



# Polarographic Studies on Anion Coordination Chemistry. Host–Guest Interactions of Hexacyclen and Pentacyclen with Pyrophosphate, Selenite, Selenate, Molybdate and Tungstate Anions

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**Abstract.** The complexation of protonated hexacyclen and pentacyclen with pyrophosphate, selenite, selenate, molybdate and tungstate anions was studied by differential pulse polarography at 25 °C. The stoichiometry and stability of the resulting anion complexes were evaluated from the pH and concentration-dependence of the peak potentials, respectively. The results established 1 : 1 anion receptor complexation in all cases. In the case of all anions studied, hexacyclen was found to form more stable anion complexes than pentacyclen. The fact that the anion-receptor complexation depends on the structural features of both the anions and the macrocycles used is indicative of a steric controlled interaction.

**Key words:** hexacyclen, pentacyclen, anion complexes, stoichiometry, stability, polarography.

## 1. Introduction

During the past two decades, the design of organic receptor molecules for the selective recognition of anionic substrates has been of increasing interest [1–6]. This is mainly due to the very important role played by anionic species in chemical as well as in biological processes [1, 2, 6]. The molecular receptors most widely used in anion coordination have been polyazamacrocycles in their protonated forms [6–18]. Due to the formation of highly charged species in aqueous solution, even at neutral pH, and their ability to form multisite hydrogen-bond networks, these cationic macrocycles are shown to be very suitable anionic receptors. It has been reasonably assumed that the electrostatic and H-bonding interactions provide the bonding forces in the resulting anion complexes, while the shape and size of the protonated macrocyclic cavity determine the bonding selectivity [7, 8, 10, 11, 15, 17, 19].

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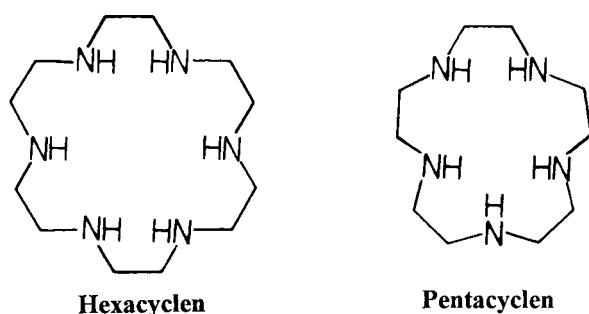


Figure 1. Structures of the macrocycles used.

Among a variety of physicochemical methods employed for the study of cation- and anion-macrocyclic interactions [4], polarographic methods are well known techniques for the study of the electrochemical behavior of macrocyclic ligands and the stability and selectivity of their complexes with various cations [20–24] and anions in solution [7, 8, 14].

Studies dealing with the interactions of polyammonium macrocycles with anionic species such as halides [9, 11, 19], nitrate [9, 11, 16], perchlorate [9–11], sulfate [11, 16], carbonate [8], phosphate [8, 14, 18], selenate [16], benzenesulfonate [9, 11], hexacyanoferrate(II) [14, 15], carboxylates [7, 9, 13, 14] and especially, nucleotides (e.g., AMP, ADP and ATP) [8, 12, 14, 17, 18] have already been reported in the literature. In this paper we report an anodic differential pulse polarographic study of hexacyclen and pentacyclen (Figure 1) complexes with pyrophosphate, selenite, selenate molybdate and tungstate anions in aqueous solution.

## 2. Experimental

Sodium salts of pyrophosphate, selenite, selenate, molybdate and tungstate and sodium hydroxide (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying. Reagent grade perchloric acid (Merck) was used as received. To obtain neutral pH and to keep the ionic strength constant, 0.1 M Tris and 0.2 M sodium perchlorate were used, which were ascertained to have no influence on the peak potential,  $E_p$ . It should be noted that the same ionic strength has already been employed for the determination of the protonation constants of hexacyclen and pentacyclen [4]. Doubly distilled deionized water was used throughout.

Hexacyclen hemihydrate and pentacyclen were obtained from the commercial salts hexacyclen $\cdot$ 3H<sub>2</sub>SO<sub>4</sub> and pentacyclen $\cdot$ 5HCl (both from Parish) as follows [11]. Weighed samples of the commercial preparations were dissolved in water and treated with stoichiometric amounts of barium carbonate (in the case of the hexacyclen salt) and silver carbonate (in the case of the pentacyclen salt). After being

mixed for 2 h at 80 °C, the hot filtrate solutions were concentrated in a rotary evaporator. Hexacyclen hemihydrate and pentacyclen were obtained by vacuum sublimation of the corresponding concentrated filtrates taken to dryness.

The polarographic and cyclic voltammetric measurements were carried out with a dropping mercury electrode (DME) in a three-electrode arrangement. The counter electrode was a platinum wire with a considerably larger surface area than that of the DME. A silver | silver chloride | saturated KCl reference electrode in a separate compartment with a dense ceramic in the bottom was directly immersed in the reaction cell. All the solutions were deaerated for 10 min with pure nitrogen gas and an inert atmosphere was maintained over the solution during the oxidation.

A Metrohm multipurpose instrument model 693VA with a Metrohm stand model 694VA and a thermal printer was used for the polarographic and cyclic voltammetric measurements. All experiments were carried out at  $25 \pm 0.1$  °C using a model FK2 Haake thermostat with a water bath.

### 3. Results and Calculation

In preliminary experiments it was found that, in aqueous solution, the macrocycles hexacyclen and pentacyclen show well defined anodic waves at DME in the Tris-buffered neutral region. The same behavior was previously reported for many polyazamacrocycles [7, 25, 26]. In dc polarograms, the plots of  $\log(i/i_d - i)$  vs. the dc potential result in straight lines with reciprocal slopes falling in the range of 29–35 mV over the entire pH range studied, emphasizing a two-electron reversible oxidation at DME. The peak currents of the differential pulse polarograms were proportional to the bulk concentration of the polyamines and also to the square root of the drop time. The corresponding cyclic voltammograms gave nearly reversible waves with  $i_{pc}/i_{pa} \approx 1$  and  $\Delta E \approx 35$  mV (see Figure 2).

Sample anodic differential pulse polarograms for the pentacyclen-selenate system at two different pH values are shown in Figure 3. As seen, the peak potential,  $E_p$ , of the anodic dissolution waves at DME due to pentacyclen shifts commonly to more positive values upon addition of the selenate anion. The peak heights decrease slightly with an increase in the anion concentration. Moreover, under similar experimental conditions, the corresponding peak potentials shift to more positive values by increasing proton concentration in solution. The observed polarographic behaviors are identical with those reported previously [7, 8, 14, 21, 23, 24], emphasizing the complex formation between the polyaza macrocycle and the anion in solution.

The peak potentials of the differential pulse polarograms were independent of the concentration of the macrocycles as well as of the buffering agent, but shifted to more negative values upon increasing the pH of the solution according to Equation (1):

$$\frac{\Delta E_p}{\Delta \log(\alpha_H)_L} = -30 \text{ mV} \quad (1)$$

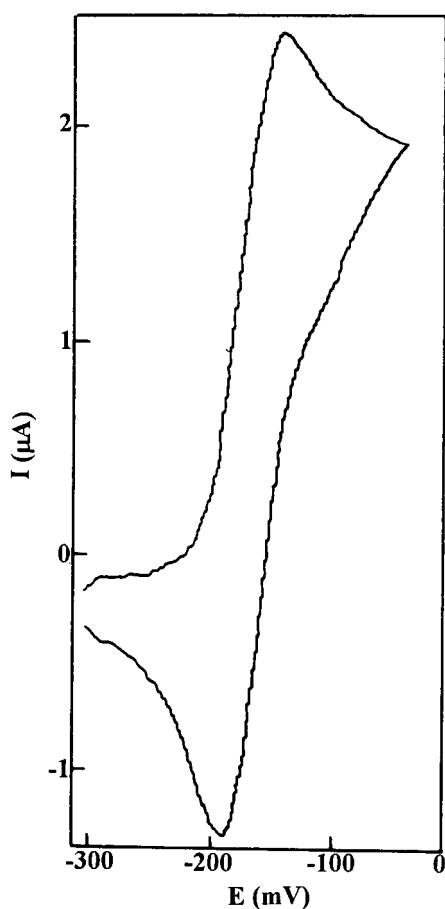
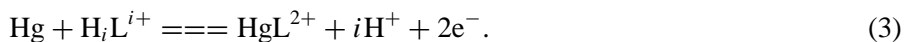


Figure 2. Cyclic voltammogram of 0.2 mM hexacyclen + 0.2 M sodium perchlorate at pH 8.6 and a scan rate of  $100 \text{ mV s}^{-1}$ .

with

$$(\alpha_{\text{H}})_{\text{L}} = [\text{L}]_{\text{F}}/[\text{L}] = 1 + K_1[\text{H}^+] + K_1K_2[\text{H}^+]^2 + \dots + K_1K_2 \dots K_i[\text{H}^+]^i \quad (2)$$

where  $K_1, K_2, \dots, K_i$  are protonation constants of the polyazamacrocycles used. The protonation constant values for the polyazamacrocycles used have already been reported in the literature [4]. Thus, based on the above mentioned facts, the 1 : 1  $\text{Hg}^{2+}$ -L complex formed can be represented as



By making the reasonable assumption that the diffusion coefficients of the  $\text{Hg}^{2+}$ -L complex and of  $\text{H}_i\text{L}^{i+}$  are equal [7, 27], the peak potential of this process can be written as [7, 23, 24].

$$(E_{\text{p}})_{\text{L}} = E_{\text{Hg}}^{\circ} + 0.0296 \log f_{\text{Hg}^{2+}} - 0.0296 \log K_{\text{HgL}}/(\alpha_{\text{H}})_{\text{L}} \quad (4)$$

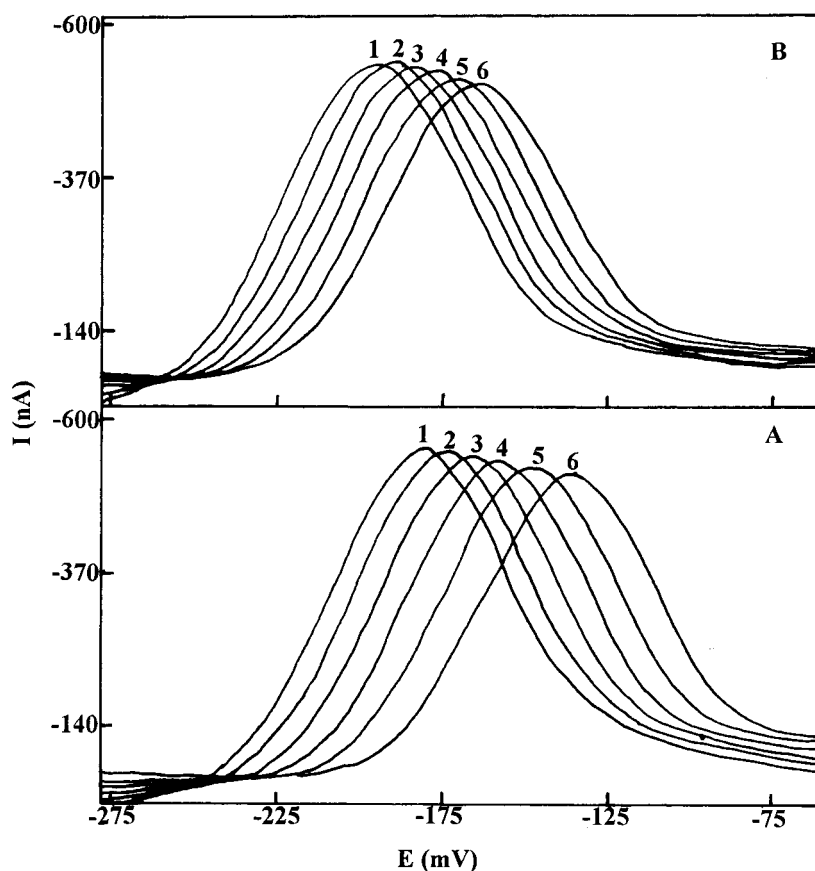


Figure 3. Anodic differential pulse polarograms of 0.2 mM pentacyclen + 0.2 M NaClO<sub>4</sub> at 25 °C and pH 8.6 (A) and 9.0 (B) in the presence of increasing amount of sodium selenate. The anion concentrations in mM are: (1) 0.0, (2) 1.0, (3) 2.0, (4) 3.0, (5), 4.0, (6) 5.0.

In contrast, in the presence of increasing concentration of the anions used, at a given pH, the  $E_p$  values shift to more positive values. With the assumption that a protonated polyamine molecule  $H_iL^{i+}$  interacts with a single anion  $A^{n-}$  to form a 1 : 1 complex  $H_iL^{i+} - A^{n-}$ , the concentration of the uncomplexed ligand,  $[L]_f$ , at DME is expressed as

$$\begin{aligned}
 [L]_f &= [L] + [HL^+] + [H_2L^{2+}] + \dots + [H_iL^{i+} - A^{n-}] \\
 &= (\alpha_H)_L[L] + \beta_L[L][H^+]^i K_1 K_2 \dots K_i [A^{n-}] \\
 &= (\alpha_H)_L'[L]
 \end{aligned}
 \tag{5}$$

where  $\beta_L$  is the 1 : 1 anion complexation constant

$$\beta_L = [H_iL^{i+} - A^{n-}] / [H_iL^{i+}][A^{n-}].
 \tag{6}$$

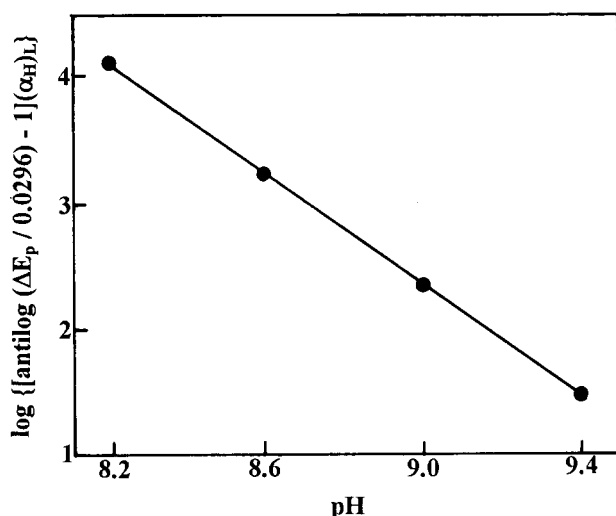


Figure 4. Plot of  $\log \{ [\text{antilog} (\Delta E_p / 0.0296) - 1] (\alpha_H)_L \}$  against pH for 0.2 mM pentacyclen + 1.0 mM  $\text{SeO}_4^{2-}$  at  $I = 0.2$  M ( $\text{NaClO}_4$ ) at 25 °C.

Thus, in the presence of anion  $A^{n-}$ , Equation (4) is modified to Equation (7):

$$(E_p)_A = E_{\text{Hg}}^\circ + 0.0296 \log f_{\text{Hg}^{2+}} - 0.0296 \log K_{\text{HgL}} / (\alpha_H)_{L'} \quad (7)$$

Then, the observed positive shift in  $E_p$  upon addition of the anions can be written as

$$\Delta E_p = (E_p)_A - (E_p)_L = 0.0296 [\log (\alpha_H)_{L'} - \log (\alpha_H)_L] \quad (8)$$

Equation (8) is simply rearranged to Equation (9).

$$[\text{antilog} (\Delta E_p / 0.0296) - 1] (\alpha_H)_L = \beta_L K_1 K_2 \dots K_i [\text{H}^+]^i [A^{n-}] \quad (9)$$

According to Equation (9), at a constant concentration of anion  $[A^{n-}]$ , a plot of the logarithm of the left hand side vs. pH should result in a straight line, with a slope corresponding to  $-i$  (Figure 4). It is noteworthy that, since the formation of the protonated charged macrocycles is strictly pH dependent [18], a relatively narrow pH range of about 8.0–9.5 was chosen in this study. Such a limited pH range has also been used in previous studies [7, 8]. On the other hand, at a given pH, a plot of the left hand side of Equation (9) against  $[A^{n-}]$  should afford straight lines passing through the origin (Figure 5). The  $\beta_L$  values can be easily determined from the slopes of such plots.

It is noteworthy that, under pH conditions where the protonated forms of the anions can also exist (i.e.,  $\text{H}_j\text{A}$ , where A denotes a completely proton-dissociated

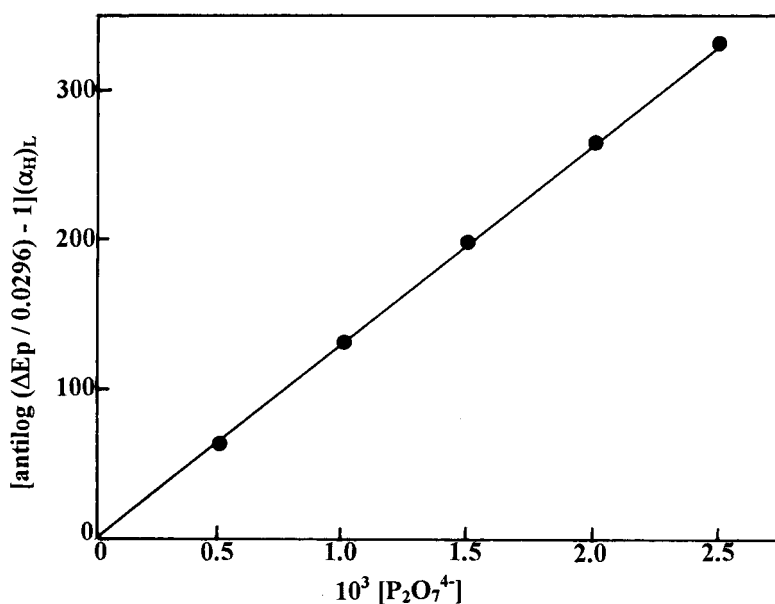


Figure 5. Plot of  $\text{antilog}(\Delta E_p/0.0296)(\alpha_H)_L$  against pyrophosphate concentration for 0.2 mM pentacyclen at pH = 9.0,  $I = 0.2$  M ( $\text{NaClO}_4$ ) and 25 °C.

form), the relationship between  $\Delta E_p$  and  $\beta_L(=[H_iL^{i-} + H_jA]/[H_iL^{i+}][H_mA])$  can be written as

$$[\text{antilog}(\Delta E_p/0.0296) - 1](\alpha_H)_L(\alpha_H)_A = \beta_L K_1 K_2 \dots K'_1 K'_2 \dots [A][H^+]^{i+j} \quad (10)$$

where  $(\alpha_H)_A = 1 + K'_1[H^+] + K'_1 K'_2 [H^+]^2 + \dots$  and  $K'_1, K'_2 \dots$  are the anion's protonation constants. In this case, the  $(i + j)$  and  $\beta_L$  values can be obtained from the slopes of the linear plots of the logarithm of the left hand side of Equation (10) vs. pH (at constant anion concentration) and the left hand side values against  $[A]$  (at constant pH), respectively. All formation constants calculated for different macrocycle–anion complexes are summarized in Table I.

#### 4. Discussion

In aqueous solution, polyazamacrocycles produce highly charged protonated cavities which can interact with anionic species. Electrostatic attraction and H-bonding are the main contributions to the stability of the resulting anion complexes. The formation of such anion complexes is strictly pH dependent so that variation in pH will result in the formation of various complex species [15, 17, 18]. The macrocycles hexacyclen and pentacyclen exhibit reversible well-behaved anodic polarograms in neutral pH buffers, which enable simple identification and characterization of their anion complexes in solution.

Table I. Formation constants for hexacyclen and pentacyclen complexes with various anions at 25 °C

Macrocyclen (L)	Anion (A)	pH range	(i + j) value	Complex formed	log $\beta$
Hexacyclen	$\text{SeO}_4^{2-}$	8.0–8.8	3.1	$\text{H}_3\text{L}^{3+} \cdot \text{A}^{2-}$	$4.13 \pm 0.05$
	$\text{SeO}_3^{2-}$	8.2–8.8	3.1	$\text{H}_3\text{L}^{3+} \cdot \text{A}^{2-}$	$4.06 \pm 0.13$
	$\text{HSeO}_3^-$	7.2–8.0	4.1	$\text{H}_3\text{L}^{3+} \cdot \text{HA}^-$	$3.87 \pm 0.08$
	$\text{P}_2\text{O}_7^{4-}$	8.2–8.8	3.0	$\text{H}_3\text{L}^{3+} \cdot \text{A}^{4-}$	$4.14 \pm 0.14$
	$\text{HP}_2\text{O}_7^{3-}$	7.2–8.2	4.0	$\text{H}_3\text{L}^{3+} \cdot \text{HA}^{3-}$	$4.23 \pm 0.08$
	$\text{MoO}_4^{2-}$	7.2–8.6	3.0	$\text{H}_3\text{L}^{3+} \cdot \text{A}^{2-}$	$2.14 \pm 0.08$
	$\text{WO}_4^{2-}$	7.2–8.6	3.1	$\text{H}_3\text{L}^{3+} \cdot \text{A}^{2-}$	$2.21 \pm 0.03$
Pentacyclen	$\text{SeO}_4^{2-}$	8.0–9.4	2.0	$\text{H}_2\text{L}^{2+} \cdot \text{A}^{2-}$	$3.64 \pm 0.7$
	$\text{SeO}_3^{2-}$	8.2–9.4	2.1	$\text{H}_2\text{L}^{2+} \cdot \text{A}^{2-}$	$3.50 \pm 0.04$
	$\text{HSeO}_3^-$	7.2–8.0	3.2	$\text{H}_2\text{L}^{2+} \cdot \text{HA}^-$	$3.35 \pm 0.05$
	$\text{P}_2\text{O}_7^{4-}$	8.2–9.4	2.0	$\text{H}_2\text{L}^{2+} \cdot \text{A}^{4+}$	$3.43 \pm 0.06$
	$\text{HP}_2\text{O}_7^{3-}$	7.2–7.8	3.1	$\text{H}_2\text{L}^{2+} \cdot \text{HA}^{3-}$	$3.87 \pm 0.03$
	$\text{MoO}_4^{2-}$	7.2–8.6	2.1	$\text{H}_2\text{L}^{2+} \cdot \text{A}^{2-}$	$2.11 \pm 0.12$
	$\text{WO}_4^{2-}$	7.2–8.6	2.0	$\text{H}_2\text{L}^{2+} \cdot \text{A}^{2-}$	$2.11 \pm 0.09$

The apparent formation constants for hexacyclen and pentacyclen complexes with pyrophosphate, selenite, selenate, molybdate and tungstate anions obtained by differential pulse polarography are listed in Table I. It should be noted that the polarographic methods can give values of the apparent formation constant under a given set of experimental conditions. But, on the microscopic level, the host-guest interactions studied certainly involve binding of the guest anions to each of the various protonated aza-macrocycles present in the ensemble average, so the explicit designation of one complex formation equation seems to be somehow misleading.

As shown in Table I, in all systems studied here only 1 : 1 receptor : anion species have been formed in solution. As usually observed in this kind of protonated amine-anion systems [11, 15, 28], for a given polyammonium receptor, the stability of the anion complexes increases with the protonation degree of the ligand. Thus, in neutral pH, the minimum protonation degree of the ligand required for making the receptor–anion interaction appreciable was found to be 2 for pentacyclen and 3 for hexacyclen (Table I).

The data given in Table I reveal that, in the case of all anions used, hexacyclen forms a more stable anion complex than does pentacyclen. Since, at the pH range studied, hexacyclen is in its triprotonated form while pentacyclen is diprotonated, the increased charge density should be the main factor contributing to the observed increased stability of the hexacyclen complexes. Moreover, molecular models in-



dicates that the resulting receptor-anion complexes are at least compatible with the sizes and shapes of the macrocyclic receptor and the substrates [12]. Thus, the smaller ring size of pentacyclen for the anions used could be disadvantageous for the ion-pair hydrogen bondings.

The stability data show that the most stable complexes are formed between the most charged species. Thus, it is obvious that the major role in second-coordination-sphere interactions between the charged species involved is played by coulombic forces, though other factors such as H-bonding and the receptors topology could also be of significance [11, 15, 28, 29]. The elongated structure of  $P_2O_7^{4-}$  facilitates the formation of multiple electrostatic and hydrogen bond interactions with the polyammonium macrocycles, resulting in the most stable complexes in the series [18]. It is interesting to note that the preference of both protonated macrocycles used for  $HP_2O_7^{3-}$  of smaller charge over  $P_2O_7^{4-}$  may be due to the availability of the  $HP_2O_7^{3-}$  proton for interaction via H-bonding with non-protonated nitrogens of the macrocycles, as pointed out in the literature [29].

It is interesting to note that, among bivalent anions used, the  $MoO_4^{2-}$  and  $WO_4^{2-}$  ions with both macrocycles are 20 to 100 times less stable than those with  $SeO_3^{2-}$  and  $SeO_4^{2-}$ . A possible reason would be the lower basicity of molybdate and tungstate anions [30] which result in their decreased tendency for H-bonding with the protonated macrocycles. Moreover, the complementarity between the topological requirements of the protonated receptors and the anionic substrates seem to be of great importance. In the cases where the anion can penetrate inside the macrocyclic cavity, a more stable complex is expected to be formed, in comparison with the case where it is located external to the receptor's cavity. Based on the experimental data, da Silva et al. [29] have suggested a structure for the inclusion complex of  $SeO_4^{2-}$  ion with the macrocycle OBISDIEN in which the selenate ion is hydrogen bonded to four protonated nitrogens inside the cavity of the macrocyclic ligand.

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