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The complexation of divalent metal ions by the cryptands 4,7,13,16-tetraoxa-1,10-diazabicyclo[8.8.2]eicosane, -[8.8.5]tricosane and -[8.8.8]hexacosane in aqueous solution

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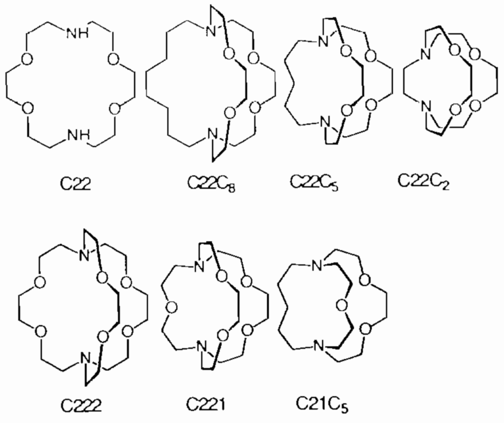
Abstract

The complexation of divalent metal ions (M^{2+}) by the cryptands 4,7,13,16-tetraoxa-1,10-diazabicyclo[8.8.2]eicosane ($C22C_2$), 4,7,13,16-tetraoxa-1,10-diazabicyclo[8.8.5]tricosane ($C22C_5$) and 4,7,13,16-tetraoxa-1,10-diazabicyclo-[8.8.8]hexacosane ($C22C_8$) to form the cryptates $[MC22C_n]^{2+}$, where $n=2$, 5 and 8, respectively, has been studied by potentiometric titration in aqueous solution at 298.2 K and $I=0.10$ mol dm^{-3} (NEt_4ClO_4). The stability constants, expressed as log K (dm^3 mol^{-1}) for $n=2$, 5 and 8, respectively, after each metal ion, are for $Mg^{2+}=3.5$, 2.1 and 2.8, $Ca^{2+}=4.68$, 2.0 and 2.6; $Sr^{2+}=4.3$, 3.0 and 2.8, $Ba^{2+}=5.28$, 2.8 and <2; $Co^{2+}=6.8$, 5.0 and <6; $Ni^{2+}=-$, 5.5 and 5.4; $Cu^{2+}=9.4$, 9.0 and 8.7, $Zn^{2+}=7.1$, 6.4 and 6.3; $Cd^{2+}=9.0$, 5.18 and 4.5, $Hg^{2+}=13.4$, $-$ and 16.5; and $Pb^{2+}=$ 11.1, 8.1 and 8.02. In some cases the formation of $[M(C22C_n)_2]^{2+}$, $[M(HC22C_n)]^{3+}$, $[M(OH)C22C_n]^+$ and $[M(OH)C22C_n]_2{}^{2+}$ is also observed. The mono and doubly protonated cryptands, $HC22C_n{}^+$ and $H_2C22C_n{}^{2+}$, are characterised by successive stability constants expressed as log K_1 (dm^3 mol^{-1}) = 10.92, 11.43 and 11.06; and log K_2 (dm^3 mol^{-1}) = 3.42, 8.10 and 8.41 for $n=2$, 5 and 8, respectively. A comparison of these data with those for related systems is made, and the effects of the structural characteristics of the cryptand and cryptate are examined

Key words: Kinetics and mechanism, Metal ion complexes, Cryptand complexes

Introduction

The ability of coronands and cryptands to selectively complex metal ions has been widely studied as a consequence of their intrinsic interest and also because of their potential for use as selective complexation agents in the development of chemical sensors and metal ion separation and extraction procedures is substantial [1–5]. Cryptands may be viewed as diazacoronands in which the two amine hydrogens have been replaced by a $-((CH_2)_2O(CH_2)_2)_x-$ or $-(CH_2)_n-$ bridge to generate a bicyclic structure. In this study we are particularly interested in the replacement of the two amine protons of the diazacoronand 4,7,13,16-tetraoxa-1,10-diazacyclooctadecane (C22) by the second type of bridge where $n=2$, 5 and 8 to give the cryptands 4,7,13,16-tetraoxa-1,10-diazabicyclo[8.8.2]eicosane ($C22C_2$), 4,7,13,16-tetraoxa-1,10-diazabicyclo-[8.8.5]tricosane ($C22C_5$) and 4,7,13,16-tetraoxa-1,10-diazabicyclo[8.8.8]-hexacosane ($C22C_8$), as shown in Scheme 1. Thus the donor atom set in C22 is the same



Scheme 1.

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as that in the three cryptands, but the $-(CH_2)_n-$ bridges modify the conformation of the 4,7,13,16-tetraoxa-1,10-diazacyclooctadecane ring and obstruct the approach of metal ions to one side of the ring.

Earlier studies show that complexation of the alkali metal ions by $C22C_2$ [6, 7], $C22C_5$ [8, 9] and $C22C_8$ [10] is largely controlled by the relative sizes of the metal ion and the ligand cavity. We now extend these studies to divalent metal ions to examine the factors controlling their complexation. This study also provides an opportunity to examine the effects of variation in donor atom numbers in cryptands of comparable cavity size through a comparison of the complexing characteristics of $C22C_5$ and 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane (C221) which possess similar sized cavities ($r \approx 1.1$ Å [11]) and six and seven donor atoms, respectively; and of $C22C_8$ and 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (C222) which possess similar sized cavities ($r \approx 1.4$ Å [11]) and six and eight donor atoms, respectively.

Experimental

Materials

The cryptands $C22C_2$ [12, 13], $C22C_5$ and $C22C_8$ [14–16] were prepared as previously described. Metal perchlorates were either purchased or were prepared from metal carbonates through reaction in water with the stoichiometric amount of $HClO_4$. In each case they were twice recrystallised from water, dried over P_2O_5 under vacuum and stored over P_2O_5 under nitrogen. Deionised water was purified with a MilliQ-Reagent system to produce water with a resistance of >15 Mohm cm. Tetraethylammonium perchlorate was prepared by the addition of NEt_4Br to a 1.0 mol dm^{-3} solution of $HClO_4$, and the resulting NEt_4ClO_4 precipitate was recrystallised from water several times until free of acid, dried to constant weight at 353–365 K and stored over P_2O_5 under nitrogen. Metal perchlorate, $HClO_4$, $C22C_n$ and NEt_4OH (BDH) titration solutions were prepared under dry nitrogen and were standardised by conventional methods. The ionic strength was adjusted to 0.10 mol dm^{-3} with NEt_4ClO_4.

Titrations

Potentiometric titrations were carried out 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 combination electrode. Titration solutions were thermostatted at 298.2±0.1 K and magnetically stirred in a water jacketted vessel which was closed to the atmosphere, apart from a vent to allow egress of a nitrogen stream which was passed through the solution to exclude atmospheric carbon dioxide. The instrumentation was calibrated by titration of 0.100 mol dm^{-3} NEt_4OH (1.00 cm^3) from the autoburette against 0.004 mol dm^{-3} $HClO_4$ (10.00 cm^3). The protonation constants, K_1 and K_2, of the cryptands were determined by titration of a solution (10.00 cm^3) 0.004 and 0.001 mol dm^{-3} in $HClO_4$ and the cryptand, respectively, with 0.100 mol dm^{-3} NEt_4OH (1.00 cm^3). The stability constants of the cryptates were determined by titrations of solutions (10.00 cm^3) 0.004 and 0.001 mol dm^{-3} in $HClO_4$ and $C22C_n$, respectively, and 0.002–0.0005 mol dm^{-3} in $M(ClO_4)_2$, with 0.100 mol dm^{-3} NEt_4OH (1.00 cm^3). (The equilibration of the $Ni^{2+}/C22C_2$ system was too slow for a reliable determination of the stability constant by this method.) All titrations were carried out in triplicate at least. The protonation constants and stability constant values were calculated using the program MINIQUAD [17].

Results and discussion

Protonation constants of the cryptands

In water at 298.2 K and $I = 0.10$ mol dm^{-3} (NEt_4ClO_4), two protonations of $C22C_n$ ($n = 2$, 5 or 8) occur:

$$H^+ + C22C_n \overset{K_1}{\rightleftharpoons} HC22C_n{}^+ \tag{1}$$

$$H^+ + HC22C_n{}^+ \overset{K_2}{\rightleftharpoons} H_2C22C_n{}^{2+} \tag{2}$$

where the protonation constants are expressed as

$$K_1 = [HC22C_n{}^+]/([H^+][C22C_n]) \tag{3}$$

and

$$K_2 = [H_2C22C_n{}^{2+}]/([H^+][HC22C_n{}^+]) \tag{4}$$

The K_1 and K_2 values appear in Table 1.

The solid state structure of $[(H_3O)C22C_5]ClO_4$ shows the oxygen of H_3O^+ to be 0.666(3) Å above the plane of the four coplanar $C22C_5$ oxygens with the lone pairs of the nitrogens directed to the centre of the cryptand cavity in an *endo–endo* conformation [9]. It is anticipated that this conformation will persist in aqueous solution with the proton residing in the $HC22C_5{}^+$ cavity. This

TABLE 1 Protonation constants for the cryptands $C22C_2$, $C22C_5$, $C22C_8$, C221 and C222, and the diazacoronand C22 at 298.2 K in 0.10 mol dm^{-3} NEt_4ClO_4 aqueous solution

Ligand	log K_1	log K_2
$C22C_2$[a]	10.92±0.05	3.42±0.05
$C22C_5$[a]	11.43±0.05	8.10±0.05
$C22C_8$[a]	11.06±0.05	8.41±0.05
C22[b]	9.20	8.02
C221[b]	11.02	7.74
C222[b]	10.00	7.53

[a] This work [b] Ref. 18

minimises the interaction of water with the proton of $HC22C_5^+$, and a predominance of analogous *endo–endo* conformations is anticipated for the other monoprotonated cryptands. The variation of K_1 for the five cryptands probably arises from their structural differences, and the lower values observed for $HC221^+$ and $HC222^+$ by comparison with those for $HC22C_5^+$ and $HC22C_8^+$, respectively, probably reflect the hydrogen bonding capacity of the additional oxygen atom in the first pair of cryptands. (A similar relationship holds for the diprotonated analogues, and may be attributable to the same cause.) The substantially lower K_1 of $HC22^+$ [18] is consistent with the greater interaction of water with the $HC22^+$ proton as anticipated for the more open structure of this monocyclic species. Other diazacoronands also have lower protonation constants than related cryptands [19].

The statistical effect of the availability of two and one protonation sites in $C22C_n$ and $HC22C_n^+$, respectively, and the repulsion between the two protonic charges in $H_2C22C_n^{2+}$ result in $K_1 > K_2$. The substantially smaller K_2 for $H_2C22C_2^{2+}$ probably reflects the destabilising effect of the particularly close proximity of the two protons in the cavity of $H_2C22C_2^{2+}$. This may result in $H_2C22C_2^{2+}$ assuming an *exo–endo* or an *exo–exo* conformation where one or both of the nitrogens direct their electron lone pairs out from the cavity so that the interaction distance between the protons is considerably increased. Similar arguments are applicable to the other cryptands. (If the *endo–endo*, *exo–endo* and the *exo–exo* conformations coexist for each $H_{(1\text{ or }2)}C22C_n^{(1\text{ or }2)+}$, the observed K_1 and K_2 are the weighted means of the different K_1 and K_2 characterising the conformers in labile equilibrium with each other.) The K_2 of H_2C22^{2+} is midway between those of the pairs $H_2C22C_5^{2+}$ and $H_2C22C_8^{2+}$, and H_2C221^{2+} and H_2C222^{2+}. This indicates that the interaction of the second protonation site with water is similar in all five diprotonated cryptands consistent with significant proportions adopting the *exo* conformation at one nitrogen at least in each case.

Stability constants of divalent metal cryptates $[MC22C_n]^{2+}$

The complexation of M^{2+} by $C22C_n$ is shown below:

$$M^{2+} + C22C_n \overset{K_{M1}}{\rightleftharpoons} [MC22C_n]^{2+} \tag{5}$$

where the stability constant is expressed as

$$K_{M1} = [MC22C_n^{2+}]/([M^{2+}][C22C_n]) \tag{6}$$

The magnitude of K_{M1} varies substantially with the nature of the cryptand and divalent metal ion as seen from Table 2 [11, 18–22]. By comparison with $[MC22]^{2+}$, $[MC22C_5]^{2+}$ and $[MC22C_8]^{2+}$, the stability of $[MC22C_2]^{2+}$ is the highest for all of the metal ions studied (except when $M^{2+} = Hg^{2+}$, which is discussed below). It appears that the optimum 'bite size' of the $\rangle NCH_2CH_2N\langle$ moiety of $C22C_2$, combined with its clam-like structure [7, 12], produces a donor atom stereochemistry which engenders a greater stability than the differing stereochemical arrays of the same number and type of donor atoms in the other three species.

The factors which may cause variations in the magnitude of K_{M1} with the nature of M^{2+} are: (i) the relative size of the metal ion [20] and the cryptand cavity [11]; (ii) the solvation energies of the metal ions [23]; (iii) the relative hardness of the metal ions and their consequent variations in affinity for oxygen or nitrogen donor atoms [24, 25]; (iv) ligand field effects [26]. The Irving–Williams series [27, 28], which largely derives from effects (ii)–(iv), predicts the following variation in complex stability constants for divalent metal ions: $Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$, albeit for less constrained ligands than $C22C_n$. While the $C22C_n$ cryptates of the similar sized Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} ions qualitatively match these predictions, those of the differently sized alkaline earth ions do not (Table 2). The variation of K_{M1} in the sequence: $Mg^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$ is consistent with Mg^{2+} being a hard acid which has a decreased affinity for nitrogen donor atoms by comparison with that of the borderline soft acid transition metal ions, with the variation in ligand field stabilisation energy in the sequence: $Co^{2+} < Ni^{2+} < Cu^{2+}$, and with the absence of such stabilisation for Mg^{2+} and Zn^{2+}.

The variation of K_{M1} in the sequence: $Mg^{2+} < Ca^{2+} > Sr^{2+} < Ba^{2+}$ for the hard metal species $[MC22C_2]^{2+}$ is consistent with the strain energy in $C22C_2$ being minimised with Ca^{2+} which has a similar ionic radius (= 1.00 Å) to Na^+, and for which the angle between the jaws of $[NaC22C_2]^+$ (89.6°) is similar to that in free $C22C_2$ (88.4°) [7]. Thus the smaller and larger radii of Mg^{2+} and Sr^{2+}, respectively, induce strain in $C22C_2$ by causing the jaws of $C22C_2$ to assume less and more than the optimum angle. However, the increase in stability observed for $[BaC22C_2]^{2+}$ does not fit this pattern and the additional formation of $[Ba(C22C_2)_2]^{2+}$

$$[BaC22C_2]^{2+} + C22C_2 \overset{K_{M2}}{\rightleftharpoons} [Ba(C22C_2)_2]^{2+} \tag{7}$$

characterised by $\log K_{M2}$ (dm^3 mol^{-1}) = 4.65, indicates a change in the relative importance of the factors affecting stability. It is possible that because of the large size of Ba^{2+} only a weak interaction occurs with the nitrogens of $C22C_2$ such that the four oxygens bind without disrupting the optimum jaw angle of the cryptand, and the second $C22C_2$ binds similarly. (A spe-

TABLE 2. Stability constants for the complexation of divalent metal ions (M^{2+}) by the cryptands $C22C_2$, $C22C_5$, $C22C_8$, C221 and C222, and the diazacoronand C22 at 298.2 K in aqueous solution

M^{2+}	Ionic[a] radius (Å)	log K ($dm^3\ mol^{-1}$)					
		$[MC22C_2]^{2+\,b}$	$[MC22C_5]^{2+\,b}$	$[MC22C_8]^{2+\,b}$	$[MC22]^{2+}$	$[MC221]^{2+}$	$[MC222]^{2+}$
Mg^{2+}	0.72	3.5±0.1	2.1±0.1	2.8±0.1		<2[c]	<2[c]
Ca^{2+}	1.00 (1.12)	4.68±0.05	2.0±0.2	2.6±0.1	1.8[d]	6.95[c]	4.4[c]
Sr^{2+}	1.18 (1.26)	4.3±0.1	3.0±0.1	2.8±0.1	2.57[d]	7.35[c]	8.0[c]
Ba^{2+}	1.35 (1.42)	5.28±0.05	2.8±0.1	<2	2.98[d]	6.30[c]	9.5[c]
Co^{2+}	0.75	6.8±0.1	5.0±0.1	<6	⩽2.5[c]	5.40[e]	⩽2.5[e]
Ni^{2+}	0.69		5.5±0.2	5.4±0.1	⩽2.5[c]	4.28[c]	⩽3.5[e]
Cu^{2+}	0.73	9.4±0.1	9.0±0.2	8.7±0.1	6.18[e] 7.59[f]	7.56[e]	6.81[e]
Zn^{2+}	0.74	7.1±0.1	6.4±0.1	6.3±0.1	3.19[e] 4.13[f]	5.41[e]	⩽2.5[e]
Cd^{2+}	0.95 (1.10)	9.0±0.2	5.18±0.05	4.5±0.1	5.31[e]	10.04[e]	7.10[e]
Hg^{2+}	1.02 (1.14)	13.4±0.1		16.5±0.1	17.85[d]	19.97[g]	18.2[d]
Pb^{2+}	1.19 (1.29)	11.1±0.1	8.1±0.3	8.02±0.05	6.90[c]	13.12[e]	12.72[e]

[a] Ref. 20 Ionic radii for six-coordination are quoted for all metal ions, and in the cases of Ca^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} the radii quoted in brackets refer to eight-coordination which is a common state for these ions. [b] This work. [c] Ref 11 [d] Ref 21. [e] Ref. 18 [f] Ref 19 [g] Ref 22 With the exceptions of the data from refs 11 and 21 which were obtained in 0.05 mol dm^{-3} NEt_4Br and 0.1 mol dm^{-3} NMe_4Cl supporting electrolyte, respectively, all other data were obtained in 0.10 mol dm^{-3} NEt_4ClO_4

ciation plot for the formation of $[BaC22C_2]^{2+}$ and $[Ba(C22C_2)_2]^{2+}$ is shown in Fig. 1.) Some support for this proposal arises from the observation (Table 2) that the hard acid metal cryptates $[CaC22C_2]^{2+}$ and $[SrC22C_2]^{2+}$ are substantially less stable than the similarly sized soft acid metal cryptates $[CdC22C_2]^{2+}$ and $[PbC22C_2]^{2+}$, respectively. This is consistent with a stronger interaction with the nitrogens in the second pair of cryptates than in the first pair, and lends plausibility to the proposal that the binding is primarily through oxygen in the two barium cryptates. A similar tendency to form 1:2 complexes with increasing metal ion size is observed for the 15C5 and 18C6 coronands in methanol where $[M15C5]^{2+}$ and $[M18C6]^{2+}$ complexes are formed when $M^{2+} = Ca^{2+}$, Sr^{2+} and Ba^{2+}, but $[M(15C5)_2]^{2+}$ and $[M(18C6)_2]^{2+}$ are formed only when $M^{2+} = Sr^{2+}$ and Ba^{2+} [29].

The variation of K_{MI} for the metal ions in the sequence: $Cd^{2+} < Hg^{2+} > Pb^{2+}$ for the cryptates in Table 2 is consistent with Hg^{2+} being of optimum size to complex with $C22C_2$ and C221 as assessed from the jaw angle requirements of the former and the estimated cavity size of the latter. (The greater stability of $[HgC221]^{2+}$ by comparison with that of $[HgC22C_2]^{2+}$ is attributable to the increased binding power arising from the extra oxygen donor atom and the more complete encapsulation of Hg^{2+} in the first species.) In addition, it appears that for the other ligands a combination of Hg^{2+} being closer to optimum size than is Cd^{2+}, and the decreased hydration energy of Hg^{2+} compared with that of Cd^{2+}, are major factors causing the Hg^{2+} complexes to be more stable than the Cd^{2+} analogues. However, Pb^{2+} should be closer to an optimum fit with $C22C_8$ and C222 than is Hg^{2+}, but this is not reflected in the relative stabilities of their cryptates. This may be a consequence of the soft acid Hg^{2+}

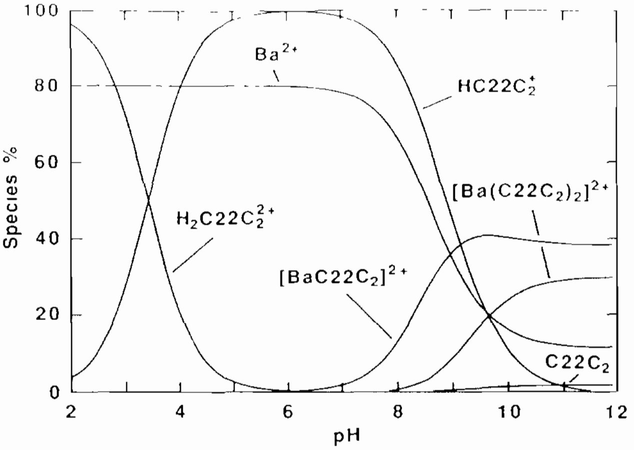

Fig 1 Speciation curves for Ba^{2+} cryptates of $C22C_2$ in aqueous 0.10 mol dm^{-3} NEt_4ClO_4 where percentages are expressed in terms of the total $C22C_2$ concentration being 100% The total Ba^{2+} and $C22C_2$ concentrations are 0.000883 and 0.001104 mol dm^{-3}, respectively

binding more strongly with the nitrogens than do the borderline soft acids Cd^{2+} and Pb^{2+}.

Comparisons of the stabilities of $[MC22C_5]^{2+}$ and $[MC22C_8]^{2+}$ with those of their respective analogues, $[MC221]^{2+}$ and $[MC222]^{2+}$, in which the number of oxygen donor atoms is increased by 1 and 2, respectively, reveal two distinct groupings according to the nature of M^{2+}. Thus for Ca^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} the stabilities of $[MC22C_5]^{2+}$ and $[MC22C_8]^{2+}$ are substantially less than those of $[MC221]^{2+}$ and $[MC222]^{2+}$, respectively, consistent with the increased stabilities of the second pair of cryptates being dominated by their extra oxygen donor atoms increasing the binding of the metal ion.

In contrast, the stabilities of $[MC22C_5]^{2+}$ and $[MC22C_8]^{2+}$ for Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} are either greater than or similar to those of $[MC221]^{2+}$ and $[MC222]^{2+}$. As the cryptand cavities are substantially larger than required to accommodate Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}, it may be inferred from the similar stabilities of $[MC22C_5]^{2+}$ and $[MC22C_8]^{2+}$ that the major interaction is between the eighteen-membered C22 ring of both cryptands and that this is dominated by interaction with the nitrogens. The observation that their stabilities are greater than those for the analogous $[MC22]^{2+}$ coronates indicates that the effect of the $-(CH_2)_5-$ and $-(CH_2)_8-$ moieties is to shield M^{2+} from interaction with water, and possibly to engender a more favourable conformation for complexation. In contrast, the presence of oxygen donor atoms in all three of the cryptand arms of $[MC221]^{2+}$ and $[MC222]^{2+}$ probably results in an attraction of M^{2+} towards the centre of the cryptand cavity, which in most cases appears to have a destabilising effect when comparisons are made with $[MC22C_5]^{2+}$ and $[MC22C_8]^{2+}$.

$[M(HC22C_n)]^{3+}$, $[M(OH)C22C_n]^{+}$ and $[M(OH)C22C_n]_2^{2+}$ complexes

The equilibrium

$$M^{2+} + H^{+} + C22C_5 \overset{K_{MH}}{\rightleftharpoons} [M(HC22C_5)]^{3+} \qquad (8)$$

where

$$K_{MH} = [M(HC22C_5)^{3+}]/([M^{2+}][H^{+}][C22C_5]) \qquad (9)$$

is characterised by log K_{MH} ($dm^6\ mol^{-2}$) = 8.69 ± 0.13, 6.0 ± 0.1 and 7.4 ± 0.2 when $M^{2+} = Co^{2+}$, Cu^{2+} and Pb^{2+}, respectively. The criterion for the detection of these species and all other species discussed herein, was that the fit of the titration data should require their presence in $\geqslant 10\%$ of the total metal ion concentration. No analogous species were detected for the other two cryptates.

The equilibrium

$$M^{2+} + OH^{-} + C22C_n \overset{K_{OH}}{\rightleftharpoons} [M(OH)C22C_n]^{+} \qquad (10)$$

where

$$K_{OH} = [M(OH)C22C_n^{+}]/([M^{2+}][OH^{-}][C22C_n]) \qquad (11)$$

is characterised by log K_{OH} ($dm^6\ mol^{-2}$) = 11.9 ± 0.1 and 21.4 ± 0.1 when $n = 2$ and $M^{2+} = Zn^{2+}$ and Hg^{2+}, respectively and 22.20 ± 0.05 and 13.9 ± 0.1 when $n = 8$ and $M^{2+} = Hg^{2+}$ and Pb^{2+}, respectively. The equilibrium

$$2M^{2+} + 2OH^{-} + 2C22C_2 \overset{K_{2OH}}{\rightleftharpoons} [M(OH)C22C_2]_2{}^{2+} \qquad (12)$$

where

$$K_{2OH} = [[M(OH)C22C_2]_2{}^{2+}]/([M^{2+}]^2[OH^{-}]^2[C22C_n]^2) \qquad (13)$$

is characterised by log K_{OH} ($dm^{15}\ mol^{-5}$) = 33.5 ± 0.2 and 26.6 ± 0.1 when $M^{2+} = Cu^{2+}$ and Zn^{2+}, respectively. Such species have also been observed in the related $C21C_5$ system [30] (Scheme 1), but the sparse nature of their characterisation in this study does not justify further discussion. This does not infer that such species are unimportant, but rather that their reliable characterisation was prevented by the precipitation of hydroxides at the higher end of the pH range studied.

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