

# Anion Complexation by Calix[3]thieno[1]pyrrole: The Medium Effect

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The interaction of calix[3]thieno[1]pyrrole, **1**, and halide and dihydrogen phosphate anions in a variety of solvents (acetonitrile, propylene carbonate, *N,N*-dimethylformamide, and dimethyl sulfoxide) has been investigated through <sup>1</sup>H NMR, conductance measurements, and titration calorimetry. <sup>1</sup>H NMR measurements reveal the sites of interaction of the ligand with the anions in CD<sub>3</sub>CN while the composition of the complex was determined through conductance measurements. A quantitative assessment of anion–ligand interactions is provided. Thus the thermodynamics of complexation of **1** with halide and dihydrogen phosphate anions in dipolar aprotic media at 298.15 K is reported. These data are interpreted in terms of the thermodynamics of transfer of reactants and product from a reference solvent (acetonitrile) to other solvents. The crucial role played by the solvent on the ability of the ligand to interact with anions and on the composition of the complex is demonstrated.

## Introduction

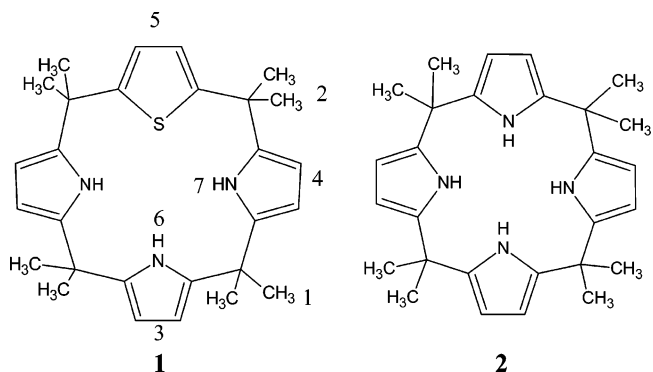
Modern supramolecular chemistry has its beginning in 1967 when Pederson<sup>1</sup> demonstrated the cation binding ability of crown ethers. This development encouraged the design of cation receptors to the extent that this area has expanded significantly in the last three and a half decades. However the number of ligands able to interact with anions is comparatively small. This is not surprising due to the various factors to be considered in the design of anion receptors. These have been discussed in an excellent paper by Dietrich.<sup>2</sup>

Calixpyrroles (products of the condensation reaction between pyrrole and acetone in acid medium)<sup>3</sup> have shown to be efficient receptors for the selective recognition of anions.<sup>4</sup> We have recently reported the thermodynamics of complexation of calix[4]pyrrole with spherical and nonspherical anions in dipolar aprotic media.<sup>5,6</sup> However we are strongly of the view that more effort is required in the field of thermodynamics of calixpyrrole chemistry. Indeed most data available on these systems are limited to stability constants in a few solvents.<sup>7–9</sup> This parameter defines quantitatively the selective or nonselective behavior of a receptor for one species relative to another in a given solvent and temperature. Quantitative knowledge of the stability of anion–calixpyrrole systems is of fundamental importance in anion recognition processes. However for a detailed thermodynamic characterization of these processes, there are several aspects to be considered such as (i) the thermodynamic origin (enthalpy and entropy) of stability of complex formation and (ii) the solvation effect of reactants and product on the thermodynamics of complexation of these systems. Another important aspect (although not considered in this paper) is that related to heat capacity measurements. In our knowledge there is little (if any) information available on heat capacity for systems involving anion binding by calix[4]pyrroles.

In this paper a detailed thermodynamic investigation of anion complexation involving calix[3]thieno[1]pyrrole, **1**, in various

dipolar aprotic media (*N,N*-dimethylformamide, DMF; dimethyl sulfoxide, DMSO; propylene carbonate, PC; and acetonitrile, MeCN) at 298.15 K is reported. The medium effect on the complexation process is discussed in terms of the transfer thermodynamics of the reactants and the product from a reference solvent (MeCN) to other solvents. In the achievement of the above objectives, several techniques (<sup>1</sup>H NMR spectroscopy, conductance measurements, and calorimetry) are explored.

The results obtained from this investigation are compared with thermodynamic data for an analogous calix[4]pyrrole derivative, **2**, previously reported by us.<sup>5</sup>



## Experimental Section

**(a) Chemicals.** Thiophene, pyrrole, and *n*-butyllithium were all purchased from Aldrich. Hexane, ethanol, and acetone (HPLC grade, Fisher) were used without further purification. Acetonitrile, MeCN (Aldrich), was first refluxed in a nitrogen atmosphere with calcium hydride for several hours and then distilled.<sup>10</sup> *N,N*-Dimethylformamide, DMF (HPLC grade, Aldrich), was dried using 4A molecular sieves (which was previously dried in an oven at 300 °C for several hours).<sup>10</sup> Propylene carbonate anhydrous, PC (99.7%, Aldrich), was used without further purification. Tetra-*n*-butylammonium fluoride, chloride, bromide, iodide, hydrogen sulfate, perchlorate, nitrate,

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and dihydrogen phosphate (Aldrich) were dried over  $P_4O_{10}$  under vacuum for several days before use.

**(b) Synthesis of Calix[3]thieno[1]pyrrole (1).** The treatment of thiophene with *n*-butyllithium followed by the addition of acetone afforded the corresponding 2,5-bis[ $\alpha$ -hydroxy- $\alpha$ , $\alpha$ -dimethylmethyl]thiophene (I) as reported earlier.<sup>11</sup> On the basis of the reactions previously employed for the formation of dipyrromethanes,<sup>12</sup> compound (I) was treated with an excess amount of pyrrole in the presence of boron trifluoride etherate to afford 2,5-bis[( $\alpha$ -pyrrolyl- $\alpha$ , $\alpha$ -dimethyl)methyl]thiophene (II). A solution of II (1 g, 3.35 mmol), pyrrole (0.2 mL, 3 mmol), and acetone (0.4 mL, 6 mmol) in MeCN (150 mL) was stirred at 0 °C under a nitrogen atmosphere. Boron trifluoride etherate (40  $\mu$ L, 0.32 mmol) was added and stirred at 0 °C for 30 min. The obtained precipitate was filtered off and recrystallized from acetone (yield 65%). Anal. Calcd for  $C_{28}H_{35}N_3S$ : C, 75.46; H, 7.92; N, 9.43. Found: C, 75.62; H, 8.01; N, 9.63.  $^1H$  NMR ( $CD_3CN$ ) (298 K),  $\delta$  (ppm): 7.84 (bs, 1H), 7.41 (bs, 2H), 6.65 (s, 2H), 5.84–5.85 (d, 2H), 5.76–5.77 (d, 4H), 1.55 (s, 12H), 1.50 (s, 12H). FAB-MS ( $m/z$ ): 446 [ $M^+$ ], found: 445.664.

**(c) Solubility Measurements.** To determine the solubility of calix[3]thieno[1]pyrrole in the various solvents, saturated solutions of **1** in the appropriate solvent were prepared. The mixtures were left in a thermostat at 298.15 K for 3 days until equilibrium was reached. Aliquots of the saturated solutions were taken from the same equilibrium mixture and analyzed gravimetrically in triplicate. Blank experiments were carried out to ensure the absence of any nonvolatile material in the pure solvent. The possibility of solvate formation of **1** in the various solvents was checked by exposing the solid to a saturated atmosphere of the appropriate solvent for several days.<sup>13</sup>

**(d)  $^1H$  NMR Measurements.**  $^1H$  NMR measurements were recorded at 298 K on a Bruker AC-300E pulsed Fourier transform NMR spectrometer. Typical operating conditions for routine proton measurements involved “pulse” or flip angle of 30°, spectral frequency (SF) of 300.135 MHz, delay time of 1.60 s, acquisition time (AQ) of 1.819 s, and line broadening of 0.55 Hz. Solutions of calix[3]thieno[1]pyrrole in the appropriate deuterated solvent ( $1\text{--}5 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ ) were placed in 5 mm NMR tubes using TMS as the internal reference to measure the spectrum of the ligand. Then additions of anion salt solutions in the same solvent ( $1\text{--}2 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ ) were made. Changes in the chemical shifts upon the addition of the anion salt relative to the free ligand were calculated.

**(e) Conductance Measurements.** Conductance measurements at 298.15 K were carried out with a Wayne-Kerr Autobalance Universal bridge, type B642. The determination of the conductivity cell constant was carried out as described elsewhere.<sup>14</sup> A solution containing the anion salt (concentration range from  $4 \times 10^{-5}$  to  $6 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ ) in the appropriate solvent was titrated with the ligand solution in the same solvent.

**(f) Titration Calorimetry.** Stability constants (expressed as  $\log K_s$ ) and enthalpies of complexation of calix[3]thieno[1]pyrrole with the appropriate anion in different solvents were determined by calorimetry using a Tronac 450 titration calorimeter<sup>15</sup> or the 2277 thermal activity monitor (TAM).<sup>16</sup> As far as the former is concerned the reliability of the equipment was tested by using the protonation reaction of tris(hydroxymethyl)aminomethane (THAM) with hydrochloric acid suggested by Wilson and Smith.<sup>17</sup> The value obtained ( $\Delta_r H^\circ = -47.5 \pm 0.6 \text{ kJ mol}^{-1}$ ) was in excellent agreement with that reported in the literature ( $-47.49 \text{ kJ mol}^{-1}$ ).<sup>18</sup> For calorimetric determinations using the Tronac 450, a solution of the ligand in the appropriate solvent ( $1 \times 10^{-3}$  to  $6 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ ) was titrated in a

**TABLE 1: Solubility and Derived Gibbs Energies of Solution of **1** in Various Solvents at 298.15 K and Transfer Gibbs Energies from Acetonitrile (Reference Solvent)**

solvent <sup>a</sup>	solubility/ $\text{mol}\cdot\text{dm}^{-3}$	$\Delta_s G^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_t G^\circ$ (MeCN $\rightarrow$ s)
MeCN	$(9.38 \pm 0.05) \times 10^{-3}$	11.57	0.00
MeOH	$(2.36 \pm 0.03) \times 10^{-3}$	15.01	3.43
EtOH	$(3.32 \pm 0.03) \times 10^{-3}$	14.15	2.58
$C_6H_5CH_3$	$(1.17 \pm 0.01) \times 10^{-2}$	11.02	−0.53
DMF	$(1.85 \pm 0.04) \times 10^{-2}$	9.89	−1.68
DMSO	$(1.06 \pm 0.04) \times 10^{-2}$	11.02	−0.55
PC	$(3.34 \pm 0.06) \times 10^{-3}$	14.13	2.56
$CHCl_3$	very soluble		
$CH_2Cl_2$	very soluble		

<sup>a</sup> Abbreviations used: MeCN, acetonitrile; MeOH, methanol; EtOH, ethanol;  $C_6H_5CH_3$ , toluene; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide; PC, propylene carbonate;  $CHCl_3$ , chloroform;  $CH_2Cl_2$ , dichloromethane.

solution (50 mL) containing the anion salt (concentration range,  $5 \times 10^{-3}$  to  $2 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$ ) in the same solvent.

For measurements carried out with the TAM calorimeter, chemical calibration was carried out. For this purpose the stability constant ( $\log K_s$ ) and the enthalpy of complexation,  $\Delta_c H^\circ$ , of 18-crown-6 and  $Ba^{2+}$  in water at 298.15 K were determined.<sup>19</sup> For complexation studies involving **1** and  $H_2PO_4^-$  anion in MeCN and PC, a solution of the ligand ( $1 \times 10^{-3}$  to  $6 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ ) was placed in the vessel and the anion salt (concentration range,  $2 \times 10^{-2}$  to  $5 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$ ) in the syringe. The dihydrogen phosphate anion salt solution was injected incrementally using a 0.5  $\text{cm}^3$  gastight motor-driven Hamilton syringe. In each titration experiment, 24 injections were made at time intervals of 35 min. Corrections for the heat of dilution of the titrant in the solvent were made. A computer program for TAM (Digitam 4.1 for Windows from Thermometric AB and Scitech Software AB, Sweden) was used to calculate the stability constant ( $\log K_s$ ) and the enthalpy of complexation ( $\Delta_c H^\circ$ ) for the process under investigation.

## Results and Discussion

**Solubilities and Derived Standard Gibbs Energies of Solution. Transfer Gibbs Energies from Acetonitrile.** Solubility measurements were performed to ensure that **1** was soluble enough in the appropriate solvent to carry out the experimental work required for the derivation of (i) thermodynamic data for the complexation process involving this ligand and various anions and (ii) the enthalpy of solution of this ligand in the appropriate solvent.

Solubility data are reported in Table 1. These are the result of several analytical measurements carried out on the same equilibrium mixture. Solvate formation was observed when a solid sample of **1** was exposed to saturated atmospheres of chloroform and dichloromethane. Given that the calculation of the standard Gibbs energy of solution,  $\Delta_s G^\circ$  requires the same composition of **1** in both phases, no further calculations were made for this ligand in these two solvents. In the absence of solvation,  $\Delta_s G^\circ$  values were calculated from  $\Delta_s G^\circ = -RT \ln S$ , where  $S$  is the solubility of the ligand on the molar scale. These are listed in Table 1. These data are referred to the standard state of  $1 \text{ mol dm}^{-3}$ . Since both the crystal lattice,  $\Delta_{cl} G^\circ$ , and the solvation Gibbs energies,  $\Delta_{sol} G^\circ$ , contribute to the  $\Delta_s G^\circ$ , the contribution of the former process is removed by the calculation of the standard transfer Gibbs energies,  $\Delta_t G^\circ$ , of **1** from a reference solvent ( $s_1 = \text{MeCN}$ ) to another  $s_2$ . These data reflect the difference in solvation of this receptor in  $s_2$  relative to  $s_1$ . Thus these values are also included in Table 1. The variations observed in  $\Delta_t G^\circ$  values for this ligand from

**TABLE 2:** Changes in the  $^1\text{H}$  NMR Chemical Shifts for (1) and Anions Complexes in (a)  $\text{CD}_3\text{CN}$  and (b)  $d_6$ -DMSO at 298 K

(a) $\text{CD}_3\text{CN}$							
	$\Delta\delta$ (ppm)						
	$\text{H}_{\text{methyl}}$ (1)	$\text{H}_{\text{methyl}}$ (2)	$\text{H}_{\text{pyrrole}}$ (3)	$\text{H}_{\text{pyrrole}}$ (4)	$\text{H}_{\text{thiophene}}$ (5)	$\text{H}_{\text{NH}}$ (6)	$\text{H}_{\text{NH}}$ (7)
free ligand (1)	1.505	1.553	5.769	5.848	6.654	7.418	7.843
$\text{F}^-$	0.060	0.037	-0.264	-0.157	0.129	3.820	
$\text{Cl}^-$	0.065	0.036	-0.239	-0.137	0.069	2.251	2.916
$\text{Br}^-$	0.047	0.002	-0.226	-0.065	0.022	0.670	0.751
$\text{I}^-$	-0.002	-0.003	-0.007	-0.004	0.008	0.090	0.048
$\text{H}_2\text{PO}_4^-$	0.050	0.010	-0.124	0.019	0.036	0.571	0.720
$\text{HSO}_4^-$	0.048	0.000	-0.002	-0.008	0.008	0.026	0.057
$\text{ClO}_4^-$	-0.002	0.007	0.000	0.007	0.009	0.008	-0.002
$\text{NO}_3^-$	0.051	0.005	-0.003	-0.003	0.007	0.069	0.077

(b) $d_6$ -DMSO							
	$\Delta\delta$ (ppm)						
	$\text{H}_{\text{methyl}}$ (1)	$\text{H}_{\text{methyl}}$ (2)	$\text{H}_{\text{pyrrole}}$ (3)	$\text{H}_{\text{pyrrole}}$ (4)	$\text{H}_{\text{thiophene}}$ (5)	$\text{H}_{\text{NH}}$ (6)	$\text{H}_{\text{NH}}$ (7)
free ligand (1)	1.504	1.538	5.729	5.703	6.689	8.576	9.111
$\text{F}^-$	-0.012	-0.004	-0.140	-0.105	0.017	3.295	
$\text{Cl}^-$	0.001	0.001	-0.017	0.007	0.002	0.041	0.071
$\text{Br}^-$	0.002	0.001	-0.007	-0.002	0.002	0.003	0.009
$\text{I}^-$	-0.003	-0.001	-0.002	-0.001	0.000	0.003	0.005
$\text{H}_2\text{PO}_4^-$	0.003	0.002	-0.017	-0.012	0.001	0.116	0.158
$\text{HSO}_4^-$	0.005	0.022	-0.011	-0.007	0.008	0.002	0.004
$\text{ClO}_4^-$	0.005	0.022	-0.017	-0.007	0.008	0.002	0.011
$\text{NO}_3^-$	0.008	0.023	0.009	-0.010	0.007	0.011	0.004

MeCN to the various solvents are rather small ranging from 3.43 to  $-1.68 \text{ kJ mol}^{-1}$  in transfers to methanol and DMF, respectively. A direct implication of this statement is that as far as this ligand is concerned its solvation changes from one medium to another are relatively small as to make any significant contribution (favorable or unfavorable) to the stability (or lack of it) of complex formation in one medium relative to another. Availability of data for an analogous derivative,<sup>5</sup> namely, **2**, shows that the replacement of one pyrrole in **2** by a thiophene unit has led to a small decrease in solubility in most solvents, except DMF. However there is a small degree of selective solvation for **1** in transfers to DMF, DMSO, and PC while for **2**,  $\Delta_r G^\circ$  values from MeCN to these solvents are  $\approx 0 \text{ kJ mol}^{-1}$ .

To assess the sites of interactions of anions with **1**, proton NMR measurements in  $\text{CD}_3\text{CN}$  and  $d_6$ -DMSO were carried out at 298 K, and these are now discussed.

**$^1\text{H}$  NMR Measurements.** For these measurements, two representative solvents were chosen, a protophobic ( $\text{CD}_3\text{CN}$ ) and a protophilic ( $d_6$ -DMSO) dipolar aprotic solvent. Table 2 reports the proton signals for the free ligand in  $\text{CD}_3\text{CN}$  and  $d_6$ -DMSO as well as the chemical shift changes that protons 1 and 2 (methyl), 3 and 4 (pyrrole), 5 (thiophene), and 6 and 7 (NH) undergo after addition of the anion salt to the ligand. As far as  $\text{CD}_3\text{CN}$  is concerned, it is observed that (i) the most significant changes are observed for the amine (6 and 7) and the pyrrolic (3 and 4) protons and (ii) the magnitude of the chemical shift changes increases with the electronegative character of the anion.

These findings provide a clear indication that **1** interacts with anions via hydrogen bond formation.

However, proton NMR studies in  $d_6$ -DMSO at 298 K (Table 2) show that, among these anions, only significant chemical shift changes in the pyrrolic (3 and 4) and amine (6 and 7) protons are observed via the addition of  $\text{F}^-$  to the ligand in this solvent. It was found that the addition of increasing amounts

**TABLE 3:** Changes in the  $^1\text{H}$  NMR Chemical Shifts for 2 and Anion Complexes in  $d_6$ -DMSO at 298 K

	$\Delta\delta$ (ppm)		
	$\text{H}_{\text{methyl}}$	$\text{H}_{\text{pyrrole}}$	$\text{H}_{\text{NH}}$
free ligand	1.522	5.700	9.269
$\text{F}^-$	0.042	-0.283	3.597
$\text{Cl}^-$	0.015	-0.025	2.090
$\text{Br}^-$	0.033	-0.057	0.304
$\text{I}^-$	-0.003	-0.008	0.003
$\text{H}_2\text{PO}_4^-$	0.045	-0.035	2.087
$\text{HSO}_4^-$	0.002	-0.001	0.006
$\text{ClO}_4^-$	0.002	-0.001	0.003
$\text{NO}_3^-$	-0.003	0.000	0.003

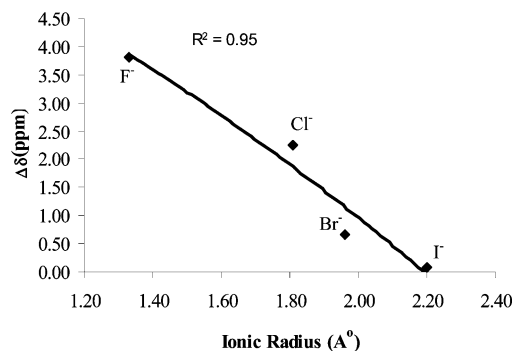
of  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HSO}_4^-$ ,  $\text{NO}_3^-$ , and  $\text{ClO}_4^-$  anion salts to **1** in  $d_6$ -DMSO caused no changes in the NMR spectra of this ligand. The  $^1\text{H}$  NMR data (Table 2) for the free ligand in these solvents show significant downfield shifts in the NH protons in moving from  $\text{CD}_3\text{CN}$  to  $d_6$ -DMSO. These are indicative that the latter solvent is likely to interact with the ligand through hydrogen bond formation between the NH protons and the basic oxygens of the solvent. Therefore the ability of the ligand to interact with anions is likely to be significantly reduced in  $d_6$ -DMSO relative to  $\text{CD}_3\text{CN}$ .

For comparison purposes  $^1\text{H}$  NMR studies for the complexation of **2** with anions were conducted in  $d_6$ -DMSO, and the results are included in Table 3. As far as **2** is concerned, significant chemical shift changes in the NH protons are observed by the addition of  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{H}_2\text{PO}_4^-$  to the ligand in this solvent. The addition of increasing amounts of  $\text{HSO}_4^-$ ,  $\text{NO}_3^-$ , and  $\text{ClO}_4^-$  did not show any significant chemical shift changes relative to the free ligand in this solvent.

Going back to data in  $\text{CD}_3\text{CN}$ , a relationship is found between the  $\Delta\delta$  values for the pyrrole NH protons and the ionic radius for halide anions<sup>20</sup> in  $\text{CD}_3\text{CN}$  (Figure 1) where the most significant change is observed for the fluoride anion. Insignificant chemical shift changes are observed for **1** and the iodide anion.

To further investigate anion complexation of  $\text{H}_2\text{PO}_4^-$  and **1** in solution, NMR titrations were conducted. Thus **1** was titrated with tetra-*n*-butylammonium dihydrogen phosphate in  $\text{CD}_3\text{CN}$ . Considerable downfield shifts of the pyrrolic NH protons are observed. The results show that the complexation is fast on the NMR time scale and furthermore suggests that the dihydrogen phosphate anion interacts with **1** through hydrogen bonding. Inspection of Figure 2 gives preliminary knowledge about the stoichiometry of the complex which appears to be 2:1 ( $\text{1/H}_2\text{PO}_4^-$ ) mole ratio. This fact is reflected in the shift observed in the resonance values of the pyrrolic NH protons.

To compare the solution binding properties of **1** relative to **2**, the chemical shift changes of the pyrrolic protons in  $\text{CD}_3\text{CN}$

**Figure 1.** Relationship between ionic radii of halide anions and  $\Delta\delta$  values for the pyrrole NH proton at 298 K.



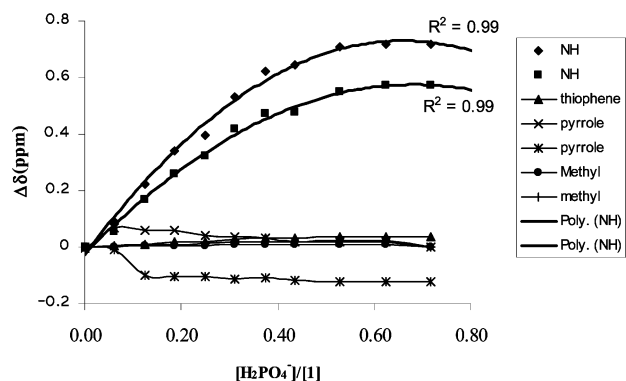


Figure 2.  $^1\text{H}$  NMR titration plot of **1** with DHP in  $\text{CD}_3\text{CN}$  at 298 K.

are considered (Table 2a). Both ligands exhibit similar pyrrole-H chemical shift changes upon the addition of excess amounts of  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , and  $\text{H}_2\text{PO}_4^-$  anions. On the other hand, the pyrrole-NH proton of **2** shows greater downfield shifts for fluoride (up to  $\Delta\delta = 5.18$  ppm)<sup>5</sup> than **1** ( $\Delta\delta = 3.82$  ppm). It appears that the replacement of one pyrrole in **2** by a thiophene ring, **1**, alters the affinity of this receptor for anions in  $\text{CD}_3\text{CN}$  solutions.

Encouraged by the NMR results, conductance measurements were carried out in order to establish the composition of the anion complexes and to gain semiquantitative information regarding the strength of complexation of the ligand with a given anion in a given medium. The results are discussed in the following section.

**Conductometric Titration.** Conductometric titrations were carried out in MeCN, DMF, DMSO, and propylene carbonate, PC, at 298.15 K. According to the ion–ligand strength, plots of molar conductance,  $\Lambda_m$  ( $\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ ), against the ligand/anion ratio showed two different patterns for complexes of moderate stability (broad break at the curvature so the composition of the complex was determined by extrapolating the lines at high and low ligand/anion mole ratios) and weak (slight or nonexistent changes) in the slope. As far as MeCN is concerned, 1:1 complexes of moderate stability were found for  $\text{F}^-$ ,  $\text{Cl}^-$ , and  $\text{Br}^-$  while a complex of 2:1 stoichiometry was formed

between  $\text{H}_2\text{PO}_4^-$  and **1** in this solvent. Representative examples of conductometric titration curves for  $\text{F}^-$  and  $\text{H}_2\text{PO}_4^-$  are shown in Figure 3. Since the electrolyte was placed in the vessel and then it was titrated with the ligand, the decrease in the conductance is attributed to the large size of the complexed anion as compared with that of the free anion. Very small changes in conductance were recorded and no slopes were observed for titrations involving iodide, nitrate, perchlorate, and hydrogen sulfate anions in this solvent. These findings were taken as indicative of the absence of interactions between this ligand and these anions in this solvent. As far as DMF is concerned, changes in the slope of the conductometric titration curve were only observed for fluoride and chloride anions. No changes were observed by the addition of the ligand to solutions containing  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{H}_2\text{PO}_4^-$ , and  $\text{HSO}_4^-$  anions. When the medium was PC the behavior observed in the conductometric titration curves for the halide anions were similar to that in MeCN where moderate complexation of **1** with  $\text{F}^-$ ,  $\text{Cl}^-$ , and  $\text{Br}^-$  was found. However in moving from MeCN to PC the composition of the complex with  $\text{H}_2\text{PO}_4^-$  is altered from a 2:1 to a 1:1 ligand/ $\text{H}_2\text{PO}_4^-$  mole ratio as shown in Figure 3.

In DMSO, complexation was only observed with the fluoride anion where the conductometric titration curve (Figure 3) shows a clear break at the 1:1 stoichiometry. No changes in the slope of the titration curves were observed for other anions ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{H}_2\text{PO}_4^-$ , and  $\text{HSO}_4^-$ ) in this solvent. These results demonstrate the striking effect of the solvent on the complexation of **1** and anions.

To examine the effect of the presence of one thiophene ring in the hybrid calixpyrrole **1**, its conductometric titration plots were compared with those of calix[4]pyrrole **2** in MeCN at 298.15 K. For the latter ligand, a stronger break in the curvature of the titration curves was observed upon complexation with anions. NMR and conductometric studies show that **1** has higher affinity for the halide anions than **2** in MeCN. Unlike **2** which shows a 1:1 ( $2/\text{H}_2\text{PO}_4^-$ ) stoichiometry in MeCN at 298.15 K, **1** shows a 2:1 ( $1/\text{H}_2\text{PO}_4^-$ ) complex in this solvent.

To explain the different binding ability of **1** for anions in different media as well as the changes observed in the

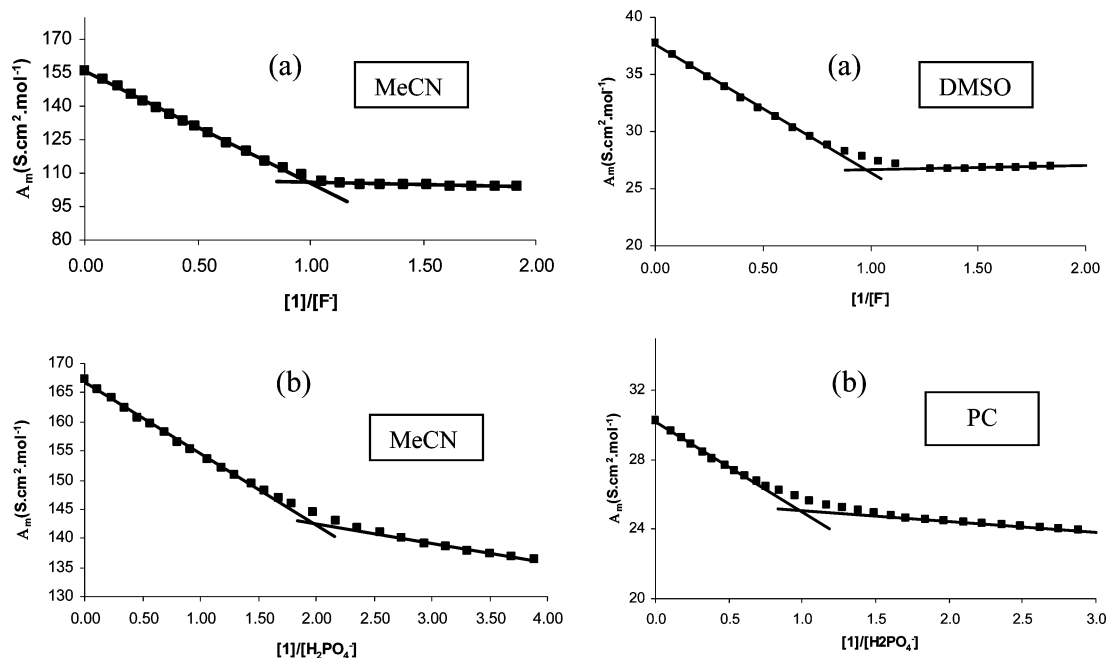


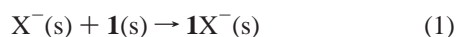
Figure 3. Conductometric titration curve for the titration of (a) the fluoride anion (with tetra-*n*-butylammonium as counterion) with **1** in MeCN and DMSO (b) dihydrogen phosphate anion (with tetra-*n*-butylammonium as counterion) in MeCN and PC at 298.15 K.

**TABLE 4: Thermodynamic Parameters for the Complexation of Anions and **1** in Acetonitrile, *N,N*-Dimethylformamide, Dimethyl Sulfoxide, and Propylene Carbonate at 298.15 K**

anion	log $K_s$	$\Delta_c G^\circ /$ kJ·mol <sup>-1</sup>	$\Delta_c H^\circ /$ kJ·mol <sup>-1</sup>	$\Delta_c S^\circ /$ J·K <sup>-1</sup> ·mol <sup>-1</sup>
Acetonitrile				
F <sup>-</sup>	5.25 ± 0.01	-29.9 ± 0.1	-31.5 ± 0.1	-5
Cl <sup>-</sup>	4.15 ± 0.07	-23.7 ± 0.4	-51.7 ± 0.5	-95
Br <sup>-</sup>	3.46 ± 0.02	-19.7 ± 0.1	-34.6 ± 0.1	-49
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	3.97 ± 0.10 (1:1)	-22.7 ± 0.1	-43.7 ± 0.4	-70
	3.72 ± 0.10 (2:1)	-21.2 ± 0.2	-17.8 ± 0.1	11
<i>N,N</i> -Dimethylformamide				
F <sup>-</sup>	3.71 ± 0.02	-21.3 ± 0.1	-9.2 ± 0.4	40
Cl <sup>-</sup>	3.48 ± 0.04	-19.8 ± 0.2	-21.3 ± 0.9	-5
Dimethyl Sulfoxide				
F <sup>-</sup>	2.12 ± 0.07	-12.1 ± 0.4	-24.5 ± 0.3	-42
Propylene Carbonate				
F <sup>-</sup>	4.37 ± 0.02	-24.9 ± 0.1	-13.5 ± 0.1	38
Cl <sup>-</sup>	4.00 ± 0.10	-22.8 ± 0.6	-18.1 ± 0.2	16
Br <sup>-</sup>	3.77 ± 0.10	-21.6 ± 0.5	-7.7 ± 0.4	46
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	4.22 ± 0.20	-24.1 ± 0.3	-21.7 ± 0.2	8

composition of **1** with H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, solvent-ion and solvent-ligand interactions need to be considered, and this will be discussed once the thermodynamics of the complexation process in the various solvents has been accomplished.

**Thermodynamics of Complexation.** As previously shown tetra-*n*-butylammonium salts are fully dissociated in MeCN, DMF, DMSO, and PC within the range of concentrations used in this work.<sup>5,6,21</sup> Therefore from the information gained from the previous section regarding the composition of the anionic complexes, thermodynamic data for 1:1 complexes of anionic species X<sup>-</sup> are referred to the process shown in eq 1

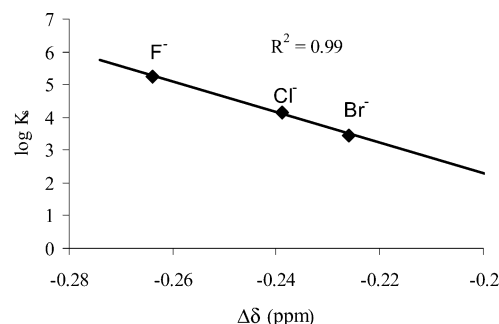


For H<sub>2</sub>PO<sub>4</sub><sup>-</sup> in MeCN, a second process takes place as shown in eq 2



Thus Table 4 lists stability constants (expressed as log  $K_s$ ), derived standard Gibbs energies,  $\Delta_c G^\circ$ , enthalpies,  $\Delta_c H^\circ$ , and entropies,  $\Delta_c S^\circ$ , of complexation of **1** and anions in MeCN, DMF, DMSO, and PC at 298.15 K. In most cases the process is enthalpically controlled, except for F<sup>-</sup> and **1** in DMF and Br<sup>-</sup> and this ligand in PC. For the F<sup>-</sup>-**1** system in PC, both the enthalpy and entropy contribute almost equally to the Gibbs energy or stability of the complex. The most striking feature of these results is found in MeCN relative to PC. Thus the selectivity trend observed for the halides is the same; however, for the former solvent, the process is enthalpically controlled, while for the latter, both enthalpy and entropy contribute to complex stability. Stability constant data are in accord with the chemical shift changes observed in the <sup>1</sup>H NMR spectra for the pyrrole proton in CD<sub>3</sub>CN at 298 K. This statement is corroborated by the linear relationship ( $r^2 \approx 0.99$ ) found between the stability constant (expressed as log  $K_s$ ) of **1** and anions and the chemical shift changes ( $\Delta\delta$ , ppm) for the pyrrole proton, as shown in Figure 4.

In an attempt to assess the effect of the thiophene ring on the complexation thermodynamics of the system, the data of calix[3]thieno[1]pyrrole are compared with those previously found for calix[4]pyrrole, **2**. Both ligands show good affinity for anions in MeCN and DMF. The most distinctive feature of the data is that the stability for anion-calix[4]pyrrole complexes

**Figure 4.** Linear relationship between log  $K_s$  and  $\Delta\delta$  values for the pyrrole proton in CD<sub>3</sub>CN at 298 K.**TABLE 5: Enthalpies of Solution of Calix[3]thieno[1]pyrrole (**1**) in Acetonitrile, *N,N*-Dimethylformamide, Dimethyl Sulfoxide, and Propylene Carbonate at 298.15 K**

MeCN		DMF	
$c/\text{mol}\cdot\text{dm}^{-3}$	$\Delta_s H/\text{kJ}\cdot\text{mol}^{-1}$	$c/\text{mol}\cdot\text{dm}^{-3}$	$\Delta_s H/\text{kJ}\cdot\text{mol}^{-1}$
$4.49 \times 10^{-4}$	15.12	$1.57 \times 10^{-4}$	20.10
$5.65 \times 10^{-4}$	15.23	$1.86 \times 10^{-4}$	19.52
$7.63 \times 10^{-4}$	15.69	$2.19 \times 10^{-4}$	19.81
$7.99 \times 10^{-4}$	15.58	$3.30 \times 10^{-4}$	19.13
$8.98 \times 10^{-4}$	15.60	$4.31 \times 10^{-4}$	19.12
		$5.36 \times 10^{-4}$	19.20
		$7.09 \times 10^{-4}$	18.81
$\Delta_s H^\circ = 15.4 \pm 0.3 \text{ kJ}\cdot\text{mol}^{-1} \text{ }^a$		$\Delta_s H^\circ = 20.8 \pm 0.4 \text{ kJ}\cdot\text{mol}^{-1} \text{ }^b$	
DMSO		PC	
$c/\text{mol}\cdot\text{dm}^{-3}$	$\Delta_s H/\text{kJ}\cdot\text{mol}^{-1}$	$c/\text{mol}\cdot\text{dm}^{-3}$	$\Delta_s H/\text{kJ}\cdot\text{mol}^{-1}$
$3.46 \times 10^{-4}$	8.74	$3.05 \times 10^{-4}$	6.28
$3.80 \times 10^{-4}$	8.28	$4.04 \times 10^{-4}$	7.88
$4.49 \times 10^{-4}$	6.93	$5.52 \times 10^{-4}$	8.95
$5.79 \times 10^{-4}$	5.60	$7.05 \times 10^{-4}$	9.20
$7.14 \times 10^{-4}$	4.39	$7.76 \times 10^{-4}$	9.28
$8.26 \times 10^{-4}$	4.24	$8.97 \times 10^{-4}$	10.64
$1.07 \times 10^{-3}$	2.36	$1.05 \times 10^{-3}$	11.12
$\Delta_s H^\circ = 16.6 \pm 0.8 \text{ kJ}\cdot\text{mol}^{-1} \text{ }^b$		$\Delta_s H^\circ = 1.5 \pm 0.1 \text{ kJ}\cdot\text{mol}^{-1} \text{ }^b$	

<sup>a</sup> Average of several measurements. <sup>b</sup> Extrapolated value at  $c = 0$ .

is greater than that for calix[3]thieno[1]pyrrole in both solvents. It is reasonable to expect that the replacement of one pyrrole unit in calix[4]pyrrole by a thiophene unit in calix[3]thieno[1]pyrrole led to a decrease in complex stability of the latter with respect to the former. In an attempt to assess the medium effect on the complexation process, we proceeded with the determination of the standard thermodynamic parameters of solution of ligand and salts in various solvents. As far as Gibbs energies are concerned, fluoride salts were found to be solvated in DMSO, MeCN, DMF, and PC, and therefore the standard Gibbs energies,  $\Delta_s G^\circ$ , were not calculated for these systems. The single ion Gibbs energies of transfer of other halide anions from MeCN (reference solvent) to other solvents are those reported in the literature<sup>22,23</sup> and these are based on the Ph<sub>4</sub>AsPh<sub>4</sub>B convention.<sup>24</sup>

In the following section, standard enthalpies of solution of **1**, free and complex anion salts in the various solvents are discussed.

**Enthalpies of Solution.** The standard enthalpies of solution,  $\Delta_s H^\circ$ , of the calix[3]thieno[1]pyrrole, tetra-*n*-butylammonium fluoride, and tetra-*n*-butylammonium dihydrogen phosphate in MeCN, DMF, DMSO, and PC at 298 K are reported in Tables 5 and 6. These values were obtained from calorimetric measurements carried out at different molar concentrations ( $c$ ) of the appropriate compound. In cases where no systematic variation in the  $\Delta_s H$  values was found by altering the concentration of

**TABLE 6: Enthalpies of Solution ( $\Delta_s H^\circ$ ) of Tetra-*n*-butylammonium Fluoride and Dihydrogen Phosphate Salts in *N,N*-Dimethylformamide, Dimethyl Sulfoxide, and Propylene Carbonate at 298.15 K**

Tetra- <i>n</i> -butylammonium Fluoride			
DMSO		PC	
<i>c</i> /mol·dm <sup>-3</sup>	Δ <sub>s</sub> <i>H</i> /kJ·mol <sup>-1</sup>	<i>c</i> /mol·dm <sup>-3</sup>	Δ <sub>s</sub> <i>H</i> /kJ·mol <sup>-1</sup>
4.64 × 10 <sup>-4</sup>	4.82	2.54 × 10 <sup>-4</sup>	19.41
5.77 × 10 <sup>-4</sup>	5.81	4.34 × 10 <sup>-4</sup>	20.79
6.97 × 10 <sup>-4</sup>	6.53	6.21 × 10 <sup>-4</sup>	21.81
8.30 × 10 <sup>-4</sup>	8.02	7.16 × 10 <sup>-4</sup>	21.70
9.19 × 10 <sup>-4</sup>	11.77	8.49 × 10 <sup>-4</sup>	22.29
1.11 × 10 <sup>-4</sup>	12.89	9.95 × 10 <sup>-4</sup>	21.63
1.27 × 10 <sup>-4</sup>	14.30		
Δ <sub>s</sub> <i>H</i> <sup>o</sup> = −11.7 ± 0.2 kJ·mol <sup>-1</sup> <i>a</i>		Δ <sub>s</sub> <i>H</i> <sup>o</sup> = 17 ± 1 kJ·mol <sup>-1</sup> <i>a</i>	
Tetra- <i>n</i> -butylammonium Dihydrogen Phosphate			
PC			
<i>c</i> /mol·dm <sup>-3</sup>	Δ <sub>s</sub> <i>H</i> /kJ·mol <sup>-1</sup>		
2.75 × 10 <sup>-4</sup>	12.93		
3.24 × 10 <sup>-4</sup>	12.27		
4.12 × 10 <sup>-4</sup>	11.92		
4.60 × 10 <sup>-4</sup>	11.21		
5.42 × 10 <sup>-4</sup>	10.97		
7.78 × 10 <sup>-4</sup>	10.31		
1.02 × 10 <sup>-4</sup>	9.14		

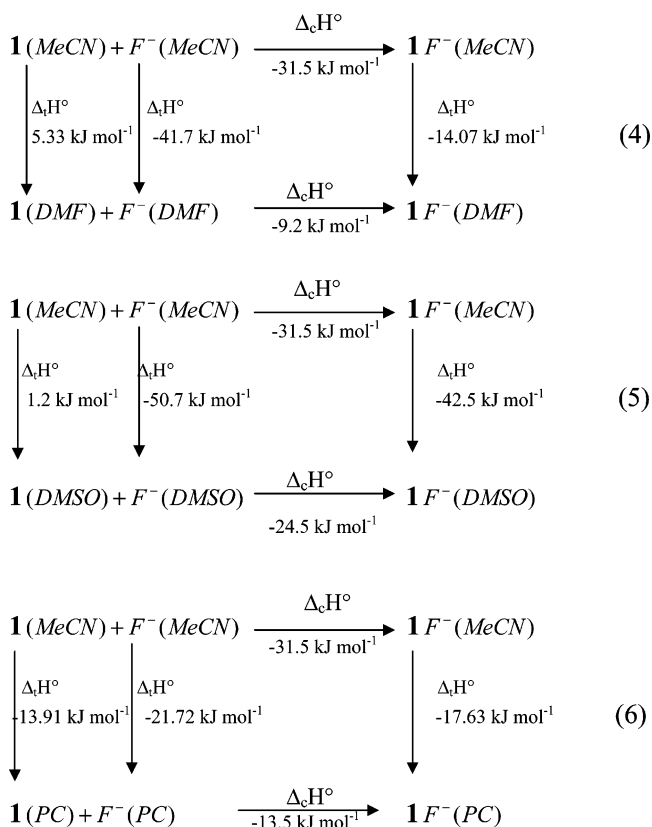
<sup>a</sup> Extrapolated value at *c* = 0.

the appropriate compound, the standard enthalpy of solution,  $\Delta_s H^\circ$ , was taken as the average of the data. When  $\Delta_s H$  values vary with changes in the electrolyte concentration, the  $\Delta_s H^\circ$  value was calculated from the intercept at *c* = 0 of a plot of  $\Delta_s H$  against the square root of the concentration, *c*<sup>1/2</sup>. Combination of these data and those reported in the literature for Bu<sub>4</sub>NF and Bu<sub>4</sub>NCl in MeCN, DMF, DMSO, and PC at 298.15 K with complexation enthalpies reported in Table 4 are now used to assess the medium effect on the complexation process, and this is discussed in the next section.

**The Medium Effect.** The medium effect on the complexation process is controlled by the differences in the solvation of the reactants and the product participating in the process in the two solvents, as shown in eq 3

$$\Delta_c P^\circ(s_1) - \Delta_c P^\circ(s_2) = \Delta_t P^\circ(\mathbf{1})(s_1 \rightarrow s_2) + \Delta_t P^\circ(X^-)(s_1 \rightarrow s_2) - \Delta_t P^\circ(\mathbf{1}X^-)(s_1 \rightarrow s_2) \quad (3)$$

This relationship reflects that for the reactants to favor complexation in *s*<sub>1</sub> relative to *s*<sub>2</sub>, these should be better solvated in the latter relative to the former solvent. The opposite is true for the anion complex. These differences are reflected in the thermodynamic parameters of transfer,  $\Delta_t P^\circ$  (*P* = *G*, *H*, *S*) of the ligand, the free anion (*X*<sup>−</sup>), and the complexed anion (*1X*<sup>−</sup>) from a reference solvent (*s*<sub>1</sub>) to another (*s*<sub>2</sub>). Availability of the  $\Delta_t H^\circ$  values for **1** and the appropriate anion from MeCN to DMF, DMSO, and PC (see Table 5) and the  $\Delta_c H^\circ$  values for these anions and **1** in these solvents (Table 4) allows the calculation of the  $\Delta_t H^\circ$  value for the anion complex from MeCN to solvents of interest through eq 3. By inserting the appropriate quantities for the halides and dihydrogen phosphate in the thermodynamic cycle (Scheme 1), it follows that as far as the fluoride–**1** system is concerned, enthalpy values for the individual processes are those shown in the cycles (Scheme 1). Transfer data for the ligand and the anion are those from Table 5. For the anion complex, the value was obtained through the cycle.

**SCHEME 1**

Taking into account eq 3, it follows that the data shown in eqs 4 and 5 demonstrate that the higher enthalpic stability of complex formation in MeCN is almost entirely due to the contribution of the free anion (lower enthalpic stability relative to DMF and DMSO respectively).

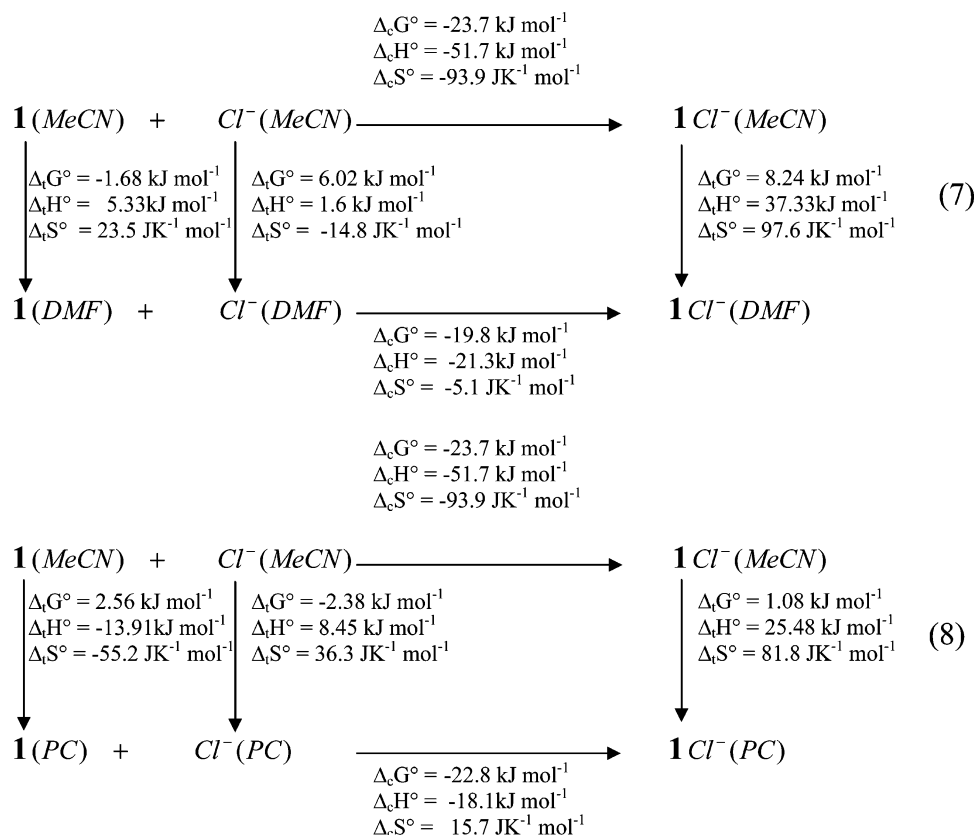
As far as the MeCN–PC solvent system is concerned (eq 6), the higher enthalpic stability of complex formation in MeCN results from the contribution of the reactants (anion and ligand) characterized by a favorable  $\Delta_t H^\circ$  value (negative) from MeCN to PC. Complexation in MeCN is not favored by the anion complex but its negative contribution is overcome by the joint contribution of ligand and anion.

As far as the chloride–**1** system is concerned (Scheme 2), availability of single-ion transfer Gibbs energy values (based on the Ph<sub>4</sub>AsPh<sub>4</sub>B convention)<sup>24</sup> allows interpretation of the medium effect on the complexation process in terms of Gibbs energies, enthalpies, and entropies, and these are now discussed. In terms of Gibbs energies, the small differences in solvation of the reactants and the product in transfers from MeCN to either DMF or PC lead to complexes of similar stability in these solvents.

The results show (eq 7) that the higher enthalpic stability of the complexation process in MeCN relative to DMF is attributed to the favorable contribution of the complex overcoming those for the ligand and the free anion (enthalpically unfavorable for complexation in MeCN). The unfavorable entropy observed in the complexation of **1** and Cl<sup>−</sup> in MeCN relative to DMF is mainly due to the higher order structure of the anion complex in MeCN relative to DMF. To a lesser extent, the free anion also contributes to the unfavorable entropy of the complexation process in MeCN relative to DMF.

As far as the MeCN–PC solvent system is concerned, the data (eq 8) show that the higher enthalpic stability of complex formation in MeCN relative to PC is almost due to the

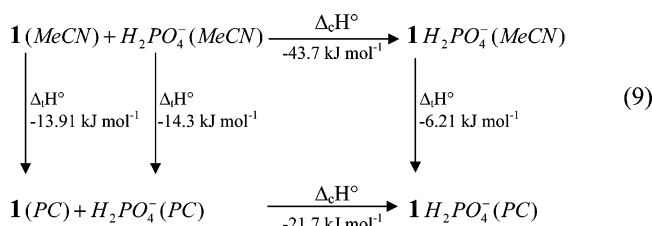
## SCHEME 2



contribution of both, the free ligand (enthalpically more stable in PC than in MeCN) and the complex (higher enthalpic stability in MeCN relative to PC).

As far as entropy is concerned, both the ligand (highly ordered in PC relative to MeCN) and the anion complex (entropically more favored in PC relative to MeCN) contribute to the unfavorable entropy of complexation in MeCN relative to PC (favorable).

Similar analysis carried out with the  $\text{H}_2\text{PO}_4^-$ –**1** system in terms of enthalpy (eq 9) shows that the anion complex is enthalpically more stable in MeCN than in PC. The opposite is true for the free anion and the ligand. These are enthalpically more stable in PC. As a result, the higher enthalpic stability of the complex in MeCN relative to PC is due to the favorable contribution of the reactants.



From the discussion of the medium effect on the complexation process, there are still some questions to be answered such as the following:

(i) Why in moving from protophobic (MeCN, PC) to protophilic (DMF, DMSO) dipolar aprotic solvents is the ability of the ligand to interact with the anions significantly reduced? Indeed in the former solvents **1** interacts with  $\text{F}^-$ ,  $\text{Cl}^-$ , and  $\text{Br}^-$ ,

in DMF this is limited to fluoride and chloride, and in DMSO **1** interacts only with the fluoride anion.

(ii) Why is the complex composition of **1** and  $\text{H}_2\text{PO}_4^-$  altered in moving from MeCN (2:1 ligand/anion complex) to PC (1:1 complex).

As far as (i) is concerned, we have previously demonstrated<sup>5</sup> that the stability of complex formation of these anions with calixpyrroles follows the same trend as that observed for the transfer of anions from a dipolar aprotic solvent (MeCN) to a protic solvent (MeOH) in that the smaller anion (high charge density) is able to interact more strongly through hydrogen bond formation than the large ones. As far as the ligand is concerned, the  $\Delta_t G^\circ$  values (indicative of the differences in solvation of **1** between two solvents) shown in Table 1 do not differ significantly as to control the extent of complex formation or lack of it in these solvents. However, the  $\Delta_t G^\circ$  value does not provide information regarding the site of ligand–solvent interaction. Protophilic aprotic solvents (basic) are likely to interact with the pyrrolic hydrogens of the ligand through hydrogen bond formation as shown in the NMR data for the free ligand (Table 2) discussed above. Therefore as the size of the anion increases, their capacity to fit into the cavity of the ligand decreases. This effect seems to be more pronounced in DMSO than in DMF. Anion solvation may play a role here since the  $\text{Cl}^-$  anion is better solvated in DMSO than in DMF ( $\Delta_t G^\circ$  ( $\text{Cl}^-$ ) (DMF  $\rightarrow$  DMSO) =  $-8.4 \text{ kJ mol}^{-1}$ , data based on the  $\text{Ph}_4\text{AsPh}_4\text{B}$  convention).

As far as (ii) is concerned, unlike the halide anions (spherical),  $\text{H}_2\text{PO}_4^-$  (tetrahedral anion) is likely to be better solvated in PC (through hydrogen bond formation between the OH group of the anion and the oxygen atoms of the solvent) and therefore steric effects are likely to exclude the possibility of forming a 2:1 ligand anion complex.



## Conclusions

From the above discussion the following conclusions can be drawn.

<sup>1</sup>H NMR measurements in CD<sub>3</sub>CN at 298 K show that **1** interacts with the halide (spherical) and dihydrogen phosphate (nonspherical) anions through the NH groups of the pyrrole rings. The larger chemical shift changes of the NH protons of **2** compared with those in **1** reveal the impact of replacing in the structure of **2**, one pyrrole by a thiophene unit.

Conductance measurements demonstrated that in MeCN, 1:1 complexes are formed between **1** and halide anions while the interaction of this ligand with dihydrogen phosphate anion in MeCN leads to the formation of a 2:1 (ligand/anion complex). The outcome of these measurements is in accord with that found from <sup>1</sup>H NMR investigations.

The medium effect on the complexation of **1** and anions has been investigated in various solvents. Thus thermodynamic aspects of complexation are discussed in two protophobic (MeCN and PC) and two protophilic (DMF and DMSO) dipolar aprotic solvents. The relevance of transfer data for the reactants and the product in the interpretation process is demonstrated. It is concluded that the solvent plays a crucial role not only on the ability of the ligand to interact with anions but also on the composition of anion complexes. The pattern observed in anion complexation by calixpyrroles is similar to that observed in cation complexation processes involving calixarenes in that interactions observed in one solvent are by no means representative of those taking place in another medium.

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