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COMMUNICATION

Protonation and stability constants for the complexation of K^+, Rb^+ and Cs^+ with 5, 11, 17, 23, 29, 35-hexakis-*tert*-butyl-37, 39, 41-trimethoxy-38, 40, 42-tris-oxoacetic acid calix[6]arene

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The stability constants for the K^+, Rb^+ and Cs^+ complexes of 5, 11, 17, 23, 29, 35-hexakis-*tert*-butyl-37, 39, 41-trimethoxy-38, 40, 42-tris-oxoacetic acid calix[6]arene have been determined, and the species present over a range of solution pH's identified.

Calixarenes that are chemically modified on the lower phenolic rim can be used as complexants for Group I metal ions. Among the most studied calixarenes are those that have uncharged ester, ketone or ether groups appended.[1] These functionalities are particularly attractive as complexants because they can act as hard donor ligands to these particular metal ions. Much of the recent work directed toward the synthesis of calixarenes as complexants for Group IA metal ions has, however, focused on the smaller calix[4]arenes. These compounds usually have uncharged methyl ether or ester substituents on the lower rim.[2-8] For the calix[4]arenes, water soluble complexes with Group I metal ions have been recently obtained with carboxylate substituted calixarenes.[9] Our interest is in developing complexants for rubidium for use as lipophilic imaging agents,[10] or for cesium for use as an extractant of the radionuclide.[11] We have therefore chosen the larger calix[6]arenes for this study.[12] A potentially useful application of calixarenes is for the complexation of these metal ions in an aqueous or hydrophilic medium. The use of homoleptic calix[6]arene carboxylates as complexants, however, will likely result in the complexes having a large negative charge at biological pH due to the multiplicity of carboxylate groups. We have therefore focused on the mixed-substituted calix[6]arene 5, 11, 17, 23, 29, 35-hexakis-*tert*-butyl-37, 39, 41-trimethoxy-38, 40, 42-tris-oxoacetic acid calix[6]arene as complexant because it has alternating carboxylic acid and methoxy groups on the lower phenolic rim.[13-15] This compound has been used for the extraction of the uranyl ion,[14, 16] but no protonation or stability constant data are available for its binding to metal ions. We have therefore evaluated the complexation properties of this compound with Rb^+ and Cs^+, in order to compare the data with that obtained using a calixspherand approach.[17, 18]

Potentiometric Methods. Owing to solubility considerations all potentiometric titrations have been carried out in a solvent mixture of 70/30 (% v/v) THF: water. This solvent mixture is prepared by first degassing each solvent separately, and then adding one to the other from a buret under a nitrogen atmosphere in order to avoid contamination from carbon dioxide. Acid and base solutions have been prepared from tetramethylammonium hydroxide (1M aqueous) and concentrated perchloric acid stock solutions. These solutions are diluted to 0.1 M with adjustments being made to account for the prior water content of these solutions. Standardization of the base solution is carried out with potassium hydrogen phthalate (KHP) using phenolphthalein/thymolphthalein as indicator. The standardized base is then used to titrate the acid solution using phenol red as indicator.

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Gravimetrically standardized solutions of the metals are prepared from the original 70/30 titrant solution using the nitrate or perchlorate salts at concentrations of 0.01 M. Titrations are carried out at a constant ionic strength of 0.1 M using tetrabutylammonium perchlorate as electrolyte so that the hydrogen ion concentration (pH) can be read directly. Single-point electrode calibration has been accomplished in this solvent system media by measurement of the pH of an accurately diluted standard acid solution at a pH of *ca.* 2). A pK_w value has been determined by subsequent addition of standard base to the above solution to a pOH of *ca.* 2, with the hydrolysis constant being the final pH reading added to the calculated pOH. Calibration and all titrations are carried out in a sealed 100 ml vessel fitted with a magnetic stirrer, N_2 inlet bubbler and outlet, electrode and temperature compensator. Initial solution volumes were generally kept at 50 ml plus the small volume contribution of the added electrolyte. Ligand pK_a values have been determined by forward and back titrations, and the data analyzed using the Fortran programs PKAS and BEST.[19] The stability constant determinations have been obtained by back titration and analyzed using BEST. The latter titrations have been carried out at 1:1 and 2:1 metal to ligand mole ratios at ligand concentrations of 0.05 to 0.1 mM. All titrations were refined to a standard deviation (sigma fit) of at most 3 x 10^{-2}.

Protonation and Stability Constants. The protonation and stability constants for the reactions shown in the Scheme are given in the Table. The ligand 5, 11, 17, 23, 29, 35-hexakis-*tert*-butyl-37, 39, 41-trimethoxy-38, 40, 42-tris-oxoacetic acid calix[6]arene is designated as L, and the proton as H. In the figure are shown the species distribution plots for both the ligand and the metal complexes over a pH range of 1.0 - 10.0.

$$M^+ + L^{3-} \underset{K_{110}}{\rightleftharpoons} ML^{2-} \underset{K_{111}}{\overset{H^+}{\rightleftharpoons}} MLH^- \underset{K_{112}}{\overset{H^+}{\rightleftharpoons}} MLH_2$$

Scheme: Protonation equilibria for the complexes

The ligand pK values show little change with successive protonations, varying over the range of 6.72 to 5.58. The stability (β_{110}) and protonation (β_{111} and β_{112}) constants show that these group I ions bind to the ligand in a 1:1 ratio for M:L, even in the presence of water as a competing ligand. Unlike divalent and trivalent metal cations such as Ca^{2+}, Ba^{2+}, Ga^{3+} and In^{3+} with this ligand, no precipitation of the metal hydroxide is observed over the pH range titrated. The values found for β_{110} show that the stability of the Rb^+ complex ML is somewhat higher than are those for K^+ or Cs^+, but the stability constants β_{112} for all the complexes MLH_2 are essentially identical. For the case of Cs^+, the concentration of the complex ML in solution is too low for a precise value of β_{110} to be obtained, but the data can be used to estimate a value of approximately unity.

Table Protonation K and Stability β (MLH) Constants of the Ligand L and the K^+, Rb^+ and Cs^+ Complexes

System	*log K_{011}*	*log K_{012}*	*log K_{013}*
L	*6.72 (0.02)*	*5.95 (0.03)*	*5.58 (0.02)*
System	*log β_{110}*	*log β_{111}*	*log β_{112}*
K^+ + L	2.1 (0.1)	9.2 (0.2)	14.90 (0.06)
Rb^+ + L	3.2 (0.3)	9.0 (0.3)	14.9 (0.3)
Cs^+ + L	~ 1	8.0 (0.2)	14.9 (0.2)

log β_{110} = log K_{110}; log β_{111} = log K_{110} + log K_{111}; log β_{112} = log K_{110} + log K_{111} + log K_{112}

The species distribution curves (Figure 1) show that at high pH values the predominant species is ML, with MLH_2 being the major species at the lower pH values. At pH values below 4, dissociation into the free ligand and metal ion occurs. The abundance of the species MHL in the pH range of 6-7 decreases along the series K^+, Rb^+, Cs^+. Indeed, for the Cs^+ ion the only complex that is present in significant concentration is MLH_2. The species distribution curves also show that the ligand has a different selectivity for these Group I cations. This difference is demonstrable for Rb^+ in basic solution, where the fraction of complex present is higher than is observed for either K^+ or Cs^+. Thus at pH 9 where the fraction of the complex ML is over 50% for Rb^+, the fractions present when M is K^+ or Cs^+ are less than 20%, with the remainder of the solution species being the free ligand and metal ion.

Our measured stability constants for these Group I cations are lower than those previously measured with other lower rim modified calixarenes. However, since the other values reported in the literature were measured in methanol as solvent,[2-8] lower values are to be anticipated in our case. Our stability constant values, therefore, are the first to be reported for these Group I cations where a calixarene ligand acts as a competitive complexant with the solvent water. Clearly, however, these values are too low for useful application in the extraction of Cs^+, or the *in vivo* imaging with radioactive Rb^+.

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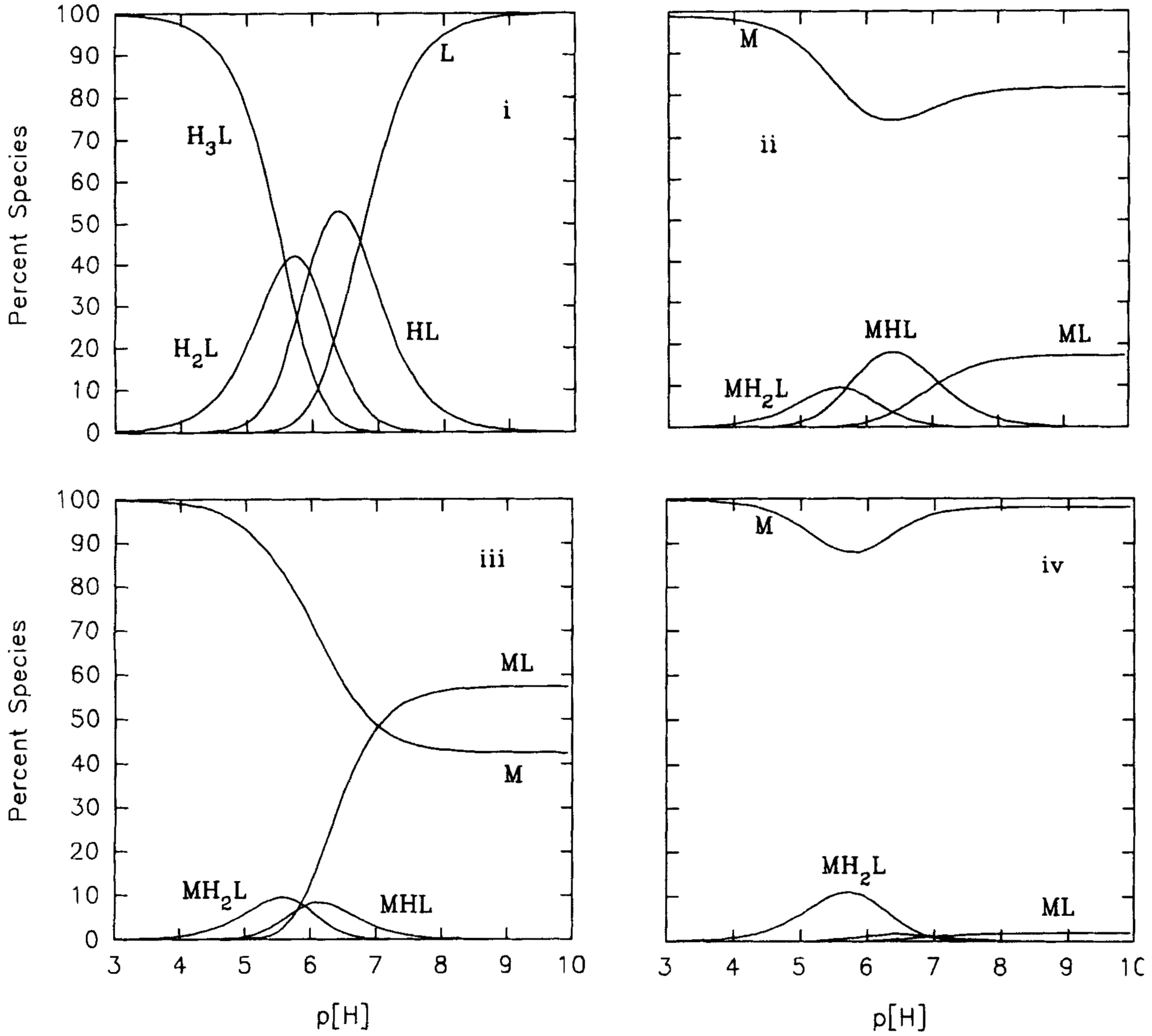

Figure 1 Species distribution curves for (i) free ligand L, (ii) M = K^+ (iii) M = Rb^+ (iv) M = Cs^+

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