

## Metal-Ion Recognition. 2.<sup>1</sup> Structural Dislocation Behavior in the Interaction of Zinc(II) and Cadmium(II) with a Series of O<sub>2</sub>N<sub>3</sub>-Donor Macrocycles

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**Abstract:** The interaction of Zn(II) and Cd(II) with a series of O<sub>2</sub>N<sub>3</sub>-donor macrocycles gives rise to new examples of "dislocation" behavior in the coordination patterns of the resulting complexes. Dislocations occur when a gradual change of properties along the ligand series induces a sudden change in coordination behavior for adjacent complexes in the series. The presence of such dislocations may form a basis for metal-ion recognition. Thus when Zn(II) and Cd(II) react with unsubstituted 17-, 18-, and 19-membered macrocycles of the above type, the trends in the stabilities for each ion parallel each other for the first two ligands [with the stability constants falling in the order Cd(II) > Zn(II)]. However, for the 19-membered-ring ligand, a dislocation of the trend is in evidence for the Cd(II) complex but not for the Zn(II): the stability of the Cd(II) complex is considerably lower than expected [the stability order is now Zn(II) > Cd(II)]. The origin of the observed dislocation along the Cd(II) series appears to be a crossover from coordination of the ether groups in the 17- and 18-membered-ring systems to their noncoordination in the 19-membered-ring system. For corresponding substituted-ligand derivatives, a similar dislocation pattern is observed and hence the dislocations appear to be primarily a function of ring size for these systems. The subtle factors underlying these effects have been elucidated by a variety of methods including solution equilibrium, NMR, molecular mechanics, and X-ray diffraction techniques. The X-ray structures of three key complexes are presented. The study serves to illustrate a discrimination mechanism that has received little attention in the past but that may be of considerable importance to a range of metal-ion discrimination behavior in other chemical and biochemical systems.

Metal-ion recognition is of fundamental importance to broad areas of both chemistry and biochemistry. In spite of this, the level of understanding of the mechanisms of such recognition is often not high. This is illustrated, for example, by the difficulty commonly experienced in attempting to predict the metal-ion binding preferences of particular biochemical sites (particularly when they incorporate mixed heteroatoms). This is so, even though thermodynamic aspects of metal-ion binding to organic ligands have been widely studied for many years. Indeed, the search for unusual metal-ion selectivity in much of this earlier work has been rather unsystematic and, for example, has typically centered on the isolated measurement of metal-ion binding constants for particular ligand types; in most cases, no clear strategy for achieving metal-ion selectivity was inherent in the experimental approach employed.

More recently, the potential of macrocyclic ligand systems, with their central cavity, for use as metal-ion selective reagents has been widely recognized.<sup>3-6</sup> In a number of studies, the metal-ion binding preferences of a series of related macrocyclic ligands incorporating gradually increasing ring sizes have been investigated. For a number of systems in which the metal ion fully occupies the macrocyclic cavity, there is a tendency for maximum stability to occur at the ligand for which the cavity size best matches the radius of the ion.<sup>3,5,6</sup> However, it is important to note that other influences frequently override this hole-size effect.<sup>7</sup>

Nevertheless, macrocyclic hole-size variation of this type has been used successfully by us in a previous study to control the relative thermodynamic stabilities of selected Ni(II) complexes; such studies have formed part of an overall program aimed at understanding more fully the factors affecting metal-ion selectivity.<sup>8-13</sup> During the course of these studies a second mechanism by which macrocyclic ligands may discriminate between metal ions has been detected.<sup>9,12,13</sup> This second process has been named *dislocation discrimination*.

Dislocation discrimination is associated with a sudden change in coordination behavior of a particular metal ion along a series

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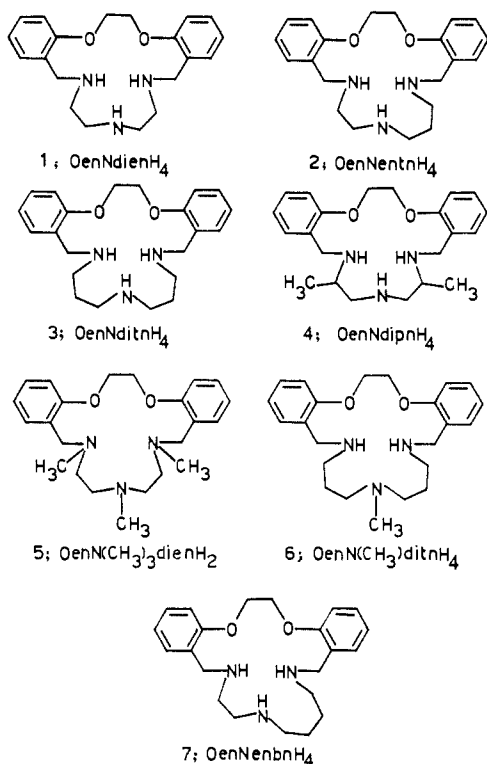
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Chart I



of closely related macrocyclic ligands. In principle, a dislocation will occur when the gradation of ligand properties along the series results in a sudden destabilization of one complex structure relative to a second. As a consequence, at the point of dislocation, adjacent complexes in the series may show major differences in their coordination geometries and/or ligand conformations. Because substantially different structures are involved, the complexes on either side of a dislocation are likely to show an enhanced difference in their respective thermodynamic stabilities over that which occurs between adjacent complexes elsewhere in the series. Thus in the absence of a dislocation, a regular gradation of metal-complex stabilities would be expected along the series. Of course, dislocations of the above type need not be restricted to macrocyclic systems although the inherent steric restraints of such systems (which arise from their cyclic nature) will tend to promote dislocation behavior.

It has been demonstrated previously that a dislocation occurs when the O<sub>2</sub>N<sub>3</sub>-donor ligands 1–3 (Chart I) coordinate to Ni(II).<sup>8</sup> For the 17- and 18-membered rings, 1 and 2, the corresponding complexes have quite similar stabilities while there is a substantial drop in stability on passing to the complex of the 19-membered macrocycle 3. Thus, the dislocation occurs for this system between the 18- and 19-membered-ring species. The 17- and 18-membered-ring complexes were postulated to have octahedral geometries in which the respective macrocycles occupy five coordination positions such that the N<sub>3</sub> portion of each macrocycle assumes a facial arrangement. Such a geometry was subsequently confirmed by X-ray diffraction to occur in the 17-membered-ring complex [Ni(OenNdienH<sub>4</sub>)(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub>.<sup>11</sup> The dislocation observed along this series was assigned to result from the increased steric crowding in the N<sub>3</sub> portion of the ligand as the number of methylene groups is increased; for the 19-membered-ring complex, a switch to meridional coordination of the N<sub>3</sub> donors is most likely induced.

Related steric clashes occur on coordination when methyl groups are appended to the N<sub>3</sub> backbone of 1 to produce 4.<sup>9</sup> Thus the stability constant for the Ni(II) complex of 1 is 10<sup>10</sup> whereas the corresponding value for the complex of 4 is 10<sup>6.9</sup>. As before, the drop in stability for the latter complex was postulated to reflect dislocation behavior centered on the N<sub>3</sub> backbone. Subsequent molecular mechanics calculations suggested that the *fac* complex

Table I. Crystal Data and Selected<sup>a</sup> Details of the Structure Determinations of [Cd(OenNdienH<sub>4</sub>)(NO<sub>3</sub>)<sub>2</sub>], [Zn(OenNdienH<sub>4</sub>)(NO<sub>3</sub>)<sub>2</sub>], and [Cd(OenNdaitnH<sub>4</sub>)(NO<sub>3</sub>)<sub>2</sub>]

	CdC <sub>20</sub> H <sub>27</sub> N <sub>5</sub> O <sub>8</sub>	ZnC <sub>20</sub> H <sub>27</sub> N <sub>5</sub> O <sub>8</sub>	CdC <sub>22</sub> H <sub>31</sub> N <sub>5</sub> O <sub>8</sub>
<i>M</i>	577.9	530.8	606.0
<i>a</i> /Å	13.545 (4)	17.512 (5)	26.214 (5)
<i>b</i> /Å	11.457 (3)	8.287 (3)	8.491 (2)
<i>c</i> /Å	7.891 (3)	15.927 (4)	11.248 (3)
$\alpha$ /deg	94.92 (2)	90	90
$\beta$ /deg	105.68 (2)	93.10 (2)	93.68 (2)
$\gamma$ /deg	100.75 (2)	90	90
<i>Z</i>	2	4	4
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
$\mu$ (Mo K $\alpha$ )/cm <sup>-1</sup>	9.07	2.39	8.34
cryst size/(mm × 10 <sup>-2</sup> )	35 × 20 × 25	42 × 26 × 28	34 × 20 × 12
no. of data in refinement <sup>b</sup>	3498	2204	2727
<i>R</i> <sup>c</sup>	0.036	0.053	0.047
<i>R</i> <sub>w</sub> <sup>d</sup>	0.037	0.053	0.048

<sup>a</sup> Further information is available in supplementary Table 1s. <sup>b</sup> Intensity measurements were made on a Philips PW1100 diffractometer, using Mo K $\alpha$  radiation. For both structures unique data with  $|F| > 6\sigma(|F_o|)$  were used in refinement. <sup>c</sup> The function minimized was  $w(|F_o| - |F_c|)^2$ , where  $w = 1/(\sum(F_o)^2)$ . <sup>d</sup>  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ .

is destabilized (relative to the *mer* complex) in this case because of steric clashes involving the appended methyl groups.<sup>11</sup> We now report an investigation of the interaction of Zn(II) and Cd(II) with the O<sub>2</sub>N<sub>3</sub>-ligand series 1–7. As part of this study, new examples of dislocation discrimination have been documented and the origins of such discrimination investigated.

### Experimental Section

Conductance and elemental analytical data were obtained as described previously.<sup>9</sup> <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on a Bruker AM300 as well as on Jeol FX90Q and FX60 spectrometers. Spectra were obtained for the metal complexes by using saturated solutions in DMSO-*d*<sub>6</sub>. The synthesis and characterization of the macrocycles 1–7 have been described previously.<sup>9,14</sup>

**log *K* Determinations.** The automated pH-titration apparatus used for the ligand protonation and metal-complex stability determinations was identical with that described elsewhere.<sup>9</sup> The general procedure employed was also similar, although the measurements were obtained with 95% methanol and (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NClO<sub>4</sub> (*I* = 0.1 M) as background electrolyte. The titrant was (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NOH (0.1 M). (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NClO<sub>4</sub> was used rather than the (CH<sub>3</sub>)<sub>4</sub>NCl employed previously for studies involving transition-metal complexes in order to avoid the strong competitive binding that occurs between Cd(II) and chloride ion.

As for previous studies involving the present ligands, 95% methanol was chosen as solvent because the enhanced solubilities of both these ligands and their complexes in this solvent mixture (relative to water) enabled the study to be extended over a wider range of compound types. Previous work<sup>8</sup> has indicated that the stability patterns exhibited for the methanol mixture are not expected to vary greatly from the patterns observed for water (although the absolute values may be somewhat lower in the latter case).

Magnesium-dried, fractionated, AR methanol and doubly distilled CO<sub>2</sub>-free water were used to prepare all solutions. The methanol was degassed before use by bubbling dry nitrogen through it for 1 h. Stability constant measurements were obtained for two to three different L:M ratios starting from either the solid metal complex or a mixture of the metal ion and the ligand in the required ratio. In most cases precipitation of complex or hydrolysis products during the titration prevented the collection of a full set of data. In all, 114 potentiometric titrations were performed during the present study. All data were refined by using a local version of the programs MINQUAD<sup>15</sup> and SUPERQUAD.<sup>16</sup> For comparison, representative sets of data were also processed by using a local version of KONST.<sup>17</sup> Within experimental error, all programs yielded identical results for a given set of titration data.

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**Table II.** Non-Hydrogen Fractional Atomic Coordinates and Thermal Parameters ( $\text{\AA}^2$ ) for  $[\text{Cd}(\text{OenNdienH}_4)(\text{NO}_3)_2]$ ,  $[\text{Zn}(\text{OenNdienH}_4)(\text{NO}_3)_2]$ , and  $[\text{Cd}(\text{OenNditnH}_4)(\text{NO}_3)_2]^a$ 

atom	x	y	z	$U_{\text{iso}}$ or $U_{\text{eq}}$	atom	x	y	z	$U_{\text{iso}}$ or $U_{\text{eq}}$
<b><math>[\text{Cd}(\text{OenNdienH}_4)(\text{NO}_3)_2]</math></b>									
Cd	0.27199 (2)	0.17652 (2)	0.40736 (3)	0.0312 (2)	C(8b)	0.3729 (3)	0.1202 (4)	0.8025 (5)	0.038 (2)
C(1a)	0.2645 (3)	0.4651 (3)	0.5539 (5)	0.037 (2)	C(7b)	0.4719 (3)	0.2166 (3)	0.8513 (5)	0.034 (2)
O(1a)	0.2365 (2)	0.3919 (2)	0.3822 (3)	0.035 (1)	C(6b)	0.5663 (3)	0.1937 (4)	0.9519 (6)	0.046 (2)
C(2a)	0.1376 (3)	0.3854 (3)	0.2675 (5)	0.032 (2)	C(5b)	0.6588 (3)	0.2779 (4)	0.9929 (7)	0.049 (3)
C(3a)	0.0578 (3)	0.4232 (4)	0.3205 (6)	0.044 (2)	C(4b)	0.6596 (3)	0.3873 (4)	0.9320 (6)	0.046 (2)
C(4a)	-0.0404 (3)	0.4090 (4)	0.1947 (7)	0.052 (3)	C(3b)	0.5672 (3)	0.4137 (3)	0.8327 (6)	0.041 (2)
C(5a)	-0.0574 (3)	0.3601 (4)	0.0221 (6)	0.047 (2)	C(2b)	0.4738 (3)	0.3281 (3)	0.7927 (5)	0.033 (2)
C(6a)	0.0234 (3)	0.3237 (3)	-0.0293 (5)	0.040 (2)	O(1b)	0.3778 (2)	0.3467 (2)	0.6955 (4)	0.035 (1)
C(7a)	0.1218 (3)	0.3342 (3)	0.0913 (5)	0.034 (2)	C(1b)	0.3767 (3)	0.4646 (3)	0.6464 (5)	0.037 (2)
C(8a)	0.2086 (3)	0.2930 (3)	0.0348 (5)	0.036 (2)	N(1)	0.0547 (2)	0.1575 (3)	0.4865 (4)	0.039 (2)
N(1a)	0.2287 (2)	0.1810 (3)	0.1023 (4)	0.032 (2)	O(1)	0.1532 (2)	0.1933 (3)	0.5666 (4)	0.043 (2)
C(9a)	0.1486 (3)	0.0721 (3)	0.0084 (5)	0.034 (2)	O(2)	0.0265 (2)	0.1178 (3)	0.3263 (4)	0.059 (2)
C(10a)	0.1786 (3)	-0.0373 (3)	0.0879 (5)	0.040 (2)	O(3)	-0.0084 (2)	0.1659 (4)	0.5691 (5)	0.079 (2)
N(1c)	0.1843 (2)	-0.0244 (3)	0.2779 (4)	0.034 (2)	N(2)	0.4962 (3)	0.2126 (3)	0.3621 (5)	0.044 (2)
C(10b)	0.2384 (3)	-0.1055 (3)	0.3852 (6)	0.040 (2)	O(4)	0.4356 (2)	0.2820 (3)	0.3768 (4)	0.050 (2)
C(9b)	0.2681 (3)	-0.0540 (3)	0.5814 (5)	0.039 (2)	O(5)	0.4575 (3)	0.1036 (3)	0.3137 (5)	0.076 (2)
N(1b)	0.3461 (2)	0.0608 (3)	0.6167 (4)	0.033 (2)	O(6)	0.5904 (2)	0.2536 (3)	0.3948 (6)	0.075 (2)
<b><math>[\text{Zn}(\text{OenNdienH}_4)(\text{NO}_3)_2]</math></b>									
Zn	0.06725 (4)	0.14110 (10)	0.22523 (5)	0.0379 (4)	O(5)	0.0658 (6)	-0.0611 (11)	0.0581 (6)	0.156 (8)
N(1a)	0.1366 (3)	0.3608 (7)	0.2548 (3)	0.035 (3)	O(6)	-0.0035 (4)	-0.2649 (8)	0.0816 (4)	0.089 (5)
N(1c)	0.0405 (3)	0.2689 (7)	0.1147 (3)	0.046 (4)	C(10b)	-0.0378 (4)	0.3289 (9)	0.1208 (5)	0.053 (5)
N(1b)	-0.0387 (3)	0.2187 (6)	0.2643 (3)	0.036 (3)	C(9b)	-0.0584 (3)	0.3601 (9)	0.2116 (5)	0.047 (4)
C(1a)	0.0004 (4)	0.2473 (9)	0.5278 (4)	0.048 (4)	C(8b)	-0.1012 (4)	0.0958 (8)	0.2653 (4)	0.042 (4)
O(1a)	0.0474 (2)	0.3042 (5)	0.4626 (3)	0.045 (3)	C(7b)	-0.1720 (4)	0.1568 (9)	0.3049 (4)	0.044 (4)
C(2a)	0.1251 (3)	0.2760 (8)	0.4714 (4)	0.037 (4)	C(6b)	-0.2436 (4)	0.1561 (9)	0.2616 (5)	0.059 (5)
C(3a)	0.1602 (4)	0.1912 (8)	0.5375 (4)	0.045 (4)	C(5b)	-0.3080 (4)	0.2153 (10)	0.2996 (7)	0.066 (6)
C(4a)	0.2376 (4)	0.1677 (9)	0.5413 (4)	0.053 (5)	C(4b)	-0.3006 (5)	0.2718 (11)	0.3797 (7)	0.073 (6)
C(5a)	0.2826 (4)	0.2314 (10)	0.4830 (4)	0.053 (5)	C(3b)	-0.2318 (4)	0.2698 (10)	0.4243 (5)	0.061 (5)
C(6a)	0.2470 (4)	0.3201 (9)	0.4171 (4)	0.048 (5)	C(2b)	-0.1678 (4)	0.2104 (8)	0.3867 (4)	0.043 (4)
C(7a)	0.1694 (4)	0.3416 (7)	0.4092 (4)	0.034 (4)	O(1b)	-0.0970 (2)	0.1961 (6)	0.4262 (3)	0.048 (3)
C(8a)	0.1348 (3)	0.4438 (8)	0.3381 (4)	0.039 (4)	C(1b)	-0.0791 (4)	0.2835 (9)	0.5021 (4)	0.052 (5)
C(9a)	0.1222 (4)	0.4769 (8)	0.1846 (4)	0.044 (4)	N(1)	0.1625 (3)	-0.0511 (7)	0.3112 (4)	0.045 (4)
C(10a)	0.1008 (4)	0.3882 (10)	0.1041 (4)	0.054 (5)	O(1)	0.0981 (3)	-0.0124 (6)	0.3368 (3)	0.052 (3)
N(2)	0.0218 (4)	-0.1417 (11)	0.1078 (5)	0.075 (6)	O(2)	0.2032 (3)	-0.1498 (6)	0.3473 (3)	0.067 (4)
O(4)	0.0234 (4)	-0.0882 (8)	0.1761 (4)	0.097 (5)	O(3)	0.1818 (3)	0.0188 (6)	0.2443 (3)	0.059 (3)
<b><math>[\text{Cd}(\text{OenNditnH}_4)(\text{NO}_3)_2]</math></b>									
Cd	0.14005 (2)	0.09094 (6)	0.48751 (5)	0.0430 (3)	N(1b)	0.0892 (2)	0.3179 (7)	0.4336 (5)	0.044 (3)
C(1a)	0.2263 (3)	0.0600 (9)	0.2053 (6)	0.050 (4)	C(8b)	0.1019 (3)	0.4019 (9)	0.3214 (6)	0.049 (4)
O(1a)	0.2279 (2)	-0.0090 (6)	0.3221 (4)	0.045 (3)	C(7b)	0.0754 (2)	0.3247 (8)	0.2153 (6)	0.041 (4)
C(2a)	0.2725 (2)	0.0034 (8)	0.3919 (6)	0.037 (4)	C(6b)	0.0294 (3)	0.3815 (10)	0.1654 (8)	0.062 (5)
C(3a)	0.3142 (3)	0.0913 (9)	0.3621 (6)	0.044 (4)	C(5b)	0.0049 (3)	0.3124 (12)	0.0667 (8)	0.066 (6)
C(4a)	0.3580 (3)	0.0963 (9)	0.4380 (7)	0.053 (4)	C(4b)	0.0265 (3)	0.1827 (11)	0.0152 (7)	0.059 (5)
C(5a)	0.3593 (3)	0.0140 (11)	0.5453 (7)	0.060 (5)	C(3b)	0.0723 (3)	0.1240 (9)	0.0627 (7)	0.054 (5)
C(6a)	0.3174 (3)	-0.0707 (10)	0.5745 (7)	0.054 (5)	C(2b)	0.0973 (3)	0.1934 (8)	0.1626 (6)	0.044 (4)
C(7a)	0.2737 (3)	-0.0797 (8)	0.4997 (6)	0.043 (4)	O(1b)	0.1421 (2)	0.1484 (6)	0.2159 (4)	0.036 (3)
C(8a)	0.2294 (3)	-0.1798 (8)	0.5335 (7)	0.047 (4)	C(1b)	0.1748 (3)	0.0446 (9)	0.1497 (7)	0.053 (5)
N(1a)	0.1911 (2)	-0.0879 (7)	0.6004 (5)	0.043 (3)	N(1)	0.2251 (2)	0.3148 (7)	0.5729 (7)	0.052 (4)
C(9a)	0.1619 (3)	-0.1990 (10)	0.6728 (8)	0.064 (5)	O(1)	0.2053 (2)	0.2774 (6)	0.4716 (5)	0.056 (3)
C(10a)	0.1280 (3)	-0.1155 (13)	0.7584 (8)	0.084 (7)	O(2)	0.2602 (2)	0.4107 (8)	0.5830 (6)	0.087 (4)
C(11a)	0.0787 (4)	-0.0611 (12)	0.7076 (9)	0.084 (7)	O(3)	0.2078 (3)	0.2511 (8)	0.6618 (5)	0.084 (4)
N(1c)	0.0790 (2)	0.0866 (8)	0.6350 (5)	0.057 (4)	N(2)	0.0676 (3)	-0.1230 (8)	0.3408 (6)	0.053 (4)
C(11b)	0.0808 (3)	0.2331 (11)	0.7077 (7)	0.067 (6)	O(4)	0.1143 (2)	-0.1229 (7)	0.3716 (5)	0.069 (4)
C(10b)	0.0609 (3)	0.3748 (10)	0.6377 (8)	0.068 (6)	O(5)	0.0398 (2)	-0.0277 (8)	0.3895 (6)	0.084 (5)
C(9b)	0.0912 (3)	0.4313 (10)	0.5357 (7)	0.061 (5)	O(6)	0.0502 (2)	-0.2126 (7)	0.2633 (6)	0.079 (4)

<sup>a</sup>All non-hydrogen atoms were refined anisotropically (see Table 2S).

**X-ray Diffraction Studies.** Colorless crystals of the nitrate complexes  $[\text{Zn}(\text{OenNdienH}_4)(\text{NO}_3)_2]$ ,  $[\text{Cd}(\text{OenNdienH}_4)(\text{NO}_3)_2]$ , and  $[\text{Cd}(\text{OenNditnH}_4)(\text{NO}_3)_2]$  were obtained by slow evaporation of the ethanol filtrates from the respective preparations given below. Crystal data and details of the structure determinations for these complexes are summarized in Table I; supplementary Table 1S contains additional details. Atom positional parameters and selected bond lengths and angles are given in Tables II and III. All the hydrogen atoms in  $[\text{Zn}(\text{OenNdienH}_4)(\text{NO}_3)_2]$  and  $[\text{Cd}(\text{OenNdienH}_4)(\text{NO}_3)_2]$  were located in difference Fourier maps and were included at these sites in the last stages of full-matrix least-squares refinement in which their thermal parameters were allowed to refine. For  $[\text{Cd}(\text{OenNditnH}_4)(\text{NO}_3)_2]$ , the hydrogen atoms attached to carbon were included in the last stages of refinement in calculated positions; the amine hydrogen atoms were located and treated as for the other two structures.

**Synthesis of Complexes.** All complexes were washed with ethanol and dried over  $\text{P}_2\text{O}_5$  in a vacuum before microanalysis.

**(Diperchlorato)(3,4,9,10-dibenzo-1,12,15-triaza-5,8-dioxacycloheptadecane)zinc(II) Monohydrate** ( $[\text{Zn}(\text{OenNdienH}_4)(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}]$ ).  $\text{OenNdienH}_4$  (0.34 g) in hot ethanol (10 mL) was added to a stirred hot solution of zinc(II) perchlorate hexahydrate (0.42 g) in hot ethanol (10 mL). The off-white solid obtained was filtered off; yield 0.43 g. Anal. Calcd for  $\text{C}_{20}\text{H}_{29}\text{Cl}_2\text{N}_3\text{O}_{11}\text{Zn}$ : C, 38.5; H, 4.7; N, 6.7. Found: C, 38.2; H, 4.8; N, 6.7.  $^{13}\text{C}$  NMR (DMSO- $d_6$ )  $\delta$  44.2, 45.1 (NHCH<sub>2</sub>CH<sub>2</sub>NH), 46.7 (ArCH<sub>2</sub>NH), 46.2 (ArCH<sub>2</sub>NH), 67.2 (CH<sub>2</sub>), 113.0, 120.7, 125.8, 129.0, 130.8, 156.3 (Ar).

**(Dinitrato)(3,4,9,10-dibenzo-1,12,15-triaza-5,8-dioxacycloheptadecane)zinc(II)** ( $[\text{Zn}(\text{OenNdienH}_4)(\text{NO}_3)_2]$ ). In a manner similar to the above, zinc(II) nitrate hexahydrate (0.33 g) yielded an off-white solid; yield 0.42 g. Anal. Calcd for  $\text{C}_{20}\text{H}_{27}\text{N}_3\text{O}_8\text{Zn}$ : C, 45.3; H, 5.1; N, 13.2; Zn, 12.3. Found: C, 45.4; H, 5.3; N, 13.1; Zn, 12.3.  $\Delta = 98 \text{ cm}^2 \text{ mol}^{-1}$  ( $\sim 10^{-3} \text{ M}$  in CH<sub>3</sub>OH, 25 °C).  $^{13}\text{C}$  NMR (DMSO- $d_6$ )  $\delta$  44.2, 45.1 (NHCH<sub>2</sub>CH<sub>2</sub>NH), 46.7 (ArCH<sub>2</sub>NH), 67.2 (OCH<sub>2</sub>), 113.1, 121.0, 125.9, 129.2, 131.0, 156.5 (Ar).

**Table III.** Selected Bond Lengths (Å) and Angles (Deg) in the Coordination Spheres of the Complexes<sup>a</sup>

	[Cd(OenN-dienH <sub>4</sub> )(NO <sub>3</sub> ) <sub>2</sub> ]	[Zn(OenN-dienH <sub>4</sub> )(NO <sub>3</sub> ) <sub>2</sub> ]	[Cd(OenN-ditnH <sub>4</sub> )(NO <sub>3</sub> ) <sub>2</sub> ]
Bond Lengths			
M-N1a	2.326 (3)	2.225 (5)	2.343 (6)
M-N1b	2.338 (3)	2.089 (5)	2.398 (6)
M-N1c	2.382 (3)	2.085 (5)	2.378 (6)
M-O1a	2.614 (3)	<i>b</i>	<i>b</i>
M-O1b	2.732 (3)	<i>b</i>	<i>b</i>
M-O1	2.318 (3) <sup>c</sup>	2.227 (5)	2.346 (5) <sup>c</sup>
M-O3		2.253 (5)	
M-O4	2.402 (3) <sup>c</sup>	2.179 (6) <sup>d</sup>	2.311 (6) <sup>c</sup>
Bond Angles			
N1a-M-N1b	139.8 (1)	99.7 (2)	161.1 (2)
N1a-M-N1c	75.5 (1)	81.9 (2)	89.9 (2)
N1b-M-N1c	76.2 (1)	86.1 (2)	78.5 (2)
N1a-M-O1a	77.4 (1)		
N1b-M-O1b	78.0 (1)		
O1a-M-O1b	64.2 (1)		
N1a-M-O1b	132.9 (1)		
N1b-M-O1a	141.2 (1)		
N1c-M-O1a	137.4 (1)		
N1c-M-O1b	151.6 (1)		
O1-M-N1a	121.9 (1)	101.1 (2)	94.8 (2)
O1-M-N1b	87.2 (1)	96.8 (2)	80.5 (2)
O1-M-N1c	92.5 (1)	175.4 (2)	126.2 (2)
O1-M-O1a	75.0 (1)		
O1-M-O1b	74.3 (1)		
O4-M-N1a	78.6 (1)	165.3 (2)	86.1 (2)
O4-M-N1b	95.9 (1)	94.2 (2)	110.6 (2)
O4-M-N1c	125.9 (1)	94.6 (2)	101.3 (2)
O4-M-O1a	78.9 (1)		
O4-M-O1b	68.6 (1)		
O1-M-O4	141.2 (1)	81.6 (2)	132.5 (2)
O1-M-O3		57.3 (2)	
O3-M-N1a		82.4 (2)	
O3-M-N1b		153.7 (2)	
O3-M-N1c		120.0 (2)	
O3-M-O4		87.1 (2)	

<sup>a</sup> Atom labels are given in Figure 2. <sup>b</sup> Intramolecular contact distances between metal and ether oxygens O1a and O1b are 4.05 and 4.44 Å in [Zn(OenNdienH<sub>4</sub>)(NO<sub>3</sub>)<sub>2</sub>] and 3.17 and 3.10 Å in [Cd(OenNditnH<sub>4</sub>)(NO<sub>3</sub>)<sub>2</sub>]. <sup>c</sup> Closest intramolecular contact distances (Å) between cadmium and other nitrate oxygen atoms fall outside conventional bond lengths; for example, in [Cd(OendienH<sub>4</sub>)(NO<sub>3</sub>)<sub>2</sub>], Cd...O2 = 3.14 and Cd...O5 = 3.04, and in [Cd(OenditnH<sub>4</sub>)(NO<sub>3</sub>)<sub>2</sub>], Cd...O3 = 2.90 and Cd...O5 = 2.96. <sup>d</sup> The closest intramolecular contact between zinc and other nitrate oxygens is to O5, 3.14 Å.

**(Dinitrato)(3,4,9,10-dibenzo-1,12,15-triaza-5,8-dioxacycloheptadecane)cadmium(II)** ([Cd(OenNdienH<sub>4</sub>)(NO<sub>3</sub>)<sub>2</sub>]). In a manner similar to the above, cadmium(II) nitrate tetrahydrate (0.34 g) yielded a white solid; yield 0.44 g. Anal. Calcd for C<sub>20</sub>H<sub>27</sub>N<sub>5</sub>O<sub>8</sub>Cd: C, 41.6; H, 4.7; N, 12.1. Found: C, 41.6; H, 4.9; N, 11.8.  $\Lambda = 95 \text{ S cm}^2 \text{ mol}^{-1}$  ( $\sim 10^{-3}$  M in CH<sub>3</sub>OH, 25 °C). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>)  $\delta$  46.5, 46.6 (NHCH<sub>2</sub>-CH<sub>2</sub>NH), 48.4 (ArCH<sub>2</sub>NH), 67.2 (OCH<sub>2</sub>), 112.6, 121.1, 125.4, 129.4, 131.4, 156.5 (Ar).

**(Nittrato) aqua(3,4,9,10-dibenzo-1,12,15-triaza-5,8-dioxacycloheptadecane)cadmium(II) perchlorate** ([Cd(OenNdienH<sub>4</sub>)(H<sub>2</sub>O)(NO<sub>3</sub>)ClO<sub>4</sub>]). In a manner similar to the above, a mixture of lithium perchlorate (0.36 g) and cadmium nitrate tetrahydrate (0.34 g) yielded an off-white solid; yield 0.42 g. Anal. Calcd for C<sub>20</sub>H<sub>29</sub>CdClN<sub>5</sub>O<sub>10</sub>: C, 37.9; H, 4.6; N, 8.9. Found: C, 38.0; H, 4.6; N, 8.5.  $\Lambda = 119 \text{ S cm}^2 \text{ mol}^{-1}$  ( $\sim 10^{-3}$  M in CH<sub>3</sub>OH, 25 °C).

**(Dinitrato)(3,4,9,10-dibenzo-1,12,16-triaza-5,8-dioxacyclooctadecane)cadmium(II)** ([Cd(OenNentnH<sub>4</sub>)(NO<sub>3</sub>)<sub>2</sub>]). OenNentnH<sub>4</sub> (0.35 g) in hot ethanol (10 mL) was added to a stirred hot solution of cadmium(II) nitrate tetrahydrate (0.34 g) in methanol (10 mL) to yield a white solid; yield 0.53 g. Anal. Calcd for C<sub>21</sub>H<sub>29</sub>CdN<sub>5</sub>O<sub>8</sub>: C, 42.6; H, 4.9; N, 11.8. Found: C, 42.6; H, 5.1; N, 11.5.  $\Lambda = 96 \text{ S cm}^2 \text{ mol}^{-1}$  ( $\sim 10^{-3}$  M in CH<sub>3</sub>OH, 25 °C). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>)  $\delta$  25.7 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 45.7, 47.5, 48.9, 49.6 (NHCH<sub>2</sub>CH<sub>2</sub>NH and NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH), 49.6, 50.0 (ArCH<sub>2</sub>NH), 67.5, 67.9 (OCH<sub>2</sub>), 112.9, 113.2, 120.9, 125.5, 126.1, 129.3, 129.5, 131.0, 131.7, 156.6, 156.7 (Ar).

**(Dinitrato)(3,4,9,10-dibenzo-1,12,16-triaza-5,8-dioxacyclononadecane)cadmium(II)** ([Cd(OenNditnH<sub>4</sub>)(NO<sub>3</sub>)<sub>2</sub>]). OenNditnH<sub>4</sub> (0.37 g) in hot ethanol (10 mL) was added to a stirred hot solution of cadmium(II) nitrate tetrahydrate (0.34 g) in ethanol (20 mL) to yield a white solid; yield 0.42 g. Anal. Calcd for C<sub>22</sub>H<sub>31</sub>CdN<sub>5</sub>O<sub>8</sub>: C, 43.6; H, 5.2; N, 11.6. Found: C, 43.5; H, 5.4; N, 11.4. <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>)  $\delta$  25.8 (CH<sub>2</sub>-

CH<sub>2</sub>CH<sub>2</sub>), 48.8, 49.2 (NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 49.8 (ArCH<sub>2</sub>NH), 66.7 (OC-H<sub>2</sub>), 114.9, 121.2, 128.3, 129.3, 131.3, 156.7 (Ar).

**(Dinitrato)(3,4,9,10-dibenzo-1,12,17-triaza-5,8-dioxacyclononadecane)cadmium(II)** ([Cd(OenNbnH<sub>4</sub>)(NO<sub>3</sub>)<sub>2</sub>]). By a similar procedure to the above, OenNbnH<sub>4</sub> (0.37 g) yielded a white solid; yield 0.40 g. Anal. Calcd for C<sub>22</sub>H<sub>31</sub>CdN<sub>5</sub>O<sub>8</sub>: C, 43.6; H, 5.2; N, 11.6. Found: C, 43.6; H, 5.3; N, 11.1.

## Results and Discussion

The present investigation has involved a series of integrated studies of the interaction of Zn(II) and Cd(II) with 1-7. Central to the study has been an investigation of the effect of systematic variation of ligand structure on stability patterns for the corresponding complexes of Zn(II) and Cd(II). In this context, ligands 1-7 can be considered to form part of a matrix of structural types in which variation in both the macrocyclic hole size and the degree of ligand substitution occurs.

**Synthesis and Characterization of Solid Complexes.** A selection of solid Zn(II) and Cd(II) complexes of macrocycles from O<sub>2</sub>N<sub>3</sub>-donor series was synthesized in order to provide well-characterized products for use in subsequent solution and X-ray diffraction studies. The complexes are mostly of type [M(mac)(NO<sub>3</sub>)<sub>2</sub>] or [M(mac)(ClO<sub>4</sub>)<sub>2</sub>] (where M = Zn and/or Cd and mac = 1-3 or 7).<sup>18</sup> These complexes are readily prepared by addition of the appropriate ligand to the corresponding metal nitrate or perchlorate in hot ethanol. Microanalytical data confirmed the 1:1 stoichiometry of the products in each case. In general, the infrared spectra of the above complexes in Nujol mulls indicated splitting of the diagnostic nitrate/perchlorate bands; this is consistent with coordination of one (or both) of these anions in the respective solid complexes. However, because of their general complexity, it was inappropriate to undertake a more detailed analysis of the respective spectra. Indeed, subsequent X-ray data for three of the complexes (see later) confirmed that simple infrared patterns would not be expected for the anion absorptions.

Where soluble, the complexes yielded conductance values that are indicative of 1:1 electrolytes in methanol (see Experimental Section). Thus in this weakly coordinating solvent, one of the anions remains coordinated. In view of the above evidence that the complex cations incorporate only one nitrate in solution, an attempt was made to isolate such a cation using perchlorate rather than nitrate as the counterion. Perchlorate was chosen because of its low coordinating ability coupled with its large size, which tends to make it a good precipitating anion. Accordingly, a synthesis was attempted in which the parent macrocycle 1 was added to Cd(II) in hot ethanol containing a mixture of nitrate and perchlorate anions. From the reaction solution a mixed-anion complex, formulated as [Cd(OenNdienH<sub>4</sub>)(H<sub>2</sub>O)(NO<sub>3</sub>)ClO<sub>4</sub>], was obtained. As for the previous dinitrate or perchlorate complexes, this species again behaved as a 1:1 electrolyte in methanol and its infrared spectrum was consistent with the above formulation. The successful isolation of this species provided additional evidence for the "persistent" coordination of one nitrate group in these complexes in solution.

**Stability Constant Determinations.** Potentiometric (pH) titrations were used to determine the protonation constants for 1-7 in 95% methanol [*I* = 0.1 M, (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NClO<sub>4</sub>] as well as stability constants for the corresponding complexes of Zn(II) and Cd(II). The values are summarized in Table IV. log *K*<sub>ML</sub> values were obtained in all cases and, for several systems, equilibria corresponding to coordination of the respective protonated (*K*<sub>MLH</sub>) ligands were also detected. As expected from charged considera-

(18) Analogous complexes of Zn(II) and Cd(II) with 4 and 6 were also isolated as white solids and characterized by spectroscopic (IR and NMR) means. Once again, conductance measurements confirmed that three of these species are 1:1 electrolytes in methanol (the fourth, the Zn(II) complex of 6, was not sufficiently soluble in methanol to obtain a conductance value). It is of interest that the tendency to form complexes exhibiting a 1:1 (macrocycle:metal) ratio is not restricted to the case where nitrate or perchlorate is the anion. Under similar conditions to those described in the Experimental Section Cd<sub>2</sub> reacts with 1 to yield the corresponding 1:1 adduct [Anal. Calcd for CdI<sub>2</sub>(C<sub>20</sub>H<sub>27</sub>N<sub>3</sub>O<sub>2</sub>): C, 33.9; H, 3.9; N, 5.9. Found: C, 33.9; H, 3.9; N, 5.9].

**Table IV.** Macrocyclic Ligand Protonation Constants and Stability Constants for the Corresponding Zn(II) and Cd(II) Complexes in 95% Methanol [ $I = 0.1 \text{ M}$ ,  $(\text{C}_2\text{H}_5)_4\text{NClO}_4$ ] at  $25^\circ\text{C}^a$ 

ligand (ring size)	ligand			complexes		
	$\log K_1$	$\log K_2$	$\log K_3$	$\log K(\text{ML}^{2+})$		$\log K(\text{MLH}^+)$
1. OenNdienH <sub>4</sub> (17)	9.69 (0.03)	8.45 (0.04)	2.01 (0.09)	Zn(II) 7.48 (0.03)	Cd(II) 8.66 (0.07)	3.72 (0.28)
2. OenNentnH <sub>4</sub> (18)	10.05 (0.08)	8.22 (0.09)	3.73 (0.08)	Zn(II) 7.13 (0.08)	Cd(II) 7.93 (0.03)	3.35 (0.22)
3. OenNditnH <sub>4</sub> (19)	10.33 (0.38)	8.36 (0.07)	5.59 (0.10)	Zn(II) 6.55 (0.01)	Cd(II) 5.33 (0.04)	3.61 (0.09)
4. OenNdipnH <sub>4</sub> (17)	9.47 (0.04)	8.25 (0.05)	1.57 (0.04)	Zn(II) 5.59 (0.11)	Cd(II) 7.94 (0.04)	3.12 (0.23)
5. OenNdien(CH <sub>3</sub> ) <sub>3</sub> H <sub>2</sub> (17)	10.05 (0.06)	7.57 (0.06)	1.94 (0.11)	Zn(II) 5.12 (0.02)	Cd(II) 6.09 (0.08)	
6. OenNditn(CH <sub>3</sub> )H <sub>4</sub> (19)	10.22 (0.11)	8.76 (0.12)	4.72 (0.12)	Zn(II) 5.89 (0.04)	Cd(II) 4.68 (0.03)	1.91 (0.30)
7. OenNenbnH <sub>4</sub> (19)	10.24 (0.03)	7.84 (0.05)	4.42 (0.07)	Zn(II) 6.04 (0.09)	Cd(II) 4.95 (0.03)	2.69 (0.15)

<sup>a</sup>All values are the mean (with standard deviation) of at least three and up to nine determinations.

tions, the  $\log K_{\text{MLH}}$  values for these latter complexes are substantially lower than the corresponding  $\log K_{\text{ML}}$  values.

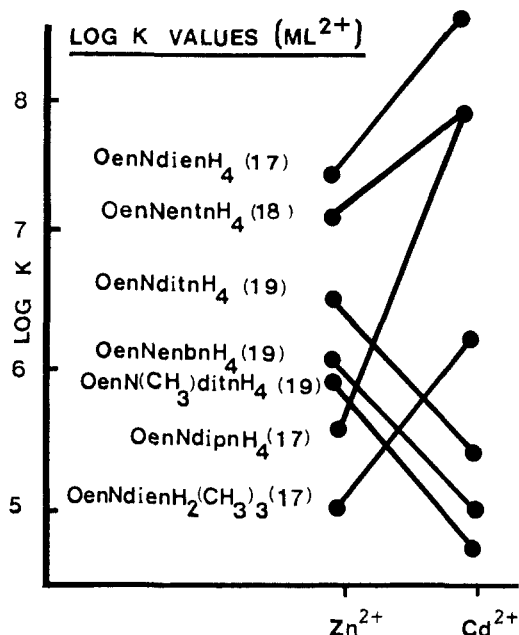
It is instructive to compare the  $\log K_{\text{ML}}$  values for the Zn(II) and Cd(II) complexes of the unsubstituted 17- to 19-membered macrocycles 1–3. For Zn(II), there is a gradual decrease in the respective constants as the ring size increases from 17- to 19-membered. Such a (regular) decrease is in accordance with that expected as less stable 6-membered chelate rings are progressively substituted for 5-membered rings along this series of complexes.

The behavior of the above ligand series toward Cd(II) is similar to that just discussed for Zn(II) for the first two members of the series. That is, there is a small drop in the  $\log K_{\text{ML}}$  value ( $\Delta \log K = 0.73$ ) on passing from the complex of the 17-membered ring 1 to that of the 18-membered ring 2. Once again, this very likely reflects the presence of the additional 6-membered chelate ring in the complex of 2 relative to that of 1. Moreover, the closeness of the stability values is in keeping with both these Cd(II) complexes having similar structures in solution. However, for the Cd(II) complex of the 19-membered ligand 3, there is a dislocation in the above  $\log K$  trend. That is, the Cd(II) species is considerably less stable than expected from the previous result—the  $K$  value is  $10^{2.6}$  lower than that of the corresponding 18-membered-ring cadmium complex and (unlike the 17- and 18-membered-ring species) the 19-membered-ring complex is now less stable than the corresponding Zn(II) species. The latter is the “natural” stability order found for these metals with polyamine ligands such as ethylenediamine or diethylenetriamine.<sup>19</sup> The data thus suggest that the Zn(II) and Cd(II) complexes of 3 have related solution structures in contrast to the corresponding complexes of 1 and 2.

The relative stabilities of the respective Zn(II) and Cd(II) complexes are illustrated in Figure 1. This figure also gives a comparison of the  $\log K$  values for the corresponding complexes of 4–7. Clearly, in all cases the 17- and 18-membered rings yield species for which the relative stability is  $\text{Cd(II)} > \text{Zn(II)}$  whereas, for the three 19-membered rings, the reverse order obtains. Thus, the relative stability of corresponding Zn(II) and Cd(II) complexes appears to be largely a function of macrocyclic hole size for these ligand systems.

As discussed above, the  $\log K$  evidence is in keeping with a structural dislocation having occurred along the Cd(II) series on passing from the 18- to the 19-membered ring with no similar dislocation being apparent in the corresponding Zn(II) series. In an attempt to investigate the above behavior further, NMR studies involving both the Zn(II) and Cd(II) systems were undertaken.

**NMR Studies.** Because of the limited solubility of the complexes in solvents such as methanol- $d_4$ , all NMR studies were performed with DMSO- $d_6$  as solvent. The proton-decoupled <sup>13</sup>C NMR spectra of a selection of the Zn(II) and Cd(II) complexes (see



**Figure 1.** Relative stabilities of the Zn(II) and Cd(II) complexes of the 17- to 19-membered rings 1–7 illustrating the dislocation that occurs along the Cd(II) complex series between the 18- and 19-membered-ring complexes (the number in parentheses after each ligand abbreviation corresponds to the macrocyclic ring size).  $\log K$  values were determined in 95% methanol with  $I = 0.1 \text{ M}$ ;  $(\text{C}_2\text{H}_5)_4\text{NClO}_4$ .

Experimental Section) gave no evidence for the presence of more than one species in the respective solutions. For each, the overall spectral pattern resembled that of the corresponding free ligand, with the expected (small) variation in the respective chemical shifts being evident. In contrast, several of the <sup>1</sup>H spectra of these complexes were more complex than those of the corresponding free ligands. For example, line broadening was observed for some or all of the aliphatic proton resonances in particular complexes (in general, the resonances for aromatic protons remained sharp), and in some complexes there was an increased number of peaks in evidence. Although <sup>1</sup>H <sup>13</sup>Cd coupling could contribute to the complexity of the Cd(II) spectra, this is clearly not a major effect since similar patterns also occurred in the spectra of individual Zn(II) complexes. The observed behavior apparently reflects the presence of chemical exchange processes (involving the coordinated ligands) which are not rapid on the NMR time scale.

It is instructive to compare the chemical shifts of the singlet corresponding to the ether methylenes in OenNdienH<sub>4</sub> (1) before and after complex formation. This signal occurs at 4.35 ppm both in the Zn(II) complex and in the free ligand whereas for the Cd(II) complex, an induced shift (to lower field) of 0.12 ppm is observed on complex formation.<sup>20</sup> Such behavior is consistent with the

(19) Smith, R. M.; Martell, A. E. *Critical Stability Constants, Amines*; Plenum: New York, 1975; Vol. 2.

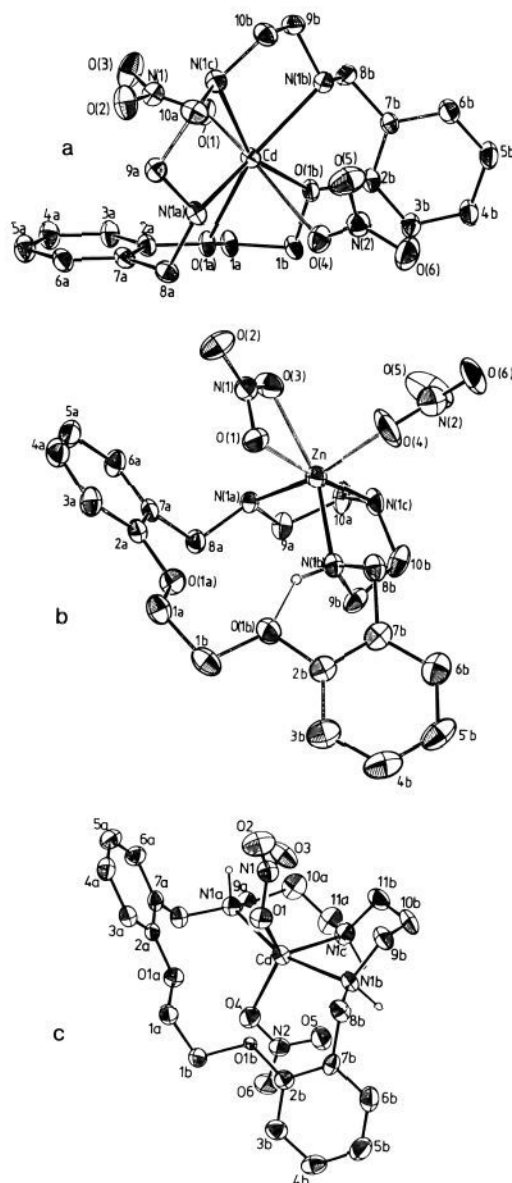
noncoordination of the ether groups in the Zn(II) complex but with their coordination in the Cd(II) analogue.

Caution needs to be exercised in extrapolating the above results to the stability studies carried out in 95% methanol. Nevertheless, the observation suggests a means for rationalizing the higher log *K* value observed for the Cd(II) complex relative to that of its Zn(II) analogue.

Because of both line broadening and overlap of the corresponding resonances in the analogous complexes of OenNentnH<sub>4</sub> (2), it was not possible to undertake similar comparisons for this (unsymmetric) system. However, comparisons were possible for the next largest ring system, OenNditnH<sub>4</sub> (3). For this ligand system, the presence of either Zn(II) or Cd(II) gave induced shifts of the above singlet (to lower field) of only 0.03 ppm in each case.<sup>20</sup> The very small shifts suggest that no significant coordination of the ether donors occurs in either complex. This observation parallels the inference from the log *K* studies that the Zn(II) and Cd(II) complexes of this ligand probably have related solution structures (in contrast to the corresponding complexes of 1 and 2).

**X-ray Diffraction Studies.** As just discussed, an important consideration in interpreting the stability variations between the complexes of the present series of O<sub>2</sub>N<sub>3</sub> ligands is the extent to which the ether oxygen donors interact with the metal ion. The X-ray structure of [Cd(OenNdienH<sub>4</sub>)(NO<sub>3</sub>)<sub>2</sub>] shows that this complex has a very distorted pentagonal-bipyramidal coordination geometry in the solid state with the Cd(II) ion lying in the cavity of the five "equatorial" donor atoms of the 17-membered macrocycle (Figure 2a); nitrate groups occupy the "axial" sites and are best described as monodentate (see Table III, footnote c) with Cd–O1 and Cd–O4 lengths falling within the range (2.31–2.44 Å) previously observed for monodentate nitrate complexes of six-coordinate Cd(II).<sup>21,22</sup> The two Cd(II) to ether oxygen bonds appear somewhat elongated [at 2.614 (3) and 2.732 (3) Å] although they fall in the range of 2.36–2.84 Å reported for similar bonds in other Cd(II) complexes.<sup>23,24</sup>

In contrast, in [Zn(OenNdienH<sub>4</sub>)(NO<sub>3</sub>)<sub>2</sub>] the macrocyclic ligand clearly adopts an arrangement that removes the ether donors from the coordination sphere.<sup>25</sup> The three nitrogen donors of the macrocycle occupy an approximately facial arrangement around the zinc, with its overall coordination number being 6; the remaining coordination positions are filled by a monodentate and a bidentate nitrate ligand (Figure 2b). The bidentate nitrate group is bonded relatively symmetrically to the zinc atom (Table III) with bond lengths [Zn–O1 = 2.227 (5) and Zn–O3 = 2.253 (6)



**Figure 2.** Molecular structures of (a) [Cd(OenNdienH<sub>4</sub>)(NO<sub>3</sub>)<sub>2</sub>], (b) [Zn(OenNdienH<sub>4</sub>)(NO<sub>3</sub>)<sub>2</sub>], and (c) [Cd(OenNditnH<sub>4</sub>)(NO<sub>3</sub>)<sub>2</sub>] illustrating the respective 7, 6, and 5 coordination numbers of these complexes.

Å] that fall within the range (2.03–2.66 Å) observed for other (usually less symmetrical) bidentate nitrate complexes of Zn(II).<sup>26</sup> The monodentate nitrate shows a longer bond to zinc, Zn–O4 = 2.179 (6) Å, than those observed (2.04–2.05 Å) in other monodentate complexes, but in these other complexes the zinc has a lower coordination number.<sup>27</sup>

In the corresponding 19-membered-ring cadmium complex the ether donors are also outside bonding distance to the metal although it appears that a very weak interaction with the metal (Cd–O1a = 3.169 and Cd–O1b = 3.098 Å) could still be present in this case.<sup>28</sup> The complex contains an approximately planar

(20) Similar studies involving an investigation of the "induced" shifts in the <sup>13</sup>C NMR spectra resulted in no systematic pattern being evident. This result is similar to that observed by us on studying the complexation of Zn(II) and Cd(II) with the analogous O<sub>2</sub>N<sub>3</sub>-donor macrocycles in DMSO-d<sub>6</sub>. Relative to the <sup>1</sup>H NMR spectra, the <sup>13</sup>C shifts tend to be more influenced by the conformational changes of the carbon backbone on coordination to Zn(II) or Cd(II) than by the small electronic effects associated with attachment of the present diamagnetic metal ions (see: Lindoy, L. F.; Lip, H. C.; Rea, J. H.; Smith, R. J.; Henrick, K.; McPartlin, M.; Tasker, P. A. *Inorg. Chem.* **1980**, *19*, 3360–3365 and references therein).

(21) Louer, M.; Louer, D.; Grandjean, D. *J. Solid State Chem.* **1976**, *17*, 231–237. Turner, R. W.; Rodesiler, P. F.; Amma, E. L. *Inorg. Chim. Acta* **1982**, *66*, L13. Viossat, B.; Khodadad, P.; Rodier, N. *Acta Crystallogr., Sect. B* **1982**, *38*, 3075.

(22) Cadmium–oxygen lengths in bidentate nitrate complexes (which are usually unsymmetrical) are generally longer and fall in a wider range (2.29–2.83 Å). See: Swaminathan, S.; Natarajan, S. *Curr. Sci.* **1967**, *36*, 513. Cameron, A. F.; Taylor, D. W.; Nuttall, R. H. *J. Chem. Soc., Dalton Trans.* **1972**, 1608–1611. Griffith, E. A. H.; Charles, N. G.; Rodesiler, P. F.; Amma, E. L. *Acta Crystallogr., Sect. C* **1983**, *39*, 331–333. Viossat, B.; Khodadad, P.; Rodier, N. *Ibid.* **1984**, *40*, 24–28. Alcock, N. W.; Curzon, E. H.; Moore, P. J. *J. Chem. Soc., Dalton Trans.* **1984**, 2813–2820.

(23) Iwamoto, R.; Wakano, H. *J. Am. Chem. Soc.* **1976**, *98*, 3764. Boman, C. E. *Acta Crystallogr., Sect. B* **1977**, *33*, 1529. Malmsten, L.-A. *Acta Crystallogr., Sect. B* **1979**, *35*, 1702.

(24) These bond lengths show a very considerable dependence on such factors as the coordination number of the cadmium and the nature of the other donor atoms present, the longest bonds (2.75–2.84 Å) being observed in an eight-coordinate complex, CdI<sub>2</sub>(1,10-diaza-18-crown-6).

(25) Hole-size considerations suggest that a small ion such as Zn(II) will have difficulty coordinating to all donor sites of the respective macrocycles if the latter adopt planar (nonfolded) conformations.

(26) Cameron, A. F.; Taylor, D. W.; Nuttall, R. H. *J. Chem. Soc., Dalton Trans.* **1972**, 1603–1608. Brassy, C.; Michaud, M.-C.; Delettre, J.; Mornon, J.-P. *Acta Crystallogr., Sect. B* **1974**, *30*, 2848–2852. Bellitto, C.; Gastaldi, L.; Tomlinson, A. A. G. *J. Chem. Soc., Dalton Trans.* **1976**, 989–992. White, A. H.; Willis, A. C. *J. Chem. Soc., Dalton Trans.* **1977**, 1377–1381. Laidoud, A.; Kheddar, N.; Briano, M. C. *Acta Crystallogr., Sect. B* **1978**, *34*, 782–788. Bernarducci, E. E.; Bharadwaj, P. K.; Lalancette, R. A.; Krogh-Jespersen, K.; Potenza, J. A.; Schugar, H. J. *Inorg. Chem.* **1983**, *22*, 3911–3920.

(27) Cameron, A. F.; Taylor, D. W.; Nuttall, R. H. *J. Chem. Soc. A* **1971**, 3402–3405. Brown, C. J.; Lewis, J. F. P. *Acta Crystallogr., Sect. C* **1984**, *40*, 368–370.

CdN<sub>3</sub> unit with a "ruffled" O<sub>2</sub>N<sub>3</sub> arrangement (Figure 2c). Overall, the coordination number is 5, with two monodentate nitrates, at normal bond lengths, completing the coordination shell. As expected, these nitrate groups are displaced more to the side of the complex away from the N<sub>3</sub> donor set [O1-Cd-O4 = 132.5 (2)°] than in the corresponding complex of the 17-membered ring [O1-Cd-O4 = 141.2 (1)°], in which electron density from the coordinated ether oxygens is present on this side.<sup>29</sup>

Although applying to the solid state, the X-ray structural data for each complex nevertheless parallel in all essential detail the

(28) However, a molecular mechanics investigation failed to reveal any evidence of significant bonding interaction between the cadmium and the ether oxygens. The starting coordinates for the calculations were those obtained from the X-ray diffraction investigation. No bonds were defined between the above-mentioned atoms, and the structure was minimized with use of a version of the Allinger force field (Allinger, N. L. *Adv. Phys. Org. Chem.* 1976, 13, 1) modified to account for the presence of the central cadmium atom (see below). The minimized structure was found to be very similar to that of the starting structure. In particular, the conformation of the flexible C-O-C-H<sub>2</sub>-CH<sub>2</sub>-O-C backbone of the macrocycle remained quite close to that found in the X-ray diffraction study—with individual bond angles in this part of the molecule all falling within 2.5° of the corresponding X-ray values. In contrast, the presence of significant Cd-ether bonding interactions (which would not be modeled by the molecular mechanics procedure used for this complex) might be expected to lead to a marked (apparent) conformational difference in the backbone observed in the X-ray study compared to that obtained from the molecular mechanics study. It should be noted that a set of force field parameters for those portions of the complex involving the cadmium atom were initially obtained by a trial and error process involving the corresponding 17-membered-ring complex, [Cd(OenNdienH<sub>4</sub>)(NO<sub>3</sub>)<sub>2</sub>]. The parameters thus defined were then used in the calculations for [Cd(OenNdienH<sub>4</sub>)(NO<sub>3</sub>)<sub>2</sub>] without alteration. While there are limitations in defining force field parameters in this manner (ideally, the force field parameter set should be derived from a range of similar structures) the procedure is nevertheless adequate for the present purpose.

(29) The mean of the O<sub>1</sub>-Cd-O<sub>1a</sub>, O<sub>1</sub>-Cd-O<sub>1b</sub>, O<sub>4</sub>-Cd-O<sub>1a</sub>, and O<sub>4</sub>-Cd-O<sub>1b</sub> angles for [Cd(OenNdienH<sub>4</sub>)(NO<sub>3</sub>)<sub>2</sub>] is 74.2° while for [Cd(OenNdienH<sub>4</sub>)(NO<sub>3</sub>)<sub>2</sub>] it is 69.1°.

proposed coordination behavior of the respective macrocycles in solution. Namely, the coordination or otherwise of the ether functions in the solid Zn(II) and Cd(II) complexes occurs in a directly analogous manner to their proposed interaction with these ions in solution.

### Concluding Remarks

Dislocation behavior of the type just discussed has been little studied in the past even though it provides a potentially powerful mechanism for achieving metal-ion discrimination within suitable systems. Apart from the implications for the design of new metal-ion specific reagents, an awareness of this mechanism will also likely contribute to a more general understanding of metal-ion recognition involving a range of other organic (including biological) substrates.

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**Supplementary Material Available:** Crystal data, details of data collection and refinement, anisotropic thermal parameters, complete lists of bond lengths and angles, and hydrogen atom coordinates (27 pages); structure factors for all three structures (49 pages). Ordering information is given on any current masthead page.

## Chemistry of Oxaziridines. 11.<sup>1</sup> (Camphorylsulfonyl)oxaziridine, Synthesis and Properties

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**Abstract:** The synthesis, reactions, properties, and crystal structure of (+)- and (-)-(camphorylsulfonyl)oxaziridines **2** are described. These optically active oxaziridines are prepared from (+)- and (-)-camphorsulfonic acid in 77% overall yield. In contrast to other optically active sulfonimines, which give on oxidation mixtures of oxaziridine diastereoisomers, oxidation of camphorsulfonimine **5** with Oxone produces only a single isomer in >90% yield. For the asymmetric oxidation of prochiral sulfides by **2**, the enantioselectivities are lower than those reported for optically active *N*-sulfamyloxaziridine **1** (5-73 vs 35-60% ee) and are discussed in terms of different active site structures for the two oxaziridines. As observed with other optically active *N*-sulfonyloxaziridines, the configuration of the oxaziridine three-membered ring in **2** controls the stereochemistry of the product, with (+)-**2** and (-)-**2** giving the opposite senses of asymmetric induction, respectively. While other *N*-sulfonyloxaziridines readily oxidize amines and epoxidize alkenes, **2** does not, even on heating. An improved method for the synthesis of Oppolzers' sultam chiral auxiliary **6** is described.

The development of reagents for the *reagent-controlled* asymmetric oxidation of prochiral alkenes, sulfides, and enolates with high enantioselectivities (>95% ee) is an important synthetic goal. To date relatively few reagents, with general applicability, have been developed. Homochiral peracids are ineffectual, affording

only low levels of asymmetric induction for the oxidation of sulfides and alkenes (0-9% ee).<sup>2</sup> Chiral organometallic peroxides are much more efficient asymmetric oxidizing reagents,<sup>3</sup> with the best

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