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Metal complexes of macrocycles in catalysis

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ABSTRACT. The reactions catalysed by metal complexes with synthetic macrocyclic ligands and, in particular, the hydrolysis reactions of esters, peptides, and other substrates are examined. Many macrocyclic coordination compounds of transition metals are active catalysts of reactions occurring at electrodes (electrocatalysis). The catalysis by macrocyclic transition metal compounds of reactions involving the oxidation of various organic substances by molecular oxygen and other oxidants, in particular, the oxygen compounds of the halogens, is described. Examples of photocatalysis with participation of macrocyclic transition metal complexes as catalysts are presented. Certain features of the electronic structure of transition metal complexes with macrocyclic ligands are considered and routes leading to further development of catalysis using such compounds are outlined.

The bibliography includes 90 references.

Contents

I.	Introduction	1150
II.	Characteristic features of metal complexes of macrocycles important for catalysis	1150
III.	Catalysis of hydrolytic reactions by macrocyclic metal complexes	1152
IV.	Electrocatalytic reactions with participation of macrocyclic metal complexes	1152
V.	Reactions involving oxidation by oxygen catalysed by macrocyclic metal complexes	1153
VI.	Other reactions catalysed by macrocyclic metal complexes	1154
VII.	Conclusion	1155

I. Introduction

Although the first systematic studies on the synthesis and properties of metal complexes of macrocyclic compounds were not carried out until the 1960s, the number of compounds of this kind described at the present time runs to several thousand. Studies on the synthesis and physicochemical characteristic of macrocyclic complexes have been surveyed in a number of monographs.[1–4]

Comparatively few studies have been devoted to the catalytic acceleration of various reactions by macrocyclic compounds but their number has increased sharply during the last decade. A general feature is manifested here: after the discovery and study of a new class of chemical compounds, their application begins to develop vigorously. This was the case, for example, with complexones and metal complexonates, which are now finding extensive applications in various branches of the national economy.

It is noteworthy that, as early as the 1970s, catalytic reactions with participation of natural macrocyclic compounds such as the porphyrins and phthalocyanines, a kind of analogue of the former, were investigated vigorously. Since a number of monographs and reviews have been devoted to this question,[5–7] the reactions catalysed by metalloporphyrins and metallophthalocyanines will not be considered as a rule in the present review. Nor will the extremely specific field of the so called phase transfer catalysis be considered. In it macrocyclic compounds (mainly crown-ethers) play the role of an agent transferring the reactive substance from one phase to another (for further details, see Hiraoka[2]).

II. Characteristic features of metal complexes of macrocycles important for catalysis

Solvated (including hydrated) metal ions can participate in many catalytic processes by themselves. Nevertheless, the incorporation of a metal ion in the cavity of a macrocycle alters its properties extremely significantly. A metal ion in a macrocyclic environment is in the first place fully or partly desolvated (dehydrated). On partial desolvation, the possibility of a fairly easy replacement of the remaining solvent molecules by the ions or molecules of the catalytic reaction substrate appears. In this case, the metal ion can function as an acid centre ("Lewis acid") and can also catalyse hydrolytic reactions such as hydrolysis, solvolysis, etc. Here one may see a certain analogy with hydrolytic enzymes such as carboxypeptidase and carbonic anhydrase, which contain in their active centres a zinc ion surrounded by electron-donating oxygen atoms of carboxylic acids or nitrogen atoms of imidazole groups. Zinc, copper, cobalt (II) and (III), and many other metal ions characterised by a marked tendency to combine with nucleophilic species can play the role of acid centres.

The electron-donating atoms of the macrocyclic ligand, coordinated in a specific way around the central metal atom, create a ligand field characterised by a definite "strength", expressed, for example, by the spectrochemical parameter $10Dg$ in an octahedral complex. Several electron-donating ligand atoms are fairly frequently arranged in approximately the same equatorial plane, leaving the axial positions relatively free for the substrate molecules or ions and one may therefore speak of the axial coordination of the substrate molecule or ion.

The possibility of such coordination is determined by the electronic structure of the central ion. For example, in the case of low-spin nickel(II) complexes the axial coordination of the substrate is difficult owing to the presence of the electron pair in the axially oriented d_{z^2} orbital and, conversely, in complexes with an unoccupied d_{z^2} orbital the σ-type axial coordination of a substrate species is entirely possible [low-spin macrocyclic iron(II), cobalt(III), etc. complexes]. The appearance of a dative π-bond of the type

LM(II)→S may play a major role in the formation of intermediate compounds of the substrate and the macrocyclic complex.

The oxidation-reduction potential of the M(n+1)L/M(n)L couple depends on the nature of the electron-donating atoms and other characteristics of the macrocyclic ligand (L). [8] The redox potential is determined by the potential of the simple solvated ions M(n+1) and M(n) and by the ratio of the stability constants of the complexes M(n)L and M(n+1)L. The greater this ratio (we shall designate it by η), the higher the redox potential of the given pair of complexes and conversely.

Among the factors which determine the ratio η, the following may be specified.

1. The nature of the electron-donating atoms in the macrocycle: the highest η is characteristic of ligands with sulphide sulphur atoms and the lowest of ligands with ether oxygen. Ligands with electron-donating amine nitrogen atoms have intermediate values of η.

2. The charge on the ligands: the ratio η diminishes with increase in the negative charge of L.

3. The size of the cavity within the macrocycle: η also increases with increase in the size of the cavity.

4. The possibility of the formation of dative π-bonds from the metal to the macrocycle leads as a rule to an increase in η.

Apart from these factors, it is essential to take into account the change in the spin state on oxidation-reduction of the complex, the difference between the effects of the ligand field on the M(n) and M(n+1) ions, the presence of alkyl substituents in the macrocycle, the change in the symmetry of the field on passing from M(n)L to M(n+1)L, etc.

By selecting the macrocyclic environment, it is possible to regulate the redox potential of the M(n+1)L/M(n)L couple which catalyses the oxidation-reduction process at a particular stage of the latter.

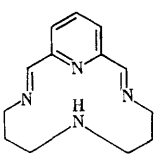
The possibility of the axial coordination of a nucleophilic molecule in the presence of an equatorial ligand and an unoccupied d_{z^2} orbital was noted above. If this orbital is occupied by a pair of electrons, the corresponding macrocyclic complex is itself converted into a nucleophile capable of combining with a proton, carbonium ions (for example, CH_3^+), and other "electrophiles". Such addition must not be hindered by a high positive charge on the complex and the nucleophiles are therefore usually macrocyclic cobalt(I) and nickel(I) complexes bearing low charges and having an unshared electron pair in the d_{z^2} orbital.

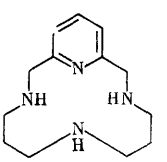
When the d_{z^2} orbital, oriented at right angles to the xy plane in which the electron-donating atoms of the macrocyclic ligand are located, is half-filled and six electrons are present in the d_{xz}, d_{yz} and d_{xy} orbitals (d^7 configuration), a kind of inorganic free radical species are produced [Co(II)L, Ni(III)L], which are capable of reacting with free radicals or generating them as a result of the homologous bond dissociation in the organic molecule.

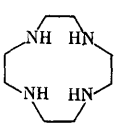
The characteristic features of the macrocyclic complexes of metal ions considered here make it possible not only to explain the mechanism of many catalytic processes but also to predict new ones. Even greater possibilities for the prediction of catalytic reactions with participation of macrocyclic complexes have arisen from the far-reaching analysis of processes in enzyme catalysis[9] and the construction on this basis of the corresponding models of the active centres of the enzymes. [10,11]

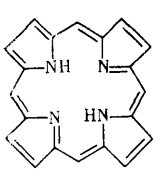
The use of the analogy between the active centres of metalloenzymes and a metal ion with its immediate environment in a complex ML, where L is a macrocyclic ligand, made it possible to discover many catalytically active compounds. In particular, using metalloporphyrins as analogues of haems and metallocorrins, it has been possible to achieve numerous catalytic processes in which metalloporphyrins and metallophthalocyanines are used. [5,6]

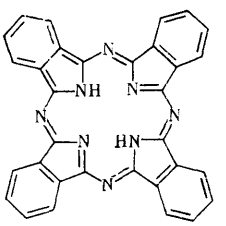
Despite the fact that several thousands of macrocyclic compounds are known nowadays, complexes with an extremely limited number of ligands (several tens) are used in catalytic reactions. In the further exposition in this review, we shall use structural formulae and the corresponding numbering of the ligands in considering the latter:

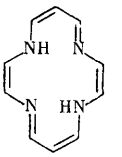

L1 (CR)

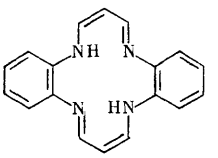

L2 (CRH)

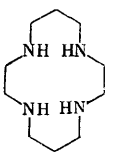

L3 (cyclene)

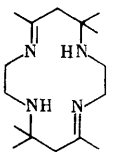

L4 (H_2P)

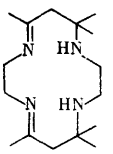

L5 (H_2Pc)

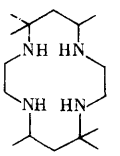

L6 (H_2TAA)

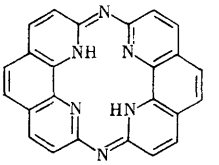

L7 (H_2DBTAA)

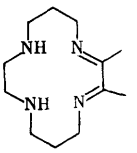

L8 (cyclam)

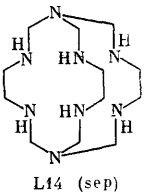

L9 (td)

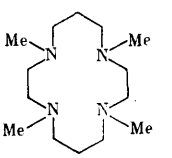

L10 (cd)

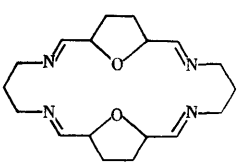

L11 (teta)

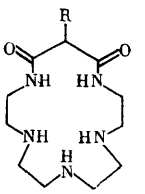

H_2L12

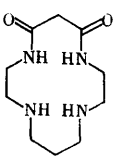

L13

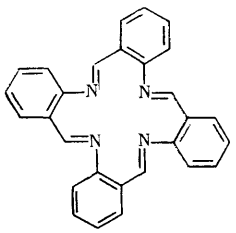

L14 (sep)


L15 (TMC)

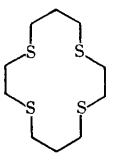

L16


H_2L17

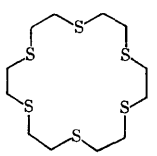

H_2L18



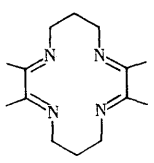
L19 (TAAB)



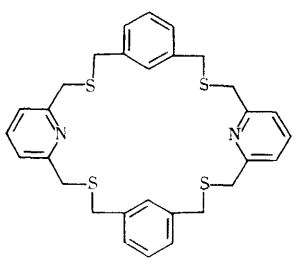
L20 (Ref.12 an S_4)



L21 (Ref.18 an S_6)



L22 (TIM)



L23

At the same time, use will be made of the conventional abbreviations for many ligands used widely in Soviet and foreign scientific literature. The ligands not illustrated here will be named in accordance with the Melson-Bush nomenclature,[1,3] which has come to be widely employed in the Soviet and foreign literature.

III. Catalysis of hydrolytic reactions by macrocyclic metal complexes

Many hydrolytic reactions (hydrolysis of peptides, esters, etc.) are catalysed by zinc-containing enzymes (for example, carboxypeptidase). The active centres of such enzymes contain a zinc ion linked to the electron-donating nitrogen atoms of the imidazole groups of histidine or the electron-donating oxygen atoms of the carboxy-groups of the glutamic acid residues. The complex $Zn(CR)^{2+}$ or ZnL1,[12] which accelerates the hydrolysis of methyl trifluoroacetate according to the scheme

$$CF_3COOMe+OH^- = CF_3COO^- + MeOH\ ,$$

by a factor of 6, can be considered as a model of this active centre.

The acceleration can be explained by the formation of a bond between the hydroxide ion and the zinc ion in the macrocyclic complex, as a result of which OH^- acquires the ability to add to the carbon atom of the ester group. The same complex $Zn(CR)^{2+}$ catalyses the hydration of acetaldehyde, i.e.

$$MeCHO+H_2O = MeCH(OH)_2\ ,$$

and the analogous CO_2 hydration reaction catalysed by carbonic anhydrase.[13] The substitution of zinc by copper(II) in the complex $M(CR)^{2+}$ increases its catalytic activity, in contrast to carbonic anhydrase. The catalytic activity of $M(CR)^{2+}$ [13] is due to the fact that it ensures the addition of the metal-coordinated hydroxide ion to the carbon atom in CO_2 or MeCHO at pH close to the physiological values.

The complexes $Zn(CR)^{2+}$ also catalyse the hydrolytic reactions of many phosphate esters, which is important as a detoxification procedure.[14] The catalytic reactions

$$(PhO)_2P(O)OC_6H_4NO_2+H_2O = (PhO)_2P(O)OH+NO_2C_6H_4OH,$$

and

$$(PhO)_2P(O)OC_6H_4NO_2+H_2O =$$

$$= (PhO)P(O)(OC_6H_4NO_2)OH+PhOH,$$

which proceed in a mixture of water and acetonitrile, have been described. The proposed mechanism of these reactions is analogous to that described above.

Similar hydrolytic reactions are catalysed not only by the complexes $Zn(CR)^{2+}$ but also by $Zn(cyclene)^{2+}$ (cyclene = L3).[15] $Zn(cyclene)^{2+}$ is even more effective than $Zn(CR)^{2+}$ in the hydrolysis of the ester $(NO_2)_2C_6H_3OP(X)(O)OEt$ (where X = Me or OEt).

The macrocyclic zinc complex $Zn([15]anN_4)^{2+}$ catalyses the hydrolysis of 4-nitrophenyl acetate.[16]

The cobalt(III) complex $[Co(cyclene)(H_2O)_2]^{3+}$ accelerates the hydrolysis of ATP with formation of ADP and phosphate.[17] The catalytic activity of this complex is manifested particularly strikingly at pH 8.6 (acceleration by a factor of 117), at pH 8.0 the ratio of the rate constants for the catalytic and non-catalytic reactions is 13.2, while at pH 7.0 it is only 2.2.

It has been suggested that cobalt(II) complexes with a chiral macrocycle containing the cyclene skeleton be used for the selective hydrolysis of specific N-terminal groups of peptides and for the conversion of L-alanine.[18]

IV. Electrocatalytic reactions with participation of macrocyclic metal complexes

Numerous studies devoted to the application of macrocyclic compounds in electrocatalysis are known. The earliest investigations concern the use of metalloporphyrins and metallophthalocyanines for the reduction of molecular oxygen at the cathode of a fuel cell.[19] Reviews of studies on this question are available in a number of monographs[5,6,20] and in a communication.[21]

The reduction of molecular oxygen at the cathode of a fuel cell is described by the overall equation[22]

$$O_2+4H^+ +4e = 2H_2O,\ E^0 = 1.229\ V.$$

However, the process is complicated by intermediate reactions and, in particular, by the reduction of oxygen to hydrogen peroxide, which is characterised by a lower redox potential:[22]

$$O_2+2H^+ +2e = H_2O_2,\ E^0 = 0.695\ V.$$

Other intermediate reactions in the reduction of O_2 to H_2O are also possible. Catalysis of the above overall reaction and of its individual stages is therefore necessary. The salts MPc and the salts of substituted porphyrins MP, especially cobalt(II), iron(II), and iron(III) salts, are used as catalysts. This is apparently associated with the ease of the formation of superoxide radical-anions O_2^- in the presence of the above complexes and their subsequent conversion into H_2O_2. It was subsequently observed that the salts of tetraazaannulenes (MTAA and MDBTAA) also exhibit a catalytic activity[23,24] these compounds being actually more active than the porphyrin and phthalocyanine salts. It may be that the salts of porphyrins, phthalocyanine and tetraazaannulenes also possess catalase activity, i.e. they accelerate the conversion of H_2O_2 into H_2O and O_2.

Studies on cobalt salts of different substituted tetraazannulenes[25] showed that the presence of various alkyl substituents in these compounds does not have a significant effect on the electrocatalytic activity of CoTAA.

Other cobalt salts of tetraaazamacrocyclic ligands [$Co(cyclam)^{3+}$, $Co(td)^{2+}$], forming intermediate dinuclear complexes with oxygen, have also been investigated as electrochemical reduction catalysts.[26] The cobalt complex with the hexaazamacrocyclic ligand L12 likewise proved to be a catalyst of the electrochemical reduction of molecular oxygen.[27]

Carbon electrodes modified by cobalt and iron salts with natural and synthetic polyazamacrocyclic ligands do not lose their activity on pyrolysis (600–800 °C). The latter actually increases.[27–33] It is naturally unlikely that the initial cobalt complexes were retained at the electrode.

The electrochemical reduction of oxygen to hydrogen peroxide at a rotating disc electrode is catalysed by the tetraazamacrocyclic cobalt complexes of cyclam (L8) or td (L9).[26] The ions $Co(cyclam)^{2+}$ also accelerate the subsequent reduction of H_2O_2 to H_2O when the conditions are altered.[34]

The electrochemical CO_2 reduction reactions, catalysed by macrocyclic coordination compounds, are of great theoretical and practical interest. Carbon dioxide is the main participant in photosynthetic reactions and in the future it may become the starting material for organic synthesis. Finally, the utilisation of CO_2 constitutes an extremely important aspect of the solution of ecological problems.

The most important electrochemical CO_2 reduction reactions are listed below with an indication of the corresponding standard potentials in an acid medium[22]:

$$CO_2 + 2H^+ + 2e = CO + H_2O,\ E^0 = -0.106\ V,$$

$$H_2CO_3 + 2H^+ + 2e = HCOOH + H_2O,\ E^0 = -0.166\ V,$$

$$2H_2CO_3 + 2H^+ + 2e = H_2C_2O_4 + 2H_2O,\ E^0 = -0.391\ V,$$

$$H_2CO_3 + 4H^+ + 4e = HCHO + 2H_2O,\ E^0 = -0.050\ V.$$

In an alkaline medium, the same reactions are characterised by different standard potentials[22]:

$$CO_3^{2-} + 3H^+ + 2e = HCO_2^- + H_2O,\ E^0 = 0.310\ V,$$

$$2CO_3^{2-} + 4H^+ + 2e = C_2O_4^{2-} + 2H_2O,\ E^0 = 0.478\ V,$$

$$CO_3^{2-} + 6H^+ + 4e = HCHO + 2H_2O,\ E^0 = 0.197\ V.$$

It is seen from the data presented that the electrochemical reduction of CO_2 can lead to the formation of a set of different products (CO, HCOOH, $H_2C_2O_4$, etc.).

Electrochemical CO_2 reduction reactions are accelerated by cobalt and nickel complexes of porphyrin and phthalocyanine[5,6,20] and also by cobalt complexes with comparatively simple tetraazamacrocyclic ligands.[35] Cobalt complexes with the "transdiene" (L9), the dimethyl-*cis*-diene (L13), and CR (L1), as well as nickel (II) complexes of CR (L1) have been investigated as catalysts of this chemical process.[36] A mechanism was proposed for the reduction of CO_2 to the final products (CO, HCOOH, $H_2C_2O_4$) and for the formation of hydrogen as a result of the reduction of the water protons (in all cases, cobalt is linked to the macrocyclic ligand):

$$\begin{array}{ccccc} Co\,(II) & \overset{+e}{\rightarrow} & Co^-(I) & \xrightarrow{+H^+} & Co\,(III)\,(H^-) \xrightarrow{+H^+} Co\,(III) + H_2 \\ & & \uparrow\downarrow{\scriptstyle +CO_2} & & \uparrow\downarrow{\scriptstyle +CO_2} \\ & & Co\,(I)\,CO_2 & & Co\,(III)\,(HCO_2^-) \overset{+H^+}{\rightleftarrows} Co\,(III) + CO + H_2O \\ & & \uparrow\downarrow & & \uparrow\downarrow{\scriptstyle +H^+} \\ & & Co\,(III) + C_2O_4^{2-} & & Co\,(III) + HCOOH\ . \end{array}$$

The electrocatalysis was carried out at a mercury cathode.

Further studies showed that nickel(II) complexes of cyclam (L8) exhibit an especially high effectiveness and selectivity in the reduction of CO_2.[37] Subsequently the mechanism of the electrochemical reduction of CO_2 was investigated in fair detail.[38]

It was established that the complex $Ni(cyclam)CO^+$ as well as the compounds $LNi(III)CO_2$ and LNi(II)CO may be formed as intermediates in the electrocatalytic reduction of CO_2.[39] The electrochemical reduction of carbon dioxide has also been observed at electrodes with a polymeric coating containing nickel complexes of tetraazaannulenes (L6, L7, etc.).[40]

The study of CO_2 as a ligand is of special interest.[41] Certain coordination compounds of cobalt(I), containing tetraazamacrocyclic compounds and carbon dioxide as ligands, have been described and characterised quantitatively.[42,43]

The bimacrocyclic cobalt complex $Co(sep)^{3+}$ (CoL14) [44] and the nickel complex $Ni(teta)^{2+}$ (NiL11) are used in electrocatalytic hydrogen evolution reactions.[45]

The electrocatalytic reduction of nitrate at a mercury electrode with formation of hydroxylamine, proceeding in accordance with the equation

$$NO_3^- + 7H^+ + 6e = NH_2OH + 2H_2O,$$

has been described.[46] The reaction is catalysed by nickel(II) and cobalt(III) complexes of cyclam (L8). The complexes of other transition metals with this ligand have a low activity.

Transition metal complexes with macrocyclic ligands also catalyse many electrochemical (anodic) oxidation processes. For example, cobalt complexes of porphyrins, phthalocyanine, and tetraazaannulenes (L6, L7) catalyse the anodic oxidation of $SO_2(H_2SO_3)$, whereas copper, nickel, and palladium complexes are catalytically inactive.[47] The catalytic activity of the tetraazamacrocyclic complexes diminishes in the sequence CoTAA ≫ CoTPhP > CoPc. The catalytic activity of carbon electrodes modified by CoTAA persists also after their pyrolysis at 800 °C.[48]

The tetraazamacrocyclic nickel complex NiL18 catalyses the anodic oxidation of benzyl alcohol to benzaldehyde; the formation of the compound Ni(III)L as an intermediate is then postulated.[49] The same reaction is catalysed by the ruthenium(IV) and ruthenium(V) complexes of tetramethylcyclam (L15).[50]

Finally, the anodic oxidation of $PhSCH_2Si(Me)_3$ in the presence of an alcohol ROH leads to the formation of $PhSCH_2OR$ and the $Si(Me)_3^+$ cations:[51]

$$PhSCH_2Si\,(Me)_3 \xrightarrow{ROH} PhSCH_2OR + Si\,(Me)_3^+ + H^+ + 2e.$$

V. Reactions involving oxidation by oxygen catalysed by macrocyclic metal complexes

Catalysis by tetraazamacrocyclic transition metal complexes M(teta) and M(td) of the reactions involving the oxidation of various substrates, in particular cyclohexene, by molecular oxygen

has long been known.[52] The oxidation reactions of hydrogen sulphide and various mercaptans, catalysed by porphyrin complexes of cobalt, iron, copper, nickel, and a number of other transition metals, have been described.[5,6] To some extent, a similar catalytic activity of macrocyclic dinuclear complexes of copper(I) and copper(II) of the type Cu_2L (L = L16) is manifested in the reactions[53,54]

$$2\,PhSH + {}^1/_2\,O_2 = PhSSPh + H_2O,$$
$$2\,PhC{\equiv}CH + {}^1/_2\,O_2 = PhC{\equiv}C{-}C{\equiv}Ph + H_2O,$$
$$PhNHNHPh + {}^1/_2\,O_2 = PhN{=}NPh + H_2O.$$

Dinuclear complexes of the type Cu_2L16 can be regarded as models of the active centres of certain copper oxidases containing the so called EPR-undetectable copper(III).

Nickel complexes with a kind of tetraazamacrocyclic ligand-anions, each containing two amide (peptide) groups (L17, L18), exhibit a high catalytic activity in reactions involving the oxidation of various substrates by molecular oxygen. These nickel complexes catalyse the oxidation of benzene to phenol, of toluene to cresol, etc.[55,56] and also the oxidation of styrene by oxygen in the presence of tetrahydroborate.[57]

The catalytic acceleration of the oxidation of 1,3-bicyclooxolan to ethylene glycol monoformate by cobalt(II) complexes of dibenzo-18-crown-6 [58] appears fairly unexpected since cobalt(II) complexes do not form any kind of stable complexes with crown-ethers.

The copper(I) and copper(II) complexes with the tetraazamacrocyclic ligand TAAB (L19) catalyse the oxidation of ascorbic acid by molecular oxygen.[59,60] Ascorbic acid free radicals and superoxide radical-anions are then formed. Under certain conditions, this reaction can proceed in the vibrational regime.[61] Tetraazaannulene complexes of iron catalyse the oxidation of hydroquinone to quinone in solution in pyridine.[62]

Finally, the oxidation of a number of alcohols to aldehydes and ketones is catalysed by thiamacrocyclic complexes of copper(II) (L20 and L21). The copper compounds of the type $CuL20^{2+}$ and $CuL21^{2+}$ can be regarded as analogues of the active centres of the so called "blue proteins".[63]

Macrocyclic complexes of transition metals catalyse the photochemical oxidation of methanol to formaldehyde. Iron(II) complexes with the tetraazamacrocyclic ligand TIM (L22)[64] as well as the cobalt(III) complexes with the ligands L9 (td) and L14 (sep) [65,66] can be used as catalysts.

VI. Other reactions catalysed by macrocyclic metal complexes

The analogy between haem-containing proteins—catalase and peroxidases—and tetraazamacrocyclic transition metal complexes suggested that the latter might exhibit catalase or peroxidase activity. Such activity has been observed in iron(III)-, cobalt(III)-, ruthenium(III)-, and osmium(IV)-pthalocyanines.[67] Somewhat later, it was established that the complex $[Fe(CRH)Cl_2]^+$ (CRH = L2) possesses catalase activity.[68] The activity of $[Fe(CRH)Cl_2]^+$ is an order of magnitude smaller than that of catalase but an order of magnitude higher than that of the iron(III) aquo-ion. Subsequently it was discovered that this iron complex exhibits a peroxidase activity in the oxidation of benzene and its substituted derivatives by hydrogen peroxide.[69] The iron(II) complex of TAAB (L19) does not exhibit an appreciable catalase activity but it does possess a pronounced peroxidase activity: in its presence, hydrogen peroxide oxidises a number of substrates. The oxidation of the dye Eriochrome Black has been characterised quantitatively.[70]

Cobalt(II) complexes of sepulchrates (sep = L14) reduce oxygen quantitatively to H_2O_2, being oxidised at the same time to $Co(sep)^{3+}$, which subsequently readily returns to the initial state $Co(sep)^{2+}$.[71]

The complexes NiL17 and NiL18 exhibit a superoxide dismutase activity.[72]

A number of reactions with participation of NaClO and PhIO as oxidants are accelerated by nickel(II) complexes of cyclam (L8) and chelating ligands (salen).[73] If $NaClO_4$ is used for the oxidation of alkenes, the catalytic activity of the macrocyclic complex is then found to be lower than that of the complexes of Schiff bases, while in the case where PhIO is employed the nickel complex of cyclam is found to be a more effective catalyst. The PhIO oxidant converts styrene and *trans*-stilbene into benzaldehyde and styrene epoxide in the presence of the dinuclear copper complex Cu_2L_{23}.[74]

The epoxidation reaction is also catalysed by nickel complexes of cyclam and its substituted derivatives, especially TMC (L15).[75] The proposed mechanism of the catalysis of the epoxidation of alkenes in the presence of nickel complexes of cyclam postulates the formation of intermediate nickel(III) or even nickel(IV) compounds. Cobalt(II) complexes of cyclam exhibit a weak catalytic activity and the $Cu(cyclam)^{2+}$ complex is altogether inactive.[76] Nickel complexes of the tetraazamacrocycles CR (L1) and TIM (L22) also possess a high catalytic activity in epoxidation reactions.[77] The catalytic acceleration of the oxidation of styrene with formation of the epoxide and benzaldehyde by the iron(III) complex of a 21-membered chiral macrocyclic ligand, containing four amide and one bipyridyl group, has been observed.[78]

A characteristic feature of the vast majority of vibrational chemical reactions is the involvement in the oxidation of the substrate (for example, malonic acid) by an oxidant (for example, bromate) of a transition metal compound as catalyst in which the metal undergoes a periodic change in the oxidation state. Such a compound may be, in particular, a macrocyclic complex.[79]

It has been observed that tetraazamacrocyclic copper(II) complexes catalyse the oxidation of malonic acid by bromate in an oscillating reaction. The oxidation state of the copper then changes from 2 to 3 and back again. The use of copper(II) complexes with teta, td, and cd (L11, L9, and L10 respectively) as catalysts has been examined.[80–83] The copper complexes with unsaturated ligands (td and cd) can, in contrast to the complex with the saturated ligand (teta), function not only as catalysts but also as substrates, i.e. the ligands cd and td can be oxidised by bromate in the vibrational mode. A similar picture is also observed when nickel complexes of the *cis*-diene cd (L10) are used as catalysts.[81–83]

The use of metal complexes with macrocyclic ligands for the catalytic acceleration of chain transfer from polymers to the monomer in radical polymerisation reactions has been examined in a number of studies. Low-spin cobalt(II) complexes with tetraazamacrocyclic ligands, in particular, with porphyrin and derivatives of tetraazaannulenes (L4, L6, L7), exhibit a catalytic activity, while cobalt complexes of td, teta, and TAAB (L9, L11, and L19 respectively) are inactive.[5,7,84] In the key stage, the radical-like compound Co(II)L reacts with hydrogen atom of the substrate and forms a radical and a cobalt hydride of the type $(H^-)Co(III)L$. This hydride then decomposes with elimination of hydrogen, while the cobalt returns to the initial state cobalt(II).

Photocatalytic reactions involving the evolution of hydrogen from water on treatment with various electron donors, photosensitisers,

and photocatalysts have been described. Cobalt(II) sepulchrates (the L14 ligand) can be used as photocatalysts.[44,85] The use of the complex $Ni(cyclam)^{2+}$ in the photocatalytic evolution of H_2 from water in a system containing a bipyridylruthenium complex (sensitiser) and ascorbic acid (electron donor) has been described.[86] It is suggested that the nickel(II) in the macrocyclic complex is reduced to Ni(I)L; this nickel(I) compound, which possesses nucleophilic properties, reacts with a proton to form the complex $(H^-)Ni(III)L$, which evolves H_2 on reaction with protons and is reduced by ascorbic acid to Ni(II)L (L = cyclam).

Even earlier, it was shown that the photocatalyst of the water reduction reaction in solutions containing bipyridylruthenium complexes as the sensitiser and europium(II) salts as the electron donor may be the cobalt complex of TIM (L22).[87]

Coordination compounds of nickel(II) with chiral macrocyclic ligands, containing sulphide sulphur in the macrocycle or amine nitrogen as well as sulphur, catalyse Grignard reactions[88,89] and, in particular, the reaction between RMgCl and vinyl bromide.

VII. Conclusion

Catalysis by metal complexes with macrocyclic ligands constitutes a new chapter in chemical science, more than 90% of the studies quoted in the literature referring to the last decade. The considerable unutilised possibilities of this field of study are indicated by the fact that, out of the several thousand macrocyclic ligands described, only a few tens, most thoroughly investigated and readily synthesised, have so far found applications in catalysis. The possibility of using macrocyclic coordination compounds to model the activity of many metalloenzymes opens the way to good future prospects. Studies of this kind are associated with the development of a new promising scientific field—biomimetic chemistry ("biomimetics"),[90] particularly that aspect of it which deals with the creation of "synzymes" (synthetic enzymes).

Macrocyclic coordination compounds are used mainly in the catalysis of oxidation-reduction processes, although a certain number of hydrolytic reactions catalysed by metal complexes of macrocycles are known. In the case of oxidation-reduction processes, the possibility of regulating the redox potentials of catalysts within wide limits by varying the parameters of the macrocyclic ligand (the size of the cavity, the number and nature of electron-donating atoms, their positions, etc.) plays an extremely significant role. The possibility of detecting "unusual" electronic states of metal ions, including radical forms [low-spin cobalt(II) and nickel(III) complexes] and nucleophiles with an unshared electron pair located on the metal atom is of great importance. Finally, the possibility of varying the geometry and the electronic structure of the ligand itself from the "usual" macroheterocyclic cyclam (L8) to a complex system with a large number of π-bonds of the type of porphyrin or phthalocyanine gives rise to good future prospects.

Studies in the field of catalysis by metal complexes of macrocycles have so far been limited to a comparatively small number of metals. The extension of the range of metals incorporated in the macrocycle for the preparation of catalytically active species can lead to new results.

Finally, we may note that the application of metal complexes of macrocycles in catalysis is associated with the solution of a series of scientific-technical problems of very great current interest, such as the creation of fuel cells, the use of solar energy, the utilisation of CO_2, etc.

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