

Selective Recognition of Carboxylate Anions by Polyammonium Receptors in Aqueous Solution. Criteria for Selectivity in Molecular Recognition¹

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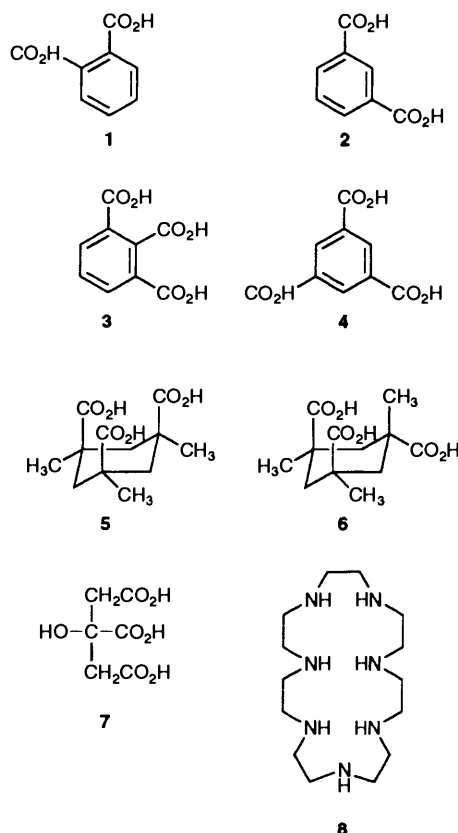
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The interaction in aqueous solution of the polyammonium receptor 1,4,7,10,13,16,19-heptaazacyclohencosane (**8**, [21]aneN₇) with the carboxylic species, 1,2-benzenedicarboxylic (**1**), 1,3-benzenedicarboxylic (**2**), 1,2,3-benzenetricarboxylic (**3**), 1,3,5-benzenetricarboxylic (**4**), *cis,cis*-1,3,5-trimethyl-1,3,5-cyclohexanetricarboxylic (**5**), *cis,trans*-1,3,5-trimethyl-1,3,5-cyclohexanetricarboxylic (**6**), and citric (**7**) acids has been followed by potentiometry and cyclic voltammetry at 298.1 K in 0.15 mol dm⁻³ NaClO₄, as well as by NMR spectroscopy. The analysis of the potentiometric and electrochemical data show the formation of 1:1 adducts. A novel method based on both potentiometry and cyclic voltammetry to establish selectivity patterns in systems presenting different protonation possibilities is introduced. Preorganization of the substrates in a shape complementary to the receptor yields interesting features such as the selective recognition of **5** over its epimer **6** and recognition of the dicarboxylic species **1** and **2** over the tricarboxylic ones **6** and **7**.

The design of receptors for selectively recognizing guests in aqueous solution is an important target according to the biological relevance of the studies in this solvent.² This goal is not easily achieved as strong solvent-guest interactions can efficiently compete with the process of selective recognition. Molecular recognition of polycarboxylic acids and amino acids has received much attention in recent years.³⁻⁸ Strong selective complexation of such guests has been achieved mainly in non-polar solvents. Receptors displaying well-preorganized binding sites have been designed for this purpose. In polar solvents and especially in water, only moderate or low selectivities have been found, however, in a few instances,⁹ when factors like π -stacking effects modulate the host-guest interaction large selectivity ratios in the binding of anions can be obtained. Preorganization plays an essential role in host-guest chemistry.¹⁰ Simple monocyclic polyammonium species have been considered as poorly organized receptors and only moderate chain-length selectivities in the binding of α,ω -dicarboxylic acids have been described for these receptors.⁶⁻⁸ However, protonation of the polyammonium macrocycles should provide a limited organization to the receptor. In any case, this degree of organization is too low to achieve strong selectivities in the binding of α,ω -dicarboxylic acids that present high conformational freedom.

In the present paper we report on the interaction of the carboxylic species, 1,2-benzenedicarboxylic (**1**), 1,3-benzenedicarboxylic (**2**), 1,2,3-benzenetricarboxylic (**3**), 1,3,5-benzenetricarboxylic (**4**), *cis,cis*-1,3,5-trimethyl-1,3,5-cyclohexanetricarboxylic (**5**), *cis,trans*-1,3,5-trimethyl-1,3,5-cyclohexanetricarboxylic (**6**), and citric (**7**) acids, with the macrocyclic receptor 1,4,7,10,13,16,19-heptaazacyclohencosane (**8**, [21]aneN₇).¹¹ We provide evidence that preorganization of the carboxylate into a shape that could be complementary to that of the protonated host plays an outstanding role in determining selectivities. Even selective recognition of one epimer over another and of dicarboxylic species over tricarboxylic ones can be achieved.

Because both host and guest are polyprotic species and interact forming adducts with a variety of degrees of proton-



ation, to evaluate selectivity at each pH value is often difficult in these systems. To overcome this problem, we present a novel method to define selectivity throughout all the pH range based on both potentiometric and electrochemical techniques. This method does not require any assumption of the location of the protons in the interacting species. The electrochemical method

is based on competitive cyclic voltammetry and can be applied to any non-electroactive species like the carboxylic compounds herein studied.

Experimental

Materials.—NaClO₄ (C. Erba, ACS grade) used as a supporting electrolyte in all potentiometric and electrochemical measurements was purified according to a procedure already described.¹² K₄[Fe(CN)₆]·3H₂O (C. Erba, ACS grade) utilized in the electrochemical measurements was used without further purification. The receptor [21]aneN₇ and its hydrochloride salt were synthesized as described in ref. 11. Acids **5** and **6** were synthesized following the procedure described in ref. 14. All the other di- and tri-carboxylic acids were purchased from Aldrich having purity greater than 99% and were used without further purification.

Electromotive Force (emf) Measurements.—The potentiometric measurements have been carried out at 298.1 K in 0.15 mol dm⁻³ NaClO₄ by using the equipment (potentiometer, burette, cell, stirrer, microcomputer, etc.) that has been fully described.¹⁵ The acquisition of the data was performed by means of the computer program PASAT.¹⁶ The reference electrode was an Ag/AgCl electrode in saturated NaClO₄. The glass electrode (Orion model 91-01) was calibrated as a hydrogen concentration probe, by titration of well-known amounts of HCl with CO₂-free NaOH solutions and determining the equivalent point by the Gran's method,¹⁷ which provides the standard potential of the cell and the ionic product of water [$pK_w = 13.73(1)$ at 298.1 K and 0.15 mol dm⁻³ NaClO₄]. The protonation constants of the polycarboxylic acids here considered have been determined for our experimental conditions (see Table 1). The protonation constants of [21]aneN₇ have been taken from ref. 18 and the equilibrium constants for the system [Fe(CN)₆]⁴⁻–[21]aneN₇ required in the calculation of distribution diagrams and in some aspects of the electrochemical study from ref. 19. The computer program SUPERQUAD¹⁹ was used to calculate all the equilibrium constants. The titration curves for each system were treated either as a single set or as separated entities without significant variations in the values of the equilibrium constants. Furthermore, the sets of data were merged together and treated simultaneously to give the final equilibrium constants. The distribution diagrams for the binary and ternary systems have been calculated by means of the computer program DISPO.²¹

Electrochemical Measurements.—Cyclic voltammetric and chronoamperometric measurements were carried out using the instrumentation previously described.¹⁹ Cyclic voltammograms were obtained using a three electrode system with gold, platinum and glassy carbon working electrodes, a platinum wire counter and a saturated calomel reference electrode (SCE). The sweep rate varied from 50 to 500 mV s⁻¹. Prior to the series of runs, the working electrodes were cleaned and activated.²² All experiments were made under an argon atmosphere in a cell thermostatted at 298.1 K. All samples were 0.15 mol dm⁻³ in NaClO₄ to maintain constant the ionic strength. The pH was adjusted to the desired values by adding appropriate amounts of HClO₄ or NaOH solutions.

To evaluate the molar fraction of complexed [Fe(CN)₆]⁴⁻, α_M , experimental and theoretical cyclic voltammograms were compared. Recently, computer assisted simulation of cyclic voltammograms has been suggested to provide an alternative procedure to analyse single and multiple ligand–metal equilibria.²³ However, the principal requirement of the technique is that the analyte of interest undergoes reversible electrochemical oxidation or reduction, deviations from reversibility and

uncompensated resistance in the cell severely limited the accuracy of quantitations in real sample analysis.²⁴ Despite the fact that other potentially useful strategies were available for cyclic voltammogram simulations, the procedure chosen for this application consisted of addition of working curves for uncomplexed [Fe(CN)₆]⁴⁻ and its complexed forms, as previously described.¹⁹ Current potential curves were calculated from the tabulated values of the current function²⁴ for one-electron reversible processes by adding the electrode currents for the free and complexed [Fe(CN)₆]⁴⁻ species, as previously described.¹⁹ Computation includes formal potentials of the [Fe(CN)₆]³⁻/[Fe(CN)₆]⁴⁻ couple, for free [Fe(CN)₆]⁴⁻ and its complexed species, and the diffusion coefficients of all the electroactive species. The latter is a significant difference with respect to other simulation procedures, in which it is assumed that all the species diffuse at the same rate.²⁶ Since the peak currents for free and complexed [Fe(CN)₆]⁴⁻ species are clearly different, a realistic simulation must include reliable values for the diffusion coefficients of these species. Formal potentials and diffusion coefficients were obtained from experimental cyclic voltammograms, the diffusion coefficients being confirmed from potential-step chronoamperometric experiments.

The α_M values were calculated from curve-fitting of experimental cyclic voltammograms by theoretical ones. A simplified procedure, involving linear fitting of a set of parameters (peak and half-peak potentials and currents) as used in quantitative resolution of overlapped peaks,²⁷ provides rapid and satisfactory results. α_M Values were also estimated from chronoamperometric measurements, providing a mean diffusion coefficient can be defined as in general metal–ligand equilibria.²⁸ Then, α_M can be calculated from the relationship $\alpha_M = (D - D_M)/(D_{ML} - D_M)$, where D_M is the diffusion coefficient for [Fe(CN)₆]⁴⁻, D_{ML} is the limiting diffusion coefficient for the system [Fe(CN)₆]⁴⁻–[21]aneN₇, and D is the actually determined mean diffusion coefficient.

Potentiostatic chronoamperograms were obtained by applying a constant potential, sufficiently positive to ensure diffusion limited current for all the species. Conventional long-time experiments have been performed to accurately determine diffusion coefficients, as recently recommended.²⁹ In all experiments, linear relationships between the observed curves and $t^{-1/2}$ were observed for times up to 3 s after the potential step. The diffusion coefficients were calculated from the experimental $i-t$ curves by: (i) least-square slope of i vs. $t^{-1/2}$ plot [Cottrell equation, $i = nFAc(\pi D)^{-1/2}t^{-1/2}$]; (ii) least-square intercept of $it^{1/2}$ vs. $t^{1/2}$ plot; and (iii) linear extrapolation of i at infinite time. Good agreement was obtained for the D values calculated by all the methods.

NMR Spectroscopy.—¹H and ¹³C NMR spectra were recorded at 200.0 and 50.3 MHz respectively, on a Varian Gemini 200 instrument using either Me₄Si or sodium 3-(trimethylsilyl)propionate (DSS) as the internal reference.

Crystal Structure Determination of Na₂[5]-4H₂O(Na₂[C₁₂H₁₆O₆]-4H₂O).—Structural determination was carried out with an Enraf–Nonius CAD4 X-ray diffractometer. A crystal (dimensions ca. 0.1 × 0.1 × 0.05 mm) of the compound was used for data collection. The compound crystallizes in the C2/c space group ($Z = 8$); lattice constants are: $a = 29.89(1)$, $b = 8.07(1)$, $c = 14.64(1)$ Å and $\beta = 106.52(4)^\circ$. Intensities were collected up to $2\theta = 40^\circ$, by using Mo-K α graphite monochromatized radiation and corrected for Lorentz and polarization effects. During data collection three standard reflections were monitored, no loss of intensity was recognized. The structure was solved, by using the 234 reflections having $I > 3\sigma(I)$, with the direct methods of MULTAN-78,³⁰ which

Table 1 Logarithms of the cumulative and stepwise protonation constants of acids 1–7 determined at 298.1 K in 0.15 mol dm⁻³ NaClO₄

Reaction	X ⁿ⁻						
	1, n = 2	2, n = 2	3, n = 3	4, n = 3	5, n = 3	6, n = 3	7, n = 3
X ⁿ⁻ + H ⁺	4.916(2) ^a	4.206(2)	5.401(2)	4.382(4)	7.289(5)	6.921(8)	5.441(2)
X ⁿ⁻ + 2H ⁺	7.678(2)	7.444(2)	9.300(2)	8.043(5)	13.47(1)	11.64(1)	9.615(4)
X ⁿ⁻ + 3H ⁺			11.945(5)	10.991(6)	17.07(2)	15.46(2)	12.359(8)
HX ⁽ⁿ⁺¹⁾⁻ + H ⁺	2.76	3.24	3.90	3.66	6.18	4.72	4.17
H ₂ X ⁽ⁿ⁺²⁾⁻ + H ⁺			2.65	2.95	3.60	3.82	2.74

^a Values in parentheses are standard deviations in the last significant figure.

Table 2 Logarithms of the cumulative and stepwise stability constants for the interaction of acids 1–7 with [21]aneN₇, determined at 298.1 ± 0.1 K in 0.15 mol dm⁻³ NaClO₄

Reaction	X ⁿ⁻						
	1, n = 2	2, n = 2	3, n = 3	4, n = 3	5, n = 3	6, n = 3	7, n = 3
L + X ⁿ⁻ + 3H ⁺	30.85(2) ^a	30.66(4)	30.89(3)	30.78(2)	31.05(7)	30.23(4)	
L + X ⁿ⁻ + 4H ⁺	38.58(2)	38.00(2)	39.24(1)	38.67(2)	39.32(4)	38.06(3)	36.82(1)
L + X ⁿ⁻ + 5H ⁺	44.03(2)	42.90(4)	46.05(2)	44.02(3)	46.46(5)	44.46(4)	42.37(1)
L + X ⁿ⁻ + 6H ⁺	48.20(2)	46.73(4)	50.97(3)	47.95(4)	52.83(4)	49.61(5)	46.53(2)
L + X ⁿ⁻ + 7H ⁺	51.42(4)	50.30(4)	54.60(4)	51.92(4)	57.63(4)	53.60(7)	50.08(2)
L + X ⁿ⁻ + 8H ⁺	53.64(3)	52.77(4)	57.64(5)	54.95(4)	61.23(5)	57.61(7)	
L + X ⁿ⁻ + 9H ⁺			60.20(5)	57.78(5)	64.31(5)	59.90(1)	
X ⁿ⁻ + H ₃ L ³⁺	3.1	3.0	3.2	3.1	3.4	2.5	
X ⁿ⁻ + H ₄ L ⁴⁺	4.5	3.9	5.2	4.6	5.2	4.0	2.7
X ⁿ⁻ + H ₅ L ⁵⁺	6.2	5.1	8.2	6.2	8.6	6.6	4.6
X ⁿ⁻ + H ₆ L ⁶⁺	8.2	6.8	11.0	8.0	12.9	9.7	6.6
X ⁿ⁻ + H ₇ L ⁷⁺	9.5	8.4	12.7	10.0	15.7	11.7	8.1

^a Values in parentheses are standard deviations in the last significant figure.

showed all the non-hydrogen atoms. An absorption correction was applied, once the structure was solved by using the DIFABS³⁰ program. The refinement was carried out by separating the parameters into two blocks, because of the low observed reflections/total parameters ratio, due to the poor quality of the crystal. For the same reason all the atoms were refined isotropically and the hydrogen atoms linked to the carbon atoms were introduced in calculated positions with thermal factors equal to those of the corresponding carbon atoms. The convergence factors were $R = 0.088$ and $R_w = 0.066$. All calculations were performed on a IBM Personal System/2 Model 80 computer with the SHELX-76 set of programs³¹ that uses the analytical approximation for the atomic scattering factors and anomalous dispersion corrections for all the atoms from ref. 33. Tables containing atomic coordinates, isotropic thermal parameters for the non-hydrogen atoms, bond distances and angles for the diacid and the coordination sphere around the sodium cations are included in the supplementary material.* The molecular plots were produced by the program ORTEP.³⁴

Results

Potentiometry.—The interaction between [21]aneN₇, **8**, and the different polycarboxylic guests studied has been investigated by potentiometry at 298.1 K in 0.15 mol dm⁻³ NaClO₄ in the pH range 3–10. The basicity constants for the carboxylic substrates determined under these experimental conditions are presented in Table 1. Table 2 shows the cumulative and the stepwise stability constants [as defined by eqns. (1) and (2), respectively] for the interaction of the fully deprotonated anionic forms of the substrates with [21]aneN₇.

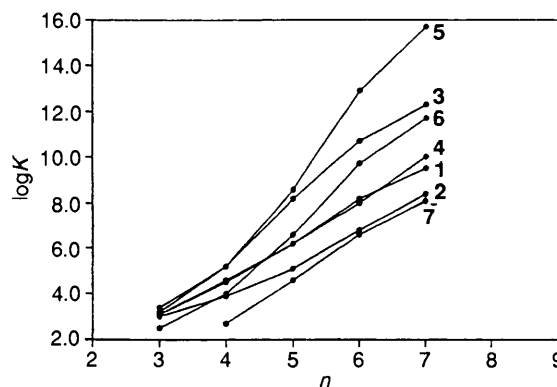
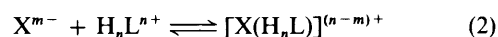
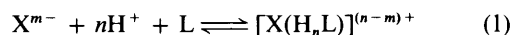


Fig. 1 Plot of the logarithms of the stepwise stability constants for the addition of the fully deprotonated carboxylic substrates to [21]aneN₇, as a function of the protonation degree of the complexed species, n



In Fig. 1, the stepwise stability constants are plotted *vs.* the protonation degree (n) of the supramolecular species. Several features deserve to be discussed. First of all, the stoichiometry found in solution for the complexes formed is always 1 : 1. Such a stoichiometry is derived from the analysis of the emf data with the computer program SUPERQUAD.²⁰ As will be discussed later, the electrochemical analyses further confirm this stoichiometry. For any protonation degree, **7** is the least interacting guest with [21]aneN₇, while, at least for the higher protonation degrees, **5** displays the largest constants (Fig. 1, Table 2). It can also be seen that **1** and **2** present larger constants than **7**; the constants of **1** being comparable to those of **4**. On the other

* For details of the CCDC deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1994, issue 1.

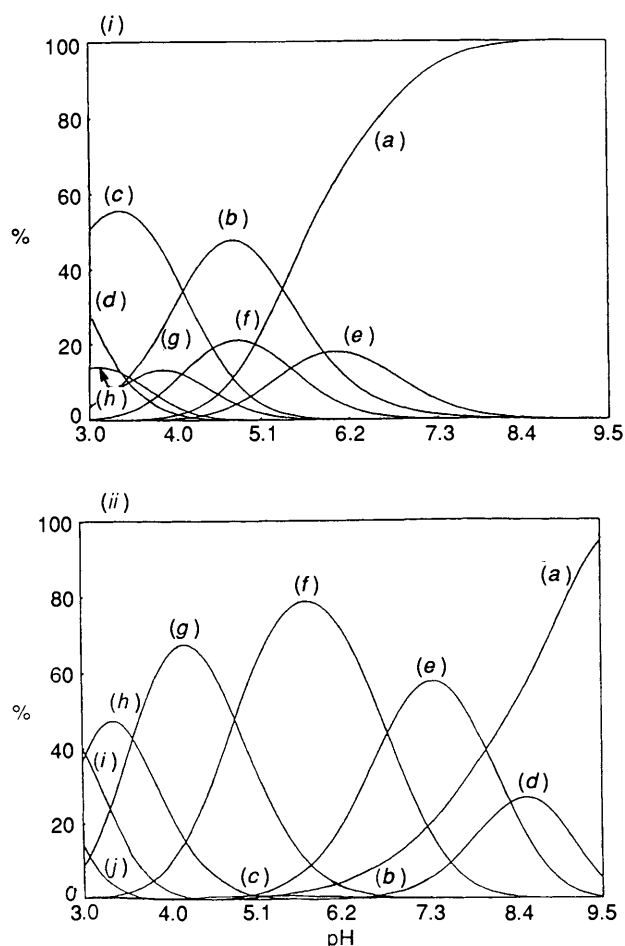


Fig. 2 (i) Distribution diagram for the species existing in equilibria as a function of pH for the system 7-[21]aneN₇; (a) 7, (b)–(d) H₇–H₃7, (e)–(h) H₄L7–H₇L7. (ii) Distribution diagram for the species existing in equilibria as a function of pH for the system 3-[21]aneN₇; (a) 3, (b) H₃, (c) H₂3, (d)–(j) H₃L3–H₉L3. Concentration for all the reagents 1×10^{-3} mol dm⁻³.

hand, in accord with similar studies, for a given substrate, the stability of the complexed species increases with the protonation degree, n . Furthermore, the differences in stability between analogous complexes of different guests increases with the protonation degree. Thus, these data suggest that very high selectivities can be achieved in these systems, as well as selective recognition of dicarboxylates derived from 1 and 2 over some of the tricarboxylates considered. However, to perform direct comparisons between stepwise stability constants and concentrations of complexed species could be misleading because of the different basicities of the guests involved (see Table 1). Basicity constants have to be somehow considered for this purpose. Nevertheless, a straight comparison between 7 and 3 can be made since their basicities are similar (Table 1). All the stepwise stability constants of 3 are about three orders of magnitude greater than those of 7. This figure [$K(3)/K(7) > 1000$] represents one of the highest selectivities up to now reported for the interaction of polycarboxylate anions with polyammonium receptors in aqueous solution. As a matter of fact, in the distribution diagram of the system 7-[21]aneN₇, calculated for 1:1 receptor–substrate molar ratio, free 7 and its protonated forms are the prevailing ones in solution, while in the corresponding distribution diagram for the system 3-[21]aneN₇, 3 is almost quantitatively complexed throughout the whole pH range (see Fig. 2).

To establish concentration selectivity ratios for all the other systems, a criterion balancing the differences in basicity should

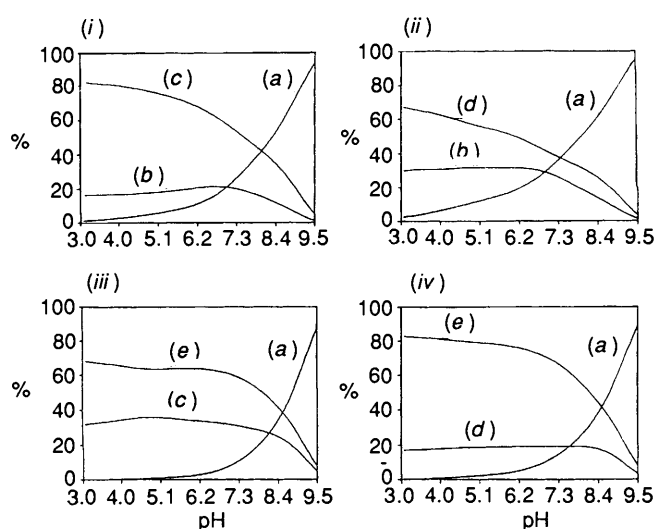


Fig. 3 Calculated overall distribution diagram for the species existing in equilibria as a function of pH for the systems: (i) 1–6-[21]aneN₇; (ii) 2–6-[21]aneN₇; (iii) 1–5-[21]aneN₇; (iv) 2–5-[21]aneN₇ (a) H_pL, (b) H₄L6, (c) H₄L1, (d) H₄L2, (e) H₄L5. Concentrations for all the reagents 1×10^{-3} mol dm⁻³. The sums of percentages of complexed species are plotted vs. pH.

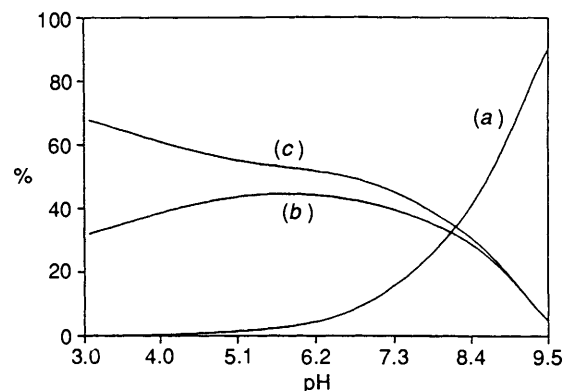


Fig. 4 Calculated overall distribution diagram for the species existing in equilibria as a function of pH for the system, 4–1-[21]aneN₇. (a) H_pL, (b) H₄L1, (c) H₄L4. Concentrations for all the reagents 1×10^{-3} mol dm⁻³. The sums of percentages of complexed species are plotted vs. pH.

be adopted. The most appropriate way is to calculate the distribution of the complexed species as a function of pH for the mixed (substrate A)–(substrate B)–[21]aneN₇ systems and to represent their overall percentages of formation. This method, which allows for attributing selectivities over all of the pH range, does not require any assumption of the location of the protons in the interacting species, which is a common source of erroneous interpretation of such a parameter.

To illustrate this method an interesting example could be the comparison of the dicarboxylic species 1 and 2 with the epimers 5 and 6. From Fig. 1, if basicity is not considered, it could be thought that complexes of 5 should predominate over those of both 1 and 2 throughout all the pH range, while complexes of 6 should prevail over those of both 1 and 2, at least for protonation degrees greater than 4. However, mixed distribution diagrams for these systems (Fig. 3) reveal that complexes of 1 and 2 clearly predominate over those of 6, the selectivity ratios being larger for 1. The reverse situation occurs for 5. A comparison between 1 and 2 obviously indicates a greater affinity of the 1,2-isomer for [21]aneN₇. In the case of 7, the selectivity ratios favouring the dicarboxylic substrates are even larger.

Similar plots allow one to conclude that 3 prevails over 4 and 1 over 2, while both tricarboxylic substrates interact more

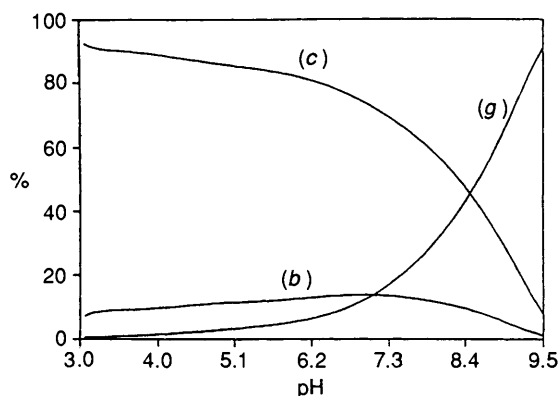


Fig. 5 Calculated overall distribution diagram for the species existing in equilibria as a function of pH for the system, 5-6-[21]aneN₇. (a) H_pL, (b) H_qL6, (c) H_rL5. Concentrations for all the reagents 1 × 10⁻³ mol dm⁻³. The sums of percentages of complexed species are plotted vs. pH.

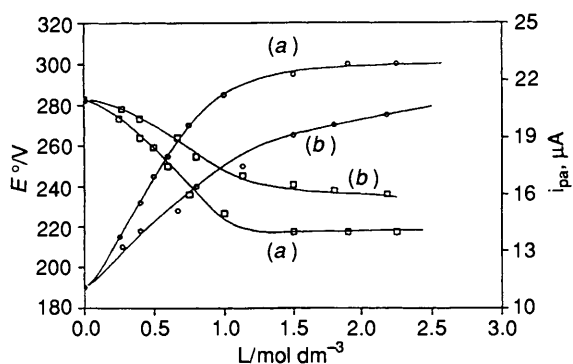


Fig. 6 Variation of the formal potential (O) and the anodic peak current (□) with the [21]aneN₇-[Fe(CN)₆]⁴⁻ molar ratio in the absence (a) and in the presence (b) of 6 at pH = 6.50. (a) c_M = 1.30 × 10⁻³ mol dm⁻³; (b) c_M = 1.30 × 10⁻³; c_X = 2.90 × 10⁻³ mol dm⁻³

strongly with [21]aneN₇ than both dicarboxylic ones. In Fig. 4, it can be seen that the more strongly interacting tricarboxylic aromatic guest 4 is recognized by [21]aneN₇ over the more strongly interacting dicarboxylic substrate 1. Thus, the general selectivity order for the aromatic substrates is 3 > 4 > 1 > 2.

Finally, it is of interest to compare the epimers 5 and 6. In Fig. 5 it is shown that for equimolar amounts of both of them and [21]aneN₇, an almost quantitative recognition of the *cis,cis*-epimer was produced.

By using this type of analysis, the complete selectivity order for the studied substrates is 3 > 5 > 4 > 1 > 2 > 6 > 7.

Electrochemistry.—Potentiometry is by far the most accurate technique to study this kind of system. However, the complexity of these systems make it advisable to use, as far as possible, alternative techniques to confirm the stoichiometry of the species as well as the extent of the interaction. In our case, competitive cyclic voltammetry (CV) has been of great help. As a matter of fact, as early as 1981,³⁵ it was pointed out that competitive cyclic voltammetry between electroactive and non-electroactive species could be a valuable tool in determining interaction strengths in anion coordination chemistry. However, as far as we know, this method has not been further developed. In this work, electrochemical data can be used to confirm the stoichiometries of the polycarboxylate-[21]aneN₇ complexes by applying an extension of the molar ratio method.³⁶

The cyclic voltammetric response for [Fe(CN)₆]⁴⁻ solutions, consisting of a one-electron reversible couple is altered significantly in presence of anionic receptors. As already

described,^{19,35,37} upon addition of increasing amounts of receptor at a given pH, the peak current decreases while the peak potentials are shifted toward more positive values. For receptor: [Fe(CN)₆]⁴⁻ molar ratios larger than unity, however, the CV pattern remains almost unchanged and consists of a one-electron diffusion-controlled reversible couple.

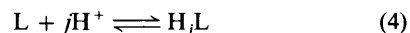
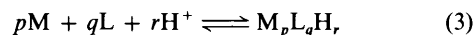
Since carboxylate anions were found to be non-electroactive and compete with [Fe(CN)₆]⁴⁻ for the coordination to the receptor, and no significant interaction between [Fe(CN)₆]⁴⁻ and the carboxylate anions occurs, addition of carboxylic species to a solution of receptor and [Fe(CN)₆]⁴⁻ determines an increase of uncomplexed [Fe(CN)₆]⁴⁻ at the expense of its complexed forms. Then, a consequent shift of the electrochemical parameters between those of free and complexed [Fe(CN)₆]⁴⁻ is observed.

For instance, curves (a) in Fig. 6 show the variation of the cyclic voltammetric formal potential and the anodic peak current with the molar ratio [21]aneN₇-[Fe(CN)₆]⁴⁻ (L-M) at pH = 6.5. Both curves exhibit a sharp break at L:M = 1, indicating the formation of a strong 1:1 complex. Curves (b) in Fig. 6 present the variation of such parameters for a series of samples containing constant concentrations of [Fe(CN)₆]⁴⁻ and 6 and varying concentrations of [21]aneN₇ at the same pH. The presence of the carboxylic species induces a shift of the electrochemical parameters towards the values corresponding to uncomplexed [Fe(CN)₆]⁴⁻; larger L:M ratios are then required to reach the limiting values of the electrochemical parameters.

Since some polymeric species have been found in crystalline compounds involving polyammonium receptors,^{37,38} it was conceivable that such a species could also be present in solution; therefore, complementary methods might be of interest to elucidate the degree of condensation of the complexed species as well as to confirm the 1:1 stoichiometry inferred from the potentiometric data.

Recent works have been published extending the classical polarographic methods³⁸ involving single and multiple ligand equilibria to cyclic voltammetry.^{23,26} However, these methods are restricted to series of mononuclear complexes and processes involving reduction of ions to metallic state or to amalgams.

Firstly, the generalized molar ratio method³⁶ has been applied to determine the stoichiometry and pH-dependent equilibrium constants of the [Fe(CN)₆]⁴⁻-[21]aneN₇ complexes for the pH values in which one can assume that only one complex predominates in solution, in which the equilibria (3) and (4) occur.



Potentiometric measurements provide the values of the corresponding equilibrium constants, β_{p,q,r} and β_j.

At a given pH, S-shaped molar ratio curves were obtained by changing the concentration of receptor with constant [Fe(CN)₆]⁴⁻ concentration. Then, chronoamperograms and simulated cyclic voltammograms (see Experimental section) were used to estimate the α_M values (α_M = p[M_pL_qH_r]/c_M) for different ligand to [Fe(CN)₆]⁴⁻ molar ratios. It can be easily demonstrated that only the adequate values of the stoichiometric coefficients, p and q, keep constant the relationship (5),

$$K_M = \alpha_M^{1/q} / [p^{1/q}(1 - \alpha_M)^{p/q}(c_L - q\alpha_M c_M/p)] \quad (5)$$

where c_M and c_L stand for the total concentrations of metal and ligand, respectively. The stability constants, β_{p,q,r}, can be easily related to the constant K_M and the protonation constants of the ligand β_j, by means of eqn. (6).

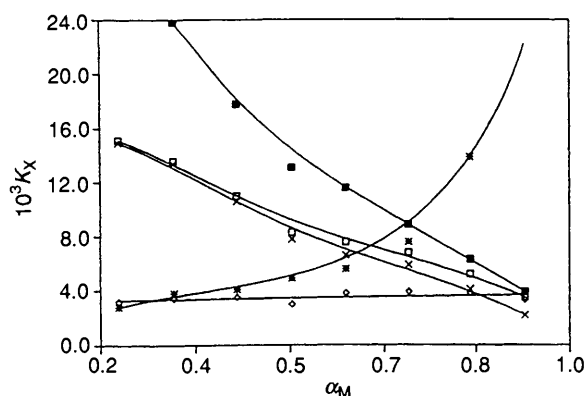


Fig. 7 Application of the generalized molar ratio method to the system $[\text{Fe}(\text{CN})_6]^{4-}$ -6-[21]aneN₇ at pH = 6.50. K_X vs. α_M only gives a horizontal line for 1:1 substrate receptor stoichiometry. (\diamond) 1:1, (\times) 2:1, (\ast) 1:2, (\square) 2:2, (\blacksquare) 3:3.

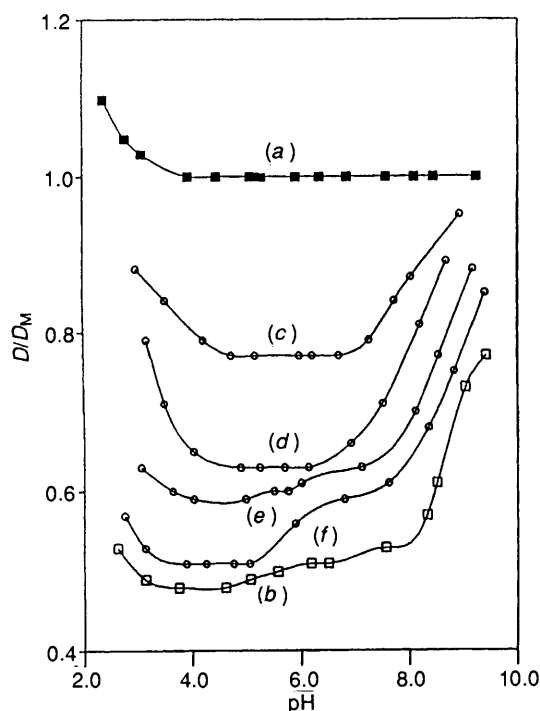


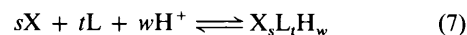
Fig. 8 Plots of the pH dependence of the chronoamperometric diffusion coefficients relative to the diffusion coefficient of uncomplexed $[\text{Fe}(\text{CN})_6]^{4-}$ at neutral pH for (a) $[\text{Fe}(\text{CN})_6]^{4-}$, (b) $[\text{Fe}(\text{CN})_6]^{4-}$ -[21]aneN₇, (c) 5- $[\text{Fe}(\text{CN})_6]^{4-}$ -[21]aneN₇, (d) 1- $[\text{Fe}(\text{CN})_6]^{4-}$ -[21]aneN₇, (e) 2- $[\text{Fe}(\text{CN})_6]^{4-}$ -[21]aneN₇, (f) 6- $[\text{Fe}(\text{CN})_6]^{4-}$ -[21]aneN₇. All the concentrations 2×10^{-3} mol dm⁻³.

$$\beta_{p,q,r} = c_M^{1-p} K_M^q (1 + \sum \beta_j [\text{H}]^j)^q [\text{H}]^{-r} \quad (6)$$

For the $[\text{Fe}(\text{CN})_6]^{4-}$ -[21]aneN₇ system, both the potentiometric and cyclic voltammetry data indicate that a single complex species predominates in the pH range 5.5–7.0. From the molar ratio method, at pH 6.5 a value of $K_M = 5.0 \times 10^4$ is estimated. From this value one can calculate $\log \beta_{1,1,4} = 39.1$, in agreement with the potentiometric value $\log \beta_{1,1,4} = 39.15$.¹⁹

Although this method cannot be directly applied to the study of the interaction of electroinactive species, as is the case of [21]aneN₇ and the carboxylic species here considered, electrochemical techniques can be used to analyse their interaction with polyazaalkanes by means of the competitive effect that is produced on the interaction $[\text{Fe}(\text{CN})_6]^{4-}$ -[21]aneN₇. To elucidate the stoichiometry of the complex species formed

between a given carboxylate anion and [21]aneN₇ in presence of $[\text{Fe}(\text{CN})_6]^{4-}$, the molar ratio method was applied to the electrochemical data monitored for a series of samples containing constant amounts of $[\text{Fe}(\text{CN})_6]^{4-}$ and carboxylate and varying concentrations of ligand at a given pH. As before, it is assumed that only one complex formation equilibrium occurs significantly in solution, in competition with the coordination of the receptor to $[\text{Fe}(\text{CN})_6]^{4-}$ [eqn. (7)].



This is accompanied by the protonation equilibria of the carboxylate anion [eqn. (8)].



The corresponding constants, $\beta_{s,t,w}$ and β_y , are known from potentiometric data, and from the electrochemical data a new series of α_M values was calculated allowing an estimate of the molar ratio α_X , being $\alpha_X = s[X_sL_tH_w]/c_X$, from the relationship (9).

$$c_X = [c_L - q/p(\alpha_M c_M - \alpha_M^{1/q})(1 - \alpha_M)^{-p/q} K_M^{-1} p^{-1/q}] / [(s/t)\alpha_X] \quad (9)$$

Then one can obtain eqn. (10).

$$K_X = \frac{p^{1/q} \alpha_X^{1/t} (1 - \alpha_M)^{p/q} K_M}{s^{1/t} \alpha_M^{1/q} (1 - \alpha_X)^{s/t}} \quad (10)$$

Providing the p , q coefficients, and the pH-dependent equilibrium constants K_M are known, K_X should take just constant values for the appropriate values of s and t , indicating the correct stoichiometry of the species formed.

For all the carboxylic substrates studied, the application of this method has led to 1:1 receptor:substrate stoichiometries, confirming the formation of polymeric species must be discharged. In Fig. 7, plots of K_X vs. α_X are presented for the system $[\text{Fe}(\text{CN})_6]^{4-}$ -[21]aneN₇-6 at pH 6.50.

The carboxylic substrate interacting most strongly with the receptor should be the one displacing the electrochemical parameters most. Therefore, this competitive effect can be quantitatively studied by comparing the formal potentials and peak currents of solutions containing equimolar amounts of $[\text{Fe}(\text{CN})_6]^{4-}$ and [21]aneN₇ with those with the same concentration of the different carboxylic acids. As Fig. 8 shows, chronoamperometrically determined diffusion coefficients clearly reveal significant variations in the competitive effect produced by the different carboxylate anions in the $[\text{Fe}(\text{CN})_6]^{4-}$ -[21]aneN₇ interaction. Points (a) in this Figure correspond to the pH dependence of the diffusion coefficient for uncomplexed $[\text{Fe}(\text{CN})_6]^{4-}$. For neutral and weakly acidic solutions the diffusion coefficient remains unchanged; however, below pH 4, its values increase as the pH decreases. This fact is attributable to the protonation of the hexacyanoferrate(II) ion.⁴⁰ Points (b) correspond to the D values for solutions with equimolar amounts of $[\text{Fe}(\text{CN})_6]^{4-}$ and [21]aneN₇. In the pH range from 4.0 to 8.0 a significant difference is obtained with respect to the diffusion coefficient for uncomplexed $[\text{Fe}(\text{CN})_6]^{4-}$. For solutions with equimolar concentrations of $[\text{Fe}(\text{CN})_6]^{4-}$, [21]aneN₇ and different acids [curves (c), (d), (e), (f)], the D values exhibit intermediate values between those corresponding to the complexed and uncomplexed $[\text{Fe}(\text{CN})_6]^{4-}$, respectively. Computer-assisted simulation of cyclic voltammograms allows us to make direct estimates of the percentages of complexed $[\text{Fe}(\text{CN})_6]^{4-}$, in the presence and absence of carboxylic substrates. This data can be compared with percentages independently obtained from the potentiometric

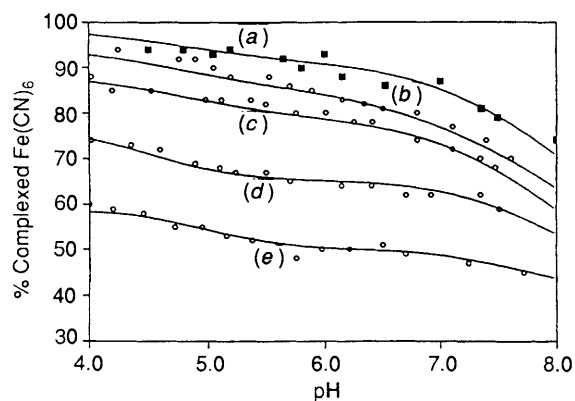


Fig. 9 Plot of the sum of percentages of $[\text{Fe}(\text{CN})_6]^{4-}$ complexed species as a function of pH for the mixed systems: (a) $[\text{Fe}(\text{CN})_6]^{4-}$ – $[\text{21}] \text{aneN}_7$; (b) $6-[\text{Fe}(\text{CN})_6]^{4-}$ – $[\text{21}] \text{aneN}_7$; (c) $2-[\text{Fe}(\text{CN})_6]^{4-}$ – $[\text{21}] \text{aneN}_7$; (d) $1-[\text{Fe}(\text{CN})_6]^{4-}$ – $[\text{21}] \text{aneN}_7$; (e) $5-[\text{Fe}(\text{CN})_6]^{4-}$ – $[\text{21}] \text{aneN}_7$. Estimated percentages obtained by means of CV (points) are compared with percentages independently obtained from the potentiometric stability constants (lines). Concentrations for all the reagents $2 \times 10^{-3} \text{ mol dm}^{-3}$.

metric stability constants by calculating the distribution of the species for the different mixed systems $[\text{Fe}(\text{CN})_6]^{4-}$ –substrate– $[\text{21}] \text{aneN}_7$ by means of the computer program DISPO.²² As shown in Fig. 9, a good agreement between the values from both techniques is observed, being the interaction order $3 > 5 > 4 > 1 > 2 > 6 > 7$.

Discussion and Conclusions

Among the studied substrates **7** is, by far, the one interacting less with $[\text{21}] \text{aneN}_7$ throughout all the pH range under consideration. In equimolar amounts all the substrates will be selectively recognized over **7** by $[\text{21}] \text{aneN}_7$. This cannot be explained, in all the cases, by different basicities of the substrates; the stepwise basicity constants of **7** are for instance lower than those of **5** and **6** and similar to those of **3** (Table 1). The reason for this behaviour should lie, therefore, in a poorer structural matching between host and guest species. Receptor $[\text{21}] \text{aneN}_7$'s protonated forms seem to present size and structural features adequate to recognize carboxyl groups organized around rigid six-membered carbon atom ring moieties. This is further evidenced by the fact that, even at pH values greater than 7, where presumably **7**, **6** and the diacids **1** and **2** are, in aqueous solution, in their fully deprotonated forms, tri- or di-anions respectively (see Table 1), both **1** and **2** interact with $[\text{21}] \text{aneN}_7$ more strongly than do **7** or **6**. In contrast with other studied systems, in which smaller or larger polyammonium macrocyclic hosts have been used,^{3,4} the charge of the anion does not solely account for the interaction strengths found. A better structural disposition of **1** and **2** for approaching the receptor and implementing the hydrogen bond network could account for this behaviour. The relevance of the shape complementarity is further confirmed when considering the case of the well organized epimers **5** and **6**. As mentioned previously, $[\text{21}] \text{aneN}_7$ selectively recognizes **5** over **6** (Fig. 6). The difference in chemical shift for the non-equivalent methylene hydrogens can be used to monitor conformational equilibria occurring upon deprotonation of those acids.¹³ Thus, for **5**, at pH values where its tri-, di- or mono-protonated forms are predominant in solution, the differences in chemical shift between the hydrogens of the methylene groups were ca. 1.4 ppm, while at pH 10, where the tricarboxylate predominates, a difference of 0.29 ppm was observed. At pH 7, where the dianion coexists in solution with 40% of other species, the difference was 0.99 ppm (see Tables 1 and 3). For **6**, at pH values where

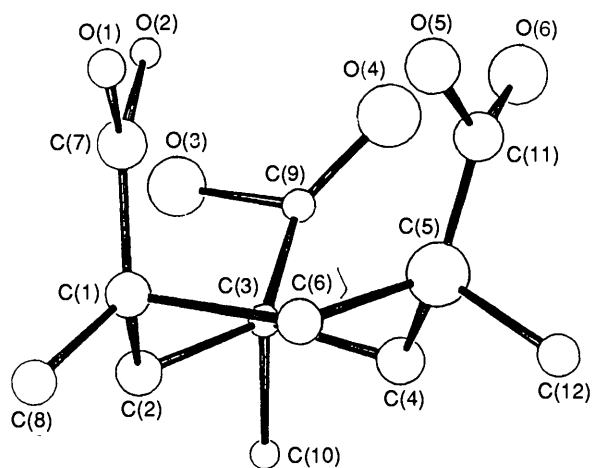


Fig. 10 ORTEP drawing for the dianion of the acid **5**

the triacid, the monoanion and the dianion predominate respectively, differences of 1.4 and 0.4 ppm were found for the non-equivalent hydrogens of two kinds of methylene groups present in the molecule; at pH 10, where the tricarboxylate predominates, differences of 0.46 and 0.73 ppm were found. These results indicate that both **5** and **6** in their tri-, di- or mono-protonated forms adopt a chair conformation with the three or two *cis*-carboxyl groups in axial disposition. For the trianions, the conformer with the three or two *cis*-carboxyl groups equatorial is found to be the most stable for **5** and **6**, respectively. The X-ray crystal structure of the disodium salt of **5**, $\text{Na}_2[\text{5}]\cdot 4\text{H}_2\text{O}$ (Figs. 10 and 11) which shows the axial arrangement of the three carboxyl groups further confirms this point.* Therefore, while in **5** all the carboxyl groups point towards the same side of the chair, in **6** one out of the three always points to the opposite side. When ^1H NMR spectra were recorded in the presence of the macrocyclic receptor $[\text{21}] \text{aneN}_7$, no significant changes were observed for **6** (Table 3) while for **5**, some interesting observations can be made. Chemical shift differences were 1.33, 1.28, 0.39 and 0.36 ppm at pH values of 5, 6, 7 and 10, respectively. Thus at pH 7, the spectroscopic parameters seem to indicate that **5** in H_4LX is still in its trianionic form. Accordingly, complexation with $[\text{21}] \text{aneN}_7$ significantly lowers the first basicity constant of **5**, approaching the one of **6**. It is noteworthy that at this pH value of 7, uncomplexed **5** is present in solution in its diprotonated form.

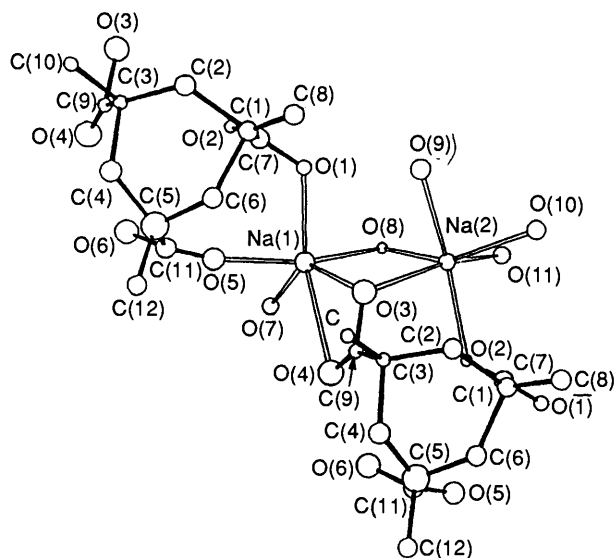
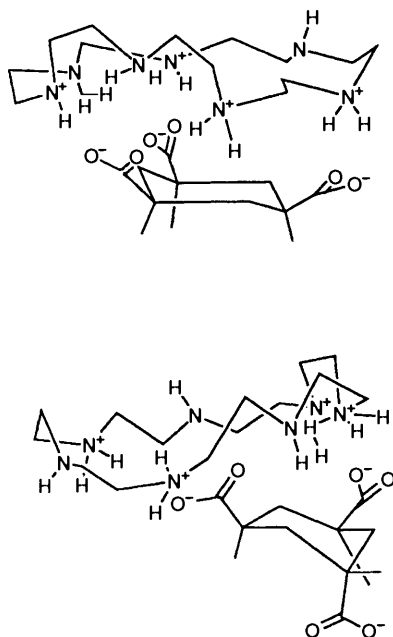
The preferential complexation of **5** over **6** suggests that $[\text{21}] \text{aneN}_7$ behaves as a flat charged surface yielding thus, a better complementarity with planar guests. Although more detailed studies are in course, preliminary molecular model-

* In the crystal lattice there are $[\text{C}_{12}\text{H}_{16}\text{O}_6]^{2-}$ anions, sodium cations and coordinated water molecules. The carboxyl groups of the anion occupy the axial positions (Fig. 11) as recognized in the crystal structure of the triacid compound (ref. 15). The mean square planes described by $\text{C}(1)\text{--}\text{C}(7)\text{--}\text{O}(1)\text{--}\text{O}(2)$ and $\text{C}(5)\text{--}\text{C}(11)\text{--}\text{O}(5)\text{--}\text{O}(6)$ are parallel within $15(2)^\circ$, and define angles of $75(2)$ and $80(2)^\circ$ respectively, with that passing through $\text{C}(3)\text{--}\text{C}(9)\text{--}\text{O}(3)\text{--}\text{O}(4)$, so as to form a three-dimensional cavity above the cyclohexane moiety. The distances between continuous oxygen atoms range from 2.46(6) to 3.16(5) Å. All the carboxylic oxygen atoms, of the dianionic species, are involved in the coordination to the sodium cations, except the O(6), which on the contrary forms the shortest contact with an oxygen atom of a water molecule $[\text{O}(6) \cdots \text{O}(9) 2.66(5) \text{ \AA}]$. Therefore we can hypothesize that the acidic hydrogen atom to be bound to this oxygen atom. The sodium cations, which are cross linked by two oxygen atoms $[\text{O}(3)$ and $\text{O}(8)]$, reach a hexa-coordination involving in the coordination sphere water oxygen atoms also (Fig. 12).

Table 3 Proton chemical shift differences (ppm) between non-equivalent methylene hydrogens for free and complexed **5** and **6**, at different pH values

5			6				
pH	Free $\Delta\delta\text{CH}_2$	Complexed $\Delta\delta\text{CH}_2$	pH	Free $\Delta\delta\text{CH}_2^a$	Complexed $\Delta\delta\text{CH}_2^a$	Free $\Delta\delta\text{CH}_2^b$	Complexed $\Delta\delta\text{CH}_2^b$
3	1.39	1.35	2	1.4	1.43	0.41	0.42
5	1.34	1.33	4	1.4	1.43	0.42	0.41
7	0.99	0.39	5	1.4	1.41	0.38	0.41
10	0.29	0.36	10	0.46	0.52	0.73	0.71

^a Methylene group between the two *cis* carboxyl groups. ^b Methylene groups between two *trans* carboxyl groups.

**Fig. 11** ORTEP drawing showing the structure of $\text{Na}_2(\mathbf{5})\cdot 4\text{H}_2\text{O}$ **Fig. 12** Possible interaction modes for the tricarboxylates of **5** and **6** with tetraprotonated [21]aneN₇

ing⁴¹ suggests that the approach and the formation of the hydrogen-bond network required to keep together the supramolecular assembly is much easier to reach in the case of **5** (Fig. 12). As a matter of fact, for **6** only two of the carboxylates can efficiently interact with the receptor. Moreover, the presence of the methyl group *cis* to the carboxyl or carboxylate groups

should make the interaction difficult. These factors may also explain the better matching of [21]aneN₇ with the diacids **1** and **2** than with **6**. For the aromatic substrates, due to their similar arrangements, charge density considerations mainly explain the selectivity order except for the interaction of the triprotonated receptor with tricarboxylates derived from **3** and **4**. In this case, a very good structural complementarity is obtained in the parallel approach of the tricarboxylate of **4** and the triprotonated host while for the tricarboxylate of **3** a normal approach to the macrocycle is preferred (as is observed for the approach of the other aromatic guests), requiring a partial unfavourable folding of the receptor.¹ In this way, the better structural factor of the tricarboxylate of **4** partially compensates the higher charge density of the tricarboxylate of **3** and very similar log *K* values are obtained for both H₃LX complexes (Table 2).

The awareness of the selectivities discussed would not have been possible without a proper criterion of selectivity. The plots showing the selectivity profiles as a function of pH calculated from the potentiometric data and their independent confirmation by cyclic voltammetry may constitute a valuable selectivity criteria for other researchers in this field.

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