Discrimination by Structural Dislocation: Thermodynamic Stabilities of the Zn^{II} and Cd^{II} Complexes of a Series of O_2N_3-Donor Macrocycles

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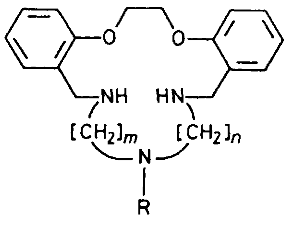
Systematic minor perturbations of ligand structures can lead to a dramatic 'dislocation' in geometry at one point along a series of metal complexes; the accompanying changes in thermodynamic stability may have important implications for strategies to achieve metal ion recognition by organic substrates; dislocation discrimination is illustrated by the complexation behaviour of a series of O_2N_3-donor macrocycles with Zn^{II} and Cd^{II}.

Establishing the factors which influence selectivity of complexation of metal ions is of considerable current interest. Metal-ion recognition by organic substrates is of major significance in chemistry and biochemistry in a number of areas which include the development of reagents for use in new analytical and hydrometallurgical processes as well as for more fully understanding the modes of metal-ion transport and storage *in vivo*.

Cyclic ligands are particularly suitable for use as selective reagents since, in addition to the usual parameters which influence the affinity of an open-chain ligand for a particular ion (*e.g.* donor atom type and chelate ring sizes), the macro-



(1)

Ring size	m	n	R	Abbreviation
17	2	2	H	$OenNdienH_4$
18	2	3	H	$OenNentnH_4$
19	3	3	H	$OenNditnH_4$
19	2	4	H	$OenNenbnH_4$
19	3	3	Me	$OenN(Me)ditnH_4$

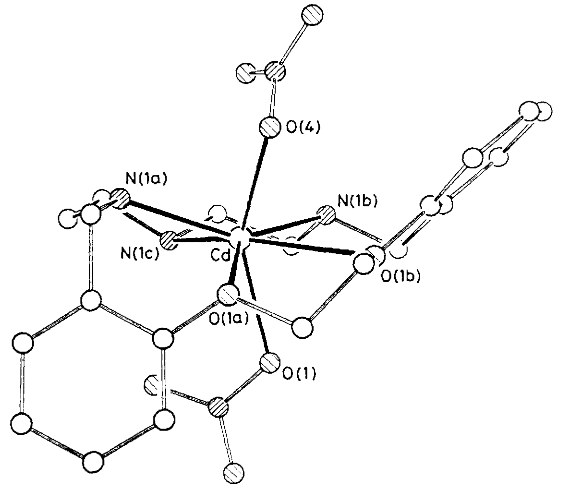


Figure 1. The structure of $[Cd(OenNdienH_4)(NO_3)_2]$. Bond lengths to Cd are N(1a), 2.326; N(1b), 2.338, N(1c), 2.382; O(1a), 2.614; O(1b), 2.732; O(1), 2.318; O(4), 2.402 Å (e.s.d. 0.003 Å throughout).

cyclic hole size can be 'tuned' to provide a donor atom cavity which exhibits an optimum fit[1] for a given metal ion. Such hole-size variations in macrocycles have been used successfully[2] to control thermodynamic stabilities of crown ether complexes of alkali- and alkaline earth-metal cations.

In this paper we consider an additional mode of macrocyclic ring-size discrimination which involves a 'dislocation' in the complexation behaviour of a particular metal ion along a series of closely related ligands. Such a 'dislocation' occurs when the gradation of properties along the ligand series triggers a substantial change in co-ordination geometry or ligand conformation in adjacent complexes in the series. This mechanism for discrimination is illustrated by the thermodynamic stabilities of Zn^{II} and Cd^{II} complexes of a series of O_2N_3-macrocylic ligands (**1**).†

Comparison of the log K_1 values for the 1 : 1 Cd^{II} complexes of the 17- and 18-membered ring ligands $OenNdienH_4$ and $OenNentnH_4$ reveals a small (but significant) decrease in stability for the complex of the latter ligand. Inspection of molecular models suggested that this decrease may reflect a slightly poorer fit of the Cd^{II} ion for the donor cavity of this larger ring macrocycle. This contention is supported by an *X*-ray structure analysis‡ of $[Cd(OenNdienH_4)(NO_3)_2]$ which shows (Figure 1) a very distorted pentagonal bi-pyramidal co-ordination geometry and although the Cd^{II} ion lies in the cavity of the five equatorial donor atoms of the 17-membered ring the bonds to the two ether oxygen atoms are long [2.614(3) and 2.732(3) Å]. In the 18-membered ring of $OenNentnH_4$ it is likely that these bonds will be even weaker if a similar co-ordination geometry is maintained. A further increase in ring size is found to be accompanied by a dramatic decrease in stability (Figure 2), with the Cd^{II} complexes of the 19-membered ring ligands $OenNditnH_4$, $OenNenbnH_4$ and $OenN(Me)ditnH_4$ being 10^2—10^3 times less stable than the related 17- and 18-membered ring species. This decrease is consistent with the 19-membered ring complexes having a substantially different geometry, possibly with one or both of the ether oxygen donors not co-ordinated.

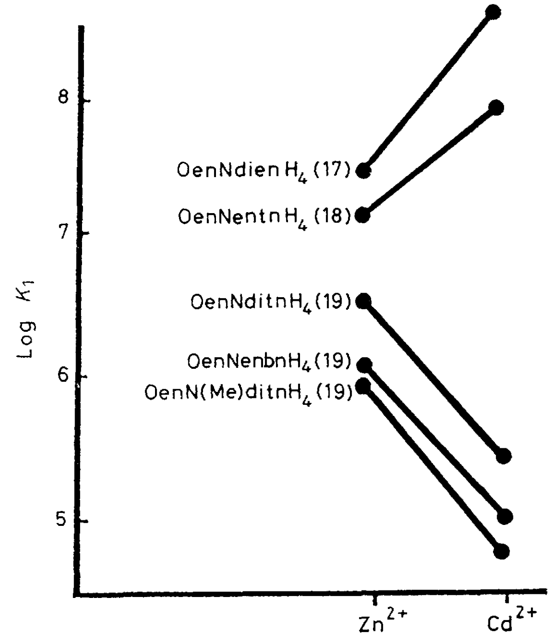


Figure 2. Log K_1 values for Zn^{II} and Cd^{II} complexes of the O_2N_3-ligands (**1**), measured in 95% MeOH at 25 °C (I = 0.1 M, Et_4NCl) as described previously.[3] Macrocyclic ring sizes are given in parentheses.

In contrast to the Cd^{II} complexes, the Zn^{II} complexes of the 17-, 18-, and 19-membered ring ligands show only a gradual systematic variation of log K_1 with ligand ring size (Figure 2). Models indicate that Zn^{II} is too small to interact with all five donors of each macrocycle if a ligand conformation similar to that in $[Cd(OenNdienH_4)(NO_3)_2]$ is adopted.

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† Details of preparation of these ligands are given in ref. 3.

‡ *Crystal data:* $[Zn(OenNdienH_4)(NO_3)_2]$, $C_{20}H_{27}N_5O_8Zn$, M = 530.8, monoclinic, space group $P2_1/n$, a = 17.512(5), b = 8.287(3), c = 15.927(4) Å, β = 93.10(2)°, Z = 4, U = 2308.0 $Å^3$, D_c = 1.527 g cm^{-3}, $\mu(Mo\text{-}K\alpha)$ = 2.39 cm^{-1}, present R factor = 0.053 for 2204 reflections with $I/\sigma(I) \geqslant 3.0$ collected on a Philips PW1100 diffractometer in the θ range 3—25°. $[Cd(OenNdienH_4)(NO_3)_2]$, $C_{20}H_{27}N_5O_8Cd$, M = 577.9, triclinic, space group $P\bar{1}$, a = 13.545(4), b = 11.457(3), c = 7.891(3) Å, α = 94.92(2), β = 105.68(2), γ = 100.75(2)°, Z = 2, U = 1146.2 $Å^3$, D_c = 1.674 g cm^{-3}, $\mu(Mo\text{-}K\alpha)$ = 9.07 cm^{-1}, present R factor = 0.036 for 3498 reflections with $I/\sigma(I) \geqslant 3.0$ collected as for the Zn complex.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

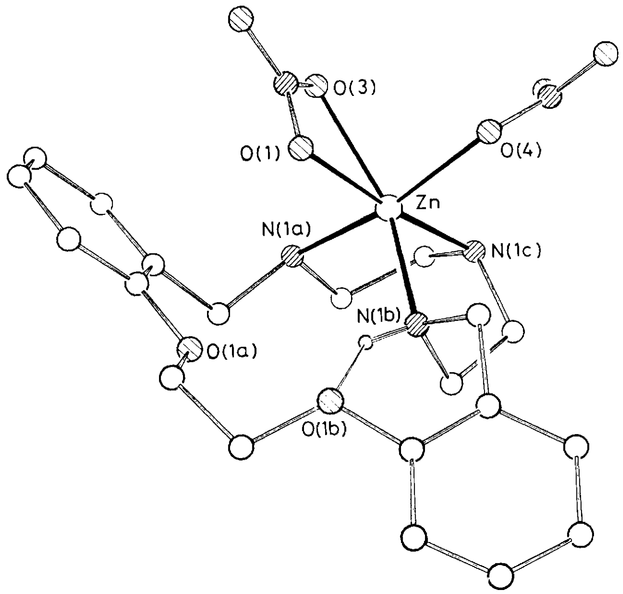

Figure 3. The structure of [Zn(OenNdienH$_4$)(NO$_3$)$_2$]. Bond lengths to Zn are N(1a), 2.225; N(1b), 2.089; N(1c), 2.085; O(1), 2.227; O(3), 2.253; O(4), 2.179 Å (e.s.d. 0.005 Å throughout). An intramolecular hydrogen bond between the hydrogen of the benzylamine nitrogen N(1b) and the ether oxygen atom O(1b) occupies part of the macrocycle cavity.

This suggests that the zinc ion may bind only to the nitrogen atoms in all these ligand systems.[4] In accordance with this the solid state structure‡ of [Zn(OenNdienH$_4$)(NO$_3$)$_2$] (Figure 3) shows an approximately facial arrangement of the three nitrogen atoms with the ether oxygens remaining unco-ordinated.

It appears that the 'dislocation' observed in the series of Cd^{II} complexes depends upon a structural change which involves non-co-ordination of the ether oxygens in the 19-membered ring complexes. Since related structures probably also occur for all of the Zn^{II} complexes, it is only for the 19-membered ring systems that the 'natural' stability order[5] for polyamine ligands of $Zn^{II} > Cd^{II}$ is observed. For the smaller rings this order is reversed—a result in keeping with the Zn^{II} and Cd^{II} complexes having different solution structures (as found in the solid state for the complexes of OenNdienH$_4$). Thus the occurrence of a structural 'dislocation' in the series of Cd^{II} complexes but not in the Zn^{II} series accounts for the overall pattern of observed variations in thermodynamic stability. It seems likely that related 'dislocation' mechanisms are of considerable importance in the metal ion discrimination behaviour which is a feature of a range of other chemical and biochemical systems.

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