the nickel complex of 5-bromo-octadehydrocorrin (XXXV) with a 5% NaOH solution in 30% H_2O_2 leads to the nickel complex of 5-bromo-15-oxo-octadehydrocorrin (XLIII).[49]



Nitration of the nickel complex of decamethyloctadehydrocorrin with a mixture of fuming HNO_3 and glacial acetic acid at 0 °C yielded the nickel complex of 10,15-dinitro-5-oxo-octadehydrocorrin (XLIV),[49] while the addition of an aqueous NaOH solution to a chloroform solution of the nickel complex (CII) at room temperature led to the isolation, together with the nickel complex of 5-oxo-octadehydrocorrin (XLII), of the complexes of 15-formyl-5-oxo-octadehydrocorrin (XLV) and

15-dichloromethyl-5-oxo-octadehydrocorrin (XLVI):[43]

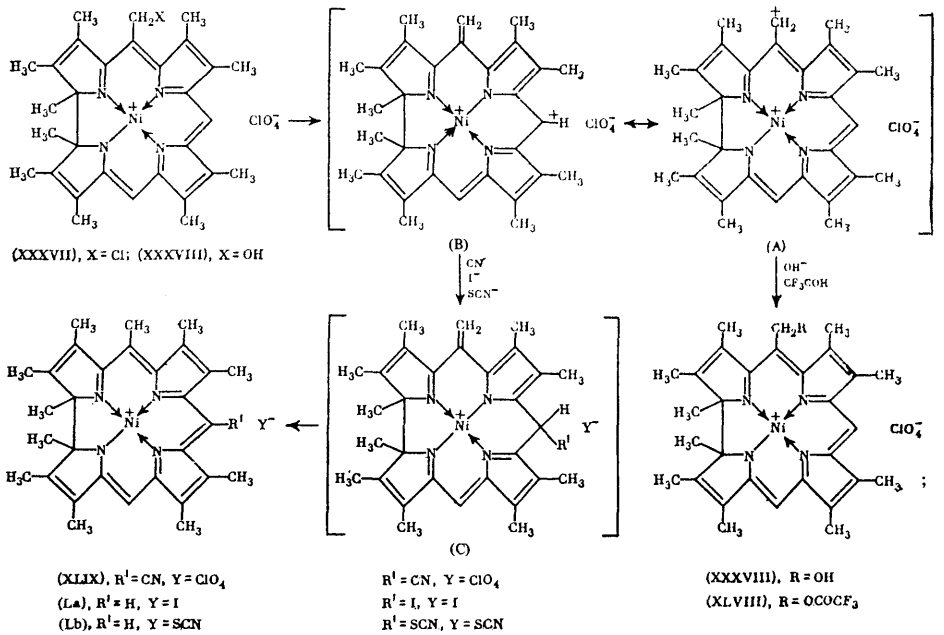


The conversion of the salts of the nickel complexes of octadehydrocorrins into neutral 5-oxo-derivatives probably proceeds as follows: initially the nucleophile adds on and the carbanion is formed, the latter being oxidised by atmospheric oxygen to the neutral nickel complex of oxo-octadehydrocorrin. The presence of electron-accepting substituents in octadehydrocorrin macrorings facilitates this reaction. In contrast to the nickel complexes, the cobalt complexes of octadehydrocorrins with electron-accepting substituents in the macroring are readily converted into cobalt(I) derivatives on treatment with bases. A whole series of oxo-complexes of substituted octadehydrocorrins, containing the $CHCl_2$, Br, CN, CHO, NO_2, and NH_2 groups in the *meso*-positions, have been obtained. The nitro-groups in the oxo-complexes are readily split off in an acid medium[43].

The oxo-group in the nickel complexes of octadehydrocorrins does not exhibit certain properties characteristic of this group. Thus, it has not been possible to convert the nickel complexes of oxo-octadehydrocorrins into the enolic forms[40]. However, when these compounds are dissolved in CF_3COOH, they are *O*-protonated with formation of hydroxy-forms, which could not be isolated. The hydroxy-complex (XLVII) is converted into the oxo-form on treatment with alkali[43,49].

The nickel complexes of octadehydrocorrins with the CH_2OH and CH_2Cl groups in the 5-position exhibit a dual reactivity in reactions with nucleophiles[51,53]. When the nickel complex of 5-chloromethyloctadehydrocorrin (XXXVII) was refluxed with a NaOH solution in alcohol, the nickel complex of 5-hydroxymethyloctadehydrocorrin (XXXVIII) was isolated and treatment with CF_3COOH resulted in the nickel complex of 5-trifluoroacetoxymethyloctadehydrocorrin (XLVIII). The reactions of the nickel complexes of 5-chloromethyl-octadehydrocorrin and 5-hydroxymethyloctadehydrocorrin (XXXVIII) with KCN, KI, and KSCN proceed differently. When the nickel complexes of 5-hydroxymethyl- (XXXVIII) and 5-chloromethyl-octadehydrocorrins were treated with a solution of KCN in aqueous alcohol at room temperature, the nickel complex of 10-cyano-1,2,3,5,7,8,12,13,17,18,19-undecamethyloctadehydrocorrin (XLIX) was isolated in both cases, i.e. the reaction with the CN^- anion proceeds with transfer of the reaction centre. When the complexes (XXXVII) and (XXXVIII) were treated with KI or KSCN, the nickel complex of undecamethyloctadehydrocorrin (L, a and b) was isolated as the iodide or thiocyanate respectively[53]:

The following reaction mechanism has been proposed: the heterolysis of the C–X bond results in the formation of an ambident cation, whose stability is enhanced owing to the redistribution of electron density as a result of the delocalisation of the positive charge over the π-electron system of the macroring. The resonance structures of the carbonium ion (A) and (B) are possible. The addition of the nucleophile to the CH_2^+ group results in the formation of the CH_2X derivative and attack on the *meso*-carbon atom produces the intermediate compound (C), which is converted into a 10-substituted 5-methyloctadehydrocorrin after the migration of the proton from the *meso*-position to the methylene group. The *meso*-iodo- and *meso*-thiocyanato-derivatives readily lose

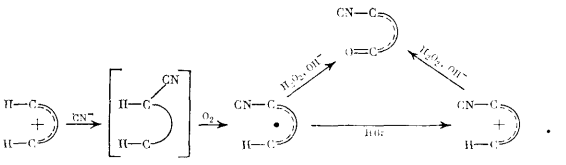


these substituents, being converted into undecamethyloctadehydrocorrin (L, a and b). The nature of the nucleophile determines the mode of reaction. This behaviour has been interpreted[51,53] on the basis of the principle of the hard and soft acids and bases (HSAB).[54,55] The CH_2^+ reaction centre formally corresponds to a hard acid, since there is a smaller possibility of the delocalisation of the charge on the primary carbon atom and, according to the HSAB principle, it should be coordinated preferentially to hard bases, i.e. OH^- and CF_3COO^-, while the reaction centre at the *meso*-carbon atom can be regarded as a soft acid which reacts preferentially with CN^-, I^-, and SCN^-.

The cationic forms of the nickel complexes of octadehydrocorrins exchange anions in the course of the reactions of the perchlorates of the nickel complexes (XXXVII) and (XXXVIII) with KSCN and KI. When the complexes (L, a and b) are dissolved in CF_3COOH, I^- and SCN^- are replaced by the CF_3COO^- anion.

The oxidation of the nickel complexes of octadehydrocorrins to the oxo-complexes on treatment with nucleophiles is sometimes accompanied by a nucleophilic substitution reaction. Several instances of nucleophilic substitution without the oxidation of the macroring are also known. When the nickel complexes of 5,10-dibromo- and 5,10-dichloro-octadehydrocorrins are treated with CH_3Li in moist THF, the formation of the oxo-complexes is accompanied simultaneously by the nuclophilic exchange of the halogens for hydrogen, while on treatment with $LiCu(CH_3)_2$ the complexes are converted into 5,10-dimethyloctadehydrocorrins[38].

The interaction of the nickel complexes of *meso*-unsubstituted octadehydrocorrins with KCN in CH_3OH leads rapidly to the formation of three products: the neutral 15-cyano-5-oxo-octadehydrocorrin and the free radicals of 5-cyano- and 5,15-dicyano-octadehydrocorrins[56,57], whose unpaired electron is delocalised over the macroring. Treatment of the radical of 5-cyano-octadehydrocorrin with HBr yielded the bromide of the nickel complex of 5-cyano-octadehydrocorrin. The oxidation of this complex with an alkaline solution of hydrogen peroxide led to the formation of the nickel complex of 5-cyano-15-oxo-octadehydrocorrin:



Treatment of the radical of dicyano-octadehydrocorrin with $HClO_4$ converts it into the perchlorate of the nickel complex of dicyano-octadehydrocorrin. This salt can be readily converted into a radical when it is chromatographed on Al_2O_3. The introduction of the cyano-group and oxidation of the salt of the nickel complex of 5-cyano-octadehydrocorrin leads to the formation of a dicyano-octadehydrocorrin radical and then a salt of the nickel complex of 5,15-dicyano-octadehydrocorrin[56,67].

V. ALKYLATION OF CORRINOIDS AND THEIR METAL COMPLEXES

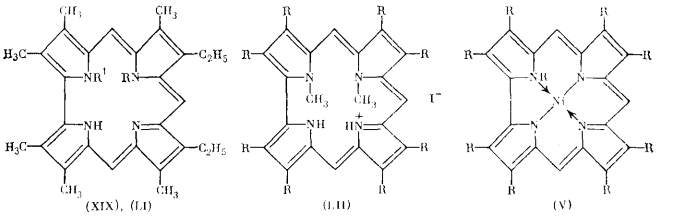
1. Alkylation of Corroles and Their Metal Complexes

Corrinoid macrocyclic compounds of all types undergo the alkylation reaction, but for each type of compound the reaction proceeds differently.

The alkylation of corroles and their metal complexes takes place at the nitrogen atoms. The reaction of the corrole anion, formed in the presence of K_2CO_3, with alkyl halides leads to the formation of a mixture of N(21)-alkylcorroles (XIX) and N(22)-alkylcorroles (LI), where R or R′ = CH_3, C_2H_5, $CH_2CH{=}CH_2$, or $(CH_3)_2C{=}CH_2$.[3,9,19,28] The N(21)-isomers are formed preferentially. In the absence of bases, alkylation does not occur. In the methylation of corrole having the $COOC_2H_5$ substituents in the 3- and 17-positions, the deactivating influence of these groups leads to the preferential formation of N(22)-methylcorrole[45].

(N(21)-Alkylcorroles are more stable than N(22)-alkylcorroles. Both isomers are aromatic and their electronic spectra contain the Soret band[28]. *N*-Alkylation increases the basicity of corroles, N(21)-methylcorroles being less basic than the N(22)-isomers: the relative acid dissociation constants of the monocations of N(21)- and N(22)-methylcorroles are 0.35 and 1.28 respectively[22].

The methylation of *N*-methylcorroles under severe conditions, for example treatment of N(21)- and N(22)-methylcorroles with CH_3I in sealed tubes (for 15 h at 100 °C) leads to the formation of N(21), N(22)-dimethylcorrole (LII), which was isolated as the iodide.

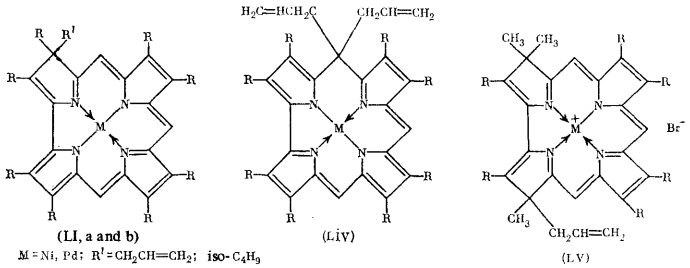


The *trans*-disposition of the *N*-alkyl groups in *N*,*N*-dialkylcorroles was demonstrated in a study of the optical rotation of a D-camphor-10-sulphonate salt[28]. The free base could not be obtained from the salt (LII). Under the same conditions, the *N*-unsubstituted corrole is also converted into *N*,*N*-dimethylcorrole and the *N*-monomethylcorrole was not isolated. Thus the rate of introduction of the second CH_3 group is higher than that of the first, i.e. *N*-alkylcorroles are more nucleophilic and basic than the *N*-unsubstituted corrole. The N(21), N(22)-dimethylcorrole salt (LII) is thermally unstable and on heating in boiling $C_6H_4Cl_2$ is converted into N(21)-methylcorrole[19]. The increased basicity of *N*,*N*-dialkyl-substituted macrocyclic compounds is a common property of corroles and porphyrins[58].

The acetylation of corroles takes place analogously to their alkylation[19]. When corrole is refluxed with acetic anhydride, N(21)-acetylcorrole is formed, its electronic spectra differing from the spectra of N(21)-alkylcorrole by the bathochromic shift of the absorption bands. The infrared spectrum of *N*-acetylcorrole has an absorption band at 1709 cm^{-1}, whose position indicates the absence of conjugation of the CO group with the chromophore of the macrocyclic compound. On an Al_2O_3 column or on treatment with NaOH, *N*-acetylcorrole is converted into *N*-unsubstituted corrole[19].

The nickel complexes of corrole anions also readily react with alkyl halides, which results in the formation of aromatic and diamagnetic N(21)-alkyl derivatives (V) whose additional alkyl group is shielded (τ = 12.6) and the molecule has no symmetry plane[9,23,26]. The reaction of the nickel complex of the corrole anion with $CH_2{=}CHCH_2Br$ leads to the formation of a mixture of the complexes of 3-alkyl-3-allylcorrole (LIII) and 5,5-diallylcorrole (LIV).[9,23,26] The nickel complex of 3-allyl-3-methylcorrole is apparently formed from the *N*-allyl

derivative via a [1,5]- or [3,3]-sigmatropic rearrangement. After the alkylation of the nickel complex with $(CH_3)_2C=CHCH_2Br$, triallylcorrole and *meso*-diallylcorrole (LIV) were isolated in addition to the 3-allyl derivative. The *meso*-derivative is not a product of the rearrangement of 3-allylcorrole, since the latter does not rearrange. The reaction of the nickel complex of corrole with isobutyl iodide leads to the formation of the 3-isobutyl derivative (LIIIb). This mode of reaction with $CH_2=CHCH_2Br$ and iso-C_4H_9I is probably due to steric factors[9].

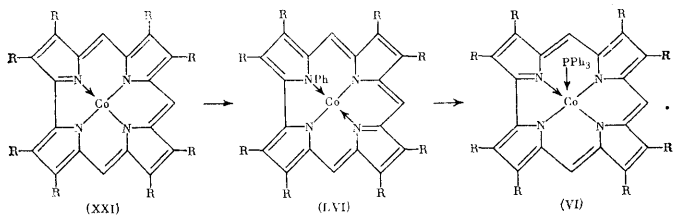


The alkylation of the nickel complex of 3,3-dialkylcorrole (LIII) with $CH_2=CHCH_2Br$ or $C_6H_5CH_2Cl$ takes place in the 17-position with formation of the salt (LV).[9]

The methylation of the pyridinium salt of the palladium complex of corrole (XVII) with CH_3I in boiling acetone in the presence of NaOH results in the formation of N(21)-methylcorrole (V, M = Pd) and 3,3-dimethylcorrole (LIII). The alkylation of the palladium complex of 3,3-dialkylcorrole with $CH_2=CHCH_2Br$ yields the palladium complex of 3,3,17-trialkyl-17-allylcorrole (LV).[27]

The alkylation of the copper complexes of corroles leads to the formation of the N(21)-alkyl derivatives[8,27,28], which split off the *N*-alkyl group on heating in 1-chloronaphthalene[27].

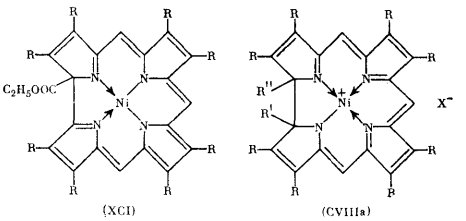
Treatment of a solution of the cobalt(III) complex of corrole (XXI) in THF with C_6H_5MgBr or C_6H_5Li results in the formation of the green crystalline cobalt(II) complex of N(21)-phenylcorrole (LVI).[30] The *N*-*p*-tolyl derivative was obtained in the same way.



Arylated Co-corroles are paramagnetic and non-planar. They are stable in the light both in the solid state and in solutions and do not form pentacoordinate cobalt(III) complexes of corroles on heating with pyridine or triphenylphosphine. The aryl group is split off at 130 °C and the resulting Co-corrole has been isolated in the form of the triphenylphosphine complex (VI). The attempts to obtain the N(21)-alkyl derivatives by alkylating Co(III)-corroles with alkylmagnesium bromide or alkyl-lithium were unsuccessful[30].

2. Alkylation of Metal Complexes of Octadehydrocorrins

The metal complexes of octadehydrocorrins also undergo the alkylation reaction. The alkylation of the nickel complexes of 1-methyloctadehydrocorrins by alkyl halides takes place in the 19-position with the formation of salts of the nickel complexes of 1,19-dialkyloctadehydrocorrins[18,21,38,40]. The CH_3, C_2H_5, n-C_3H_7, $CH_2=CHCH_2$, and $C_6H_5CH_2$ substituents have been introduced in this way into the 19-position[18]. Although the 19-position is not the usual reaction centre for electrophilic reactions, substituting in the 19-position in 1-methyloctadehydrocorrins causes the minimum interference with the conjugation of the system in the transition state. The alkylation of the nickel complexes of 1-ethoxycarbonyloctadehydrocorrins (XCI) also takes place in the angular position and leads to the formation of the nickel complexes of 19-alkyl-1-ethoxycarbonyloctadehydrocorrins (CVIIIa). The 19-methyl-,[59] alkyl-, and 19-(3,3-dimethylallyl)-derivatives[29] have been obtained in this way.



Since the cobalt complexes of 1-methyloctadehydrocorrins have not been isolated, their alkylation has been scarcely investigated. However, treatment of a solution of the cobalt complex of 1-methyloctadehydrocorrin with CH_3I in an inert gas atmosphere results in the formation of the 1,19-disubstituted derivative[2].

The methylation of the nickel complexes of 1,19-dimethyloctadehydrocorrins takes place in the *meso*-position but only to a slight extent. The methylation of the nickel complex of octa-alkyl-1,19-dimethyloctadehydrocorrin with CH_3I in the presence of $SnCl_4$ leads to the formation of the 5-methyl derivative in 6% yield [47].

Reductive methylation has been used to introduce the CH_3 group into the *meso*-position in the octadehydrocorrin macroring, which results in the formation of 10-methyloctadehydrocorrin (LVII).[60] The reductive methylation of salts of the nickel complexes of octadehydrocorrin (III) takes place as follows. On treatment with CH_3I in the presence of sodioanthracene in anhydrous THF in an inert gas atmosphere, the CH_3 group enters the 10-position with the simultaneous opening of the macroring and the formation of the nickel complex of undecamethylbiladiene (LVIII), the anthracene radical-anion functioning as an electron transferring agent in this reaction and participating in the formation of the anionic form $(III)^-$:

$$(III) + 2NaC_{14}H_{10} \rightarrow Na^+(III)^- + 2C_{14}H_{10} + NaI \ .$$

After the addition of CH_3I, the complex (LVIII) is formed:

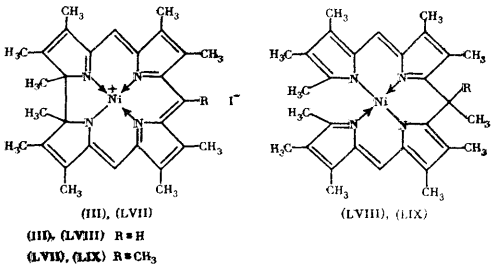
$$Na^+(III)^- + CH_3I \rightarrow (LVIII) + NaI \ .$$

The oxidation of this complex leads to the formation of the cyclic system (LVII):

$$(LVIII) + I_2 \rightarrow (LVII) + 2HI \ .$$

Repeated reductive methylation of undecamethyloctadehydrocorrin (LVII) again leads to the addition of the CH_3 group in the 10-position and ring opening with formation of

the complex (LIX), which does not cyclise into the nickel complex of octadehydrocorrin even under severe conditions[60] as a consequence of the presence of two geminal CH_3 groups[15].



(III), (LVII)

(III), (LVIII) R = H

(LVII), (LIX) R = CH_3

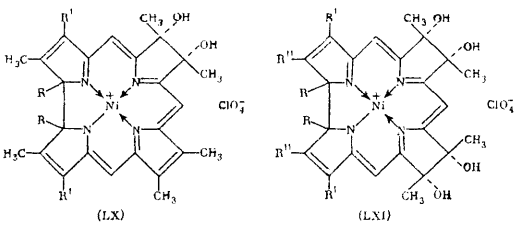
(LVIII), (LIX)

VI. REACTIONS INVOLVING THE β,β-DOUBLE BONDS

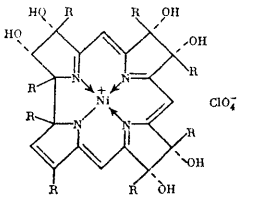
1. Hydroxylation of the Nickel Complexes of Octadehydrocorrins

The octadehydrocorrin macroring contains 10 double bonds, 6 of which are involved in a system of conjugated C=C and C=N bonds constituting the chromophore, which is characteristic of both octadehydrocorrin and corrins, while the four β,β-double bonds are cross-conjugated in relation to the chromophore and are characteristic only of octadehydrocorrins.

One of the few reactions involving the β,β-double bonds is hydroxylation of the metal complexes of octadehydrocorrin on treatment with OsO_4.[61-64] The hydroxylation of the nickel complexes of decamethyl- and 1,19-diethoxycarbonyl-octamethyl-octadehydrocorrins[62,65] as well as the nickel and cobalt complexes of octadehydrocorrins containing the $C_6H_5CH_2O$ substituents in the 3- and 17-positions[63] results in the formation of a mixture of the corresponding 7,8-dihydroxy-derivatives (LX) and 7,8,12,13-tetrahydroxy-derivatives (LXI), i.e. the *B* and *C* rings are involved in the reaction in the first place. The composition of the mixture of compounds (LX) and (LXI) depends on the amount of OsO_4.[62] The reaction of OsO_4 with the nickel complexes of octadehydrocorrins containing the residues of acetic and propionic acids in the *A* and *D* rings proceeds analogously[64]. After the hydroxylation of octadehydrocorrins with free 2- and 18-positions, 2,3,7,8,12,13-hexahydroxycorrin (LXII) and 2,3,7,8,12,13,17,18-tetrahydroxycorrin (LXIII) were isolated in addition to the 7,8-diols and 7,8,12,13-tetraols[61,62,65]. As a consequence of the *trans*-disposition of the 1,19-substituents and the *cis*-hydroxylation, which takes place on either side of the plane of the octadehydrocorrin molecule, a mixture of diastereoisomeric racemates is formed.

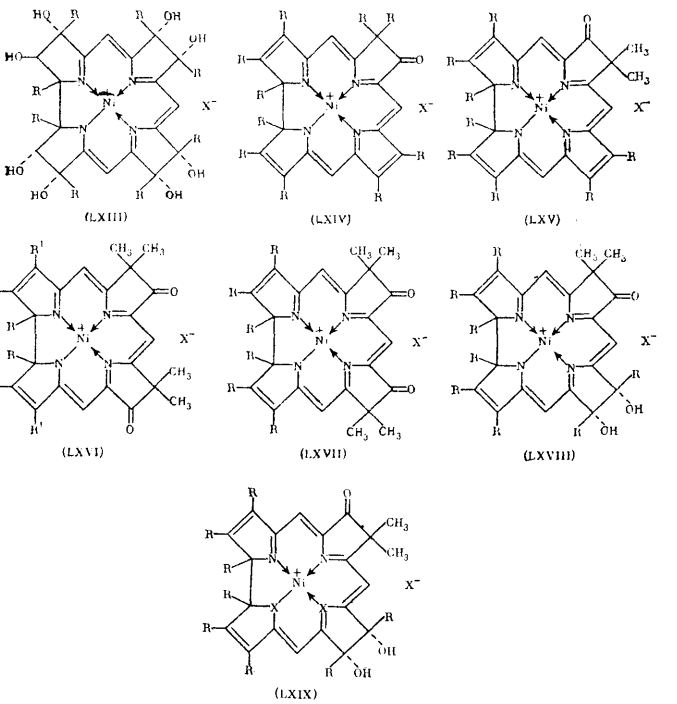


(LX) (LXI)



(LXII)

On treatment with H_2SO_4, the β-dihydroxy-derivatives of corrinoids undergo the pinacol rearrangement, which leads to the formation of ketones containing the *gem*-dimethyl group. The diol (LX) is converted into a mixture of the two monomers (LXIV) and (LXV), which could not be separated[64]. After the pinacol rearrangement of the tetraol (LXI), the two diketones (LXVI) and (LXVII) were isolated. Brief treatment of tetradehydrocorrin having OH groups in the *A* and *D* rings with H_2SO_4 led to the isolation of only the hydroxyketone (LXVI, R′ = OH), in which the OH groups of the *A* and *D* ring are retained[63]. Of the three possible products of the rearrangement of each tetraol (LXI), it was possible to isolate only the diketones (LXVI) and (LXVII):[64]

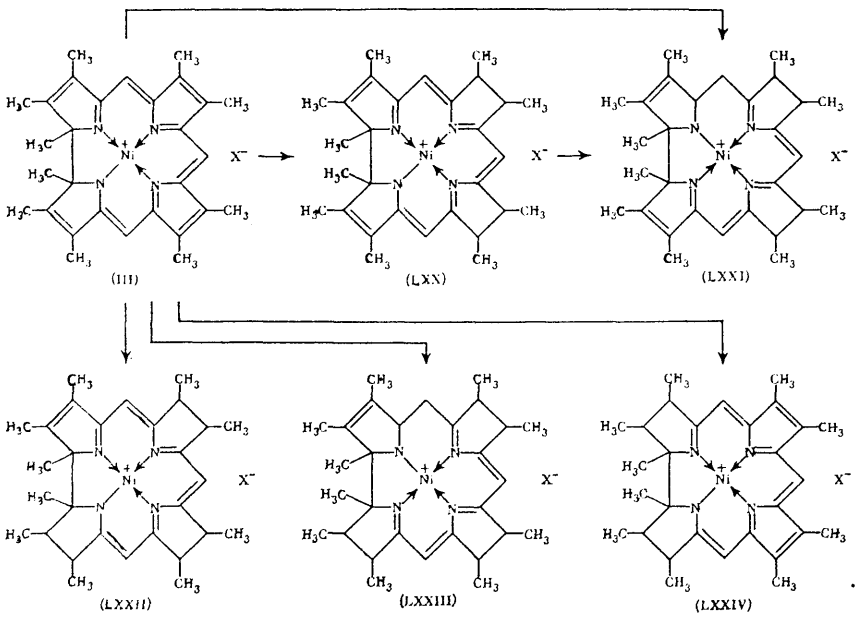


(LXIII) (LXIV) (LXV)

(LXVI) (LXVII) (LXVIII)

(LXIX)

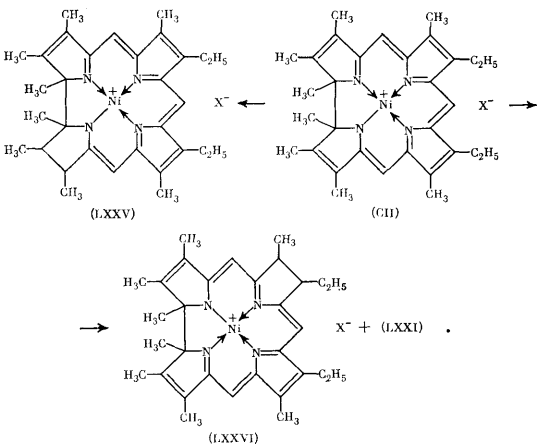
The products of the pinacol rearrangement, namely the mono- and di-ketones, can again undergo the hydroxylation reaction. After treatment with OsO_4, the mixture of the monoketones (LXIV) and (LXV) is converted into a mixture of the dihydroxyketones (LXVIII) and (LXIX). The amount of the dihydroxyketone (LXVIII) is three times greater than that of the dihydroxyketone (LXIX), apparently because the two CH_3 groups in the 8-position hinder the hydroxylation of the *C* ring[65]. The structures of the dihydroxyketones were confirmed by the products of their pinacol rearrangement: compound (LXVIII) is converted into a mixture of the diketones (LXVI) and (LXVII), while compound (LXIX) gives rise to only the diketone (LXVI).[61,62,65]



2. Hydrogenation of the Metal Complexes of Octadehydrocorrins

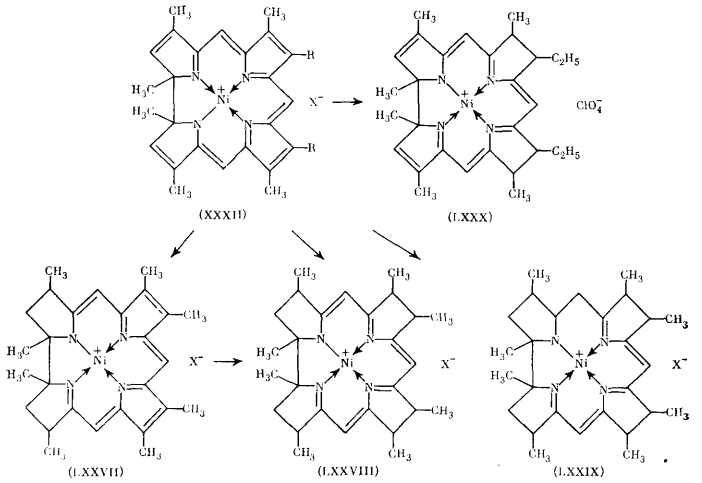
The second reaction involving the β,β-double bonds of the octadehydrocorrin macroring is hydrogenation, which leads under different conditions to a series of macrocylic compounds intermediate between corrins and octadehydrocorrins as regards degree of oxidation. The course of the hydrogenation reaction is greatly influenced by the β-substituents[66]. Hydrogenation of the metal complexes of octadehydrocorrins having alkyl groups in the 1-, 2-, 18-, and 19-positions involves in the first place the β,β-double bonds of the *B* and *C* rings. In the presence of Raney nickel at 100 °C and 100 atm, the nickel complex of decamethyloctadehydrocorrin is converted into the nickel complex of *AD*-tetradehydrocorrin(LXX),[66,67] which is also formed after reduction of the complex (III) in boiling acetic acid[67]. Further reduction of the *AD*-tetradehydrocorrin or the complex (III) over the 10% Pd/C catalyst (20 °C, 100 atm, 26 h) involves the addition of H_2 in the 4- and 5-positions of the macroring with formation of the complex (LXXI).[66] Vigorous hydrogenation of the complex (III) leads to the formation of *A*-hydrocorrin (LXXII) in which there is a β,β-double bond only in the *A* ring[67]. The most highly hydrogenated product is isocorrin (LXXIII), obtained on hydrogenation of the complex (III) over Raney nickel at 160 °C and 120 atm.[66]

The selective hydrogenation of the *B* and *C* rings in β-substituted octadehydrocorrins is a consequence of the steric hindrance generated by the substituents in the 1-, 2-, 18-, and 19-positions. However, the hydrogenation of the complex (III) over the 10% Pd/C catalyst in acetic acid leads to the reduction of the β,β-double bonds of the *A* and *D* rings and the formation of *BC*-tetradehydrocorrin (LXXIV).[66] The replacement of the CH_3 substituents in the 8- and 12-positions by the more bulky C_2H_5 groups changes the mode of reaction: the hydrogenation of the nickel complex of 8,12-diethyloctamethyloctadehydrocorrin (CII) over Raney nickel at 160 °C and 120 atm results in the formation of the nickel complex of *ABC*-hexadehydrocorrin (LXXV).[66] The hydrogenation of the octadehydrocorrin (CII) over the 5% $Pd/BaSO_4$ catalyst (20 °C, 100 atm, 5 days) leads to the formation of a mixture of the hexadehydrocorrin (LXXVI) and the complex (LXXI).[66] After the hydrogenation of the octadehydrocorrin (CII) or *AD*-tetradehydrocorrin under severe conditions, the didehydrocorrin (LXXII) was isolated[66]:



In the hydrogenation of the nickel complexes of octadehydrocorrins unsubstituted in the 2- and 18-positions [compound (XXXII)] and in the 2-, 3-, 17-, and 18-positions, H_2 adds in the first place to the β,β-double bonds of the *A* and *D* rings: the hydrogenation of the complex (XXXII) (20 °C, 50 atm) leads to the formation of a mixture of *BC*-tetradehydrocorrin (LXXVII) and the corrin (LXXVIII), while under more severe conditions the corrin (LXXVIII) was isolated with an admixture of the 4,5-dihydrocorrin (LXXIX). A mixture of corrin and 4,5-dihydrocorrin was also obtained on hydrogenation of the *BC*-tetradehydrocorrin (LXXVII).[66] The hydrogenation of the complex (XXXII) at 100 °C leads to the formation of *AD*-tetradehydrocorrin (LXXX),[2] while hydrogenation over Raney nickel at 100 °C and 100 atm yielded corrins[67,68]. The hydrogenation of the

nickel complex of 1,7,8,12,13,19-hexamethyloctadehydrocorrin over Raney nickel (20 °C, 50 atm) leads to the formation of the nickel complex of *BC*-tetradehydrocorrin[66].

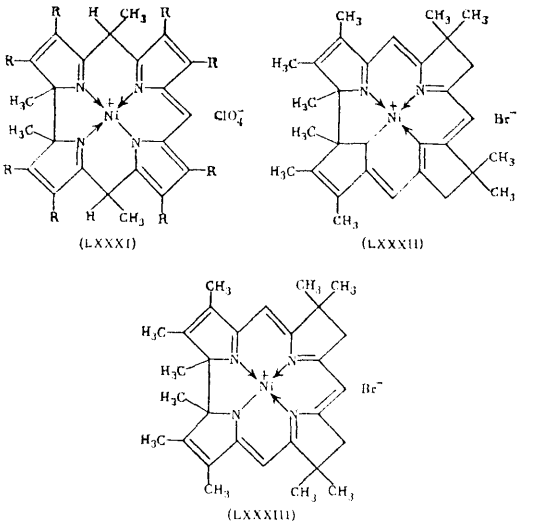


All the products of the hydrogenation of the nickel complexes of corrinoids containing 6 or 8 double bonds are capable of being dehydrogenated in the *B* and *C* rings in air and in the presence of basic catalysts[69]. The nickel complexes of corrins with unsubstituted 2-, and 18-positions[67,68] or 2-, 3-, 17-, and 18-positions[66,67] are converted into *BC*-tetradehydrocorrins, while the nickel complexes of *AD*-tetradehydrocorrins are converted into complexes of octadehydrocorrins[66,67]. The preferential dehydrogenation of the *B* and *C* rings is probably due to the steric hindrance in the region of the angular CH_3 groups or reflects the greatest acidity of the protons in the *B* and *C* rings compared with the acidity of those in the *A* and *D* rings.

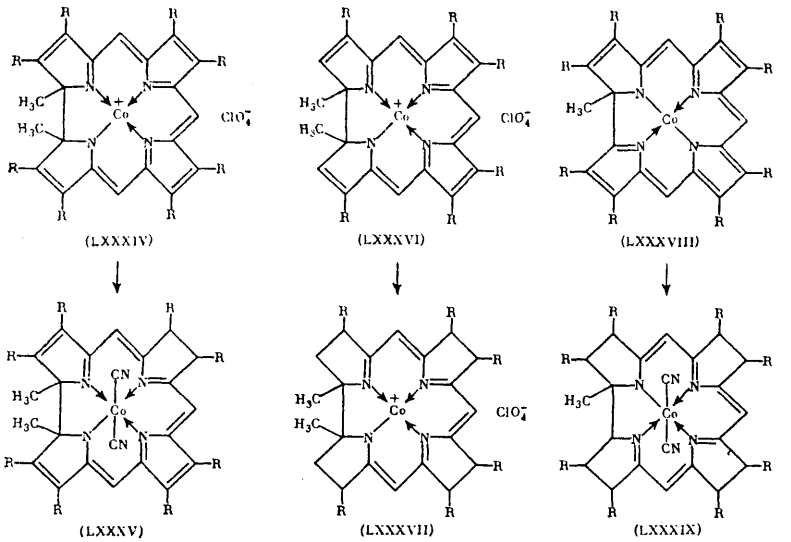
In the hydrogenation over platinum of the nickel complex of β-alkyloctadehydrocorrin containing CH_3 groups in the 5- and 15-positions, one mole of H_2 adds on and an unstable amorphous orange product (LXXXI),[15] whose electronic spectrum resembles that of the nickel complex of dipyrrolylmethene, is formed.

The hydrogenation of the nickel complex of 7,8,12,13-tetrahydroxyoctadehydrocorrin (LXI, R′ = H) over the Pd/C catalyst leads to a corrin, while the hydrogenation under the same conditions of the tetraol containing the $C_6H_5CH_2O$ substituents in the 3- and 17-positions results only in the elimination of the $C_6H_5CH_2$ groups.[63]

The hydrogenation of the diketones (LXVI) and (LXVII) over Raney nickel at 150 °C and 10 atm involves the CO groups and leads to the tetradehydrocorrins (LXXXII) and (LXXXIII).[65]

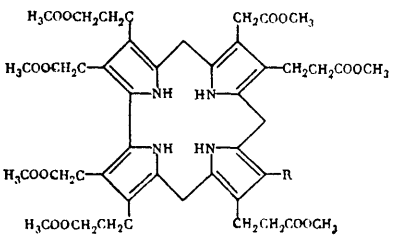


The hydrogenation of the cobalt complexes of octadehydrocorrin takes place analogously. The hydrogenation of the cobalt complex of octa-alkyl-1,19-dimethyloctadehydrocorrin (LXXIV) over Raney nickel at 100 °C and 100 atm results in the formation, after treatment with NaCN, of the dicyanocobalt complex of *AD*-tetradehydrocorrin (LXXXV),[15] which has also been obtained by the hydrogenation of the complex (LXXXIV) in methanol containing acetic acid over the 10% Pd/C catalyst at 80–82 °C and 85 atm.[70] The cobalt complexes of octadehydrocorrins (LXXXVI) with unsubstituted 2- and 18-position are converted into the corrins (LXXXVII) on hydrogenation at 175 °C and 100 atm,[38,68] while the



dicyanocobalt complex of corrin (LXXXIX), whose electronic spectrum is identical with that of cyanocobaltamin, was obtained in the form of an amorphous substance from the cobalt complex of 1-methyloctadehydrocorrin (LXXXVIII) under the same conditions after treating the hydrogenation product with CN^- ions[38].

When β-substituted octadehydrocorrins are hydrogenated, asymmetric carbon atoms are produced and the reaction products are mixtures of stereoisomers. The hydrogenation of the nickel complex of 1,19-dimethyloctadehydrocorrin (Raney nickel, 20 °C, and 25 atm or 160 °C and 100 atm), which has no β-substituents, led to another corrin complex[71,72]. The nickel complex of 1,19-dimethyloctadehydrocorrin is converted into crystalline corrin already at 20 °C and atmospheric H_2 pressure after 1 h.[72] The nickel complex of octadehydrocorrin acts itself as the catalyst of the hydrogenation proper: when a solution of the nickel complex of octadehydrocorrin is heated at 160 °C and 80–100 atm for 4 h without a catalyst, corrin is formed. The hydrogenation of the cobalt complex of 1,19-dimethyloctadehydrocorrin at 20 °C and 25 atm leads to a mixture of dicyanocobalt complexes of corrin and 4,5-dihydrocorrin after treatment of the product with CN^- ions; in the absence of treatment with cyanide ions, the perchlorate of the cobalt complex of corrin was isolated[72].



(XC)

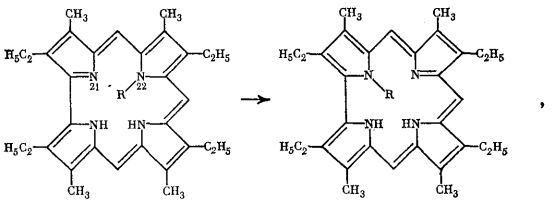
On hydrogenation over platinum, octa-alkylcorrole is converted into an unstable product, which is rapidly reoxidised in air to the initial corrole[3]. The hydrogenation of corroles containing the CH_3OOCCH_2 and $CH_3OOCCH_2CH_2$ groups in the β-positions over platinum oxide leads to colourless readily oxidisable crystalline corrologens (XC).[41]

VII. REARRANGEMENTS OF CORRINOIDS AND THEIR METAL COMPLEXES

The metal complexes of 1-alkyl- and 1,19-dialkyl-octadehydrocorrins as well as the metal complexes and the free bases of *N*-alkylcorroles undergo thermal rearrangements.

1. The Rearrangements of Corroles and Their Metal Complexes

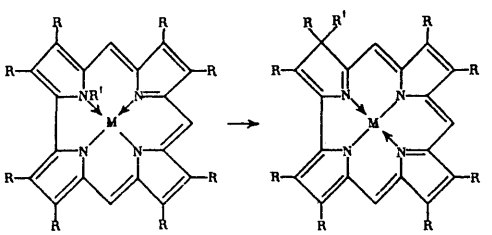
When *N*-alkylcorroles and their metal complexes are heated, the *N*-alkyl groups migrate to another N atom or to the 3-position in the macroring. N(22)-Methyl- and N(22)-allylcorroles (LI, a and b) are converted into N(21)-methyl and N(21)-allyl-corroles (XIX, a and b) on refluxing in toluene[19,21,28]. The thermal isomerisation of N(22)-allylcorrole in cumene[28] and the isomerisation of N(22)-3,3-dimethylallylcorrole (LIc) [19,28] showed that the migration proceeds via a free-radical mechanism.



(LI a–c) (XIX a–c)

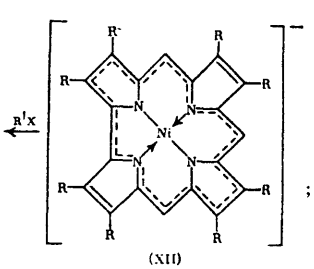
(a) R = CH_3; (b) R = $CH_2CH{=}CH_2$; (c) R = $CH_2CH{=}C(CH_3)_2$.

Heating of the nickel complexes of N(21)-alkylcorroles in chlorobenzene (130 °C, 90 min) leads to the formation of complexes of 3,3-dialkylcorroles (LIII).[9,21,23] The steric factor plays a major role in these reactions; migration of bulky alkyl substituents is the faster[23]. Thus N(21)-ethyl- and N(21)-propyl-corroles rearrange in boiling benzene, while the reaction of the Ni-corrole anion (XII) with $CH_2{=}CHCH_2Br$ or iso-C_4H_9I leads immediately to the nickel complex of the 3,3-disubstituted corrole[3,21,23]. The driving force of this arrangement is apparently the formation of a strong C–C σ-bond instead of the weak C–N σ-bond as well as the decrease of steric strain and the gain of the energy of stabilisation by the ligand field[21].



(V) (LIII)

M = Ni, Pd.

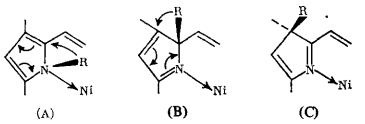


(XII)

The thermal arrangement of the metal complexes of *N*-alkylcorroles can proceed either via two [1,5]-sigmatropic shifts (A) → (B) → (C) or via the metal-[1,3]-sigmatropic shift (A) → (C). A choice between these two possibilities has not been made but preference has been given to the first possibility[9].

The rearrangement of the palladium complexes of N(21)-alkylcorroles takes place analogously; on heating in o-$C_6H_4Cl_2$, they are converted into complexes of 3,3-dialkylcorroles (LII).[27,28] The temperature of the rearrangements of the palladium complexes is higher than that of the nickel complexes probably as a consequence of the steric hindrance due to the large bulk of palladium.

The copper complexes of N(21)-ethylcorroles are converted into the complexes of *N*-unsubstituted corroles, while the complexes of N(22)-ethylcorroles are cleaved[28].

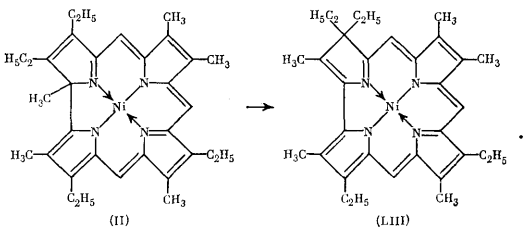


(A) (B) (C)

2. The Rearrangement of the Nickel Complexes of 1-Substituted Octadehydrocorrins

The thermal rearrangements of the metal complexes of 1-substituted and 1,19-disubstituted octadehydrocorrins take place with an alteration in the type of the tetrapyrrole macroring and the formation of more conjugated compounds.

On refluxing in o-$C_6H_4Cl_2$, the nickel(II) complexes of 1-methyloctadehydrocorrins are converted into the complexes of 3,3-dialkylcorroles (LIII).[18,21,29,56] The structure of the nickel complex of 2,2-dialkylcorrole was initially attributed to the thermal isomerisation product, since the nickel complex of 2-methylcorrole is formed in the case of 1-methyloctadehydrocorrin with an unsubstituted 2-position (XVI):[18,56]

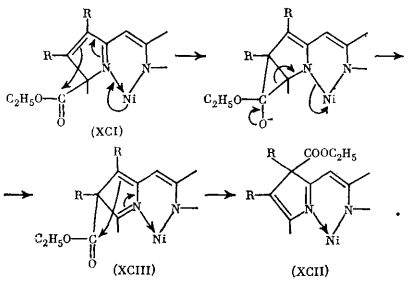


(II) (LIII)

However, it was found that the migration of the substituent from the 1-position takes place in two stages: initially to the 2-position with formation of 2,2-dialkylcorrole, which is followed by the shift of the substituent with the greater capacity for migration to the 3-position[21,29]. This sequence of reactions was demonstrated in the transformation of the nickel complex of 2,3,12,17-tetraethyl-1,7,8,13,18-pentamethyloctadehydrocorrin into the nickel complex of 3,3-diethylcorrole, whose formation is possible when 2-ethyl-2-methylcorrole is formed initially and then 3,3-diethylcorrole is produced as a consequence of the greater mobility of the ethyl group[29]. The migration of the angular CH_3 group from the 1-position to the 3-position can be regarded as a sigmatropic shift[73]. The capacity of substituents for migration varies in the sequence $CH_2{=}CHCH_2 > COOC_2H_5 > C_2H_5 > CH_3$.[21,29] The mechanism of the rearrangement of the nickel complexes of 1-substituted octadehydrocorrins was confirmed experimentally in the thermolysis of the nickel complex of 1-ethoxycarbonyloctadehydrocorrin (XCI), which is converted into the complex of 3-alkyl-3-ethoxycarbonylcorrole (XCII) on heating in boiling chlorobenzene, while on standing in the solid state (20 °C, 2 days) or in CH_2Cl_2 (12 h) in the dark it is converted into the complex (XCIII) containing the $COOC_2H_5$ group in the 2-position; the latter rearranges to the complex of 3,3-disubstituted corrole (XCII) on heating for 1 h in chlorobenzene[59].

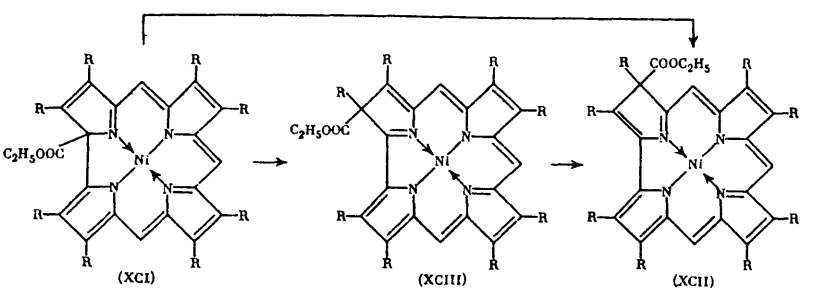
3. Rearrangements of the Metal Complexes of 1,19-Disubstituted Octadehydrocorrins

The metal complexes of 1,19-disubstituted octadehydrocorrins rearrange either into porphyrin complexes or into corrole complexes depending on the type of the angular substituents. The nickel complexes of 1,19-dialkyloctadehydrocorrins are converted into porphyrin complexes, while the nickel complexes of 1,19-diethoxycarbonyl- and 19-allyl-1-ethoxycarbonyl-octadehydrocorrins are converted into complexes of 3,3-disubstituted corroles. When the nickel complexes of octa-alkyl-1,19-diethoxycarbonyloctadehydrocorrins are heated in chlorobenzene, the complexes of 3-alkyl-3-ethoxycarbonylcorroles (XCII) are formed[20,56], the first stage involving the elimination of one angular $COOC_2H_5$ group and the formation of the nickel of 1-ethoxycarbonyloctadehydrocorrin (XCI), which was isolated when 1,19-diethoxycarbonyloctadehydrocorrin was treated cautiously with aqueous alkali. When the complex is heated in chlorobenzene, compound (XCII) is formed[29]. The migration of the ester group is either a [1,5]-sigmatropic shift analogous to the [1,5]-alkyl migration or the reaction mechanism involves the participation of the nickel atom and constitutes the sequence (XCI) → (XCIII) → (XCII).



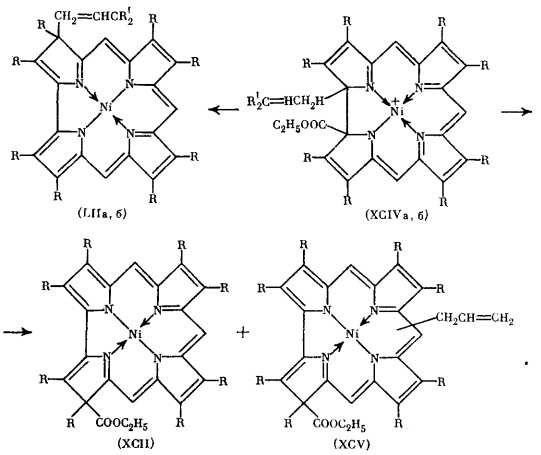
(XCI) (XCIII) (XCII)

The rearrangement of the nickel complex of octa-alkyl-19-allyl-1-ethoxycarbonyloctadehydrocorrin (XCIVa, R′ = H) takes place analogously; on treatment with NaOH, this compound is converted into the complex of 3-alkyl-3-allylcorrole (LIIa, R′ = H).[29] The rearrangement of the nickel complex of 19-ethoxycarbonyl-1-dimethylallyloctadehydrocorrin (XCIVb, R′ = CH_3) leads to the formation of the nickel complex of 3-ethyl-3-dimethylallylcorrole (LIIb. R′ = CH_3), i.e. takes place without the inversion of the

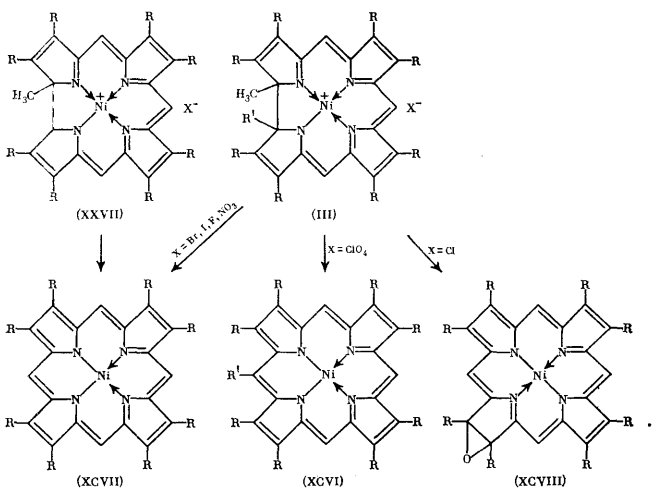


(XCI) (XCIII) (XCII)

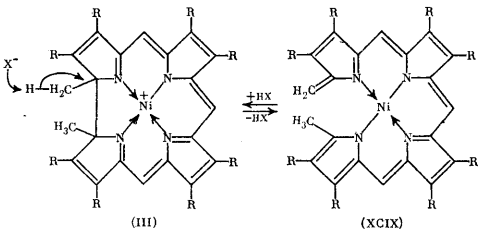
allyl substituent[42]. It is therefore probable that the allyl group migrates via two [1,5]-sigmatropic shifts C(1) → C(2) → C(3), as in the migration of the ester group. The thermal rearrangement of the nickel complex of 19-allyl-1-ethoxycarbonyloctadehydrocorrin (XCIVa) at 180 °C leads to the formation of a mixture of the complexes of 3-ethoxycarbonyl-3-methylcorrole (XCII) and the *meso*-allyl-3-ethoxycarbonylcorrole (XCV).[29]



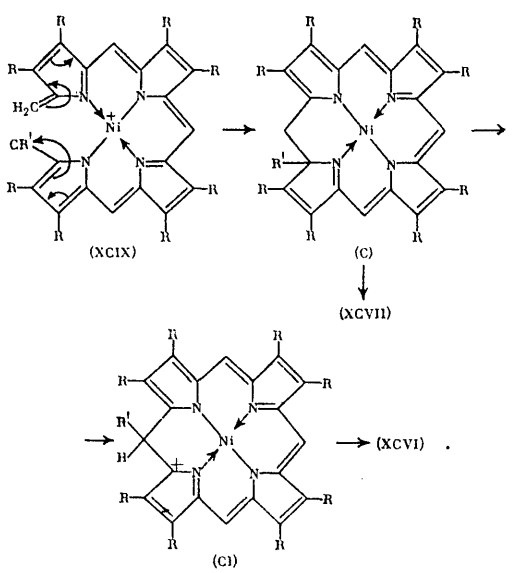
The thermal rearrangement of the salts of the nickel complexes of 1,19-dialkyloctadehydrocorrins take place with expansion of the macroring and consists in the conversion of octadehydrocorrins into porphyrins[21,24,43,74]. The pathway followed in this reaction depends on the nature of the anion: the perchlorates give rise to *meso*-alkylporphyrins (XCVI), while the iodides, bromides, fluorides, and nitrates produce the *meso*-unsubstituted porphyrins (XCVII); the third type of rearrangement is that of chlorides into 2,3-epoxy-5-methylchlorin (XCVIII).[43,74] The salts of the nickel complexes of 1-methyloctadehydrocorrins are converted into *meso*-unsubstituted porphyrins.



The first stage of the octadehydrocorrin–porphyrin rearrangement involves the elimination of a proton from one of the angular groups on attack by the anion, which acts as a base. This entails the dissociation of the C(1)–C(19) bond in the macroring of the type of the Hoffman elimination with formation of a neutral complex of bilatriene (XCIX).[24] The complex (XCIX), containing the benzylidene group instead of the methylene group, was isolated in the rearrangement of the bromide of the nickel complex of 19-benzyl-1-methyloctadehydrocorrin[74]. One of the angular groups, usually a methyl group, is a source of the fourth *meso*-carbon atom in the formation of the intermediate complex (C), which undergoes the following transformations: in the case of the I^-, Br^-, F^-, and NO_3^- anions, a second angular group is split off and the nickel complex of the *meso*-unsubstituted porphyrin is formed.



It has been shown that in the thermolysis of the iodide [of the nickel complex] of octa-alkyl-1,19-dimethyloctadehydrocorrin the angular CH_3 group is split off in the form of CH_3I, which suggests that the anion eliminates the angular group on nucleophilic attack[74]. In the case of the ClO_4^- anion, which is a weak nucleophile, the 19-alkyl group migrates and the *meso*-substituted porphyrin is formed. Since the ClO_4^- anion has oxidising properties, the rearrangement of the perchlorates apparently proceeds via the cationic form (CI), which is converted after oxidation into the porphyrin (XCVI).[74] In the thermolysis of the perchlorates of the nickel complexes of octadehydrocorrins containing the CH_3, C_2H_5, C_3H_7, C_4H_9, C_5H_{11}, $CH_2CH{=}CH_2$, and $COOC_2H_5$ groups in the 19-position, the substituents migrate without the isomerisation of the carbon skeleton with the exception of the allyl group, which is converted into the propenyl group[74]. Only the *meso*-alkylporphyrins are formed in the rearrangement of the perchlorates of the nickel complexes of 1,19-dialkyloctadehydrocorrins with unsubstituted 2- and 18-positions, i.e. there is no migration of the alkyl group to a neighbouring free β-position[74].



The thermolysis of the chlorides of the nickel complexes of 1,19-dimethyloctadehydrocorrins leads to the formation of complexes of 2,3-epoxy-5-methylchlorins (XCVIII) and *meso*-unsubstituted porphyrins, i.e. one angular CH_3 group migrates to the *meso*-position and the β,β-double bond of the neighbouring pyrrole ring is oxidised. Since the nickel complexes of porphyrins are insensitive to this type of oxidation by air, the substrate must be a non-aromatic product, for example, compound (XCIX) or the cyclic derivative (C).[43]

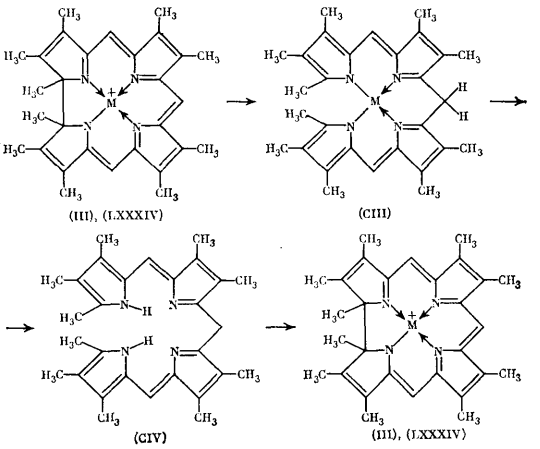
The presence of substituents in the *meso*-positions of 1,19-dialkyloctadehydrocorrins does not influence the rearrangement. For example, the iodides of the nickel complexes of octa-alkyl-5-cyano-1,19-dimethyloctadehydrocorrin and octa-alkyl-5,15-dicyano-1,19-dimethyloctadehydrocorrin are converted into the nickel complexes of the corresponding 5-cyano- and 5,15-dicyano-porphyrins on thermolysis[43].

The thermolysis of the cobalt complexes of octa-alkyl-1,19-dimethyloctadehydrocorrins leads to the formation of the corresponding cobalt complexes of porphyrins[75].

4. The Reductive Opening of the Macroring of the Metal Complexes of Octadehydrocorrins

The metal complexes of octadehydrocorrins are extremely stable. The cobalt and nickel atoms cannot be removed from these compounds without disrupting the macroring[75].

The interconversions of the nickel and cobalt complexes of the octadehydrocorrins (III) and (LXXXIV) have been achieved by treatment with reducing agents, which leads to the opening of the macroring between the C(1) and C(19) atoms with formation of the metal complexes of bilatrienes or the tautomeric biladienes, which are readily demetallated and can be recyclised to the metal complexes of octadehydrocorrins on treatment with $(CH_3COO)_2Ni$ or $(CH_3COO)_2Co$ in air.



The following mechanism for this migration has been proposed[79]: the metal complex of octadehydrocorrin, for example, the nickel complex (III), combines with two electrons under reductive conditions (in the presence of H_2S or $Na_2S_2O_4$) and is converted into a negatively charged complex, which, after the dissociation of the C(1)–C(19) bond, into the metal complex of 22,24-dihydrobilatriene and the latter is converted, after protonation at C(10), into a neutral complex of biladiene (CIII). On treatment with CF_3COOH, HCl, or even H_2S, the latter is demetallated and the resulting biladiene (CIV) can be reconverted into the metal complex of the octadehydrocorrin on treatment with nickel or cobalt acetate in the presence of atmospheric oxygen. The cobalt complexes of octadehydrocorrins are much more reactive than the corresponding nickel complexes; the opening of their rings takes place under very mild conditions (H_2S, room temperature)[76] and on treatment with HBr these compounds are converted into the monohydrobromides of bilatrienes-*abc*.[75]

The C(1)–C(19) bond is ruptured also on hydrogenation of the nickel complex of 3,17-benzyloxyoctadehydrocorrin over the 10% Pd/C catalyst, the resulting metal complex of biladiene recyclising in air at 20 °C.[63]

The principle of the reductive ring opening has been used to obtain the cobalt complex of 7,8-dihydroxy-, 7,8,12,13-tetrahydroxy-, 8.13-dioxo-, and 8,12-dioxo-decamethyloctadehydrocorrins, which could not be obtained by another procedure[76,77].

The stability of the nickel complexes of the tetrapyrrole macrorings with respect to reducing agents increases on successive saturation of the β,β-double bonds in the *B* and *C* rings:

$$(LXXXIV) < (III) < (LX) < (LXVI) = (LXVII) < (LXI) \quad .$$

The cobalt complexes are so labile that substitution on the periphery of the macroring does not play an appreciable role.

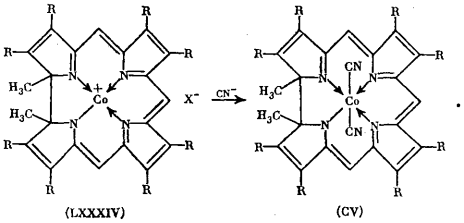
VIII. THE CHANGE IN THE OXIDATION AND COORDINATION STATES OF THE METALS IN THE METAL COMPLEXES OF CORROLES AND OCTADEHYDROCORRINS

1. The Redox Reactions of Corrinoid Compounds

The oxidation-reduction properties of vitamin B_{12} and its derivatives have been the subject of lively interest, since the oxidation state of the cobalt atom of cobalamin changes in the enzymatic B_{12}-dependent reaction[78].

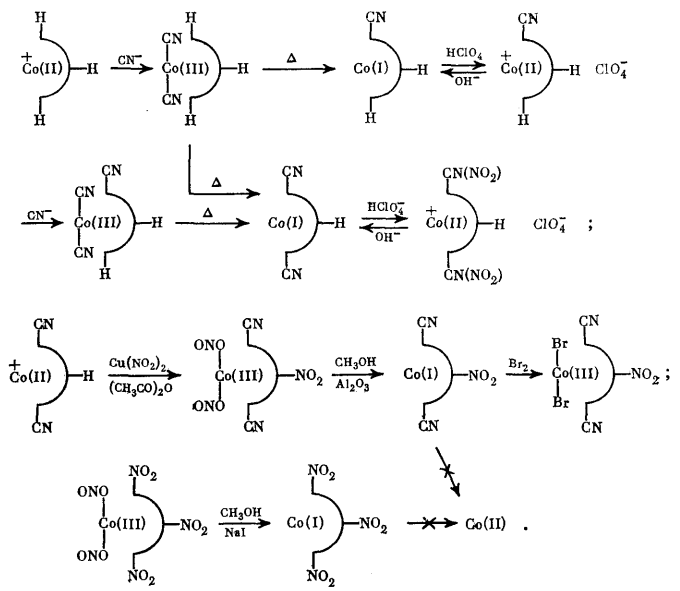
In recent years octadehydrocorrins have attracted attention as models of viatmin B_{12}. Ready interconversion of different oxidation states of cobalt takes place in the cobalt complexes of octadehydrocorrins (LXXXIV), in contrast to the stability of the bivalent nickel in the octadehydrocorrin complexes.

When the cobalt(II) complex of octa-alkyl-1,19-dimethyl-octadehydrocorrin is treated with a cyanide, the CN group does not enter the macroring. Instead a green diamagnetic dicyanide (CV) is formed, where two CN groups are located in the axial positions at the Co atom, which is oxidised to the tervalent state[15,63,75,79,80]. When cobalt(II) complexes of octadehydrocorrins are treated with $Cu(NO_3)_2$ in acetic anhydride, simultaneous nitration of the *meso*-positions of the macroring and the formation of a cobalt(III) complex with the ONO axial ligand take place; the *meso*-unsubstituted octadehydrocorrin is then converted into a mixture of 5,15(10)-dinitro- and 5,10,15-trinitro-octadehydrocorrins, while 5,15-dicyano-octadehydrocorrin is converted into 5,15-dicyano-10-nitro-octadehydrocorrin. On treatment with methanol, they are converted into salts of the cobalt(II) complexes of the corresponding octadehydrocorrins[75,79].



Cobalt(III) complexes of octadehydrocorrins can be obtained also from the cobalt(I) complexes. Treatment of the cobalt(I) complexes of 5,15-dicyano-10-nitro- and 5,10,15-trinitro-octadehydrocorrins with Br_2 leads to the formation of the dibromides of the cobalt(III) complexes of the corresponding octadehydrocorrins[75].

Cobalt(I) complexes of octadehydrocorrins are formed from both the cobalt(II) complexes[75] and from the cobalt(III) complexes[75,79]. When salts of the cobalt(II) complexes of monocyano- and dicyano-octadehydrocorrins were treated with alkali, neutral cobalt(I) complexes were obtained. This reaction is reversible; on treatment with $HClO_4$, the cobalt(I) complexes are converted into salts of the cobalt(II) complexes. The introduction of three electron-accepting substituents greatly stabilises the cobalt(I) complexes, which do not change on treatment with $HClO_4$. The thermolysis of the dicyanide of the cobalt(III) complex of the *meso*-unsubsituted octadehydrocorrin leads to the cobalt(I) complex of 5-cyano- and 5,15-dicyano-octadehydrocorrins, the latter being formed also on heating the dicyanide of the cobalt(III) complex of 5-cyano-octadehydrocorrin. The migration of the CN group from the Co atom to a C atom is probably an intermolecular process[75]. Treatment of the dinitrites of the cobalt(III) complexes of tri-*meso*-substituted octadehydrocorrins with NaI or Al_2O_3 in methanol also leads to the completion of the cobalt(I) complexes. The interconversions of the cobalt complexes of octadehydrocorrins can be represented schematically as follows:



The reduction of the cobalt(II) complexes of octadehydrocorrins on treatment with NaOH in aprotic solvents or with KOH in the form of a complex with a cyclic polyether also leads to the formation of cobalt(I) complexes, which are slowly reoxidised by atmospheric oxygen to the initial compounds[81]. It has been suggested[81] that an electron is transferred from the OH^- anion, which is unsolvated, to the cobalt(II) complex of octadehydrocorrin; in the reduction of the cobalt(II) complexes to the cobalt(I) complexes on treatment with $(C_2H_5)_3N$, the electron transfer from the amine to the cobalt(II) complex of octadehydrocorrin takes place via an outer-sphere mechanism. The reaction of the cobalt(II) complex of 1,19-diethoxycarbonyloctamethyloctadehydrocorrin (CVIIIb) with $NaBH_4$ in DMF also leads to a cobalt(I) complex[82]. The cobalt(I) complexes of octadehydrocorrins are stable, remaining unchanged in air for several hours. Their treatment with pyridine or triphenylphosphine does not alter the electronic spectrum[79]. Treatment of the cobalt(I) complexes with $FeCl_3$ or I_2 entails their instantaneous conversion into the cobalt(II) complexes[4,81].

The reduction of the nickel(II) and cobalt(II) complexes of octa-alkyl-1,19-diethoxycarbonyloctadehydrocorrins (CVIIIb) in THF has been studied with the aid of optical spectra and EPR.[14] The formation of one- and two-electron reduction products was observed in both cases. The product of the one-electron reduction of the nickel complex is a very stable free radical, formed on addition of one electron to the lowest unoccupied π orbital of the ligand. The first reduction potential of the initial cation in DMF (−0.30 V) indicates the stability of the radical and corresponds to one-electron reduction. The one-electron reduction of the cobalt(II) complex leads to the formation of a neutral cobalt(I) complex, i.e. in contrast to the nickel(II) complexes, the electron adds to the central metal ion, whose oxidation state changes. When reduced nickel and cobalt complexes of octadehydrocorrins are treated with oxidants (I_2, $FeCl_3$), the initial compounds are quantitatively regenerated[14].

Further reduction of the cobalt(I) complex of octadehydrocorrin and of the free radical of the nickel(II) complex also proceeds as a one-electron process, which leads in both cases to complexes of the bivalent metals with two additional electrons in the ligand π orbital. The oxidation of these substances in air results in the regeneration of approximately 90% of the products of the first reduction stage. Both nickel and cobalt complexes of octadehydrocorrins can be reduced further, but the compounds formed were not identified and the products of the preceding reduction stage cannot be regenerated on oxidation in air.

The reduction of the cobalt complexes of octadehydrocorrins constitutes a series in which the oxidation state of the central cobalt ion changes as follows: (II) → (I) → (II) with consecutive addition of one electron, and the final change from cobalt(I) to cobalt(II) must be a result of electron transfer from the cobalt(I) ion to the ligand together with competitive reduction of the ligand[14].

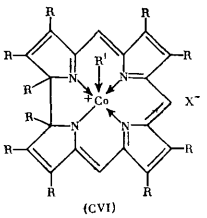
The electrolytic reduction of salts of the cobalt(II) complexes of 5,15-dicyano- and 5,15-dinitro-octadehydrocorrins at a platinum electrode leads to the formation of stable cobalt(I) complexes[73,79]. The reduction of the cobalt complexes of mono- and di-substituted octadehydrocorrins as well as unsubstituted octadehydrocorrins is a reversible one-electron process. The cobalt(I) complexes are stabilised with respect to oxidation in the presence of strong electron-accepting substituents in the macroring.

The reduction of the cobalt(III) complexes of corroles (XXI) with an Na film in THF *in vacuo* and also with $NaBH_4$ or $(C_4H_9)_4NOH$ in DMF leads to the formation of Co(II)-corrole anions (XII), which are reconverted in air into the initial cobalt(III) complexes of corroles[13,31]. The first reduction potential $E_{1/2} = -0.26$ eV. The enhancement of the electron-donating properties of the axial ligands hinders the reduction of the central cobalt ion[30]. When pyridine is added to solutions of the square-planar or pyramidal cobalt(III) complexes of corroles, $E_{1/2}$ becomes −0.54 eV in all cases as a consequence of the formation of the octahedral dipyridine complex[30]. According to other data[13], the potential of the reduction of Co(III)-corrole to the Co(II)-derivative is −0.34 eV in DMF and −0.47 eV in the presence of pyridine. All the redox processes are of the one-electron type and are

reversible[30], while the oxidation of the corrole bases is a quasi-reversible process[83].

2. The Coordination Properties of the Cobalt Atom in Complexes of Corrinoids

The central cobalt atom in the cobalt(II) complexes of octadehydrocorrins can be both tetracoordinate and pentacoordinate. The cobalt(II) complexes of octadehydrocorrins readily coordinate in the axial position one pyridine molecule[13] and also CH_3OH and DMF [13,14] with formation of pentacoordinate square-planar cobalt(II) complexes of octadehydrocorrin (CVI), [13,81] the unpaired electron being delocalised from the d_{z^2} orbital of the cobalt(II) atom over the coordinate bond between cobalt and the nitrogen atom of pyridine[13,82].

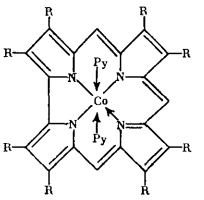


(CVI)

When pyridine and polyvinylpyridine are coordinated to the cobalt(II) complexes of 2,18-substituted octadehydrocorrin, the formation constants of the pentacoordinate complexes increase with enhancement of the electron-accepting properties of the β-substituents[84]. There is a linear relation between $\lg K$ for the coordination of pyridine and the σ_m constants of the β-substituents[84]. The constants of the coordination of substituted pyridines and aliphatic amines to the cobalt(II) complex of 8,12-diethyloctamethyloctadehydrocorrin have also been determined and correlations have been established between the coordination constants and the basicity of 4-substituted pyridines, on the one hand, and the coordination constants and the σ constants of the pyridine substituents, on the other[81]. The complexes of aliphatic amines and Co-octadehydrocorrins are less stable than the pyridine complexes. A mechanism has been proposed for the formation of these complexes, which consists in the amine giving up two electrons to the cobalt(II) complex in stages, the first electron being transferred to the cobalt atom via an outer-sphere mechanism and the resulting cobalt(I) complex and the electron-deficient amine combining to give a pentacoordinate cobalt(II) complex of octadehydrocorrin[81].

The coordination state of the cobalt(II) complexes of octadehydrocorrins depends on the nature of the anion[85]. The perchlorates and nitrates are tetracoordinate complexes, while the acetates and bromides are pentacoordinate. The nickel complexes of octadehydrocorrins are tetracoordinate in all the known cases and the nature of the anions does not affect this.

The cobalt(III) of corroles form both 1 : 1 and 1 : 2 adducts with pyridine and other amines[86]. The addition of an excess of pyridine to solutions of the square-planar or pyramidal complexes of corroles leads to the formation of the octahedral dipyridinecobalt(III) complexes of corroles (CVII), which are stable only in the presence of an excess of pyrine[30].



(CVII)

Correlations have been established between the formation constants of the penta- and hexa-coordinate cobalt(III) complexes of corroles and the basicity of the 4-substituted pyridines and between the constants of the coordination of 4-substituted pyridines to Co(III)-corroles and the σ constants of the pyridine substituents[86].

IX. REACTIONS OF SUBSTITUENTS IN THE CORRINOID MACRORINGS

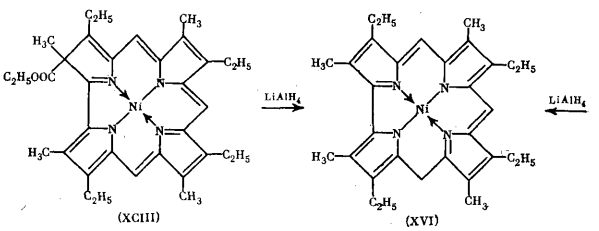
The reactions of substituents in the octadehydrocorrin macroring have been little investigated. The reactions of substituents in the 1- and 19-positions have been studied in greatest detail, since their removal leads to the formation of other types of tetrapyrrole macrorings.

When the nickel and cobalt complexes of 1,19-diethoxy carbonyloctadehydrocorrins are treated with alkaline agents, the ester is hydrolysed and the resulting carboxylic acids are carboxylated, while treatment with a solution of $(C_4H_9)_4$. .NOH in methanol yielded complexes of the tetrabutylammonium salt of 1-carboxyoctadehydrocorrin[14]. Rapid treatment of the nickel complex of 1,19-diethoxycarbonyloctadehydrocorrin (CVIIIb, R′ = $COOC_2H_5$) with a solution of NaOH in water[29] or methanol[59] leads to the nickel complex of 1-ethoxycarbonyl octadehydrocorrin.

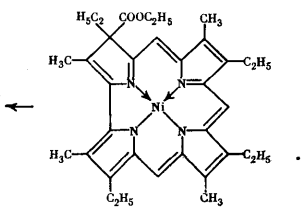
When the nickel complexes of 1-ethoxycarbonyl- and 1,19-diethoxycarbonyl-octadehydrocorrins (XCI) and (CVIIIb) are reduced with $LiAlH_4$, one ester group is eliminated and corrole and 1-ethoxycarbonyloctadehydrocorrin are formed respectively[59]. The nickel complex of 19-ethoxycarbonyl-1-methyloctadehydrocorrin (CVIIIa) is readily converted into the nickel complex of 1-methyloctadehydrocorrin on treatment with NaOH in methanol[29,40] or with sodium in alcohol[59].

The cobalt complexes are more reactive. When the cobalt complex of 1,19-diethoxycarbonyloctadehydrocorrin is treated with a solution of NaOH in methanol at 20 °C, the cobalt complex of corrole is formed[40].

Ester substituents at any saturated carbon atom are readily removed. When the nickel complexes of corroles, (XCII) and (XCIII), containing the $COOC_2H_5$ groups at C(3) and C(2) are reduced with $LiAlH_4$, they are both rapidly converted into the same corrole (XVI): [59]



(XCIII) (XVI)



(XCII)

The hydrogenation of the nickel complex of 3,17-dibenzyloxyoctamethyloctadehydrocorrin over the 10% Pd/C catalyst in alcohol at 20 °C leads to the formation of the nickel complexes of 17-benzyloxy-3-hydroxy- and 3,17-dihydroxyoctadehydrocorrins[63]. The oxidation of triphenylphosphinecobalt(III) complexes of octa-alkylcorroles with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone results in the formation of 3,17-diformyl derivatives[30]. Thermolysis of the nitrate of the nickel complex of decamethyloctadehydrocorrin probably involves the transformation of the CH_3 group in the 3-position into the CN group via the mechanism $-CH_3 \rightarrow -CH{=}NOH \rightarrow -CN$; the nitrosation is caused by the nitrous vapours formed on decomposition of the NO_3^- anion[74]. An analogous reaction occurs in the thermolysis of the nitrate of the nickel complex of octa-alkyl-1,19-diethoxycarbonyloctadehydrocorrin[29,56].

The metal complexes of octadehydrocorrins with propionic acid residues in the β-positions readily undergo reactions characteristic of carboxylic acids. They are esterified on refluxing in methanol in the presence of $HClO_4$.[87] The esterification of the CH_2CH_2COOH groups in the 8- and 12-positions, which are less sterically shielded, proceeds more readily than the esterification of the same groups in the 2- and 18-positions. The reactions of metal complexes of octadehydrocorrins containing the CH_2CH_2COOH groups with epoxyethane leads to the corresponding esters which are the products of the addition of one epoxyethane molecule[87].

Thus the metal complexes of octadehydrocorrins have unusual chemical properties, whose study makes a considerable contribution to the chemistry of complex compounds and tetrapyrrole macrocyclic compounds.

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