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Thermodynamics of Anion–π Interactions in Aqueous Solution

Paloma Arranz-Mascarós,[†] Carla Bazzicalupi,[‡] Antonio Bianchi,*[,‡] Claudia Giorgi,[‡] Maria-Luz Godino-Salido,[†] Maria-Dolores Gutiérrez-Valero,[†] Rafael Lopez-Garzón,*[,†] and Matteo Savastano[‡]

[†]Department of Inorganic and Organic Chemistry, University of Jaen, 23071, Jaen, Spain
[‡]Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3, 50019 Sesto Fiorentino, Italy

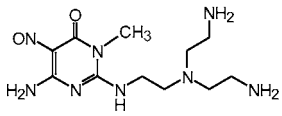
Supporting Information

ABSTRACT: Thermodynamic parameters ($\Delta G°$, $\Delta H°$, $T\Delta S°$), obtained by means of potentiometric and isothermal titration calorimetry (ITC) methods, for the binding equilibria involving anions of high negative charge, like SO_4^{2-}, SeO_4^{2-}, $S_2O_3^{2-}$ and $Co(CN)_6^{3-}$, and nitroso-amino-pyrimidine receptors in water suggested that anion–π interactions furnish a stabilization of about −10 kJ/mol to the free energy of association. These anion–π interactions are almost athermic and favored by large entropic contributions which are likely due to the reduced hydrophobic pyrimidine surface exposed to water after anion aggregation, and the consequent reduced disruptive effect on the dynamic water structure. The crystal structure of the $\{H_4L[Co(CN)_6]\}\cdot 2H_2O$ complex showed strong anion–π interactions between $Co(CN)_6^{3-}$ and the protonated H_4L^{3+} receptor. The CN···centroid distance (2.786(3) Å), occurring with a cyanide N atom located almost above the centroid of the pyrimidine ring, is the shortest distance till now reported for the interaction between CN^- ions and heteroaromatic rings.

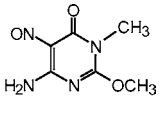
Selective binding of anions in water is a challenging target, due to the variety of their structures, to their high hydration free energies, to the occurrence that they often exist in narrow pH ranges and that the noncovalent interactions used to bind anions are weak and not easy to design. Fortunately, noncovalent interactions are individually weak but collectively strong and, accordingly, it is possible to construct polyfunctional receptors capable of strong and selective anion binding.[1]

Among noncovalent forces, anion–π interactions recently came into the focus of attention.[2] The nature of such interactions has been described by many crystallographic studies[2,3] as well as by theoretical[2,3a,b,4] and experimental[2,3e,i,5,6] works. A recent overview of experimental results, mostly based on the binding of halogenide anions in organic solvents, led to the conclusion that the binding free energy ($-\Delta G°$) for this attractive force is less than 1 kcal/mol (4 kJ/mol) for each interacting phenyl ring and that anion–π interactions are poorly effective for selective anion binding but offer potential applications in catalysis and transport within synthetic and biological systems.[2a] Actually, a greater binding free energy has been reported for anion–π interactions. The estimations were often made by extracting, with the help of reference systems, the anion–π contribution from the combined contributions of anion–π and H-bond interactions. Nevertheless, as recently pointed out, model structures and solvation effects may affect the magnitude of the measured term.[6] Furthermore, such quantifications can be complicated by the tendency of salts to form ion-pairs when solvents of low polarity are employed.

We have recently shown that protonated forms of the ligand HL, a tren (tris(2-aminoethyl)amine) molecule attached to a nitroso-amino-pyrimidine, are able to bind inorganic (SO_4^{2-}, PO_4^{3-}, AsO_4^{3-}, $HgCl_4^{2-}$, CrO_4^{2-}) and nucleotidic (AMP, ADP, ATP) anions forming stable complexes in aqueous solution.[7,8] In the crystal structures of $[H_3L(HgX_4)]$ (X = Cl, Br)[7] and $[H_3L(CdI_4)]$[9] the ammonium groups of the protonated tren moiety form salt-bridges with the anions while the electron-poor pyrimidine ring is engaged in strong anion–π interactions. In the case of $[H_3L(HgCl_4)]$, the Cl-centroid distance (3.134 Å) is, to date, the shortest among all observed halogenide–pyrimidine distances.



HL



L1

In the case of SO_4^{2-}, the only anion within the considered group that does not bear protonation in the investigated pH range, a good linear correlation was exhibited between the binding free energies and the receptors charge (H_2L^+, H_3L^{2+}, and H_4L^{3+}) according to the relationship $-\Delta G° = 5.4(\pm 0.2)x + 8.9(\pm 0.4)$ (x = receptor charge). This relationship provides two energetic contributions: the first one (−5.4 ± 0.2 kJ/mol) is the free energy increment for a unitary increment of ligand charge, while the second one (−8.9 ± 0.4 kJ/mol) is the residual free energy contribution at zero ligand charge ($x = 0$) which was associated with the anion–π interaction.[7]

We have now verified by means of new potentiometric (pH-metric) titrations performed in the presence of a large excess of SO_4^{2-} (see Supporting Information (SI)), that the uncharged HL ligand binds this anion with a free energy of association $\Delta G° = -10.0(3)$ kJ/mol (Table 1) that well compares with the value derived from the linear correlation. Protonated forms of HL also bind other anions, such as SeO_4^{2-}, $S_2O_3^{2-}$, and $Co(CN)_6^{3-}$ that, like SO_4^{2-}, do not protonate under our

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Table 1. Thermodynamic Parameters for the Formation of Anion Complexes with HL in 0.1 M NMe_4Cl at 298.1 K[a]

	log *K*					
	potentiometry	linear corr.	ITC	$-\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$T\Delta S°$ (kJ/mol)
$HL + SO_4^{2-}$	1.76(5)	1.6(1)	1.7(1)	10.0(3)	0.6(7)	11(1)
$H_2L^+ + SO_4^{2-}$	2.53(5)[b]			14.4(3)	−5.0(4)	9.4(4)
$H_3L^{2+} + SO_4^{2-}$	3.41(2)[b]			19.5(1)	−3.3(4)	16(1)
$H_4L^{3+} + SO_4^{2-}$	4.42(2)[b]			25.2(1)	18.0(4)	43.2(4)
$HL + S_2O_3^{2-}$		2.19(4)	1.9(1)	10.8(6)[c]	2.3(2)	13.1(8)
$H_2L^+ + S_2O_3^{2-}$	2.83(7)			16.1(4)	*d*	
$H_3L^{2+} + S_2O_3^{2-}$	3.34(8)			19.1(5)	*d*	
$H_4L^{3+} + S_2O_3^{2-}$	3.95(9)			22.5(5)	*d*	
$HL + SeO_4^{2-}$		2.05(2)	2.1(1)	12.0(6)[c]	3.34(9)	15.3(7)
$H_2L^+ + SeO_4^{2-}$	2.68(6)			15.3(6)	9.9(2)	25.2(8)
$H_3L^{2+} + SeO_4^{2-}$	3.34(6)			19.0(3)	5.2(1)	24.2(4)
$H_4L^{3+} + SeO_4^{2-}$	3.96(8)			22.6(5)	15.2(4)	37.8(9)
$HL + Co(CN)_6^{3-}$		1.87(1)	2.0(1)	11.4(6)[c]	−2.43(7)	9.0(7)
$H_2L^+ + Co(CN)_6^{3-}$	2.72(6)			15.2(6)	9.99(2)	25.2(6)
$H_3L^{2+} + Co(CN)_6^{3-}$	3.44(5)			19.6(3)	7.26(3)	26.9(3)
$H_4L^{3+} + Co(CN)_6^{3-}$	4.24(6)			24.22(3)	*e*	

[a]Unless otherwise noted, log*K* and $\Delta G°$ values were potentiometrically determined. [b]Taken from ref 7. [c]Values determined by ITC. [d]Not determined due to $S_2O_3^{2-}$ decomposition. [e]Not determined due to insufficient complex solubility.

experimental conditions to form 1:1 complexes (Table 1). Also for these anions the binding free energies give rise to good linear correlations with ligand charge (Figure 1) providing

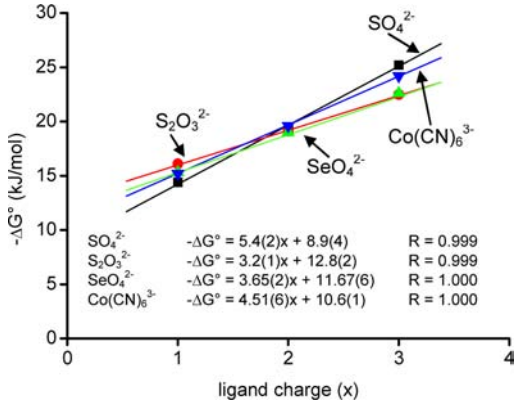

Figure 1. Linear correlation between the ligand charge and the free energy change of anion binding by H_2L^+, H_3L^{2+}, and H_4L^{3+}.

estimated binding constants of log *K* = 2.05(2), log *K* = 2.19(4), and log *K* = 1.87(1) ($-\Delta G°$ in the range 10.7−12.8 kJ/mol) for the association of the neutral HL ligand with SeO_4^{2-}, $S_2O_3^{2-}$, and $Co(CN)_6^{3-}$, respectively (Table 1).

X-ray analysis of the crystalline $\{H_4L[Co(CN)_6]\}\cdot 2H_2O$ complex showed that H_4L^{3+} actually binds $Co(CN)_6^{3-}$ through the formation of salt-bridges and strong anion−π interactions (Figure 2), although in the crystal structure the interacting partners do not form defined $\{H_4L[Co(CN)_6]\}$ pairs. In this complex, ligand protonation involves the primary amino groups of the tren moiety and the oxygen atom of the nitroso group, in agreement with previous solution studies.[9] The $[Co(CN)_6]^{3-}$ anions lie on crystallographic inversion centers, so that the asymmetric unit contains half of two non-equivalent anions, giving rise to a H-bond network involving protonated nitrogen and oxygen ligand atoms (Figure 2 and SI Figures S1 and S2). These anions establish anion−π interactions with the pyrimidine ring. One cyanide N atom is located almost above the centroid of the pyrimidine ring, just 2.786(3) Å apart from

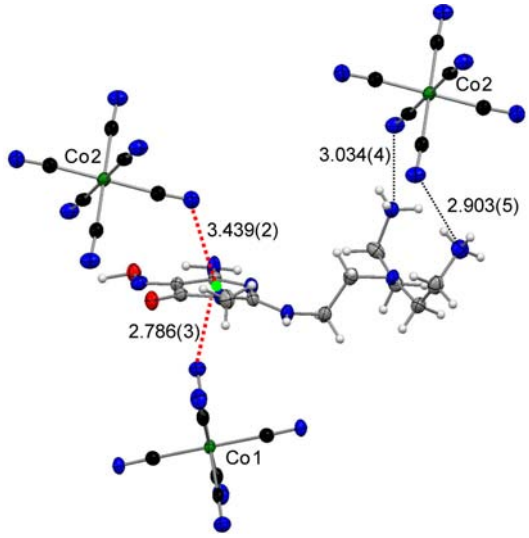

Figure 2. Portion of the crystal structure of $\{H_4L[Co(CN)_6]\}\cdot 2H_2O$ showing the H_4L^{3+} receptor with interacting $Co(CN)_6^{3-}$ anions.

it, and forms an angle ($\alpha 1$ in Figure 3a) of 9.9(1)° with the normal to the ring plane, while this normal forms an angle of 46.2(2)° with the C≡N group ($\alpha 2$ in Figure 3a).

A search carried out by the CSD system[10] evidenced that such N···centroid distance is the shortest distance till now reported for the interaction between metal-bound CN^- ions (no structures were found for free CN^-) and heteroaromatic rings (Figure 3b,c). This search also evidenced that the C≡N group is rarely normal to the ring plane, but it is usually tilted with the $\alpha 2$ angle mainly falling in the 65−85° range (Figure 3c). Nevertheless, the C≡N group is far from being coplanar with the ring in structures showing strong interaction; for instance, $\alpha 2$ is below 65° in structures with d < 3.1 Å. Actually, $\alpha 2$ is about 46° in $\{H_4L[Co(CN)_6]\}\cdot 2H_2O$. The anion−$\pi$ interaction of the second $[Co(CN)_6]^{3-}$ is weaker: d = 3.439(2), $\alpha 1$ = 24.5(1)°, $\alpha 2$ = 81.5(2)° (Figures 2, 3).

Binding equilibria were also studied by isothermal titration calorimetry (ITC) (see SI for experimental details) to

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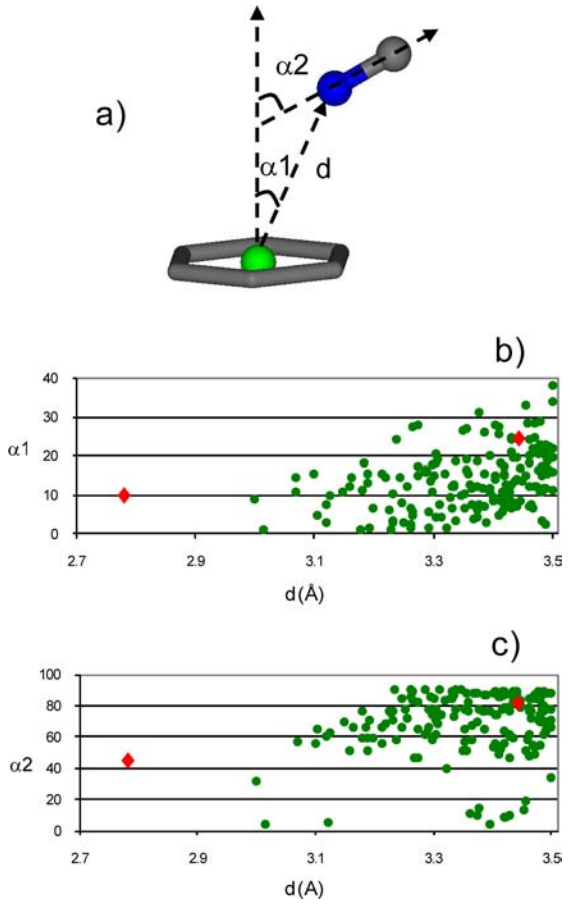

Figure 3. (a) Geometrical parameters used for the description of the C≡N···π interactions. (b, c) Comparison of the structural data obtained from the CSD search (green) with those of the $\{H_4L[Co(CN)_6]\}\cdot 2H_2O$ crystal structure (red).

determine the enthalpy changes collected in Table 1 along with the derived entropy contributions. ITC measurements, performed by adding a large excess of anion to HL solutions, made it possible to determine stability constants and enthalpy changes (Table 1) for anion binding by the uncharged ligand. Interestingly, these stability constants are very similar to the values given by the free energy-ligand charge correlations. Although these results give confidence about the existence of anion complexes of the uncharged HL in solution, the possibility that such complexes are formed by pure anion−π interactions is reasonably questionable in the absence of further evidence. We can exclude that in a solvent like water the formation of such complexes involves ion-pairs, instead of isolated anions, but we cannot exclude that other forces than anion−π interactions may contribute to complex stability.

Interesting results were obtained analyzing the anion binding properties of L1, the pyrimidine residue of HL, for which there are no contributions from the polyamine chain and does not contain any group that could be effective for anion binding in water. The study, conducted by ITC (see SI), showed that L1 form 1:1 anion complexes and furnished stability constants and enthalpy changes listed in Table 2. The stability of L1 complexes is only slightly smaller than the stability of the HL analogues (Tables 1, 2), revealing that contributions from the polyamine chain to the stability of HL complexes are almost insignificant. Also solvent effects do not seem to discriminate anion binding by HL and L1, since both enthalpic and entropic

Table 2. Thermodynamic Parameters for the Formation of Anion Complexes with L1 Determined by ITC in 0.1 M NMe_4Cl at 298.1 K

	log K	$-\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$T\Delta S°$ (kJ/mol)
L1 + SO_4^{2-}	1.5(1)	8.6(6)	3.28(9)	11.9(7)
L1 + $S_2O_3^{2-}$	1.91(9)	10.9(5)	1.37(7)	12.3(6)
L1 + SeO_4^{2-}	1.85(6)	10.6(2)	1.78(4)	12.4(2)
L1 + $Co(CN)_6^{3-}$	1.77(8)	10.1(5)	−1.96(3)	8.1(5)

contributions to the formation of equivalent complexes by the two ligands are fairly similar.

On the basis of these results, and considering that other weak forces, in particular hydrogen bonding, are not expected to give significant contributions to the association of such anions with L1 in water, we believe that the thermodynamic parameters determined for anion binding by the neutral HL and L1 ligands might be reasonably associated to anion−π interactions. The free energy change for such anion−π interactions in water, ranging from −8.6 to −12.0 kJ/mol, is indicative of a relatively weak binding, although it is about 2−3 times higher than that expected for a single phenyl ring interacting with halogenide anions in organic solvents.[2a] It has been recently shown by means of computational methods that a significant stability of anion−π complexes with neutral ligands, can be expected in solvents with a large dielectric constant, like water, that stabilize the polar resonance structures of the ligand.[11] Indeed, nitroso-amino-pyrimidines like HL and L1 exhibit strong polarization of their electronic structure[9,12] and, accordingly, HL and L1 form strong anion−π interactions in water.

It is noteworthy that these anion−π interactions are almost athermic and favored by large entropic contributions (Tables 1, 2). Similar thermodynamic features are typical of association processes occurring in solution with large desolvation effects. Since these anion−π interactions take place with modest charge neutralization, the favorable entropic term is likely because the anion−pyrimidine aggregation reduces the hydrophobic pyrimidine surface exposed to water and minimizes its disruptive effect on the dynamic water structure.

In conclusion, we have found that (i) the combination of salt-bridge and anion−π interactions may offer the opportunity to determine the individual contribution of each type of interaction, (ii) the free energy change ascribed to the formation of anion−π interactions between HL and L1 with anions of high negative charge like SO_4^{2-}, SeO_4^{2-}, $S_2O_3^{2-}$, and $Co(CN)_6^{3-}$ in water is about −10 kJ/mol, 2−3 times greater than the free energy change estimated for anion−π interactions between a phenyl ring and halogenide anions in organic solvents, (iii) the favorable free energy for the anion−π interactions in this study are due to large and favorable entropic contributions likely originating from desolvation phenomena. Nevertheless, entropic contributions to binding processes are rarely due to sole solvent effects, but can be better described as the sum of different components some of which can be subjected to molecular design.[13] Accordingly, despite their weakness, anion−π interactions can afford additional instruments to cope successfully with the challenging objective of designing anion receptors.

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■ ASSOCIATED CONTENT

Supporting Information

Full experimental details and crystallographic information. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

rlopez@ujaen.es; antonio.bianchi@unifi.it

Notes

The authors declare no competing financial interest.

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