Electrochemical and Spectroelectrochemical Investigations of Mono- and Binuclear Cobalt(II) Complexes of "Figure-Eight" Octapyrrolic Macrocycles

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In this paper, electrochemical investigations of a set of three cyclooctaphyrin complexes containing divalent cobalt are reported. These complexes are the homodinuclear cobalt-cobalt complex Co_2L_1 with the ligand H_4L_1, the mononuclear cobalt complex CoH_2L_2 and the heterodinuclear copper(II)-cobalt complex $CoCuL_2$ with the ligand H_4L_2. All of these species undergo two reduction and three oxidation processes, all of which are reversible one-electron transfers. The two reduction and first two oxidation steps are ligand-centered, as confirmed by spectroelectrochemical investigations. In contrast, the third oxidation corresponds to a metal-centered reversible one-electron transfer. The metal-centered oxidation steps occur at lower potentials than the third oxidation steps of the free bases. UV/Visible spectral changes observed during oxidation confirm a metal-centered oxidation generating a cobalt(III) cation, which is rather unusual when compared with cobalt porphyrin complexes, in which the oxidation of the metal usually occurs before the oxidation of the ligand.

Introduction

The chemical and biological properties of vitamin B12 and its derivatives have generated considerable interest in the chemical investigation of cobalt complexes.[1]

Since functional mimics of multielectronic redox enzymes may involve two or more metal centers, numerous cofacial metalloporphyrins have been synthesized and cofacial cobalt porphyrins have been studied to evaluate their ability to carry out the tetraelectronic electrocatalytic reduction of O_2 to H_2O.[2]

Cobalt porphyrins are well-known systems and their redox behavior has been extensively studied;[3] however, cobalt complexes of larger polypyrrolic macrocycles have not yet been investigated. Although numerous macrocyclic polypyrrolic ligands have been synthesized,[4–10] their complexation properties with transition metals remain scarce in the literature[11–13] and only a few cobalt complexes have been characterized.[14,15]

Cyclooctapyrrolic ring systems have recently been synthesized.[16–18] They possess a "figure-eight" conformation delimiting two tetrapyrrolic complexation sites that are able to accommodate up to two divalent cations as shown in crystallographic structures.[19–21] However, due to their twisted geometry, the two tetrapyrrolic sites do not share the same plane. They are separated by a dihedral angle of approximately 60°. These cyclooctaphyrins (COP) have allowed the preparation and characterization of several cobalt complexes: Co_2L_1 with the ligand H_4L_1 [[34]COP(1.1.1.0.1.1.1.0)] as well as CoH_2L_2 and $CoCuL_2$ with the ligand H_4L_2 [[32]COP(1.0.1.0.1.0.1.0)] (Figure 1).

The aim of the present electrochemical investigation was to determine whether or not cyclooctaphyrins are able to stabilize cobalt(I) and/or cobalt(III), as is usually observed in porphyrins.[23–25] In order to study the solvent effects, electrochemical investigations were performed using rotating disk and cyclic voltammetry in two media differing in their solvation properties: benzonitrile (PhCN) and dichloromethane (CH_2Cl_2). Spectroelectrochemistry was used to identify the electron transfer sites (ligand versus metal).

The present results on cobalt cyclooctaphyrins can then be compared with our previous studies on three series of cyclooctaphyrin metallocomplexes for which only ligand-centered electron transfers were observed.[26,27]

Results and Discussion

Electrochemical Studies

The redox behavior of the three cobalt cyclooctaphyrin complexes were determined by cyclic voltammetry (CV) and rotating disk voltammetry (RDV) in dry PhCN + 0.1 M $TBAPF_6$ solutions at room temperature (25 °C).

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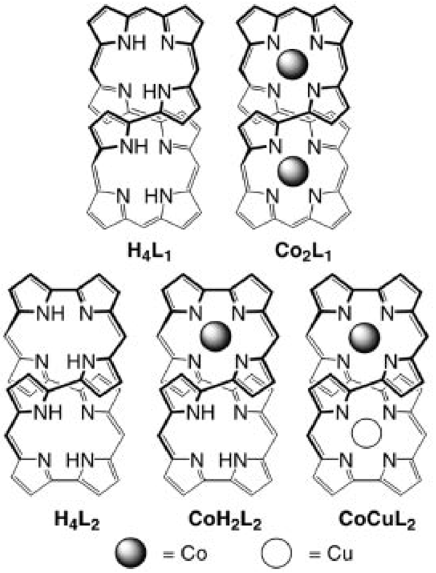

Figure 1. Free bases and complexes studied in the two cyclooctaphyrin series; the ethyl groups on the pyrroles are omitted for clarity; the compounds are named [−]COP(-.-.-.-.-.-) after the nomenclature proposed by Franck for polypyrrolic macrocycles[22]

RDV on Co_2L_1 presents two reduction (−1.96 and −1.33 V/Fc) and four oxidation waves (−0.42, 0.06, 0.30 and 0.63 V/Fc) (Figure 2). All waves are of similar amplitude and wave analysis using Tomeš criteria[28] give slopes close to 56.4 mV, the expected value for reversible one-electron processes, for the two reduction and the first three oxidation steps, whereas the fourth oxidation step has a slope of 90 mV (Table 1).

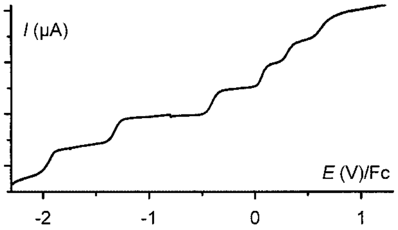

Figure 2. Rotating disk voltammetry on Co_2L_1 (≈10^{-4} M) in PhCN +0.1 M Bu_4NPF_6, at a Pt working electrode; scan rate: 0.05 V/s. $N = 2000$ rpm

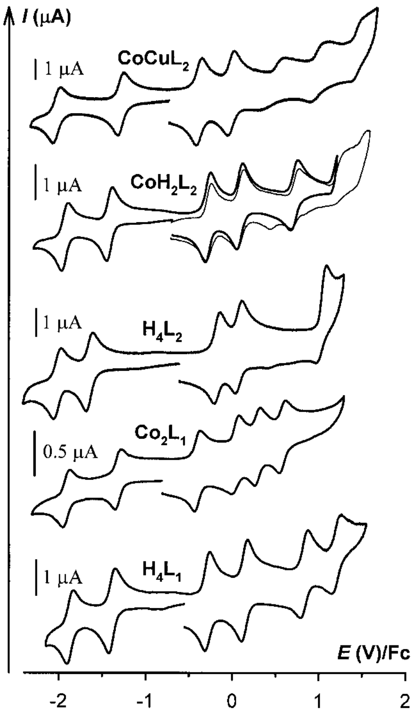

Figure 3. Cyclic voltammetry on H_4L_1, Co_2L_1, H_4L_2, CoH_2L_2 and $CoCuL_2$ in PhCN +0.1 M Bu_4NPF_6, at a Pt working electrode; scan rate: 1 V/s for H_4L_2 and 0.05 V/s for H_4L_1, Co_2L_1, CoH_2L_2 and $CoCuL_2$. c ≈10^{-4} M.

The results from the cyclic voltammetric study of Co_2L_1 (Figure 3) confirms the reversibility of each of the two one-electron reduction processes, as well as the first three one-electron oxidation steps. In contrast with the results from the rotating disk voltammetric study, the fourth oxidation step is also reversible. This reversibility was confirmed by monitoring the peak current (I_p) and the peak potentials (E_p) with increasing scan rates: E_p remained invariant with ν for sweep rates up to 5 V/s, the peak current ratio remained close to unity for all ν, and the peak potential difference ($\Delta E = E_{pc} - E_{pa}$) was approximately 60 mV.

A particular behavior is observed for the second oxidation step when the vertex potential is fixed after the third or fourth oxidation steps with sweep rates higher than 0.1 V/s. As shown in Figure 4 (a) the reverse peak of step II disappears on increasing the sweep rates and a new peak is observed at −0.11 V/Fc. Such behavior may be due to slow

Table 1. Redox potentials obtained by rotating disk voltammetry, in PhCN +0.1 M Bu_4NPF_6, at a Pt working electrode; scan rate: 0.05 V/s. $E = (E_{pc}+E_{pa})/2$; potentials vs. Fc

Compound	E red$_2$ ($E_{3/4} - E_{1/4}$)	E red$_1$ ($E_{3/4} - E_{1/4}$)	E ox$_1$ ($E_{3/4} - E_{1/4}$)	E ox$_2$ ($E_{3/4} - E_{1/4}$)	E ox$_3$ ($E_{3/4} - E_{1/4}$)	E ox$_4$ ($E_{3/4} - E_{1/4}$)	E ox$_5$ ($E_{3/4} - E_{1/4}$)
Co_2L_1	−1.96 V (62 mV)	−1.33 V (60 mV)	−0.42 V (62 mV)	0.06 V (56 mV)	0.30 V (54 mV)	0.63 V (90 mV)	–
CoH_2L_2	−1.95 V (63 mV)	−1.41 V (61 mV)	−0.29 V (57 mV)	0.09 V (60 mV)	0.74 V (68 mV)	1.37 V (89 mV)	–
$CoCuL_2$	−2.01 V (65 mV)	−1.28 V (62 mV)	−0.39 V (57 mV)	−0.03 V (61 mV)	0.57 V (73 mV)	1.08 V (84 mV)	1.47 V (77 mV)

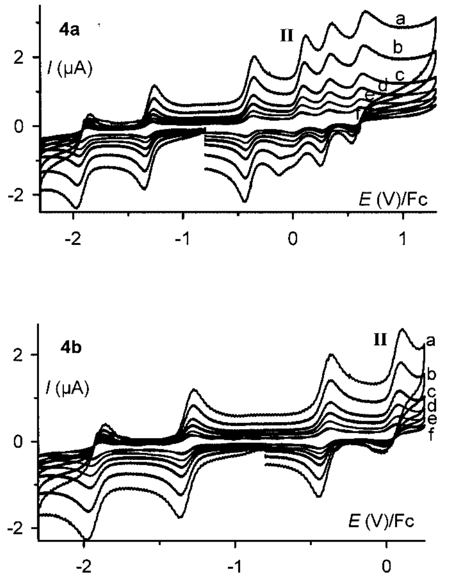

Figure 4. Series of cyclic voltammograms of Co_2L_1 ($\approx 10^{-4}$ M) with different scan rates in PhCN +0.1 M Bu_4NPF_6, performed at a Pt working electrode; scan rates for: a) 1 V/s; b) 0.5 V/s; c) 0.2 V/s; d) 0.1 V/s; e) 0.05 V/s; f) 0.02 V/s; for 4a potential range from −2.30 V to +1.30 V/Fc, and for 4b potential range from −2.30 V to +0.25 V/Fc.

geometric rearrangements occurring during the third oxidation process, preventing the molecule from returning to its initial structure again in the CV time scale ($\nu > 0.1$ V/s). The fact that the disappearance of a peak and the appearance of a new peak is not observed when the third oxidation has not been reached [Figure 4 (b)], confirms that these geometric rearrangements occur in the tricationic species.

It should be mentioned that the third and the fourth oxidation processes observed for Co_2L_1 using CV (Table 2) and rotating disk voltammetry (Table 1) occur at potentials that are less positive by 400 mV relative to those of the free bases, and by 200 mV relative to those of complexes with non-electroactive metals. This could be an indication of metal-centered electron transfers, which would explain the above hypothesis concerning the geometric changes that occur during the third oxidation process.

The two reduction and first two oxidation steps of the other two cobalt complexes, CoH_2L_2 and $CoCuL_2$, are similar to those of the free base H_4L_2.[26,27] After the second oxidation step, the complexes have a distinct behavior. When using RDV and CV, CoH_2L_2 presents a third one-electron oxidation that occurs at 0.73 V/Fc, which is 280 mV less positive than the third oxidation of the free base (Table 2). A fourth one-electron oxidation step is observed at +1.27 V/Fc (Figure 3). These data are in agreement with a metal-centered oxidation process for the third oxidation step of CoH_2L_2.

The complex $CoCuL_2$ presents three additional one-electron oxidation steps after the second oxidation. The third oxidation occurs at +0.57 V/Fc, 440 mV less positive than that of the free base (Table 2). This is consistent with the third oxidation process occurring at the cobalt center. The fourth and fifth oxidation steps are observed at +1.08 and +1.47 V/Fc (Figure 3).

It has been shown that in cobalt porphyrin complexes, the redox potential of the $Co^{III/II}$ couple is dependent on both the solvent and the supporting electrolyte. Indeed, strong coordinating solvents facilitate the oxidation of the metal, whereas in non-bonding solvents the redox potential is shifted towards positive potentials.[23−25,29−31] On the other hand, the redox potentials of ligand-centered electron transfers are less sensitive to solvation changes than metal-centered processes. For these reasons, a new set of measurements in non-coordinating CH_2Cl_2 was performed to study the solvent effects on the redox potentials when going from benzonitrile to dichloromethane.

In CH_2Cl_2, the reduction and first two oxidation steps of Co_2L_1 are similar to that described previously in PhCN. The third oxidation step is shifted to more positive potentials by 300 mV, while the fourth oxidation step is no longer observed under these experimental conditions. The addition of a strong axial ligand in dichloromethane is expected to shift the redox potential of a metal-centered electron transfer.[23−25] Therefore, pyridine was added to confirm that the third oxidation process is metal-centered. After the addition of pyridine, the third oxidation step shifts cathodically towards the value observed in PhCN (Figure 5). The

Table 2. Redox potentials obtained by cyclic voltammetry, in PhCN (at a Pt working electrode) and in CH_2Cl_2 (on a GC working electrode) +0.1 M Bu_4NPF_6; scan rate: 0.1 V/s. $E = (E_{pc}+E_{pa})/2$; potentials vs. Fc

Compound	Solvent	E red$_2$ (Volt)	E red$_1$ (Volt)	E ox$_1$ (Volt)	E ox$_2$ (Volt)	E ox$_3$ (Volt)	E ox$_4$ (Volt)	HL gap (Volt)
H_4L_1	PhCN	−1.88	−1.40	−0.30	0.13	0.83	1.21	1.10
	CH_2Cl_2	−1.78	−1.49	−0.38	0.14	0.87	1.19	1.11
Co_2L_1	PhCN	−1.92	−1.32	−0.41	0.03	0.29	0.58	0.91
	CH_2Cl_2 + Py	−1.89	−1.40	−0.45	0.07	0.39	0.69	0.95
	CH_2Cl_2	−1.96	−1.43	−0.48	0.08	0.59	−	0.95
H_4L_2	PhCN	−2.02	−1.64	−0.18	0.08	1.01	1.06	1.46
	CH_2Cl_2	−1.97	−1.66	−0.23	0.11	1.12	1.12	1.43
CoH_2L_2	PhCN	−1.93	−1.41	−0.28	0.09	0.73	1.27	1.13
	CH_2Cl_2	−2.02	−1.57	−0.41	0.05	0.78	−	1.16
$CoCuL_2$	PhCN	−2.01	−1.28	−0.39	−0.03	0.57	1.08/1.47	0.89
	CH_2Cl_2	−2.11	−1.39	−0.46	0.00	0.74	1.10/−	0.93

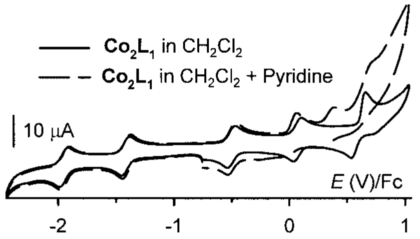

Figure 5. Cyclic voltammetry on Co_2L_1 ($5 \cdot 10^{-4}$ M) (solid line) and on Co_2L_1 +12 equivalents of pyridine (dashed line) in CH_2Cl_2 +0.1 M Bu_4NPF_6, at a Pt working electrode (scan rate: 0.1 V/s)

redox potentials determined are presented in Table 2. All of the above results demonstrate that the third oxidation step corresponds to the oxidation of Co^{II} to Co^{III}.

Under the same experimental conditions, a large potential shift (170 mV) is observed for the third oxidation step of $CoCuL_2$, and only a small shift (50 mV) is observed for CoH_2L_2 (Table 2). Such a small shift is characteristic of poor axial coordination by the cobalt ion. This can be explained in the following way: as this is a mononuclear complex of the smallest cyclooctaphyrin, it is possible that the ligand is more tightly wrapped around the cobalt cation, thus hindering the access for axial coordination to a greater extent relative to $CoCuL_2$.

Spectroelectrochemistry

In order to determine the electron transfer sites, spectroelectrochemical studies were carried out. Comparison of the spectral changes during electrolysis of the cobalt complexes with the spectra of the parent compounds (free base and complexes with non-electroactive metals) allowed us, in most cases, to assign the electron transfer sites in the cobalt complexes.

For each cobalt complex, the reduction processes produce spectral evolutions with well-defined isosbestic points. The spectra obtained after electrolysis revert quantitatively to the initial spectrum by stepwise electrochemical restoration of the starting cyclooctaphyrin. This result indicates that the two electroreduced species are stable in the time scale of the spectroelectrochemical experiments, i.e. about 30 min, which is a good indication of the high stability of the electrogenerated species under these experimental conditions. Spectral changes seen for the cobalt complexes are similar to those observed for the parent compounds [a blue shift for Co_2L_1; Figure 6 (a) and red shifts for CoH_2L_2 and $CoCuL_2$; Figure 6 (c and e)], which confirms that the reductions are ligand-centered. For complexes CoH_2L_2 and $CoCuL_2$, the presence of an intense and sharp absorption band (Soret-like) is observed after the second reduction process, as seen previously for metallocomplexes of cyclooctaphyrins with the same ligand.[27]

The three oxidation steps also produce spectral evolutions with well-defined isosbestic points, even for $CoCuL_2$ [Figure 6 (f)], for which the third oxidation process is quasi-reversible when using CV. The initial spectra could be quantitatively recovered by stepwise reduction of the electrogenerated species, which indicates the high stability of the generated species.

The fourth and further oxidations could not be studied for CoH_2L_2 and $CoCuL_2$ since their oxidation steps occur too close to the electrolyte discharge.

Spectral evolutions for the two first oxidations are similar to those of the free bases (blue shift for Co_2L_1 [Figure 6 (b)] and red shift for CoH_2L_2 and $CoCuL_2$ [Figure 6 (d and f)], which are characteristic of ligand-centered oxidations, thus generating the corresponding dications. Spectral evolutions for the third oxidation step differ for each complex studied.

For Co_2L_1 and CoH_2L_2, the spectral evolutions for the third oxidation step are quite different from those observed for the free base. The intensity of the band changes, while no changes are observed in the absorption wavelength. This is a good indication of a metal-centered oxidation process.

For $CoCuL_2$, the changes involving the third oxidation step are more significant; indeed the absorption bands at 388 and 646 nm decrease in intensity, whereas new bands appear at 331 and 424 nm.

The Unexpected Synthesis of the Radical Cation $CoH_2L_2^+$

As only a few cobalt complexes were available, we considered the possibility of the insertion of a second cobalt cation in the mononuclear complex by in situ complexation. As no spectroscopic data were available for the dinuclear cobalt complex of the ligand H_4L_2, in situ complexation in a mixture of methanol/dichloromethane (1:1) was tested with copper since the UV/Visible spectra of the mononuclear copper complex and the homodinuclear copper complex are already available. In situ complexation of copper to the ligand H_4L_2 confirmed the formation of the mononuclear complex [for 1 equiv. of $Cu(CF_3SO_3)_2$] and the dinuclear complex [for 2 equiv. of $Cu(CF_3SO_3)_2$]. The spectra shift to the red when going from the free base to the mono- and dinuclear copper complex, as shown in Figure 7 (a).

The same experiment was carried out with the cobalt salts $Co(CF_3SO_3)_2$ and $Co(OH)_2$. The first observation was that the complexation kinetics are much slower for cobalt than for copper. The characteristic spectrum of the mononuclear complex was observed eight hours after the introduction of the cobalt salt for a stoichiometric mixture. Further spectral changes were observed only when a large excess (saturated solution) of the cobalt(II) salt was added to the mononuclear complex. The observed spectrum indicated the presence of a new species X in solution [Figure 7 (b)]. Compound X was prepared by dissolving the free base H_4L_2 (5.3 mg) in 30 mL of a mixture of methanol/dichloromethane (1:1). 3000 equivalents of $Co(OH)_2$ were added to the solution, and the suspension was stirred overnight. The excess solid was removed by filtration. The solution was dried over $MgSO_4$ and then filtered. Finally, the solvent was removed under vacuum. A dark blue powder was obtained. The UV/Visible spectrum of X is identical to the spectrum observed when using spectroelectrochemistry after the first oxidation process of CoH_2L_2; this implies that the radical cation $CoH_2L_2^{\bullet +}$ is formed. Rotating disk voltammetry on the prepared compound shows potentials that are similar

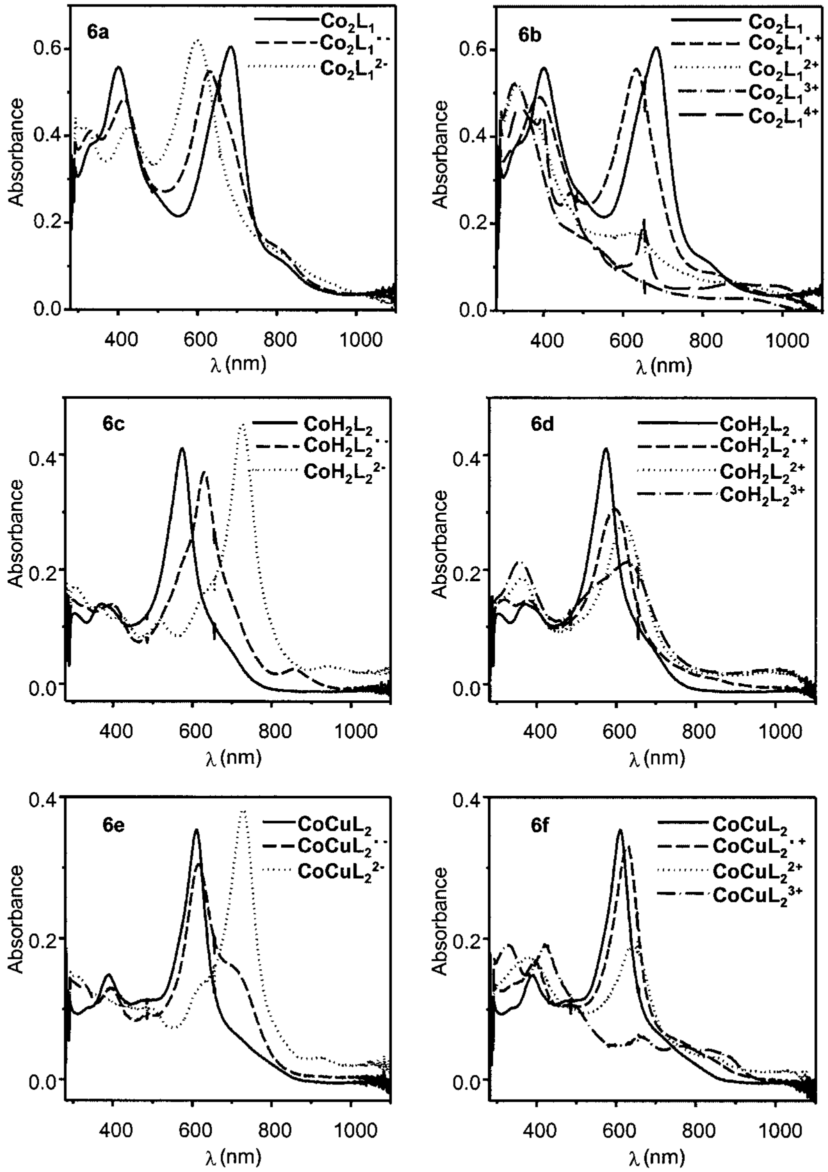

Figure 6. Spectroelectrochemistry on Co$_2$L$_1$, CoH$_2$L$_2$ and CoCuL$_2$, in PhCN +0.1 M Bu$_4$NPF$_6$; reduction [Figure 6 (a)] and oxidation processes [Figure 6 (b)] of Co$_2$L$_1$. Reduction [Figure 6 (c)] and oxidation processes [Figure 6 (d)] of CoH$_2$L$_2$; reduction [Figure 6 (e)] and oxidation processes [Figure 6 (f)] of CoCuL$_2$; $c \approx 10^{-5}$ M

to those observed for the complex CoH$_2$L$_2$; however, instead of an oxidation at −0.28 V/Fc, a reduction current is observed (Figure 8). The spectroelectrochemical reduction of X at −0.4 V/Fc produces spectral evolutions with well-defined isosbestic points that lead to the spectrum of neutral CoH$_2$L$_2$.

All these observations confirm that the prepared species X is in fact the radical cation of the complex CoH$_2$L$_2$. Mass spectrometry also confirms that X is a mononuclear cobalt complex (m/z = 537 [M + H]$^{2+}$, expected mass for C$_{68}$H$_{86}$CoN$_8$: 1073). In situ complexation did not allow us to prepare a new homodinuclear complex to extend our electrochemical studies. No explanation about the formation of this radical has been established. However, since the first oxidation step of the complex CoH$_2$L$_2$ occurs at a very low potential, the possible presence of an oxidizing agent as an impurity in the cobalt salt (3000 equiv.) used in excess or oxygen (even our experimental conditions are not suitable for this kind of reaction),[32] could be responsible for the chemical reaction generating the radical cation.

Discussion

The main difference between the free bases and the cobalt complexes (see Tables 1 and 2) that belong to the same COP ligand series involves the redox potentials beyond the second oxidation process. The third oxidations for the cobalt complexes occur at potentials much less positive than those observed for the free bases, and correspond to the oxidation of Co^{II} to Co^{III}. The redox potential of the latter step is solvent-dependent, as expected for metal-centered electron

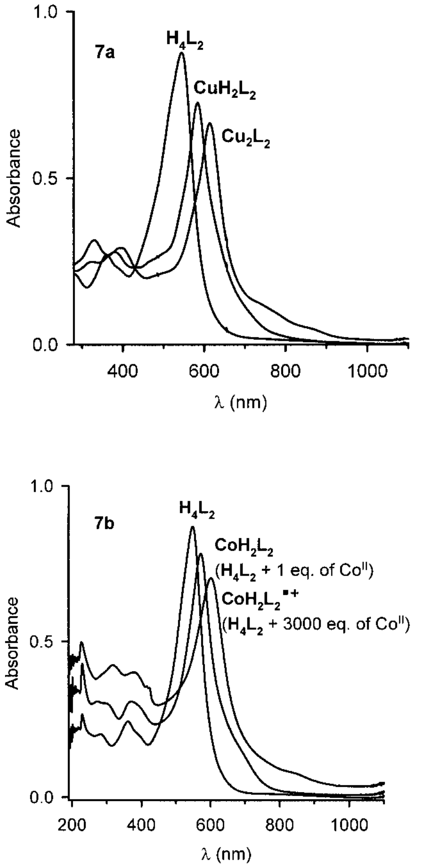

Figure 7. UV/Visible absorption spectra of H_4L_2 ($\approx 10^{-5}$ M) and spectral evolutions for in situ complexation in a mixture of methanol/dichloromethane (1:1) with metallic divalent salts; 7a for in situ complexation with Cu^{II} and 7b for in situ complexation with Co^{II}

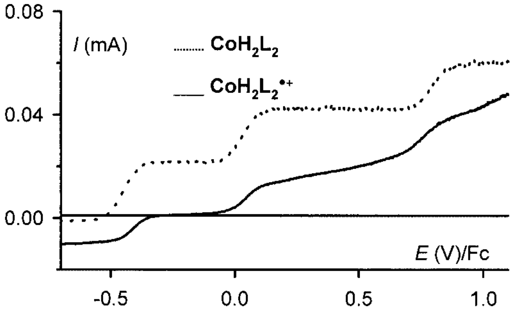

Figure 8. Rotating disk voltammetry on CoH_2L_2 and $CoH_2L_2^+$ in CH_2Cl_2 + 0.1 M Bu_4NPF_6, at a Glassy Carbon (GC) working electrode; scan rate: 0.01 V/s. N = 2000 rpm; $c \approx 10^{-4}$ M

transfers and as observed previously for porphyrins.[23,24] This behavior is due to the conversion of a preferred square-planar coordination for the Co^{II} to an octahedral coordination for the Co^{III} ion. Thus, a coordinating solvent like PhCN will be axially coordinated by metals, thus stabilizing the Co^{III} ion. This stabilization will facilitate the generation of Co^{III}, such that the potential will be cathodically shifted relative to the values determined in CH_2Cl_2.

All the studies undertaken confirm that COP do not stabilize the Co^{I} species at all. This is not the case for previously studied cobalt complexes.[24] COP behave like corrphycenes[33] and porphycenes,[34] and differ vastly from porphyrins, which usually stabilize cobalt(I) in the tetrapyrrolic ring system. The observed $Co^{II/III}$ redox potentials in COP are much more positive than those observed previously in tetrapyrrolic ring systems (−0.07 V/Fc for corrphycene,[33] +0.195 V/Fc for porphycene[34] and +0.30 V/Fc for porphyrins[35]). Such positive potentials are in agreement with the fact that cyclooctaphyrins destabilize Co^{III} in the corresponding "tetrapyrrolic" coordination site of COP. Within the COP series, Co_2L_1 stabilizes the cobalt(III) atom to a greater extent than other COP complexes such as CoH_2L_2 and $CoCuL_2$. Comparison with previously studied cobalt tetrapyrrolic macrocyclic complexes was not possible since the oxidation of the cobalt ion occurs before ring oxidation for these complexes. For the COP complexes, the oxidation of the cobalt ion occurs after the generation of the dication.

Spectral changes for the free base and the cobalt complex are similar during the two reduction and first two oxidation steps, indicating that these four redox steps occur on the ligand, generating the radical anion and the dianion during reduction, and the radical cation and the dication during oxidation. The free base presents a non-reversible behavior for the second reduction step for prolonged electrolysis: the spectral changes are similar to those observed for metal complexes for at least the first ten minutes. Thus, we can conclude that this electron transfer is also ligand-centered.

The third oxidation presents different spectral changes for the free base and the metal complex, which is consistent with a metal-centered electron transfer process. The spectral changes during this third oxidation for the cobalt complex mainly involve the intensity of the absorption bands. This type of behavior is also characteristic of a metal-centered electron transfer process, as generally it induces smaller geometric or topographic changes in the molecule.

For the other cobalt complexes similar conclusions are obtained from the spectroelectrochemical results. In addition, their behavior in two different solvents provides confirmation of the nature of the electron transfers.

Conclusion

All cyclooctaphyrin cobalt complexes undergo two reduction processes and a first and a second oxidation process, all one-electron, reversible and ligand-centered. Beyond the second oxidation, the redox behavior is different for each complex. They all possess a third one-electron reversible oxidation process centered at the metal ($Co^{2+} \rightarrow Co^{3+}$). The homodinuclear cobalt complex also undergoes a fourth oxidation step that is one-electron and reversible, and centered at the second cobalt cation; no further oxidations are observed. For the monocobalt complex, another oxidation is observed (ligand-centered), as well as two other oxidation steps observed in the case of the heterodinuclear cobalt-copper complex. Spectroelectrochemistry confirms the nature of the electron transfers. The metal-centered steps are affected by the solvent coordination properties. A shift towards cathodic potentials is observed for these steps in PhCN, except in the case of the monocobalt complex. An attempt to obtain the homodinuclear cobalt complex of the COP(1.0.1.0.1.0.1.0) series[32] led to the formation of the monocobalt complex radical cation. Under our experimental conditions, no cobalt-centered reductions are observed.

Experimental Section

General Remarks: In most of the cases the electrochemical measurements were carried out in a glove box (less than 3 ppm of H_2O and less than 2 ppm of O_2) at room temperature (25 ± 2 °C) in PhCN containing 0.1 M $TBAPF_6$ in a classical three electrode cell, connected to a PAR (model 273) potentiostat, interfaced with a PC computer. The working electrode was a platinum (Pt) disk electrode (diameter: 2 mm), used either motionless as in cyclic voltammetry (v = 20 mV/s to 5 V/s) or as a rotating disk electrode. The auxiliary and the pseudo-reference electrodes were platinum wires. PhCN (Aldrich, 99 %) was dried for two days over $CaCl_2$ (anhydrous, Fluka, 97 %), and distilled on P_2O_5 (Prolabo) under reduced pressure in an inert atmosphere (Argon). Bu_4NPF_6 was dried in an oven (65 °C) under vacuum for two days. Bu_4NPF_6 was dissolved in PhCN inside the glove box and the solution was then percolated over activated alumina. The available potentials at a platinum working electrode ranged from −2.5 to +1.8 V/Fc.

Some measurements were carried out under classical conditions out of the glove box, in CH_2Cl_2 containing 0.1 M $TBAPF_6$ in a three electrode cell. The electrochemical cell was connected to a computerized multipurpose electrochemical device (Autolab PGSTAT T20) controlled by GPSE software. The working electrode was a glassy carbon (GC) disk electrode (diameter: 3 mm), used either motionless as in cyclic voltammetry (v = 20 mV/s to 5 V/s) or as a rotating disk electrode. The auxiliary electrode was a platinum wire, and the reference electrode was Ag/AgCl/KCl (sat.) electrode. All potentials are referred to the ferrocene/ferrocenium (Fc/Fc^+) couple used as internal standard.

Spectroelectrochemical measurements were carried out in PhCN in a home-made quartz cell, having an optical pathway of 1 mm. The working electrode was a platinum grid (1000 mesh) placed in the optical pathway. The reference and the auxiliary electrodes were platinum wires separated by cotton from the solution in individual compartments. The cell was filled in the glove box, and hermetically closed, then it was placed in a diode array spectrophotometer (Hewlett−Packard 8453), and the spectra were recorded during electrolysis.

2,3,7,8,12,13,16,17,21,22,26,27,31,32,35,36-Hexadecaethyloctaphyrin-(1.1.1.0.1.1.1.0)ato-dicobalt(II) (Co_2L_1): The dinuclear cobalt(II) complex Co_2L_1 was prepared by dissolving the free base H_4L_1 (52 mg, 0.05 mmol) in 50 mL of absolute DMF, by gently heating the solution under argon. A solution of cobalt(II) acetate tetrahydrate (125 mg, 0.5 mmol) dissolved in 15 mL of DMF was added to the ligand and the solution was refluxed for three hours. After cooling to room temperature, 50 mL of toluene was added to the solution as well as 150 mL of ice water. The organic layer was washed several times with water, dried over Na_2SO_4 and finally the solvent was removed under vacuum. Recrystallization under argon in a mixture of acetonitrile/t-butylmethyl ether (4:1) gave Co_2L_1 as a black powder. Yield 36 mg (65 %). MS (FAB): *m/z* = 1156 [M^+] (100 %). $C_{70}H_{86}Co_2N_8$ (1157.4): calcd. C 72.64, H 7.49, N 9.68; found C 72.36, H: 7.49, N: 9.42. IR (CsI): ṽ = 2962, 2930, 2869, 1663, 1577, 1492, 1464, 1450, 1371, 1314, 1275, 1205, 1170, 1141, 1110, 1055, 1029, 1018, 986, 960, 925, 848, 835, 809, 746, 679 cm^{-1}. UV/Vis (CH_2Cl_2) λ_{max} (ε) = 347 sh (34400), 401 (51500), 682 nm (55600 M cm^{-1}). M.p. >300 °C.

2,3,6,7,11,12,15,16,20,21,24,25,29,30,33,34-Hexadecaethyloctaphyrin-(1.01.0.1.0.1.0)atocobalt(II) (CoH_2L_2): The mononuclear cobalt(II) complex CoH_2L_2 was prepared by dissolving the free base H_4L_2 (102 mg, 0.1 mmol) in a mixture of 30 mL of dichloromethane and 1 mL of triethylamine under an inert atmosphere. $Co(OAc)_2$ $4H_2O$ (55 mg, 0.22 mmol) in 15 mL of methanol was added to the solution. The mixture was stirred at room temperature for six hours and the solvent removed under vacuum. At all times the solution temperature was maintained below 25 °C. The remaining compound was chromatographically filtered through aluminum oxide (5 × 2 cm column) with a hexane/dichloromethane mixture (1:3) and finally recrystallized from an acetonitrile/dichloromethane/methanol mixture (1:1:1). CoH_2L_2 was obtained as green crystals. Yield 86 mg (80 %). MS (FAB): *m/z* = 1073 (100 %) $[M]^+$. $C_{68}H_{86}CoN_8$ (1074.4): calcd. C 76.02, H: 8.07, N 10.43; found C 76.07, H 8.10, N 10.40. IR (KBr): ṽ = 2962, 2929, 2869, 1570, 1531, 1507, 1464, 1389, 1270, 1224, 1210, 1187, 1153, 1122, 1109, 1056, 1004, 953, 873, 829, 764 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 272 (34000), 370 (34000), 571 (91000), 674 nm (20000 M cm^{-1}). M.p. > 300 °C.

2,3,6,7,11,12,15,16,20,21,24,25,29,30,30,33,34-Hexadecaethyloctaphyrin-(1.01.0.1.0.1.0)atocobalt(II)copper(II) ($CoCuL_2$): The heterodinuclear cobalt copper complex $CoCuL_2$ was obtained by dissolving the mononuclear cobalt complex CoH_2L_2 (107 mg, 0.1 mmol) in 50 mL of CH_2Cl_2. $Cu(OAc)_2$ H_2O (20 mg) dissolved in methanol was added to the solution and the mixture was stirred for one hour at room temperature. The solvent was removed under vacuum and the compound purified by chromatographic filtration through aluminum oxide (5 × 1 cm column) with a mixture of toluene/hexane (1:2). The unique fraction was finally recrystallized from a hexane/dichloromethane (1:1) mixture yielding $CoCuL_2$. MS (FAB): *m/z* = 1134 (100 %) $[M]^+$, 1151 (20) $[M + 1/2O_2]^+$. $C_{68}H_{84}CoCuN_8$ (1136.0): calcd. C 71.9, H 7.45, N 9.86; found C 71.52, H 7.49, N 9.98. IR (CsI): ṽ = 2961, 2928, 2867, 1561, 1520, 1496, 1464, 1387, 1369, 1266, 1228, 1187, 1153, 1122, 1108, 1060, 1006, 954, 874, 833, 782 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 389 (37000), 608 nm (87000 M cm^{-1}). M.p. > 300 °C.

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