Dislocation Discrimination: The Interaction of Zinc(II) and Cadmium(II) with Dibenzo-substituted Macrocyclic and Open-chain Tetra-amines

Kenneth R. Adam,[a] Christopher W. G. Ansell,[b] Keith P. Dancey,[b] Laurel A. Drummond,[b] Anthony J. Leong,[a] Leonard F. Lindoy,[a]* and Peter A. Tasker[b]*†

[a] *Department of Chemistry and Biochemistry, James Cook University, Queensland 4811, Australia*
[b] *School of Chemistry, Polytechnic of North London, London N7 8DB, U.K.*

Thermodynamic stabilities have been determined for zinc(II) and cadmium(II) complexes of a series of macrocyclic and open-chain tetra-amines; for the 14- to 16-membered macrocyclic systems a dislocation in the stability pattern occurs for zinc(II) at the 16-membered ring complex while, for cadmium(II), the dislocation occurs at the 15-membered ring species resulting in an enhanced stability difference [$Zn^{II}>Cd^{II}$] for the complexes of this latter ring.

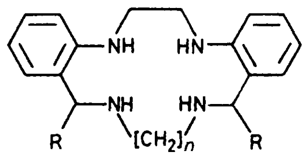
Selective complex formation by macrocyclic ligands is of considerable current interest.[1—3] As part of a wider programme in this area, we have previously investigated a little-studied discrimination mechanism termed 'dislocation discrimination'.[4] Such discrimination involves the occurrence of a dislocation in the complexation behaviour of a particular metal ion along a series of closely related ligands.

In a previous study,[3] we have investigated the complexation of Zn^{II} and Cd^{II} by 17- to 19-membered O_2N_3-donor macrocycles. Along these respective complex series, a dislocation in the expected $\log_{10}K$ values occurs for the Cd^{II} complex of the 19-membered ring whereas no similar dislocation is apparent along the Zn^{II} series. This different complexation behaviour for Zn^{II} and Cd^{II} has been demonstrated to provide a basis for discriminating between these ions. Further, with these ligands, the 'natural' stability order of $Zn^{II}>Cd^{II}$ found for simple polyamine ligands[3] is reversed for the complexes of the 17- and 18-membered rings but reverts to the normal order for the complexes of the 19-membered ring.

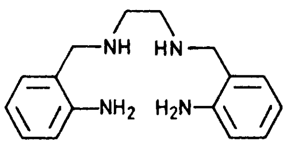
We now report a new example of dislocation discrimination involving Zn^{II} and Cd^{II} complexes of the smaller (N_4-donor) macrocycles (**1**)—(**3**)‡ which contain 14- to 16-membered rings; the macrocycles (**1**)—(**3**) were obtained by reduction of their corresponding di-imine precursors.[5] Stability patterns for the Zn^{II} and Cd^{II} complexes were determined potentiometrically (pH titration in 95% methanol) and are given in Figure 1. For Zn^{II}, the 14- and 15-membered rings yield $\log_{10}K$ values which are quite similar whereas there is a sudden drop in stability for the complex of the 16-membered ring. The behaviour for Cd^{II} is quite different: in this case a dislocation in stability occurs between the 14- and 15-membered rings with the value for the 15-membered ring complex being lower than expected. The stability then increases for the 16-

† *Present address:* Research Department, Imperial Chemical Industries plc, Organics Division, P.O. Box No. 42, Hexagon House, Blackley, Manchester M3 3DA, U.K.

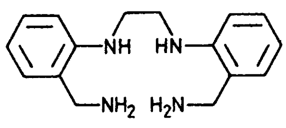
‡ (**1**): 5,6,7,8,9,10,15,16,17,18-decahydrodibenzo[*e,m*][1,4,8,11]-tetra-azacyclotetradecine; (**2**): 6,7,8,9,10,11,16,17,18,19-decahydro-5*H*-dibenzo[*e,n*][1,4,8,12]tetra-azacyclopentadecine; (**3**): 5,6,7,8,9,10,11,12,17,18,19,20-dodecahydrodibenzo[*e,o*][1,4,6,13]-tetra-azacyclohexadecine; (**4**): 5,11-diethyl-6,7,8,9,10,11,16,17,18,19-decahydro-5*H*-dibenzo[*e,n*][1,4,8,12]tetra-azacyclopentadecine; (**5**): *N,N'*-bis-(*o*-aminobenzyl)ethylenediamine; (**6**): *N,N'*-bis-[*o*-(aminomethyl)phenyl]ethylenediamine.



(1) n = 2, R = H
(2) n = 3, R = H
(3) n = 4, R = H
(4) n = 3, R = Et



(5)



(6)

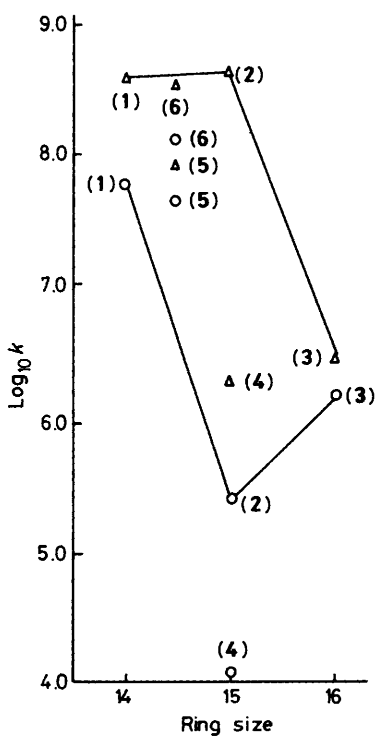


Figure 1. $Log_{10}K$ values for formation of the 1:1 complexes of Zn^{II} and Cd^{II} with (**1**)—(**6**). The stabilities were obtained potentiometrically in 95% methanol (I = 0.1 M, Et_4NClO_4) at 25 °C. All values are the mean of between 2 and 5 individual determinations at varying metal : ligand ratios. In all cases individual $\log_{10}K$ values fell within 0.1 of the mean (and usually within 0.05). △, Zn^{II}; ○, Cd^{II}.

membered ring species. Thus, relative to the 14-membered and 16-membered ring systems, the 15-membered ring shows enhanced recognition for Zn^{II} over Cd^{II}.

In order to probe the generality of this enhanced recognition for Zn^{II}, the stabilities of the Zn^{II} and Cd^{II} complexes of the corresponding 15-membered diethylated (*meso*) derivative (**4**)[6]‡ were determined. Although both $\log_{10}K$ values are lower than those for the unsubstituted 15-membered macrocycle (**2**), the diethyl derivative still maintains the discrimination observed for the parent ring. The lower $\log_{10}K$ values obtained with the disubstituted macrocycle presumably reflect the effect of increased steric hindrance on complexation; nevertheless, the stability difference for Zn^{II} and Cd^{II} is clearly not markedly dependent on the presence or absence of diethyl substitutuents.

In parallel experiments, the interaction of the above ions with the open-chain ligands (**5**)[7]‡ and (**6**)[7]‡ was investigated. Both ligands can be considered to be analogues of the 15 membered macrocycle (**2**). For each open-chain system, the $\log_{10}K$ values are unremarkable (see Figure 1) with the respective Zn^{II} complexes being only slightly more stable than the corresponding Cd^{II} species. Thus, the discrimination observed for the 15-membered ring (**2**) clearly depends on its cyclic nature; nevertheless, the behaviour does not constitute ring-size discrimination of the most common type.[1,2] The latter solely involves the match or otherwise of the metal-ion for the radius of the available macrocyclic hole.

In contrast to the stability pattern for the Zn^{II} complexes of (**1**)—(**3**), the complexes of the *larger* Cd^{II} ion show *decreased* stability as the ring size *increases* from 14 to 15 members (even though the stability again rises as the hole size is further increased in the 16-membered ring). The enhanced discrimination ability shown by the 15-membered ring thus appears to be a consequence of the different dislocation patterns which occur when these cyclic ligands interact with Zn^{II} and Cd^{II}. Overall, the study thus documents a new example of dislocation discrimination: a discrimination mechanism of potential importance to a number of other metal-containing chemical and biochemical systems.

We thank the S.E.R.C. and I.C.I. (U.K.) for a Co-operative Research Grant as well as the Australian Research Grants Scheme and the Australian Institute of Nuclear Science and Engineering for assistance.

Received, 6th December 1985; Com. 1730

References

1 R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb, and J. J. Christensen, *Chem. Rev.*, 1985, **85**, 271.
2 K. Henrick, P. A. Tasker, and L. F. Lindoy, *Prog. Inorg. Chem.*, 1985, **33**, 1.
3 K. R. Adam, K. P. Dancey, B. A. Harrison, A. J. Leong, L. F. Lindoy, M. McPartlin, and P. A. Tasker, *J. Chem. Soc., Chem. Commun.*, 1983, 1351.
4 K. R. Adam, A. J. Leong, L. F. Lindoy, H. C. Lip, B. W. Skelton, and A. H. White, *J. Am. Chem. Soc.*, 1983, **105**, 4645.
5 P. G. Owston, R. Peters, E. Ramsammy, P. A. Tasker, and J. Trotter, *J. Chem. Soc., Chem. Commun.*, 1980, 1218.
6 K. Henrick, P. M. Judd, P. G. Owston, R. Peters, P. A. Tasker, and R. W. Turner, *J. Chem. Soc., Chem. Commun.*, 1983, 1253.
7 C. W. G. Ansell, M. McPartlin, P. A. Tasker, and A. Thambythurai, *Polyhedron*, 1983, **2**, 83.