Non-symmetrical Schiff Base Complexes.
Experimental Support to an Intramolecular, Non-Symmetrical Activation Process and Synthesis of a New Type of Tetraaza Macrocyclic Complexes

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Abstract

The 'half-unit' (AEH) obtained by reacting equimolar quantities of pentane-2,4-dione and diaminoethane may be used to produce non-symmetrical tetradentate Schiff base. The species under examination results from the condensation of an (AEH) unit with 3-(ethoxymethylene)-2,4-pentanedione. This ligand and its copper(II) and nickel(II) complexes display two carbonyl groups which, according to various physical probes, are very different; one is strongly affected by a $COCH_3$ substituent while the other (which is far remote from this substituent) is almost unaffected. However, both groups are amenable to condensation with ethylenediamine to yield a new type of macrocyclic complex. The properties of the related 13-acetyl-5,7-14-trimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,12,14-tetraenato-(2-) copper(II) and nickel(II) are reported.

It is well known that in a series of metal complexes involving macrocyclic ligands, the chemical behaviour and the physical properties depend strongly on the nature of the peripheral substituents on the chelate ring [1–3]. For instance, condensation of Schiff base complexes (M.A) (Fig. 1) with ethylenediamine only occurs if R_2 is an electron-withdrawing group such as —COOR or —COR, the resulting products being N_4-macrocyclic complexes $(M.A'_{Ac})$ [4]. Moreover, it has been demonstrated that these electron-withdrawing groups favour the reduction of the metal in agreement with a decrease of its electron density [5]. The influence of the substituents on electron distribution within the chelate ring has been studied by ^{13}C NMR and electronic spectroscopy [6]. A relationship between the chemical shifts of the C-2 and, to a lesser extent, C-3 nuclei and the ability of the C=O groups to react with ethylenediamine has also been reported [6].

All these studies are devoted to symmetrical molecules and the two C=O groups involved in the condensation process are identical. In this paper we present data obtained for non-symmetrical nickel-(II) and copper(II) complexes belonging to the
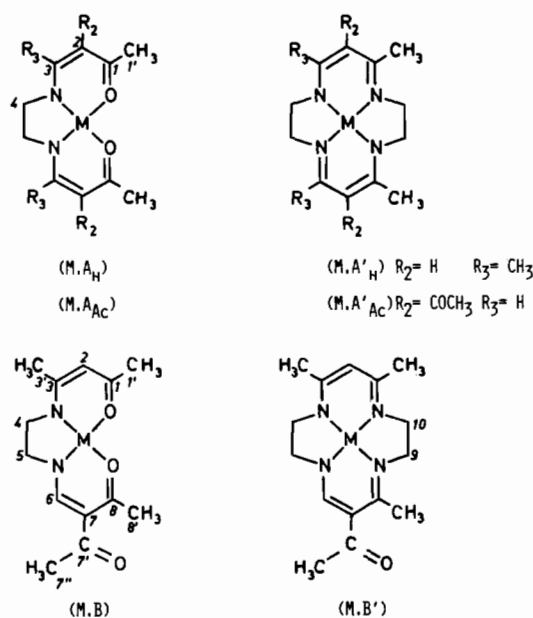

Fig. 1. Complexes with their abbreviations.

(M.B) and (M.B') types. The (M.B) complexes are expected to show two significantly different C=O groups and the attention has been focused on a comparative study of substituent effects in symmetrical and nonsymmetrical species. Various spectroscopies (IR, ^1H and ^{13}C NMR, mass, electronic and EPR) as well as electrochemical measurements have been used to characterize the complexes and to give materials for the comparison.

The complexes of interest are illustrated in Fig. 1.

Experimental

Microanalyses were performed by the Service Central de Microanalyses du CNRS, Lyon. Infrared spectra of KBr discs were recorded using a Perkin-Elmer 577 spectrometer, visible spectra using a Cary 14 spectrophotometer. Mass spectra were

obtained using a VG Micromass 7070F spectrometer. Proton and ^{13}C NMR spectra were run on a Bruker WH90 using TMS (^{1}H spectra) and CDCl$_3$ (^{13}C spectra) as internal reference. All chemical shifts (^{1}H and ^{13}C) are given in ppm *versus* TMS using CDCl$_3$ as solvent. EPR spectra were obtained on a Bruker 200 TT spectrometer.

A 'home-made microcomputer-controlled instrument' with ohmic resistance compensation was used for cyclic voltammetry and polarographic studies [7]. A platinum auxiliary electrode and an Ag/AgCl (0.1 M KCl) reference electrode were used in conjunction with a dropping mercury electrode. All voltammograms were recorded at ambient temperature, at 0.5 V s^{-1}; nickel complexes: 10^{-3} M in CH$_3$CN/ Et$_4$NClO$_4$ (Fluka) 0.1 M medium. All solutions were degassed with argon for 15 min before measurements.

3-(ethoxymethylene)-2,4-pentadione and 7-amino-4-methyl-5-aza-3-heptene-2-one (AEH)

They were prepared according to literature processes [8, 9].

3-acetyl-9-methyl-5-diaza-dodeca-3,9-diene-2,11-dione (B)

A solution of 5.5 g of 3-(ethoxymethylene)-2,4-pentanedione (3.5 × 10^{-2} mol) in absolute ethanol (60 cm^3) was added dropwise upon stirring to a solution of 5 g of AEH (3.5 × 10^{-2} mol) in 50 cm^3 of absolute ethanol. At the end of the addition, a white precipitate appeared. The solution was concentrated and the fine white material collected by filtration, washed with absolute ethanol and diethyl ether, and subsequently dried. The yield was 6 g (70%). *Anal.* Calcd. for C$_{13}$H$_{20}$N$_2$O$_3$: C, 61.90; H, 7.94, N, 11.11. Found: C, 61.63; H, 8.06; N; 11.13.

3-acetyl-9-methyl-5,8-diazadodeca-3,9-diene-2,11-dionato(2-) nickel(II) (Ni.B)

To the ligand (4g, 1.7 × 10^{-2} mol) dissolved in methanol (100 cm^3) was added upon stirring 4.2 g of nickel(II) ethanoate dihydrate (1.7 × 10^{-2} mol). An orange colour appeared readily and the solution was heated to reduce the volume to *ca.* 40 cm^3. Water was added and an orange precipitate appeared upon cooling. This compound was filtered, washed with ethanol and diethyl ether, and subsequently dried. The yield was 3.5 g (70%). *Anal.* Calcd. for C$_{13}$H$_{18}$N$_2$O$_3$Ni: C, 50.65; H, 5.84; N, 9.08; Ni, 18.83. Found: C, 50.60; H, 5.84; N, 9.05; Ni, 18.70.

3-acetyl-9-methyl-5,8-diazadodeca-3,9-diene-2,11-dionato(2-)copper(II) (Cu.B)

The above procedure was followed. From the resulting purple solution, all the solvent was evaporated and diethyl ether added, leaving a purple precipi-
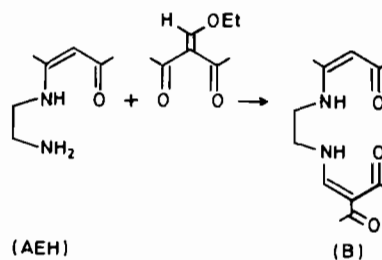

Fig. 2. Chemical reaction for the preparation of a nonsymmetrical Schiff base (B).

tate which was filtered and washed with diethyl ether. The yield was similar. *Anal.* Calcd. for C$_{13}$-H$_{18}$N$_2$O$_3$Cu: C, 49.76; H, 5.74; N, 8.93; Cu, 20.26. Found: C, 49.61; H, 5.68; N, 8.84; Cu, 19.81.

13-acetyl-5,7,14-trimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,12,14-tetraenato(2-)nickel(II) (Ni.B')

This macrocycle was isolated by application of the method from ref. 8. The (Ni.B) product in dry ethylenediamine was stirred and heated to reflux under argon. The solid dissolved to give a red solution which was refluxed for 30 min. Water was added after cooling. The red precipitate that formed was removed by filtration and washed with copious amounts of water, then with ethanol, and finally with diethyl ether and subsequently dried. The yield was 35%, based on the starting complex. *Anal.* Calcd. for C$_{15}$H$_{22}$N$_4$ONi: C, 54.22; H, 6.62; N, 16.87; Ni, 17.45. Found: C, 54.02; H, 6.73; N, 16.70; Ni, 17.33.

13-acetyl-5,7,14-trimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,12,14-tetraenato(2-)copper(II) (Cu.B')

The same procedure was followed. The solution turned blue, then green. The cooled solution was left to stand overnight without adding water. The resulting green precipitate was collected by filtration, dissolved in CH$_2$Cl$_2$ and filtered again. The solvent was then removed, leaving the green macrocyclic product with a yield of 35% based on the starting complex. *Anal.* Calcd. for C$_{15}$H$_{22}$N$_4$OCu: C, 53.33; H, 6.52; N, 16.59; Cu, 18.81. Found: C, 53.01; H, 6.40; N, 16.45; Cu, 18.65.

Results and Discussion

As previously reported, non-symmetrical Schiff bases are conveniently prepared from the 'half-unit' (AEH) according to the scheme depicted in Fig. 2. In the present case, AEH is reacted with 3-(ethoxymethylene)-2,4-pentanedione to yield 3-acetyl-9-methyl-5,8-diazadodeca-3-9-diene-2,11-dione (B) which may be complexed by nickel and copper ions. Although the two coordinated C=O groups in the (M.B) complexes are obviously dissimilar, both are

TABLE I. Mass Spectra.

	(B)	(Ni.B)	(Cu.B)	(Ni.B')	(Cu.B')
$M^{+\bullet}$ [a]	252(13)[b]	308(100)	313(100)	332(100)	337(100)
$M-CH_3^+$	–	293(60)	298(3)	317(32)	322(4)
$M-Q^+$ [c]	141(2)	197(15)	202(21)	–	–
$M-Q'^+$ [d]	–	169(68)	174(92)	–	–
$M-Q'-H^+$	112(100)	–	–	–	–
CH_3CO^+	43(30)	–	–	–	–

[a]Molecular ion. [b]Relative intensities. [c]$Q = CH_3C(N=CH_2)CHCOCH_3$. [d]$Q' = HC(N=CH_2)C(COCH_3)_2$.

TABLE II. ^{13}C Chemical Shifts (ppm *vs.* TMS).

	CH3				CH2				CH	C	C=N		C=O or C=N		C=O
	3'	1'	8'	7"	4	5	9	10	2	7	3	6	1	8	7'
Ni.A$_H$)[a]	20.9	24.2			52.9				99.4		164.5		176.8		
(Ni.A$_{Ac}$)[a]			28.3 28.9	28.9 28.3		58.4				113.9		159.4		188.0	194.0
(Ni.B)	21.4	24.5	28.9 29.1	29.1 28.9	52.3	59.9			100.2	114.0	165.5	159.5	177.3	188.7	194.6
(A$_H$)	18.4	28.6			43.4				95.9		162.7		195.3		
(B)	18.7	27.0	28.9	31.9	43.6	50.5			96.7	112.1	162.8	160.5	194.8	196.1	201.0
(Ni.A'$_{Ac}$)		20.9	28.4			59.2	54.1			111.8		156.3		167.0	194.5
(Ni.B')	20.9	21.3 21.6	21.6 21.3	28.5	53.0	60.6	54.8	52.8	97.8	112.0	159.0[b]	156.9	159.3[b]	166.5	193.7

[a]See also reference 6. [b]These assignments may be reversed.

seemingly able to react with ethylenediamine to afford the corresponding macrocyclic complexes (M.B').

Mass Spectroscopy

The ligand (B) and the related complexes (M.B) and (M.B') were characterized by mass spectroscopy. The relevant data are reported in Table I.' In all cases, the observation of the molecular ion allows an unambiguous identification. For the free ligand, the intensity of the corresponding peak at m/e = 252 is as usual rather low [10]. However, it became the prevailing signal in the spectra of the complexes. The fragmentation pattern of the Schiff base (B) and of its complexes (M.B) and more particularly the production of the 'half-unit' Q and Q' (Table I) are characteristic [10, 11] of such types of molecules. In marked contrast to this behaviour, one may note the great stability of the macrocyclic compounds (M.B'). Finally, it may be emphasized that no peak attributable to a symmetrical species has been found.

Infrared Spectroscopy

Infrared spectra of the (M.B) and (M.B') complexes show a band attributable to the uncomplexed C=O group at 1635 cm^{-1} (Ni.B), 1620 cm^{-1} (Ni.B'), 1640 cm^{-1} (Cu.B), and 1620 cm^{-1} (Cu.B'). Strong overlap of the C=C, C=N and coordinated C=O stretching mode results in a broad absorption from 1600 to 1550 cm^{-1}. It is noteworthy that in the (M.B') spectra, no absorption occurs at *ca.* 1700 cm^{-1} in accordance with a wide electronic delocalization over the six-membered rings [12].

NMR Spectroscopy

The ^{13}C NMR data related to the free ligand (B) and to the two nickel complexes (Ni.B) and (Ni.B') are listed in Table II together with the data obtained for the related symmetrical species. The assignments are made based on ^{1}H-coupled spectra and chemical shift values. It may be emphasized that the (Ni.B) spectrum is merely the sum of the (Ni.A$_H$) and Ni.A$_{Ac}$) spectra. Therefore the assignments are straightforward. They are then easily extended to the other compounds. The only ambiguities concern the methylic carbons, which are of little interest.

The effects of complexation and cyclization may be deduced from a comparison throughout the series of symmetrical or non-symmetrical compounds.

TABLE III. ^{1}H Chemical Shift (ppm *vs.* TMS).

	CH$_3$				CH$_2$	CH		NH
	3'	1'	8'	7"	4, 5, 9, 10	2	6	
$(A_H)^a$	2.00	2.13			3.47(m)	4.98		11.4
$(A_{Ac})^a$			2.53	2.28	3.61(m)		7.85(d)	10.8(d)
(B)	1.82	1.97	2.45	2.17	3.48(m)	4.97	7.65(d)	11.0
(Ni.B)	1.96	1.96	2.44	2.30	3.18(m)	5.03	7.50	
$(Ni.A'_H)^a$	1.90	1.90	1.90		3.12	4.58		
$(Ni.A'_{Ac})$			2.41	2.29	3.33		7.71	
Ni.B')	1.98	1.98	2.41	2.30	3.29(m)	4.71	7.71	

^{a}See also references 20, 21, 22.

As expected, the C-1 and C-8 nuclei are the most affected.

As previously mentioned, the large differences observed between the chemical shift of similar carbons in the symmetrical complexes (Ni.A$_H$) and (Ni.A$_{Ac}$) have been attributed [6] to the inductive effect of the COCH$_3$ group. It is noteworthy that the same differences are found between the two moieties of the non-symmetrical complex (Ni.B), implying that the effect of the peripheral COCH$_3$ group is restricted to the moiety to which it is directly linked. Furthermore, the chemical shift differences are much smaller in the free ligand (B) than in the nickel complex, evidencing the polarizing influence of the metal centre.

These conclusions may be extended to the macrocyclic complex (Ni.B').

The ^{1}H data (Table III) are in agreement with the proposed structures. However, the ^{1}H spectrum of the free Schiff base (B) supports the occurrence of the tautomeric form depicted in Fig. 2. A broad signal observed at 11 ppm is attributed to the NH protons and results from the overlap of a doublet (J = 13 Hz) and a singlet. The doublet is due to a coupling of the NH with the CH of the enamine group since the resonance of the latter proton is also a doublet ($\delta = 7.64$ ppm, $^3J_{HH} = 13$ Hz). This assignment is supported by double-irradiation experiments. Further, the NH signals vanish upon complexation while the CH doublet turns into a singlet.

Electronic Spectra

Modifications of the electron distribution within the chelate ring under the influence of peripheral substituents have been previously invoked to explain the variation of the electronic spectra throughout the series of symmetrical complexes (Ni.A) and (Ni.A') [13]. The frequency of the lowest-energy band, which is attributed to a transition from the d_π (d_{xz} and d_{yz}) orbital to the d_σ (d_{xy}) orbital, is blue-shifted when electron-withdrawing groups are substi-

TABLE IV. Lowest Energy d–d Band in Nickel(II) and Copper(II) Complexes (CH$_2$Cl$_2$ solutions).

Complexes	ν (cm^{-1})		Ref.
	M = Ni	M = Cu	
(M.A$_H$)	17,600	18,400	6, 23
		18,200	
(M.A$_{Ac}$)	19,000	18,400	6
(M.B)	18,350	18,350	
(M.A'$_H$)	17,900	16,200	22
(M.A'$_{Ac}$)	19,600	17,800	13
(M.B')	18,870	16,660	

tuted for H at R$_2$ [6, 13]. These groups are assumed to cause an electron-drift mainly by a π-path, the metal–ligand σ-bond being affected only indirectly [14]. From the data reported in Table IV it is obvious that this conclusion may be extended to (Ni.B) and (Ni.B'). Furthermore, the frequencies related to these non-symmetrical species lie between those of the corresponding symmetrical complexes.

Surprisingly, the influence of the substituent is reduced in the (Cu.A) and (Cu.B) complexes with respect to their nickel homologues. However, this influence becomes clearly discernible in (Cu.A') and (Cu.B').

An interesting remark concerns the dependence of the (Cu.B) spectrum on the solvent. The lowest-energy band which occurs at 18,350 cm^{-1} in CH$_2$-Cl$_2$ is shifted to 12,200 cm^{-1} in ethylenediamine whereas a second band appears at 16,300 cm^{-1}. Although it is well known that electronic spectra of copper complexes do not afford unambiguous criteria of structure [15], the observed behaviour could be tentatively related to a change in the coordination geometry around the copper ion.

TABLE V. ESR Data (CH_2Cl_2, $CH_3C_6H_5$ solutions: ratio 4/1).

	g_{iso}[a]	A_{iso}[a] $(10^{-4}$ cm$^{-1})$	$g_{\parallel}$[b]	$A_{\parallel}$[b] $(10^{-4}$ cm$^{-1})$	$g_{\perp}$[b]	$A_{\perp}$[b,c] $(10^{-4}$ cm$^{-1})$
(Cu.B)	2.093	87	2.182	214	2.033	23.5
(Cu.B) + En	2.113	68	2.212	–	2.085	–
(Cu.B')	2.071	93	2.137	220	2.021	29.5

[a]293 K spectra;   [b]113 K spectra;   [c]Calculated using the relation $A_{iso} = 1/3 (2A_{\perp} + A_{\parallel})$.

TABLE VI. Electrochemical Data (Reduction).

Complexes	Polarography		Cyclic Voltammetry[b]				nb·e⁻ exchanged
	$E_{1/2}$ (volts)	log $i/i_d - i$ (slope in mV/log unit)	Ep_c (volts)	Ep_a (volts)	ΔEp (mV)	I_{pc}/I_{pa}	
(Ni.A$_{Ac}$)	−1.68[c]						
(Ni.B)	−1.88	58	−1.91	−1.85	60	0.78	1
(Ni.A$_H$)	−2.04[c]						
(Ni.B')	−2.46	68	−2.50	−2.44	60	0.94	1

[a]*Vs.* Ag/Ag⁺; sweep rate 200 mV mn^{-1};   [b]*Vs.* Ag/Ag⁺; sweep rate 500 mV s^{-1};   [c]Values from ref. 4, *vs.* SCE.

ESR

The powder spectra of (Cu.B) and (Cu.B') show broad signals not amenable to a detailed analysis. Data related to solution spectra are reported in Table V. At room temperature, four lines are observed as expected for monomeric copper(II) species. At low temperature, the usual 'tetrahedral' spectra are seen with $g_{\parallel} > g_{\perp}$. The occurrence of superhyperfine structures on the $g_{\perp}$ signals allows a clear differentiation between (Cu.B) and (Cu.B') which show five and nine lines, respectively. This in accordance with coupling of the free electron with two and four nitrogens.

Two points deserve further comments: (i) a complex signal involving seven lines is observed at $g = 4.02$ in the glass spectrum of (Cu.B) (CH_2Cl_2, $CH_3C_6H_5$ as solvent): the presence of this $\Delta M = 2$ transition indicates interaction of the spin with two copper nuclei and suggests formation of dimers upon freezing; (ii) the (Cu.B) spectrum is markedly dependent on the solvent used. At room temperature, addition of ethylenediamine to the CH_2Cl_2 solution results in a decrease of $|A_{iso}|$ from 87×10^{-4} cm^{-1} to 68×10^{-4} cm^{-1}. At low temperature, poor resolution prevents a precise determination of the hyperfine coupling constants but it appears that ethylenediamine causes an increase of the g-values (from 2.033 to 2.085 for $g_{\perp}$ and from 2.182 to 2.212 for $g_{\parallel}$). These effects [16, 17] are consistent with the formation of an adduct between the planar chelate (Cu.B) and ethylenediamine. From the observed g-values a square-pyramidal structure is inferred for

this adduct. No 'half-field' transition is observed in the presence of ethylenediamine.

Electrochemical Study

Jäger *et al.* [5] have measured polarographic half-wave potentials related to the reduction process $NiL + e^- \rightarrow (NiL)^-$ for a series of nickel(II) complexes involving quadridentate Schiff base ligands. It appears that when electron-withdrawing groups are substituted for H at R_2, reduction becomes easier. This is related to a decrease of the electron density on the nickel atom. The data reported in Table VI allow this conclusion to be extended to non-symmetrical complexes. Furthermore, the influence of one substituent ($COCH_3$) is markedly lower than the effect of two substituents in the related symmetrical complexes.

Conclusions

The data emphasize the influence of the peripheral substituent ($COCH_3$) on the electron distribution in symmetrical (M.A and M.A') and non-symmetrical (M.B and M.B') complexes. When examining the metallic centre, Ni(II) or Cu(II), the effect related to one substituent (M.B or M.B') is markedly lower than the effect of two substituents (M.A or M.A'), as expected. However, when considering the ligand, it appears that the influence of the substituent on the non-symmetrical species (M.B and M.B') is restricted to the moiety to which it is bonded.
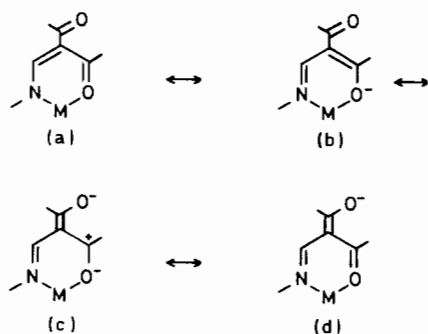
Fig. 3. Resonance structures for (Ni.B).

Furthermore, this influence is almost identical in magnitude to that observed in the related symmetrical species. This behaviour results in a significant difference between the two coordinated C=O groups in the (M.B) complexes as examplified by the ^{13}C NMR data. In spite of this difference, the two C=O actually react with ethylenediamine to afford the tetraazamacrocyclic complexes (M.B').

It is not unreasonable to suppose that the negatively charged ethylenediamine first reacts with C-8, which is positively charged due to the influence of the acetyl group. Indeed, COCH$_3$ is expected to decrease the electron density on the C-8 atoms via resonance participation of structure c (Fig. 3). This interpretation is supported by the downfield shift of C-8 with respect to C-1.

However, a different mechanism is needed to explain ring closure which involves the 'non activated' (C-1)=O group. It is interesting to recall here that electronic and ESR spectra related to the (Cu.B) complex in the presence of ethylenediamine (En) suggest the formation of an adduct (Cu.B) En in a preliminary step. Recently, Melson proposed a multistep mechanism to account for the reaction of the symmetrical complexes (M.A$_{Ac}$) with En [18]. In the first step, formation of a six-coordinated (M = Ni) or a five-coordinated (M = Cu) adduct is postulated. The second step would involve deprotonation of the coordinated NH$_2$ group of ethylenediamine and subsequent attack of this nucleophile at the carbon atom of a coordinated C=O group of the ligand. The third step would be ring closure through condensation of the remaining NH$_2$ with the second C=O group.

Our data are consistent with the occurrence of steps I and II in the case of the non-symmetrical complexes (M.B). As previously noted, the reactivity of the second C=O group which is remote from the electron-withdrawing group (COCH$_3$) is expected to be low even in the presence of the metal ions. Indeed, the ^{13}C NMR data evidence the polarizing effect of the nickel ion on (C-8)=O but not on (C-1)=O. Therefore we suggest that a thermodynamic template effect should be operative in this third step and,

consequently, that the driving force of the first condensation would be better considered as a kinetic effect.

Finally, reaction of the non-symmetrical complexes (M.B) with ethylenediamine may be used to produce the novel tetraazamacrocyclic complexes (M.B'). The presence of one functional group appended to the macrocyclic ligand offers the opportunity for affixing a superstructure designed to obtain biomimetic properties, according to the works of Busch [19].

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