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An equilibrium study on bivalent metal complexes with 1,5,9,13,17,21-hexaazacyclotetracosane ([24]aneN_6) in aqueous solution

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The macrocycle 1,5,9,13,17,21-hexaazacyclotetracosane (L = [24]aneN_6) was synthesized as both its HNO_3 and HCl salts. The protonation and stability constants with Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} have been determined potentiometrically in 1.0 mol dm^{-3} KNO_3 aqueous solution at 25 °C. For all these metal ions only mononuclear complexes are formed. In the case of the HNO_3 salt log K_{ML} obtained is 10.66 ± 0.02 for $[NiL]^{2+}$, 14.87 ± 0.04 for $[CuL]^{2+}$, 10.68 ± 0.01 for $[ZnL]^{2+}$ and 8.27 ± 0.01 for $[CdL]^{2+}$, whereas in the case of the HCl salt log K_{ML} is 16.47 ± 0.02 for $[CuL]^{2+}$ in 1.0 mol dm^{-3} KCl aqueous solution at 25 °C. The results for the metal complexes with [24]aneN_6 were compared with those for the M^{2+}–[18]aneN_6 (1,4,7,10,13,16-hexaazacyclooctadecane) system and discussed in terms of a ring effect. The smaller K_{CuL} in the nitrate system compared with that in the chloride system suggests an affinity of the macrocycle towards Cl^-.

Large macrocyclic compounds with six or more possible co-ordination sites have attracted interest because of their ability to bind more than one metal ion in the macrocyclic framework, their catalytic activity as enzyme models and in anion co-ordination chemistry.[1–11] Complex formation of a series of polyazacycloalkanes [3*k*]aneN_k (k = 3–12) with metal ions has been extensively studied;[12–23] it has been shown that binuclear complexes are formed when $k \geqslant 6$. It has also been found that the protonated forms of the polyazacycloalkane [18]aneN_6 (1,4,7,10,13,16-hexaazacyclooctadecane) bind various anions such as citrate (3-carboxy-3-hydroxypentan-1,5-dioate), succinate, Cl^-, NO_3^-, *etc.*;[2,24] however, the stability of these complexes is weak or moderate (log K from 1 to 3).

On the other hand, the formation constants of a series of polyazacycloalkanes [4*k*]aneN_k (k = 3 or 4) with metal ions have been reported.[25–28] The thermodynamic stability of the above macrocyclic complexes is usually larger than those of the analogous open-chain polyamine complexes and is variously attributed to either an entropic or enthalpic effect or both. Furthermore, Lehn and co-workers[2] showed that the fully protonated species of [24]aneN_6 (1,5,9,13,17,21-hexaazacyclotetracosane) and [32]aneN_8 (1,5,9,13,17,21,25,29-octaazacyclodotriacontane) form stable complexes with various inorganic, organic and metal complex anions. However, much less is known about complex formation for the polyazacycloalkanes [4*k*]aneN_k ($k \geqslant 6$).[25,27] It is interesting to determine whether [24]aneN_6 can capture more than one metal ion in the macrocyclic framework or to bind large ions such as those of the rare-earth metals.

In the present study we have synthesized [24]aneN_6 which contains six nitrogen donor atoms and determined its protonation and stability constants with Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} in aqueous solution by potentiometry. The results obtained are compared with those for the M^{2+}–[18]aneN_6 system.

Experimental

Preparation of 1,5,9,13,17,21-hexaazacyclotetracosane ([24]aneN_6)

The macrocycle [24]aneN_6 was synthesized as its HNO_3 and HCl salts by the method of Dietrich *et al.*[29] The nitrate salt was recrystallized from a mixture of ethanol and water (50% v/v) (Found: C, 29.5; N, 23.1; H, 6.85. Calc. for $C_{18}H_{50}N_{12}O_{19}$: C, 29.3; N, 22.8; H, 6.80%).

Materials

A CO_2-free solution of KOH was prepared by dissolving KOH pellets (Wako pure chemicals, super special grade) in doubly distilled water. It was kept in a polyethylene bottle with soda-lime guard tubes, which was directly connected to a Metrohm auto burette (E665/9). The concentration was determined by means of a pH-metric titration against a standard sulfamic acid solution. Aqueous solutions of the nitrate salts of Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} were obtained by dissolving the solid hydrated salts (Wako pure chemicals, special grade) without further purification in doubly distilled water. The concentrations of the metal ions were determined by standard ethylenedinitrilotetraacetate titration. Potassium nitrate (Wako pure chemicals, special grade) was recrystallized twice from water. A 1.0 mol dm^{-3} stock solution of KNO_3 or KCl was prepared and used as an ionic medium for the pH measurements.

pH-Metric measurements

The pH-metric titrations were carried out in a 1.0 mol dm^{-3} KNO_3 or KCl solution at 25 °C by using a Horiba Digital pH meter (F-8 AT) and a Horiba combination glass electrode (6237-10C). The volume of the titration vessel was 60 cm^3. The solution in the vessel was stirred continuously by using a magnetic stirrer. A stream of nitrogen, presaturated with water vapour by bubbling it through a 1.0 mol dm^{-3} KNO_3 or KCl solution, was passed into the sample solution. The entire cell was thermostatted at 25.0 ± 0.1 °C. For the determination of the protonation constants the cell was filled with about 20 cm^3 of a 1.0 mol dm^{-3} KNO_3 or KCl solution containing [24]aneN_6 (*ca.* 1.0 mmol) and HNO_3 or HCl (*ca.* 9.0 mmol) in excess. For the titrations a standard KOH solution was dispensed from a Metrohm auto burette (E665/9). The pH meter was adjusted by standard pH solutions (pH 4.01 and 6.86, Wako pure chemicals). The ionic product of water was determined in a 1.0 mol dm^{-3} KNO_3 or KCl aqueous solution at 25 °C and found to be 13.75 ± 0.01 and 13.83 ± 0.01, respectively.

Table 1 Experimental details of the pH measurements at 25 °C

	Initial concentration/mmol dm^{-3}			pH range		
	Metal	[24]aneN_6	H^+	measured	computed	Data points
Ion						
H^{+a}		0.9953	7.844	2.8–11.5	6.9–11.0	66
Ni^{2+a}	1.064	0.9982	7.912	2.7–11.1	7.5–7.8	8
Cu^{2+a}	0.5862	0.9970	7.801	2.8–11.2	6.6–10.0	29
Cu^{2+a}	1.100	0.9970	7.756	2.8–11.2	5.8–10.7	36
Zn^{2+a}	1.026	0.9979	7.836	2.7–10.9	7.6–8.0	11
Cd^{2+a}	1.017	0.9979	7.804	2.7–11.1	8.1–8.4	11
H^{+b}		1.020	7.968	2.8–11.3	7.4–10.8	54
Cu^{2+b}	0.4530	1.034	7.893	2.8–11.2	5.6–10.7	57

[a] For [24]aneN_6·6HNO_3 in 1.0 mol dm^{-3} KNO_3 aqueous solution. [b] For [24]aneN_6·6HCl in 1.0 mol dm^{-3} KCl aqueous solution.

Table 2 Stepwise protonation constants of [24]aneN_6 in 1.0 mol dm^{-3} KNO_3 and KCl aqueous solutions at 25 °C, together with those for [18]aneN_6.[32] The values in parentheses are estimated standard deviations in the last significant figures

	[24]aneN_6·6HNO_3 [a]	[24]aneN_6·6HCl [b]	[18]aneN_6·6HCl [c]
$\log K_1$	10.96(1)	11.27(1)	10.15
$\log K_2$	10.32(1)	10.57(1)	9.48
$\log K_3$	9.61(1)	9.92(1)	8.89
$\log K_4$	8.61(1)	9.23(1)	4.27
$\log K_5$	7.74(1)	8.32(1)	2.21
$\log K_6$	7.05(1)	7.44(1)	1.0

[a] This work, 1.0 mol dm^{-3} KNO_3. [b] This work, 1.0 mol dm^{-3} KCl. [c] From ref. 32, 0.15 mol dm^{-3} $NaClO_4$ aqueous solution at 25 °C.

The hydrogen-ion concentration was obtained from the measured pH values by the method suggested by Irving *et al.*[30] The protonation constants of the macrocycle and the formation constants of the metal complexes were evaluated on the basis of the pH-metric titration data using the computer program PSEQUAD.[31] The initial concentrations of the reagents and the range of pH measured in each titration are summarized in Table 1. In the case of Cu^{2+} the titrations were carried out for metal to macrocycle molar ratios of 1 : 1 and 1 : 2, while in the other cases the titrations were performed at a molar ratio of 1 : 1. At a molar ratio of 2 : 1 precipitation occurred in the titrations at about pH 6.

Electronic spectral measurements

The electronic spectrum of an aqueous solution of the nickel complex was recorded on a Hitachi U-3200 spectrophotometer.

Results and Discussion

Protonation of [24]aneN_6

The stepwise protonation constants for the macrocycle [24]aneN_6 are given in Table 2, together with those reported for [18]aneN_6[32] for comparison. The results show that [24]aneN_6 behaves as a strong base in each protonation step. The protonation constants for [24]aneN_6 are higher than those of related macrocycles previously reported,[2,29] which may be ascribed to the high ionic strength of 1.0 mol dm^{-3} used in the present study.

The protonation constants for [24]aneN_6·6HNO_3 are all less than the corresponding values for [24]aneN_6·6HCl in each protonation step. This behaviour is probably due to the electrostatic interaction between the counter anions and the nitrogen atoms of the macrocycles. The smaller chloride ions will probably interact more strongly with the protonated macrocycle than do the nitrate ions; hence the positive charges on the protonated macrocycle will decrease and become less repulsive, resulting in the enhancement of its basicity in chloride solution.

It is interesting to compare the protonation constants for [24]aneN_6 with those for [18]aneN_6. As is seen in Table 2, [18]aneN_6 behaves as a strong base in the first three protonation steps, but as a much weaker base in the last three. Additionally it is less basic than the larger macrocycle [24]aneN_6 in each protonation step. These behaviours can be rationalized in terms of the electrostatic repulsion among the positive charges on the protonated cyclic polyamines. In [24]aneN_6, where the nitrogen atoms are bridged by $(CH_2)_3$ chains, the positive charges on the protonated nitrogen atoms in the ligand are more distant from each other than in [18]aneN_6 having shorter ethylene chains between the nitrogen atoms; thus, the protonated species of [24]aneN_6 would be more stable than those of [18]aneN_6.

Fig. 1(*a*) and 1(*b*) show the distribution diagrams of the individual protonated species in the systems H^+–[24]aneN_6 and H^+–[18]aneN_6, respectively. In the neutral pH region highly charged species, H_4L^{4+}, H_5L^{5+} and H_6L^{6+}, are formed for [24]aneN_6, while for [18]aneN_6 only H_3L^{3+} is predominantly formed. This result suggests that the macrocycle [24]aneN_6 is more promising for anion co-ordination than is [18]aneN_6.

Complex formation

The formation constants for the complexes of the bivalent metal ions with the macrocycle [24]aneN_6 are summarized in Table 3, together with those reported for [18]aneN_6.[18,19,32,33] The results show that [24]aneN_6 forms only mononuclear complexes with the metal ions investigated. In the Cu^{2+}–[24]aneN_6 system protonated complexes are also formed, however for the other metal ions protonated complexes were not observed. This is because deprotonation of [24]aneN_6 occurs at a higher pH ($\geqslant$6) than that of [18]aneN_6; hence the complex formation of Cu^{2+} with [24]aneN_6 takes place at about pH 6, whereas the other metal ions form complexes at pH $>$8. Fig. 2(*a*) and 2(*b*) show the distribution diagrams of the individual species for Cu^{2+}–[24]aneN_6 in the nitrate and chloride systems, respectively, which were calculated by using the equilibrium data in Table 3 as a function of pH. In the Cu^{2+}–[24]aneN_6 system the formation constants for the nitrate

Table 3 Logarithms of the formation constants (log K_{ML}) of the bivalent metal complexes with [24]aneN_6 in 1.0 mol dm^{-3} KNO_3 and KCl solution at 25 °C and with [18]aneN_6 in 0.15 mol dm^{-3} $NaClO_4$ solution at 25 °C. Values in parentheses are standard deviations in the last significant figures

	log K					
			[18]aneN_6·6HCl			
Reaction [a]	[24]aneN_6·6HNO_3 Cu	[24]aneN_6·6HCl Cu	Ni [c]	Cu [d]	Zn [e]	Cd [f]
$M + L \rightleftharpoons ML$ [b]	14.87(4)	16.47(2)	19.6(2)	24.40(2)	18.70(1)	18.80(1)
$M + L + H \rightleftharpoons M(HL)$	25.02(4)	26.97(1)	23.7(3)	27.40(5)	22.63(3)	
$M + L + 2H \rightleftharpoons M(H_2L)$	33.17(3)	35.18(1)		30.88(4)		
$M + L + 3H \rightleftharpoons M(H_3L)$	39.46(3)	41.70(1)				
$M + L + 4H \rightleftharpoons M(H_4L)$	45.59(5)	47.72(2)				
$ML + H \rightleftharpoons M(HL)$	10.15	10.50	4.1	3.00	3.93	
$M(HL) + H \rightleftharpoons M(H_2L)$	8.15	8.21		3.48		
$M(H_2L) + H \rightleftharpoons M(H_3L)$	6.29	6.52				
$M(H_3L) + H \rightleftharpoons M(H_4L)$	6.12	6.02				

[a] Charges omitted for clarity. [b] log K 10.66(2) (M = Ni), 10.68(1) (Zn) and 8.27(1) (Cd). [c] Ref. 33. [d] Ref. 32. [e] Ref. 18. [f] Ref. 19.

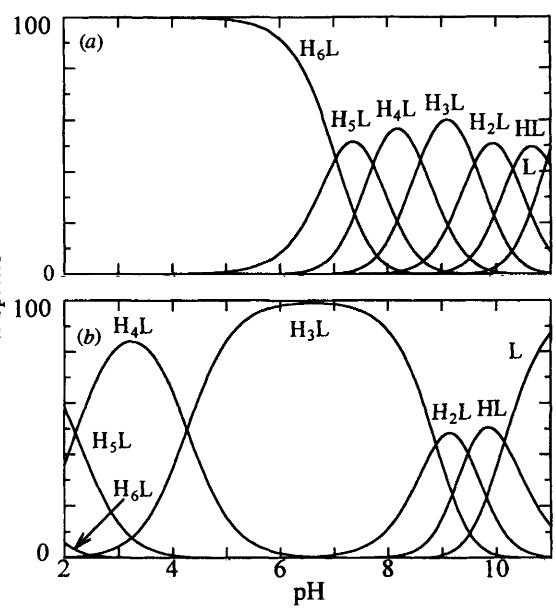

Fig. 1 Distribution diagrams for (*a*) H^+–[24]aneN_6 and (*b*) H^+–[18]aneN_6

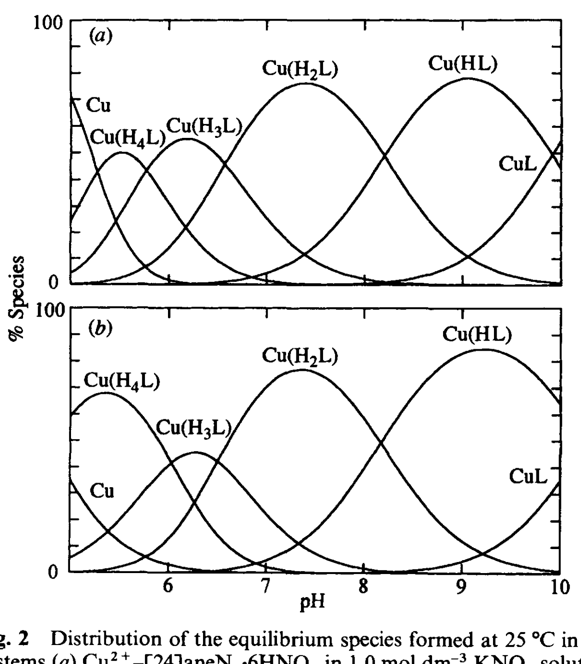

Fig. 2 Distribution of the equilibrium species formed at 25 °C in the systems (*a*) Cu^{2+}–[24]aneN_6·6HNO_3 in 1.0 mol dm^{-3} KNO_3 solution and (*b*) Cu^{2+}–[24]aneN_6·6HCl in 1.0 mol dm^{-3} KCl solution

Table 4 Electronic spectral data for the nickel(II) complexes with macrocyclic polyamine ligands

Complex	λ_{max} (ε) [a]	
$[Ni([18]aneN_6)]^{2+}$	530 (11) [b]	345 (11) [b]
$[Ni([24]aneN_6)]^{2+}$	628 (2.8)	387 (11)

[a] λ_{max} given in nm, ε in dm^3 mol^{-1} cm^{-1}. [b] Taken from ref. 21.

solution are smaller than those for the chloride solution. This result suggested that the $[Cu([24]aneN_6)]^{2+}$ complex interacts with the chloride ion more strongly than with the nitrate ion.

The $[Cu([18]aneN_6)]^{2+}$ complex shows a poor tendency for protonation compared with $[Cu([24]aneN_6)]^{2+}$, as seen from log $K_{M(HL)}$ in Table 3. Its first and second protonation constants are similar to each other, suggesting that the two sites in the complex are so far apart as not to interfere with each other. Furthermore, the small value of the protonation constant indicates that all donor atoms are involved in the complex formation. On the other hand, the first and second stepwise protonation constants of the $[Cu([24]aneN_6)]^{2+}$ complex are large and similar to the third and fourth stepwise protonation constants of the free macrocycle. This finding indicates that at least two nitrogen atoms are not co-ordinated to Cu^{2+} within $[Cu([24]aneN_6)]^{2+}$.

The electronic spectral data for aqueous solutions of the nickel(II) complexes with the macrocycles [24]aneN_6 and [18]aneN_6 obtained in the range 300–900 nm are given in Table 4. The $[Ni([24]aneN_6)]^{2+}$ complex showed a spectrum typical for an octahedral high-spin nickel(II) chromophore, analogous to that reported for $[Ni([18]aneN_6)]^{2+}$, in which full octahedral co-ordination of the hexadentate ligand to nickel(II) is reached.[33] The difference between the spectral features of these two complexes is the low-energy shift experienced by $[Ni([24]aneN_6)]^{2+}$ with respect to $[Ni([18]aneN_6)]^{2+}$, which is ascribed to the stronger ligand field for the latter complex coinciding with its higher thermodynamic stability.

The stability constants for the complexes Ni^{2+}, Cu^{2+} and Zn^{2+} with [24]aneN_6 follow a typical Irving–William series.[34] For the d^{10}-metal complexes the formation constant of $[Zn([24]aneN_6)]^{2+}$ is larger than that of $[Cd([24]aneN_6)]^{2+}$. This difference is similar to that for d^{10}-metal complexes with open-chain polyamines or with macrocyclic polyamines containing less than five nitrogen donor atoms. This finding suggests that the decrease in stability constant for d^{10}-metal complexes with [24]aneN_6 results from the increase in the number of unco-ordinated nitrogen donor atoms or the presence of six-membered rings.[35]

Acknowledgements

The present work was partially supported by a Grant-in-Aid for Scientific Research in the Priority Area of 'Synthesis and Solute Structure Analysis of Rare Earth Complexes of New Macrocyclic Polyamines having Some Pendant Arms' (No. 07230295) from the Ministry of Education, Science and Culture, Japan. All calculations were performed at the Computer Centre of Fukuoka University.

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Received 22nd March 1996; *Paper* 6/02010K