Contribution from the Department of Chemistry, Polytechnic of North London, London N7 8DB, United Kingdom, and the Department of Chemistry and Biochemistry, James Cook University of North Queensland, Queensland 4811, Australia

Studies of Macrocyclic Ligand Hole Sizes. 1. X-ray Structures of the Nickel Bromide Complexes of the Diimine and Reduced Forms of a 16-Membered Macrocyclic Ring Incorporating O_2N_2 Donors

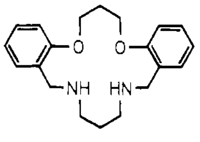
HILARY J. GOODWIN,[1a] KIM HENRICK,[1a] LEONARD F. LINDOY,*[1b] MARY McPARTLIN,[1a] and PETER A. TASKER*[1a]

Received November 5, 1981

Comparative X-ray diffraction structures of the nickel bromide complexes of the 16-membered macrocycles 3,4:10,11-dibenzo-1,13-diaza-5,9-dioxacyclohexadecane (**1**) and 3,4:10,11-dibenzo-1,13-diaza-5,9-dioxacyclohexadeca-1,12-diene (**2**) have been obtained. Macrocycle **2** is the diimine precursor of **1**. Both nickel complexes have similar trans-bromo, pseudooctahedral coordination geometries with the O_2N_2-donor sets being either planar or very nearly planar. In each complex the nickel atom lies in the hole of the macrocycle with both sets of aromatic rings inclined to the same side of the respective donor atom planes. Largely as a consequence of decreased O-N bites in the chelate rings containing the imine linkages, the hole size in the coordinated diimine macrocycle **2** is smaller than in its coordinated analogue **1**. However the effective "covalent" radius for the sp^2 nitrogens in the former complex is also smaller (than the sp^3 radius in the latter) and this partially compensates for the above difference in ring size. Both macrocycles appear to fit high-spin nickel well. [Ni(macrocycle **1**)Br_2]: space group *Cc*, $a = 16.835$ (5) Å, $b = 15.337$ (4) Å, $c = 8.181$ (2) Å, $\beta = 95.30$ (2)°, $R = 0.046$ for 1826 four-circle diffractometer data with $I > 3\sigma(I)$. [Ni(macrocycle **2**)Br_2]: space group $Cmc2_1$, $a = 16.540$ (3) Å, $b = 15.703$ (5) Å, $c = 7.905$ (1) Å, $R = 0.039$ for 852 four-circle diffraction data with $I > 3\sigma(I)$.

Introduction

Macrocyclic O_2N_2-donor ligands such as the 16-membered ring **1**[2] have been investigated previously as potential metal ion selective reagents. As part of these investigations, we have considered kinetic,[3-5] thermodynamic,[5-9] and structural[3,5,7-9] aspects of the interaction of Co(II), Ni(II), Cu(II), and Zn(II) with a range of such macrocycles incorporating different ring sizes and/or substituents. Related work on the coordination chemistry of the corresponding precursor diimine macrocycles (such as **2**) have also been carried out.[10,11] The effective hole sizes of the respective macrocycles were of particular interest in these studies of transition-metal complexes in view of the possibility of discovering useful ring-size effects such as metal ion discrimination of the type which is characteristic of the crown ethers toward non-transition-metal ions. Indeed, the kinetic and thermodynamic stabilities of the Ni(II) complexes of the 14- to 17-membered amine macrocycles of the above type reach a peak at the 16-membered ring.[4,6] Consideration of likely lengths for the metal-donor bonds suggested that both the 15- and 16-membered macrocycles should provide rings which fit high-spin Ni(II) well. In agreement with this, X-ray studies[3,12] have shown that there is very little difference between the hole sizes of the 15-membered macrocycle before and after coordination to nickel although some conformational differences do occur. We now report details of the X-ray structure determination of the nickel bromide complex of the 16-membered ring macrocycle **1** together with the results of a comparative study of the corresponding complex of the diimine macrocycle **2**. On the basis of their spectral and other properties, both of these complexes have previously been assigned trans pseudooctahedral coordination geometries.[2,10]


1; O-tn-N-tnH$_4$

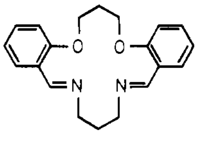

2; O-tn-N-tn

Table I. Crystal Data and Selected Details[a] of Structure Determination

	[Ni(O-tn-N-tn)Br_2]	[Ni(O-tn-N-tnH_4)Br_2]
mol formula	$C_{20}H_{22}Br_2N_2NiO_2$	$C_{20}H_{26}Br_2N_2NiO_2$
M_r	540.94	544.97
space group	$Cmc2_1$	*Cc*
a/Å	16.540 (3)	16.835 (5)
b/Å	15.703 (5)	15.337 (4)
c/Å	7.905 (1)	8.181 (2)
β/deg		95.30 (2)
Z	4	4
θ range/deg[b]	3-30	3-30
$\lvert F_o\rvert/\sigma(\lvert F_o\rvert)$ for data used in refinement	6	6
no. of data used in refinement	852	1826
$R = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$[c]	0.039	0.046

[a] Further information is available in supplementary material Table 1. [b] Intensity measurements were made on a Philips PW1100 diffractometer. [c] The function minimized was $\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$, where $w = 1/\sigma(F_o)^2$.

Apart from the implications of the structural details to the past selectivity studies, the subtle changes that may occur on introduction of unsaturation into a coordinated macrocycle such as **1** are themselves of considerable intrinsic interest and

---

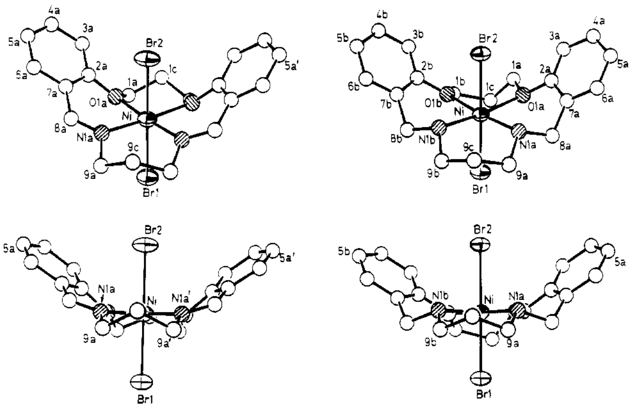
(1) (a) Polytechnic of North London. (b) James Cook University of North Queensland.
(2) Grimsley, P. G.; Lindoy, L. F.; Lip, H. C.; Smith, R. J.; Baker, J. T. *Aust. J. Chem.* **1977**, *30*, 2095. Armstrong, L. G.; Grimsley, P. G.; Lindoy, L. F.; Lip, H. C.; Norris, V. A.; Smith, R. J. *Inorg. Chem.* **1978**, *17*, 2350.
(3) Ekstrom, A.; Lindoy, L. F.; Lip, H. C.; Smith, R. J.; Goodwin, H. J.; McPartlin, M.; Tasker, P. A. *J. Chem. Soc., Dalton Trans.* **1979**, 1027.
(4) Ekstrom, A.; Lindoy, L. F.; Smith, R. J. *Inorg. Chem.* **1980**, *19*, 724.
(5) Adam, K. R.; Anderegg, G.; Lindoy, L. F.; Lip, H. C.; McPartlin, M.; Rea, J. H.; Smith, R. J., Tasker, P. A. *Inorg. Chem.* **1980**, *19*, 2956.
(6) Anderegg, G.; Ekstrom, A.; Lindoy, L. F.; Smith, R. J. *J. Am. Chem. Soc.* **1980**, *102*, 2670.
(7) Adam, K. R.; Lindoy, L. F.; Lip, H. C.; Rea, J. H.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1981**, 74.
(8) Lindoy, L. F.; Lip, H. C.; Rea, J. H.; Smith, R. J.; Henrick, K.; McPartlin, M.; Tasker, P. A. *Inorg. Chem.* **1980**, *19*, 3360.
(9) Adam, K. R.; Anderegg, G.; Henrick, K.; Leong, A. J.; Lindoy, L. F.; Lip, H. C.; McPartlin, M.; Smith, R. J.; Tasker, P. A. *Inorg. Chem.* **1982**, *21*, 4048.
(10) Armstrong, L. G.; Lindoy, L. F. *Inorg. Chem.* **1975**, *14*, 1322.
(11) Lindoy, L. F.; Lip, H. C.; Power, L. F.; Rea, J. H. *Inorg. Chem.* **1976**, *15*, 1724. Armstrong, L. G.; Lindoy, L. F.; McPartlin, M.; Mockler, G. M.; Tasker, P. A. *Ibid.*, **1977**, *16*, 1665.
(12) Tasker, P. A.; Trotter, J.; Lindoy, L. F. *J. Chem. Res., Miniprint* **1981**, 3834.

0020-1669/82/1321-3261$01.25/0

Table II. Atomic Fractional Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$)

atom	*x*	*y*	*z*	*U*
		$[Ni(O\text{-}tn\text{-}N\text{-}tn)Br_2]$		
Ni	0	2513 (1)	2500	*a*
Br(1)	0	3683 (1)	4707 (6)	*a*
Br(2)	0	1380 (1)	211 (6)	*a*
O(1a)	916 (4)	3197 (4)	1153 (11)	49 (2)
N(1a)	926 (5)	1939 (5)	3685 (13)	49 (2)
C(1c)	0	4000 (10)	−693 (32)	66 (6)
C(1a)	747 (6)	3497 (6)	−607 (14)	51 (2)
C(2a)	1544 (5)	3561 (5)	2012 (14)	46 (2)
C(3a)	1809 (6)	4390 (6)	1664 (14)	53 (2)
C(4a)	2520 (5)	4681 (7)	2535 (16)	62 (3)
C(5a)	2922 (7)	4182 (7)	3616 (16)	65 (3)
C(6a)	2630 (6)	3381 (8)	4017 (16)	68 (3)
C(7a)	1922 (6)	3061 (5)	3249 (13)	49 (2)
C(8a)	1628 (6)	2224 (6)	3844 (13)	54 (2)
C(9a)	770 (6)	1089 (6)	4424 (15)	55 (2)
C(9c)	0	1070 (10)	5509 (31)	59 (5)
		$[Ni(O\text{-}tn\text{-}N\text{-}tnH_4)Br_2]$		
Ni	5000	2403 (1)	5000	*a*
Br(1)	5073 (1)	3697 (1)	6888 (2)	*a*
Br(2)	4907 (1)	1057 (1)	3129 (2)	*a*
O(1a)	6023 (4)	1744 (5)	6496 (9)	37 (2)
O(1b)	4240 (5)	1741 (5)	6657 (10)	40 (2)
N(1a)	5825 (5)	2936 (6)	3585 (12)	39 (2)
N(1b)	4010 (5)	2886 (5)	3676 (11)	37 (2)
C(1c)	5332 (7)	1665 (8)	8922 (16)	54 (3)
C(1a)	5844 (8)	1192 (8)	7901 (17)	55 (3)
C(2a)	6651 (6)	1444 (6)	5635 (13)	34 (2)
C(3a)	6929 (7)	606 (8)	5756 (15)	48 (3)
C(4a)	7573 (7)	354 (8)	4859 (16)	47 (3)
C(5a)	7923 (8)	957 (9)	3901 (18)	60 (3)
C(6a)	7619 (7)	1794 (8)	3750 (16)	51 (3)
C(7a)	6972 (6)	2048 (7)	4621 (14)	39 (2)
C(8a)	6641 (7)	2950 (7)	4433 (15)	45 (3)
C(9a)	5600 (7)	3809 (8)	2866 (16)	51 (3)
C(1b)	4431 (7)	1556 (8)	8390 (15)	48 (3)
C(2b)	3508 (6)	1403 (7)	5992 (13)	37 (2)
C(3b)	3288 (7)	560 (8)	6302 (15)	49 (3)
C(4b)	2559 (9)	241 (10)	5582 (17)	67 (4)
C(5b)	2068 (8)	775 (9)	4522 (18)	63 (4)
C(6b)	2302 (8)	1634 (8)	4238 (16)	51 (3)
C(7b)	3031 (7)	1943 (7)	4976 (15)	43 (3)
C(8b)	3296 (6)	2862 (7)	4635 (14)	40 (2)
C(9b)	4081 (7)	3755 (7)	2943 (16)	47 (3)
C(9c)	4781 (6)	3803 (7)	1883 (14)	43 (3)

[a] These atoms were assigned anisotropic thermal parameters—see Table 2 (supplementary material).



$[Ni(O\text{-}tn\text{-}N\text{-}tn)Br_2]$ $[Ni(O\text{-}tn\text{-}N\text{-}tnH_4)Br_2]$

Figure 1. Structures of $[Ni(O–tn–N–tn)Br_2]$ and $[Ni(O–tn–N–tnH_4)Br_2]$.

Table III. Selected[a] Interatomic Bond Lengths/Å and Angles/Deg

	$[Ni(O\text{-}tn\text{-}N\text{-}tn)Br_2]$	$[Ni(O\text{-}tn\text{-}N\text{-}tnH_4)Br_2]$	
		part a	part b
	Bonds		
Ni-Br(1)	2.534 (4)	2.511 (2)	
Ni-Br(2)	2.538 (4)	2.566 (2)	
C(1c)-C(1)	1.47 (1)	1.45 (2)	1.55 (2)
C(1)-O(1)	1.50 (1)	1.48 (2)	1.45 (2)
O(1)-C(2)	1.37 (1)	1.40 (1)	1.40 (1)
C(2)-C(3)	1.40 (1)	1.37 (2)	1.38 (2)
C(2)-C(4)	1.40 (1)	1.39 (1)	1.38 (2)
C(6)-C(7)	1.41 (1)	1.41 (2)	1.40 (2)
C(7)-C(8)	1.48 (1)	1.49 (2)	1.51 (2)
C(8)-N(1)	1.25 (1)	1.48 (1)	1.49 (1)
N(1)-C(9)	1.48 (1)	1.50 (2)	1.47 (2)
C(9)-C(9c)	1.54 (2)	1.53 (2)	1.63 (2)
	Angles		
Br(1)-Ni-Br(2)	178.0 (2)	178.4 (1)	
Br(1)-Ni-O(1)	88.8 (2)	91.6 (2)	89.1 (2)
Br(1)-Ni-N(1)	90.2 (3)	92.0 (3)	91.8 (3)
Br(2)-Ni-O(1)	89.8 (2)	88.0 (2)	89.4 (2)
Br(2)-Ni-N(1)	91.0 (3)	89.5 (3)	88.5 (3)
C(1)-C(1c)-C(1)	114.7 (13)	113.8 (11)	
C(1c)-C(1)-O(1)	111.8 (12)	109.7 (10)	112.1 (10)
C(1)-O(1)-C(2)	118.2 (7)	114.8 (8)	114.5 (8)
C(1)-O(1)-Ni	119.2 (6)	118.5 (7)	127.1 (6)
C(2)-O(1)-Ni	120.1 (7)	116.6 (6)	118.3 (6)
O(1)-C(2)-C(7)	115.8 (7)	115.8 (9)	117.1 (9)
C(2)-C(7)-C(8)	125.1 (8)	121.2 (10)	120.4 (10)
C(7)-C(8)-N(1)	126.2 (9)	110.9 (9)	112.6 (9)
C(8)-N(1)-Ni	126.5 (7)	112.8 (7)	111.7 (7)
C(8)-N(1)-C(9)	116.4 (9)	111.2 (9)	109.6 (8)
C(9)-N(1)-Ni	117.1 (6)	114.6 (7)	116.9 (7)
N(1)-C(9)-C(9c)	112.5 (10)	112.6 (10)	111.8 (9)
C(9)-C(9c)-C(9)	112.1 (17)	114.0 (10)	

[a] A full list is given in the supplementary material. Details of the O_2N_2 coordination planes are given in Figure 2.

such knowledge is of potential use for the design of macrocyclic reagents.

Experimental Section

Green crystals (butanol) of the respective complexes were prepared as described previously.[2,10] Crystal data and details of the structure determination are summarized in Table I. Additional details are given in the supplementary material. Atomic fractional coordinates and isotropic thermal parameters are listed in Table II.

Results and Discussion

The X-ray determinations confirm the expected six-coordinate trans-bromide geometries for $[Ni(O–tn–N–tn)Br_2]$ and $[Ni(O–tn–N–tnH_4)Br_2]$ (Figure 1).[2,10] Comparisons of selected interatomic bond lengths and bond angles for both systems are given in Figure 2 and Table III. Apart from the different bond lengths to nickel for the three donor atom types (O, N, Br), the most marked distortions from regular octahedral coordination are the considerable deviations from 90° that are observed for several of the angles subtended at nickel by adjacent donor atoms of the macrocycle. The O_2N_2-donor set presented by the macrocycle is planar in the diimine complex and close to planar in $[Ni(O–tn–N–tnH_4)Br_2]$, for which the maximum deviations of the O and N atoms from the O_2N_2 plane are ±0.02 Å. For each complex the chelate rings incorporating the aromatic rings are bent to the same side of the respective O_2N_2 planes in an analogous manner to that found previously for the corresponding 15-membered ring complexes of type $[Ni(O–en–N–tnH_4)X_2]$ (X = Cl, NCS).[3,13]

The Ni–Br bond distances in both complexes are unremarkable and fall near the sum (2.53 Å) of the respective covalent radii.[14] The two Ni–Br bond lengths in $[Ni(O–tn–N–tnH_4)Br_2]$ are significantly different, and comparison of the two structures suggests that the difference may be related

---

(13) Battaglia, L. P.; Corradi, A. B.; Mangia, A. *Inorg. Chim. Acta* **1980**, *39*, 211.

(14) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

Table IV. Torsion Angles/Deg in the Inner Great Rings of the Ligands in [Ni(O–tn–N–tn)Br$_2$] and [Ni(O–tn–N–tnH$_4$)Br$_2$]

	[Ni(O–tn–N–tn)Br$_2$]	[Ni(O–tn–N–tnH$_4$)Br$_2$] part a	[Ni(O–tn–N–tnH$_4$)Br$_2$] part b
C(1)′–C(1c)–C(1)–O(1)[a]	−76	88	−52
C(1c)–C(1)–O(1)–C(2)	−109	166	161
C(1)–O(1)–C(2)–C(7)	−152	−163	136
O(1)–C(2)–C(7)–C(8)	−8	−2	−1
C(2)–C(7)–C(8)–N(1)	−19	−67	67
C(7)–C(8)–N(1)–C(9)	−178	−160	162
C(8)–N(1)–C(9)–C(9c)	132	176	−177
N(1)–C(9)–C(9c)–C(9)′	74	73	−72

[a] Primes denote atoms in the symmetry-related half of the molecule [Ni(O–tn–N–tn)Br$_2$] or in the alternative part (a or b) of the molecule [Ni(O–tn–N–tnH$_4$)Br$_2$].

to nonbonding contacts. In [Ni(O–tn–N–tnH$_4$)Br$_2$], the shortest contacts to the bromine atoms are intramolecular: Br(2)···HN(1a) (2.77 Å); Br(2)···HN(1b) (2.68 Å); Br(1)···H(1c2) (2.68 Å). However for the diimine complex where the Ni–Br distances are equal, the shortest (intramolecular) contacts to bromine atoms are larger: Br(1)···H(1c2) (2.92 Å) and Br(2)···H(1a1) (3.01 Å).[15]

For the diimine complex, a crystallographic mirror plane containing C(1c), Br(1), Ni, Br(2), and C(9c) is present; the bond lengths in the macrocycle are generally similar to corresponding values in the nickel complexes of O–en–N–tnH$_4$[3,13] as well as to related parts of the macrocycle in [Ni(O–tn–N–tnH$_4$)Br$_2$]. However for the latter complex the halves of the molecule are not crystallographically equivalent and the six-membered chelate ring incorporating the two oxygen donors is unsymmetrical. There is an approximately planar arrangement of the four atoms Ni, O(1a), O(1b), and C(1a) with the chelate ring folding about O(1b)···C(1a). The distortion in this chelate ring is reflected by significantly different Ni–O and C–C bond lengths [bonds from the central carbon C(1c) of the ring] in the a and b halves of the molecule. Torsion angles between corresponding parts of the chelate ring in both halves of the molecule are also very different (Table IV).

Each of the Ni–O bond lengths in the complexes is longer than the sum of the Pauling covalent radii of octahedral nickel (1.39 Å) and oxygen (0.66 Å),[14] and this has been a common feature of nickel–ether oxygen bond lengths in other complexes.[3] A literature search revealed that such bonds show considerable variation about a mean distance (12 bonds) of 2.15 Å.[16] The lengths of the Ni–O bonds in the diimine complex thus fall very close to this mean value while both values for [Ni(O–tn–N–tnH$_4$)Br$_2$] are greater than the mean value. The unequal Ni–O bond lengths in this latter complex parallel a similar situation in [Ni(O–en–N–tnH$_4$)Cl$_2$].[3] In both of these complexes the inequalities in the vicinity of the oxygen donors probably reflect the relatively weak binding of the latter to the nickel ion. As a consequence, the oxygen donors would be able to position themselves such that a minimization of any cumulative macrocyclic-ring strain occurs. Since no similar effects are apparent in the structure of [Ni(O–tn–N–tn)Br$_2$] (the two trimethylene chelate rings incorporating the two oxygen atoms or the two nitrogen atoms both have low-energy chair conformations in this case), it might be concluded that the donor atoms in the diimine macrocycle are more ideally positioned for binding to Ni(II) than in O–en–N–tnH$_4$ or O–tn–N–tnH$_4$.

Both Ni–N bond lengths of 2.058 (9) and 2.041 (9) Å in [Ni(O–tn–N–tnH$_4$)Br$_2$] fall in the range (2.03–2.16 Å) observed for the coordinate bonds from neutral sp^3-hybridized N atoms in high-spin nickel complexes of macrocyclic ligands.[3] The Ni–N bond lengths of 2.009 (9) Å in the diimine complex show the expected shortening resulting from the presence of sp^2-hybridized nitrogens[17] and lie in the range of 1.92–2.10 Å observed for other high-spin nickel complexes of imine ligands.[18]

The sum of the bond angles about each sp^2 nitrogen is 360°; however, some deviation from the ideal of 120° occurs for individual angles. The introduction of imine linkages into the macrocyclic system results in further unsaturation in the chelate rings containing aromatic moieties, and an appreciable decrease in the O–N bite in these chelate rings occurs (Figure 2). This reduction in bite appears to be especially influenced by the shorter (double) C(8)–N(2) bond distance as well as the greater Ni–N(1)–C(8) angle in [Ni(O–tn–N–tn)Br$_2$]. In contrast the N–N and O–O bites in the remaining two chelate rings show little variation between the two structures. Thus it seems that the shorter Ni–O bond lengths in the diimine complex once again largely reflect steric dictates arising from the remaining fused rings of the coordinated macrocycle, and in particular, the smaller N–O bites of the adjacent conjugated chelate rings appear to be a major influence.

As a consequence of the effects just discussed, the hole size of the coordinated macrocycle in the diimine complex might be expected to be reduced relative to that in [Ni(O–tn–N–tnH$_4$)Br$_2$], and a similar reduction has been proposed for other cyclic systems on introduction of unsaturation.[19] The introduction of two sites of unsaturation has been shown to result in an increased ligand field toward low-spin nickel, which approximates that found for the corresponding saturated macrocycle containing one less atom in the macrocyclic ring.

For the present systems, the radius of the hole defined by the O$_2$N$_2$-donor set has been calculated as the mean distance of the donor atoms from their centroid, and the values ob-

---

(15) H(1c2) and H(1a1) are hydrogen atoms attached to C(1c) and C(1a), respectively. There is no convincing evidence that the inequality in the Ni–Br bond lengths in the diimine complex is due to H bonding. Indeed, in the related chloro complex, [Ni(O–en–N–tnH$_4$)Cl$_2$], there is a well-defined intermolecular H bond to one of the chlorine atoms, but no inequality of the Ni–Cl bonds occurs (see ref 3).

(16) The wide variation of metal–ether bond distances (1.99–2.31 Å) apparent in the literature suggests that these systems exhibit a broad, shallow potential well in their respective bond energy diagrams. High-spin nickel to ether oxygen bond lengths in both macrocyclic and nonmacrocyclic complexes were calculated from atomic parameters in the Cambridge Crystallographic Data Centre files by using the CSSR programs (see ref 5). The following references were used: Johnston, D. L.; Horrocks, W. D. *Inorg. Chem.* **1977**, *10*, 687. Prout, C. K.; Walker, C.; Rossotti, F. J. C. *J. Chem. Soc. A* **1971**, 556. Sacconi, L.; Van der Zee, J. J.; Shields, K. G.; Kennard, C. H. L. *Cryst. Struct. Commun.* **1973**, *2*, 229. Louis, R.; Metz, B.; Weiss, R. *Acta Crystallogr., Sect. B* **1974**, *B30*, 774. Lalancette, R. A.; Macchia, D. J.; Furey, W. F. *Inorg. Chem.* **1976**, *15*, 548. Bullock, J. I.; Ladd, M. F. C.; Povey, D. C. *J. Chem. Soc., Dalton Trans.* **1977**, 2242. Barnes, J. C.; Sesay, L. J.; Nicholls, B. H. *Inorg. Nucl. Chem. Lett.* **1977**, *13*, 153. Louis, R.; Agnus, Y.; Weiss, R. *Acta Crystallogr., Sect. B.* **1979**, *B35*, 2905.

(17) Because of the higher s-orbital character in the sp^2 hybrids, these are not as diffuse as sp^3 hybrids; the effective radius of the nitrogen is decreased and greater overlap occurs producing a decrease in the corresponding Ni–N distance (see: Huheey, J. E. "Inorganic Chemistry", 2nd ed.; Harper and Row: New York, 1978; p 142). In addition, with sp^2 hybridization there is a prospect of metal to ligand π-bond formation—the presence of which would further shorten the Ni–N bond.

(18) Fleischer, E. B.; Klem, E. *Inorg. Chem.* **1965**, *4*, 637. Hawkinson, S. W.; Fleischer, E. B. *Ibid.* **1969**, *8*, 2402. Johnston, D. L.; Horrocks, W. D. *Ibid.* **1971**, *10*, 687. Meyers, J. F.; Kennard, C. H. L. *J. Chem. Soc., Chem. Commun.* **1972**, 77. Richardson, M. F. *Can. J. Chem.* **1974**, *52*, 3716. Corradi, A. B.; Palmieri, C. G.; Nardelli, M.; Pelizzi, C. *J. Chem. Soc., Dalton Trans.* **1974**, 150. Sheldrick, G. M.; Stotter, D. A. *Ibid.* **1975**, 666. Alyea, E. C.; Ferguson, G.; Restivo, R. J. *Inorg. Chem.* **1975**, *14*, 2491. Lalancette, R. A.; Macchia, D. J.; Furey, W. F. *Ibid*, **1976**, *15*, 548. Boge, E. M.; Mockler, G. M.; Sinn, E. *Ibid.* **1977**, *16*, 467. Cumming, H. J.; Hall, D.; Wright, C. E. *Acta Crystallogr., Sect. B*, **1977**, *B33*, 1636. Cairns, C.; McFall, S. G.; Nelson, S. M.; Drew, M. G. B. *J. Chem. Soc., Dalton Trans.* **1979**, 446. Freyberg, D. P.; Mockler, G. M.; Sinn, E. *Inorg. Chem.* **1979**, *18*, 808.

(19) Martin, L. Y.; Sperati, C. R.; Busch, D. H. *J. Am. Chem. Soc.* **1977**, *99*, 2968. Tait, A. M.; Lovecchio, F. V.; Busch, D. H. *Inorg. Chem.* **1977**, *16*, 2206.

Table V. Radius/Å of the "Hole" Defined by the O_2N_2-Donor Set

	$[Ni(O\text{-}tn\text{-}N\text{-}tn)Br_2]$	$[Ni(O\text{-}tn\text{-}N\text{-}tnH_4)Br_2]$
N(1a)···CE[a]	2.079	2.132
N(1b)···CE	2.079	2.156
O(1a)···CE	2.067	2.137
O(1b)···CE	2.067	2.116
mean	2.07	2.14[b]

[a] The centroid of the positions of the atoms O(1a), O(1b), N(1a), and N(1b), i.e., $x_{CE} = {}^1/_4\Sigma x_{O(1a)etc}$, $y_{CE} = {}^1/_4\Sigma y_{O(1a)etc}$, and $z_{CE} = {}^1/_4\Sigma z_{O(1a)etc}$. [b] The corresponding mean value for the 15-membered ring complex $[Ni(O\text{-}en\text{-}N\text{-}tnH_4)Cl_2]$ is 2.09 Å (N···CE = 2.065 and 1.974 Å; O···CE = 2.165 and 2.157 Å). See ref 12.

tained, together with the value for the corresponding nickel chloride complex of the 15-membered ring, O–en–N–tnH_4, are listed in Table V. For the 16-membered rings, a reduction in hole size (as defined above) of 0.07 Å occurs when two imine linkages are present, and for this latter case, the radius is within 0.02 Å of the value for the 15-membered ring complex in which no imine linkages are present. However if the hole sizes obtained by the above procedure are corrected for the "modified[20] covalent radii" for sp^2 nitrogen and sp^3 nitrogen, respectively, then the difference in macrocyclic hole size seen in Table V is much less pronounced. In spite of the considerable uncertainity in the various estimated radii, the results suggest that the cavity available to the nickel ion in each 16-membered ring complex is close[21] to 1.39 Å—the literature covalent radius for this ion. Similar considerations suggest that the corresponding 15-membered macrocycle, O–en–N–tnH_4, will also provide a favorable cavity for Ni(II) in accordance with the reported structural and solution data for this system.[3,4,6]

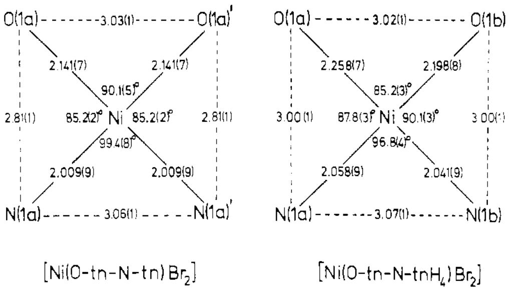


Figure 2. Comparison of bond lengths/Å and angles/deg within the donor atom planes of the macrocycles in $[Ni(O\text{–}tn\text{–}N\text{–}tn)Br_2]$ and $[Ni(O\text{–}tn\text{–}N\text{–}tnH_4)Br_2]$.

Concluding Remarks

Introduction of unsaturation into the macrocyclic ring of the present systems leads to a reduction in ring size. However, the "modified covalent radius"[20] of the sp^2 nitrogens is also smaller so that the cavity available to the nickel ion is only slightly reduced. This result emphasizes the need to allow for such effects when macrocycles are compared that contain similar donor atoms but have different patterns of unsaturation adjacent to these donor atoms. In addition, it has implications for the future design of macrocycles containing unsaturation for use as metal ion selective reagents.

Acknowledgment. H.J.G., K.H., M.M., and P.A.T. thank the Science Research Council (U.K.) for diffractometer equipment and computing facilities. L.F.L. acknowledges the Australian Research Grants Committee for support and the Australian Institute of Nuclear Science and Engineering for a travel grant.

Registry No. Ni(macrocycle **1**)Br_2, 66793-46-2; Ni(macrocycle **2**)Br_2, 52659-70-8.

Supplementary Material Available: Further details of the structure determinations together with listings of interatomic bond lengths and angles, least-squares planes and deviations, and structure factors (22 pages). Ordering information is given on any current masthead page.

---

(20) The effective radii or "modified covalent radii" of the two nitrogen atom donor types were estimated by taking the mean of respective Ni–N bond lengths for a range of high-spin nickel complexes and subtracting 1.39 Å [the Pauling covalent radius for high-spin Ni(II)] from each: a radius for sp^2 nitrogen of ~0.66 Å (based on 25 high-spin nickel–imine bonds obtained from the structures listed in ref 18) and a radius for sp^3 nitrogen of ~0.72 Å. The latter value is based on the 89 high-spin nickel to secondary amine bonds given in the following papers: Bosnich, B.; Mason, R.; Pauling, P. J.; Robertson, G. B.; Tobe, M. L. *J. Chem. Soc., Chem. Commun.* **1965**, 97. Pajunen, A.; Luukkonen, E. *Suom. Kemistil. B* **1969**, *42*, 172. Clausen, A.; Hazell, A. C. *Acta Chem. Scand.* **1970**, *24*, 2811. Biagini, S.; Cannas, M. *J. Chem. Soc. A* **1970**, 2398. Whimp, P. O.; Bailey, M. F.; Curtis, N. F. *Ibid.* **1970**, 1956. Riley, P. E.; Seff, K. *Inorg. Chem.* **1972**, *11*, 2993. Meyers, J. F.; Kennard, C. H. L. *J. Chem. Soc., Chem. Commun.* **1972**, 77–78. Curtis, N. F.; Swann, D. A.; Waters, T. N. *J. Chem. Soc., Dalton Trans.* **1973**, 1408. Guha, S. *Acta Crystallogr., Sect. B* **1973**, *B29*, 2167. Richardson, M. F. *Can. J. Chem.* **1974**, *52*, 3716. Kramarenko, F. G.; Polynova, T. N.; Porai-Koshits, M. A.; Halyi, V. P. C.; Mitrofanova, N. D. *Zh. Strukt. Khim.* **1974**, *15*, 161. Cumming, H. J.; Hall, D.; Wright, C. E. *Acta Crystallogr., Sect. B* **1977**, *B33* 1636. Zompa, L. J.; Margulis, T. N. *Inorg. Chim. Acta* **1978**, *28*, L157. Freeman, H. C.; Guss, J. M. *Acta Crystallogr., Sect. B* **1978**, *B34*, 2451. Goldberg, M. J.; Marsh, R. E. *Ibid.* **1979**, *B35*, 960. Cairns, C.; McFall, S. G.; Nelson, S. M.; Drew, M. G. B. *J. Chem. Soc., Dalton Trans.* **1979**, 446. Freyberg, D. P.; Mockler, G. M.; Sinn, E. *Inorg. Chem.* **1979**, *18*, 808. Louis, R.; Agnus, Y.; Weiss, R. *Acta Crystallogr., Sect. B* **1979**, *B35*, 2905. Margulis, T. N.; Zompa, L. J. *J. Chem. Soc., Chem. Commun.* **1979**, 430. Pavelcik, F.; Kettmann, V.; Majer, J. *Collect. Czech. Chem. Commun.* **1979**, *44*, 1070. Battaglia, L. P.; Corradi, A. B.; Mangia, A. *Inorg. Chim. Acta* **1980**, *39*, 211. Drew, M. G. B.; Hollis, S. *Acta Crystallogr., Sect. B* **1980**, *B36*, 1944. Drew, M. G. B.; Hollis, S. *Ibid.* **1980**, *36*, 2629.

(21) From the "modified covalent radii" for nitrogen given in the previous reference and a value of 0.76 Å for ether oxygen (calculated from data in ref 16) the "apparent" cavity occupied by Ni(II) was estimated to have a radius of 1.36 Å in $[Ni(O\text{–}tn\text{–}N\text{–}tn)Br_2]$ and 1.40 Å in $[Ni(O\text{–}tn\text{–}N\text{–}tnH_4)Br_2]$. The corresponding approximate value for $[Ni(O\text{–}en\text{–}N\text{–}tnH_4)Cl_2]$ is 1.35 Å. All these values are near the Pauling covalent radius of 1.39 Å for high-spin Ni(II). This concept of an "apparent" cavity, although somewhat hypothetical, nevertheless appears to be a useful indicator of the match of a metal ion for a particular macrocyclic ring. Although caution must be exercised because of the uncertainties in the various radii, the above estimates are nevertheless consistent with the results from the kinetic and thermodynamic studies on the nickel complexes of the 14- to 17-membered (diamine) macrocycles. These studies suggested that the 16-membered macrocycle provides a slightly better fit for Ni(II) than does its 15-membered analogue and that the optimum hole size may well lie between those provided by these two ring sizes (see ref 4 and 6).