Co^{2+} Translocation in a Terpyridine–Cyclam Ditopic Receptor

Miguel E. Padilla-Tosta,[a] José M. Lloris,[a] Ramón Martínez-Máñez,*[a] Teresa Pardo,[a] Felix Sancenón,[a] Juan Soto,[a] and M. Dolores Marcos[b]

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The coordination behaviour of the ditopic receptor of 1-[*p*-(2,2′:6′,2′′-terpyrid-4′-yl)tolyl]-1,4,8,11-tetraazacyclotetradecane (L^1) towards Co^{2+} in acetonitrile/water (70:30, v/v) has been investigated. At acidic pH values, the L^1–H^+–Co^{2+} system shows an oxidation wave at 150 mV vs. SCE, characteristic of Co^{2+} in a bis(terpyridine) environment. Upon addition of OH^-, a reduction in the intensity of the wave at 150 mV is observed and a new oxidation wave appears at 1.30 V. This new wave is close to that found for $[Co(cyclam)]^{2+}$ under similar working conditions. The electrochemical data thus suggest that there is a pH-controlled translocation of the Co^{2+} ion from the bis(terpyridine) to the cyclam environment. A similar inference can be made from the results of UV/Vis studies. A thermodynamic characterization of the L^1–H^+–Co^{2+} system has also been carried out. Stability constants have been determined in acetonitrile/water (70:30, v/v, containing 0.1 mol dm^{-3} nBu_4NClO_4 at 25 °C) using potentiometric techniques. The following species were found: $[Co(L^1)_2H_4]^{6+}$, $[Co(L^1)_2H_3]^{5+}$, $[Co(L^1)H]^{3+}$, $[Co(L^1)]^{2+}$, and $[Co(L^1)(OH)]^{+}$. The 2:1 ligand-to-metal species $[Co(L^1)_2H_4]^{6+}$ and $[Co(L^1)_2H_3]^{5+}$ are assigned to complexes where Co^{2+} is coordinated by two terpyridine units. The $[Co(L^1)H]^{3+}$, $[Co(L^1)]^{2+}$, and $[Co(L^1)(OH)]^{+}$ species are assigned to complexes where the Co^{2+} cation is in the cyclam binding domain. The pH-induced Co^{2+} jumping between coordination sites is discussed in terms of the different basicities of cyclam and terpyridine. Co^{2+} jumping between coordination sites has also been studied by the sequential acidification of basic mixtures of L^1 and Co^{2+}. Under these conditions, the translocation was observed at a different pH value than when an acid-to-basic path was followed. The effect of anions such as phosphate and chloride on the translocation process has also been studied. In the presence of phosphate, translocation occurs at pH = 11 rather than at pH ≈ 8. The phosphate–L^1 and phosphate–L^1–Co^{2+} systems have been characterized by potentiometry and a remarkably good agreement has been found between the electrochemical and potentiometric data.

Introduction

The appropriate arrangement of suitably predisposed individual molecular elements has recently resulted in the development of systems such as sensors, switches, molecular devices, etc.[1] This has led to the exploration of interesting new effects arising from particular molecular organisations or specific assemblies of individual components with the aim of mimicking the more complex functions observed in biological systems.[2] Among known molecular functions is that of translocation.[3] It has been argued that the translocation process (positional changes of atoms in a molecule) resembles mechanical processes at the macroscopic level but is operative on the molecular scale.[4] Compounds used for such studies generally have in common the property of bi- or multistability. Thus, mechanical microscopically based translocation processes involve interconversion between two structurally different states in bi- or multistable systems. To construct such systems, several suitable components have to be coupled in a specific manner. The prerequisites of the final device are a molecule containing multiple binding sites (a polytopic ligand), a guest (organic or inorganic) capable of being bound by the binding domains, and a suitable switching mechanism to induce jumping of the guest between sites on the polytopic receptor. For instance, several examples have been reported where bound cations shift from one site to another in ditopic receptors as a result of redox triggering.[5] In these systems, the shift arises as a result of the dependence of the binding preference of the metal ion on its oxidation state. Besides redox triggering, ionically controlled translocation is also possible. We describe herein a translocation process found in the interaction of Co^{2+} with the ditopic ligand 1-[*p*-(2,2′:6′,2′′-terpyrid-4′-yl)tolyl]-1,4,8,11-tetraazacyclotetradecane (L^1) possessing 2,2′:6′,2′′-terpyridine and 1,4,8,11-tetraazacyclotetradecane (cyclam) coordination domains. We have found the metal ion jumping between these two coordination sites to be ionically governed by protons. This pH-induced jumping is discussed in terms of the basicities of the cyclam and terpyridine units and the values of the formation stability constants. The effect of certain anions on the translocation process has also been studied.

Results and Discussion

The design of artificial systems for studying translocation processes requires careful choice of each individual component. We have assembled two coordination sites (terpyri-

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[a] Departamento de Química, Universidad Politécnica de Valencia,
Camino de Vera s/n, 46071 Valencia, Spain
Fax: (internat.) + 34-96/387-7349
E-mail: rmaez@qim.upv.es
[b] Institut de Ciència dels Materials de la Universitat de València (ICMUV),
P. O. Box 2085, 46071 Valencia, Spain

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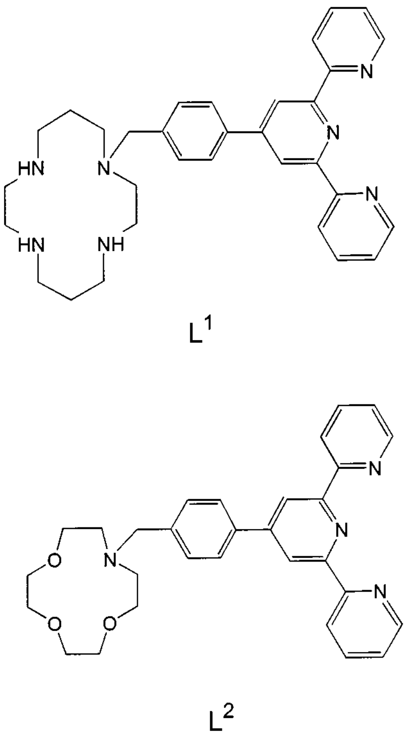


Scheme 1

dine and cyclam), both of which are capable of coordinating transition metal ions.[6] The use of an appropriate mediator (i.e. protons) makes it possible to control the relative affinity of each binding domain towards a certain metal cation. Terpyridine and cyclam components were chosen in view of the large difference in basicity between their nitrogen atoms. Besides this difference, the terpyridine-cyclam couple also has to meet an important thermodynamic requirement; the stability constants of each binding domain with a certain metal ion must be adequately complemented by the basicities of the binding atoms in order to observe, when the pH value is modulated, jumping between coordination sites (see below).

Terpyridine and cyclam were covalently linked by reaction of 4′-[4-(bromomethyl)phenyl]-2,2′:6′,2′′-terpyridine with an excess of 1,4,8,11-tetraazacyclooctadecane (cyclam) in dichloromethane in the presence of triethylamine as a base, to give the ditopic receptor L^1 (see Scheme 1). Details of the synthesis have been published elsewhere.[7] L^1 is insoluble in water and therefore the coordination studies were carried out in acetonitrile/water (70:30, v/v) mixtures. The use of other solvent mixtures such as dioxane/water or DMSO/water was also precluded by inadequate solubility.

Once the ditopic ligand had been synthesized, the next step was the choice of a suitable metal ion. Co^{2+} was selected in view of the fact that its coordination environment, in both the cyclam and terpyridine moieties, can easily be monitored by electrochemical techniques. Co^{2+} in a bis(terpyridine) coordination environment displays a very characteristic oxidation process at ca. 200 mV vs. SCE, whereas when coordinated by cyclam the oxidation to Co^{3+} becomes much more difficult.

Acidified solutions of Co^{2+} and L^1 (molar ratio L^1/Co^{2+} = 2:1) show a reversible oxidation wave at 150 mV with a ratio between the cathodic and anodic peak intensities, i_{pc}/i_{pa}, of ca. 1. This value is very close to the oxidation potential found for the complex $[Co(MePhtpy)_2]^{2+}$ [MePhtpy = 4′-(4-methylphenyl)-2,2′:6′,2′′-terpyridine] under similar working conditions. However, whereas the oxidation wave of the $[Co(MePhtpy)_2]^{2+}$ complex does not change as a function of the pH value, the addition of OH^- to the $Co^{2+}-L^1$ system leads to a decrease in the intensity of the wave at 150 mV and the appearance of an oxidation process at higher anodic potential (1.35 V). The new wave is similar to that found for the $[Co(cyclam)]^{2+}$ complex in acetonitrile/water. Figure 1 shows the electrochemical behaviour of the $Co^{2+}-L^1$ system at certain pH values. The data suggest that a translocation occurs,[8] which is schematically represented in Scheme 2. Figure 2 shows a plot of the intensity of the oxidation wave of the Co^{2+}−bis(terpyridine) core as a function of the pH value for the L^1-Co^{2+} system.

The large difference in intensity between the 150 mV and 1.35 V waves merits comment. This is not an unexpected behaviour and can be attributed to the low diffusion coefficient of the bis(terpyridine) complex and to adsorption processes observed for the oxidation of the cyclam−Co^{2+} species. Moreover, the oxidation wave at 1.35 V is cathodically shifted when the pH value is very basic, probably due to the formation of hydroxo complexes.

The jumping of Co^{2+} between the terpyridine and cyclam environments can also be observed by UV/Vis spectrophotometry. The visible spectrum of $Co^{2+}-L^1$ is pH-dependent. At acidic pH values, a poorly defined band with a maximum centred at 515 nm is found. When the solution is basified, a dramatic decrease in its intensity is observed. The spectra of the $Co^{2+}-L^1$ system under acidic and basic conditions closely resemble those found for the complexes $[Co(MePhtpy)_2]^{2+}$ and $[Co(cyclam)]^{2+}$, respectively.

The electrochemical and UV/Vis experiments thus suggest that there is a proton-induced jumping of the cobalt cation between the two different sites on the ditopic receptor L^1. In addition, we have completed the study with a thermodynamic characterization of the system. The thermodynamic behaviour of polyamines such as cyclam can be adequately studied by potentiometry. However, this technique is not generally suitable for solution studies on polypyridines. Potentiometry, as a technique for deducing stability constants in polyamines, is based on the competition between the metal ion and protons to bind to the N donor atoms. The nitrogen atoms in polyamines are sufficiently basic to react with protons even in the presence of metal ions to give the protonated free receptors. Thus, a requirement for the deduction of stability constants by means of potentiometry is that both the free receptor and the complex must be observable in the pH range studied (usually 2−10). This is generally the case with polyamines, but not with terpyridines due to their lower basicities. However, although simple titrations of terpyridine in the presence of a metal ion would not lead to accurate determinations of

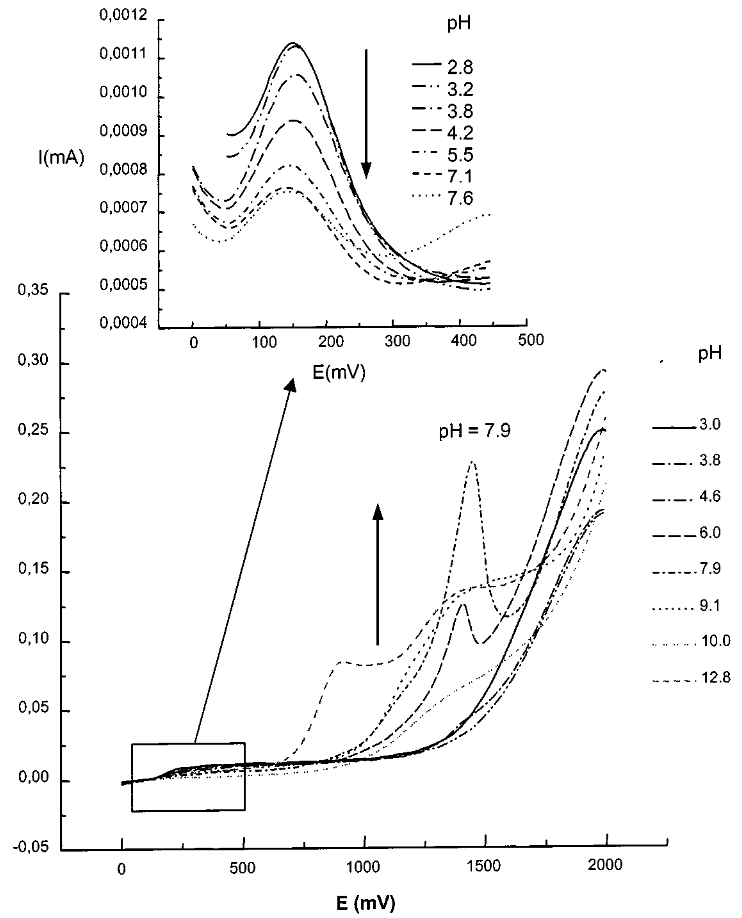
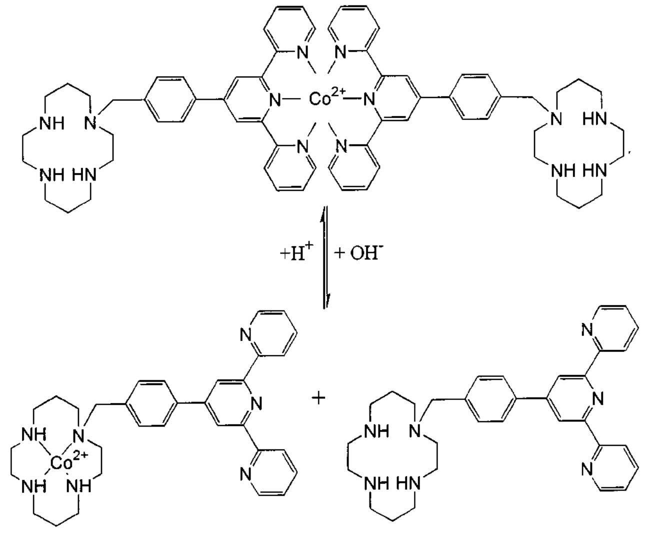


Figure 1. Electrochemical behaviour of the L^1-Co^{2+} system at various pH values using rde and differential pulse voltammetry



Scheme 2

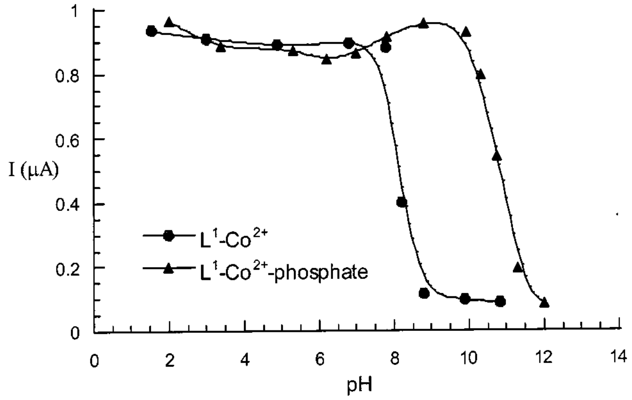


Figure 2. Intensity of the oxidation potential of the Co^{2+}−bis(terpyridine) core at 150 mV vs. SCE as a function of the pH value and in the presence of phosphate for the L^1-Co^{2+} system

the stability constants, more complex experiments can be designed for the thermodynamic characterization of terpyridine−metal mixtures. Thus, a terpyridine−metal solution might be treated with a ligand (appropriate for potentiometric study) that strongly competes with terpyridine in binding the metal cation. At this point, it is important to state that receptor L^1 does indeed meet the requirement outlined above; terpyridine is covalently coupled to a polyamine that, as suggested by the electrochemical experiments, strongly reduces the affinity of the Co^{2+} for the coordination environment of the former. Therefore, one should be able to carry out standard potentiometric experiments to thermodynamically characterize the $L^1-H^+-Co^{2+}$ system.

The first step involved the determination of the protonation constants of L^1 by titrating previously acidified solutions of the ligand in acetonitrile/water (70:30, v/v, 0.1 mol dm^{-3} tetrabutylammonium perchlorate) with KOH.

Although L^1 has seven possible protonation sites, only five constants could be measured, indicating that two protonation processes are too acidic to be determined (see Table 1).

Table 1. Protonation constants (log*K*) of L^1, mftpy, and cyclam [mftpy = 4′-(4-methylphenyl)-2,2′:6′,2′′-terpyridine; cyclam = 1,4,8,11-tetraazacyclooctadecane] in acetonitrile/water (70:30, v/v) containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate at 25 °C

Reaction	L^1 log*K*	mftpy log*K*	cyclam log*K*
$L + H^+ \rightleftarrows (HL)^+$ [a]	9.75(4)[b]	4.35(2)	11.62(2)
$L + 2\,H^+ \rightleftarrows (H_2L)^{2+}$	15.40(4)	6.80(2)	21.85(3)
$L + 3\,H^+ \rightleftarrows (H_3L)^{3+}$	19.71(3)	8.05(1)	23.22(2)
$L + 4\,H^+ \rightleftarrows (H_4L)^{4+}$	23.33(4)		
$L + 5\,H^+ \rightleftarrows (H_5L)^{5+}$	26.21(5)		
$(HL)^+ + H^+ \rightleftarrows (H_2L)^{2+}$	5.65	2.45	10.23
$(H_2L)^{2+} + H^+ \rightleftarrows (H_3L)^{3+}$	4.31	1.25	1.37
$(H_3L)^{3+} + H^+ \rightleftarrows (H_4L)^{4+}$	3.62		
$(H_4L)^{4+} + H^+ \rightleftarrows (H_5L)^{5+}$	2.88		

[a] Charges have been omitted for the sake of clarity. − [b] Values in parentheses are standard deviations in the last significant figure.

In order to compare the protonation behaviour of the ditopic receptor with those of the individual components, the stepwise protonation constants of the cyclam as well as those of 4′-[(4-methyl)phenyl]-2,2′:6′,2′′-terpyridine were also determined in acetonitrile/water (70:30, v/v) mixtures (see Table 1). Three and two protonation processes were observed for the cyclam and terpyridine units, respectively. The protonation constants obtained in acetonitrile/water (70:30, v/v) solutions are in good agreement with the analogous constants reported in water.[9] Cyclam displays two very basic protonation processes in water with log*K* values for the processes cyclam + $H^+ \rightleftarrows$ Hcyclam$^+$ and Hcyclam$^+$ + $H^+ \rightleftarrows H_2$cyclam^{2+} of 11.5 and 10.5, respectively. In contrast, the third and fourth protonation processes are much less basic with log*K* values of 1.5 and 0.9. Terpyridine shows less basic character in water. Only two protonation constants could be determined, with log*K* values for the processes H^+ + tpy $\rightleftarrows$ Htpy$^+$ and Htpy$^+$ + $H^+ \rightleftarrows H_2$tpy^{2+} of 4.65 and 3.5. It can be concluded that the difference in basicity found between the terpyridine and the cyclam in water is retained in acetonitrile/water and probably also in the ditopic ligand L^1. Comparison of the basicity constants of L^1 with those of the individual components (see Table 1) suggests that the first two protonation processes occur at the cyclam core, the third and fourth protonations at the terpyridine, whereas the final protonation process relates to the attack of a proton at the cyclic polyamine.

Potentiometric studies aimed at determining the nature of the L^1-Co^{2+} complexes in solution have also been carried out in acetonitrile/water (70:30, v/v) by titrating previously acidified solutions containing the ligand and the metal ion in a 2:1 molar ratio with KOH. The potentiometric data were fitted with a model where the following complexes were found: $[Co(L^1)_2H_4]^{6+}$, $[Co(L^1)_2H_3]^{5+}$, $[Co(L^1)H]^{3+}$, $[Co(L^1)]^{2+}$, and $[Co(L^1)(OH)]^+$. Table 2 shows the formation stability constants for these complexes.

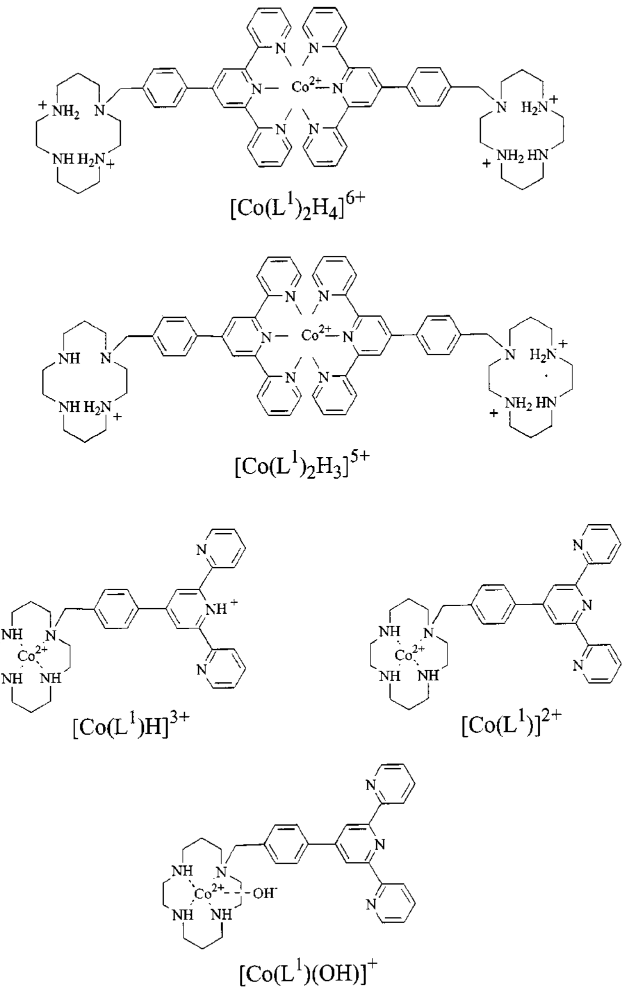
Table 2. Stability constants (log*K*) for the formation of Co^{2+} complexes of L^1 in acetonitrile/water (70:30, v/v) containing 0.1 mol dm^{-3} nBu$_4$NClO$_4$ at 25 °C

Reaction	log*K*
$Co^{2+} + 2\,L^1 + 4\,H^+ \rightleftarrows [Co(L^1)_2H_4]^{6+}$	47.20(5)[a]
$Co^{2+} + 2\,L^1 + 3\,H^+ \rightleftarrows [Co(L^1)_2H_3]^{5+}$	42.81(4)
$Co^{2+} + L^1 + H^+ \rightleftarrows [Co(L^1)H]^{3+}$	18.82(4)
$Co^{2+} + L^1 \rightleftarrows [Co(L^1)]^{2+}$	12.76(3)
$Co^{2+} + L^1 + H_2O \rightleftarrows [Co(L^1)(OH)]^+ + H^+$	0.83(5)

[a] Values in parentheses are standard deviations in the last significant figure.

The 2:1 ligand-to-metal species $[Co(L^1)_2H_4]^{6+}$ and $[Co(L^1)_2H_3]^{5+}$ are attributed to complexes where the cobalt(II) is coordinated by two terpyridine units. The additional presence of protons in these complexes indicates that the peripheral cyclam groups are protonated.

The 1:1 ligand-to-metal complexes $[Co(L^1)H]^{3+}$, $[Co(L^1)]^{2+}$, and $[Co(L^1)(OH)]^+$ are attributed to species where the cobalt ion is coordinated by the cyclam binding unit. Scheme 3 shows the assignments of the various com-



Scheme 3

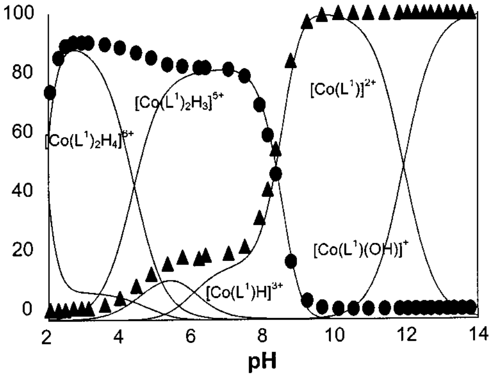


Figure 3. Distribution diagram of the various species derived from the $L^1-H^+-Co^{2+}$ system and a plot of the overall percentages of the Co^{2+}−cyclam (s) and Co^{2+}−bis(terpyridine) complexes (•) as a function of the pH value

plexes existing in solution. Figure 3 shows the distribution diagram for the $L^1-H^+-Co^{2+}$ system. The Co^{2+}−cyclam complexes have formation stability constants very similar to those reported for the Co^{2+}−cyclam$-H^+$ system. For instance, the stability constant for the formation of the complex $[Co(cyclam)]^{2+}$ is $\log K = 12.71$,[9] which is very close to the value found for the process $Co^{2+} + L^1 \rightleftarrows [Co(L^1)]^{2+}$, i.e. $\log K = 12.76$. This indicates that the presence of a bulky terpyridylphenyl group attached to the cyclam core and the use of acetonitrile/water solutions instead of pure water does not significantly modify the coordination behaviour of the cyclic tetraamine. The $\log K$ value for the formation of the bis(terpyridine)−cobalt(II) complex, $Co^{2+} + 2\,tpy \rightleftarrows [Co(tpy)_2]^{2+}$, is 18.6.[9] The analogous stability constant for $Co^{2+} + 2\,L^1 \rightleftarrows [Co(L^1)_2]^{2+}$ cannot be obtained from the potentiometric titrations of the $Co^{2+}-H^+-L^1$ system. However, it can be approximately deduced from the stability constant for the process $Co^{2+} + 2\,L^1 + 4\,H^+ \rightleftarrows [Co(L^1)_2H_4]^{6+}$, assuming that the process $[Co(L^1)_2]^{2+} + 4\,H^+ \rightleftarrows [Co(L^1)_2H_4]^{4+}$ would have an approximate value of 30.80 [$\log K = 30.80$ is calculated as twice $\log K = 15.40$ corresponding to the $L^1 + 2\,H^+ = (H_2L^1)^{2+}$ process]. This gives a stability constant for the process $Co^{2+} + 2\,L^1 \rightleftarrows [Co(L^1)_2]^{2+}$ of ca. 16.40, which suggests that $\log K$ for the formation of the Co^{2+}−bis(terpyridine) complex of L^1 in acetonitrile/water is of the same order of magnitude as that reported for the formation of the $[Co(tpy)_2]^{2+}$ complex.

Figure 3 also shows a plot of the overall percentages of the Co^{2+}−cyclam and Co^{2+}−bis(terpyridine) species as a function of the pH value. A pH-dependent coordination pattern can be seen, with cyclam complexes as the main species at basic pH values and bis(terpyridine) complexes being present at a level of 80% or more at pH < ca. 8. Remarkably, the translocation process represented in Figure 3 is in good agreement with the electrochemical data presented in Figure 2.

To fully understand how translocation operates one should be aware of the relationship between stability constants and ion jumping. The easiest system one can picture is a receptor containing two coordination sites (A and B), both of which can either be protonated or form a complex with a certain metal ion M. Let us assume that the stability constant for the $A + M \rightleftarrows AM$ process is larger than that for $B + M \rightleftarrows BM$. Under these circumstances, only when the protonation constant for $A + H \rightleftarrows AH$ is larger than that for $B + H \rightleftarrows BH$ can a complete pH-controlled translocation be observed. Therefore, to observe ionically governed pH-induced jumping of the metal ion between coordination sites, a requirement that has to be fulfilled is a difference in basicity and binding strength towards the metal ion in favour to the more basic binding sites. The translocation process then works as follows: When the proton concentration is low (basic pH values), the metal ion is coordinated by the more basic centre (stronger complex); when the proton concentration is increased, the more basic centre becomes protonated, inducing the jumping of the metal ion to the less basic binding domain. The $Co-L^1-H^+$ system is similar to that described above, the only difference being the presence of 2:1 ligand-to-metal complexes. To observe translocation in this case, the formation stability constant for complexation of the metal ion at the less basic centre (terpyridine) has to be less than twice that for complexation at the more basic coordination environment (cyclam). Bearing in mind that this requirement is fulfilled in the $Co^{2+}-L^1$ system, one would expect pH-induced jumping between coordination sites, as is indeed observed {$Co^{2+} + L^1 \rightleftarrows [Co(L^1)]^{2+}$; $\log K = 12.71$ for Co^{2+} in the cyclam environment, and $Co^{2+} + 2\,L^1 \rightleftarrows [Co(L^1)_2]^{2+}$; $\log K \approx 16.4$ for Co^{2+} in the bis(terpyridine) environment}. At basic pH values, Co^{2+} jumping occurs from the bis(terpyridine) environment to the more basic cyclam binding domain. This process can be represented by the chemical reaction $[Co(L^1)_2H_3]^{5+} \rightleftarrows [Co(L^1)]^{2+} + L^1 + 3\,H^+$; $\log K = -30.05$. As can be seen, the $[Co(L^1)]^{2+}/[Co(L^1)_2H_3]^{2+}$ ratio is controlled by the proton concentration. The more basic the solution, the greater the proportion of Co^{2+} in the cyclam.

We also synthesized the receptor L^2 by reaction of 4′-[(4-bromomethyl)phenyl]-2,2′:6′,2′′-terpyridine and 4,7,10-trioxa-1-azacyclododecane. L^2 is similar to L^1 in the sense that it also contains two coordination sites of different basicities. Although we have not carried out potentiometric studies on L^2 in acetonitrile/water, we have found in the literature that cobalt forms 1:1 complexes with the ligand 1,7-dioxa-4,10-diazacyclododecane (L^3) with a stability constant for the process $Co^{2+} + L^3 \rightleftarrows [Co(L^3)]^{2+}$ of $\log K = 6.01$.[10] A similar order of magnitude is presumed for the process $Co^{2+} + L^2 \rightleftarrows [Co(L^2)]^{2+}$. Therefore, as the value of the stability constant of the bis(terpyridine) complex ($\log K \approx 16$) is greater than twice the formation stability constant of Co^{2+} with the oxa-aza ligand, for the $Co^{2+}-L^2-H^+$ system one would expect the bis(terpyridine) species to be predominant over the entire pH range. Indeed, the electrochemical data reveal a unique oxidation process at ca. 150 mV attributable to the presence of Co^{2+} in a bis(terpyridine) coordination environment and the intensity of the electrochemical wave does not change over the pH range studied. There is no evidence for any translocation process. This highlights the importance of a careful choice of each element in the design of systems displaying pH-modulated translocations.

Ionically controlled metal ion jumping has been demonstrated for the interaction a terpyridine−cyclam ditopic receptor with Co^{2+}. In addition, we have studied some factors that might have an effect on the translocation.

The first effect concerns the fact that demetallation from cyclam is slower than the process of metal incorporation into the macrocycle. This is a well-known effect and is generally operative in cyclic polyamines. The influence of this effect on the Co^{2+} jumping between coordination sites has been studied by monitoring the electrochemical behaviour of basic mixtures of L^1 and Co^{2+} upon their stepwise acidification. Under these conditions, the Co^{2+} ion remains in the cyclam core until pH ≈ 6. Further acidification induces translocation to give bis(terpyridine) species. At neutral pH value, the most stable complex is that involving the bis(terpyridine) and Co^{2+}−cyclam species are transformed to this thermodynamically favoured arrangement. However, this process is very slow; at pH = 7, only after two weeks was a partial translocation of the Co^{2+} from the cyclam to the bis(terpyridine) observed.

The operation of this kinetic process gives a hysteresis loop. Hysteresis phenomena in the solid state are well documented.[11] In contrast, studies of hysteresis loops in solution are, to the best of our knowledge, scarce.[12] This hysteresis phenomenon arises as a consequence of the existence of a bistable system coupled with a large kinetic activation barrier. Although the system is far from comparable with other well-known systems and is far too simple to be of any application, it complies with the very basic requirements for information storage: the existence of two metastable states (Co^{2+} in cyclam and Co^{2+} in terpyridine) for a given environmental condition (neutral solutions) that can be readily interconverted by the variation of an external parameter (pH).

A different approach that might affect the pH value at which translocation occurs involves the addition of anions. If the relative affinities of a certain anionic guest towards Co^{2+}−cyclam and Co^{2+}−terpyridine complexes are different, then a modulation of the translocation might be achieved. To examine this attractive possibility, we studied the Co^{2+} jumping between coordination sites in the presence of phosphate and chloride anions. A plot of the intensity of the Co^{2+}/Co^{3+} oxidation wave in the bis(terpyridine) environment as a function of the pH value in the presence of phosphate is shown in Figure 2. Translocation from the terpyridine to the cyclam environment in the presence of phosphate occurs at pH ≈ 11, quite different from the pH value (8) at which ion jumping is observed in the absence of this anion. In contrast, chloride does not affect the pH value of translocation. It is noteworthy that although some molecular systems have been described where a translocation effect is induced by redox triggering or by the pH value, there have been very few examples reported in the literature where ion jumping is modulated by the presence of anions.[13]

Table 3. Stability constants (log*K*) for the formation of phosphate complexes of L^1 in acetonitrile/water (70:30, v/v) containing 0.1 mol dm^{-3} $n\mathrm{Bu_4NClO_4}$ at 25 °C

Reaction	log*K*
$L^1 + PO_4^{3-} + 2\,H^+ \rightleftarrows [L^1H_2PO_4]^-$	26.37(4)[a]
$L^1 + PO_4^{3-} + 3\,H^+ \rightleftarrows [L^1H_3PO_4]$	35.63(3)
$L^1 + PO_4^{3-} + 4\,H^+ \rightleftarrows [L^1H_4PO_4]^+$	43.21(3)
$L^1 + PO_4^{3-} + 5\,H^+ \rightleftarrows [L^1H_5PO_4]^{2+}$	47.25(3)

[a] Values in parentheses are standard deviations in the last significant figure.

We also carried out potentiometric studies to thermodynamically characterize the L^1−phosphate−H^+ and L^1−Co^{2+}−phosphate−H^+ systems. Table 3 shows the stability constants for the formation of the phosphate complexes of L^1 in acetonitrile/water (70:30, v/v). Potentiometric techniques give information about the stoichiometries of the formed complexes, but do not give direct information concerning the nature of the species. Therefore, it is not straightforward to deduce whether the protons in the complexes are bonded to the phosphate or to L^1. Nevertheless, bearing in mind the pH ranges of existence of the various phosphate species and the pH ranges of existence of the protonated $(H_jL^1)^{j+}$ species, we can tentatively assign the complex $[(L^1)H_2(PO_4)]^-$ to the interaction of $(L^1H)^+$ with HPO_4^{2-}, and the complexes $[(L^1)H_3(PO_4)]$, $[(L^1)H_4(PO_4)]^+$, and $[(L^1)H_5(PO_4)]^{2+}$ to the interaction of the anion $H_2PO_4^-$ with $(L^1H)^+$, $(L^1H_2)^{2+}$, and $(L^1H_3)^{3+}$, respectively.

Table 4 shows the stability constants for the formation of the complexes of the L^1−Co^{2+}−phosphate−H^+ system. The following complexes were found: $[Co(L^1)_2H_5(PO_4)]^{4+}$, $[Co(L^1)_2H_4(PO_4)]^{3+}$, $[Co(L^1)_2H_3(PO_4)]^{2+}$, $[Co(L^1)_2H_2(PO_4)]^+$, and $[Co(L^1)(OH)(PO_4)]^{2-}$. Taking into account the pH ranges of existence of the PO_4^{3-}, HPO_4^{2-}, and $H_2PO_4^-$ species and the distribution diagram of the L^1−Co^{2+}−phosphate−H^+ system in Figure 4, we tentat-

Table 4. Stability constants (log*K*) for the formation of complexes of L^1 with Co^{2+} and phosphate in acetonitrile/water (70:30, v/v) containing 0.1 mol dm^{-3} $n\mathrm{Bu_4NClO_4}$ at 25 °C

Reaction	log*K*
$2\,L^1 + Co^{2+} + PO_4^{3-} + 5\,H^+ \rightleftarrows [Co(L^1)_2H_5(PO_4)]^{4+}$	68.12(5)[a]
$2\,L^1 + Co^{2+} + PO_4^{3-} + 4\,H^+ \rightleftarrows [Co(L^1)_2H_4(PO_4)]^{3+}$	62.22(4)
$2\,L^1 + Co^{2+} + PO_4^{3-} + 3\,H^+ \rightleftarrows [Co(L^1)_2H_3(PO_4)]^{2+}$	54.65(4)
$2\,L^1 + Co^{2+} + PO_4^{3-} + 2\,H^+ \rightleftarrows [Co(L^1)_2H_2(PO_4)]^+$	46.00(4)
$L^1 + Co^{2+} + PO_4^{3-} + H_2O \rightleftarrows [Co(L^1)(OH)(PO_4)]^{2-} + H^+$	9.30(4)

[a] Values in parentheses are standard deviations in the last significant figure.

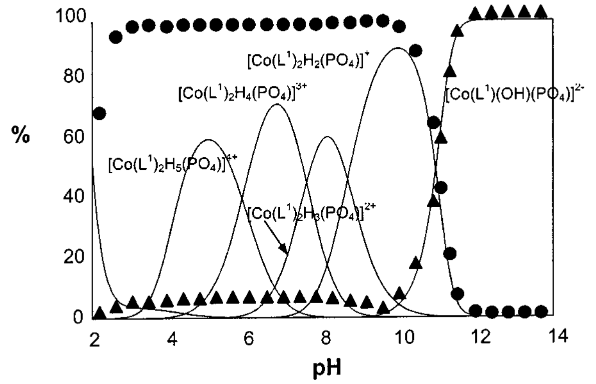


Figure 4. Distribution diagram of the various species derived from the $L^1-H^+-Co^{2+}$−phosphate system and a plot of the overall percentages of the Co^{2+}−cyclam (▲) and Co^{2+}−bis(terpyridine) complexes (●) as a function of the pH value

ively assign the complex $[Co(L^1)_2H_2(PO_4)]^+$ to the interaction of $HPO_4{}^{2-}$ with $[Co(L^1)_2H]^{3+}$, and the complexes $[Co(L^1)_2H_5(PO_4)]^{4+}$, $[Co(L^1)_2H_4(PO_4)]^{3+}$, and $[Co(L^1)_2H_3(PO_4)]^{2+}$ to the interactions of $H_2PO_4{}^-$ with $[Co(L^1)_2H_3]^{5+}$, $[Co(L^1)_2H_2]^{4+}$, and $[Co(L^1)_2H]^{3+}$, respectively. On this basis, the stability constant for the process $[Co(L^1)_2H_3]^{5+} + H_2PO_4{}^- \rightleftarrows [Co(L^1)_2H_5(PO_4)]^{4+}$ is, for instance, $\log K = 3.79$.

The 2:1 ligand-to-metal species $[Co(L^1)_2H_5(PO_4)]^{4+}$, $[Co(L^1)_2H_4(PO_4)]^{3+}$, $[Co(L^1)_2H_3(PO_4)]^{2+}$, and $[Co(L^1)_2H_2(PO_4)]^+$ are attributed to complexes where the cobalt(II) is in a bis(terpyridine) environment, whereas in the complex $[Co(L^1)(OH)(PO_4)]^{2-}$ the Co^{2+} cation is coordinated by the cyclam domain. Figure 4 also shows a plot of the overall percentages of the Co^{2+}−cyclam and Co^{2+}−terpyridine species as a function of the pH value. There is a remarkable agreement between this plot and the electrochemical data presented in Figure 2. The modulation induced in the translocation process by the presence of phosphate suggests that this anion has a greater affinity for Co^{2+}−terpyridine than for Co^{2+}−cyclam complexes. The net result is that translocation occurs at higher pH values than in the absence of phosphate.

Conclusions

In conclusion, we have studied the ionically induced translocation of Co^{2+} in the ditopic receptor L^1, which contains two binding sites, cyclam and terpyridine, of different basicities. The solution mixture L^1-Co^{2+} has been thermodynamically characterized using potentiometric techniques. The pH value at which the translocation takes place can be modified by following a basic-to-acidic path or by the addition of suitable anions. In the latter case, the different affinities of the phosphate anion for the species existing in solution produces a remarkable shift in the pH value at which ion jumping is observed.

Experimental Section

The ditopic ligand L^1 was prepared according to a published method;[7] L^2 was synthesized according to ref.[14]; all other reagents were commercially available and were used as received. − Potentiometric titrations were carried out in acetonitrile/water (70:30, v/v, 0.1 mol dm^{-3} tetrabutylammonium perchlorate) under nitrogen in a water-thermostatted (25.0 ± 0.1 °C) reaction vessel. The titrant was added by means of a Crison 2031 microburette. The potentiometric measurements were made using a Crison 2002 pH meter and a combined glass electrode. The titration system was automatically controlled by a PC using a program that monitors the e.m.f. values and the volume of titrant added. The electrode was calibrated as a hydrogen ion concentration probe by titration of precise amounts of HCl with CO_2-free KOH solution and determining the equivalent point by Gran's method,[15] which gives the standard potential E'° and the ionic product of water ($K'_w = [H^+][OH^-]$). The concentrations of the metal ion solutions were determined using standard methods. The computer program SUPERQUAD[16] was used to calculate the protonation and stability constants. The titration curves for each system (ca. 250 experimental points corresponding to at least three titration curves; pH = $-\log[H^+]$ range investigated 2−10; concentration of the ligand and metal ion ca. $1.2 \cdot 10^{-3}$ mol dm^{-3}) could be treated either as a single set or as separate entities without significant variations in the values of the stability constants. Finally, the data set was merged and treated as one to give the stability constants. Electrochemical experiments were carried out in acetonitrile/water (70:30, v/v, 0.1 mol dm^{-3} tetrabutylammonium perchlorate) using a Tacussel IMT-1 programmable function generator connected to a Tacussel PJT 120-1 potentiostat. The working electrode was platinum with a saturated calomel reference electrode separated from the solution under study by a salt bridge containing the solvent/supporting electrolyte. The auxiliary electrode was a platinum wire.

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[1] See, for example: P. L. Boulas, M. Gómez-Kaifer, L. Echegoyen, *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 216−247. − J.-M. Lehn, *Supramoleular Chemistry*, VCH, Weinheim, **1995**. − M. D. Ward, *Chem. Ind.* **1997**, 640−645. − I. Rubinstein, S. Steinberg, Y. Tor, A. Shanzer, J. Sagir, *Nature* **1988**, *332*, 426−429. − R. A. Bissell, A. Prasanna de Silva, H. Q. N. Gunaratne, P. L. M. Lynch, G. E. M. Maguire, K. R. A. S. Sandanayake, *Chem. Soc. Rev.* **1992**, *21*, 187−195. − P. R. Ashton, R. Ballardini, V. Balzani, I. Baxter, A. Credi, M. C. T. Fyfe, M. T. Gandolfi, M. Gómez-López, M. V. Martínez-Díaz, A. Piersanti, N. Spencer, J. F. Stoddart, M. Venturi, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **1998**, *120*, 11932−11942. − S. Creager, C. J. Yu, C. Bamdad, S. O'Connor, T. MacLean, E. Lam, Y. Chong, G. T. Olsen, J. Luo, M. Gozin, J. F. Kayyem, *J. Am. Chem. Soc.* **1999**, *121*, 1059−1064.

[2] A. E. Doering, D. A. Nicoll, Y. Lu, L. Lu, J. N. Weiss, *J. Biol. Chem.* **1998**, *273*, 778−783. − D. Tortorella, D. Sesardic, C. S. Dawes, E. London, *J. Biol. Chem.* **1995**, *270*, 27446−27452.

[3] G. De Santis, L. Fabbrizzi, D. Iacopino, P. Pallavicini, A. Perotti, A. Poggi, *Inorg. Chem.* **1997**, *36*, 827−832. − P. Isenring, B. Forbush, *J. Biol. Chem.* **1997**, *272*, 24556−24562. − M. Verkhovskaya, M. Verkhovsky, M. Wikstrom, *J. Biol. Chem.* **1992**, *267*, 14559−14562. − V. Amendola, L. Fabbrizzi, C. Mangano, P. Pallavicini, A. Perotti, A. Taglietti, *J. Chem. Soc., Dalton Trans.* **2000**, 185−189.

[4] R. Ballardini, V. Balzani, M. T. Gandolfi, L. Prodi, M. Venturi, D. Philip, H. S. Ricketts, J. F. Stoddart, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1301−1303.

[5] L. Zelikovichi, J. Libman, A. Zhanzer, *Nature* **1995**, *374*, 790–792. – A. Livoreil, C. O. Dietrich-Buchecker, J. P. Sauvage, *J. Am. Chem. Soc.* **1994**, *116*, 9399–9400. – C. Canevet, J. Libman, A. Shanzer, *Angew. Chem. Int. Ed. Engl.* **1996**, *36*, 2657–2660. – C. Belle, J.-L. Pierre, E. Saint-Amar, *New J. Chem.* **1998**, 1399–1402.

[6] J. P. Sauvage, J. P. Collin, J. P. Charnbron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola, L. Flamigni, *Chem. Rev.* **1994**, *94*, 993–1019. – G. W. Gokel (Ed.), in: *Advances in Supramolecular Chemistry*, JAI Press Inc., Greenwich, Connecticut, USA, **1993**. – L. F. Lindoy (Ed.), in: *The Chemistry of Macrocyclic Ligand Complexes*, University Press, Cambridge, U.K., **1989**.

[7] M. E. Padilla-Tosta, J. M. Lloris, R. Martínez-Máñez, A. Benito, J. Soto, T. Pardo, M. A. Miranda, M. D. Marcos, *Eur. J. Inorg. Chem.* **2000**, 741–748. – M. E. Padilla-Tosta, J. M. Lloris, R. Martínez-Máñez, T. Pardo, J. Soto, A. Benito, M. D. Marcos, *Inorg. Chem. Commun.* **2000**, *2*, 45–48.

[8] Due to the ditopic nature of the receptor L^1, the process of Co^{II} displacement is more probably intramolecular (translocation is the term used in this case) although it has to be pointed out that an intermolecular rearrangement cannot be completely ruled out.

[9] R. M. Smith, A. E. Martell (Eds.), *Critical Stability Constants*, Plenum, New York, **1974–1989**; A. E. Martell, R. M. Smith, R. M. Motekaitis, NIST Critical Stability Constants of Metal Complexes Database, Texas A & M University, College Station, **1993**.

[10] E. Luboch, A. Cygan, J. Biernat, *Inorg. Chim. Acta* **1983**, *68*, 201–204. – F. Arnaud-Neu, M. Sanchez, R. Yahya, M. J. Schwing-Weill, *Helv. Chim. Acta* **1985**, *68*, 456–464.

[11] J. F. Létard, P. Guionneau, L. Rabardel, J. A. K. Howard, A. E. Goeta, D. Chasseau, O. Kahn, *Inorg. Chem.* **1998**, *37*, 4432–4441. – J. Kröber, E. Codjovi, O. Kahn, F. Grolière, C. Jay, *J. Am. Chem. Soc.* **1993**, *115*, 9810–9811. – H. Bolvin, O. Kahn, B. Vekhter, *New J. Chem.* **1991**, *15*, 889–895.

[12] M. Sano, H. Taube, *Inorg. Chem.* **1994**, *33*, 705–709. – U. Kölle, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 956–958.

[13] M. Montalti, L. Prodi, *Chem. Commun.* **1998**, 1461–1462.

[14] M. E. Padilla-Tosta, J. M. Lloris, R. Martínez-Máñez, M. A. Miranda, J. Soto, M. D. Marcos, *Eur. J. Inorg. Chem.*, submitted.

[15] G. Gran, *Analyst (London)* **1952**, *77*, 661. – F. J. Rossotti, H. J. Rossotti, *J. Chem. Educ.* **1965**, *42*, 375.

[16] P. Gans, A. Sabatini, A. Vacca, *J. Chem. Soc., Dalton Trans.* **1985**, 1195–1200.

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