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## Studies of Macrocyclic Ligand Hole Sizes. 2.<sup>1</sup> X-ray Structures of the Nickel Chloride Complexes of Analogous 15-Membered Macrocycles Containing O<sub>2</sub>N<sub>2</sub><sup>-</sup>, N<sub>4</sub><sup>-</sup>, and S<sub>2</sub>N<sub>2</sub>-Donor Sets

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X-ray diffraction structures of the nickel chloride complexes of the N<sub>4</sub>-donor and S<sub>2</sub>N<sub>2</sub>-donor macrocycles 3,4:9,10-dibenzo-1,5,8,12-tetraazacyclopentadecane (N<sub>4</sub>-mac) and 3,4:9,10-dibenzo-1,12-diaza-5,8-dithiacyclopentadecane (S<sub>2</sub>N<sub>2</sub>-mac) have been obtained and compared with the previously determined structure of the analogous complex of the O<sub>2</sub>N<sub>2</sub> macrocycle 3,4:9,10-dibenzo-1,12-diaza-5,8-dioxacyclopentadecane (O<sub>2</sub>N<sub>2</sub>-mac). All complexes contain corresponding 15-membered macrocyclic rings and show trans-chloro, pseudooctahedral coordination geometries with the X<sub>2</sub>N<sub>2</sub>-donor (X = O, N, S) sets being nearly planar. In each complex the nickel atom lies in the hole of the macrocycle, with both aromatic rings inclined to the same side of the respective donor atom planes when X = O or S and to opposite sides when X = N. A general procedure for estimating the match of a metal ion for a particular macrocyclic ring is described: the hole size given by the mean distance of the donor atom positions from their centroid is "corrected" for the mean covalent radii of the donor atom types present to yield the apparent cavity available to the metal ion. This is then compared with the covalent radius of the metal ion involved. The results for the present systems suggest that all three macrocycles fit high-spin nickel well. Even though the radius of the sulfur donors is considerably larger than those of oxygen or nitrogen, this difference appears to be largely compensated by the greater "circumference" of the inner ring in the sulfur-containing macrocycle (resulting from the pressure of four long C-S bonds) so that the cavity presented to nickel remains nearly ideal. [Ni(N<sub>4</sub>-mac)Cl<sub>2</sub>]: space group P2<sub>1</sub>/c, *a* = 12.151 (3) Å, *b* = 18.934 (6) Å, *c* = 11.253 (2) Å, β = 115.98 (8)°, *R* = 0.059 for 1459 four-circle diffraction data with *I* > 2σ(*I*). [Ni(S<sub>2</sub>N<sub>2</sub>-mac)Cl<sub>2</sub>]: space group P2<sub>1</sub>/n, *a* = 19.334 (4) Å, *b* = 13.128 (9) Å, *c* = 7.999 (1) Å, β = 99.05 (3)°, *R* = 0.032 for 4127 four-circle diffraction data with *I* > 3σ(*I*).

### Introduction

As part of a series of studies involving the design and synthesis of macrocyclic ligands of potential use as metal ion selective reagents, the solution behavior of a variety of such ligands toward a number of transition-metal ions has been investigated.<sup>3-9</sup> Particular attention has been given to a search for macrocycle hole-size discrimination effects, and for example, such effects were observed in the kinetic and thermodynamic behavior of a series of nickel complexes of 14- to 17-membered O<sub>2</sub>N<sub>2</sub>-donor macrocycles.<sup>5,6</sup> In parallel to these studies, X-ray diffraction structural determinations of selected compounds have also been performed.<sup>3,4,7,8</sup> Of particular interest have been the hole sizes of the respective macrocycles and their relationship to the observed metal ion chemistry; in these studies the radius of the hole defined by the O<sub>2</sub>N<sub>2</sub>-donor sets was calculated as the mean distance of the positions of the donor atoms from their centroid. A previous study<sup>1</sup> has shown that substitution of two imine linkages for two secondary amine linkages in the 16-membered O<sub>2</sub>N<sub>2</sub>-donor ring leads to only a very minor reduction in the cavity size available to nickel when allowance is made for the effectively smaller radius of sp<sup>2</sup> nitrogen over sp<sup>3</sup> nitrogen.

Up to the present, little structural information is available on the effects of variation of donor atom type on hole size

Table I. Crystal Data and Selected<sup>a</sup> Details of Structure Determinations of [Ni(N<sub>4</sub>-mac)Cl<sub>2</sub>] and [Ni(S<sub>2</sub>N<sub>2</sub>-mac)Cl<sub>2</sub>]

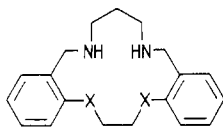
	[Ni(N <sub>4</sub> -mac)Cl <sub>2</sub> ]	[Ni(S <sub>2</sub> N <sub>2</sub> -mac)Cl <sub>2</sub> ]
mol formula <sup>b</sup>	C <sub>20</sub> H <sub>28</sub> Cl <sub>4</sub> N <sub>4</sub> Ni	C <sub>15</sub> H <sub>24</sub> Cl <sub>2</sub> N <sub>2</sub> NiS <sub>2</sub>
<i>M<sub>r</sub></i>	524.99	474.17
space group	P2 <sub>1</sub> /c	P2 <sub>1</sub> /n
<i>a</i> /Å	12.151 (3)	19.334 (3)
<i>b</i> /Å	18.934 (6)	13.128 (9)
<i>c</i> /Å	11.253 (2)	7.991 (2)
β/deg	115.98 (8)	99.05 (3)
<i>Z</i>	4	4
θ range/deg <sup>c</sup>	3-25	3-25
<i>F<sub>o</sub></i>  /σ(  <i>F<sub>o</sub></i>  ) for data used in refinement	4	6
no. of data in refinement	1459	4127
<i>R</i> = Σ   <i>F<sub>o</sub></i>   -   <i>F<sub>c</sub></i>   /Σ  <i>F<sub>o</sub></i>   <sup>d</sup>	0.059	0.032
<i>R<sub>w</sub></i> <sup>e</sup>	0.059	0.036

<sup>a</sup> Further information is available in the supplementary material, Table 1S. <sup>b</sup> The N<sub>4</sub>-mac complex contains a CH<sub>2</sub>Cl<sub>2</sub> solvate molecule. This shows complex disorder near an inversion center. Two sites are represented by atoms C(1s), Cl(1s), Cl(2s) and C(2s), Cl(3s), Cl(4s) in Table II with site occupation factors 0.59 and 0.22, respectively. A third site (occupation factor 0.19) has its C atom coincident with Cl(4s) and its Cl atoms coincident with C(2s) and with Cl(4s)', related to Cl(4s) in Table II by 1 + *x*, 1 - *y*, -*z*. Refinement with this model was accomplished by adjusting the site occupation factors for C(2s) and Cl(4s) (see Table II) to take account of the overlaid third site. <sup>c</sup> Intensity measurements were made on a Philips PW1100 diffractometer using Mo Kα radiation. <sup>d</sup> The function minimized was Σw(|*F<sub>o</sub>*| - |*F<sub>c</sub>*|)<sup>2</sup> where w = 1/(σ(*F<sub>o</sub>*))<sup>2</sup>. <sup>e</sup> *R<sub>w</sub>* = [Σw(|*F<sub>o</sub>*| - |*F<sub>c</sub>*|)<sup>2</sup>/Σw|*F<sub>o</sub>*|<sup>2</sup>]<sup>1/2</sup>.

within a given macrocyclic ligand framework. In an attempt to redress this deficiency, the X-ray structures of three high-spin nickel complexes of type [Ni(mac)Cl<sub>2</sub>] (macrocycle (mac) = 1-3) are now compared.<sup>10</sup>

- (1) Part 1: Goodwin, H. J.; Henrick, K.; Lindoy, L. F.; McPartlin, M.; Tasker, P. A. *Inorg. Chem.* **1982**, *21*, 3261.
- (2) (a) Polytechnic of North London. (b) James Cook University of North Queensland.
- (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) 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.
- (5) Lindoy, L. F.; Lip, H. C.; Rea, J. H.; Smith, R. J.; Henrick, K.; McPartlin, M.; Tasker, P. A. *Ibid.* **1980**, *19*, 3360.
- (6) Anderegg, G.; Ekstrom, A.; Lindoy, L. F.; Smith, R. J. *J. Am. Chem. Soc.* **1980**, *102*, 2670.
- (7) Ekstrom, A.; Lindoy, L. F.; Smith, R. J. *Inorg. Chem.* **1980**, *19*, 724.
- (8) Adam, K. R.; Anderegg, G.; Henrick, K.; Leong, A. J.; Lindoy, L. F.; Lip, H. C.; McPartlin, M.; Smith, R. J.; Tasker, P. A., to be submitted for publication in *Inorg. Chem.*
- (9) 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.
- (10) Lindoy, L. F.; Smith, R. J. *Inorg. Chem.* **1981**, *20*, 1314.

- (10) Details of the structure of [Ni(O<sub>2</sub>N<sub>2</sub>-mac)Cl<sub>2</sub>] have been published previously,<sup>3</sup> and a full report of the corresponding dithiocyanato complex has also appeared. See: Battaglia, L. P.; Corradi, A. B.; Mangia, A. *Inorg. Chim. Acta* **1980**, *39*, 211.



- 1, X = O ( $O_2N_2$ -mac)
- 2, X = NH ( $N_4$ -mac)
- 3, X = S ( $S_2N_2$ -mac)

### Experimental Section

Blue crystals of  $[Ni(S_2N_2\text{-mac})Cl_2]^9$  were obtained on recrystallization of this complex from methanol.  $[Ni(N_4\text{-mac})Cl_2]^{11}$  was recrystallized from dichloromethane to yield blue crystals. Crystal data and details of the structure determinations are summarized in Table I. Further details are given in the supplementary material together with additional data for  $[Ni(O_2N_2\text{-mac})Cl_2]$ . Atomic fractional coordinates and isotropic thermal parameters in the former two complexes are listed in Table II.

Hydrogen atoms attached to carbon atoms were included in calculated positions (Table 2S, supplementary material) and refined with common thermal parameters. Hydrogen atoms attached to nitrogen atoms (Table 1S, supplementary material) were inserted in positions found in difference-Fourier maps. Their positional and isotropic thermal parameters were refined for  $[Ni(S_2N_2\text{-mac})Cl_2]$ . However, only a common isotropic thermal parameter for amino hydrogens was refined for  $[Ni(N_4\text{-mac})Cl_2]$ .

### Results and Discussion

In accordance with the evidence from other physical measurements, the X-ray structural determinations indicate that the  $N_4$ -donor and  $S_2N_2$ -donor complexes have *trans*-dichloro structures, which are related to that found previously for  $[Ni(O_2N_2\text{-mac})Cl_2]$ .<sup>3</sup> In all three complexes the coordination geometries are best described as distorted octahedral (Figure 2a-c). A comparison of selected bond lengths and angles for the complexes is given in Table III and Figure 3; torsion angles in the inner great rings are compared in Table 7S (supplementary material). The distortions from octahedral symmetry are reflected by the considerable variation of bond lengths and angles, which occur about the nickel atom in each complex. The  $N_4$ -donor complex has pseudo-two-fold symmetry whereas the other two complexes show approximate mirror symmetry; the lengths of most of the chemically equivalent bonds in the two halves (a and b) of each molecule are the same within experimental error (see Table III). Exceptions to this are the Ni-O lengths in  $[Ni(O_2N_2\text{-mac})Cl_2]$  and the Ni-S lengths in  $[Ni(S_2N_2\text{-mac})Cl_2]$  where the bonds differ by 0.102 and 0.046 Å, respectively (see Figure 3). Related variations in Ni-O bond lengths were also found in the nickel bromide complex of the analogous 16-membered  $O_2N_2$  macrocycle.<sup>1,12</sup> In the ( $O_2N_2$ -mac) and ( $S_2N_2$ -mac) ligands the gauche conformation of the ethane linkage in the five-membered chelate rings coupled with the saddle-shaped conformation of the macrocycles (vide infra) require the pairs of Ni-O or Ni-S bonds to be nonequivalent. In all these mixed-donor systems, the ether and thioether donor atoms are expected to bind more weakly to nickel than the nitrogen donors. As a consequence, any cumulative ring strain in the complexes arising from the presence in each of three six-membered fused rings might be expected to be accommodated by variation of the bond lengths and/or angles in the remaining (five-membered) chelate ring incorporating the oxygen or sulfur donors. Such an effect appears to be a source of the unequal bond lengths mentioned above. In addition, the conformations of the five-membered rings in  $[Ni(O_2N_2\text{-mac})Cl_2]$  or  $[Ni(S_2N_2\text{-mac})Cl_2]$  each have an uneven distribution of the ethane bridge with respect to the

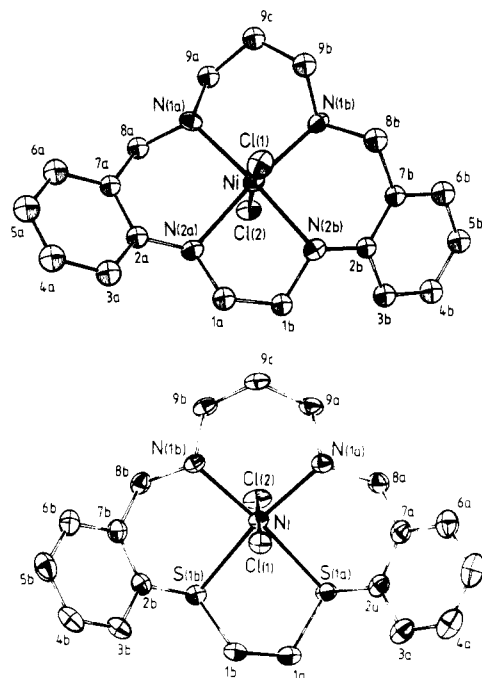


Figure 1. Views of  $[Ni(N_4\text{-mac})Cl_2]$  and  $[Ni(S_2N_2\text{-mac})Cl_2]$  showing atom labels and thermal ellipsoids (30% probability).

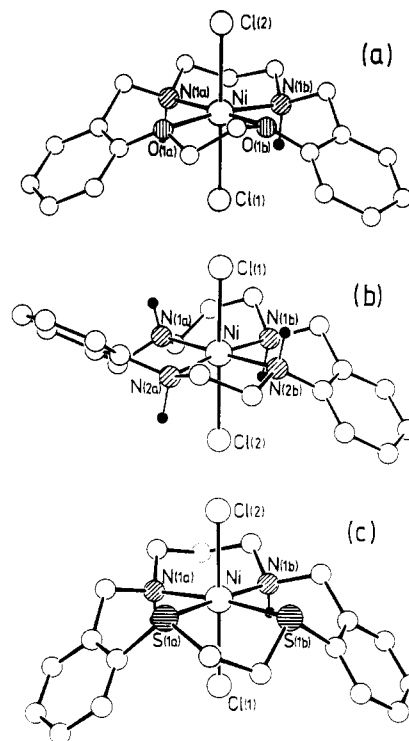


Figure 2. Comparative views of the macrocycle conformations in (a)  $[Ni(O_2N_2\text{-mac})Cl_2]$ , (b)  $[Ni(N_4\text{-mac})Cl_2]$ , and (c)  $[Ni(S_2N_2\text{-mac})Cl_2]$ .

donor atom planes of the respective macrocycles. Each bridge is bent away from the normal gauche arrangement toward an envelope conformation. In contrast, the five-membered ring in  $[Ni(N_4\text{-mac})Cl_2]$  is much closer to a regular gauche arrangement.

The axial Ni-Cl bonds in the ( $S_2N_2$ -mac) complex show a small but significant difference in length. The longer bond is observed for Cl(1), which experiences the shortest intramolecular contacts: Cl(1)⋯H(1Na), 2.60; Cl(1)⋯H(1Nb), 2.70; Cl(1)⋯H(1b2), 2.77 Å; cf. Cl(2)⋯H(9b1), 2.85 Å. A similar situation was reported<sup>1</sup> for nonequivalent *trans* Ni-Br

(11) Owston, P. G.; Peters, R.; Tasker, P. A., unpublished work.

(12) Even greater variations of metal-ether oxygen bond lengths occur in *cis* complexes of related ligands. See: Armstrong, L. G.; Lindoy, L. F.; McPartlin, M.; Mockler, G. M.; Tasker, P. A. *Inorg. Chem.* **1977**, *16*, 1665. Lalancette, R. A.; Macchia, D. J.; Furey, W. F. *Ibid.* **1976**, *15*, 548.

**Table II.** Fractional Atomic Coordinates and Thermal Parameters/ $\text{\AA}^2$  for  $[\text{Ni}(\text{N}_4\text{-mac})\text{Cl}_2]$  and  $[\text{Ni}(\text{S}_2\text{N}_2\text{-mac})\text{Cl}_2]$ 

atom	x	y	z	$U(\text{iso})$ or $U(\text{eq})$
[Ni(N <sub>4</sub> -mac)Cl <sub>2</sub> ]				
Ni(1)	0.09036 (14)	0.15576 (8)	0.24698 (16)	0.0327 (8)
Cl(1)	0.1925 (3)	0.1421 (2)	0.4893 (3)	0.052 (2)
Cl(2)	-0.0147 (3)	0.1532 (1)	0.0029 (3)	0.042 (2)
N(1a)	-0.0078 (8)	0.2419 (5)	0.2589 (8)	0.033 (6)
N(2a)	-0.0509 (8)	0.0829 (4)	0.2357 (9)	0.037 (6)
N(1b)	0.2288 (8)	0.2192 (4)	0.2418 (9)	0.037 (6)
N(2b)	0.1842 (8)	0.0610 (4)	0.2429 (8)	0.032 (6)
C(1a)	0.0087 (11)	0.0135 (6)	0.2717 (12)	0.044 (3)
C(2a)	-0.1292 (10)	0.1016 (6)	0.2942 (11)	0.039 (3)
C(3a)	-0.1647 (11)	0.0538 (6)	0.3645 (11)	0.051 (3)
C(4a)	-0.2438 (11)	0.0750 (6)	0.4178 (13)	0.057 (4)
C(5a)	-0.2850 (11)	0.1416 (6)	0.4025 (12)	0.058 (4)
C(6a)	-0.2494 (10)	0.1915 (6)	0.3356 (12)	0.052 (4)
C(7a)	-0.1733 (10)	0.1726 (5)	0.2762 (11)	0.038 (3)
C(8a)	-0.1393 (10)	0.2262 (6)	0.2010 (11)	0.042 (3)
C(9a)	0.0176 (10)	0.3051 (5)	0.1998 (11)	0.044 (3)
C(9c)	0.1445 (9)	0.3339 (6)	0.2777 (11)	0.045 (3)
C(9b)	0.2505 (10)	0.2814 (6)	0.3310 (12)	0.049 (3)
C(1b)	0.0939 (9)	0.0029 (5)	0.2099 (11)	0.041 (3)
C(2b)	0.2587 (10)	0.0626 (6)	0.1704 (11)	0.036 (3)
C(3b)	0.2504 (10)	0.0101 (6)	0.0814 (12)	0.045 (3)
C(4b)	0.3207 (11)	0.0140 (6)	0.0121 (12)	0.052 (4)
C(5b)	0.3985 (11)	0.0698 (6)	0.0355 (12)	0.052 (3)
C(6b)	0.4092 (11)	0.1227 (6)	0.1231 (12)	0.052 (3)
C(7b)	0.3367 (10)	0.1197 (6)	0.1903 (6)	0.038 (3)
C(8b)	0.3471 (10)	0.1803 (6)	0.2858 (12)	0.049 (3)
C(1s) <sup>a</sup>	-0.4649 (21)	0.3656 (13)	0.2721 (25)	0.058 (7)
Cl(1s) <sup>a</sup>	-0.4130 (9)	0.3722 (6)	0.1501 (11)	0.144 (4)
Cl(2s) <sup>a</sup>	-0.4207 (7)	0.3398 (4)	0.3871 (8)	0.101 (2)
C(2s) <sup>a</sup>	-0.5143 (23)	0.4229 (13)	0.1948 (27)	0.124 (9)
Cl(3s) <sup>a</sup>	-0.4459 (28)	0.3477 (17)	0.2220 (34)	0.139 (11)
Cl(4s) <sup>a</sup>	-0.4955 (11)	0.4645 (5)	0.0480 (11)	0.125 (4)
[Ni(S <sub>2</sub> N <sub>2</sub> -mac)Cl <sub>2</sub> ]				
Ni	0.19433 (1)	0.18633 (2)	-0.10657 (3)	0.0307 (1)
Cl(1)	0.18409 (3)	0.05734 (4)	0.11032 (7)	0.0388 (3)
Cl(2)	0.20368 (4)	0.31382 (4)	-0.32211 (8)	0.0511 (4)
S(1a)	0.12648 (3)	0.31748 (5)	0.02249 (8)	0.0395 (3)
S(1b)	0.29038 (3)	0.26935 (4)	0.07769 (8)	0.0377 (3)
N(1a)	0.1028 (1)	0.1232 (1)	-0.2379 (2)	0.036 (1)
N(1b)	0.2610 (1)	0.0849 (1)	-0.2046 (2)	0.034 (1)
C(1b)	0.2474 (1)	0.2892 (2)	0.2634 (3)	0.049 (1)
C(2b)	0.3487 (1)	0.1673 (2)	0.1403 (3)	0.036 (1)
C(3b)	0.3779 (1)	0.1518 (2)	0.3098 (3)	0.043 (1)
C(4b)	0.4281 (1)	0.0770 (2)	0.3504 (4)	0.052 (2)
C(5b)	0.4490 (1)	0.0182 (2)	0.2256 (4)	0.056 (2)
C(6b)	0.4183 (1)	0.0310 (2)	0.0583 (4)	0.051 (1)
C(7b)	0.3679 (1)	0.1065 (2)	0.0117 (3)	0.040 (1)
C(8b)	0.3355 (1)	0.1173 (2)	-0.1720 (3)	0.043 (1)
C(9b)	0.2396 (1)	0.0618 (2)	-0.3874 (3)	0.043 (1)
C(9c)	0.1668 (1)	0.0192 (2)	-0.4277 (3)	0.044 (1)
C(1a)	0.1846 (1)	0.3550 (2)	0.2150 (3)	0.053 (2)
C(2a)	0.0554 (1)	0.2451 (2)	0.0758 (3)	0.040 (1)
C(3a)	0.0333 (1)	0.2494 (2)	0.2328 (4)	0.052 (1)
C(4a)	-0.0277 (2)	0.1985 (2)	0.2564 (4)	0.063 (2)
C(5a)	-0.0654 (2)	0.1432 (2)	0.1274 (4)	0.064 (2)
C(6a)	-0.0421 (1)	0.1365 (2)	-0.0286 (4)	0.054 (2)
C(7a)	0.0179 (1)	0.1885 (2)	-0.0567 (3)	0.042 (1)
C(8a)	0.0385 (1)	0.1847 (2)	-0.2318 (3)	0.043 (1)
C(9a)	0.1074 (1)	0.0926 (2)	-0.4150 (3)	0.045 (1)

<sup>a</sup> Site occupation factors for these atoms are given in Table I.

bonds in a complex of a related 16-membered ring.

In all three complexes the four donor atoms of the respective macrocycles are close to planar. The maximum deviation of the nitrogen atoms from the equatorial plane in  $[\text{Ni}(\text{N}_4\text{-mac})\text{Cl}_2]$  is 0.06 Å. For the  $\text{O}_2\text{N}_2$  and  $\text{S}_2\text{N}_2$  systems the maximum deviations of the donor atoms are 0.06 and 0.05 Å, respectively.

The Ni-N bond lengths in the three complexes (Figure 3) all fall within the range of 2.03–2.16 Å observed for the co-

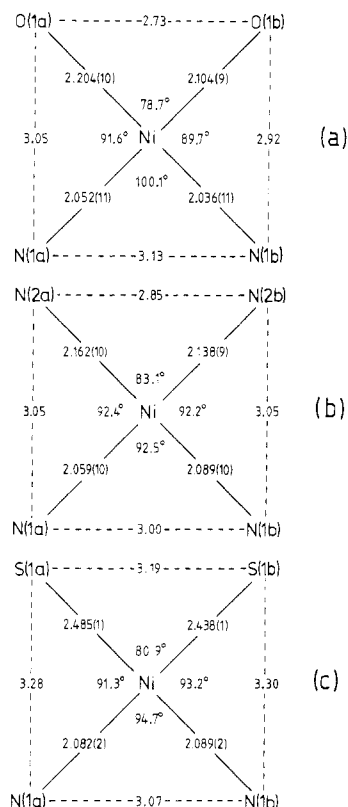
**Table III.** Selected<sup>a</sup> Bond Lengths/Å and Angles/Deg in the Complexes  $[\text{Ni}(\text{N}_4\text{-mac})\text{Cl}_2]$  and  $[\text{Ni}(\text{S}_2\text{N}_2\text{-mac})\text{Cl}_2]$ 

	[Ni(N <sub>4</sub> -mac)Cl <sub>2</sub> ] X = N(2a) or N(2b)		[Ni(S <sub>2</sub> N <sub>2</sub> -mac)Cl <sub>2</sub> ] X = S(1a) or S(1b)	
	part a	part b	part a	part b
Distances <sup>b</sup>				
Ni-Cl(1)	2.465 (3)		2.453 (1)	
Ni-Cl(2)	2.471 (3)		2.429 (1)	
Ni-N(1)	2.059 (10)	2.089 (10)	2.082 (2)	2.089 (2)
Ni-X	2.162 (10)	2.138 (9)	2.485 (1)	2.438 (1)
C(1)-C(1)'	1.49 (2)		1.491 (4)	
C(1)-X	1.47 (1)	1.48 (1)	1.824 (3)	1.830 (3)
X-C(2)	1.42 (2)	1.46 (2)	1.777 (3)	1.771 (2)
C(2)-C(7)	1.43 (2)	1.39 (2)	1.399 (3)	1.397 (3)
C(7)-C(8)	1.49 (1)	1.54 (2)	1.514 (4)	1.509 (3)
C(8)-N(1)	1.47 (1)	1.49 (2)	1.490 (3)	1.486 (3)
N(1)-C(9)	1.47 (2)	1.49 (2)	1.487 (3)	1.486 (3)
C(9)-C(9c)	1.50 (1)	1.53 (2)	1.515 (3)	1.502 (4)
Angles <sup>b</sup>				
Cl(1)-Ni-Cl(2)	172.8 (1)		179.6 (1)	
Cl(1)-Ni-X	90.0 (3)		94.5 (1)	
Cl(1)-Ni-N(1)	92.1 (3)	85.5 (3)	85.7 (1)	87.0 (1)
Cl(2)-Ni-X	84.9 (3)	88.9 (2)	85.4 (1)	89.2 (1)
Cl(2)-Ni-N(1)	93.2 (2)	90.6 (3)	93.9 (1)	93.1 (1)
X-Ni-X'	83.1 (4)		80.9 (1)	
X-Ni-N(1)	92.4 (4)	92.2 (4)	91.3 (1)	93.2 (1)
X-Ni-N(1)'	173.6 (4)	174.9 (4)	173.9 (1)	171.3 (1)
N(1)-Ni-N(1)'	92.5 (4)		94.7 (1)	
C(1)-C(1)-X	111 (1)	111.9 (9)	115.5 (2)	109.1 (2)
C(1)-X-Ni	105.8 (7)	106.5 (7)	104.0 (1)	98.8 (1)
C(1)-X-C(2)	116 (1)	116.7 (9)	109.8 (1)	103.2 (1)
C(2)-X-Ni	119.7 (7)	117.4 (6)	102.0 (1)	102.9 (1)
X-C(2)-C(7)	117 (1)	118 (1)	115.5 (2)	117.1 (2)
C(2)-C(7)-C(8)	123 (1)	122 (1)	122.5 (2)	122.9 (2)
C(7)-C(8)-N(1)	113.8 (8)	111.3 (8)	113.0 (2)	112.7 (2)
C(8)-N(1)-Ni	111.1 (6)	112.1 (7)	114.6 (1)	113.0 (1)
C(8)-N(1)-C(9)	111.6 (8)	107.8 (7)	110.7 (2)	110.0 (2)
C(9)-N(1)-Ni	112.0 (8)	109.9 (8)	114.4 (2)	114.0 (1)
N(1)-C(9)-C(9c)	113.4 (8)	112.3 (8)	113.2 (2)	113.1 (2)
C(9)-C(9c)-C(9)'	117.8 (9)		116.3 (2)	

<sup>a</sup> Complete lists of bond lengths and angles are given in the supplementary material (Tables 4S and 5S). <sup>b</sup> Primes denote atoms from the alternative part of the molecule. Atom C(9c) is the central atom of the trimethylene bridge.

ordinate bonds from neutral  $sp^3$ -hybridized N atoms in high-spin nickel complexes of macrocyclic ligands.<sup>3</sup> In each complex, the corresponding pairs of Ni-N bonds are equal within experimental error. In  $[\text{Ni}(\text{N}_4\text{-mac})\text{Cl}_2]$  the nickel is closer to the benzylamino nitrogens, N(1a) and N(1b), than to the anilino nitrogens, N(2a) and N(2b). The difference of 0.07 Å between the lengths (mean values) of the two Ni-N bond types appears to be a consequence of the smaller chelate ring containing N(2a) and N(2b), which defines a relatively unfavorable N-Ni-N bond angle ( $82^\circ$ ). A related situation exists in the other two complexes, where the angles subtended by the donor atoms of each five-membered chelate ring at nickel are both considerably less than  $90^\circ$ . In the  $\text{O}_2\text{N}_2$ - and  $\text{S}_2\text{N}_2$ -donor complexes the O-Ni and S-Ni bond lengths each fall in the respective ranges of 1.99–2.31 Å (Ni-O)<sup>1</sup> and 2.38–2.53 Å (Ni-S),<sup>13</sup> found for related bonds to high-spin

- (13) Loub, J.; Podlahova, J. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 409. Podlahova, J.; Loub, J.; Novak, C. *Acta Crystallogr., Sect. B* **1972**, *28*, 1623. Louis, R.; Metz, B.; Weiss, R. *Ibid.* **1974**, *30*, 774. Obodovskaya, A. E.; Shkol'nikova, L. M.; Zavodnik, V. E.; Annev, N. V. R.; Kochin, S. G.; Kogan, V. A.; Osipov, O. A. *Koord. Khim.* **1976**, *2*, 197. Delaunay, J.; Kappenstein, C.; Hugel, R. *Acta Crystallogr., Sect. B* **1976**, *32*, 2341. Boge, E. M.; Mockler, G. M.; Sinn, E. *Inorg. Chem.* **1977**, *16*, 467. Delaunay, J.; Kappenstein, C.; Hugel, R. P. *J. Chem. Res., Miniprint* **1978**, *48*, 801. Keturah, C.; Tasker, P. A.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1978**, 1057. Choong, W.; Stephenson, N. C.; Ali, M. A.; Malik, M. A.; Phillips, D. J. *Aust. J. Chem.* **1979**, *32*, 1199. Louis, R.; Agnus, Y.; Weiss, R. *Acta Crystallogr., Sect. B* **1979**, *35*, 2905.



**Figure 3.** Comparison of bond lengths/Å and angles/deg within the donor atom planes of the macrocycles in (a)  $[\text{Ni}(\text{O}_2\text{N}_2\text{-mac})\text{Cl}_2]$ , (b)  $[\text{Ni}(\text{N}_4\text{-mac})\text{Cl}_2]$ , and (c)  $[\text{Ni}(\text{S}_2\text{N}_2\text{-mac})\text{Cl}_2]$ . The esd's for ligand bites and bond angles in parts a, b, and c are  $\leq 0.01$ ,  $\leq 0.01$ ,  $\leq 0.004$  Å and  $\leq 0.5$ ,  $\leq 0.4$ ,  $\leq 0.1^\circ$ , respectively.

**Table IV.** Calculated Values for the Hole Sizes of the Coordinated Macrocycles

complex	$D/\text{Å}$ , diameter of macrocyclic hole (uncorrected) <sup>a</sup>	$R_A/\text{Å}$ , "apparent" radius of metal ion cavity <sup>b</sup>
$[\text{Ni}(\text{O}_2\text{N}_2\text{-mac})\text{Cl}_2]^c$	4.18	1.35 <sup>d</sup>
$[\text{Ni}(\text{N}_4\text{-mac})\text{Cl}_2]$	4.22	1.39
$[\text{Ni}(\text{S}_2\text{N}_2\text{-mac})\text{Cl}_2]$	4.54	1.39

<sup>a</sup> Calculated as twice the mean distance of the donor atom positions from their centroid. <sup>b</sup> Derived from the calculated diameter by correcting for the mean of the covalent radii of the donor atoms present, i.e.,  $R_A = D/2 - \bar{r}_x$ , where  $r_x$  = "modified covalent radius" of donor(s) calculated from data in the Cambridge Crystallographic Data Centre files (see text and ref 20). <sup>c</sup> Identical values were obtained for  $[\text{Ni}(\text{O}_2\text{N}_2\text{-mac})(\text{NCS})_2]$ . <sup>d</sup> The Pauling radius for high-spin Ni(II) is 1.39 Å.

nickel in other complexes.

The macrocycles in the  $\text{O}_2\text{N}_2$  and  $\text{S}_2\text{N}_2$  complexes both have a "saddle-shaped" configuration (see Figure 2). This "saddle-shaped" distortion from planarity is more marked in the  $\text{S}_2\text{N}_2$  complex in which the benzylamino chelate rings are inclined at 19 and 17° to the same side of the coordination plane (cf. 13 and 11° on the  $\text{O}_2\text{N}$  complex),<sup>14,15</sup> and the aliphatic chelate rings are inclined at 19 and 16° to the other side of the coordination plane (cf. 8 and 11° on the  $\text{O}_2\text{N}_2$  complex).<sup>14</sup> In these two complexes, the hydrogen atoms

attached to the two nitrogens forming the six-membered trimethylene chelate ring are orientated toward the same side of the chelate ring, and a chair conformation occurs in each case.

In contrast, in the coordinated macrocycle in  $[\text{Ni}(\text{N}_4\text{-mac})\text{Cl}_2]$ , the hydrogen atoms attached to adjacent nitrogen donors fall alternatively on opposed sides of the donor atom plane. This gives rise to a "skew-boat"<sup>16</sup> conformation for the six-membered chelate ring incorporating N(1a) and N(1b) and leads to the benzylamino chelate rings adopting a "step-shaped"<sup>17</sup> configuration, being inclined at 8 and 11° to opposite sides of the coordination plane. The different conformations of the aliphatic bridges in the three complexes are manifest by the different torsion angles (Table 7S (supplementary material)), particularly about the C(1)-X and C(9)-C(9c) bonds.

A comparison of the respective macrocycle donor atom planes is given in Figure 3. The relative macrocyclic hole sizes, calculated as twice the mean distance of the donor atoms from their centroid, are tabulated in Table IV. It is apparent that the hole sizes in the  $\text{O}_2\text{N}_2$  and  $\text{N}_4$  systems are quite similar, and this is not unexpected in view of the similarity of the covalent radii of oxygen and nitrogen. Defined in this way, the hole size in the  $\text{S}_2\text{N}_2$  system is much larger, and this can in part be ascribed to the larger covalent radius of thioether sulfur, which leads to the introduction of four long sulfur-carbon bonds in the macrocyclic ring. Relative to the mean C(1)-O and mean C(2)-O bond lengths in  $[\text{Ni}(\text{O}_2\text{N}_2\text{-mac})\text{Cl}_2]$ , the corresponding mean C-S bond lengths in  $[\text{Ni}(\text{S}_2\text{N}_2\text{-mac})\text{Cl}_2]$  are longer by 0.37 and 0.41 Å, respectively, in good agreement with the difference of 0.38 Å between the Pauling covalent radii<sup>18</sup> for sulfur (1.04 Å) and oxygen (0.66 Å). Thus the "circumference" of the macrocyclic great ring is effectively increased, and this is reflected by the larger bites of the chelate rings containing sulfur donors (Figure 3).

Since the nonequivalent donor atoms in the three macrocycles have different covalent radii, it is clearly not appropriate to compare directly the hole sizes given in Table IV when attempting to predict the "fit" of each ring for the nickel ion. Allowance for the respective donor atom radii must first be made. Estimates of the required radii have been obtained: data in the Cambridge Crystallographic Data Centre files (accessed via the CSSR programs)<sup>19</sup> were used to obtain the mean lengths of bonds between high-spin nickel and ether, thioether, and secondary-amine donor functions, and 1.39 Å (the Pauling covalent radius of nickel)<sup>18</sup> was subtracted from each mean. The following values were obtained: O, 0.76 Å (based on 12 bonds);<sup>1</sup> N(sp<sup>3</sup>), 0.72 Å (based on 89 bonds);<sup>1</sup> S, 1.05 Å (based on 17 bonds).<sup>13</sup> Since these "modified covalent-radii" values are derived solely from high-spin nickel complexes containing donor types similar to those in the complexes under study, their use for hole-size estimation was considered more appropriate than any of the published covalent radii.<sup>20</sup>

(16) Buckingham, D. A.; Sargeson, A. M. *Top. Stereochem.* **1971**, *6*, 219.  
 (17) The very different macrocycle conformations in  $[\text{Ni}(\text{N}_4\text{-mac})\text{Cl}_2]$  and  $[\text{Ni}(\text{O}_2\text{N}_2\text{-mac})\text{Cl}_2]$  or  $[\text{Ni}(\text{S}_2\text{N}_2\text{-mac})\text{Cl}_2]$  parallel similar conformational differences observed by X-ray for a number of transition-metal complexes of the related, open-chain tetradentate ligand *N,N'*-ethylenebis(salicylideneaminato). For this latter ligand system, the frequency with which both structural types occur strongly suggests that the energy difference between them is small. The ethylene bridge between the two sp<sup>2</sup> nitrogen atoms has an envelope conformation when the complex has a symmetrical saddle (or umbrella) shape but a gauche conformation when a symmetrical stepped geometry occurs. See: Calligaris, M.; Nardin, G.; Randaccio, L. *Coord. Chem. Rev.* **1972**, *7*, 385. Maslen, H. S.; Walters, T. N. *Ibid.* **1975**, *17*, 137.

(18) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960.  
 (19) Details are given in ref 4.

(14) Similar values are observed<sup>10</sup> in  $[\text{Ni}(\text{O}_2\text{N}_2\text{-mac})(\text{NCS})_2]$ .

(15) Angles of the benzene rings a and b to the respective macrocycle donor planes:  $[\text{Ni}(\text{O}_2\text{N}_2\text{-mac})\text{Cl}_2]$ , 38 and 39°;  $[\text{Ni}(\text{S}_2\text{N}_2\text{-mac})\text{Cl}_2]$ , 51 and 49°;  $[\text{Ni}(\text{N}_4\text{-mac})\text{Cl}_2]$ , 33 and 41°.

For an estimation of a radius for the cavity occupied by the nickel in each complex, a general procedure of subtracting the mean of the "modified covalent radii" of all the donor atoms from the uncorrected radius of the macrocyclic hole was employed. While obviously such a procedure has its limitations, it does have the virtue of being applicable to a range of macrocyclic complexes and allows comparisons even when different types and/or numbers of donor atoms are present or irregular coordination geometries occur.<sup>21</sup> No other simple semiquantitative procedure for comparing the hole sizes from crystallographic data in such complexes appears to have been proposed previously.

The radii ( $R_A$ ) of the apparent cavities occupied by nickel, for each of the present complexes calculated as above, are listed in Table IV. Both the  $N_4$ - and  $S_2N_2$ -donor complexes give values that are identical with the Pauling radius for octahedral nickel of 1.39 Å while the value of 1.35 Å for the  $O_2N_2$ -donor complex is only slightly less than this radius.<sup>22</sup> It is apparent that the cavities in all three macrocyclic complexes are close to ideal for high-spin nickel. Previously it has been postulated that, along a series of saturated tetraaza macrocycles of increasing ring size, it is the 15-membered macrocycle that will provide the ring of best fit for high-spin nickel.<sup>23</sup> Hence, it is not unexpected that the present 15-membered  $N_4$  macrocycle also provides a ring of nearly optimum size for this ion, especially since the X-ray structural data confirm the absence of any major strain in the various chelate rings of the nickel complex.

Since the hole size in the free  $O_2N_2$  macrocycle in a "planar" configuration has been shown to be the same as that in  $[Ni(O_2N_2\text{-mac})Cl_2]$  and  $[Ni(O_2N_2\text{-mac})NCS_2]$ ,<sup>21</sup> it seems unlikely that undue strain is present in the chelated rings of

this macrocycle even though some conformational changes do occur on coordination. Indeed, along the series of 14- to 17-membered  $O_2N_2$  macrocycles, both the kinetic and thermodynamic stabilities of the nickel complexes reach a maximum at the 16-membered macrocycle although the values for the 15-membered ring system are only slightly lower.<sup>5,6</sup> This evidence suggests that both ring sizes fit high-spin nickel well, with the optimum hole size perhaps falling between the holes provided by these two ring sizes.

Clearly, for  $[Ni(S_2N_2\text{-mac})Cl_2]$ , the cavity occupied by nickel is again nearly ideal. However, whether the hole size occurring in the macrocycle corresponds to the "natural" (that is, least strained) value or whether some ring expansion (with an accompanying increase in energy) has occurred on incorporation of the nickel atom is difficult to answer in the absence of other studies. Nevertheless, there is little evidence for the presence of marked additional chelate ring strain in this complex, and this suggests that the enlarged macrocyclic ring "circumference"<sup>24</sup> discussed previously is quite effective in compensating for the larger covalent radii of the sulfur donors.

### Concluding Remarks

The procedure described provides a means of obtaining a generalized picture of hole sizes in macrocyclic systems for comparison purposes. Although it may well be of wider applicability, its use for comparing the present closely related macrocyclic complexes seems particularly appropriate. The results indicate that substitution of two ether oxygens or two thioether sulfurs for two  $sp^3$  nitrogens in the 15-membered  $N_4$  macrocycle gives new macrocycles that are also capable of providing nearly ideal cavities for high-spin nickel(II). Although such cavities could differ from the "natural" hole in the metal-free system, there is little evidence that this is an important consideration for the present complexes.

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**Registry No.**  $Ni(N_4\text{-mac})Cl_2$ , 82891-97-2;  $Ni(S_2N_2\text{-mac})Cl_2$ , 76137-02-5.

**Supplementary Material Available:** Further details of the structure determinations together with listings of interatomic bond lengths and angles, least-squares planes and deviations, structure factors, and data for  $[Ni(O_2N_2\text{-mac})Cl_2]$  additional to those published previously<sup>3</sup> (50 pages). Ordering information is given on any current masthead page.

- (20) The "modified covalent-radius" values obtained for N (0.72 Å) and S (1.05 Å) are quite close to the corresponding Pauling covalent radii of 0.70 and 1.04 Å whereas the value for O (0.76 Å) is larger than the Pauling radius of 0.66 Å. The latter value was originally derived from carbon-oxygen bond lengths in organic compounds. However, all three radii correspond reasonably well to other values (based solely on bond lengths in compounds containing homonuclear bonds) of 0.74 (for both O and N) and 1.04 Å (for S). See: Sharpe, A. G. "Inorganic Chemistry"; Longmans, Green and Co.: New York, 1980; pp 127-129.
- (21) Tasker, P. A.; Trotter, J.; Lindoy, L. F. *J. Chem. Res., Miniprint* **1981**, 3834.
- (22) An alternative procedure involving subtraction of the donor atoms' "modified covalent radii" from the corresponding observed metal-donor bond lengths and then taking the mean value of the lengths, which remains as the radius ( $R$ ) of the metal ion cavity, gives virtually identical results:  $[Ni(O_2N_2\text{-mac})Cl_2]$ ,  $R = 1.36$  Å;  $[Ni(N_4\text{-mac})Cl_2]$ ,  $R = 1.39$  Å;  $[Ni(S_2N_2\text{-mac})Cl_2]$ ,  $R = 1.38$  Å. However, this procedure is not applicable to metal-free macrocycles. In contrast, the procedure outlined in the main text does not suffer from this disadvantage and thus allows direct comparison of the hole sizes in metal-free macrocycles and their metal complexes.
- (23) Busch, D. H. *Acc. Chem. Res.* **1978**, *11*, 392 and references therein.

- (24) As evidenced by the increased donor atom bites involving the sulfur donors.