

The complexation of divalent metal ions by the cryptand 4,7,13-trioxa-1,10-diazabicyclo[8.5.5]eicosane (C21C₅) in water and 95% methanol/water solutions

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Abstract

A potentiometric titration study of the complexation of divalent metal ions (M²⁺) by the cryptand 4,7,13-trioxa-1,10-diazabicyclo[8.5.5]eicosane (C21C₅) to form the cryptate [M.C21C₅]²⁺ at 298.2 K and *I* = 0.1 (NEt₄ClO₄) yielded the apparent stability constants, expressed as log(*K*/dm³ mol⁻¹), for Mg²⁺ = 2.3 and 3.25, Ca²⁺ = 2.3 and 3.6, Mn²⁺ = 4.1 and 5.23, Co²⁺ = 4.4 and 6.14, Ni²⁺ = 4.2 and 6.0, Cu²⁺ = 9.33 and 8.19, Zn²⁺ = 6.4 and 6.2, Cd²⁺ = 5.0 and 5.86, and Pb²⁺ = 8.3 and 7.6, where the first and second values pertain to water and 95% methanol/water solutions, respectively. Under the same conditions the mono- and doubly protonated cryptands, HC21C₅⁺ and H₂C21C₅²⁺, were characterised by the apparent successive protonation constants expressed as log(*K*₁/dm³ mol⁻¹) = 11.6 and log(*K*₂/dm³ mol⁻¹) = 7.73 and 5.93 in water and in 95% methanol/water, respectively. The formation of [M.HC21C₅]³⁺ and [M(OH).C21C₅]⁺ was also observed for M²⁺ = Cu²⁺ and Pb²⁺. These data are discussed in terms of the structural characteristics of the cryptand and cryptate, and are compared with data from related systems.

Introduction

The coronands and cryptands have generated considerable interest as they represent the first synthetic ligands capable of selectively complexing alkali metal ions according to size and thereby mimic antibiotics such as valinomycin and monensin, and possibly some of the molecular moieties responsible for selective alkali metal ion transport across biological membranes [1–5]. Studies of the alkali metal ions have tended to dominate the complexation chemistry of the coronands and cryptands, and apart from the alkaline earth metal ions [6,7], the complexation of divalent metal ions has been less systematically studied. Such studies of divalent metal ion complexation encompass higher metal ion surface charge densities, directional bonding, crystal field effects, and wide variations in Lewis acid characteristics, which may superimpose on the metal ion/ligand cavity size ratio which dominates the chemistry of alkali metal ion coronates and cryptates.

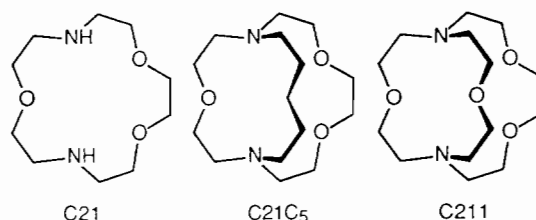
In this study we have selected the cryptand 4,7,13-trioxa-1,10-diazabicyclo[8.5.5]eicosane (C21C₅) as it has the same set of donor atoms and fifteen membered

ring as the coronand 4,7,13-trioxa-1,10-diazacyclopentadecane (C21). It also possesses a similar sized preformed cavity to the cryptand 4,7,13,16-tetraoxa-1,10-diazabicyclo[8.5.5]eicosane (C211) although the -(CH₂)₅- chain of C21C₅ lacks the electron donating oxygen atom of the second -CH₂CH₂OCH₂CH₂- moiety of C211, as seen in Scheme 1 [8–13]. Thus C21C₅ may be viewed as a ligand intermediate in character between C21 and C211 affording interesting comparisons.

Experimental

Materials

4,7,13-Trioxa-1,10-diazabicyclo[8.5.5]eicosane (C21C₅) was prepared as previously described [8].



Scheme 1.

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Metal perchlorates were either prepared from metal carbonates through reaction with the stoichiometric amount of perchloric acid, or were purchased. In either case they were twice recrystallised from water, and were dried with P_2O_5 under vacuum and stored over P_2O_5 under nitrogen. Tetraethylammonium perchlorate was prepared by the addition of tetraethylammonium bromide to a 1.0 mol dm^{-3} solution of perchloric acid, and the resulting NEt_4ClO_4 precipitate was recrystallised from water several times until free of acid, and was dried to constant weight at 353–365 K and was then stored over P_2O_5 under nitrogen. Methanol was purified and dried as in the literature [14], and deionised water was purified with a MilliQ-Reagent system to produce water with a resistance of $> 15 \text{ Mohm cm}$. Stock 95% methanol/water stock mixture was prepared by volume. The metal perchlorate, perchloric acid (all 0.10 mol dm^{-3} in NEt_4ClO_4) and tetraethylammoniumhydroxide (BDH) titration solutions were standardised by conventional methods.

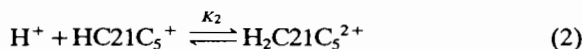
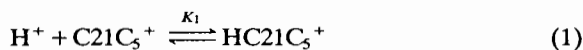
Titration

Potentiometric titrations were carried out in both water and 95% methanol/water using a Metrohm E665 Dosimat autoburette interfaced to a Laser XT/3-8086 PC in conjunction with an Orion SA720 potentiometer and an Orion Ross Sureflow 81-72 BN combination electrode. All titrations were performed at 298.2 ± 0.1 in a water jacketed vessel which was closed apart from a vent to allow egress of nitrogen. A stream of nitrogen was bubbled through the titration solution to exclude atmospheric carbon dioxide, and the solution was stirred using a magnetic stirrer. The pH electrode was calibrated by titration of $0.100 \text{ mol dm}^{-3} NEt_4OH$ (1.00 cm^3) from the autoburette against $0.004 \text{ mol dm}^{-3} HClO_4$ (10.00 cm^3) to determine E_0 and pK_w . (Under the conditions of these studies $pK_w = 13.8$ and 14.9 in water and 95% methanol/water, respectively). The apparent protonation constants K_1 and K_2 of $C21C_5$ were determined by titration of a solution (10.00 cm^3) 0.004 and $0.001 \text{ mol dm}^{-3}$ in $HClO_4$ and $C21C_5$, respectively, with $0.100 \text{ mol dm}^{-3} NEt_4OH$ (1.00 cm^3). The apparent stability constants of $[M.C21C_5]^{2+}$, $[M.HC21C_5]^{3+}$ and $[M(OH).C21C_5]^+$ were determined by titrating similar solutions containing $M(ClO_4)_2$. For each metal ion at least two titrations in which the metal ion/ligand concentration was varied were performed. The apparent protonation constants and apparent stability constant values were determined using the program MINIQUAD [15].

Results and discussion

Apparent protonation constants for $C21C_5$

In water and 95% methanol/water at 298.2 K and $I = 0.10$ (NEt_4ClO_4) two protonations of $C21C_5$ occur:



where the successive apparent protonation constants are expressed as:

$$K_1 = [HC21C_5^+]/([H^+][C21C_5]) \quad (3)$$

and

$$K_2 = [H_2C21C_5^{2+}]/([H^+][HC21C_5^+]) \quad (4)$$

The K_1 and K_2 values appear in Table 1. The value of K_1 is independent of the nature of the solvent. This suggests that the proton resides in the cryptand cavity bound to a nitrogen in the *endo* conformation such that the lone pair of electrons are directed towards the cavity centre. In the solid state crystallographic studies of metal cryptates show that both nitrogens adopt this conformation such that the cryptand is in the *endo-endo* conformation and the maximum lone pair electron density is directed towards the region of positive charge [10–12]. Such an *endo-endo* conformation for $C21C_5$ minimises the effect of solvent on proton association in the formation of $HC21C_5^+$ and a predominance of this conformation may explain the invariance of K_1 observed in this study. (The $C21C_5$ cavity is too small to accommodate a water molecule.) The electronic repulsion of the two protonic charges in $H_2C21C_5^{2+}$ results in $K_1 > K_2$. In addition the destabilising effect of the close proximity of the two protons in the

TABLE 1. Protonation constants for 4,7,13-trioxo-1,10-diazabicyclo[8.5.5]eicosane ($C21C_5$) and related ligands at 298.2 K and $I = 0.10$ (NEt_4ClO_4) in water and 95% methanol/water

Ligand	$\log K_1$	$\log K_2$
$C21C_5^a$	11.6 ± 0.2	7.73 ± 0.05
Water		
$C21C_5^a$	11.6 ± 0.2	5.93 ± 0.05
95% Methanol/water		
$C211^b$	11.32	8.14
Water		
$C211^c$	11.59	7.12
95% Methanol/water		
C21	8.76 ^b	8.04 ^b
Water	9.26 ^d	8.12 ^d

^aThis work. ^bRefs. 16 and 17. ^cRef. 18—supporting electrolyte is $0.1 \text{ mol dm}^{-3} Me_4NCl$. ^dRef. 19.

cavity of $\text{H}_2\text{C}_21\text{C}_5^{2+}$ in the *endo-endo* conformation may result in one or both of the nitrogens adopting the *exo* conformation where the lone pair is directed out into the solvent and the interaction distance is considerably increased in what is now the *endo-exo* or *exo-exo* conformation of $\text{H}_2\text{C}_21\text{C}_5^{2+}$. As a consequence a proton at the *exo* site is now exposed to solvent interactions and as a consequence K_2 is expected to reflect variations in the nature of the solvent. In simplistic terms the 95% methanol/water solvent more effectively stabilises HC_21C_5^+ , by comparison with $\text{H}_2\text{C}_21\text{C}_5^{2+}$, than does water. The proportion of $\text{H}_2\text{C}_21\text{C}_5^{2+}$ existing in the *endo-endo*, *endo-exo*, and probably the *exo-exo* conformation (each of which should possess different K_2 values), may also vary with the nature of the solvent.

The closely related cryptand 4,7,13,16-tetraoxa-1,10-diazabicyclo[8.5.5]eicosane (C211) is characterised by K_1 values [16,17] in water and 95% methanol/water solution which are similar to those characterising C_21C_5 (Table 1). This suggests that the replacement of the methylene group in the latter species by an ether oxygen in the former has no direct effect on K_1 . However, it is anticipated that this replacement will have some effect on the flexibility of the cryptand molecular framework, and therefore on the proportions of the *endo-endo*, *endo-exo* and *exo-exo* conformations existing in solution, which in turn may explain the difference in the K_2 values characterising HC_21C_5^+ and HC_211^+ (Table 1).

The K_1 of the diazacoronand C21 in water [16,19] is substantially less than the K_1 values characterising C_21C_5 and C211 (Table 1). This is consistent with the nitrogen protonation site in monocyclic C21 being less able to compete for a proton with water than is the case with bicyclic C_21C_5 and C211. It is also consistent with the suggestion that the *endo* conformation of the nitrogen protonation site in the latter two species has only a small interaction with the solvent. This relatively low K_1 characterising C21 is also observed for several smaller and larger diazacoronands [19]. The K_2 of C21 is similar to those of C_21C_5 and C211 which may indicate that the solvent interaction of the second protonation site is similar in all three species consistent with the second protonation sites of $\text{H}_2\text{C}_21\text{C}_5^{2+}$ and $\text{H}_2\text{C}_211^{2+}$ adopting the *exo* conformation.

Apparent stability constants of divalent metal cryptates $[\text{M}.\text{C}_21\text{C}_5]^{2+}$

The complexation of M^{2+} by C_21C_5 is:



where the apparent stability constant is expressed as:

$$K = [\text{M}.\text{C}_21\text{C}_5^{2+}] / ([\text{M}^{2+}][\text{C}_21\text{C}_5]) \quad (6)$$

The magnitude of K varies substantially with the nature of the divalent metal ion and the solvent (Table 2). The factors which may cause variations in the magnitude of K with the nature of M^{2+} are: the relative size of the metal ion [20] and the C_21C_5 cavity (approximately spherical of radius 80 pm [8]); the relative hardness of the metal ions and their consequent variations in affinity for oxygen over nitrogen donor atoms [21, 22], and crystal field effects [23]. The relatively low values of K characterising the Mg^{2+} and Ca^{2+} cryptates are attributable to the hard acid nature of these metal ions and their consequently greater affinity for oxygen over nitrogen donor atoms. Thus water is better able to compete with C_21C_5 for Mg^{2+} and Ca^{2+} than is the case for the other metal ions in Table 2, which are classified as borderline or soft acids and show a greater affinity for nitrogen donor atoms. The Irving-Williams series [24, 25], which largely reflects ligand dipole-metal ion electrostatic effects and crystal field effects for simpler ligands than those considered here, predicts that the stability of metal complexes should vary in the sequence $\text{Ca}^{2+} < \text{Mg}^{2+} < \text{Mn}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} \gg \text{Zn}^{2+}$. This trend, prevails in both water and 95% methanol/water for $[\text{M}.\text{C}_21\text{C}_5]^{2+}$, with the exception of Ca^{2+} and Ni^{2+} (Table 2) which may probably be attributed to the constraining geometry of C_21C_5 . On the basis of the Gutmann donor numbers, D_N , of water (33.0) and methanol (23.5) [26-28]* it is expected that water will compete more effectively with C_21C_5 for M^{2+} than will methanol and this expectation holds for $\text{M}^{2+} = \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Mn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}$ and Cd^{2+} , as indicated by the increased stability of $[\text{M}.\text{C}_21\text{C}_5]^{2+}$ in 95% methanol/water. However, as it is probable that some coordination sites remain occupied by solvent in the cryptate, and that the number of such sites may vary with M^{2+} , this simple dependence on D_N may be disrupted, as appears to be the case for $\text{Cu}^{2+}, \text{Zn}^{2+}$ and Pb^{2+} .

Similar trends in stability are also observed for $[\text{M}.\text{C}_211]^{2+}$ [16, 29, 30] and $[\text{M}.\text{C}_21]^{2+}$ [14, 17] (Table 2), and it is clear that the different geometries and number of electron pair donating atoms in the three ligands result in a maximum of about an order of magnitude difference in stability. This suggests a common dominant factor determining stability which

*Reference 26 gives $D_N=19$ and 18, respectively, determined in dilute solution in 1,2-dichloroethane where the hydrogen bonding structure of methanol and water is disrupted. It is suggested in refs. 27 and 28 that $D_N=23.5$ and 33.0 are more appropriate to pure methanol and water, respectively.

TABLE 2. Apparent stability constants for the complexation of divalent metal ions (M^{2+}) by 4,7,13-trioxa-1,10-diazabicyclo[8.5.5]icosane ($C21C_5$) at 298.2 K and $I=0.10$ (NEt_4ClO_4) in water and 95% methanol/water

M^{2+}	Ionic radius ^a (pm)	$\log(K/dm^3 mol^{-1})$			
		$[M.C21C_5]^{2+b}$ water	$[M.C21C_5]^{2+b}$ 95% methanol/water	$[M.C211]^{2+}$ water	$[M.C21]^{2+}$ water
Mg^{2+}	72	2.3 ± 0.1	3.25 ± 0.05	2.5^c	
Ca^{2+}	100 (112)	2.3 ± 0.1	3.6 ± 0.1	2.50^c	
Mn^{2+}	83	4.1 ± 0.1	5.23 ± 0.05		
Co^{2+}	75	4.4 ± 0.1	6.14 ± 0.05	$< 4.7^d$	5.05^e
Ni^{2+}	69	4.2 ± 0.1	6.0 ± 0.2	$< 4.5^d$	5.22^d
Cu^{2+}	73	9.33 ± 0.05	8.19 ± 0.05	7.78^d	3.73^c
Zn^{2+}	74	6.4 ± 0.2	6.2 ± 0.2	$< 5.3^d$	4.05^d
Cd^{2+}	95	5.0 ± 0.1	5.86 ± 0.05	$< 5.5^d$	7.17^d
Pb^{2+}	119 (129)	8.3 ± 0.1	7.6 ± 0.1	7.93^d	8.15^d
					5.34^e
					6.46^e
					5.85^e

^aRef. 20. Ionic radii for six-coordination are quoted for all metal ions, and in the cases of Ca^{2+} and Pb^{2+} the radii quoted in brackets refer to eight-coordination which is a common state for these two ions. ^bThis work. ^cRefs. 29, 30 — unlike the other K data in the Table, these data were obtained in $0.05 mol dm^{-3} NEt_4Br$ supporting electrolyte. ^dRef. 16. ^eRef. 19.

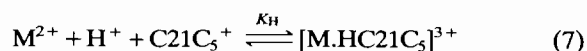
in the case of Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} is probably the preference to bond with the two amine nitrogens. This coincides with the observation that Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} complexes of C21 and related diazacoronands show no enhanced stability over the analogous complexes formed by 1,4-diazabutane, 4-oxa-1,7-diazaheptane and 4,7-dioxa-1,10-diazadecane. Thus for these diazacoronands and cryptands there is no observable macrocyclic effect [19].

The lower stabilities of $[Mg.C21C_5]^{2+}$, $[Ca.C21C_5]^{2+}$ and their C211 analogues place them in the approximate positions anticipated from the Irving–Williams series relative to the stabilities of the other metal ions in Table 2. This indicates that the hardness of these metal ions and their expected greater affinity for oxygen electron pair donating atoms does not enhance the stability of their $[M.C21C_5]^{2+}$ and $[M.C211]^{2+}$ species by comparison with those of the softer metal ions. It now becomes significant to make comparisons with $[Li.C211]^+$ and $[Na.C211]^+$ in water for which $\log(K/dm^3 mol^{-1}) = 5.5$ and 3.2 , respectively [29, 30]. The Li^+ ion ($r = 76$ pm) fits into the C211 cavity to form an *inclusive* cryptate in which it is completely desolvated, and this is considered to be the source of its relatively high stability compared to that of $[Na.C211]^+$ which exists as an *exclusive* cryptate as a consequence of Na^+ ($r = 102$ pm) being too large to enter the C211

cavity [10–13]. (The alkali metal ions also reflect the decrease in the number of oxygen atoms on going from $[M.C211]^+$ to $[M.C21C_5]^+$ ($M = Li, Na, K$ or Cs) as evidenced by the stability constant of $[M.C211]^+$ being several orders of magnitude greater than that for $[M.C21C_5]^+$ in a given solvent [9, 13].) On the basis of ionic radii it might be anticipated that $[M.C211]^{2+}$ to $[M.C21C_5]^{2+}$ should exist as inclusive and exclusive cryptates when $M = Mg$ and Ca , respectively, and that a corresponding difference in stability should arise similar to that observed for the alkali metal ions. That this is not so suggests that the cryptands cannot compete so effectively for the alkaline earths ions as a consequence of their higher solvation energies, and that as a consequence both the selectivities and the stabilities of the alkaline earth cryptates are decreased.

$[M.HC21C_5]^{3+}$ and $[M.(OH).C21C_5]^+$ complexes

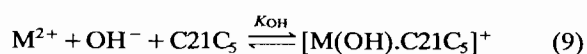
The equilibria



where

$$K_H = [M.HC21C_5^{3+}] / ([M^{2+}][H^+][C21C_5]) \quad (8)$$

and



where

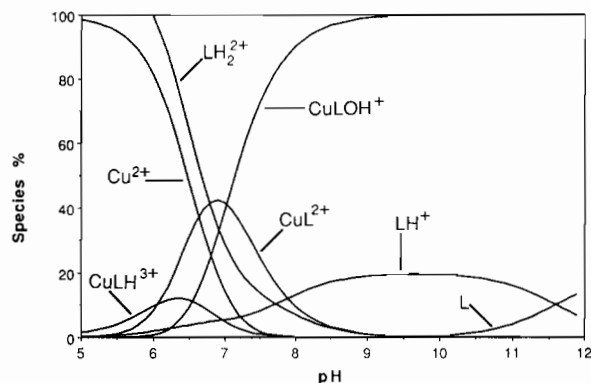


Fig. 1. Speciation curves for Cu^{2+} complexes of $\text{C}21\text{C}_5$ (L) in water. Total Cu^{2+} concentration = $0.0010 \text{ mol dm}^{-3}$, the total $\text{C}21\text{C}_5$ concentration = $0.0012 \text{ mol dm}^{-3}$ and $I = 0.10$ (NEt_4ClO_4).

$$K_{\text{OH}} = \frac{[\text{M}(\text{OH})\cdot\text{C}21\text{C}_5^+]}{([\text{M}^{2+}][\text{OH}^-][\text{C}21\text{C}_5])} \quad (10)$$

are observed in water for $\text{M}^{2+} = \text{Cu}^{2+}$ and Pb^{2+} . In water $\log(K_{\text{H}}/\text{dm}^6 \text{ mol}^{-2})$ and $\log(K_{\text{OH}}/\text{dm}^6 \text{ mol}^{-2}) = 15.4 \pm 0.2$ and 16.1 ± 0.2 , respectively, when $\text{M}^{2+} = \text{Cu}^{2+}$, and 15.6 ± 1.0 and 13.7 ± 0.2 , respectively when $\text{M}^{2+} = \text{Pb}^{2+}$. It is envisaged that the cryptand is only bound to M^{2+} through the unprotonated nitrogen of $\text{HC}21\text{C}_5^+$ in $[\text{M}\cdot\text{HC}21\text{C}_5]^3+$ and that only a weak interaction occurs between M^{2+} and the cryptand ether oxygens. A species distribution for the Cu^{2+} in water is shown in Fig. 1. In 95% methanol/water the same species are observed for Pb^{2+} and $\log(K_{\text{H}}/\text{dm}^6 \text{ mol}^{-2}) = 14.5 \pm 0.2$ and $\log(K_{\text{OH}}/\text{dm}^6 \text{ mol}^{-2}) = 15.2 \pm 0.2$. For Cu^{2+} in 95% methanol/water $\log(K_{\text{H}}/\text{dm}^6 \text{ mol}^{-2}) = 14.6 \pm 0.2$, but the titration data is compatible with the dimeric hydroxo species $[\text{Cu}(\text{OH})\cdot\text{C}21\text{C}_5]_2^{2+}$ ($K_{(\text{OH})_2} = \frac{[\text{M}(\text{OH})\cdot\text{C}21\text{C}_5^+]}{([\text{M}^{2+}][\text{OH}^-][\text{C}21\text{C}_5]^2)}$, and $\log(K/\text{dm}^{15} \text{ mol}^{-5}) = 37.2 \pm 0.3$) being the dominant species at high pH rather than the monomeric species ($\log(K_{\text{OH}}/\text{dm}^6 \text{ mol}^{-2}) = 23.1 \pm 0.2$). The observation of these species coincides with $[\text{Cu}\cdot\text{C}21\text{C}_5]^{2+}$ and $[\text{Pb}\cdot\text{C}21\text{C}_5]^{2+}$ being the most stable of the $[\text{M}\cdot\text{C}21\text{C}_5]^{2+}$ species studied (Table 2).

Acknowledgements

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