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Photochemical- and pH-switching Properties of a New Photoelastic Ligand Based Upon Azobenzene. Basicity and Anion Binding

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The synthesis of a new cylindrical macrotricyclic ligand (L) based upon two 1,4,7,13-tetramethyl-1,4,7,10,13,16-hexaazacyclooctadecane rings connected *via* two azobenzene pillars is described. The ligands displays photoelastic properties: light absorption at 366 nm produces *trans* → *cis* isomerization of the azobenzene moieties with formation of *trans-cis* ($L_{E\text{-}Z}$) and *cis-cis* ($L_{Z\text{-}Z}$) isomers. Recovery of the thermodynamically more stable *trans-trans* ($L_{E\text{-}E}$) isomer can be obtained by thermal back-isomerization or visible light (430 nm) absorption. The isomeric composition of L solution depends upon pH: for $pH < 5.5$ the $L_{E\text{-}E}$ form is the unique species in solution, while increasing amounts of Z species are formed at increasing pH. The protonation constants of $L_{E\text{-}E}$ have been determined in $0.1\,mol\,dm^{-3}$ Me_4NNO_3 solution at $298.1 \pm 0.1\,K$. The protonated species of L form stable inclusion complexes with anionic species such as $[Co(CN)_6]^{3-}$.

Keywords: Photoelastic ligands; Chemical switches; Macrocycles; Anion coordination

INTRODUCTION

Azobenzene has been used, as structural component of many macrocyclic molecules, to obtain photo-responsive ligands capable of changing their shape upon light absorption, since in solution it gives rise to a photostationary state in which, depending on the irradiation wavelength, different amounts of the *trans* (*E*) and *cis* (*Z*) isomers coexist [1–13]. In the solid state, ligands containing azobenzene units in the Z (*cis*) conformation are relatively stable, while in solution they isomerize faster and faster with increasing temperature and decreasing solvent polarity to form the thermodynamically more stable *E* (*trans*) isomers. The *E* and *Z* isomers display quite different ligational properties, being characterised by different dispositions of

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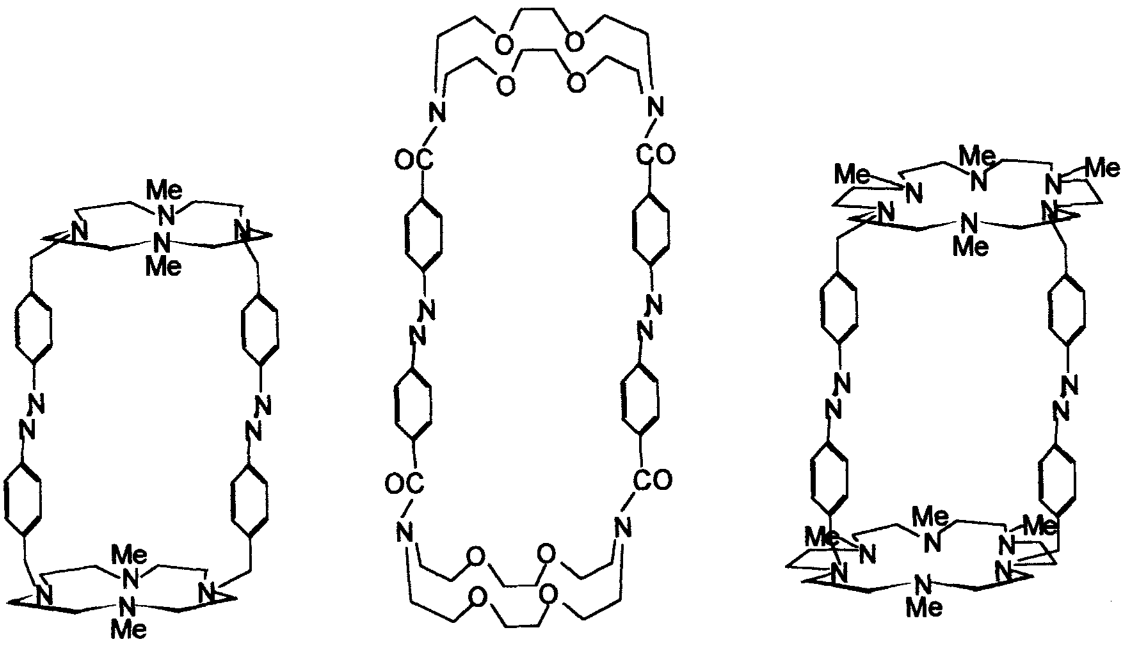
donor atoms and different architectures of the host cavities, and then binding selectivity can be achieved upon ligand irradiation.

Binding selectivity towards cationic and, more recently, anionic species is commonly achieved by proton-mediated switching (pH-switching) taking advantage of the protonation equilibria involving most of the ligands in solution. From this point of view polyazacycloalkanes have proved particularly useful owing to the convergent array of binding groups within their molecular structure [14–16].

In a recent paper [13] we reported the new macrotricyclic ligand L1 (Fig. 1), composed of two tetraazamacrocyclic rings linked together by two azobenzene pillars, which combine photoelastic characteristics and pH-mediated binding properties, evidencing as combination of these two switching mechanisms leads to the modulation of the ligational properties of this molecules in both the cavity size and the availability of the binding sites. The synthesis of this ligand was suggested by a previous work by Shinkai *et al.* [8] describing a similar cylindrical molecule (L2 in Fig. 1) based on two 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane rings connected *via* amidic linkage to azobenzene pillars, which displays photoresponsive ligational properties towards metal cations.

Considering that protonated forms of macrocyclic polyamines are very efficient in anion binding, we have now synthesised a new cylindrical ligand constituted by two azobenzene pillars and two hexaazamacrocycles, in the attempts to obtain a receptor able to form highly protonated (highly charged) species which, in principle, should form very stable complexes with anionic species in solution. In the present paper we describe the synthesis of this ligand, its photochemical and pH-switching



L1 L2 L

FIGURE 1 Photoelastic compounds containing two azobenzene pillars.

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properties as well as its binding ability towards large anions.

RESULTS AND DISCUSSION

Photochemical Behaviour

In agreement with the behaviour of ligand L1 [13], also L is expected to form, upon irradiation in solution, the $L_{E\text{-}E}$, $L_{E\text{-}Z}$ and $L_{Z\text{-}Z}$ (Fig. 2) isomers. In the case of L1, however, it was possible to identify and quantify the three isomers by means of ^{1}H and ^{13}C NMR spectroscopy, while for L we were not able to perform a similar characterisation, since the NMR spectra obtained for this molecule in different solvents, at different pH values and at different temperatures were not amenable to analysis due to the presence of extremely broad bands. In the previous case (L1) the simultaneous use of the data obtained from ^{1}H NMR and UV-VIS absorption spectrophotometry allows us to calculate the molar absorption coefficient of the three isomers, furnishing the spectrum of each form [13]. The results obtained indicated that the spectrum of the *E-Z* form of L1 is composed of exactly half the spectrum of the *E-E* form and half the spectrum of the *Z-Z* form. As a consequence of such spectral characteristics, the UV-VIS absorption data alone could not be used to calculate the molar fraction distribution of the three species; only the total amount of the *E* and *Z* forms of azobenzene groups, independent of their belonging to a particular isomer, could be obtained. Similarly, the absorption data obtained for L are not useful to perform the speciation of the system. Nevertheless, these absorption data furnished interesting information regarding the ligand properties.

The absorption spectrum of L in acidic solution is similar to that of the parent compound *E*-azobenzene [2], indicating that L is in the *E-E* form, and no significant interaction between this chromophore and the two polyamine macrocycles occurs. The same behaviour was also observed for L1 [13]. However, while the *E-E* form is the unique L1 isomer present in

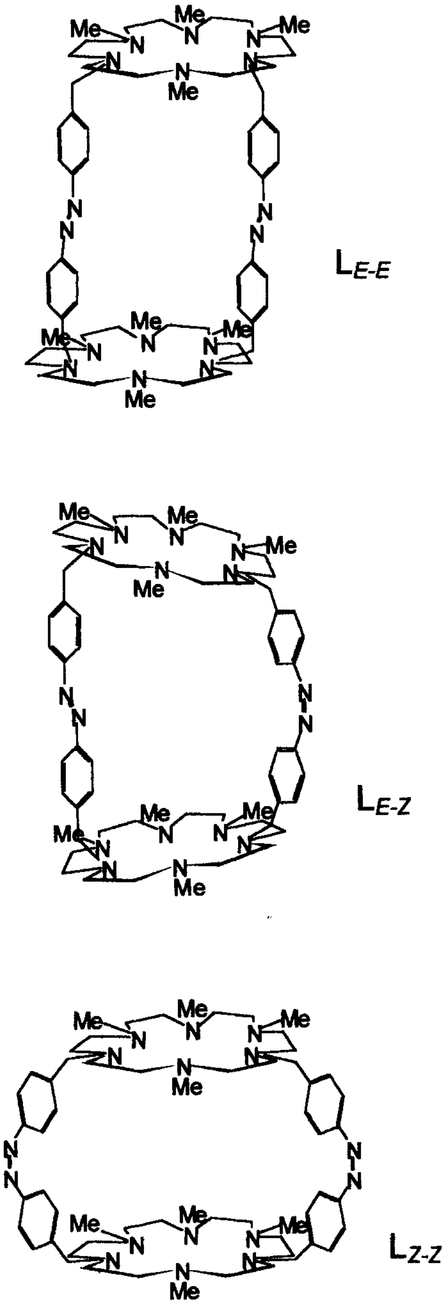

FIGURE 2 Schematic representation of the three isomeric forms of L.

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solution over all the pH range, in the case of L appreciable amounts of Z isomers are found in alkaline solution. As can be seen in Figure 3, which displays the absorption spectra of L1 obtained at different pH's after equilibration of the solutions at 298 K in the dark, the spectra (isomeric composition) change in a discontinuous manner with pH, evidencing pH ranges (1.0–5.5, 6.4–8.3, 8.8–12.0) in which they are almost invariant. The spectrum of L obtained in the pH range 1.0–5.5 doesn't change at lower pH values (pH = 0), suggesting that, under such conditions, $L_{E\text{-}E}$ is practically the unique ligand isomer present in solution. The interconversion process between *E* and *Z* forms is reversible at the different pH's, although upon pH changes long times are required to recovery the equilibrium conditions. It is to be noted that for the first time molecules with azobenzene pillars in Z conformation, the thermodynamically less stable conformation for azobenzene, are observed in absence of light irradiation.

Irradiation of this compound at 366 nm and pH 1.0 results in spectral variations (Fig. 4) that are in agreement with the formation of Z forms, denoted by the disappearance of the 327 nm band typical of the *E* form and appearance of the 430 nm band typical of the *Z* form. As shown by Figure 4, a photostationary state is reached in 60 minutes in which more than 50% of the total amount of *E* azobenzene bridges are transformed into Z, indicating that a significant amount of the Z-Z species is formed. The lack of total conversion into the Z-Z form is due to the photochemical reversibility of the isomerization. Therefore an equilibrium that depends on the relative ratio of the molar absorption coefficients ($\varepsilon_E/\varepsilon_Z$) at the excitation wavelength is reached. For example at 313 nm the amount of *E* to *Z* conversion is lower because at this wavelength the difference between the molar absorption coefficients of the Z and *E* forms is lower. The quantum yield for the isomerization of the first azobenzene, (measured after 1 minute irradiation), is practically independent of the solution pH, as can be confirmed by inspection of the inset in Figure 4.

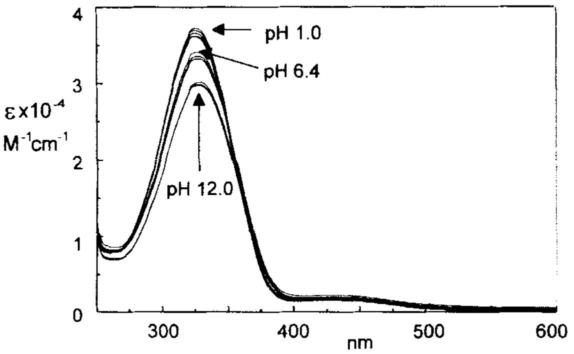

FIGURE 3 Absorption spectra of dark equilibrated solutions of compound L at different of pH values.

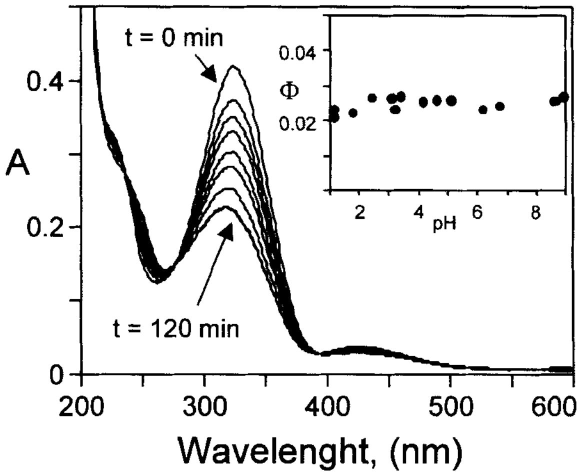

FIGURE 4 Spectral modifications upon irradiation of compound L at 366 nm, pH 1.0; irradiation times t = 0, 2, 4, 6, 10, 15, 25, 60, 120 min. Curves for 60 and 120 min. are coincident. Inset: pH dependence of the quantum yield (Φ), calculated after 1 min irradiation.

The amount of Z forms obtained upon irradiation increases with increasing pH. As can be seen in Figure 5, where the molar absorbances at 327 nm of spectra reported in Figure 3 are plotted along with the corresponding absorbances after irradiation of the sample at 366 nm during 60 minutes, also the composition of the photostationary state obtained after irradiation varies in a discontinuous manner with pH, evidencing pH ranges in which it is

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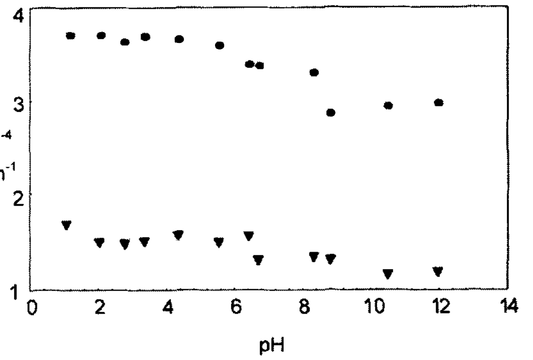

FIGURE 5 Molar absorbances at 327 nm of L aqueous solutions at different pH registered before (●) and after (▼) irradiation at 366 nm during 60 min. The samples used are the same employed to obtain the spectra in Figure 3.

almost invariant. The Z forms display a larger absorbance than the E forms at 430 nm (Fig. 4). According to this observation, irradiation at this wavelength gives rise to the Z → E back-conversion, evidencing the reversibility of the process.

The recovery of the thermodynamically more stable E forms, from irradiated solution containing large amounts of Z forms, can be obtained spontaneously (thermal recovery). The rate of such thermal recovery increases with increasing temperature for a given pH, while at a given temperature it increases with decreasing pH (Fig. 6). It is noteworthy that in very acidic solutions ($\mathrm{pH} \leq 1$) the recovery of $L_{E\text{-}E}$, from solutions containing significant amounts of the $L_{Z\text{-}Z}$ isomer, takes place *via* two consecutive reactions (Fig. 6a), the first one characterised by a greater rate constant, which can be ascribed to the $L_{Z\text{-}Z}$, → $L_{E\text{-}Z}$ interconversion, and the second one in which $L_{E\text{-}E}$ is formed from $L_{E\text{-}Z}$ at a lower rate. At higher pH the two processes are not perceptible (Fig. 6b).

This behaviour can be explained by considering that in very acidic solutions both macrocyclic rings of L are highly protonated (highly charged) and thus a large repulsion between them is expected. According to molecular models [17], the distance between the two macrocyclic rings of L increases in the order $L_{Z\text{-}Z} < L_{E\text{-}Z} < L_{E\text{-}E}$, the largest effect being observed form $L_{Z\text{-}Z}$ to $L_{E\text{-}Z}$. Hence, the faster $L_{Z\text{-}Z}$, → $L_{E\text{-}Z}$ interconversion produces an important reduction of the electrostatic repulsion between the two protonated macrocyclic rings, while the successive $L_{E\text{-}Z} \rightarrow L_{E\text{-}E}$ interconversion, determining a lower effect, takes place at lower rate. At higher pH's the kinetic data indicate that the two Z → E processes are independent, accounting for the conversion of total Z forms to total E forms independent of the different isomers.

This type of argument can also explain why the amount of Z species in solution at equilibrium, in absence of irradiation, decreases with decreasing pH, and the fact that upon irradiation larger amounts of the $L_{Z\text{-}Z}$ form are produced at higher pH values (Fig. 5).

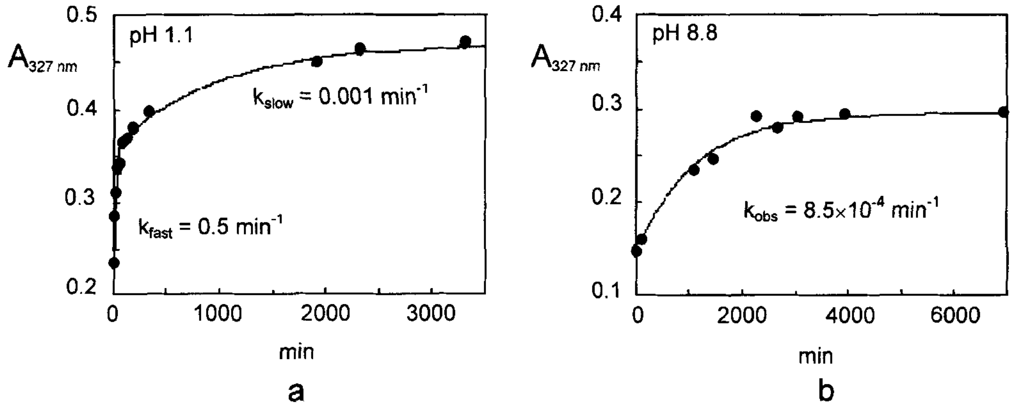

FIGURE 6 Thermal recovery at 40°C, followed at 327 nm, of $L_{E\text{-}E}$ after irradiation at 366 nm: (a) pH = 1.1, (b) pH = 8.8.

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After these considerations it would be interesting to know which protonated species of L are present in solution at the different pH's.

Basicity Properties and Anion Binding

In the previous study dealing with L1, it was possible to determine the basicity properties of all three ligand isomers (*E-E*, *E-Z*, *Z-Z*) since, as said above, it was possible to determine by means of NMR spectra the percentage of each isomer in solution [13]. As already discussed, a similar speciation can not be performed with the new L ligand. Nevertheless, we have been able to determine the basicity properties of the $L_{E\text{-}E}$ isomer.

We have seen before, that in absence of irradiation $L_{E\text{-}E}$ is the unique species in acidic solution, and upon alkalinization the expected amount of Z forms is produced in a long time. Hence, by using acidic solutions of L, as starting material, it has been possible to determine the protonation constants (Tab. I) of the $L_{E\text{-}E}$ isomer, by means of common potentiometric (pH-metric) titrations in aqueous solution, before an appreciable amount of Z forms are produced.

As can be seen, in the pH range investigated (2.5–10.5) $L_{E\text{-}E}$ behaves as a nonaprotic base. Under our experimental conditions binding of the first four protons cannot be resolved as separate single-proton transfer processes (Tab. I), but simultaneous protonation of both macrocyclic moieties is observed. Such behaviour is typical of symmetrical ligands in which the protonation sites are largely separated. For higher protonation degrees, however, the repulsion between positive charges becomes considerable and ligand protonation takes place in successive stages (Fig. 7).

TABLE I Protonation constants of L determined in 0.1 mol dm^{-3} NMe_4Cl at 298.1 ± 0.1 K

Reaction	Log K
$L + 2H^+ = H_2L^{2+}$	20.85(6)[a]
$H_2L^{2+} + 2H^+ = H_4L^{4+}$	16.9(9)
$H_4L^{4+} + H^+ = H_5L^{5+}$	7.0(1)
$H_5L^{5+} + H^+ = H_6L^{6+}$	6.4(1)
$H_6L^{6+} + H^+ = H_7L^{7+}$	5.0(1)
$H_7L^{7+} + H^+ = H_8L^{8+}$	3.0(1)
$H_8L^{8+} + H^+ = H_9L^{9+}$	2.6(1)

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

We have shown above that in absence of irradiation, at equilibrium, the isomeric composition changes in a discontinuous manner with pH, evidencing pH ranges (1.0–5.5, 6.4–8.3, 8.8–12.0) in which it is almost invariant. The $L_{E\text{-}E}$ isomer is almost the unique species present in the most acidic range, the strong electrostatic repulsion between the highly protonated macrocyclic rings favouring such elongated conformation. Hence, in agreement with the distribution diagram of Figure 7 and the spectral data of Figure 5, species H_nL^{n+} with $n \geq 6$, formed

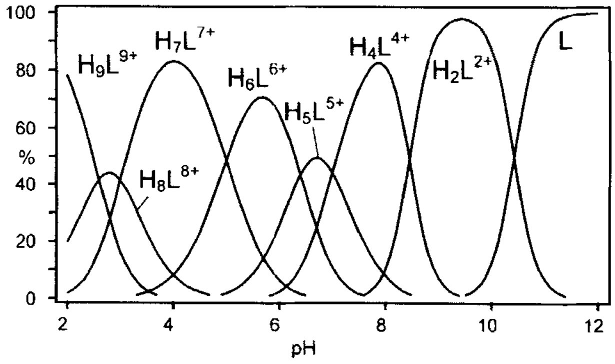

FIGURE 7 Distribution diagram of the protonated species formed by $L_{E\text{-}E}$ as a function of pH.

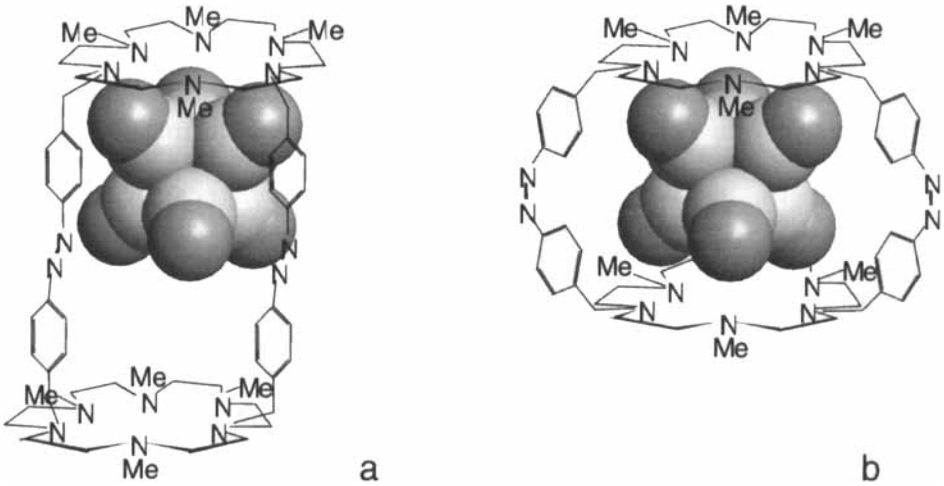

FIGURE 8 Schematic representation of the inclusion complexes formed by $[Co(CN)_6]^{3-}$ with protonated species of $L_{E\text{-}E}$ (a) and $L_{Z\text{-}Z}$ (b).

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during the potentiometric titrations, maintain the *E-E* conformation, while species with $n \leq 5$ slowly produce, in two different steps, the amount of Z forms expected at equilibrium.

Protonation of polyamines controls the ability of such molecules to associate with chemical species, competing with the formation of metal complexes and promoting anion binding. In this sense, protonation itself is a sort of chemical switch. Considering the ability of L to form highly protonated (highly charged) species in solution, and the possibility of modulating size and shape of the ligand cavity, the present photoelastic ligand could be relevant in molecular recognition processes involving anionic substrates. A preliminary study performed by means of spectrophotometric measurements [22] in $1.0\,\mathrm{mol\,dm^{-3}}$ HCl solution reveals that association of $(H_{12}L_{E\text{-}E})^{12+}$ with a highly charged anion, such as $[Co(CN)_6]^{3-}$, gives rise to the stable anion complex $\{(H_{12}L_{E\text{-}E})[Co(CN)_6]\}^{9+}$ ($\log K = 3.7(1)$). Molecular models [17] indicate that the cavity of the ligand in its elongated form ($L_{E\text{-}E}$) is too long to allow simultaneous interaction of both protonated hexaaza macrocyclic rings with the anion. Hence, in $\{(H_{12}L_{E\text{-}E})[Co(CN)_6]\}^{9+}$ the anion is expected to be in contact with only one hexaaza macrocyclic unit, as sketched in Figure 8a. On the other hand, switching the ligand structure to the $L_{Z\text{-}Z}$ form should give rise to a more stable complex in which both protonated macrocyclic units interact with the anion in a sandwich like fashion (Fig. 8b).

Further work will be undertaken to get more insight into the photochemical- and pH-switching processes involving anion recognition by L.

EXPERIMENTAL SECTION

Synthesis of L

L was synthesised by following the procedure previously reported for L1 [13]. The synthesis of 1,4,7,13-tetramethyl-1,4,7,10,13,16-hexaazacyclooctadecane was reported elsewhere [18].

A solution of bis(4-bromomethyl-phenyl)-diazene (1.77 g, 4.8 mmol) in warm dry CH_3CN was added, over a period of 3 hours, to a refluxing solution of 1,4,7,13-tetramethyl-1,4,7,10,13,16-hexaazacyclooctadecane (1.51 g, 4.8 mmol) in dry CH_3CN containing Na_2CO_3 (1.1 g, 1.0 mmol). The mixture was refluxed during 6 hours, then cooled at room temperature and filtered. The resulting solution was evaporated to dryness on a rotary evaporator. The crude product was dissolved in 100 cm^3 of water and extracted several times with chloroform. The chloroform solution was dried over anhydrous Na_2SO_4 and evaporated to dryness on a rotary evaporator. The orange solid, obtained after evaporation, was washed several times with cyclohexane, dissolved in ethanol and treated with concentrated HCl solution to obtain the solid L·12HCl compound, which was filtered, washed with ethanol and dried in vacuum at 35°C (yield 1.2 g, 34%). MS m/z 1044 ($[M+H]^+$). Anal. Calcd for $C_{60}H_{108}N_{16}Cl_{12}$: C, 48.72; H, 7.36; N, 15.15. Found: C, 48.4; H, 7.4; N, 14.9.

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Spectrophotometric Measurements

The electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer equipped with a 1 cm cell thermostated at 298 K.

Irradiation Experiments

Light excitation was performed by a medium pressure mercury arc lamp. Interference filters (Oriel) were used to select narrow spectral ranges with maximum wavelength at 366 nm. The irradiated solution was contained in a 1 cm spectrophotometric quartz cell. The intensity of the incident light (1.1×10^{-6} Einstein min^{-1} at 366 nm) was measured by ferrioxalate actinometry [19].

Potentiometric Measurements

Potentiometric (pH-metric) measurements ($pH = -\log [H^+]$) were carried out in a degassed 0.1 mol dm^{-3} Me_4NCl, at 298.1 ± 0.1 K, by using the equipment and the methodology that has been already described [20]. The combined Ingold 405 S7/120 electrode was calibrated as a hydrogen concentration probe by titrating known amounts of HCl with CO_2-free Me_4NOH solutions and determining the equivalent point by Gran's method [21] which allows to determine the standard potential E^o and the ionic product of water ($pK_w = 13.83(1)$ at 298.1 K in 0.1 mol dm^{-3} Me_4NCl). All measurements were performed in the pH ranges 2.5–10.5. In all experiments the concentration of **L** was about 8×10^{-4} mol dm^{-3}. Three measurements (about 120 data points) were performed to determine the protonation constants of **L** in its *E-E* form, processing the e.m.f. data by means of the computer programs HYPERQUAD [22]. Solutions containing the unique $L_{E\text{-}E}$ isomer were prepared in 0.1 mol dm^{-3} HCl solution and allowed to equilibrate at 298 K in the dark for many hours. The absence of Z forms was spectophotometrically verified before and after each titration.

Acknowledgements

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