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Supramolecular interactions of hexacyanocobaltate(III) with polyamine receptors containing a terminal anthracene sensor☆

Laura Rodríguez [a], Sérgio Alves [b], João C. Lima [b], A. Jorge Parola [b], Fernando Pina [b,*], Conxa Soriano [c], Teresa Albelda [d], Enrique García-España [d,*]

[a] *Departament de Química Inorgànica, Universitat de Barcelona, Martí i Franquès 1, 08028 Barcelona, Spain*
[b] *Departamento de Química, Centro de Química Fina e Biotecnologia–REQUIMTE, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Monte de Caparica, Portugal*
[c] *Departament de Química Orgánica, Facultat de Farmacia, Universitat de València, Burjassot, Spain*
[d] *Departament de Química Inorgànica, Facultat de Química, Universitat de València, C/Dr. Moliner 50, 46100 Burjassot (València), Spain*

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Abstract

The fluorescence emission properties of a series of chemosensors containing a polyamine receptor bearing an anthracene signaling unit were studied. The fluorescence emission intensity is dependent on the protonation degree of the receptor, the fully protonated form exhibiting the highest emission intensity. By removing protons from the nitrogens a quenching effect can be observed, due to an electron-transfer from the amine to the excited fluorophore. The rate constant of the quenching process is exponentially dependent on the distance of the nitrogen from which the electron is transferred ($\beta = 0.6\,\text{Å}^{-1}$). The ability of the chemosensors for signaling anions was tested through the model anion hexacyanocobaltate(III). The temperature dependence of the association constants shows that at least for this compound, the change in solvation entropy is probably the controlling parameter to account for the binding.

Keywords: Supramolecular; Polyamine; Anthracene; Fluorescent; Chemical sensors

1. Introduction

In recent years, chemosensors capable of detecting the presence of anions have been subjected to some attention, due to the importance of these species in many biological processes [1]. A chemosensor can be defined as a molecule containing a signaling unit, a spacer and a receptor (Scheme 1) [2]. One great challenge in the design of chemosensors concerns the receptor unit, because differently from cations, the binding of anions is usually much weaker. Chemosensors containing polyamine receptors are versatile ligands since they can coordinate both metal ions and anions depending on their protonation state.

We are particularly interested in the use of these chemosensors to signal the supramolecular interactions with anions, in order to study the bonding occurring at the second coordination sphere. The driving force for the binding of anions is believed to be the electrostatic attraction, together with the possibility of hydrogen bond formation. However, less attention has been paid to the solvation effects. In this work, the interaction of hexacyanocobaltate(III) with the polyammonium receptors **L1**–**L7** (see Scheme 2) is reported. The receptors were designed to obey Scheme 1: namely they all contain a polyamine chain attached to an anthracene fluorescent unit whose emission should be affected by the binding of an anion to the receptor:

$$[Co(CN)_6]^{3-} + H_3O^+ + h\nu \rightarrow [Co(CN)_5(H_2O)]^{2-} + HCN \quad (1)$$

The hexacyanocobaltate(III) anion is known to undergo a photoaquation reaction (Eq. (1)) and this fact can also be used to obtain information about the supramolecular structures of the adducts in solution. It was shown that the fully protonated forms of polyamine macrocyclic receptors, e.g. [24]ane-$N_6H_6^{6+}$ and [32]ane-$N_8H_8^{8+}$, give rise to 1:1 adducts with $[Co(CN)_6]^{3-}$ and other metal cyanide complexes and that the quantum yield of photoreaction (1)

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* Corresponding authors. Tel.: +351-21-2948355; fax: +351-21-2948550.
E-mail addresses: fjp@dq.fct.unl.pt (F. Pina), enrique.garcia-es@uv.es (E. García-España).

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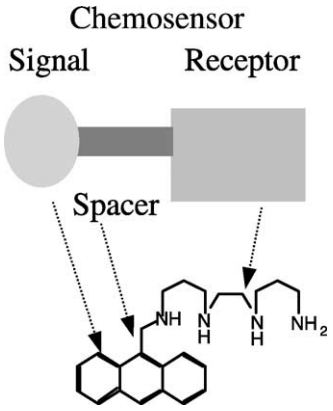
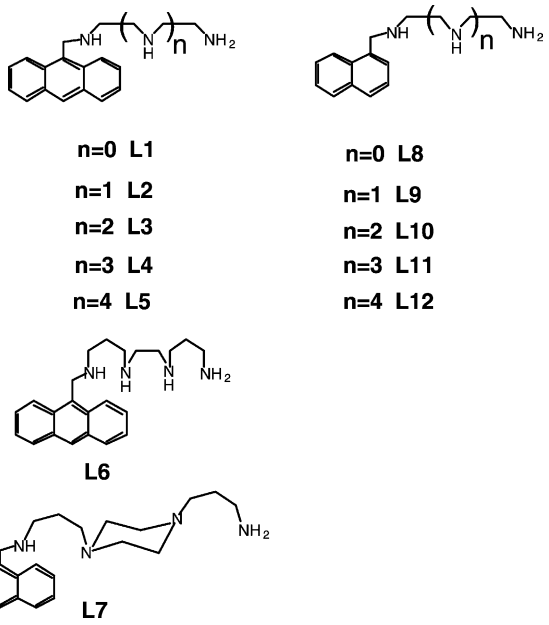


Scheme 1.



Scheme 2.

is reduced respectively by a factor of 2 or 3 when hexacyanocobaltate(III) anion was involved in those adducts [3,4]. Such discrete quenching effect was taken as an indication of defined structures involving respectively three or four of the cyanide ligands linked by hydrogen bonds to the protonated nitrogens of the polyamine. The photoaquation reaction of hexacyanocobaltate(III) can thus be used as a structural probe in solution for this and other adducts involving polyamine chains.

2. Experimental

2.1. Synthesis

Ligands **L3**–**L6** were available from previous studies [5–7]. Ligands **L1**, **L2** and **L7** were synthesized according to similar procedures [5–7]. Ethylenediamine (Merck, >99%) was distilled prior to use. Diethylenetriamine (Aldrich, 99%), 1,4-bis(3-aminopropyl)-piperazine (Aldrich, >99%) and 9-anthracenecarboxaldehyde (Aldrich, 97%) were used as received. Absolute ethanol, chloroform, dichloromethane and 37% hydrochloric acid were of analytical grade. ^{1}H NMR spectra were recorded on a Bruker ARX 400 MHz spectrometer, using residual solvent peak as reference. Elemental analysis were made in a Thermo Finnigan-CE Instruments Elemental Analyzer 1112 series or in an Elementar VarioEL analyzer.

2.2. N1-(9-Anthrylmethyl)-1,2-ethanediamine dichlorhydrate (*L1*·2HCl)

9-Anthracenecarboxaldehyde (1.03 g, 5.0 mmol) and ethylenediamine (1.7 ml, 25 mmol) were stirred for 72 h in a mixture of 125 ml of absolute ethanol and 75 ml of $CHCl_3$. Sodium borohydride (1.9 g, 50 mmol) was then added and the resulting solution stirred overnight. The solvent was removed at reduced pressure. The resulting residue was treated with water and the compound was repeatedly extracted with CH_2Cl_2 (three times 30 ml). The organic phase was washed with H_2O, dried over anhydrous sodium sulfate, and the solvent was evaporated to give the free amine, which was dissolved in 20 ml of absolute ethanol and precipitated as its hydrochloric salt. 76% yield. ^{1}H NMR of the non-protonated amine in $CDCl_3$, δ_H (ppm): 2.88 (t, 2H), 2.94 (t, 2H), 4.75 (s, 2H), 7.46 (t, 2H), 7.54 (t, 2H) 8.01 (d, 2H), 8.35 (d, 2H), 8.40 (s, 1H). Anal. calcd. for $C_{17}H_{20}Cl_2N_2{\cdot}0.5H_2O$: C 61.45, H 6.37, N 8.43. Found: C 61.2, H 6.1, N 8.1.

2.3. N1-(2-Aminoethyl)-N2-(9-anthrylmethyl)-1,2-ethanediamine trichlorhydrate (*L2*·3HCl)

9-Anthracenecarboxaldehyde (1.03 g, 5.0 mmol) and diethylenetriamine (2.7 ml, 25 mmol) were stirred for 72 h in a mixture of 125 ml of absolute ethanol and 75 ml of $CHCl_3$. Sodium borohydride (1.9 g, 50 mmol) was then added and the resulting solution stirred overnight. The solvent was removed at reduced pressure. The resulting residue was treated with water and the compound was repeatedly extracted with CH_2Cl_2 (three times 30 ml). The organic phase was dried with anhydrous sodium sulfate, and the solvent was evaporated to give the free amine, which was dissolved in 20 ml of absolute ethanol and precipitated as its hydrochloric salt. This compound was then purified by re-dissolving it in basic H_2O, repeatedly extracting with CH_2Cl_2 (three times 30 ml), drying the organic phase with anhydrous sodium sulfate and evaporating the solvent to give the free amine, which was then dissolved in 20 ml of absolute ethanol and again precipitated as its hydrochloric salt. 64% yield. ^{1}H NMR (D_2O), δ_H: 3.1–3.5 (m, 8H), 4.81 (s, 2H), 7.30 (t, 2H), 7.41 (t, 2H), 7.73 (d, 2H), 7.86 (d, 2H), 8.15 (s, 1H). Anal. calcd. for $C_{19}H_{26}Cl_3N_3{\cdot}H_2O$: C 54.23, H 6.71, N 9.99. Found: C 54.2, H 6.5, N 9.7.

2.4. 3-(4-{3-[(9-Anthrylmethyl)amino]propyl}piperazino)-propylamine tetrachlorhydrate (**L7**·3HCl)

9-Anthracenecarboxaldehyde (1.03 g, 5.0 mmol) and 1,4-bis(3-aminopropyl)-piperazine (5.1 ml, 25 mmol) were stirred for 72 h in a mixture of 125 ml of absolute ethanol and 75 ml of $CHCl_3$. Sodium borohydride (1.9 g, 50 mmol) was then added and the resulting solution stirred overnight. The solvent was removed at reduced pressure. The resulting residue was treated with water and the compound was repeatedly extracted with CH_2Cl_2 (three times 30 ml). The organic phase was dried with anhydrous sodium sulfate, and the solvent was evaporated to give the free amine, which was dissolved in 20 ml of absolute ethanol and precipitated as its hydrochloric salt. 56% yield. ^{1}H NMR (D_2O), δ_H: 1.85 (s, 4H), 2.76 (t, 2H), 2.93 (t, 2H), 3.00 (t, 2H), 3.08 (t, 2H), 3.25 (s, 4H), 3.54 (s, 4H), 4.56 (s, 2H), 7.16 (t, 2H), 7.27 (t, 2H), 7.57 (d, 2H), 7.70 (d, 2H), 7.96 (s, 1H). Anal. calcd. for $C_{25}H_{38}Cl_4N_4·5H_2O$: C 47.93, H 7.72, N 8.94. Found: C 47.9, H 7.6, N 8.9.

2.5. Electromotive force (emf) measurements

Potentiometric titrations were carried out at 298.1 ± 0.1 K in 0.15 mol dm^{-3} NaCl. The experimental procedure (burette, potentiometer, cell, stirrer, microcomputer, etc.) has been fully described elsewhere [8]. The acquisition of the emf data was performed with the computer program PASAT [9]. The reference electrode was an Ag/AgCl electrode in saturated KCl solution. The glass electrode was calibrated as an hydrogen-ion concentration probe by titration of previously standardized amounts of HCl with CO_2-free NaOH solutions and determining the equivalent point by the Gran's method [10] which gives the standard potential, $E^{\circ\prime}$, and the ionic product of water. The computer program HYPERQUAD [11] was used to calculate the protonation constants. The titration curves for each system (ca. 100 experimental points corresponding to at least three measurements, pH range investigated 2–10, concentration of **L** ranging from 5×10^{-4} to 5×10^{-3} mol dm^{-3}) were treated either as a single set or as separated curves without significant variations in the values of the stability constants. Finally, the sets of data were merged together and treated simultaneously to give the final stability constants.

2.6. Spectrophotometric and spectrofluorimetric titrations

Absorption spectra were recorded on a Shimadzu UV-2510 PC, UV-Vis recording spectrophotometer and fluorescence emission on SPEX Jobin-Yvon Fluorolog 3 spectrofluorimeter. HCl and NaOH were used to adjust the pH values that were measured on a Metrohm 713 pH meter. All the measurements were carried out in 0.15 mol dm^{-3} NaCl. Linearity for the fluorescence emission was checked in the concentration range used. The absorbance of the excitation wavelength was maintained lower than ca. 0.15. When excitation was carried out at wavelengths different from the isosbestic points, a correction for the absorbed light was performed.

The fluorescence emission titration curves were carried out using the acidity constants obtained from potentiometric measurements, except for the **L1** and **L2** where their solubility is not enough for potentiometry. In this case the fitting was achieved including the acidity constants as variable parameters.

2.7. Fluorescence decay measurements

The samples were excited at 337 nm using a coaxial flash lamp (IBH, 5000 system) filled with nitrogen. The lamp pulses are monitored by a synchronization photomultiplier, the PM signal is shaped in a constant fraction discriminator (Canberra 2126) and directed to a time to amplitude converter (TAC, Canberra 2145) as start pulses. Emission wavelength (450 nm) is selected by a monocromator (Oriel 77250) imaged in a fast photomultiplier (9814B Electron Tubes Inc.), the PM signal is shaped as before and delayed before entering the TAC as stop pulses. The analogue TAC signals are digitized (ADC, ND582) and stored in a PC. The analysis of the decays is carried out with the method of modulating functions extended by global analysis as implemented by Striker et al. [12].

3. Results and discussion

3.1. Fluorescence properties of the ligands in aqueous solution

In Fig. 1A, absorption, fluorescence emission and excitation spectra for compound **L7** (pH = 1.0) are presented. Absorption and fluorescence spectra of compounds **L1**–**L6** of the same series present the same features, typical from anthracene-substituted receptors. While the absorption spectra hardly change with pH, the emission intensity is strongly pH dependent, as can be seen in Fig. 1B, where a fluorimetric titration curve is shown for the same compound **L7**.

As reported for many other analogs containing naphthalene or benzene [13,14] removing protons from the nitrogens of the chain causes the occurrence of an electron-transfer from the lone pair of the amine to the excited fluorophore, leading to the quenching of the fluorophore emission [15–18].

The electron-transfer quenching rate constant, k_q, for each species, can be obtained from the Stern–Volmer equation, adapted to an intramolecular process (Eq. (2)):

$$\frac{I_0}{I} = 1 + k_q \tau_0 \quad (2)$$

where I_0 and τ_0 are respectively the emission and the lifetime of the fully protonated form ($\tau_0 \approx 12$ ns in aerated

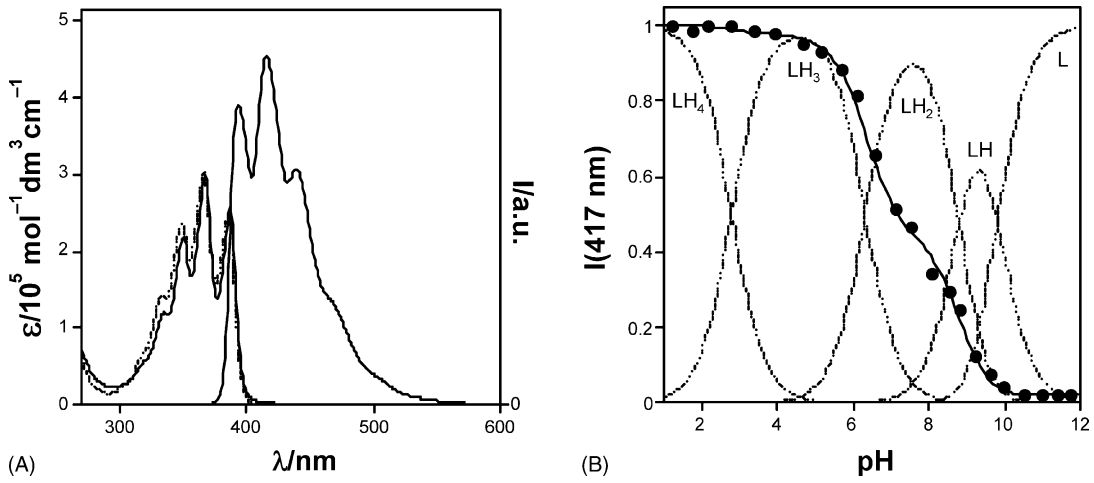


Fig. 1. (A) Absorption (—), fluorescence emission and excitation spectra (···) for compound **L7**, pH = 1.0. (B) Normalized fluorescence emission titration curve for **L7** in 0.15 mol dm^{-3} NaCl superimposed to the molar fraction distribution of the various species obtained by potentiometry. The following protonation constants were obtained at 298.1 ± 0.1 K in 0.15 mol dm^{-3} NaCl: $\log K_{L,LH} = 9.83(1)$, $\log K_{LH,LH_2} = 8.82(2)$, $\log K_{LH_2,LH_3} = 6.34(3)$, $\log K_{LH_3,LH_4} = 2.80(8)$.

solutions), and I the emission of a less protonated form, which can be calculated from the coefficients of the fittings such as the one shown in Fig. 1B. Following the same treatment recently reported [19] for the series **L8**–**L12** and assuming an identical protonation sequence,[1] we have represented the fluorescence emission quenching constants as a function of the through-bond distance that separates the anthracene moiety from the nearest unprotonated nitrogen (Fig. 2).[2] The result in Fig. 2 illustrates the dramatic dependence on the distance evidenced by the quenching effect. From the exponential dependence, a β factor of ca. 0.6 Å^{-1} is obtained, close to the 0.5 Å^{-1} value reported previously for the series **L8**–**L12**.

3.2. Interaction with the hexacyanocobaltate(III) anion

The fully protonated forms of the present family of compounds exhibit an intense fluorescence emission, which can be used to signal the binding of anionic receptors. The quenching of the fluorescence emission intensity at 416 nm (λ_{exc} = 387 nm) of compounds **L1**–**L5**, at pH = 1.0, upon addition of increasing hexacyanocobaltate(III) concentrations is presented in Fig. 3.

According to Fig. 3, the hexacyanocobaltate(III) adducts with compounds **L1**–**L5** are still emissive. This result contrasts with the one obtained for the analogs **L8**–**L12**, containing the naphthalene fluorophore, where almost complete quenching of the adduct was obtained [19]. This different behavior can be ascribed to the lower energy level of the anthracene triplet when compared with naphthalene (see Scheme 3) allowing only partial (thermally activated) energy transfer.

Time correlated single photon counting measurements were carried out for the series. The fluorescence decays in the presence of hexacyanocobaltate(III), collected at 450 nm (λ_{exc} = 337 nm) are best fitted with sums of two exponentials, with a longer decay time (τ_2) equal to the decay of

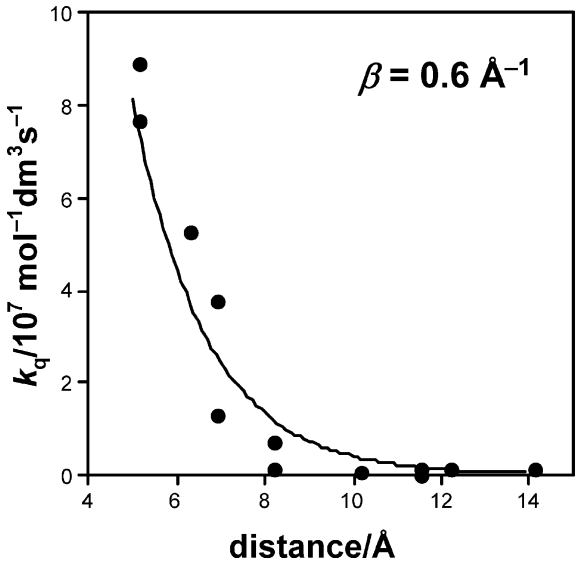


Fig. 2. Quenching rate constants obtained from Eq. (1) using data from fluorimetric titration plots (such as the one in Fig. 1B) as a function of through-bond chromophore-deprotonated nitrogen distance.

[1] The deprotonation sequence can be obtained by representing the ^{1}H NMR and ^{13}C NMR chemical shifts as a function of pH. A detailed study of the deprotonation sequence was recently reported for the naphthalene analogs, **L8**–**L12** [19]. Previous potentiometric and spectroscopic data for compounds **L3**–**L6** and data obtained in this work for compounds **L1**, **L2** and **L7** suggest that also in the case of the **L1**–**L7** series, a similar protonation pattern holds. The first protons are removed from the central nitrogens of the chain and the more basic amino group is the primary at one of the ends of the molecule.

[2] Protonation constants and fluorimetric titrations for ligands **L1**–**L6** are presented as supplementary material

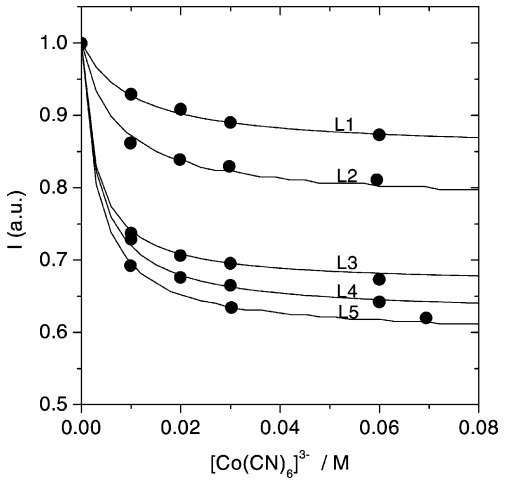
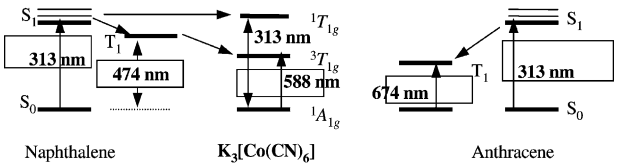


Fig. 3. Normalized fluorescence intensity at 416 nm (λ_{exc} = 387 nm) of compounds **L1**–**L5** at pH = 1.0 as a function hexacyanocobaltate(III) concentration.



Scheme 3.

the ligand in the absence of quencher, and a shorter decay time (τ_1), whose amplitude increases with increasing concentration of quencher. Table 1 shows the results from global analysis of the fluorescence decays of **L2** with increasing concentrations of hexacyanocobaltate(III).

The shorter decay time can easily be attributed to the chemosensor emission within the adduct and the largest one to the free ligand. The respective changes in amplitude exhibit a dependence on the metal complex concentration as expected. Moreover, the ratio τ_1/τ_2 is 0.85, in good agreement with the ratio between the respective steady state fluorescence emission intensities for **L2**, shown in Fig. 3.

The time resolved fluorescence data points to a static quenching mechanism. The lack of dynamic quenching allows the use of the fluorescence emission intensity parameter to determine the association constants with hexacyanocobaltate(III) for the series **L1**–**L5**, following the method previously reported by Lehn and coworkers [20]. At 25 °C, the

Table 1
Decay times (τ_1, τ_2) and normalized pre-exponential factors (a_1, a_2) from global analysis of time correlated single photon counting decays of compound **L2** at pH = 2.0 for several hexacyanocobaltate(III) concentrations

$K_3[Co(CN)_6]$ (M)	τ_1 (ns)	τ_2 (ns)	a_1	a_2	χ^2
0	10.5	12.3	–	1.0	1.0
8.63×10^{-5}	10.5	12.3	–	1.0	1.2
1.30×10^{-3}	10.5	12.3	0.30	0.70	1.1
4.65×10^{-3}	10.5	12.3	0.73	0.27	1.3

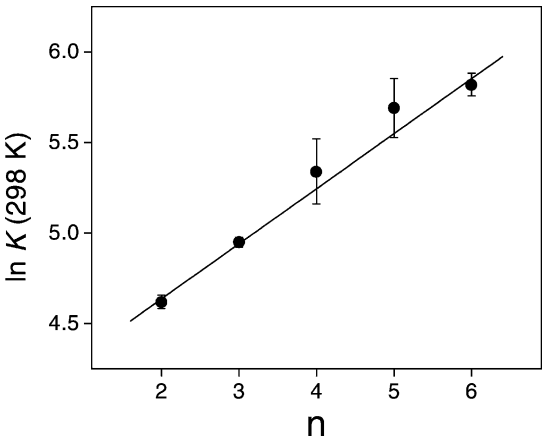


Fig. 4. Logarithm of the complexation constant of ligands **L1**–**L5** with hexacyanocobaltate(III) at pH = 1.0 and 298 K, obtained from the fitting of fluorescence data.

logarithm of the association constants in HCl 0.1 M is plotted in Fig. 5. These values are one order of magnitude lower than those reported for the adducts of hexacyanocobaltate(III) with polyamine macrocycles, e.g. [24]ane-N_6 ($\ln K$ = 9.0 [21]), and increases with the positive charge of the ligand, suggesting that the free energy for complexation is dominated by the electrostatic interaction of the positively charged ligand with the negatively charged hexacyanocobaltate(III) (see Fig. 4).

In order to split the enthalpic and enthropic terms, the temperature dependence of the association constants was inspected. The values of ΔH and ΔS were obtained from Van't Hoff plots of the constants, and are presented in Fig. 5.

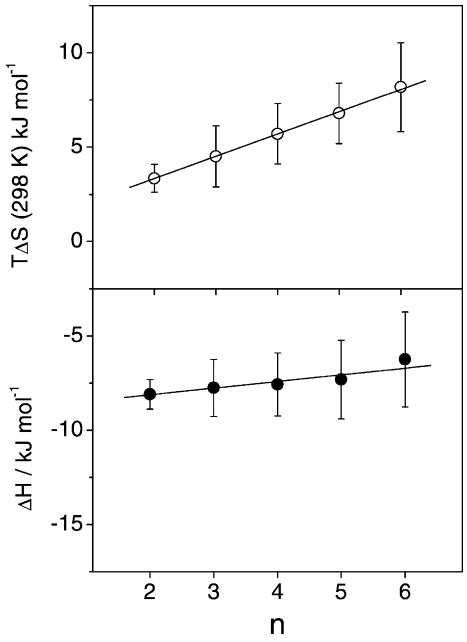


Fig. 5. Enthalpy and entropy contributions to the free energy of complexation of ligands **L1**–**L5** with hexacyanocobaltate(III) at pH = 1.0 and 298 K.

The entropy term is positive, increasing slightly with n (number of nitrogens), while the enthalpy is negative and shows a smaller variation with n. Despite that both terms significantly contribute to the free energy, the trend observed in the constants is clearly associated to the positive enthropic term. Since in the gas phase an association reaction has a negative entropy change, the positive values in Fig. 5 must be associated with the solvation entropy difference between products and reagents. This difference is positive because water has a more loose structure around the bigger and less charged adduct than around the smaller and heavily charged free ligand and free hexacyanocobaltate(III).

The enthalpic term is usually associated to the electrostatic, dipolar and hydrogen bonding interaction inside the adduct. The small variation with n could reflect a constancy in the stabilizing interactions inside the adduct, i.e. a constant number of hydrogen bonds along the series **L1**–**L5**.

More information about the hydrogen bonding contribution to the stabilization of the adduct was obtained by measuring the photoaquation quantum yields of the hexacyanocobaltate(III) complex in the presence of **L5**. This ligand was chosen since it is the one exhibiting the largest association constant. In a typical experiment, the metal complex (5×10^{-3} M) was irradiated at 313 nm, pH = 1.0, in the presence of **L5** (2×10^{-4} M).

The overall photoaquation quantum yield (Eq. (1)) results from contributions due to: (i) direct excitation of free hexacyanocobaltate (trivial contribution); (ii) excitation of the hexacyanocobaltate(III) fraction attached to the chemosensor; and (iii) excitation of the chemosensor fraction involved in the adduct, followed by energy transfer to the metal complex, and subsequent photoreaction. The observed quantum yield ($\phi = 0.24$) can thus be accounted for by a contribution of the free metal complex ($\phi = 0.30$) [3,4], linked metal complex ($\phi = 0.2$) [22], and a small contribution of photoproduct due to the energy transfer from the chemosensor to the receptor, within the adduct ($\phi = 0.2$) whose efficiency is 0.55.

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