electronic studies of several quadruply bonded complexes (ref 46). The computer program used to perform the Fourier transform analyses was written and developed by Mr. Glen E. Kellogg, Chemistry Department, University of Arizona. We also acknowledge the Department of Energy, Contract DE-ACO2-80ER10746, and the University of Arizona for partial support of this work. D.L.L. is an Alfred P. Sloan Fellow.

Registry No. $Mo_2(O_2CCH_3)_4$, 14221-06-8; $[Mo_2(O_2CCH_3)_4]^+$, 88326-46-9; Mo, 7439-98-7.

Specification of the Bonding Cavities Available in Metal-Binding Sites: A Comparative Study of a Series of Quadridentate Macrocyclic Ligands

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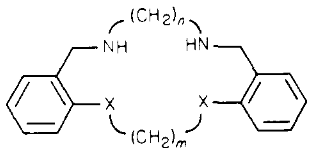
Abstract: A method for specifying the size of bonding cavities available to metal ions in metal-binding sites has been applied to a series of seven nickel(II) complexes of dibenzo-substituted quadridentate macrocycles and two free ligands. The procedure allows the goodness-of-fit of a metal ion for the binding site to be estimated by correcting the "hole size" of the donor set for the radii of the donor atoms. For the series of macrocyclic ligands considered, the resulting "bonding cavity" radii are shown to increase by ~0.05 Å for each additional atom in the inner great ring. Changing the donor atom type is found to have a relatively small influence on bonding cavity radii. Data from three new X-ray structure determinations of 14-membered macrocyclic species are considered in the survey; the structures determined are the nickel chloride complex of 3,4:9,10-dibenzo-1,12-diaza-5,8-dioxacyclotetradecane [Ni(O-en-N-enH_4)Cl_2], the nickel thiocyanate complex of 3,4:9,10-dibenzo-1,5,8,12-tetraazacyclotetradecane [Ni(N-en-N-enH_4)$(NCS)_2$], and the metal-free macrocyclic ligand (N-en-N-enH_4). The conformation of metal-free (N-en-N-enH_4) is very similar to that in its nickel complex [Ni(N-en-N-enH_4)$(NCS)_2$] and also to that found for the related O_2N_2 ligand in [Ni(O-en-N-enH_4)Cl_2]. Both the N_4 and O_2N_2 14-membered ligands impose a ring-size constriction on the coordinated high-spin Ni(II) ion; this constriction is more severe for the O_2N_2 ligand. [Ni(O-en-N-enH_4)Cl_2]·$CHCl_3$: space group $P\bar{1}$, a = 11.525 (3) Å, b = 11.307 (3) Å, c = 9.757 (2) Å, α = 106.74 (2)°, β = 90.78 (2)°, γ = 103.22 (2)°, R = 0.075 for 1233 four-circle diffractometer data with $F \geq \sigma(F)$. [Ni(N-en-N-enH_4)$(NCS)_2$]: space group $C2/c$, a = 15.280 (4) Å, b = 9.765 (2) Å, c = 15.488 (4) Å, β = 108.13 (3)°, R = 0.038 for 2151 four-circle diffractometer data with $F \geq \sigma(F)$. (N-en-N-enH_4): space group $P2_1/c$, a = 11.844 (3) Å, b = 8.118 (2) Å, c = 17.788 (4) Å, β = 100.53 (3)°, R = 0.068 for 1049 four-circle diffractometer data with $F \geq \sigma(F)$.

The fit of a metal ion for its surrounding coordination shell is a parameter of major importance in influencing the chemical properties of the resulting metal complex. While in simple ligand systems it is normally found that the respective donor atoms take up positions that yield near ideal metal–ligand bond lengths, this is often not the case when the ligands are restricted by steric constraints. Constraints of this type have been postulated to be the origin of unusual behavior in a range of metal-containing systems in both chemistry and biochemistry. In previous work, Busch et al.[2] have used force-field calculations to probe such constraints in Ni(II) and Co(III) complexes of tetraaza macrocycles.

We have been concerned with the theoretical and practical aspects of the use of macrocyclic ligands as metal ion selective reagents and have also been concerned with matching ring sizes in such ligands to the radii of particular metal ions. As part of this study, X-ray structure determinations of a series of closely related macrocyclic compounds **1** containing O_2N_2-, N_4-, and S_2N_2-donor sets have been completed[3-5] and a simple procedure developed for assessing the fit of the metal ion for a given macrocyclic cavity. A particular aim of these studies has been to correlate the hole-size variations in macrocycles of the general type **1** with the previously documented transition metal ion chemistry of these systems.[6-10] In the latter studies unusual, and potentially useful, ring-size discrimination effects have been observed in both the thermodynamic and kinetic behavior of a number of such compounds.[9,10]



1, X = O, NH, S; n = 2, 3; m = 2-4

A comparison of the macrocycle hole size in the dibromonickel(II) complex of **1** (X = O; n = m = 3) with that in its

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Table I. Crystal Data and Selected[a] Details of the Structure Determinations of [Ni(O-en-N-enH_4)Cl_2], [Ni(N-en-N-enH_4)$(NCS)_2$], and N-en-N-enH_4

mol formula	$C_{19}H_{23}Cl_2N_2NiO_2$[b]	$C_{20}H_{24}N_6NiS_2$	$C_{18}H_{24}N_4$
M	547.19	471.29	296.42
a, Å	11.525 (3)	15.280 (4)	11.844 (3)
b, Å	11.307 (3)	9.765 (2)	8.118 (2)
c, Å	9.757 (2)	15.488 (4)	17.788 (4)
α, deg	106.74 (2)	(90)	(90)
β, deg	90.78 (2)	108.13 (3)	100.53 (3)
γ, deg	103.22 (2)	(90)	(90)
Z	2	4	4
space group	$P\bar{1}$	$C2/c$	$P2_1/c$
F(000)	444	984	640
μ(Mo Kα), cm^{-1}	10.00	10.27	0.39
crystal size, mm	0.32 × 0.20 × 0.12	0.21 × 0.18 × 0.10	0.22 × 0.15 × 0.12
no. of data in refinement[c]	1233	2151	1049
R[d]	0.075	0.038	0.068
R_w[e]	0.076	0.038	0.071

[a] Further information is available in the supplementary material, Table 1S. [b] A monochloroform solvate. [c] Intensity measurements were made on a Philips PW1100 diffractometer, using Mo Kα radiation. For all three structures unique data with $|F| > 6\sigma(|F_o|)$ were used in refinement. [d] The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/(\sigma(F_o))^2$. [e] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

diimine analogue has been published.[4] It was found that introduction of the imine linkages leads to only a very small reduction in the size of the cavity available to nickel after allowance is made for the smaller covalent radius of sp^2 compared with sp^3 nitrogen. In a further study,[3] the effect of donor atom variation on the macrocyclic hole size in the 15-membered ring structure **1** (m = 2; n = 3) was investigated. Substitution of two ether oxygens or two thioether sulfurs for two sp^3 nitrogens in **1** (X = NH; m = 2; n = 3) leads to macrocyclic ligands which, like the N_4 ring, are capable of providing a near ideal cavity for high-spin Ni(II). Even though the covalent radius of the sulfur donors is greater than those of oxygen or nitrogen, this difference appears to be largely compensated for by the greater "circumference" of the inner great ring of the S_2N_2-donor macrocycle resulting from the presence of four long C–S bonds in the ring.

As an extension of the above studies, the X-ray structures of high-spin nickel complexes of the 14-membered macrocycles **1** (X = O; m = n = 2; O-en-N-enH_4) and **1** (X = NH; m = n = 2; N-en-N-enH_4) are now presented together with details of the structure of the metal-free macrocycle, N-en-N-enH_4. Hole-size data for these compounds are compared with those obtained previously for related 15- and 16-membered macrocyclic compounds. In all, hole-size calculations involving nine X-ray structure determinations have been performed as part of the present investigation. Taken together, these results serve to illustrate the utility of the procedure for comparing relative cavity sizes in different ring systems.

Experimental Section

Blue crystals of [Ni(O-en-N-enH_4)Cl_2]·$CHCl_3$ were obtained on recrystallization of the unsolvated complex[6] from chloroform. Several attempts to obtain crystals of the analogous dichloro complex, [Ni(N-en-N-enH_4)Cl_2], were all unsuccessful. However, mauve crystals of [Ni(N-en-N-enH_4)$(NCS)_2$] were obtained from a methanol/acetonitrile solvent mixture and these were used for the structural analysis. Crystal data and details of the structure determinations are summarized in Table I; supplementary Table 1S contains additional details and Table 10S lists atomic fractional coordinates and isotropic thermal parameters.

Amine hydrogens in [Ni(O-en-N-enH_4)Cl_2]·$CHCl_3$ and all hydrogen atoms in [Ni(N-en-N-enH_4)$(NCS)_2$] and (N-en-N-enH_4) were inserted in positions found in difference Fourier maps. Their positional parameters were not refined, but a common thermal parameter was refined in each structure. Hydrogen atoms attached to carbon atoms in [Ni(O-en-N-enH_4)Cl_2]·$CHCl_3$ were included in calculated positions "riding" on the appropriate carbon atom, and a common thermal parameter was refined.

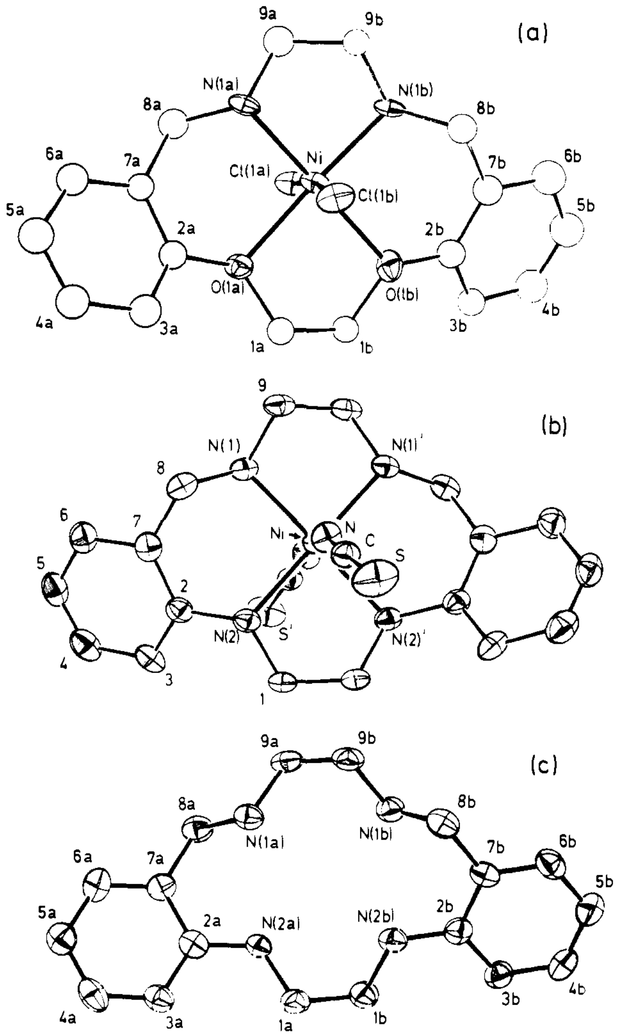

Figure 1. The structures of (a) [Ni(O-en-N-enH_4)Cl_2]·$CHCl_3$, (b) [Ni(N-en-N-enH_4)$(NCS)_2$], and (c) (N-en-N-enH_4), showing atom labels used in tables.

Results and Discussion

The complexes [Ni(O-en-N-enH_4)Cl_2]·$CHCl_3$ and [Ni(N-en-N-enH_4)$(NCS)_2$] both have trans-octahedral geometries (Figure 1a,b), similar to those found previously for high-spin complexes of the analogous 15- and 16-membered macrocycles. Bond distances and angles in the coordination planes defined by the macrocyclic ligands are compared in Figure 2. Tables II and III list additional selected bond lengths and angles for the above two complexes as well as for the metal-free macrocycle, (N-en-N-enH_4).

In both complexes the four donor atoms of the macrocycle are nearly planar with the maximum deviation from the respective coordination planes being 0.10 Å for the O_2N_2 system and 0.12 Å for the N_4 system. The N_4-donor complex has a crystallographic 2-fold axis passing through the midpoints of the ethane bridges, whereas the O_2N_2 system shows pseudo-C_2 symmetry with some small differences between chemically equivalent bond lengths and angles in the two halves (a and b) of the molecule (Figure 2 and Table III). A difference in the two Ni–Cl bond lengths is also apparent in [Ni(O-en-N-enH_4)Cl_2], and this difference appears to be a consequence of intermolecular hydrogen bonding between the Cl(2) and H(N1a) atoms (see Table III). Similar intermolecular H bonding also occurs[7] in the nickel chloride complex of the analogous 15-membered O_2N_2 macrocycle. An interesting feature of the structure is that the geometry about the oxygen atoms in the O_2N_2-donor complex is almost identical with that about the corresponding nitrogen atoms in the N_4-donor complex (see Table III). The five-membered chelate rings in both complexes have normal gauche conformations and, as a consequence

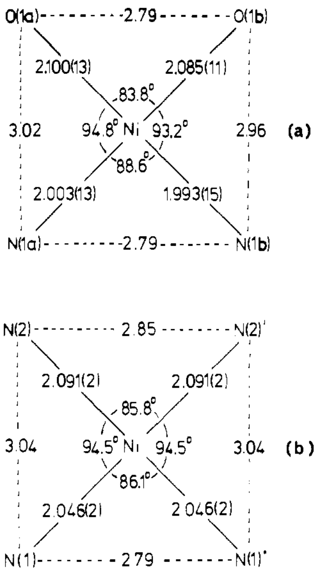

Figure 2. Comparison of the bond lengths (Å) and angles (deg) in the macrocyclic donor-atom planes in (a) [Ni(O-en-N-enH_4)Cl_2]·$CHCl_3$ and (b) [Ni(N-en-N-enH_4)$(NCS)_2$].

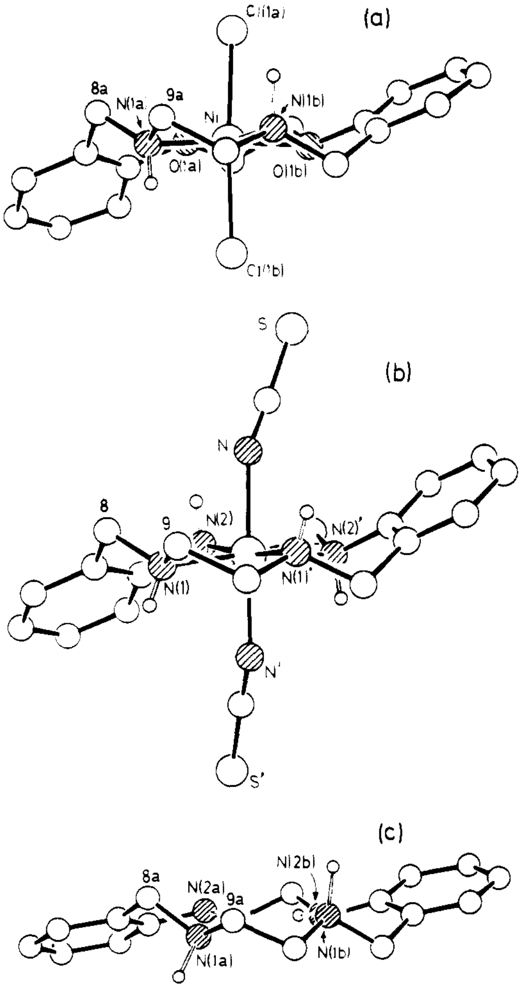

Figure 3. Comparison of the macrocycle conformations in (a) [Ni(O-en-N-enH_4)Cl_2]·$CHCl_3$, (b) [Ni(N-en-N-enH_4)$(NCS)_2$], and (c) (N-en-N-enH_4).

of this and the sp3 hybridization of each nitrogen, the N–H bonds alternate on either side of the coordination plane in [Ni(N-en-N-enH_4)$(NCS)_2$] (see Figures 3b and 4b).

Both complexes have an overall "step-shaped" geometry which is similar to that in [Ni(N-en-N-tnH_4)Cl_2] {(N-en-N-tnH_4) = **1**; X = NH; $m = 2$; $n = 3$} and contrasts with the "saddle-shaped"

Table II. Molecular Dimensions in the Coordination Sphere for [Ni(O-en-N-enH_4)Cl_2]·$CHCl_3$ and [Ni(N-en-N-enH_4)$(NCS)_2$]

	[Ni(O-en-N-enH_4)Cl_2] {X = O(1), Y = Cl(1)} part a	part b	[Ni(N-en-N-enH_4)$(NCS)_2$] {X = N(2), Y = N}
(a) Distances,[a] Å			
Ni-N(1)	2.003 (13)	1.993 (15)	2.046 (2)
Ni-X	2.100 (13)	2.085 (11)	2.091 (2)
Ni-Y	2.419 (7)	2.455 (7)	2.108 (2)
(b) Angles, deg			
N(1)-Ni-N(1')	88.6 (6)		86.1 (1)
X-Ni-X'	83.8 (5)		85.8 (1)
N(1)-Ni-X	94.8 (5)	93.2 (5)	94.5 (1)
N(1)-Ni-X'	172.4 (7)	175.2 (5)	173.1 (1)
Y-Ni-Y'	172.6 (2)		176.3 (1)
Y-Ni-N(1)	97.1 (5)	96.1 (5)	86.8 (1)
Y-Ni-X	86.2 (4)	85.3 (4)	91.0 (1)
Y-Ni-O(1')	90.3 (4)	87.4 (4)	
Y-Ni-N(1')	90.1 (5)	87.1 (5)	
(c) Angles Involving Ni at Donor Atoms, deg			
Ni-N(1)-C(8)	110.4 (10)	113.2 (12)	110.6 (2)
Ni-N(1)-C(9)	103.4 (10)	103.7 (11)	104.9 (2)
Ni-X-C(1)	105.4 (11)	105.3 (9)	104.9 (2)
Ni-X-C(2)	117.9 (10)	119.0 (12)	115.8 (2)
(d) Thiocyanate Ligand in [Ni(N-en-N-enH_4)$(NCS)_2$]			
C-N	1.158 (3) Å; C-S		1.621 (3) Å
C-N-Ni	156.0 (2)°; S-C-N		178.4 (3)°

[a] Primes indicate atoms in the alternative part (a or b) of the molecule [Ni(O-en-N-enH_4)Cl_2] and in the symmetry-related half of the molecule of [Ni(N-en-N-enH_4)$(NCS)_2$].

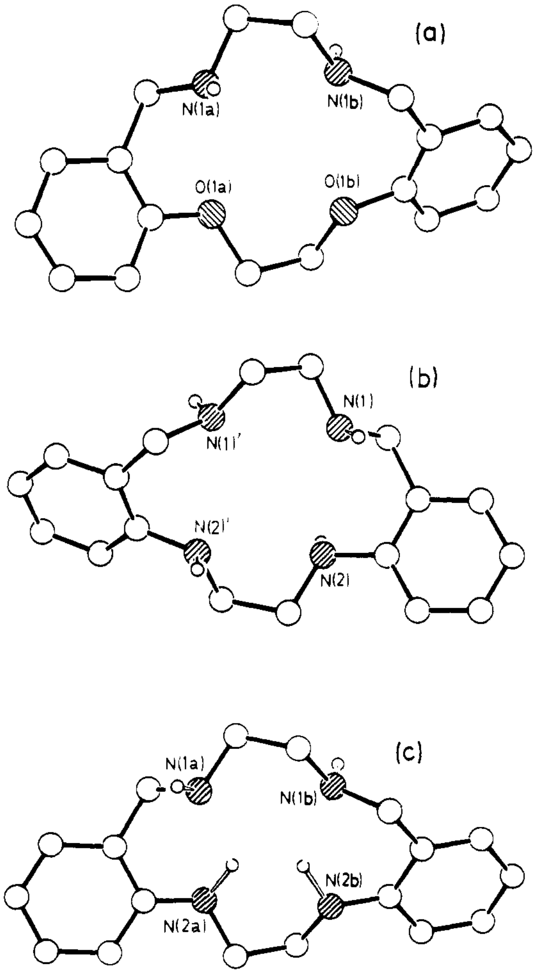

Figure 4. Amino-hydrogen locations in (a) [Ni(O-en-N-enH_4)Cl_2]·$CHCl_3$, (b) [Ni(N-en-N-enH_4)$(NCS)_2$], and (c) (N-en-N-enH_4). For ease of comparison the nickel and coordinated anions are not shown in a and b.

Table III. Molecular Dimensions in the Macrocyclic Residues for [Ni(O-en-N-enH_4)Cl_2], [Ni(N-en-N-enH_4)$(NCS)_2$], and (N-en-N-enH_4)

	[Ni(O-en-N-enH_4)Cl_2] {X = O(1) and Y = Cl(1)}		[Ni(N-en-N-enH_4)$(NCS)_2$] {X = N(2) and Y = N}	(N-en-N-enH_4) {X = N(2)}	
	part a	part b		part a	part b
			(a) Bond Lengths,[a] Å		
C(1)-C(1′)	1.501 (26)		1.533 (8)	1.534 (9)	
C(1)-X	1.445 (22)	1.465 (23)	1.481 (4)	1.449 (9)	1.468 (10)
X-C(2)	1.416 (22)	1.396 (25)	1.450 (4)	1.391 (9)	1.407 (9)
C(2)-C(3)	1.338 (34)	1.404 (24)	1.391 (5)	1.406 (12)	1.405 (11)
C(2)-C(7)	1.391 (26)	1.401 (30)	1.407 (4)	1.406 (10)	1.406 (12)
C(3)-C(4)	1.453 (29)	1.406 (32)	1.399 (6)	1.387 (11)	1.405 (11)
C(4)-C(5)	1.360 (29)	1.304 (36)	1.365 (5)	1.393 (13)	1.386 (13)
C(5)-C(6)	1.390 (37)	1.389 (30)	1.398 (5)	1.385 (13)	1.410 (12)
C(6)-C(7)	1.421 (27)	1.452 (33)	1.394 (5)	1.394 (10)	1.391 (11)
C(7)-C(8)	1.529 (33)	1.571 (24)	1.520 (4)	1.506 (11)	1.521 (10)
C(8)-N(1)	1.474 (26)	1.449 (26)	1.485 (4)	1.479 (10)	1.480 (9)
N(1)-C(9)	1.489 (29)	1.515 (19)	1.476 (4)	1.457 (10)	1.471 (9)
C(9)-C(9′)	1.508 (28)		1.526 (7)	1.514 (10)	
N(1)-H(N1)	1.13	0.89	0.83	1.11	1.18
N(2)-H(N2)			0.92	1.12	1.15
N(1)···H(N2)				2.01	1.99
H(N1)···Y[b]		2.42			
			(b) Angles, deg		
X-C(1)-C(1′)	107.8 (17)	108.7 (13)	108.8 (1)	110.6 (6)	109.4 (6)
C(1)-X-C(2)	119.5 (16)	118.5 (13)	118.0 (2)	119.7 (6)	119.5 (5)
X–C(2)-C(3)	117.2 (16)	120.7 (18)	120.8 (3)	123.6 (7)	118.7 (7)
X–C(2)-C(7)	119.2 (19)	116.9 (15)	118.7 (3)	117.8 (7)	119.1 (6)
C(3)-C(2)-C(7)	123.5 (18)	122.4 (20)	120.5 (3)	118.5 (6)	122.2 (7)
C(2)-C(3)–C(4)	118.1 (19)	116.5 (19)	120.0 (3)	121.2 (7)	120.3 (8)
C(3)-C(4)-C(5)	121.9 (24)	122.7 (20)	120.3 (3)	119.9 (8)	121.6 (7)
C(4)-C(5)-C(6)	116.5 (20)	123.3 (24)	119.8 (4)	119.4 (7)	117.5 (7)
C(5)-C(6)-C(7)	124.1 (18)	117.5 (22)	121.4 (3)	121.5 (7)	122.1 (8)
C(2)-C(7)-C(6)	115.6 (20)	117.5 (17)	117.9 (3)	119.5 (7)	119.8 (7)
C(2)-C(7)-C(8)	124.5 (17)	124.1 (18)	123.4 (3)	120.9 (6)	120.0 (6)
C(6)-C(7)-C(8)	119.9 (16)	118.3 (19)	118.7 (3)	119.6 (6)	120.0 (7)
C(7)-C(8)-N(1)	108.9 (18)	108.1 (16)	108.6 (2)	109.5 (6)	110.8 (6)
C(8)-N(1)-C(9)	116.2 (17)	118.1 (14)	118.1 (2)	113.2 (6)	112.7 (6)
N(1)-C(9)-C(9′)	106.2 (17)	106.8 (14)	107.0 (1)	109.7 (6)	110.5 (6)

(c) Chloroform Solvate for [Ni(O-en-N-enH_4)Cl_2]·$CHCl_3$

C-Cl(2)	1.701 (31) Å	Cl(2)–C-Cl(3)	105.3 (20)°
C-Cl(3)	1.767 (39) Å	Cl(2)-C-Cl(4)	106.9 (15)°
C–Cl(4)	1.765 (36) Å	Cl(3)–C–Cl(4)	106.7 (19)°

[a] Primes indicate atoms in the alternative part (a or b) of the molecules [Ni(O-en-N-enH_4)Cl_2] or (N-en-N-enH_4) and in the symmetry-related half of the molecule in [Ni(N-en-N-enH_4)$(NCS)_2$]. [b] Related to Cl(1b) in Table 10S by $-x$, $1-y$, $1-z$.

geometry found for the related complexes of **1** with X = O (*m* = 2 or 3; *n* = 3).[3,4] For [Ni(N-en-N-enH_4)$(NCS)_2$], the benzene rings are inclined at 35° to the "NiN_4" plane whereas the corresponding angles in [Ni(O-en-N-enH_4)Cl_2]·$CHCl_3$ are 31° and 34°.

The overall conformation of the metal-free macrocycle, (N-en-N-enH_4), is very similar to that in its nickel thiocyanate complex. However, in the free macrocycle, two intramolecular bonds of type N—H···N are present (Table III and Figure 4). Figures 3 and 4 show that the conformations of the macrocycles in the complexes [Ni(O-en-N-enH_4)Cl_2] and [Ni(N-en-N-enH_4)$(NCS)_2$] correspond closely to that of the free ligand (N-en-N-enH_4).

Bond lengths and angles for chemically equivalent bonds in the coordinated and metal-free macrocycle are also generally very similar (Table III). However, the C(8)–N(1)–C(9) angles in both halves of the free macrocycle are closer to tetrahedral values (113.2° and 112.7°) than in its complex (118.1°). This may be manifestation of additional strain in the coordinated ring system which arises from expansion of the ring after incorporation of the nickel ion (see below).

The macrocyclic Ni–N bond lengths in the N_4-donor complex (Figure 2) are all slightly shorter than the mean length (2.11 Å) of 89 secondary amine to high-spin nickel bonds reported in the literature.[4] In the O_2N_2 system, the Ni–N bonds are even shorter, and at 2.003 (13) and 1.993 (15) Å appear to be the shortest such bonds so far reported for high-spin Ni(II) (literature range: 2.04–2.33 Å).[4] Similarly, the Ni–O bond lengths of 2.100 (13) and 2.085 (11) Å in this latter complex are significantly shorter than the mean value of 2.15 Å found for a range of other Ni(II)–O(ether) bonds in high-spin complexes.[4] Consideration of the nickel-donor atom bond distances in the O_2N_2-macrocyclic complex thus suggests that appreciable ring-size constriction of the nickel-donor atom bonds occurs in [Ni(O-en-N-enH_4)Cl_2]. The ring-size constriction on the nickel-donor atom bond lengths in [Ni(N-en-N-enH_4)$(NCS)_2$] is less, but is still significant, leading to the unusual situation in which the bonds from the neutral nitrogen atoms in the macrocycle are shorter than those from the anionic thiocyanate nitrogen atoms.

The suggestion[13] that the hole size in the 14-membered "cyclam-type" ligands may be slightly less than the optimum for high-spin Ni(II) is supported by the data (Table IV) for (N-en-N-enH_4) which is a dibenzo derivative of cyclam. The radius of the hole in the metal-free ligand, calculated as the mean distance of the donor atoms from their centroid, at 2.03 Å is smaller than the value (2.07 Å) found for its nickel complex (Table IV). The observation that the minimum-strain form of (N-en-N-enH_4) provides an "N_4" cavity which is too small for high-spin Ni(II) accounts for the especially facile Ni(II) → Ni(III) conversion

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[11] No similar H bonding is present in the N_4-donor complex.

[12] Battaglia, L. P.; Corradi, A. B.; Mangia, A. *Inorg. Chim. Acta* **1980**, 39, 211–216.

[13] It has been postulated previously that some hole size constriction toward high-spin Ni(II) will occur for saturated tetraaza macrocycles with great rings which are less than 15-membered: Busch, D. H. *Acc. Chem. Res.* **1978**, 11, 392–400 and references therein.

Table IV. Hole-Size Data for O_2N_2-, N_4-, and S_2N_2-Donor Macrocycles of Type 1

compound	ring size	donor set	D,[a] Å	R_A,[b] Å	R_A/R_P[c]	ref
$[NiLCl_2]\cdot CHCl_3$ ($X = O; n = m = 2$)	14	O_2N_2	4.09	1.31	0.94	*d*
$[NiLCl_2]$ ($X = O; n = 2; m = 3$)	15	O_2N_2	4.18	1.35	0.97	3
$[NiL(NCS)_2]$ ($X = O; n = 2; m = 3$)	15	O_2N_2	4.18	1.35	0.97	12
$[NiLBr_2]$ ($X = O; n = m = 3$)	16	O_2N_2	4.28	1.40	1.01	4
L ($X = O; n = 2; m = 3$)[e]	15	O_2N_2	4.18, 4.30			5
$[NiL(NCS)_2]$ ($X = NH; m = n = 2$)	14	N_4	4.13	1.35	0.97	*d*
$[NiLCl_2]$ ($X = NH; n = 2; m = 3$)	15	N_4	4.22	1.39	1.00	3
L ($X = NH; m = n = 2$)	14	N_4	4.05			*d*
$[NiLCl_2]$ ($X = S; n = 2; m = 3$)	15	S_2N_2	4.54	1.39	1.00	3

[a] Diameter of the macrocyclic hole (uncorrected). Defined as twice the mean distance of the donor atom positions from their centroid. [b] "Apparent" radius of the metal ion cavity. Derived from the calculated diameter by correcting for the mean of the covalent radii of the donor atoms presented, i.e., $R_A = D/2 - r_X$, where r_X = "effective covalent radius" of donors as calculated from data in the Cambridge Crystallographic Data Centre files (see text and ref 3). [c] R_P is 1.39 Å, the Pauling covalent radius for high-spin Ni(II). [d] This work. [e] This macrocycle crystallizes with two independent molecules per assymmetric unit (ref 5).

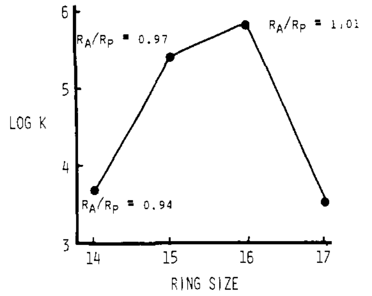

Figure 5. The relationship between hole size and thermodynamic stability for nickel complexes of the O_2N_2 macrocycles (**1**, X = O).

which has been observed[14] in complexes of this ligand. The corresponding hole size in $[Ni(O\text{-en-}N\text{-en}H_4)Cl_2]$ is 2.05 Å.

For the above complexes, the "apparent"[15] cavity size occupied by the nickel ion was calculated by obtaining the mean distance of the positions of the donor atoms from their centroid and substracting the mean "effective covalent radius" of the donor atoms from this value. The "effective covalent radii" of the different donor atom types were estimated,[3,4] by taking the mean of a range of similar donor-nickel bond distances (see previously) to those in the complexes under study and subtracting from each mean the Pauling covalent radius for high-spin nickel. This procedure allows direct comparison of the macrocyclic hole sizes in metal-free macrocycles as well as in the corresponding metal complexes and enables comparisons even when irregular coordination geometries or different numbers or types of donor atoms are present. It is also applicable to three-dimensional cage ligand systems.

The results of the hole-size calculations for the compounds just discussed are given in Table IV together with those for closely related systems whose structures were determined previously. The data clearly show that for both the O_2N_2 and N_4 ligands the radius of the cavity available to nickel increases by 0.04–0.05 Å for each additional atom in the macrocyclic ring.

As expected for $[Ni(O\text{-en-}N\text{-en}H_4)Cl_2]\cdot CHCl_3$, the radius of the cavity available to nickel (1.31 Å) is substantially less than the Pauling radius for high-spin Ni(II) (1.39 Å). The nickel radius falls between the radii obtained for the cavities in the analogous 15-membered (1.35 Å)[3] and 16-membered (1.40 Å)[4] rings. Both the kinetic[9] and thermodynamic[10] stabilities of the complexes of these 14- to 16-membered macrocyclic rings reflect the match of the nickel ion to the respective macrocyclic cavities. Along this O_2N_2-donor series, the stabilities reach a maximum at the 16-membered ring complex with both the 15- and 16-membered compounds being considerably more stable than the 14-membered complex. The correlation between thermodynamic stability and the ratio of apparent cavity to metal covalent radius (R_A/R_P) is illustrated in Figure 5.

In the complexes of the 14- and 15-membered rings the radius of the hole (as defined by the mean distance of the donor atoms from their centroid) is slightly smaller in the O_2N_2 ligand than in the analogous N_4 ligand (see Table IV). This can be partly attributed to the larger circumference of the N_4 ligand, which results from the longer carbon to anilino-nitrogen bonds in the complex compared with the analogous carbon to phenoxy-oxygen bonds in the complex of the O_2N_2 ligand (see C(1)–X and X–C(2) lengths in Table III). Correction of the respective macrocyclic holes for the radii of the donor atoms present leads to a further reduction in the cavity size of the O_2N_2 macrocycle relative to its N_4 analogue. This is a consequence of the larger "effective covalent radius" used for oxygen (0.76 Å) than for nitrogen (0.72 Å).

Concluding Remarks

The results obtained in the present investigation are completely consistent with those presented previously.[3,4] In addition, all the results accord well with the known chemistry of the respective compounds. Thus, the concept of an "apparent" cavity, although somewhat hypothetical, nevertheless appears to be a useful indicator of the match of a metal ion for a given macrocyclic ring. A knowledge of this latter aspect is of fundamental importance to the design and synthesis of new macrocycles for use as metal ion selective reagents.

Finally, it has not escaped us that the procedure outlined for obtaining hole-size data for macrocyclic compounds may well have wider applicability. It should prove useful for investigating the complexes of a range of other ligand types as well as for the study of metal-containing biological molecules such as the metalloenzymes. In the latter case it appears to be particularly suitable for the analysis of "entatic state" phenomena; we are currently undertaking an investigation in this area.

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Registry No. 1 ($X = NH$; $n = m = 2$), 88589-00-8; $[Ni(O\text{-en-}N\text{-en}H_4)Cl_2]\cdot CHCl_3$, 88588-98-1; $[Ni(N\text{-en-}N\text{-en}H_4)(NCS)_2]$, 88588-99-2.

Supplementary Material Available: Further details of the structure determinations together with listings of interatomic bond lengths and angles, least-squares planes, structure factors, torson angles, atomic coordinates, and isotropic thermal parameters (35 pages). Ordering information is given on any current masthead page.

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(14) Seghi, B.; Ansell, C. W. G.; Baillie, P. J.; Buttafava, A.; Fabbrizzi, L.; Henrick, K.; McPartlin, M.; Tasker, P. A. "Composes Macrocycliques"; Strasbourg, 1982, p 39, and paper in preparation. $E_{1/2}$ for Ni(II) → Ni(III) in $[Ni(N\text{-en-}N\text{-en}H_4)](ClO_4)_2$ is 0.47 V (measured in acetonitrile relative to the ferrocinium/ferrocene couple, as outlined in Fabbrizzi: Fabbrizzi, L. *J. Chem. Soc., Chem. Commun.* **1979**, 1063–1065).

(15) The "apparent" metal ion cavity as calculated may differ from the actual cavity since the calculation is based on the over simplificiation that the various donor-atom radii are fixed. Nevertheless, the ratio of the "apparent" radius to the Pauling radius (R_A/R_P in Table IV) does provide a relative measure of the fit of a metal ion for a given macrocyclic ring.