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Complexes of macrocycles with pendant arms as models for biological molecules

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Abstract

Recent literature results on inorganic models related to metalloenzymes which transport electrons or activate small molecules are discussed in this review. The molecular systems are essentially restricted to macrocyclic or polydentate ligands preferentially containing nitrogen atoms and pendant arms. The discussion is mainly concerned with aspects such as spectroscopic, electrochemical and chemical characterization of the systems and electro- or photo-activation of small molecules.

Keywords: Aza-macrocyclic ligands; Pendant substituents; Small molecules; Photocatalysis; Vibrational spectra; Electrocatalysis; Reduction; Bioinorganic models

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1. Introduction

The synthesis of aza-macrocyclic compounds received considerable attention during the last decade because of their relationship to biomimetic and catalytic systems and the applications of this type of chelating agents to biology and medicine. They have applications in modern chemical techniques such as magnetic resonance imaging, imaging with radioisotopes and radiotherapy, i.e. techniques where metal complexes with extreme kinetic and thermodynamic stability toward metal release are required [1,2].

There has been a particular interest in the preparation and characterization of coordination compounds with aza-macrocyclic ligands with pendant substituents for the reasons given above [3–7]. The complexation properties of polyaza-macrocycles are governed mainly by the macrocyclic ring size. *N*-Functionalization of these macrocycles may enhance their metal-ion selectivity and the stability of metal complexes depending on the coordination properties of the pendant arms [3].

The systems to be considered in this review are essentially restricted to macrocyclic or polydentate ligands preferentially containing nitrogen atoms and pendant arms. Properties of the compounds considered in this review are mainly restricted to UV–vis and IR spectroscopy, surface phenomena, electrochemical and chemical characterizations of the systems and electro- or photo-activation of small molecules, i.e. CO_2 [8,9].

Molecular recognition of DNA, RNA and related biomolecules by complexes with aza-macrocyclic ligands has attracted great interest [10,11]. A critical survey of this important field and the main biomimetic models based on this kind of ligands are made in this work.

2. General remarks

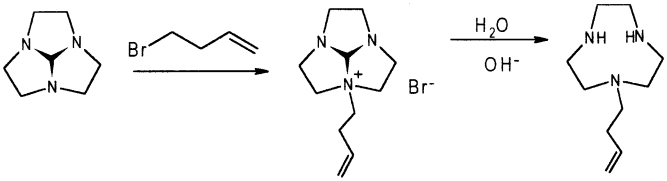
General aspects about the synthesis and characterization of complexes with aza-macrocyclic ligands possessing pendant substituents and particular examples related to recently studies on equilibria in solution are described in this section.

2.1. Synthesis and characterization

Work on the preparation of complexes with aza-macrocyclic ligands containing pendant substituents has increased during the last five years [4–7,12,13]. They have been characterized by several conventional techniques. Also, the X-ray crystallographic structure has been determined for most of them [14–24].

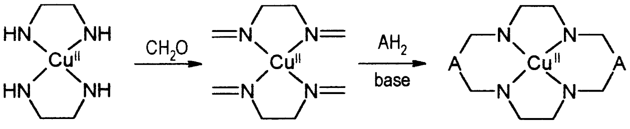
The most relevant aza-macrocyclic ligands and complexes synthesized in the above-mentioned period range from 9 to 24 atoms. They predominantly show no extended π-delocalization, i.e. the synthesis of porphyrins, phthalocyanines, naphthalocyanines and related derivatives with pendant substituents are scarce compared with those ligands possessing a highly saturated ring.

Peackock et. al. reported a general method for the preparation of nine-membered mono-*N*-substituted derivatives, as shown in Scheme 1. A variety of methods have been used to ensure the isolation of singly substituted products, some of which are not general and most of which require chromatography to separate the singly substituted product from the multiply-substituted by-products [25].



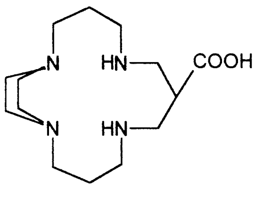
Scheme 1.

Diethylmalonate acts as an efficient locking fragment in the Cu(II) directed synthesis of 14-membered tetraaza-macrocycles. For example, in the reaction of $[Cu(1,2\text{-diaminoethane})2]^{2+}$ with two equivalents of diethylmalonate in the presence of formaldehyde and triethylamine the 1,4,8,11-tetraazacyclotetradecane-6,6,13,13-tetracarboxylic acid, tetraethyl ester Cu(II) diperchlorate complex salt is formed, as shown in Scheme 2 [26].

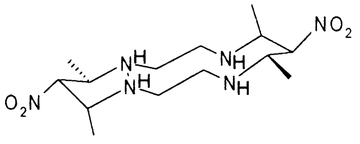


Scheme 2.

On the other hand, syntheses and X-ray characterization of Ni(II) complexes with ligands derived from tetraazacyclopentadecane with a pendant arm, as shown in **L1**, were described recently. These complexes form octahedral paramagnetic species where axial coordination of the pendant arm to the metal leads to a 1D chain compound, i.e. the C-pendant attached directly to the macrocyclic ring acts as a bridging group [27].



L1



L2

The new pendant-arm macrocycle ligand **L2** forms a Cu(II) complex which has recently been synthesized. Its crystal structure revealed a rare example of genuine square-planar coordination [28].

Complexation reactions of several tetraaza-macrocycles with Group 6 metal carbonyls form compounds (Fig. 1) with a stoichiometry dependent on the size of the macrocycle and on the metal [29].

Moore et al. [30] have reported the synthesis and characterization of 12-membered ring ligands (Scheme 3) and their corresponding Ni(II), Cu(II) and Zn(II) complexes. Recently, there have been a number of studies in which coordinating 2-pyridylmethyl pendant arms have been attached to the N atom(s) of aza-macrocycles [31,32]. This is usually achieved by direct alkylation of all of the available macrocyclic secondary amino groups with 2-chloromethylpyridine. In this way, new macrocyclic ligands have been produced with one, two or three 2-pyridylmethyl pendant arms. Scheme 4 shows one example of this type of synthesis. The crystal structure for the Zn derivative shows a distorted square-pyramidal geometry, with the Zn atom 0.59 Å above the plane of the macrocyclic ring in the direction of the coordinated pendant pyridyl group [31].

Bazzigalupi et al. reported the synthesis of the ligands **L3**, **L4** and **L5**. These compounds behave as versatile building blocks for the assembly of 1,4-dibenzoaza- or oxaaza-macrocycles [33].

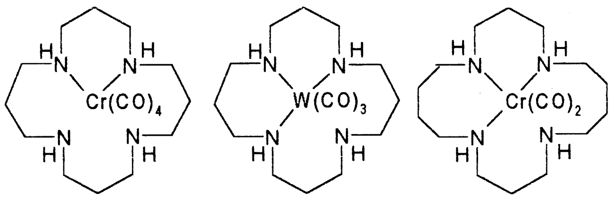
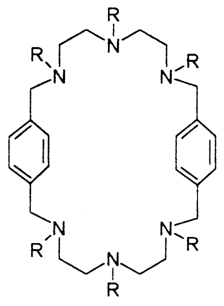
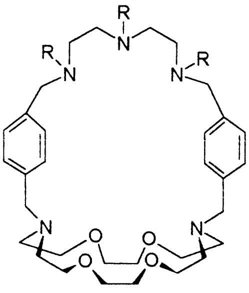


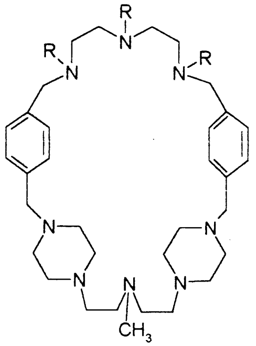
Fig. 1. Reactions of complexation of several tetraaza-macrocycles with Group 6 metal carbonyls.



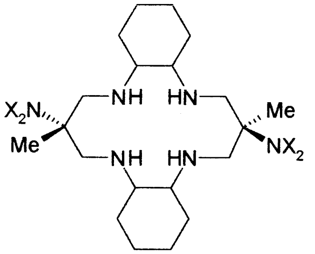
L3



L4



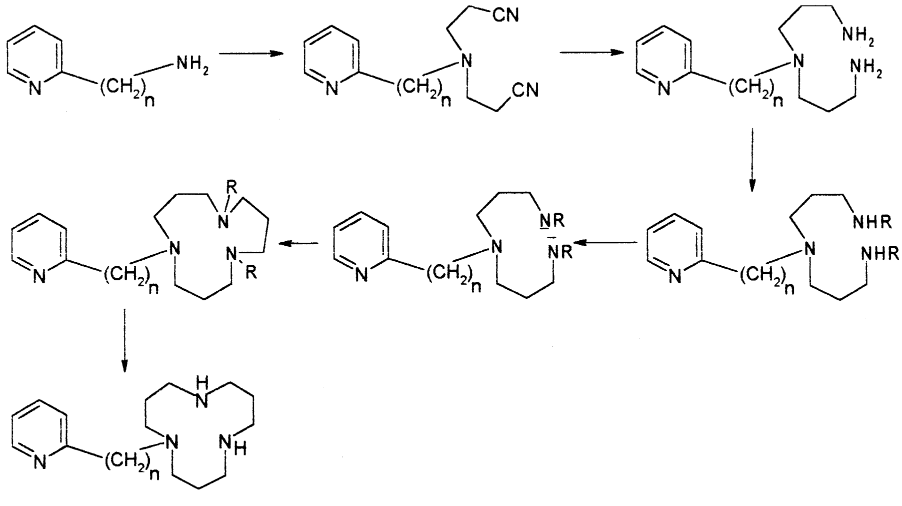
L5



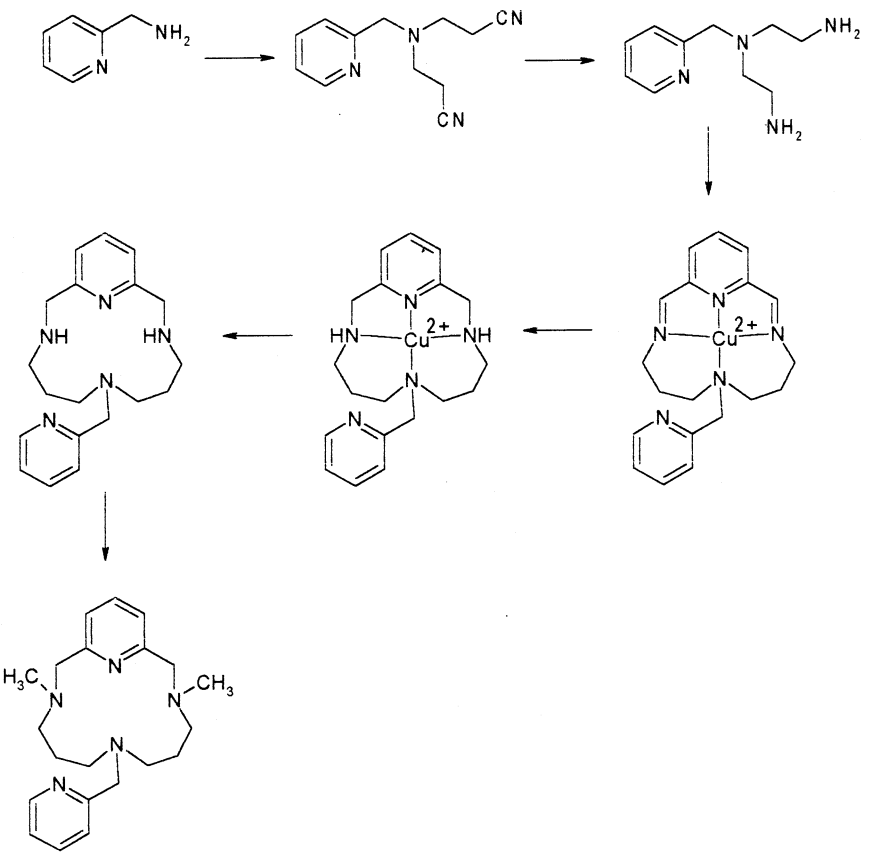
X = O, H

L6

Lawrence et al. have synthesized the ligand **L6** by reaction of bis(*trans*-cyclohexane-1,2-diamine)copper(II) with formaldehyde and nitroethane in a basic aqueous solution. This rigid polycyclic macrocycle, based on a 14-membered tetraazacy-



Scheme 3.



Scheme 4.

cloalkane frame, may exist as a number of isomers and spectroscopic and chiro-optical properties of the isolated complexes were reported [34,35]. Reduction of the nitro groups with zinc in aqueous acid produces the corresponding compounds with a pendant primary amine as metal-free hydrochloride salts in good yield.

One interesting property of these systems is related to protonation equilibrium involving the pendant amine. The stability of complexes formed by multidentate and macrocyclic ligands with six coordinate first row d-block transition metal di-cations generally follows the Irving-Williams sequence (Mn < Fe < Co < Ni < Cu > Zn). Attempts to modify this pattern of selectivity ligands have been designed to enforce a tetrahedral geometry on a metal [36,37] and the macrocycles described here were developed as part of ongoing studies in this area. These matters will be discussed next.

2.2. Equilibrium species

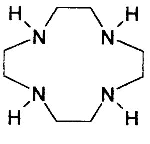
2.2.1. Coordinating pendant arms

An important characteristic of aza-macrocyclic compounds is the existence of multiple equilibria between species in solution. Indeed, aza-macrocyclic ligands with a saturated framework are basic compounds which undergo multiple *N*-aza protonation reactions. Introduction of pendant groups (*N*-pendant) in the ligand, e.g. $N\text{–}RO^-$, $N\text{–}RCOO^-$, $N\text{–}RCONH_2$, etc., add one additional site that might be protonated. Interactions via nitrogen atoms with the media would be lost depending on the number of the protonable *N*-pendant groups introduced.

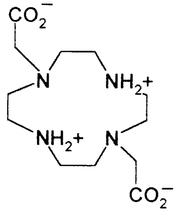
The presence of this kind of pendant groups also induces additional inter- and intramolecular equilibria exchanges, intramolecular bonds, coordination ability and selectivity for ionic monoatomic species, stereochemical, structural and conformational exchanges in the complexes among others changes. Several systems and equilibria are considered next with some emphasis on the protonation reactions.

The complexation of alkali metal ions by multidentate ligands involves sequential solvent displacement at the metal center and ligand conformational changes that sometimes results in selective complexation of a particular alkali metal ion, as exemplified by antibiotic complexes, coronates and cryptates [38].

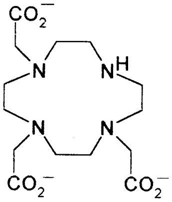
Cyclen, **L7**, and its derivatives, **L8**, **L9** and **L10**, are more stable than its homologous complexes from cyclam, especially when the divalent metal ion is one of large ionic radius [39,40].



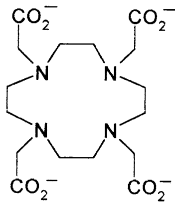
L7



L8



L9



L10

In addition, **L8** binds in a *cis*-octahedral fashion to Ni(II) through the four nitrogen atoms and two carboxylate groups. These units form dimers via an apparently symmetrical hydrogen bond from the non-bonding oxygen of a carboxylate group to a lone proton originated from a perchloric acid molecule of crystallization [41]. A similar structure is confirmed for the Zn(II) complex by ^{13}C-NMR. Cyclam coordinates in its most stable *trans* configuration by appending car-

Table 1

L7, **L8**, **L9** and **L10** pK_a values [a]

[b] Equilibria	**L7**	**L8**	**L9**	**L10**
$L^{x-}+H^+ \overset{K_1}{\rightleftharpoons} HL^{(x-1)-}$	11.32	11.45	11.59	11.73
$HL^{(x-1)-}+H^+ \overset{K_2}{\rightleftharpoons} H_2L^{(x-2)-}$	9.72	9.54	9.24	9.40
$H_2L^{(x-2)-}+H^+ \overset{K_3}{\rightleftharpoons} H_3L^{(x-3)-}$	<2.3	4.00	4.43	4.50
$H_3L^{(x-3)-}+H^+ \overset{K_4}{\rightleftharpoons} H_4L^{(x-4)-}$	<2.3	2.36	3.48	4.19

[a] $\text{Log}_{10} K_x = pK_{ax}$.

[b] $x = 2, 3, 4$ and 0, for **L8**, **L9**, **L10** and **L7**, respectively.

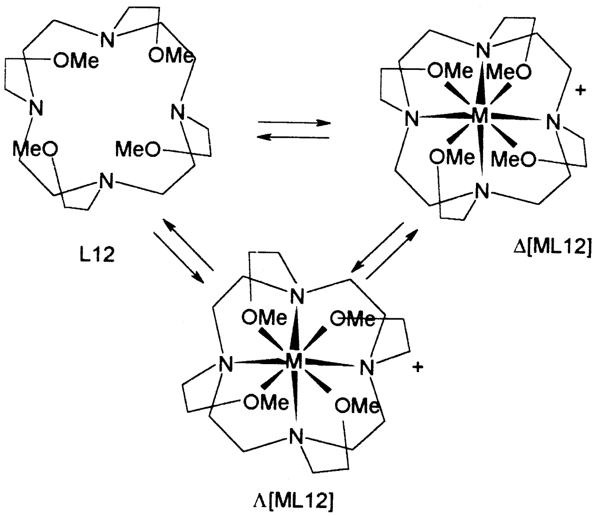
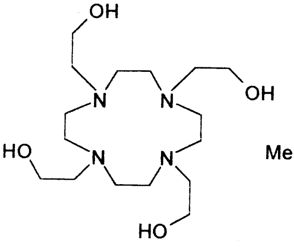


Fig. 2. Enantiomerization for the Δ and Λ square antiprismatic $[\mathbf{ML12}]^+$ (M = Li, Na, K) complexes.

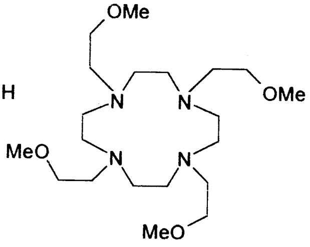
boxymethyl groups to the diagonally related nitrogen atoms, one below the macrocyclic plane and the other above [42].

Protonation constants were measured by potentiometric titration of **L7**, **L8**, **L9** and **L10** with tetraethyl ammonium hydroxide, using tetraethyl ammonium perchlorate to keep the ionic strength constant. Table 1 shows the results of these measurements which merit some comments. A trend toward higher basicity at the first protonation site as the number of carboxylate groups increases is observed. Also, the first carboxylate site is more basic than is normally seen for α-amino acids ($pK_a = 2.0–2.5$). Internal hydrogen bonding appears to be responsible for the disparity of magnitudes in the pK_a values for carboxylic groups. Formation constants for complexes with divalent Co, Ni, Cu, Zn, Cd and Pb were also communicated [41]. Distribution diagrams of these species at different pH values were calculated [41].

The ligand **L11** was the first pendant-arm tetraaza-macrocycle in which equilibrium and kinetic studies of inter and intramolecular exchange processes involving alkali-metal complexes were quantitatively studied [43,44].



L11

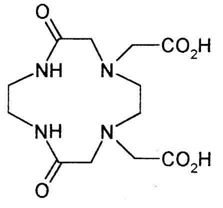


L12

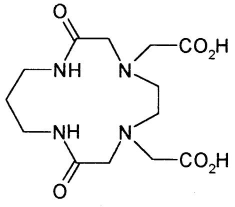
The stabilities of complexes [**ML11**]$^+$ and [**ML12**]$^+$ (M = Li, Na, K, Rb, Cs, Ag), were determined in several solvents [38,42]. In the [**ML11**]$^+$ family, the differences between equilibrium constants were attributed to changes with the metal's ionic radii of opposing contributions from the M$^+$ solvation energy and from the ability of **L11** to adopt an optimum conformation in the coordination to the metal. It is possible to conclude that the complexes of the parent macrocycle cyclen are less stable than those from **L11** [38,42].

The enantiomerization of the Δ and Λ square antiprismatic [**ML12**]$^+$ (M = Li, Na, K; Fig. 2) were studied by ^{13}C-NMR; this phenomenon occurs much more rapidly than the intermolecular exchange of the ligands. An exception must be made for [**KL11**]$^+$ in which the enantiomerization occurs predominantly through the intermolecular exchange of **L11** [45].

Neutral complexes of Co^{2+}, Ni^{2+}and Cu^{2+}, with the macrocyclic ligands **L13** and **L14** and their protonation equilibria leading to species $[\mathrm{MLH}_{-1}]^-$ and $[\mathrm{MLH}_{-2}]^{2-}$ have been studied [46].



L13



L14

The electronic spectra in solution for MLH_{-2} species are quite different from those of the corresponding ML species. This experimental observation has been attributed to a change in the coordination geometry as a result of amide nitrogen atom deprotonation. Dissociation constants for the complexes mentioned above are shown in Table 2. The $\mathrm{p}K_{[\mathrm{MLH}_{-1}]^-}$ values are significantly higher than $\mathrm{p}K_{[\mathrm{MLH}_{-1}]^{2-}}$ for **L13** ligands. However, $\mathrm{p}K_{[\mathrm{MLH}_{-1}]^-}$ values are lower than $\mathrm{p}K_{[\mathrm{MLH}_{-1}]^{2-}}$ for **L14** ligands. Such large differences in the acid–base properties of the two macrocyclic ligand, i.e. **L13** and **L14**, compounds are due to a difference of only one –CH$_2$– group in the ligand ring system.

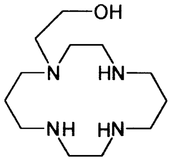
The stability constants for the monometallic complexes formed from ligands of monohydroxyethylated tetraaza-macrocycles **L15**, **L16** and the tri-hydroxyethylated

Table 2
pK_a dissociation constants for [**ML13**] and [**ML14**] (M = Co, Ni, Cu) [a]

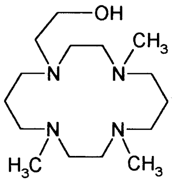
Equilibria	Co		Ni		Cu	
	L13	**L14**	**L13**	**L14**	**L13**	**L14**
$\mathrm{ML} \overset{K_{\mathrm{MLH}_{-1}}}{\rightleftharpoons} [\mathrm{MLH}_{-1}]^- + \mathrm{H}^+$	9.52	10.62	9.30	10.68	7.30	7.38
$[\mathrm{MLH}_{-1}]^- \overset{K_{\mathrm{MLH}_{-1}}}{\rightleftharpoons} [\mathrm{MLH}_{-2}]^{2-} + \mathrm{H}^+$	12.23	10.26	13.90	9.78	10.41	6.05

[a] $\mathrm{Log}_{10} K_x = \mathrm{p}K_{ax}$.

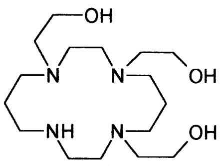
macrocycle **L17**, with Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} have been determined in aqueous solution [47].



L15

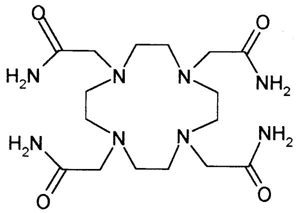


L16



L17

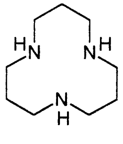
The tri-hydroxyethylated macrocycle complexes reach equilibrium, at each titration point, within 5 min from the addition of each aliquot of base. By contrast, the equilibration reactions of mono-hydroxyethylated ligands were slower processes. These results indicated that the ease of metal-ion coordination to the tetraazamacrocycles, afforded by pendant hydroxyethyl groups, required a minimum of two hydroxyethyl groups located on adjacent nitrogen atoms.



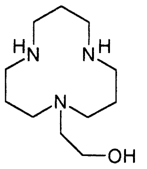
L18

Wainwright et al. have proposed that formation of the complex between **L18** and Cd(II) is indicative of an increased stabilization [48] with regard to that of related macrocyclic Cd(II) complexes, whose pendant substituents are different from those in **L18**. Indeed, the [Cd**L18**]$^{2+}$ complex, fully formed even in 1 M HNO_3, must have an unusually large complex stability constant, $pK > 21$. This value must be compared with $pK = 14.3$ and 23.3 for the respective complexes of Cd^{2+} and Cu^{2+} with cyclen and $pK = 14.6$ and 15.2 for those complexes of the pendant-arm alcohol **L11**. Moreover, the complex crystallographic structure shows a pseudo square-antiprismatic geometry that allows intramolecular interconversions between two enantiomeric forms.

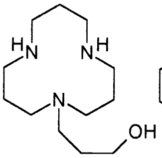
Catalytic hydrolysis of acetate, phosphates, and β-lactams of Zn(II) complexes with macrocyclic triamines [12]aneN_3, **L19**, and cyclen in aqueous solution have been intensively studied [49] to elucidate the role of Zn(II) in hydrolytic zinc enzymes such as carbonic anhydrase, alkaline phosphatase, and β-lactamase II. Hydrolysis is thought to involve the Zn(II)–OH^- species as the active nucleophile for some enzyme models and is now widely accepted for hydrolytic zinc enzymes. A site-directed mutagenesis study disclosed two Zn(II) ions at the active center: one surrounded by three histidine residues and the other by two histidine residues [50]. Here again, the relative nucleophile was proposed to be the Zn(II)–OH^- species.



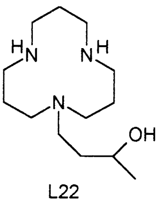
L19



L20

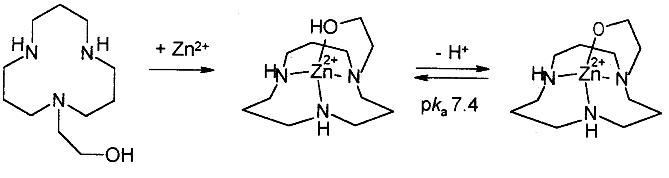


L21



L22

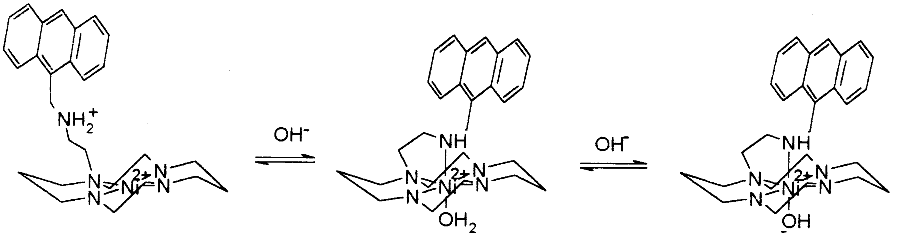
Zn(II) complexes of **L20**, **L21** and **L22**, parent to **L19**, have revealed that the pendant alcohol of $[\mathrm{Zn}\mathbf{L20}]^{2+}$ deprotonates with an extremely low pK_a value of 7.4 to become an alkoxide anion donor at the fourth coordination site [51], as shown Eq. (1). This fact is used to explain that the serine residue located at the center of zinc enzymes can be deprotonated at physiological pH.



L20 Zn^{II}L20 Zn^{II}H$_{-1}$L20 (1)

The alkoxide-coordinating complex Zn(II)H_{-1}**L20** was crystallized as the dimeric complex (Zn(II)H_{-1}**L20**)$_2$ in an aqueous solution of **L20** and Zn(ClO$_4$)$_2$ at pH 9. This alkoxide Zn(II)H_{-1}**L20** catalyzes the 4-nitrophenyl acetate hydrolysis, and kinetic study at pH 9.3, has established the second-order rate constant, which is almost four times greater than the corresponding value for the Zn(II)**L20**–OH$^-$. The model shows for the first time that the Zn(II)-bound alkoxide is a better nucleophile than the Zn(II)-bound hydroxide.

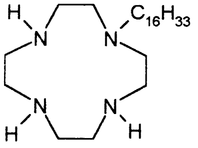
Equilibria related to the species depicted in Eq. (2) show the existence of OH$^-$ coordinated al high pH values [51]. Also, the protonated species is yellow, square planar and low-spin whereas the deprotonated form is blue–violet, octahedral and high-spin. A potential application of the equilibria in Eq. (2) is the control of the luminescence of groups in the pendant arm.



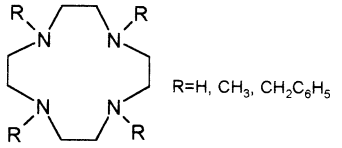
(2)

2.2.2. *Non-coordinating pendant arms*

Macrocyclic ligands with non-coordinating *n*-alkyl pendant arms also participate in various equilibria and may have some practical applications. The lipophilic Zn(II) complex with hexadecylcyclen, **L23**, is almost insoluble in water but becomes soluble in the presence of the triton X-100 surfactant [49]. In the Zn(II) complex, monodeprotonation of the Zn(II)-bound H_2O yields a binuclear OH-bridged complex, (Zn**L23**)$_2$OH$^-$, and a monomeric Zn(II)**L23**–OH$^-$ species. Besides, the complex Zn(II)**L23** possesses a higher catalytic activity than the related complex of cyclen with Zn(II) in the hydrolysis of 4-nitrophenyl acetate, bis(4-nitrophenyl)phosphate, and tris(4-nitrophenyl)phosphate. The catalytic activity increased with pH and leveled off at pH 10. It was concluded from these experimental observations that the active species was Zn(II)**L23**–OH$^-$. The higher effective concentration of the lipophilic substrate coexisting with the complex in the micelles accounts for the enhanced catalytic activity. Therefore, the lipophilic Zn(II)–hexadecylcyclen is probably one of the best candidates to be used in the detoxification treatment of poisonous phosphotriesters.



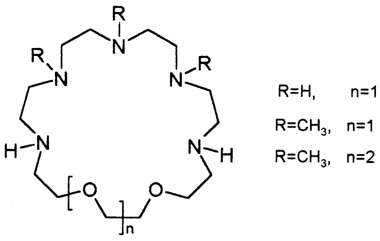
L23



L24

An equilibrium between the five-coordinate Ni(II) complexes with **L24** (R = CH_3, $CH_2C_6H_5$), and its planar Ni(II) complexes species in water or a water/ethanol mixture has been reported [52]. In non-planar compounds of Ni(II), spectral data leads to the conclusion that steric factors determine the ligand field strength more than the size of the macrocycle. By contrast, both factors play significant roles in the ligand field strength of square planar complexes. The equilibrium between the high-spin, five-coordinate, [Ni(**L24**)(H_2O)]$^{2+}$ complexes and the planar [Ni**L24**]$^{2+}$ is dominated by complex solvation factors.

There are other macrocyclic ligands containing nitrogen and oxygen as donor atoms in their framework. While they can act as anionic or neutral substrates, they sometimes behave as 'compartmental' macrocyclic receptors with different donor atoms at opposite sides of the molecule. In this arrangement, the structure has two binding sites with different hard–soft characteristics. Examples of these ligands are the oxaaza-macrocycles **L25** [53].



L25

Moreover, the **L25** ($R = H$, $n = 1$) ligand behaves as a tetraprotic base, with K_1–K_4 = 9.57, 8.87, 7.70 and 3.41, respectively, in $NaClO_4$ or NEt_4ClO_4. The higher basicity exhibited by **L25** ($R = H$, $n = 1$) with respect to **L25** ($R = CH_3$, $n = 1$) and **L25** ($R = CH_3$, $n = 2$) can be explained taking into account the presence of three tertiary nitrogens in the latter macrocycles.

3. Vibrational spectra of aza-macrocycles and their interaction with metal surfaces

This section is devoted to the interpretation of the vibrational spectra of the structure of the aza-macrocycles, free, in metal complexes and when they are interacting with metal surfaces.

A brief number of references, concerned with experimental techniques and normal-coordinate treatments which are applied to the investigation of these vibrational problems are also reviewed.

Since published studies of this nature with pendant macrocycles are rare (see Section 3.2.2), this section mainly considers non-substituted macrocycles and those having short chain substituents.

A detailed interpretation of the interactions of these species with metal surfaces could be of interest to people engaged in the design of modified electrodes for electrocatalytic studies (see Section 4.2).

3.1. Vibrational spectra techniques

IR reflection and surface enhancement Raman spectroscopy (SERS) are the most appropriate techniques to interpret the macrocycle–surface interaction. Different IR reflection techniques have been used: diffuse, reflection–absorption and attenuated total reflection (ATR). All of them, using specific accessories, have been reviewed and compared [54–56]. Fundamental aspects of SERS were analyzed by Schatz [57]. Aroca and Price [58] observed that tin island films used in surface IR experiments give rise to an electromagnetic enhancement of the IR absorption spectrum; the surface enhancement of the IR (SEIR) absorption was shown for evaporated nanometric films of 5,14-pentacenedione and naphthalic 1,8:4,5-dianhydride.

IR specular reflectance has been used in the study of glass type systems; preparative difficulties arise when attempting to record IR transmission spectra of glasses [59]. Reflection-absorption has been largely used to characterize adsorbates on metal surfaces [60–62], also in the study of the electrode–electrolyte interphase [63] and in the determination of the molecular orientation and stacking of the molecules deposited onto the surface [64]. Diffuse-reflection has been reviewed in the far, medium and near IR [65,66].

Most of SERS studies use the conventional Raman apparatus; the signal enhancement depends on the characteristics of the surface, the nature of the adsorbate, and on the incident wavelength. Colloids [67–69] and electrodes surface preparation [70] has been largely reported. There is little information about techniques to deposit metal on glass [71]. Most common techniques to deposit adsorbates onto different substrates are evaporation [72] and high-vacuum evaporation [73,74]; in both cases this procedure is accompanied by film thickness control. Molecular characterization of the film is a fundamental requirement to establish a correlation between the molecular structure, long-range molecular organization and physical properties of the film.

Several organic and organometallic molecules have been investigated in surface studies by means of IR-reflection and SERS [75–77]. Gold, copper and silver surfaces have the d band lower than the Fermi level; this means that they enhance the vibrational signals. In the case of copper colloidal solutions or metal deposited as islands, the band corresponding to the surface plasmons is observed in the near IR [78,79].

3.2. Aza-macrocycles and surface interactions

Tetraaza-macrocycles, in particular phthalocyanines and its derivatives, are interesting organic dyes which can be used in electrophotography, optical data recording and solar energy conversion [80–84], because their thin films have strong light absorption in the longer wavelength region (700–900 nm) of semiconductor lasers. Their photoactivity in the near-IR region depends on the extended π-electron conjugated macrocyclic systems. In order to search for electrooptic properties very well characterized surfaces should be prepared: the molecules must be deposited as thin films with a unique molecular stacking and orientation [74].

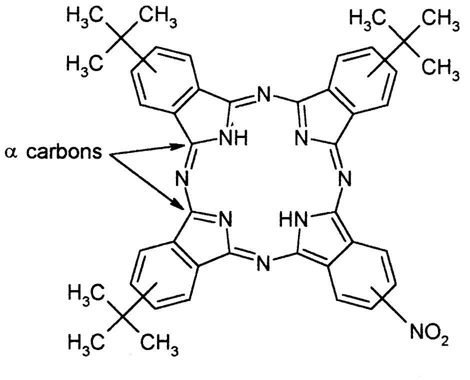
3.2.1. Porphyrins, phthalocyanines, and naphthalocyanines

Vibrational spectra of metalloporphyrins have been studied exhaustively because of their biological importance as prosthetic groups of a variety of heme proteins. Thus, many review articles have been published on this subject, and most of them discuss the vibrational spectra of metalloporphyrins together with those of heme proteins [85]. Recently, Nakamoto [86] has reviewed several articles concerning these macrocycles and discussed the state of the art of the normal coordinate analysis, the assignment of the structure-sensitive vibrations, the metal-macrocycle ring coordination, the metal–metal bonded porphyrins and the π–π complex formation and dimerization.

Metallophthalocyanines, M(Pc), are known for their high thermal stability and very low solubility in any solvents. The A_{2g} in plane vibrations become Raman active, similar to metalloporphyrins, under resonance conditions. Several IR and Raman spectra of M(Pc) and M(Pc) containing axial ligands have been reported by many investigators [87,88]. Melendres et al. [89] carried out a normal coordinate analysis on Fe(Pc). As expected, extensive vibrational coupling occurs among the local coordinates so that simple description cannot be justified; the Fe–N force constant was reported to be 1.0 mdyn $Å^{-1}$. Hutchinson et al. [90] assigned the νM–N modes of different metal isotopes of M(Pc). Aroca et al. [91] characterized the lanthanide series of bisphthalocyanine complexes of $LnPc_2^t$ (free radical green material) and the corresponding blue material ($LnHPc_2^t$) by using Raman and

SERS, IR and visible spectroscopy; interconversion of the green to blue material was observed by heating Langmuir–Blodgett (LB) assemblies and KBr pellets of the green material. Oxidation–reduction process was inferred to occur in the organic ring and the oxidation state of the central metal atom is not affected. Well-characterized LB multilayer assemblies of PrPc_2 and the tetra-*tert*-butyl derivative PrPc_2^t were exposed to NO_x (NO_2/N_2O_4) gas and the effect of gas adsorption was monitored using visible and IR spectroscopy [92]; the high sensitivity surface-enhanced resonance-Raman spectroscopy (SERRS) allowed one to observe the reversible chemical absorption of NO_2 on a monomolecular LB layer of PrPc_2 and PrPc_2^t.

Palys et al. [93] studied the resonance Raman spectra of monolayers of transition metal phthalocyanines; the spectra reveal specific interaction with the support. The mechanism in the case of ZnPc monolayers was elucidated by using Raman spectra and MNDO calculations. The α-atoms (see H_2**L26**) dominate the interaction with the support and the usually assumed D_{4h} geometry does not represent the true energy minimum but the mean of two mesomeric forms. The IR active *v*ZnN (Eg) vibration was observed at 329 cm^{-1} and the observed ZnN distance is 1.980 Å. Sheng-Gao et al. [94] prepared novel asymmetrically substituted metal-free Pc, nitro-*tert*-butylphthalocyanine, H_2**L26**, which resulted suitable for fabrication as a thin film using the LB technique.



H_2L26

Due to their extended π-electron-delocalized system, naphthalocyanines (H_2Nc), exhibit strong absorption bands in the near IR region [95]. This spectral characteristic and their photoconductive properties make the Nc compounds suitable candidates for applications in solar energy conversion and laser electrophotography [96]. Despite this importance, vibrational studies on Nc compounds are scarce. Kaplan et al. reported the IR energy of the most intense absorptions of some Nc metal complexes [97]. Yanagi et al. studied the IR spectra of various Nc complexes in the transmission and reflection absorption geometries [98]. Aroca et al. studied the vibrational spectra (Raman, Resonance Raman, SERRS and IR) of H_2Nc and

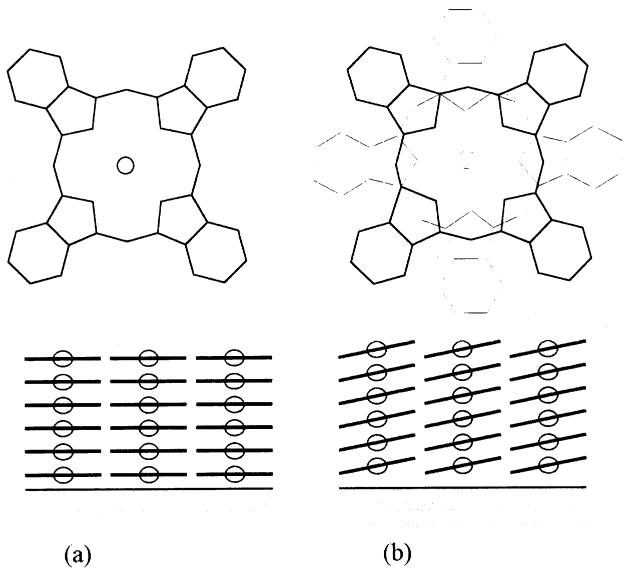


Fig. 3. Molecular stacking for **ML26** crystals: (a) metal free H_2**L26** and Zn**L26**; (b) Al**L26**Cl, Ga**L26**F and VO**L26** (adapted from Ref. [98]).

CuNc compounds [72]. A recent publication deals with a vibrational interpretation of the structure of the solid H_2Nc and their Co(II), VO^{2+} and Pb(II) complexes [99]; the metal–macrocycle stretching mode was observed at 330, 308 and 273 cm^{-1}, respectively. The Co and VO ions slightly disturb the structure of the Nc moiety, constraining the whole system to adopt a deformed warped stereochemistry in the same way that in MPc macrocycles [100].

Little work dealing with vibrational studies of the macrocycle–surface interaction has been published for naphthalocyanine and its metal complexes. One deals with the ZnNc complex for which the orientation onto different substrates has been inferred from IR reflection–absorption spectroscopy and other measurements [73]; three types of molecular orientations were assigned for the deposited thin films depending on NaCl, graphite and glass at 250°C. The orientation of different metal complexes of naphthalocyanine was studied by X-ray diffraction, IR spectroscopy, transmission electron microscopy and electron diffraction [98]: metal-free H_2Nc and ZnNc took the face-to-face, eclipsed stacking, *P* orientation, in which their molecular planes came into a parallel contact to the substrate surface; AlNcCl and GaNcF, and VONc took the eclipsed, slipped stacking, *I* orientation, holding their molecular planes slightly inclined to the substrate surface, as shown in Fig. 3.

Gobernado-Mitre et al. [72] studied the molecular organization of CuNc onto different substrates using IR and SERS; a tilted, close to face-on molecular orientation in the evaporated films on KBr and Ag was inferred from the transmission and reflection–absorption FT-IR spectroscopy. The medium-intensity Raman line at 223 cm^{-1} was ascribed to a deformation with a large Cu–N stretching contribution. An IR and theoretical interpretation of the structure and orientation of H_2Nc and its Cu(II) complex deposited onto a smooth copper surface has been recently proposed [101]; the electronic density on the copper ion, resulting from complexation, moves to the copper surface during the interaction. The differences between the spectra of the complex dispersed in KBr and those of the complex deposited onto a KBr monocrystal and onto a smooth copper surface, shown in the Fig. 4, support the existence of the metal–macrocycle interaction.

The substrate–adsorbate interaction constrains the macrocycle complex to adopt a deformed warped structure. Theoretically, the preferred orientation onto the surface and the energy of the interaction were evaluated through a simplified molecular model and using INDO/1 and extended Hückel semiempirical methods. The most probable orientation is plane parallel with the copper ion interacting with the surface. This interaction is stabilized to about 913 kJ mol^{-1} in comparison with that of the macrocycle ligand, which is tilted with respect to the surface. This orientation is mainly due to an out-of-plane position of the hydrogen atoms of the coordination site. The spectral variations, in particular the frequency shifting of CuNc interacting with the copper surface, were more significant in comparison with that observed by Aroca et al. [72] for the interaction of the same complex with a silver substrate. This confirms that the nature of the surface plays an important role in the adsorbate–substrate interaction. The complex–surface interaction of the CuNc–Cu system is favored due to the geometrical coincidence between the

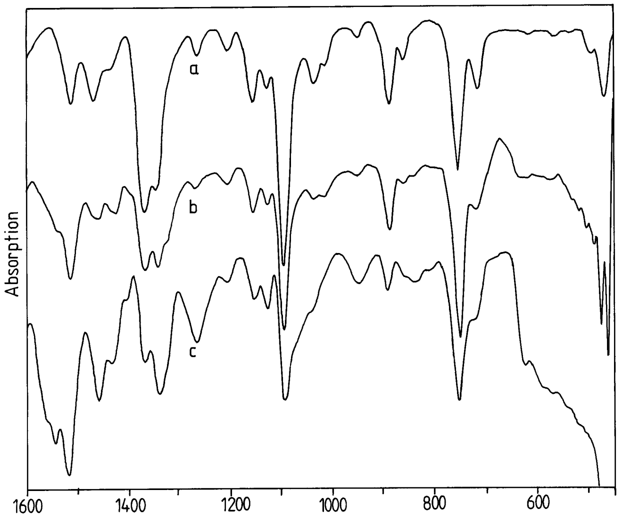


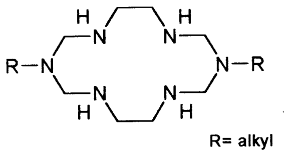
Fig. 4. (a) IR spectrum of Cu**L26** dispersed in KBr; (b) IR transmission spectrum of Cu**L26** onto a KBr monocrystal; (c) specular reflectance IR spectrum of Cu**L26** onto a smooth Cu surface for an incident radiation angle of 45°, in the region 1600–450 cm^{-1} [105].

nitrogen atoms of the coordination site in the complex and the copper atoms of the surface.

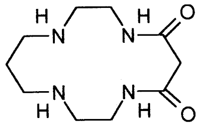
3.2.2. Hexaaza-macrocycles, tetraaza-macrocycles, and miscellaneous macrocycles

A vibrational study including the Raman and IR spectra and an extended normal coordinate treatment and semiempirical calculation performed at the INDO/1 level for the hexaaza-macrocycle shown in the H_2**L32** and its Cu(II) complex was recently published [102]. Bands at about 390 and 280 cm^{-1} were ascribed to νCuN; a force constant $F_{CuN} = 1.0$ mdyn Å^{-1} represents the observed bands quite well. The optimized CuN distance 1.84 Å is rather short in comparison with several other complexes (2.1 Å). This low force constant for such a short distance was interpreted in terms of a low positive charge on the copper atom. INDO/1 calculations confirmed this hypothesis suggesting that a relatively high total charge density is located on the coordination site. Thus, an eventual redox reaction with gases such as CO_2 should involve the central metal ion.

An IR assignment of vibrations of the pendant arms in **L27** has been carried out [103]. The specular reflectance IR spectra of the macrocycles cyclam and cyclamdione, **L28**, and their copper complexes on a smooth copper surface have been published [104].



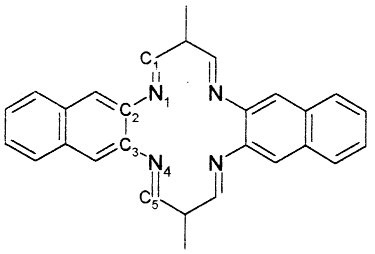
L27



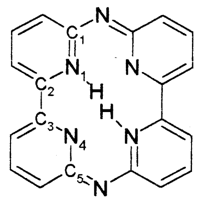
L28

Spectral modifications by metal (Cu and Ni) complexation were ascribed to structural changes; the νCuN mode was assigned to bands observed at 437 cm^{-1} in cyclam and at 430, 388 and 334 cm^{-1} in cyclamdione. The spectral behavior was interpreted in terms of a unique structural arrangement and the structure and orientation of each system was the same, i.e. the orientation of the cyclam molecules is plane parallel to the surface with the interaction being directed by the nitrogen lone pair electrons, and the cyclamdione compounds are decidedly perpendicular to the surface, the interaction being through the CO groups. In the case of the cyclamdione compounds the substrate–adsorbate interaction is of shorter range than of the cyclam systems; the CO groups are probably responsible for that characteristic.

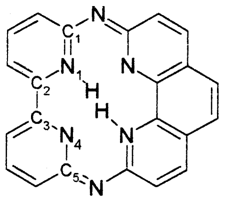
For a series of macrocycles with four, six and eight N atoms in the macrocycle ring, H_2**L29**, H_2**L30**, H_2**L31**, H_2**L32** and H_2**L33** a theoretical study by using the INDO/1 method and a molecular model has been proposed to determine the stability of the complex formation and to interpret the energetic process of the complex surface



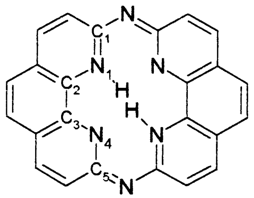
H_2**L29**



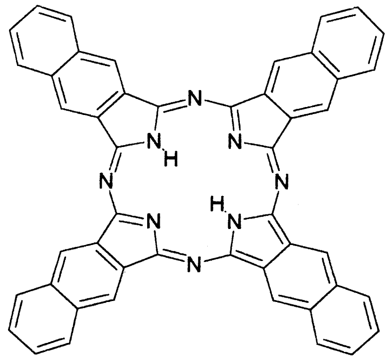
H_2**L30**



H_2**L31**



H_2**L32**



H_2**L33**

interaction [105a]; the effect of increasing the π-electronic system was also studied in the hexaaza ligands. Furthermore, the structure of the tetraaza and hexaaza ligands H_2**L30**–H_2**L32** and their Cu(II) and Ni(II) complexes was optimized by means of the INDO/1 method and the bond characteristics were evaluated throughout the Wiberg index [101,102].

Complex surface interactions were characterized following the same methodology used for the study of naphthalocyanine, H_2**L33**, and its Cu(II) complex deposited onto a copper surface [101]; the model interaction is displayed in Fig. 5. The optimized distance between the complex and the copper surface was about 2.0 Å in all the cases. This distance is in the range of a van der Waals-type interaction. The complex–surface interaction for the Ni(II) with all the ligands was stronger than that for the corresponding Cu(II) complexes.

The analysis of the Wiberg index values, bonds orders and the total energy for the ligands, complexes and for the sustrate–adsorbate corresponding systems suggests

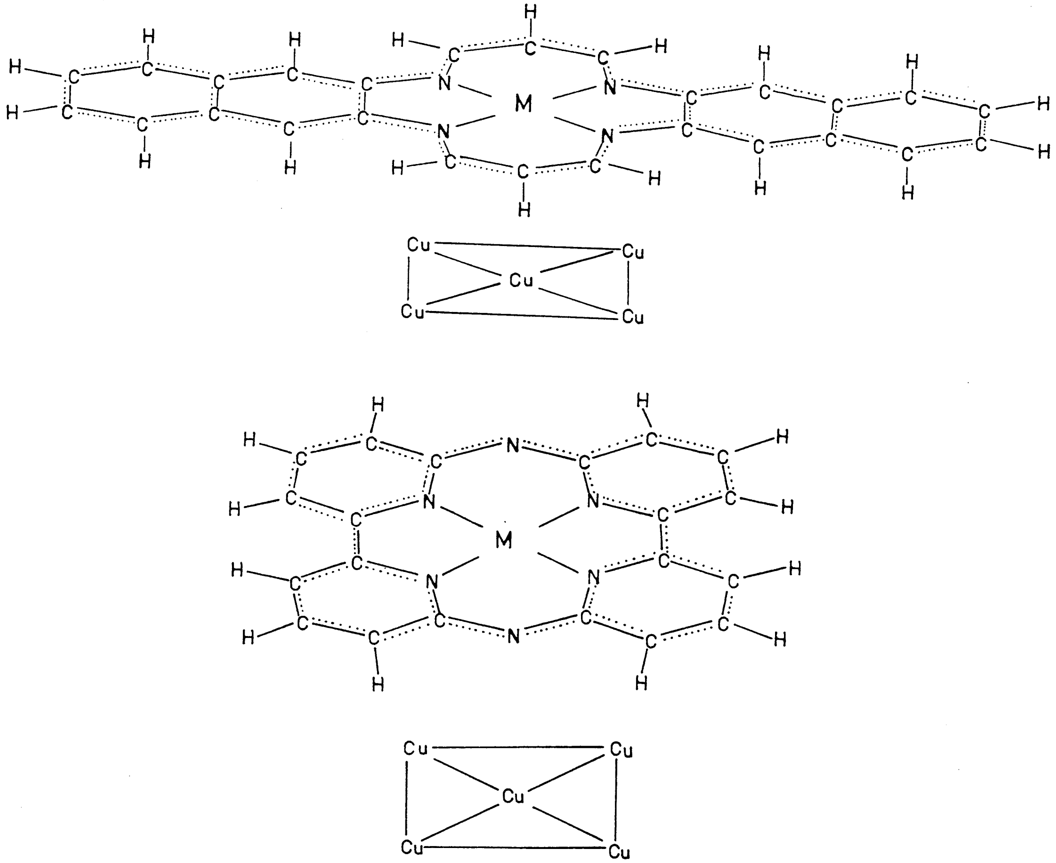


Fig. 5. Diagram of the adsorbate–substrate interaction model, (a) H_2**L33**; (b) Cu**L33** (naphthalene rings are omitted for simplicity).

that the metal–ligand coordination involves an important π-electronic redistribution around the cation by surface effect. Moreover the complex–surface interaction is favored by increasing both the π-electronic system around the coordination site and the number of the nitrogen atoms in the macrocycle ring. This interaction is less energetic when the stability of the complex increases.

Some attempts have been made to prepare *N*-alquil pendant derivatives from H_2**L30** and H_2**L32** [105b], in order to study their interaction with metal surfaces and to compare these results with those of the non-pendant systems.

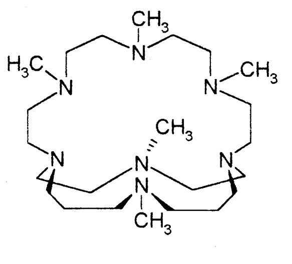
4. Electroactivation of small molecules

4.1. General remarks

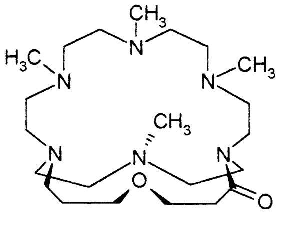
Many coordination compounds with aza-macrocyclic ligands are electrocatalytically active in many redox reactions involving small molecules. For example, porphyrins, phthalocyanines and other iron and cobalt aza-macrocyclic complexes have successfully been used in the electroreduction of oxygen [106–113], oxidation of hydrazine [114,115], oxidation of thiols [116,117] and reduction of nitric oxide [118] among others. It has also been found that vitamin B12 is an efficient catalyst for oxygen reduction [119–121], and oxidation of hydrazine [121,122] and thiols [123,124].

The effect of substituents on phthalocyanines [125,126] and porphyrins [127–130] upon the electrocatalytic reduction of oxygen and thiols has been systematically studied.

The electrocatalytic activity depends on the metal, on the kind of ligands [106] and on the substituents in the case of aza-macrocyclic ligands [15,107,125,131]. The role of the change in the complex geometry on the redox process is one of the most important factors to be considered [19]. Modulation of redox potentials by using specific substituents to simulate a biochemical system [132] is far from a straightforward systematization because several electronic, structural and energetic factors may simultaneously affect the potential [126,133–136]. In some cases, however, the experimental results are not too difficult to explain. For example, only a one two-electron reduction process is observed with Cu_2**L34** while two one-electron reduction processes are observed with Cu_2**L35** [137]. This experimental fact can be rationalized in terms of the rigidity of the **L34** ligand.



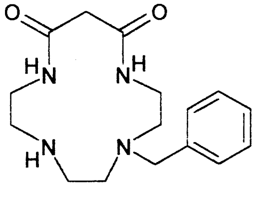
L34



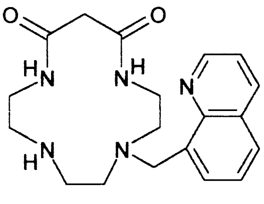
L35

Electroreduction of some Ni(II) complexes with *N*-alkyl substituted tetraazamacrocyclic ligands in aqueous solutions show a more favorable Ni(I) stabilization potential than the Ni(I) complex with the non-substituted ligand. However, Ni(I) stabilization is not changed when the ligands are C-alkyl substituted. These facts have been explained in terms of different solvation energy [134].

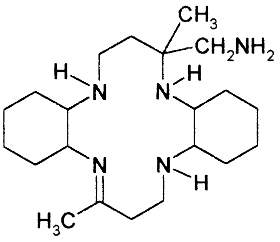
Ligands **L36** and **L37** stabilize Ni(III) but not Cu(III). Size of the different metals and coordination through the pendant substituents accounts for the observed behavior [138]. However Cu(III) is stabilized in the case of **L38**, which is explained in terms of the favorable size of the macrocycle and the presence of aminomethyl substituent in that case [139].



L36



L37



L38

Increasing hydrophobicity by appropriate substitutions allow the use of some complexes as biological models. Dendritic porphyrins with pendant multifunctionality have been synthesized [135]. The first, second and third generation of dendritic Zn(II) porphyrin, shown in Fig. 6, has been obtained. The insertion of a dendrimer around a porphyrin core could alter the polarity of the surroundings of the electrophore and modify its electrochemical behavior. Dendritic porphyrins could therefore be regarded as models for electron-transfer proteins like cytochrome-C, which exhibits oxidation potentials 300–400 mV more positive in aqueous solutions than those of similarly coordinated heme model systems that lack the hydrophobic peptide shell.

4.2. Electrocatalytic reduction of CO_2

Electrocatalytic reduction of CO_2 has been widely studied in recent years because of its role in environmental problems and energy production. Since its reduction requires up to eight electrons, many metals were employed as electrocatalysts [140–142]. Several coordination compounds, adsorbed on an electrode or in solution, were also employed as selective catalysts [139,143–158]. In particular, nickel–cyclam derivatives were extensively used [159–167] for these studies. Electrochemically generated nitrile and ester radicals were also found to be good catalysts in the oxalate oxidation [168].

Non-macrocyclic complexes, employed with similar aims, merit a brief comment: palladium-phosphines [169], rhenium-, ruthenium- and rhodium-pyridines [170–172] reduced CO_2 to CO, and rhodium-phosphines [173]. Ruthenium-bipyridines and polypyridines [174–176] instead lead to HCO_2^-.

The mechanisms for the electrochemical reduction of CO_2 with Ni(II) tetraazamacrocycles and the reduction of the complexes with pulse-radiochemically generated

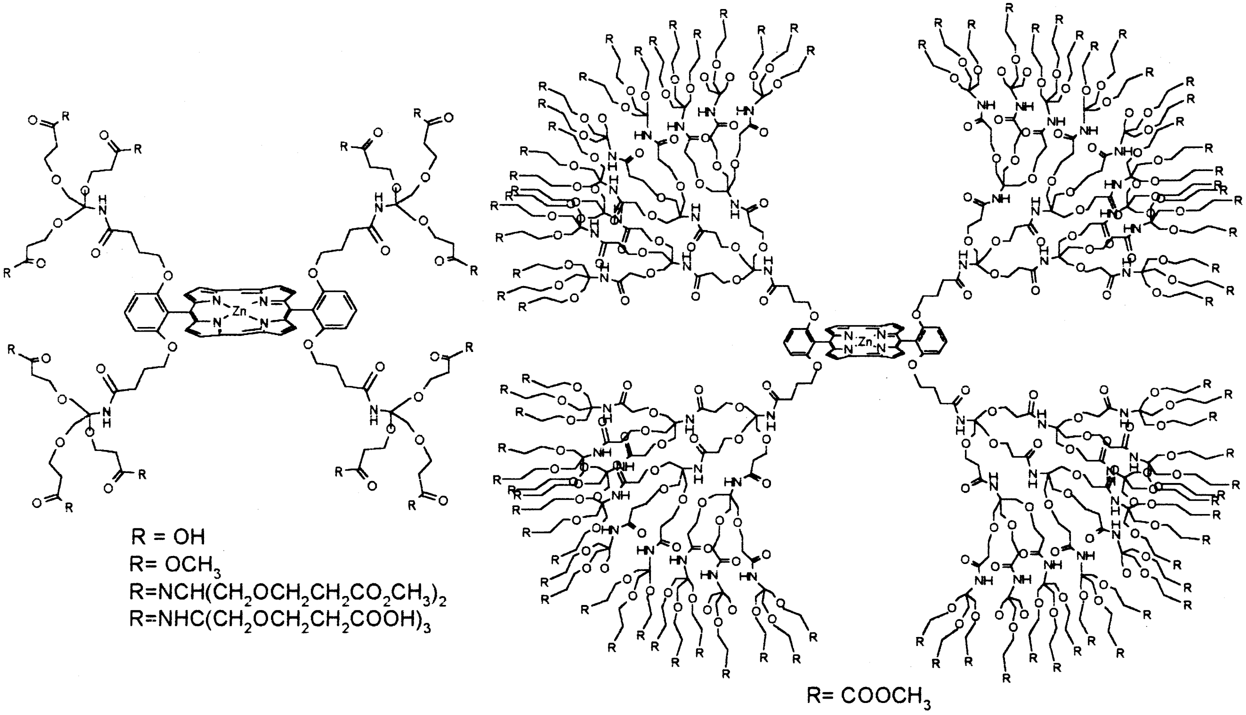


Fig. 6. First-, second- and third-generation of dendritic Zn(II) porphyrin (adapted from Ref. [135]).

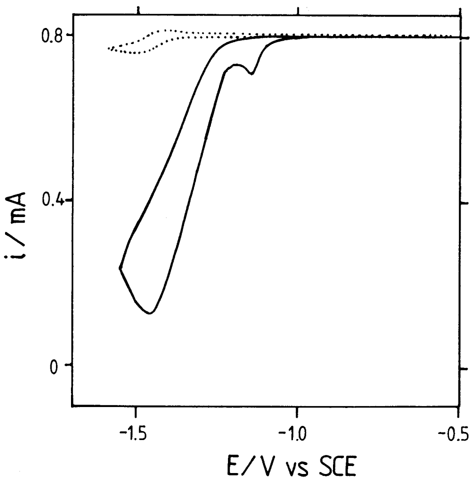
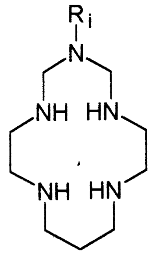


Fig. 7. Cyclic voltammograms under a CO_2 atmosphere: (...), $[Ni\ (cyclam)]^{2+}$; (—), $[Ni\mathbf{L39}]^{2+}$ ($R = CO\text{–}C_6H_4$), in 10^{-4} M aqueous solutions (adapted from Ref. [146]).

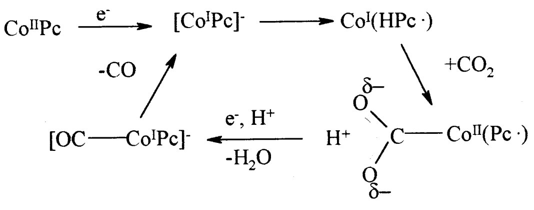
$CO_2^{\bullet -}$ are claimed to be different [134] (see below). Electrocatalyzed reductions of CO_2, where Ni(II) complexes of ligands derived from *N*-pendant substituted aza-cyclam, **L39**, are used as catalysts, have been communicated [146]. In these compounds, the values of the Ni(III)/Ni(II) and Ni(II)/Ni(I) redox potentials are affected by the substituents nature. It has also been found that the electrocatalytic activity is maintained in spite of the substitution of a CH_2 in cyclam by an NH in aza-cyclam because the structure around the metal remains the same and the Ni(I) and Ni(III) oxidation states are stabilized. It has also been found that CO is the main electroreduction product as in the nickel–cyclen derivatives. By contrast, changes in the macrocycle, i.e. modifications in the 5,6,5,6-chelate rings, would affect the electrocatalytic activity.



$R=CH_3, C_{16}H_{33}, CO\text{-}CH_3,$
$CO\text{-}C_6H_5$, etc (see ref. 146)

L39

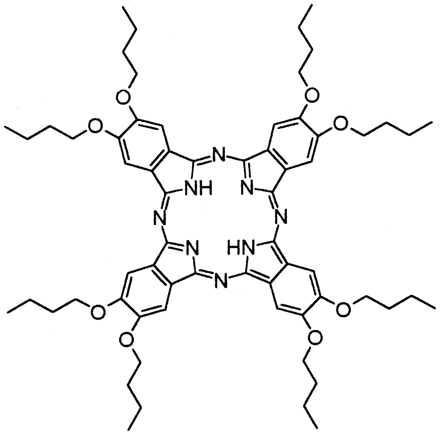
The dramatic effect observed in the cyclic voltammograms of $[Ni\mathbf{L39}]^{2+}$ ($R = \text{–}COC_6H_5$) in a CO_2 atmosphere is shown in Fig. 7. The cathodic peak current is increased by a factor of 2500 in relation to the one in a nitrogen atmosphere [146].



Scheme 5.

In CO_2, the cathodic peak is increased only by a factor of 4.5 compared with nitrogen when the catalyst, [Ni**L24**]$^{2+}$ (R = CH_3), has a ligand with a 12-membered ring [147]. However, in this reaction the main product is formic acid instead of CO. In addition, it has been demonstrated that the planar form of the complex is electrochemically active and not the distorted one.

The effect of substituents on the cobalt(II) phthalocyanine-catalyzed electroreduction of CO_2 has recently been investigated [150]. A greater yield and selectivity for CO_2, relative to the unsubstituted macrocyclic complex, was found with Co**L40** on a modified graphite electrode.



H_2L40

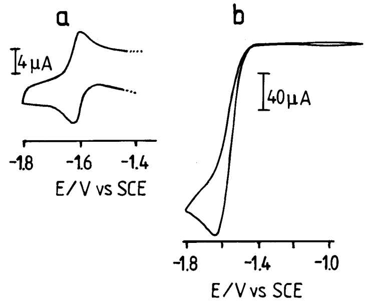
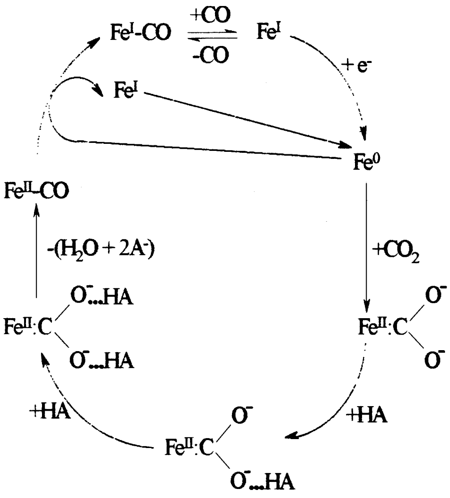


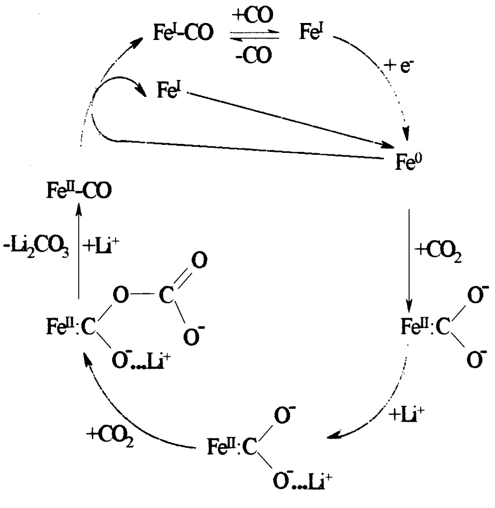
Fig. 8. Cyclic voltammogram for Fe(III) (tetraphenylporphyrin) Cl in: (a), absence of CO_2 (glassy carbon electrode); (b), under 1 atm. of CO_2 in CF_3CH_2OH 1.47 M (mercury electrode) (adapted from ref. [177]).



Scheme 6.

The enhancement of the activity is explained in terms of the donor effect of the substituent which would make the metal center a better nucleophile for the coordination of CO_2. The proposed mechanism is depicted in Scheme 5 [150].

Iron(0) porphyrin has been shown to catalyze the electrochemical reduction of CO_2 in DMF. The catalytic efficiency and life time of this catalyst are however rather low. Saveant and co-workers [149,177] demonstrated that the addition of weak Brønsted acids such as 1-propanol, 2-pyrolidone, and CF_3CH_2OH or Lewis acid such as Mg^{2+}, Ca^{2+}, Ba^{2+}, Li^+, and Na^+ resulted in a considerable



Scheme 7.

improvement of the catalysis of CO_2 by Fe(0) tetraphenylporphyrins. Both the catalytic currents and the lifetime of the catalyst increase without significant formation of hydrogen. The authors have also shown that typical cyclic voltammogram for Fe(III)(tetraphenylporphyrin)Cl in the absence of CO_2 exhibits three successive waves corresponding to the reversible formation of the Fe(II), Fe(I) and Fe(0) complexes. Typical enhancements and changes of the Fe(I)/Fe(0) wave in nitrogen and CO_2 in the presence of the Brønsted acid, CF_3CH_2OH, are shown in Fig. 8.

The observed voltammograms and results from the preparative electrolysis suggest the mechanism depicted in Scheme 6 [149,177].

Added cations also change the catalytic activity by the mechanism shown in Scheme 7.

The order of reactivity $Mg^{2+} = Ca^{2+}$ and $Ba^{2+} > Li^{+} > Na^{+}$ resulted from the enhancement of the Fe(I)/Fe(0) wave. These cations accelerate the catalytic process by creating ion-pairing with the negatively charged oxygen atoms of CO_2 after it coordinates to the iron atom. This mechanism, proposed by Saveant et al., is shown in Scheme 7 [149,177]. The nature of the synergetic effect is, therefore, similar to the action of a weak Brønsted acid, i.e. where hydrogen binding in Scheme 6 has been replaced by ion-paring in Scheme 7.

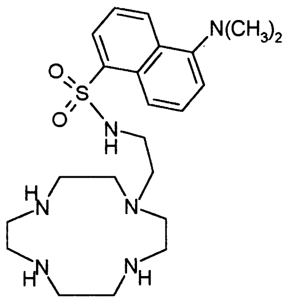
5. Photoactivation of CO_2

The photochemical and photophysical properties of various macrocycles will be reviewed below. Literature reports about the photophysical properties of macrocyclic compounds with pendant arms or macrocycles intercalated between pendant arms of a host are examined in Section 5.1.

These studies show the potential that such compounds may have for various photochemical applications, i.e. to the photocatalyzed reduction of CO_2 and/or to the removal of industrial pollutants like sulfites. In addition, the progress made in understanding the mechanism of the CO_2 reduction when Ni(II) or Co(II) macrocycles are used as catalysts, is discussed in Section 5.2.

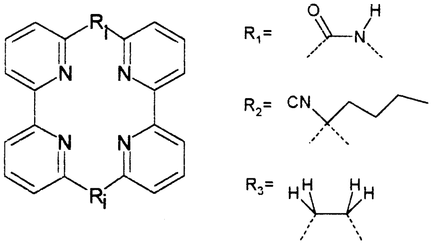
5.1. General remarks

Macrocyclic complexes with pendant arms have shown interesting properties as probes and model molecules in biochemical processes. The complexes of a dansylamido-pendant cyclen, **L41** [10], with Zn(II), Cd(II) and Cu(II) were prepared in order to elucidate interactions of the Zn(II) ions in the catalytic sites of zinc enzymes.



H_3L41

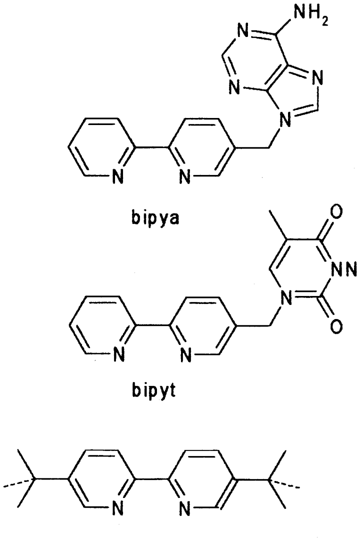
Such compounds of the new macrocycle are more stable than the homologous cyclen derivatives. Coordination to Zn^{2+} produces an hypsochromic shift of the UV absorption band to 323 nm (5.36×10^3 M^{-1} cm^{-1}). By contrast, the absorption spectrum of the free, mostly deprotonated, ligand has an absorption at 330 nm (4.95×10^3 M^{-1} cm^{-1}). Charge effects on the electronic levels of the naphthyl chromophore offer a possible rational explanation for the spectral changes. A broad absorption band centered at 305 nm (7.55×10^3 M^{-1} cm^{-1}) appears when the ligand is coordinated to Cu(II). The change in the spectrum is in accordance with a new electronic transition, i.e. a charge transfer from the macrocycle nitrogens to Cu(II). The emission of the free ligand exhibits a maximum at 555 nm when irradiated at 300 nm. The emission depends, however, on the degree of protonation. For example, a 25% increase in the emission intensity follows deprotonation of the dansylamide-pendant from H_3**L41**$^{2+}$ to **L41** at pH 12. A blue shift of the emission to 528 nm and a 4.9% increase in the quantum yield is observed when deprotonation–complexation is effected with Zn^{2+}. The change may be related to changes in the energy gap and availability of n–π* excited states. Coordination of the ligand to Cu^{2+} and Co^{2+} quenches the emission by increasing the conversion to lower lying non emissive states. By contrast to these ligands with luminescent pendants, a number of macrocyclic complexes, **L42**, where the luminescence originated in excited states of the macrocycle have been prepared [178].



L42

In nonaqueous solvents, coordination to Li^+ enhances the luminescence with respect to the free ligand. It is possible that coordination increases the energy of the n–π* excited state relative to the luminescent π–π*. Several structural factors may contribute to a 103 times enhancement of the luminescence in the 14-membered macrocycle, i.e. R_2, versus only a 3.5 times enhancement of the fluorescence in the macrocycle with a 16-membered ring, i.e. R_1. The role of keto-enol reorganization in the excited state is considered a possible reason for the disparity between these macrocycles. A comparison with a 16-membered ring macrocycle where the keto-enol reorganization was prevented, i.e. between one with R_2 and another with R_3, could have demonstrated such a proposition.

Photophysical studies about the luminescence and intramolecular energy transfer between two metallocomplexes were investigated in Ru(II), Os(II) and Re(II) complexes of derivatized 2,2′-bipyridine, **L43** [179], including the possibility of intramolecular energy transfer between two of the complexes kept together by means of their hydrogen-bonded thymine and adenosine pendant arms.



bipya

bipyt

dbbipy

L43

The UV–vis absorption and luminescence spectra of the complexes exhibited only small departures from those of the complexes with underivatized bipy. Pendant adenosine and thymine groups do not quench the emission of the compounds and have little effect on the position of the metal to ligand charge transfer excited state. The NMR spectra of the pair $Ru(dbbipy)_2$ $(bipya)^{2+}/Os(dbbipy)_2$ $(bipyt)^{2+}$ with the counter ion PF_6^- revealed the association of the metallocomplexes with a small association constants, i.e. 60 M^{-1} in CD_3CN and 123 M^{-1} in CD_2Cl_2. In a similar manner, the pair $Ru(dbbipy)_2$ $(bipya)^{2+}/Re(bipyt)(CO)_3Cl$ associates with $K = 17.9$ M^{-1}. The experimental observation of an intramolecular energy transfer is hindered, however, by the weak association of the complexes [179].

Considerations about the exoergonicity of the processes lead to the conclusion that Ru to Os and Re to Ru energy transfer processes should be possible. The role

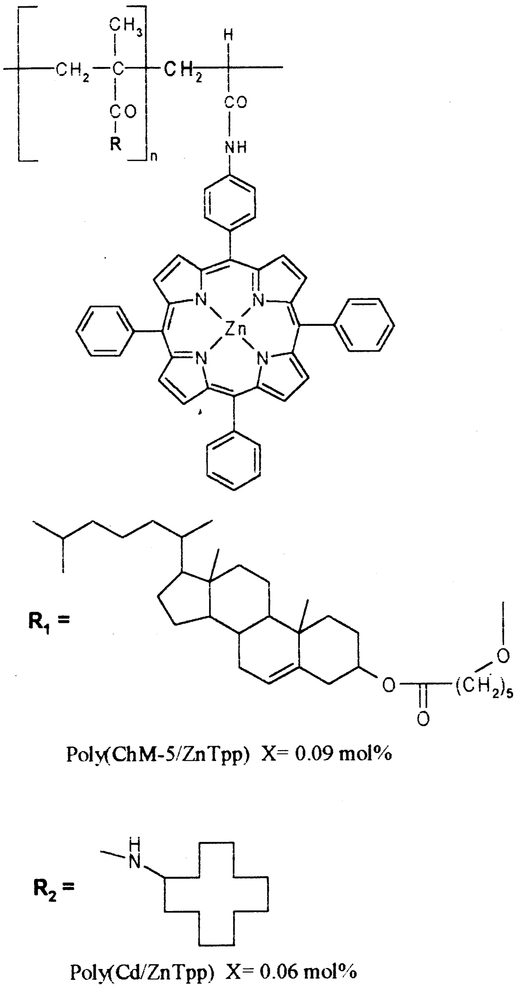


Fig. 9. Cinc(II) tetraphenyl-porphyrins with different polymeric pendant substituents.

of electronic and nuclear factors suggest that through space (Forster) and through bond (Dexter) account for the Ru to Os [179].

By contrast, calculations show that a Forster (dipole–dipole) mechanism must play an insignificant role in a Re to Ru energy transfer. In other experiments, the luminosphore/chromophore has been intercalated between pendant arms [180]. The photophysical behavior of Zn(II) tetraphenylporphyrin (Fig. 9), compartmentalized in the hydrophobic cluster of cyclododecyl (R_2) pendant groups, shows a behavior different than in other hydrophobic pendant groups of amphiphilic polyelectrolyte. Typically, the phosphorescence of Zn(II) tetraphenylporphyrin in aqueous solution is blue shifted ca. 40 nm compared with clusters of lauryl, adamantyl and naphthyl groups.

The phosphorescence and the E-type delayed fluorescence are also temperature dependent. In the R_2 (see Fig. 9) containing terpolymer, a fraction of the Zn(II) tetraphenylporphyrin is forced into sterically distorted structures with a higher energy T_1 state. The higher energy T_1 state is responsible of the blue-shifted emission. Consistent with this idea, the lifetime of the T_1 state in poly(A/Cd/ZnTPP) becomes longer than in poly(A/La/ZnTPP) (see Fig. 9). The decay profiles of the T–T absorptions show a biexponential functional behavior. The longest lived component being is extremely long by comparison with other conditions, e.g. 50 times that of Zn(II) tetraphenylporphyrin in ethanol or toluene at 300 K and twice the lifetimes measured in the corresponding glasses at 77 K. The T-dependence suggests that the Cd acts as a rigid matrix where the Zn(II) tetraphenylporphyrin resides in the distorted configuration. The lengthening of the luminosphore lifetime was also achieved by covalently linking a small number of Zn(II) tetraphenylporphyrin to polymetacrylate-bearing cholesterol side chains [181]. The extremely long triplet lifetimes, i.e. 18 ms for the first order decay of the luminescence in *n*-hexane solutions of poly(ChM-5/ZnTPP), led the authors to propose that, even in a diluted solution, the Zn(II) tetraphenylporphyrin exists in an intramolecular assembly of the pendant cholesterol mesogens with liquid crystalline order. Such an order should thoroughly prevent the T–T annihilation of the Zn(II) tetraphenylporphyrin triplets.

5.2. Mechanism of the CO_2 catalyzed reduction

Related to the catalyzed photochemical or electrochemical reduction of CO_2, the reduction of $Ni(cyclam)^{2+}$, by CO_2^- and H has been rationalized in terms of adducts that respectively dissociate in $Ni(cyclam)^+$ [182]. However, neither adduct exhibited absorption bands in a spectral region where they could be observed in flash-photochemical and pulse radiochemical experiments.

$$Ni^{II}(cyclam)^{2+} + CO_2 \rightarrow Ni(cyclam)CO_2^+ \quad k = 6.7 \times 10^9\ M^{-1}\ s^{-1} \tag{3}$$

$$Ni(cyclam)CO_2^+ \rightarrow Ni^I(cyclam)^+ + CO_2 \quad k = 2.0 \times 10^6\ s^{-1} \tag{4}$$

The rate constant for the dissociation of $Ni(cyclam)CO_2^+$ into the Ni(I) complex and CO_2 is $2.0 \times 10^6\ s^{-1}$ and the rate constant for the reduction of $Ni(cyclam)^{2+}$ by CO_2^-, is $k_a = 6.7 \times 10^9\ M^{-1}\ s^{-1}$ (Eqs. (3) and (4)).

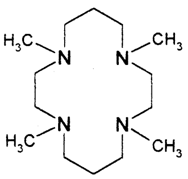
A comparison between the equilibrium association constants of CO_2 and H^+ to $Ni(cyclam)^+$, i.e. 6.2×10^{-2} and 1.6×10^{-2} M, respectively, revealed the thermochemical advantage of binding CO_2 with regard to protons. Also, comparison between Co(I) and Ni(I) reveal stronger bonds for the former metal center, a condition probably related to a smaller Jahn–Teller effect in low-spin d^8 than in d^9. However, the overall kinetic and thermochemical parameters make $Ni(cyclam)^+$ a selective CO_2 reductant over a larger pH range than $Co(cyclam)^+$. Indeed, protonation of Ni(I) is favored over addition of CO_2 when $pH < 2$. Also the authors concluded that, in the catalytic reduction of $CO_{2.}$ there is no addition to an Ni–H bond. Time-resolved spectroscopy allowed Rodgers et al. to measure the rate constant of CO addition to $Ni(cyclam)^+$ [183], Eq. (5).

$$Ni(cyclam)^+ + CO \rightarrow Ni(cyclam)CO^+ \quad k = 2.0 \times 10^9\ M^{-1}\ s^{-1} \tag{5}$$

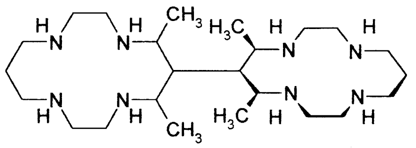
A spectral transformation from λ_{max} 470 to 350 nm is assigned to conformational isomerization with a rate constant $k = 1.8\ s^{-1}$. The authors speculate that such an isomerization is due to the inversion of two amino groups, i.e. from an *RRSS* configuration to a *RSRS* one. This observation is in accordance with a previous literature report where the isomerization of several pulse-radiochemically generated Ni(I) macrocycles is reported to take place over several milliseconds [134]. The authors also found that electrochemically and pulse radiochemically generated Ni(I) complexes have different lifetimes. It is argued that different isomers are generated by these two techniques. On the basis of this report, particular care must be taken when electrochemical properties are used for the rationalization of the catalysis by Ni macrocycles of the thermal and photochemical CO_2 reduction. It is also proposed in this work that various Ni(I) tetraaza-macrocycles undergo decomposition by an intramolecular reduction of imine groups, a process that may occur in aqueous solutions when reactions with CO_2 and H^+ are too slow to compete. The [Ni**L24**]$^{2+}$ ($R = CH_3$) is a better catalysis for the photoinduced CO_2 reduction than [Ni**L44**]$^{2+}$ [147].

Indeed, the reduction process is 14 times faster than with [Ni**L44**]$^{2+}$ and there is a different distribution of products. While CO and formic acid are the main products of the [Ni**L24**]$^{2+}$ ($R = CH_3$) catalysis, with [Ni**L44**]$^{2+}$ the major product formed is H_2 followed by CO yield. Formation of Ni(III) transient products is proposed in order to account for a two-electron donation to CO_2 and/or H^+. New bimacrocyclic Ni(II) complex, from **L45**, largely exceeds the catalytic activity of the mononuclear complex [184]. Photochemical experiments show that the complex produces CO faster and is more selective towards the reduction of CO_2 versus H^+ than the cyclam monomer.

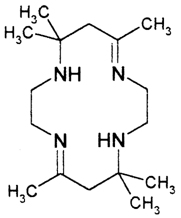
The main difference between the binuclear and mononuclear complexes is that methyl groups occupy the axial positions of the bicyclic macrocycle. Such a structure must reduce the ability to coordinate water.



L44



L45



L46

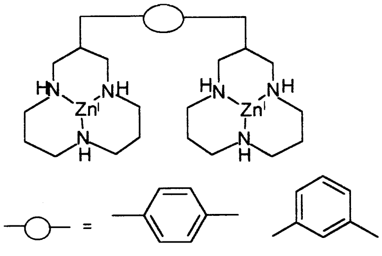
Work on the photocatalyzed reduction of CO_2 with several Co(II) macrocycles, with *p*-terphenyl, TP, functioning as photosensitizer and a tertiary amine, D, as a sacrificial reagent, has shown that redox potentials and steric constraints, associated with the macrocycles structure, are important factors controlling the catalytic activity [185]. In the photoinduced reduction by the *p*-terphenyl radical, transient spectra showed the sequential formation of the Co(I)**L46**$^+$ complex and the S–Co(III)**L46**–CO_2^+ complex, where S = solvent. Indeed, the decay of Co(I) intermediates is strongly related to the redox potential. It was established that CO_2 binds to Co(II)**L46** with $k = 1.7 \times 10^8\ M^{-1}\ s^{-1}$ and dissociates with $k = 6.5 \times 10^{-4}$

s^{-1}. These studies were carried out in a mixed acetonitrile/methanol solvent to avoid the proton reduction from any strong proton donor, e.g. TP. The proposed multi-step mechanism, offers the best rationale for the new experimental observations. The association of CO_2 to Co(I)**L46**$^+$ was also investigated as a function of the pressure in order to determine the reaction's activation volume [186]. Electrostriction due to charging the carboxylate and axial bond length changes appear to have considerable influence in the volume change of -17.7 ml mol^{-1}. Similar mechanistic studies on the reduction of CO_2 have been carried out with several porphyrins, P, of Co and Fe [187,188]. Reduction of the Co(II) complex by pulse radiolysis in aqueous acidic or neutral solutions shows the formation and decay of Co(I)P. The Co(I) compounds are stable in organic solvents and do not react with CO_2. It takes an extra reduction equivalent, i.e. to the radical-anion Co^0P, to observe such a reaction. That Co^0P is the active reductant was also verified by cyclic voltammetry. The work with Fe^iP ($i = 0$, I, II) show some similarities with heme proteins. The Fe(I) oxidation state is the active reductant of CO_2 and the formation of the Fe(II)–CO products. A turnover of 70 molecules of CO per porphyrin molecule was measured for the photocatalyzed reduction.

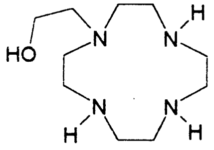
6. Inorganic models related to metalloenzymes

Metal complexes with macrocyclic ligands have been designed as chemical models of hydrolytic metalloenzymes. These enzymes contain Zn(II) as the central ion which promotes the formation of the nucleophile for the hydrolysis of many important biological molecules. Kimura et al. [51] synthesized a Zn(II) ethanol pendant 1,5,9-triazacyclodecane complex, Zn(II)**L20**, as a chemical model for serine-involving enzymes. This complex deprotonates at physiological pH to become a strong nucleophile than the pendant-less complex toward 4-nitrophenylacetate. The same group [189] further studied the activation mechanism of the alcoholic groups in Zn(II) enzymes using the novel Zn(II) complex Zn(II)**L47**, in the catalytic hydrolysis of carboxyesters.

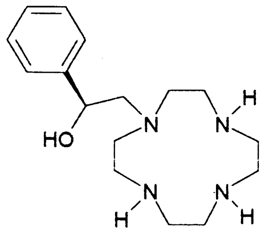
They found that at 25°C the complex deprotonates with a pK_a of 7.60 to give an OH^--bound complex which activates the pendant alcoholic group generating a strong nucleophile for the 4-nitrophenyl acetate hydrolysis. The results may explain the nucleophilicity of serine at the active site of Zn(II) hydrolytic enzymes.



Scheme 8.



L47

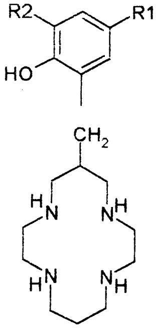


L48

A phosphatase model system was designed by complexing Zn(II) with the 1,4,7,10-tetraazacyclododecane ligand bearing a benzyl alcohol pendant group [190], **L48**, which may serve to understand the participation of Ser-102 and Zn(II) in the catalytic activity of alkaline phosphatase.

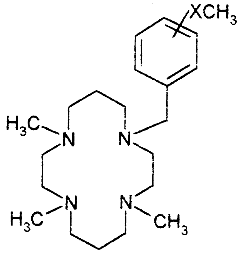
The selective hydrolysis of phosphate esters by Zn(II) complexes of dimers derived from triazacyclopolydecanes was studied by Chapman and Breslow [191]. Two molecules of the ligand were linked by spacer groups of different length and geometry (Scheme 8). They found that the distance between the metal binding sites determines the selectivity of the catalytic performance. The 1,4-phenyl and 1,3-phenyl linkers were the most effective in promoting the hydrolysis of *p*-nitrophenylphosphate. The authors suggested that as in the enzyme alkaline phosphatase, the two zinc ions in the dimers coordinate to the phosphate group. They proposed a different mechanism for the hydrolysis of the diester, bis(*p*-nitrophenyl)phosphate; one Zn(II) ion binds to the phosphate group and the other one provides a nucleophilic oxide ion.

Zhu et al. [192] synthesized [Zn**L49**]$^{2+}$ complexes with phenolic-pendants as model of carbonic anhydrase. It was found that the electron-withdrawing substituents on the phenyl group tend to decrease the pK_a values of coordinated phenolate. In the hydrolysis of *p*-nitrophenyl acetate, the hydrolytic activity of the complex increased with the decrease of the pK_a values.



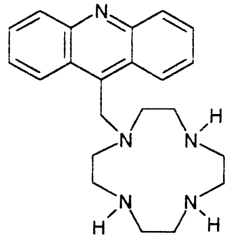
R1 = R2 = H
R1 = R2 = Br
R1=Br R2= H

L49



X=O, N, S

L50



L51

Schmid et al. [193] synthesized [Ni**L50**]$^{2+}$ with *ortho*- or *para*-substituted benzylic pendant groups, as model compounds for coenzyme F430, a cofactor which contains Ni coordinated to tetrapyrrole. The Ni(II) complex with a methylthio group in the *ortho*-position on the pendant ring in the macrocyclic ligand by treatment with reducing agent produced, although in small amounts thiol and methane. In the case of the *para*-methylthio substituted Ni(II) complex methane formation was not detected, indicating that the proximity of the methylthio group to the metal center is an important factor.

Further studies on Ni(II) and Cu(II) complexes of 14-membered tetraaza-macrocyclic ligand with methylthio- and methoxy-substituted aliphatic pendant chains [194] have shown that the participation of the side chain in the coordination with the ion metal takes place only when the methylthio group is present.

A novel Zn(II) complex of tetraazacyclodecane bearing acridine pendant groups, **L51**, has been synthesized to study the molecular recognition of a specific nucleobase in nucleic acid [11]. The complex showed selective binding to deoxythimidine in aqueous solution at physiological pH. The introduction of the acridine pendant involves an additional stacking π–π interaction with thymine base which makes this artificial receptor a higher specific host toward deoxythimidine compared with the pendant less tetraazacyclododecane complex.

Acknowledgements

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