J. Chem. Eng. Data **2004,** *49,* 133−137 **133**

Binding of Phosphate, Pyrophosphate, and Hexacyanoferrate(II) by Fully *N*-Methyl Substituted Polyammonium Cations in Aqueous Solution

Francesco Crea, Alessandro De Robertis, Concetta De Stefano,* Claudia Foti, and Silvio Sammartano

Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica dell'Università,
Salita Sperone 31, I-98166 Messina (Vill. S. Agata), Italy

In this study, we determined the stability of some fully *N*-methyl substituted polycation−inorganic polyanion complexes by potentiometric measurements at $t = 25$ °C. As for other previously studied similar systems, the stability of ALH_r species (A = amine; L = inorganic polyanion; $r = 1, 2, ... m$, with $m \geq n$, n = maximum protonation degree of the amine) is a function of the charges involved in the formation equilibrium. The basicity of the polyanion also plays a fairly significant role. The stability of these species is compared with that of analogous species of unsubstituted amines and with that of polyammonium−carboxylate complexes. Simple predictive stability relationships are given.

Introduction

Open chain polyammonium cations form fairly stable complexes with inorganic and organic polyanions.[1−6] The most important factor determining the stability of these species is the number of positive and negative charges in the reactants. In general, the simple relationship

$$\log K_{ij} = \text{const} \times \zeta \qquad (1)$$

is sufficient to explain ~80% of the stability of different species formed in a given system. In eq 1, ζ is the charge product

$$\zeta = z_+|z_-| \qquad (2)$$

relative to the formation equilibrium

$$\mathrm{AH}_i^{\,i+} + \mathrm{H}_j\mathrm{L}^{(z-j)-} = \mathrm{ALH}_r^{(j+i-z)} \qquad (3)$$

[$z_+ = i+$; $z_- = (z - j)-$; $r = i + j$]. In some cases, species with stoichiometric coefficients of A or L ≠ 1 can also be formed. Other factors may contribute to the stability of these species, in particular hydrogen bonding. As concerns the structure of open chain polyammonium cations, differences in the stability of polyanion complexes can be due to the length of the alkyl chain and to *N*-alkyl substitution. Recently we compared the analogous complexes formed by two series of amines, $\mathrm{C}_{(2n-2)}\mathrm{N}_n\mathrm{H}_{(5n-2)}$ (unsubstituted) and $\mathrm{C}_{3n}\mathrm{N}_n\mathrm{H}_{7n}$ (fully methyl substituted), with some carboxylic anions.[7] Here we report the results of a similar investigation involving some inorganic anions, namely, *o*-phosphate, pyrophosphate, and hexacyanoferrate(II). For the purpose of comparison, the $\mathrm{PO_4}^{3-}$-unsubstituted polyammonium cation system was studied too. The polyamines studied in this work, together with abbreviations, are reported in Table 1.

Table 1. Amines Considered in This Work

amines	abbreviation
$\mathrm{H_2N{-}(CH_2)_2{-}NH_2}$ ethylenediamine	en
$\mathrm{H_2N{-}(CH_2)_2{-}NH{-}(CH_2)_2{-}NH_2}$ diethylenetriamine	dien
$\mathrm{H_2N{-}(CH_2)_2{-}NH{-}(CH_2)_2{-}NH{-}(CH_2)_2{-}NH_2}$ triethylenetetramine	trien
$\mathrm{H_2N{-}(CH_2)_2{-}NH{-}[(CH_2)_2{-}NH]_3{-}(CH_2)_2{-}NH_2}$ 3,6,9,12-tetrazatetradecane-1,14-diamine (pentaethylenesamine)	penten
$\mathrm{(CH_3)_2N{-}(CH_2)_2{-}N(CH_3)_2}$ *N*, *N*, *N*′, *N*′-tetramethylethylenediamine	tmed
$\mathrm{(CH_3)_2N{-}(CH_2)_2{-}[N(CH_3){-}(CH_2)_2]_2{-}N(CH_3)_2}$ 1,1,4,7,10,10-hexamethyltriethylenetetramine	hmtt
$\mathrm{(CH_3)_2N{-}(CH_2)_2{-}N(CH_3){-}(CH_2)_2{-}N(CH_3)_2}$ *N*, *N*, *N*′, *N*′, *N*′′-pentamethyldiethylenetriamine	pmdt

Experimental Section

Chemicals. All the amines studied in this work [Aldrich or Sigma products] were purified by transformation into the corresponding hydrochlorides and were used in this form. Tetrasodium diphospate (Analar BDH), hexacyanoferrate(II) [used in the form of tetrasodium salt (Fluka puriss.)], and pyrophosphoric and hexacyanoferrate(II) acids (Fluka purum) were used without further purification and standardized against sodium carbonate. Disodium hydrogen phosphate and sodium chloride (Fluka, puriss.) were prepared by weighing pure salts previously dried in a stove at 110 °C. The purity of all the ligands, checked by potentiometric titrations, was always >99.5%. Standard solutions of NaOH and HCl were prepared by diluting concentrated Fluka ampules and were standardized against potassium biphthalate or sodium carbonate, respectively. All the solutions were made up using freshly prepared, twice distilled $\mathrm{CO_2}$-free water ($R = 18$ MΩ cm^{-1}).

Apparatus and Procedure. The measurements were carried out using three different pieces of potentiometric apparatus: (1) a Metrohm model 665 automatic titrant dispenser coupled with a Crison model 2002 potentiometer and a combination Orion-Ross 8172 glass electrode; (2) a

---

* To whom correspondence should be addressed. E-mail: destefano@chem.unime.it. Fax: +39-(0)90-392827.

10.1021/je034133m CCC: $27.50

Metrohm model 665 automatic titrant dispenser coupled with a Metrohm model 654 potentiometer and a combination Orion-Ross 8102 glass electrode; (3) a Metrohm model 605 potentiometer equipped with an Orion combination glass electrode (Ross type 8102) and a Metrohm model 654 motorized buret. The estimated accuracies of these systems were ±0.15 mV and ±0.003 cm^3 for electromotive force (emf) and titrant volume readings, respectively. Pure nitrogen was bubbled through the solutions in titration cells in order to avoid O_2 and CO_2 inside, and the solutions were magnetically stirred.

Twenty-five milliliters of the solution containing the ligand (HPO_4^{2-}, $P_2O_7^{4-}$, or $Fe(CN)_6^{4-}$) and the amine hydrochloride under study were titrated with standard NaOH up to pH ∼ 11. Titrations were performed without adding background salt. Concentrations used in the experiments were $C_{amine} = 8-40$ mmol L^{-1} and $C_{anion} = 1.7-50$ mmol L^{-1}. Separate titrations of HCl at the same ionic strength (adjusted with NaCl) as the sample under study were carried out to determine standard electrode potential $E°$. The pH values were obtained in the concentration scale ($pH \equiv -\log C_H$).

Calculations. The computer program ESAB2M[8] was used to calculate the purity of the reagents and to refine all the parameters related to the calibration of the electrode system. Calculations were carried out using the nonlinear least-squares computer programs BSTAC[9] and STACO.[10] These are able to compute the complex formation constants and the parameters for their dependence on ionic strength and to refine analytical concentrations and electrode constants as the standard potential and the slope of the system. BSTAC and STACO can allow for variations in ionic strength during titration. The dependence of formation constants on ionic strength was taken into consideration using the Debye−Hückel type equation (K = formation constant; ${}^{T}K$ = formation constant at infinite dilution):[11]

$$\log K = \log {}^{T}K - z^{*}I^{1/2}/(2 + 3I^{1/2}) + CI + DI^{3/2} \quad (4)$$

where the empirical parameters C and D, independent of the chemical nature of the reactants and depending only on the stoichiometry of the reaction, are

$$C = c_0 p^{*} + c_1 z^{*} \quad (5)$$

$$D = dz^{*} \quad (6)$$

with

$$z^{*} = \Sigma(\text{charges})^2_{\text{reactants}} - \Sigma\,(\text{charges})^2_{\text{products}}$$

$$p^{*} = \Sigma\,(\text{moles})_{\text{reactants}} - \Sigma(\text{moles})_{\text{products}}$$

Values previously found for empirical parameters[11] were $c_0 = 0.11$, $c_1 = 0.20$, and $d = -0.075$. These equations have been extensively tested in the ionic strength range $0 < I$/mol $L^{-1} \leq 1$. In our experimental conditions, the ionic strength was always <0.03 mol L^{-1} and, therefore, the use of such an empirical equation did not involve significant errors. Concentrations and formation constants are given on the molarity scale. In the calculations, it is necessary to take into account the protonation constants of the amines and the carboxylic ligands. Moreover, protonated amines form weak complexes with Cl^- (amine hydrochlorides are used) and inorganic anions form weak complexes with Na^+ (coming from the NaOH titrant), and all these species must be considered as well. Protonation constants and weak complex formation constants have already been reported for amines[12] and inorganic polyanions.[13] Distribution diagrams and simulated titration curves were obtained using the computer program ES4ECI.[9]

Table 2. Overall Formation Constants for the Amine−H$^+$−Polyanion Species at I = 0 mol L^{-1} and t = 25 °C

indexes[a]	anion	log β_{pqr}		
$p\ q\ r$		tmed	pmdt	hmtt
1 1 2	PO_4^{3-}	23.44 ± 0.06[b]	23.24 ± 0.07[b]	24.1 ± 0.1[b]
1 1 3		31.03 ± 0.04	32.29 ± 0.06	33.16 ± 0.08
1 1 4		36.49 ± 0.06	38.42 ± 0.08	40.01 ± 0.06
1 1 5			40.7 ± 0.1	44.73 ± 0.09
1 1 6				46.3 ± 0.1
1 1 1	$P_2O_7^{4-}$	12.2 ± 0.1	12.2 ± 0.1	11.9 ± 0.1
1 1 2		21.91 ± 0.04	22.13 ± 0.03	21.29 ± 0.08
1 1 3		29.07 ± 0.02	30.53 ± 0.02	30.65 ± 0.06
1 1 4		34.36 ± 0.02	36.39 ± 0.04	37.64 ± 0.04
1 1 5		35.41 ± 0.09	39.38 ± 0.06	42.81 ± 0.06
1 1 6			40.5 ± 0.3	45.52 ± 0.08
1 1 7				46.1 ± 0.1
2 1 4		40.16 ± 0.08		
2 1 5		45.9 ± 0.1		
1 1 1	$Fe(CN)_6^{4-}$	12.1 ± 0.1	12.0 ± 0.1	
1 1 2		19.77 ± 0.7	22.70 ± 0.02	
1 1 3		22.92 ± 0.8	26.42 ± 0.02	
1 1 4		23.9 ± 0.1	28.71 ± 0.03	
1 1 5			29.84 ± 0.07	
2 1 4		36.9 ± 0.1	47.9 ± 0.1	

indexes[a]	anion	log β_{pqr}		
$p\ q\ r$		dien	trien	penten
1 1 2	PO_4^{3-}	24.4 ± 0.2	24.30 ± 0.3	23.83 ± 0.14
1 1 3		33.85 ± 0.05	34.19 ± 0.10	33.66 ± 0.04
1 1 4		40.30 ± 0.10	41.84 ± 0.10	42.69 ± 0.03
1 1 5		44.25 ± 0.15	47.84 ± 0.15	50.17 ± 0.03
1 1 6			50.25 ± 0.2	55.66 ± 0.02
1 1 7				59.24 ± 0.03
2 1 4				64.54 ± 0.10
2 1 5				71.63 ± 0.06

[a] Indexes refer to the reaction $pA^0 + qL^{z-} + rH^+ = A_pL_qH_r^{(r-qz)}$. [b] ±3 std dev.

Results

Polyammonium Cation−Polyanion Complexes. Overall formation constants relative to the reaction

$$pA^0 + qL^{z-} + rH^+ = A_pL_qH_r^{(r-qz)} \quad (7)$$

are reported in Table 2. The errors associated with the most important (stable) species are quite low, considering the complexity of the systems, and make reliable the discussion about the relevance of the species formed. To compare different systems, it is necessary to consider effective formation equilibria, given by eq 3; the relative equilibrium constants are shown in Table 3, together with some previously reported[14−16] stability data for analogous systems of unsubstituted amines. The same table includes the log K_{ij}/ζ ratio to show how the charges involved in eq 3 explain the stability of these species.

A first inspection of the data in Table 3 gives the following information: (a) all the species considered have fairly similar stability, and this is consistent with the prevalence of electrostatic effects observed in the formation of this type of complex in many analogous systems; (b) closer scrutiny of the data reveals the trend

$$PO_4^{3-} > P_2O_7^{4-} > Fe(CN)_6^{4-}$$

Table 3. log K_{ij} (Equation 3) for the H^+−Polyamine−Polyanion Species at t = 25 °C and I = 0 mol L^{-1}

reaction	log K_{ij}		log K_{ij}/ζ	
	tmed	en	tmed	en
$HA^+ + HPO_4^{2-} = A(PO_4)H_2^-$	2.0	1.5[a]	1.1	0.75[a]
$H_2A^{2+} + HPO_4^{2-} = A(PO_4)H_3^0$	3.9	3.0	1.0	0.75
$H_2A^{2+} + H_2PO_4^- = A(PO_4)H_4^+$	2.2	1.6	1.1	0.8
$HA^+ + P_2O_7^{4-} = A(P_2O_7)H^{3-}$	3.0	3.1[b]	0.75	0.8[b]
$HA^+ + HP_2O_7^{3-} = A(P_2O_7)H_2^{2-}$	3.2	3.4	1.1	0.8
$H_2A^{2+} + HP_2O_7^{3-} = A(P_2O_7)H_3^-$	4.7	4.0	0.8	1.1
$H_2A^{2+} + H_2P_2O_7^{2-} = A(P_2O_7)H_4^0$	3.3	2.6	0.8	0.7
$H_2A^{2+} + H_3P_2O_7^- = A(P_2O_7)H_5^+$	2.0	1.4	1.0	0.7
$H_2A^{2+} + A(P_2O_7)H_2^{2-} = A_2(P_2O_7)H_4^0$	3.5	2.8	0.9	0.7
$H_2A^{2+} + A(P_2O_7)H_3^- = A_2(P_2O_7)H_5^+$	2.0		1.0	
$HA^+ + Fe(CN)_6^{4-} = A[Fe(CN)_6]H^{3-}$	3.0	2.8[c]	0.75	0.7[c]
$H_2A^{2+} + Fe(CN)_6^{4-} = A[Fe(CN)_6]H_2^{2-}$	5.0	4.8	0.6	0.6
$H_2A^{2+} + HFe(CN)_6^{3-} = A[Fe(CN)_6]H_3^-$	3.8	3.6	0.6	0.6
$H_2A^{2+} + H_2Fe(CN)_6^{2-} = A[Fe(CN)_6]H_4^0$	2.3	2.9	0.6	0.7
$H_2A^{2+} + A[Fe(CN)_6]H_2^{2-} = A_2[Fe(CN)_6]H_4^0$	2.4		0.6	

reaction	log K_{ij}		log K_{ij}/ζ	
	hmdt	dien	hmdt	dien
$HA^+ + HPO_4^{2-} = A(PO_4)H_2^-$	1.7	2.3	0.85	1.15
$H_2A^{2+} + HPO_4^{2-} = A(PO_4)H_3^0$	2.6	3.0	0.65	0.75
$H_2A^{2+} + H_2PO_4^- = A(PO_4)H_4^+$	1.5	2.2	0.75	1.1
$H_3A^{3+} + H_2PO_4^- = A(PO_4)H_5^{2+}$	2.3	2.5	0.8	0.8
$HA^+ + P_2O_7^{4-} = A(P_2O_7)H^{3-}$	3.0	3.2[b]	0.75	0.8[b]
$H_2A^{2+} + P_2O_7^{4-} = A(P_2O_7)H_2^{2-}$	4.7	5.4	0.6	0.7
$H_2A^{2+} + HP_2O_7^{3-} = A(P_2O_7)H_3^-$	3.5	4.2	0.6	0.7
$H_2A^{2+} + H_2P_2O_7^{2-} = A(P_2O_7)H_4^0$	2.7	3.9	0.7	1.0
$H_3A^{3+} + H_2P_2O_7^{2-} = A(P_2O_7)H_5^+$	4.2	4.6	0.7	0.8
$H_3A^{3+} + H_3P_2O_7^- = A(P_2O_7)H_6^{2+}$	3.0	3.4	1.0	1.1
$HA^+ + Fe(CN)_6^{4-} = A[Fe(CN)_6]H^{3-}$	2.8	2.5[c]	0.7	0.6[c]
$H_2A^{2+} + Fe(CN)_6^{4-} = A[Fe(CN)_6]H_2^{2-}$	5.3	4.9	0.7	0.6
$H_3A^{3+} + Fe(CN)_6^{4-} = A[Fe(CN)_6]H_3^-$	7.5	7.2	0.6	0.6
$H_2A^{2+} + HFe(CN)_6^{3-} = A[Fe(CN)_6]H_3^-$	4.7			
$H_3A^{3+} + HFe(CN)_6^{3-} = A[Fe(CN)_6]H_4^0$	5.5	5.4	0.6	
$H_3A^{3+} + H_2Fe(CN)_6^{2-} = A[Fe(CN)_6]H_5^+$	4.2		0.7	0.6
$H_3A^{3+} + A[Fe(CN)_6]H_3^- = A_2[Fe(CN)_6]H_6^{2+}$	2.6	2.6	0.9	0.9

reaction	logK_{ij}		logK_{ij}/ζ	
	hmtt	trien	hmtt	trien
$HA^+ + HPO_4^{2-} = A(PO_4)H_2^-$	2.6	2.3	1.3	1.1
$H_2A^{2+} + HPO_4^{2-} = A(PO_4)H_3^0$	3.5	3.3	0.9	0.8
$H_2A^{2+} + H_2PO_4^- = A(PO_4)H_4^+$	3.1	3.8	1.5	1.9
$H_3A^{3+} + H_2PO_4^- = A(PO_4)H_5^{2+}$	3.1	3.6	1.0	1.2
$H_4A^{4+} + H_2PO_4^- = A(PO_4)H_6^{3+}$	4.1	3.7	1.0	0.9
$HA^+ + P_2O_7^{4-} = A(P_2O_7)H^{3-}$	2.7	2.8	0.7	0.7
$H_2A^{2+} + P_2O_7^{4-} = A(P_2O_7)H_2^{2-}$		5.5		0.9
$HA^+ + HP_2O_7^{3-} = A(P_2O_7)H_2^{2-}$	2.5		0.8	
$H_2A^{2+} + HP_2O_7^{3-} = A(P_2O_7)H_3^-$	3.7	5.3	0.6	0.9
$H_3A^{3+} + HP_2O_7^{3-} = A(P_2O_7)H_4^0$	6.0	6.6	0.7	0.7
$H_3A^{3+} + H_2P_2O_7^{2-} = A(P_2O_7)H_5^+$	4.4	5.6	0.7	0.9
$H_4A^{4+} + H_2P_2O_7^{2-} = A(P_2O_7)H_6^{2+}$	6.6	6.4	0.8	0.8
$H_4A^{4+} + H_3P_2O_7^- = A(P_2O_7)H_7^{3+}$	4.9	4.3	1.2	1.1

reaction	log K_{ij} penten	log K_{ij}/ζ penten
$HA^+ + HPO_4^{2-} = A(PO_4)H_2^-$	1.6	0.8
$H_2A^{2+} + HPO_4^{2-} = A(PO_4)H_3^0$	2.4	0.6
$H_3A^{3+} + HPO_4^{2-} = A(PO_4)H_4^+$	3.3	0.55
$H_4A^{4+} + HPO_4^{2-} = A(PO_4)H_5^{2+}$	5.0	0.6
$H_5A^{5+} + HPO_4^{2-} = A(PO_4)H_6^{3+}$	7.4	0.7
$H_5A^{5+} + H_2PO_4^- = A(PO_4)H_7^{4+}$	3.8	0.8
$A(PO_4)H_5^{2+} + HPO_4^{2-} = A(PO_4)H_6^0$	2.0	0.5
$A(PO_4)H_6^{3+} + HPO_4^{2-} = A(PO_4)H_7^+$	3.6	0.6

[a] Reference 14. [b] Reference 15. [c] Reference 16.

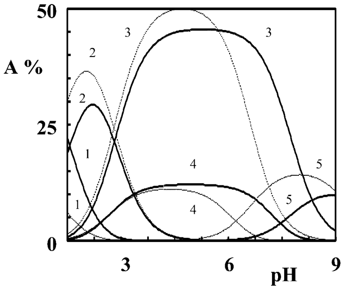

Figure 1. Speciation diagram of the systems diamine−$Fe(CN)_6^{4-}$ at I = 0 mol L^{-1} and t = 25 °C. Full line, en; dotted line, tmed (A = en or tmed). (1) $A[Fe(CN)_6]H_4^0$. (2) $A[Fe(CN)_6]H_3^-$. (3) $A[Fe(CN)_6]H_2^{2-}$. (4) $A_2[Fe(CN)_6]H_4^0$. (5) $A[Fe(CN)_6]H^{3-}$.

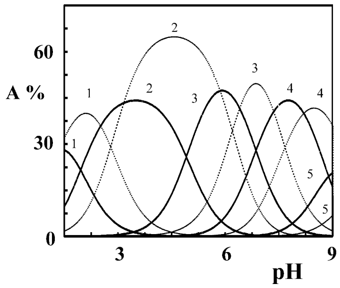

Figure 2. Speciation diagram of the systems tetramine−PO_4^{3-} at I = 0 mol L^{-1} and t = 25 °C. Full line, hmtt; dotted line, trien (A = hmtt or trien). (1) $A(PO_4)H_6^{3+}$. (2) $A(PO_4)H_5^{2+}$. (3) $A(PO_4)H_4^+$. (4) $A(PO_4)H_3^0$. (5) $A(PO_4)H_2^-$.

which may account for the differing abilities of these anions to form hydrogen bonds; (c) from the values of log K_{ij}, it is not possible to observe any difference between the complexing ability of unsubstituted and substituted polyammonium cations. Nevertheless, some quite important differences can be evidenced, by drawing the speciation profiles of analogous amines, as shown in Figures 1 and 2. In Figure 1, we compare the distribution of species in the analogous systems en−$Fe(CN)_6^{4-}$ and tmed−$Fe(CN)_6^{4-}$: differences in formation percentages are not significant, but there is a significant shift to lower pH values for the formation of all tmed species. For the hmtt−PO_4^{3-} and trien−PO_4^{3-} systems (Figure 2), we observe a similar trend, but the formation percentage of one of the species here, $A(PO_4)_5^{2+}$, is significantly higher for the unsubstituted amine. Analogous observations can be made for the other systems. Small differences in formation percentages can be found by investigating the various systems, while the shift to lower pH values was found for all the systems containing substituted amines.

Stability−Charge Relationships. As already found in many other investigations (see refs 3 and 17 and references therein), the charges involved in the formation reaction play a fundamental role in the stability of the various complexes. This is clearly shown in Figure 3 where log K_{ij} for inorganic complexes of N-methylsubstituted amines (including SO_4^{2-} species, from ref 18) is plotted versus ζ. Linearity is very good, and we obtain

$$\log K_{ij} = a\zeta \tag{8}$$

with a = 0.70 ± 0.04 and r = 0.997 (linear correlation coefficient). For the analogous species of unsubstituted amines (refs 10 and 14−16 and this work), we have a = 0.67 ± 0.03. We have already suggested using $\underline{n} = \zeta/2$ as a crude approximation of the number of possible salt bridges in order to estimate the free energy contribution per bond, ΔG_b^0:

$$\Delta G_b^0 = \Delta G_{ij}^0/\underline{n}$$

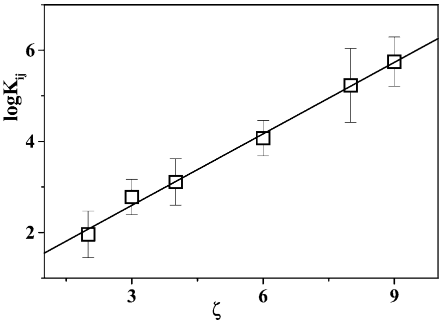

Figure 3. Dependence on ζ (charge product, eq 2) of log K_{ij} (eq 3) for the formation of fully *N*-methyl substituted polyammonium cation−inorganic polyanion, at $I = 0$ mol L^{-1} and $t = 25$ °C. Error bars are $\bar{\sigma} = \sigma/\sqrt{N}$ (N = number of complexes considered).

Table 4. Free Energy Contributions per Bond for Some Classes of Polyammonium Cation−Polyanion Complexes, at $I = 0$ mol L^{-1} and $t = 25$ °C

	substituted amines		unsubstituted amines	
anion	N^a	$-\Delta G_b{}^{0\ b}$	N^a	$-\Delta G_b{}^{0\ b}$
$SO_4{}^{2-}$ [d]	9	7.4 ± 0.4[c]	26	6.4 ± 0.2[c]
$PO_4{}^{3-}$	12	10.7 ± 0.6	34	8.5 ± 0.3
$P_2O_7{}^{4-}$	22	8.2 ± 0.3	71	8.2 ± 0.2
$Fe(CN)_6{}^{4-}$	12	7.4 ± 0.3	32	6.8 ± 0.2
$P_3O_{10}{}^{5-}$ [e]			49	7.5 ± 0.2

[a] N = number of species taken into account. [b] kJ mol^{-1} $\underline{n}^{-1}$. [c] ±Std dev. [d] Reference 18. [e] Reference 10.

Using the values reported above, we have

$$-\Delta G_b{}^0 = (8.0 \pm 0.5)\ \text{kJ mol}^{-1}\ \underline{n}^{-1}$$

$$-\Delta G_b{}^0 = (7.6 \pm 0.3)\ \text{kJ mol}^{-1}\ \underline{n}^{-1}$$

for substituted and unsubstituted amines, respectively. To give quantitative information about the differences in stability of the different inorganic anions, we report $\Delta G_b{}^0$ values for the complexes of these anions in Table 4. The general trend, valid for both substituted and unsubstituted amine complexes, is

$$PO_4{}^{3-} > P_2O_7{}^{4-} > P_3O_{10}{}^{5-} > SO_4{}^{2-} \approx Fe(CN)_6{}^{4-}$$

This trend is the same as that indicated by the basicity of these inorganic ligands.[13] A more sophisticated empirical relationship, which also accounts for the basicity of the inorganic anion, is

$$\log K_{ij} = b_0 + b_1\zeta + b_2 \log K_1^{\mathrm{H}}$$

(log K_1^{H} is the first protonation constant of the polyanion), with $b_0 = 0.29 \pm 0.10$, $b_1 = 0.564 \pm 0.011$, and $b_2 = 0.066 \pm 0.009$.

Discussion

The $\Delta G_b{}^0$ values reported in Table 4 indicate first that the maximum deviation is about ±2 kJ mol^{-1} $\underline{n}^{-1}$, and this quantity can be assumed as a measure of the "residual" contributions (positive or negative) to the stability of different factors. The latter include hydrogen bonding, steric, and solvation effects due to *N*-alkyl substitution, the length of the alkyl chain, the flexibility of ligands, charge dispersion, the acid−base properties of both amine and anion, and so forth. The overall average for all the inorganic complexes of both substituted and unsubstituted amines is $-\Delta G_b{}^0 = 7.8 \pm 0.4$ kJ mol^{-1} $\underline{n}^{-1}$, and therefore the residual effects account for ~25% of the stability of these species.

The $\Delta G_b{}^0$ values reported in this paper for species of substituted or unsubstituted polyammonium cations with inorganic anions can be compared with the values obtained for analogous species of the same cations with carboxylic anions. For malonate, citrate, 1,2,3-propanetricarboxylate, and 1,2,3,4-butanetetracarboxylate, we obtained[7] $a = 0.52$ and $a = 0.58$ (eq 1) for substituted and unsubstituted amines, respectively. Therefore, we may calculate

$$-\Delta G_b{}^0 = 5.9\ \text{kJ mol}^{-1}\ \underline{n}^{-1}$$

$$-\Delta G_b{}^0 = 6.6\ \text{kJ mol}^{-1}\ \underline{n}^{-1}$$

for the two types of complex. The overall average gives $-\Delta G_b{}^0 = 6.3 \pm 0.4$ kJ mol^{-1} $\underline{n}^{-1}$ for all the species formed by the above carboxylic ligands with polyammonium cations. As a general conclusion, the effect of *N*-alkyl substitution on the stability of the species considered is quite small (often comparable with experimental error) for both inorganic and organic anions. This was recently confirmed in a study[19] that includes both potentiometric and calorimetric investigations. Moreover, the entropic term $T\Delta S°$, for analogous species of substituted and unsubstituted amines, does not show statistically significant differences and the comparison of inorganic and organic anion systems gives significant evidence for a difference of ~1.5 kJ mol^{-1} $\underline{n}^{-1}$ in favor of inorganic species. This is consistent with the findings of previous comparative studies of the ΔG^0 and $T\Delta S^0$ values associated with the formation of organic and inorganic species with amine polycations.[20]

The stability data reported in this paper are also consistent with literature findings for $PO_4{}^{3-}$ and $SO_4{}^{2-}$ complexes of macrocyclic polyammonium cations.[21,22] For these species too, a significant difference ($PO_4{}^{3-} > SO_4{}^{2-}$) was observed, due to the different hydrogen bonding capabilities of the two inorganic ligands.

Literature Cited

(1) Bianchi, A.; Micheloni, M.; Paoletti, P. Thermodynamic Aspects of the Polyazacycloalkane Complexes with Cations and Anions. *Coord. Chem. Rev.* **1991**, *110*, 17−113.

(2) Izatt, R. M.; Pawlak, K.; Bradshaw, J. S. Thermodynamic and Kinetic Data for Macrocycle Interaction with Cation, Anions and Neutral Molecules. *Chem. Rev.* **1995**, *95*, 2529−2586.

(3) Daniele, P. G.; Prenesti, E.; De Robertis, A.; De Stefano, C.; Foti, C.; Giuffrè, O.; Sammartano, S. Binding of Inorganic and Organic Polyanions by Protonated Open Chain Polyamines in Aqueous Solution. *Ann. Chim.* (*Rome*) **1997**, *87*, 415−447.

(4) Lehn, J. M. *Supramolecular Chemistry, Concepts and Perspectives*; VCH: Weinheim, 1995.

(5) *Supramolecular Chemistry of Anions*; Bianchi, A., Bowman-James, K., Garcia-España, E., Eds.; Wiley: New York, 1997.

(6) Schneider, H. J.; Yatsimirsky, A. *Principles and Methods in Supramolecular Chemistry*; Wiley: Chichester, 2000.

(7) Cascio, S.; De Robertis, A.; De Stefano, C.; Sammartano, S. The effect of *N*-alkyl substitution on the binding of polycarboxylic anions by linear polyammonium cations. *J. Solution Chem.* **2000**, *29*, 1101−1114.

(8) De Stefano, C.; Princi, P.; Rigano, C.; Sammartano, S. Computer Analysis of Equilibrium Data in Solution. ESAB2M: An Improved Version of the ESAB Program. *Ann. Chim.* (*Rome*) **1987**, *77*, 643−675.

(9) De Stefano, C.; Mineo, P.; Rigano, C.; Sammartano, S. Ionic Strength Dependence of Formation Constants. XVII. The Calculation of Equilibrium Concentrations and Formation Constants. *Ann. Chim.* (*Rome*) **1993**, *83*, 243−277.

(10) De Stefano, C.; Foti, C.; Giuffrè, O.; Mineo, P.; Rigano, C.; Sammartano, S. Binding of Tripolyphosphate by Aliphatic Amines: Formation, Stability and Calculation Problems. *Ann. Chim.* (*Rome*) **1996**, *86*, 257−280.

(11) (a) Daniele, P. G.; De Stefano, C.; Foti, C.; Sammartano, S. The Effect of Ionic Strength and Ionic Medium on the Thermodynamic

Parameters of Protonation and Complex Formation. *Curr. Top. Solution Chem.* **1997**, *2*, 253−274. (b) Daniele, P. G.; De Robertis, A.; De Stefano, C.; Sammartano, S.; Rigano, C. On the Possibility of Determining the Thermodynamic Parameters for the Formation of Weak Complexes Using a Simple Model for the Dependence on Ionic Strength of Activity Coefficients. Na^+, K^+ and Ca^{2+} Complexes of Low Molecular Weight Ligands in Aqueous Solution. *J. Chem. Soc., Dalton Trans.* **1985**, 2353−2361.

(12) (a) Casale, A.; Foti, C.; Sammartano, S.; Signorino, G. Thermodynamic Parameters for the Protonation of Some Polyamines $C_{(2n-2)}N_nH_{(5n-2)}$ in NaCl Aqueous Solution at Different Ionic Strengths. *Ann. Chim.* (*Rome*) **1998**, *88*, 55−70. (b) Cascio, S.; De Robertis, A.; Foti, C. Protonation of polyamines in NaCl aqueous solution and binding of Cl^- by polyammonium cations. *Fluid Phase Equilib.* **2000**, *170*, 167−181.

(13) (a) Daniele, P. G.; De Robertis, A.; De Stefano, C.; Gianguzza, A.; Sammartano, S. Salts Effects on the Protonation of Ortho-Phosphate Between 10 and 50 °C, in Aqueous Solution. A Complex Formation Model. *J. Solution Chem.* **1991**, *20*, 495−515. (b) Capone, S.; De Robertis, A.; Sammartano, S.; Rigano, C. Studies on Hexacyanoferrate(II) Complexes. Formation Constants for Alkali Metal, Ammonium and Calcium(II) Complexes at Different Temperatures and Ionic Strengths in Aqueous Solution. *Thermochim. Acta* **1986**, *102*, 1−14. (c) De Robertis, A.; Rigano, C.; Sammartano, S. Studies on Hexacyanoferrate(II) Complexes. Potentiometric Determination of Protonation Constants in Li^+, Na^+, K^+, $NH_4{}^+$ and Ca^{2+} Chloride Media and Formation Constants, in Aqueous Solution at 25 °C, Using H^+-Glass and Potassium Ion Selective Electrodes. *Ann. Chim.* (*Rome*) **1984**, *74*, 33. (d) De Stefano, C.; Foti, C.; Gianguzza, A. Ionic Strength Dependence of Formation Constants. Part XIX. The Effect of Tetramethylammonium, Sodium and Potassium Chlorides on the Protonation Constants of Pyrophosphate and Triphosphate at Different Temperatures. *J. Chem. Res.* **1994** (S), *464* (M), 2639−2661.

(14) De Robertis, A.; De Stefano, C.; Gianguzza, A.; Sammartano, S. Binding of Polyanions by Biogenic Amines. I. Formation and Stability of Protonated Putrescine and Cadaverine Complexes with Inorganic Anions. *Talanta* **1998**, *46*, 1085−1093.

(15) De Stefano, C.; Foti, C.; Giuffrè, O.; Sammartano, S. Formation and Stability of Pyrophosphate Complexes with Aliphatic Amines in Aqueous Solution. *Talanta* **1996**, *43*, 707−717.

(16) De Stefano, C.; Foti, C.; Giuffrè, O. Binding of Hexacyanoferrate(II) by Aliphatic Amines in Aqueous Solution. *J. Solution Chem.* **1996**, *25*, 155−165.

(17) De Robertis, A.; De Stefano, C.; Foti, C.; Giuffrè, O.; Sammartano, S. Thermodynamic parameters for the binding of inorganic and organic anions by biogenic polyammonium cations. *Talanta* **2001**, *54*, 1135−1152.

(18) Foti, C.; Pettignano, A.; Sammartano, S. Thermodynamic parameters for the binding of sulphate by open chain polyammonium cations. *Ann. Chim.* (*Rome*) **2002**, *92*, 1067−1075.

(19) De Robertis, A.; De Stefano, C.; Pettignano, A. Thermodynamic parameters for the binding of polycarboxylic anions by fully methyl substituted linear polyammonium cations. *Ann. Chim.* (*Rome*) **2002**, *92*, 13−25.

(20) De Robertis, A.; De Stefano, C.; Giuffrè, O.; Sammartano, S. ΔG^0 and $T\Delta S^0$−Charge Relationships for the Binding of Inorganic and Organic Anions by Open Chain Polyammonium Cations: A Short Review. *Ann. Chim.* (*Rome*) **1999**, *89*, 23−35.

(21) Arranz, P.; Bencini, A.; Bianchi, A.; Diaz, P.; Garcia-España, E.; Giorni, C.; Luis Santiago, V.; Querol, M.; Valtancoli, B. Thermodynamics of sulphate anion binding by macrocyclic polyammonium receptors. *J. Chem. Soc., Perkin Trans.* **2001**, *2*, 1765−1770.

(22) Bazzicalupi, C.; Bencini, A.; Bianchi, A.; Cecchi, M.; Escuder, B.; Fusi, V.; Garcia-España, E.; Giorni, C.; Luis Santiago, V.; Taccagni, G.; Marcelino, V.; Paoletti, P.; Valtancoli, B. Thermodynamics of phosphate and pyrophosphate anions binding by macrocyclic polyammonium receptors. *J. Am. Chem. Soc.* **1999**, *121*, 6807−6815.

Received for review July 11, 2003. Accepted October 19, 2003. We thank the University of Messina for financial support (PRA).

JE034133M