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Ni^{II} and Zn^{II} complexes of the hexadentate macrocyclic ligand *cis*-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine

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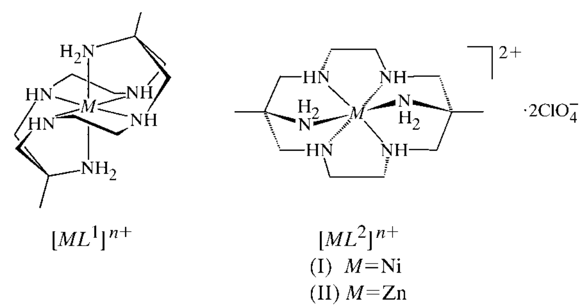
The title pendent-arm macrocyclic hexaamine ligand binds stereospecifically in a hexadentate manner, and we report here its isomorphous Ni^{II} and Zn^{II} complexes (both as perchlorate salts), namely (*cis*-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine-κ^6N)nickel(II) diperchlorate, [Ni($C_{12}H_{30}N_6$)](ClO_4)$_2$, and (*cis*-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine-κ^6N)zinc(II) diperchlorate, [Zn($C_{12}H_{30}N_6$)](ClO_4)$_2$. Distortion of the N—*M*—N valence angles from their ideal octahedral values becomes more pronounced with increasing metal-ion size and the present results are compared with other structures of this ligand.

Comment

The coordination chemistry of the isomeric pendent-arm macrocycles *trans*- and *cis*-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine (L^1 and L^2, respectively) has revealed a number of interesting variations in the structural and physical properties of their complexes. Complexes of the hexadentate-coordinated *trans* isomer (Curtis *et al.*, 1987; Bernhardt *et al.*, 1989, 1990, 1991; Borzel *et al.*, 1998) are more common than the corresponding *cis* complexes (Bernhardt *et al.*, 1992, 1993, 1997; Lye *et al.*, 1994). It is an interesting feature that L^1 and L^2 can only bind in one configuration when coordinated as hexadentates, so the structure of the organic ligand determines the isomerism of the resulting complexes.

The hexadentate *trans* isomers coordinate such that the metal is coplanar with the four secondary amines, and the pendent amines bind in *trans* coordination sites. By contrast, in the corresponding *cis* isomers, the macrocycle adopts a folded conformation and the pendent amines coordinate in *cis* sites. Molecular-mechanics calculations (Bernhardt & Comba, 1991) predicted that the *cis* isomer L^2, bound as a hexadentate, would be able to complex both small and large metal ions, whereas the hexadentate-coordinated *trans* isomer could only accommodate metals up to a certain size, until one or both axial *M*—N bonds were broken as a consequence of strain in the complex. These computational results have been borne out by subsequent experimental data.

The two complexes [NiL^2](ClO_4)$_2$, (I), and [ZnL^2](ClO_4)$_2$, (II), are isomorphous and the absolute configuration was determined in each case. The Ni^{II} and Zn^{II} crystals studied here, both grown from racemic solutions, were found to be enantiomorphs. Views of the two complex cations are shown in Figs. 1 and 2. The folded conformation of the macrocycle is evident, with the coordinated four secondary amines having the same absolute configuration *i.e. RRRR* (*SSSS*). Each complex cation has (non-crystallographic) C_2 symmetry; the principal axis bisects the N5—*M*—N6 angle, and the *M*—N bond lengths separate into three distinct pairs (Tables 1 and 3). Both macrocyclic five-membered chelate rings adopt the same conformation ($\delta\delta$ or $\lambda\lambda$), where the C—C bond in each ring is oblique to the C_2 axis. This conformation was predicted (Bernhardt & Comba, 1991) to be dominant for complexes containing both small and large metal ions, and indeed no other conformation of a hexadentate-coordinated complex of L^2 has been identified. Hydrogen bonding between perchlorate-O atoms and most amine-H atoms is found (Tables 2 and 4). These hydrogen bonds result in chains comprising cations linked by perchlorate anions extending along the *b* axis.



The *M*—N bond lengths in both structures are typical of hexaamine complexes of Ni^{II} and Zn^{II}, and are significantly longer than those observed in the respective *trans* isomers: [NiL^1](ClO_4)$_2$ 2.07$_{sec}$ and 2.13$_{prim}$ Å (Curtis *et al.*, 1987); [ZnL^1](ClO_4)$_2$ 2.10$_{sec}$ and 2.21$_{prim}$ Å (Bernhardt *et al.*, 1991), where subscripts sec and prim indicate secondary and primary N atoms, respectively. This is a feature that has now been observed in the *trans* and *cis* isomers of a number of complexes in this series (Co^{III}, Cr^{III}, Ni^{II} and Zn^{II}), where the *trans* isomers invariably exhibit unusually short *M*—N bond lengths in contrast to the corresponding coordinate bond lengths in the *cis* isomers, which are normal. Molecular-

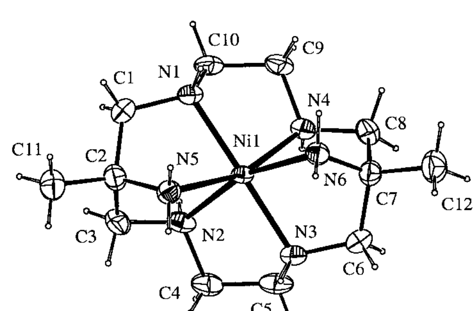


Figure 1
View of (I) showing 30% probability ellipsoids.

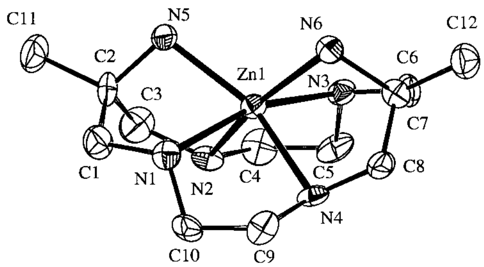


Figure 2
View of (II) showing 30% probability ellipsoids (H atoms omitted).

mechanics calculations predicted this disparity some time ago (Bernhardt & Comba, 1991).

The valence angles involving the metal centres (Tables 1 and 3) indicate that the larger Zn^{II} ion exhibits a greater distortion from octahedral geometry than its Ni^{II} analogue. This again is a general trend across the series of known structures of L^2 complexes ranging from the smallest (Co^{III}; Bernhardt *et al.*, 1997) to the largest (Pb^{II}; Lye *et al.*, 1994). There are a number of structural indicators of this distortion. It may be viewed as a pseudo-trigonal twist of the N1–N2–N5 and N4–N3–N6 octahedral faces, by analogy with tris-bidentate complexes. This definition is somewhat limited in this case as there is no threefold axis in complexes of L^2. A more reliable indicator of the distortion present in these complexes is the N5—*M*—N6 valence angle, which increases with the *M*—N bond length, and this is illustrated in Fig. 3. The Cd^{II} (Bernhardt *et al.*, 1992) and Pb^{II} (Lye *et al.*, 1994) structures exhibit somewhat exaggerated bite angles caused by (or resulting in) coordination of perchlorate anions, and their structures approximate distorted square-antiprismatic geometries (N_6O_2). It is difficult to say whether the presence of these weakly bound ions (M—O > 3.0 Å) in the Cd^{II}/Pb^{II} structures significantly perturb the valence angles involving the coordinated macrocycle or, conversely, whether these distortions are driven by the macrocycles, which prize open the N5—*M*—N6 angles thus making room for incoming ligands.

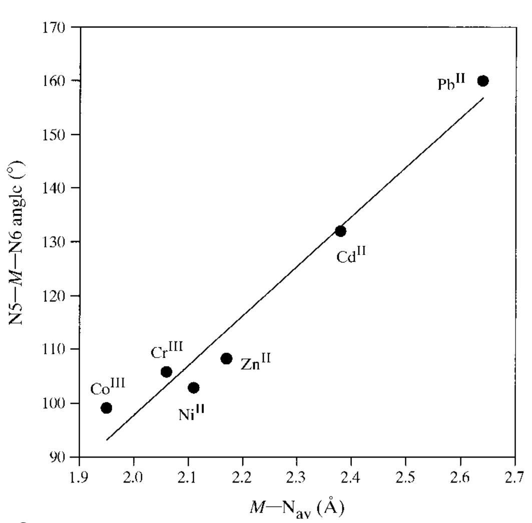


Figure 3
Plot of observed N5—*M*—N6 angle (°) as a function of average *M*—N bond length (Å) for hexadentate-coordinated complexes of L^2.

The observed distortions from octahedral geometry with increasing *M*—N bond length were predicted by molecular-mechanics calculations. However, electronic contributions from transition metal ions will oppose distortions away from octahedral geometry (ligand-field stabilization energy), and neglecting this effect can lead to an overestimation of the observed distortion (Bernhardt & Comba, 1993). That is, the geometries of the d^{10} Zn^{II} and Cd^{II} complexes represent true ligand-dictated distortions, whereas the Co^{III}, Cr^{III} and Ni^{II} structures reflect a balance between ligand-directed steric and metal-based electronic effects.

Experimental

The title complexes were both synthesized readily by mixing equimolar amounts of the metal ion and ligand hydrochloride salt (L^2·6HCl) in water adjusted to pH 7 with NaOH solution. Both compounds were precipitated by addition of excess $NaClO_4$. Crystals of each complex were obtained by slow evaporation of their aqueous solutions.

Compound (I)

Crystal data

$[Ni(C_{12}H_{30}N_6)](ClO_4)_2$
M_r = 516.03
Monoclinic, $P2_1$
a = 9.198 (4) Å
b = 12.771 (1) Å
c = 9.880 (5) Å
β = 113.09 (2)°
V = 1067.6 (7) Å^3
Z = 2
D_x = 1.605 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 10–14°
μ = 1.210 mm^{-1}
T = 295 (2) K
Prism, purple
0.50 × 0.50 × 0.50 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.404, T_{max} = 0.546
2097 measured reflections
1971 independent reflections
1892 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 24.98°
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 15$
$l = -11 \rightarrow 10$
3 standard reflections
frequency: 120 min
intensity decay: <5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.117
S = 1.084
1971 reflections
278 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0981P)^2 + 0.2008P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.57 e Å^{-3}
$\Delta\rho_{min}$ = −0.83 e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = 0.03 (3)

Table 1
Selected geometric parameters (Å, °) for (I).

Ni—N1	2.075 (5)	Ni—N6	2.124 (5)
Ni—N3	2.077 (5)	Ni—N4	2.126 (5)
Ni—N5	2.096 (5)	Ni—N2	2.147 (5)
N1—Ni—N3	171.0 (2)	N5—Ni—N4	161.63 (18)
N1—Ni—N5	78.39 (19)	N6—Ni—N4	79.5 (2)
N3—Ni—N5	107.0 (2)	N1—Ni—N2	91.0 (2)
N1—Ni—N6	106.6 (2)	N3—Ni—N2	82.9 (2)
N3—Ni—N6	79.5 (2)	N5—Ni—N2	81.3 (2)
N5—Ni—N6	102.9 (2)	N6—Ni—N2	162.4 (2)
N1—Ni—N4	83.47 (19)	N4—Ni—N2	101.98 (19)
N3—Ni—N4	91.33 (19)		

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1C^{i}	0.91	2.41	3.192 (10)	144
N2—H2···O1D	0.91	2.49	3.283 (10)	146
N3—H3···O2B^{ii}	0.91	2.14	3.039 (8)	167
N3—H3···O2B'^{ii}	0.91	2.08	2.917 (11)	152
N4—H4···O2A	0.91	2.38	3.213 (7)	151
N4—H4···O2D	0.91	2.57	3.271 (9)	135
N5—H5A···O2D^{ii}	0.90	2.56	3.056 (8)	116
N5—H5A···O2D'^{ii}	0.90	2.09	2.819 (10)	137
N5—H5B···O1C^{i}	0.90	2.62	3.389 (13)	144
N6—H6A···O2B^{iii}	0.90	2.31	3.120 (8)	150
N6—H6A···O2B'^{iii}	0.90	2.64	3.53 (3)	168
N6—H6B···O2C^{ii}	0.90	2.50	3.341 (10)	156
N6—H6B···O2C'^{ii}	0.90	2.49	3.382 (13)	170

Symmetry codes: (i) $1-x, \frac{1}{2}+y, 1-z$; (ii) $1+x, y, z$; (iii) $-x, \frac{1}{2}+y, -z$.

Compound (II)

Crystal data

$[Zn(C_{12}H_{30}N_6)](ClO_4)_2$	$D_x = 1.611$ Mg m^{-3}
$M_r = 522.69$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 25 reflections
$a = 9.075$ (1) Å	$\theta = 10$–14°
$b = 12.891$ (1) Å	$\mu = 1.439$ mm^{-1}
$c = 9.963$ (3) Å	$T = 295$ (2) K
$\beta = 112.438$ (9)°	Prism, colourless
$V = 1077.3$ (4) Å^3	0.30 × 0.13 × 0.10 mm
$Z = 2$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.073$
ω–2θ scans	$\theta_{max} = 24.97°$
Absorption correction: ψ scan (North *et al.*, 1968)	$h = 0 \rightarrow 10$
$T_{min} = 0.779$, $T_{max} = 0.866$	$k = 0 \rightarrow 15$
2115 measured reflections	$l = -11 \rightarrow 10$
1987 independent reflections	3 standard reflections
916 reflections with $I > 2\sigma(I)$	frequency: 120 min
	intensity decay: <5%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0782P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.060$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.175$	$\Delta\rho_{max} = 0.72$ e Å^{-3}
$S = 0.987$	$\Delta\rho_{min} = -0.66$ e Å^{-3}
1987 reflections	Absolute structure: Flack (1983)
258 parameters	Flack parameter = −0.04 (5)
H-atom parameters constrained	

Table 3
Selected geometric parameters (Å, °) for (II).

Zn1—N6	2.128 (14)	Zn1—N1	2.170 (13)
Zn1—N5	2.134 (12)	Zn1—N4	2.219 (13)
Zn1—N3	2.141 (15)	Zn1—N2	2.255 (12)
N6—Zn1—N5	108.9 (6)	N3—Zn1—N4	89.7 (5)
N6—Zn1—N3	77.4 (5)	N1—Zn1—N4	79.7 (5)
N5—Zn1—N3	113.7 (6)	N6—Zn1—N2	156.5 (5)
N6—Zn1—N1	114.7 (6)	N5—Zn1—N2	80.0 (6)
N5—Zn1—N1	76.9 (5)	N3—Zn1—N2	79.2 (5)
N3—Zn1—N1	161.5 (5)	N1—Zn1—N2	88.3 (5)
N6—Zn1—N4	78.2 (6)	N4—Zn1—N2	102.5 (5)
N5—Zn1—N4	156.4 (5)		

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1A^{i}	0.91	2.54	3.33 (2)	146
N2—H2···O1C	0.91	2.57	3.39 (2)	150
N3—H3···O2B^{ii}	0.91	2.28	3.14 (2)	158
N3—H3···O2C'^{ii}	0.91	1.99	2.88 (2)	166
N4—H4···O2A	0.91	2.48	3.300 (16)	151
N4—H4···O2D	0.91	2.48	3.165 (18)	133
N5—H5B···O2D^{ii}	0.90	2.61	3.12 (2)	116
N5—H5B···O2D'^{ii}	0.90	2.18	2.853 (19)	132
N6—H6A···O2C^{ii}	0.90	2.37	3.22 (2)	158
N6—H6A···O2B'^{ii}	0.90	2.29	3.18 (2)	169
N6—H6B···O2B^{iii}	0.90	2.41	3.201 (19)	147
N6—H6B···O2C'^{iii}	0.90	2.42	3.30 (3)	165

Symmetry codes: (i) $1-x, y-\frac{1}{2}, 1-z$; (ii) $1+x, y, z$; (iii) $-x, y-\frac{1}{2}, -z$.

In both structures, rotational disorder in one of the perchlorate anions (about the Cl2—O2A bond) was modelled by refining atoms O2B/O2B', O2C/O2C' and O2D/O2D' with complementary occupancies and applying tetrahedral restraints to the O atoms of each contributor.

For both compounds, data collection: *CAD*-4 *Manual* (Enraf–Nonius, 1988); cell refinement: *SET*4 in *CAD*-4 *Manual*; data reduction: *Xtal*3.2 (Hall *et al.*, 1992); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1588). Services for accessing these data are described at the back of the journal.

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