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Synthesis and electrochemical behavior of a tetrametallated cobalt porphyrin

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Abstract

Reported is the chemistry of a new polynuclear cobalt porphyrin complex obtained by complexing the pyridine residues of *meso*-tetra(4-pyridyl)porphinate cobalt(III) chloride with ruthenium(III)–EDTA ions. The complex exhibited reversible spectroelectrochemical behavior, with two successive redox processes at $E° = 0.080$ and 0.295 V versus SHE associated with the peripheral Ru(III)EDTA and central Co(III) ions, respectively. An enhanced electrocatalytic activity in the reduction of molecular oxygen was observed for the tetrametallated cobalt porphyrin, involving a cooperative effect between the cobalt(III) center and the peripheral Ru(II)–EDTA groups.

Introduction

Metalloporphyrins containing peripheral metal complexes attached to the macrocyclic ring are of great interest, since they can exhibit enhanced photocatalytic or electrocatalytic properties in comparison to the typical porphyrins [1–6]. The reactivity of these complexes is expected to be strongly influenced by cooperative interactions [7–9] involving the central and peripheral metal ions. In order to evaluate this point, we have investigated the spectroscopic and electrochemical properties of a new polynuclear cobalt porphyrin complex (Fig. 1), derived from *meso*-tetra(4-pyridyl)porphinate cobalt chloride, [CoTPyP]Cl, by complexing the pyridine residues with ruthenium(III)–EDTA ions.

Experimental

The $[Ru(HEDTA)(H_2O)]\cdot 3H_2O$ and $[CoTPyP(H_2O)Cl]$ complexes were prepared according to the methods previously described [10–14]. The tetrametallated cobalt porphyrin was isolated as a solid of composition $Na_4[CoTPyP(H_2O)Cl(RuEDTA)_4]\cdot 8H_2O$ according to the following procedure. $[CoTPyP(H_2O)Cl]$ was solubilized in aqueous 0.025 M HCl solution and mixed with $[Ru(HEDTA)(H_2O)]\cdot 3H_2O$ at a mole ratio of 1:5. The pH of the mixture was carefully adjusted to 5 with NaOH. The red–brown solution was concentrated to a minimum volume in a flash evaporator, at 60 °C, and cooled at room temperature. By adding a few drops of dilute hydrochloric acid, the polynuclear complex precipitated leaving the excess of $[Ru(HEDTA)(H_2O)]$ in solution. The solid was collected on a filter, suspended in a small volume of water, and the mixture was carefully neutralized with NaOH. The resulting solution was evaporated to dryness. The solid was washed with ethanol, and dried in a vaccuum desiccator. *Anal.* Calc. for $C_{80}H_{88}O_{40}N_{16}ClNa_4CoRu_4$: C, 36.1; H, 4.0; N, 8.4. Found: C, 36.1; H, 4.1; N, 8.5%.

Cyclic voltammetry was carried out with a Princeton Applied Research (PAR) instrument, consisting of a model 173 potentiostat and a model 175 universal programmer. Glassy carbon electrodes ($A = 0.23$ cm^2) were employed for the measurements, using the conventional Luggin capillary arrangement with the Ag/AgCl ($I = 1$ M KCl) reference electrode ($E° = 0.222$ V versus SHE) in aqueous solution. A platinum wire was used as the auxiliary electrode.

The electronic spectra were recorded on a Hewlett-Packard model 8452-A diode array spectrophotometer. For the spectroelectrochemical measurements, the PAR 173 potentiostat was used in parallel with the diode array spectrophotometer. A three electrode system was designed for a rectangular quartz cell of 0.025 cm internal optical pathlength. A gold minigrid was used as a transparent working electrode, in the presence of a small Ag/AgCl reference electrode and a platinum auxiliary electrode. Stopped-flow kinetics were carried out with a Durrum D-110 instrument, equipped with a Kel-F flow system.

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Results and discussion

The $[Ru(EDTA)(H_2O)]^-$ ion, generated from the deprotonation of the $[Ru(HEDTA)(H_2O)]$ complex in acetate buffer ($4 < pH < 6$), exhibits a great affinity for pyridine ligands [13] and it is expected to form stable complexes with tetra(4-pyridyl)porphyrins by coordinating at the peripheral pyridyl groups, as in Fig. 1. Unfortunately, the direct reaction is precluded by the very small solubility of $[CoTPyP(H_2O)Cl]$ in aqueous and polar solvents compatible with the $[Ru(EDTA)(H_2O)]^-$ ion. The best results were obtained by solubilizing the $[CoTPyP(H_2O)Cl]$ complex in 0.025 M HCl, and reacting with $[Ru(HEDTA)(H_2O)]$ while the pH was gradually raised to 5, as described in 'Experimental'. The formation of the polynuclear cobalt porphyrin complex can be readily observed, since the product, in contrast with the starting cobalt porphyrin, is very soluble in neutral aqueous solution.

The tetrasubstituted complex, $[Co^{III}TPyP(Ru^{III})_4]$, was isolated from concentrated solutions, exhibiting consistent analytical results. The complex, analogously to several substituted [Ru(EDTA)] complexes, is susceptible to dissociation reactions, existing in equilibrium with $[Ru(EDTA)H_2O]^-$ ions. For this reason, in order to prevent the dissociation of the tetrasubstituted species, an excess of $[Ru(EDTA)(H_2O)]^-$ was employed in all the experiments.

The electronic spectrum of the $[Co^{III}TPyP(Ru^{III})_4]$ complex (Fig. 2), is similar to that of $[Co^{III}TPyP]^+$ in 0.1 M HCl, exhibiting the characteristic Soret and β bands at 435 and 550 nm, in comparison to 432 and 541 nm for the cobalt porphyrin. The α band is only poorly defined around 595 nm. As in the case of the substituted tetraphenyl porphyrins [15], the bathochromic shifts observed in the spectra reflect the increase in the electron acceptor properties of the pyridyl group induced by the $[Ru^{III}EDTA]^-$ ions. The electronic spectrum does not exhibit any variation in the pH range from 5 to 8, suggesting that the pK_a of the coordinated water molecule is higher than 8.

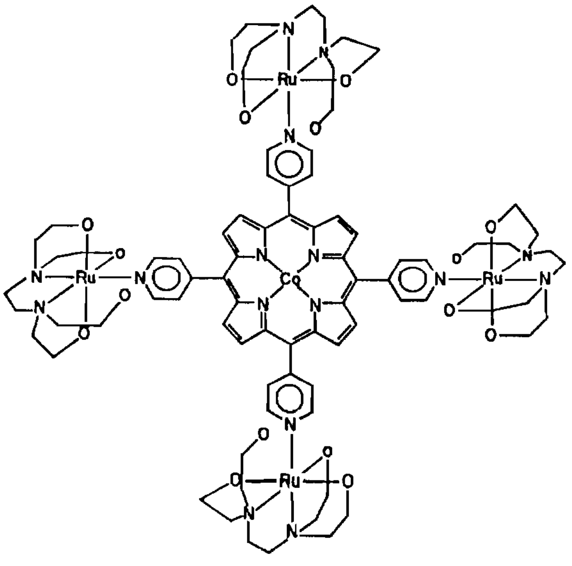

Fig. 1. Structure of $[CoTPyP(Ru)_4]$.

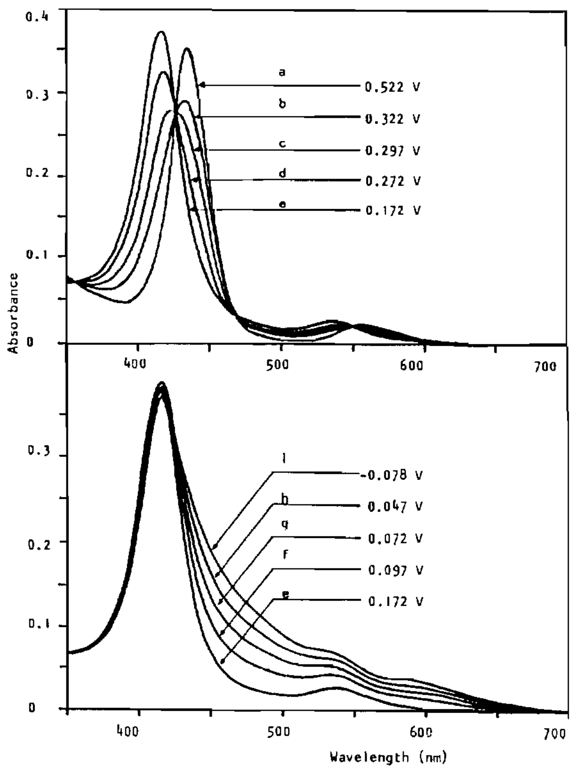

Fig. 2. Spectroelectrochemical bahavior of the [Co-TPyP(RU)$_4$] complex (0.1 mM) in aqueous solution at several applied potentials (in V vs. SHE), in the presence of 1.0 mM $[RuEDTA(H_2O)]^-$, 0.025 M acetate buffer and 0.25 M sodium trifluoroacetate (298 K).

The spectroelectrochemical behavior of the polynuclear cobalt porphyrin is illustrated in Fig. 2. By gradually decreasing the applied potentials, two successive reversible processes have been observed at $E° = 0.295$ and 0.080 mV, respectively. The first one leads to pronounced changes in the electronic spectra, shifting the Soret, β and α bands to 416, 536 and 596 nm, respectively, with isosbestic points at 356, 428, 470 and 548 nm. This type of behavior is typical of redox processes involving changes in the oxidation state of the central metal ion. The observed $E°$ value is also similar to that reported for the cobalt(III) 4-tetramethylpyridylporphyrin complex [16]. The second process leads to an absorbance increase around 460 nm, with minor changes in the intensity of the Soret and β bands. The E° value is close to those previously reported for ruthenium–EDTA complexes containing substituted pyridines. These complexes, in the reduced form, also exhibit characteristic metal-to-ligand charge-transfer bands in the visible [13]. Therefore, the second process is consistent with the reduction of the peripheral $Ru^{III}EDTA$ groups in the polynuclear cobalt porphyrin. Analogously to the examples from literature, the absorption band at 460 nm can be assigned to a ruthenium(II)-to-pyridine, $d_\pi \rightarrow p_\pi^*$ charge-transfer transition.

Typical cyclic voltammograms for the $[Co^{III}TPyP(Ru^{III})_4]$ complex, obtained in the presence of excess of $[Ru^{III}(EDTA)(H_2O)]^-$, are shown in Fig. 3. The composite waves can be deconvoluted in terms of two reversible waves, with $E^\circ = 0.080$ and -0.010 V, corresponding to monoelectronic redox processes associated with the peripheral $[Ru^{III}EDTA]$ and the free $[Ru^{III}(EDTA)(H_2O)]^-$ complexes, respectively. Surprisingly, there is little or no evidence for the redox waves expected for the $Co^{III/II}$ center, around 0.29 V. We presume that the electrode process involving the $Co^{III/II}$ redox couple is too slow to be detected in the cyclic voltammograms. This kind of behavior has been observed for several cobalt(III) complexes and is probably due to the large reorganization energies required for electron transfer in these systems [17].

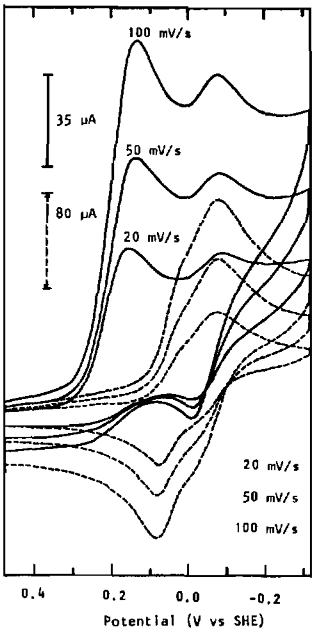

Fig. 3. Cyclic voltammograms of $[CoTPyP(Ru)_4]$, 1.7 mM in (– – –) argon or 0.10 mM in (——) dioxygen saturated aqueous solution at several scan rates, in the presence of 1.0 mM $[RuEDTA(H_2O)]^-$, 0.050 M acetate buffer, pH 5.0, and 0.25 M sodium trifluoracetate (298 K).

In the presence of dioxygen, the voltammograms (Fig. 3) exhibit a strong cathodic peak superimposed to the redox waves of the $[Co^{III}TPyP(Ru^{III})_4]$ complex. This peak can be observed even in the presence of very small amounts of the complex, e.g. in concentrations around 1 µM, corresponding to the reduction of dioxygen catalyzed by the polymetallated porphyrin.

The catalytic waves are better seen by subtracting the voltammograms obtained under dioxygen and argon atmospheres in identical conditions, in order to exclude the electrochemical waves of the catalyst and of the $[Ru^{III}(EDTA)H_2O]^-$ complex in excess (Fig. 4). The value obtained by dividing the catalytic peak currents for the reduction of dioxygen by the calculated value for the reversible monoelectronic O_2/O_2^- couple, has been previously employed [5] to estimate the number of electrons involved in the process. In our case, the results were around 1.6 ± 0.2, using catalyst concentrations in the range of 1 to 500 µM, suggesting the formation of hydrogen peroxide as the immediate product of reduction of dioxygen. A detailed study using rotating ring disk electrodes is being carried out to elucidate this point.

It should be noticed that under the conditions of this work, the electrochemical reduction of dioxygen in the absence of the polymetallated porphyrin occurs below -0.4 V. The $[Ru^{III}(EDTA)(H_2O)]^-$ complex also exhibits some catalytic activity in the electrochemical reduction of dioxygen; however, its efficiency is rather small in comparison to that observed in the presence of the polymetallated porphyrin.

At high concentrations of the porphyrin, e.g. 1 mM, the catalytic peak is located near the redox

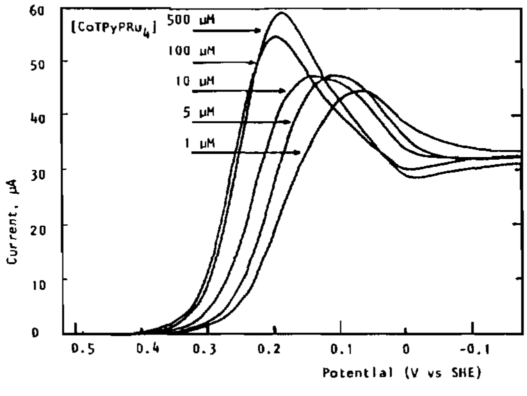

Fig. 4. Catalytic currents obtained by subtracting the cathodic waves in dioxygen and argon saturated solutions for the $[CoTPyP(Ru)_4]$ complex at several concentrations, scan rate = 20 mV s^{-1}, in the presence of 1.0 mM $[RuEDTA(H_2O)]^-$, 0.025 M acetate buffer, pH 5.0, and 0.25 M sodium trifluoracetate.

potential of the Co(III/II) couple. The reduction of dioxygen can be carried out by the cobalt(II) species with little participation of the peripheral Ru^{III}–EDTA groups. However, as the concentration of the catalyst decreases, for instance, from 1 mM to 1 μM, the catalytic peak moves in the direction of the redox potential of the peripheral Ru(III/II)–EDTA groups. The intensities of the catalytic currents remain practically the same, indicating that the decrease in the concentration of the catalyst is compensated by an increase in its efficiency promoted by the peripheral ruthenium(III/II) complexes.

Stopped-flow kinetic experiments were carried out for this system, starting from the reduced $[Co^{II}TPyP(Ru^{II})_4]$ complex (0.5 μM) and reacting with air or dioxygen saturated solutions in the presence of acetate buffer (0.05 M, pH 5), $[RuEDTA(H_2O)] = 1$ mM, [sodium trifluoroacetate] = 0.25 M, 298 K. In all the experiments the polymetallated cobalt porphyrin was completely oxidized. The kinetics monitored at the Soret and charge-transfer bands were too fast, proceeding within the mixing time of the stopped-flow equipment (2 ms). Therefore, we conclude that by means of rapid electron transfer reactions, the peripheral Ru^{II}–EDTA complexes regenerate the Co(II) ion in the active site, overcoming the slow electrode process which otherwise would limit the efficiency of the electrocatalytic process.

Acknowledgements

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