Inorg. Chem. **1989**, *28*, 4531-4535 **4531**

Acknowledgment. This work was supported by the National Science Foundation. We thank Rhenium Alloys, Inc., for material support, Scott Horn for technical assistance, and Todd Johnson for a skilled contribution at a critical moment.

Registry No. $ReH_3(PMe_2Ph)_4$, 79245-24-2; $ReCl_3(PMe_2Ph)_3$, 15613-32-8; $[ReH_4(PMe_2Ph)_4]BF_4$, 123674-41-9; PhCCPh, 501-65-5; CH_3CN, 75-05-8; CO, 630-08-0; D_2, 7782-39-0; $[HNEt_3]Br$, 636-70-4; ethylene, 74-85-1.

Supplementary Material Available: Listings of anisotropic thermal parameters (Table S1) and full crystallographic data (Table S2) (3 pages); a listing of observed and calculated structure factors (Table S3) (10 pages). Ordering information is given on any current masthead page.

Contribution from the Research School of Chemistry, Australian National University, Canberra,
Australia Capital Territory 2601, Australia, and School of Chemistry,
Macquarie University, Sydney, New South Wales 2109, Australia

Synthesis and Structural Studies of Nickel(II) Complexes of 14-Membered *trans*-N_2O_2 and *trans*-N_2S_2 Quadridentate Macrocycles

Paul A. Duckworth,[†] Frederick S. Stephens,[‡] Kevin P. Wainwright,[†,§] K. D. V. Weerasuria,[†]
and S. Bruce Wild*,[†]

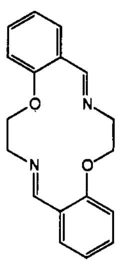
Received May 1, 1989

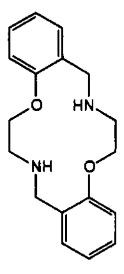
Triphenylphosphine reacts with 2-(2-azidoethoxy)benzaldehyde in an aza-Wittig reaction to give a 98% yield of the unsaturated 14-membered *trans*-N_2O_2 diimine macrocycle 6,7,15,16-tetrahydrodibenzo[*f*,*m*][1,8,4,11]dioxadiazacyclotetradecine (**1**), presumably via seven-membered 2,3-dihydro-1,4-benzoxazepine (**7**). Reduction of diimine **1** with lithium aluminum hydride gives the *trans*-N_2O_2 diamine macrocycle 6,7,8,9,15,16,17,18-octahydrodibenzo[*f*,*m*][1,8,4,11]dioxadiazacyclotetradecine (**2**). The structure of $[NiCl_2(\mathbf{2})]$ has been determined by X-ray diffraction. The dichloronickel(II) complex of the corresponding *trans*-N_2S_2 macrocycle 6,7,8,9,15,16,17,18-octahydrodibenzo[*f*,*m*][1,8,4,11]dithiadiazacyclotetradecine (**4**) has also been prepared and structurally characterized. For $[NiCl_2(\mathbf{2})]$ at −150 °C: space group $P\bar{1}$ (No. 2), $a = 9.092$ (4) Å, $b = 9.803$ (4) Å, $c = 10.431$ (4) Å, $\alpha = 92.34$ (3)°, $\beta = 104.34$ (3)°, $\gamma = 97.31$ (3)°, $Z = 2$, $R = 0.044$ for 1309 data with $I > 3\sigma(I)$. For $[NiCl_2(\mathbf{4})]\cdot 0.5H_2O$ at −150 °C: space group $P2_1/n$ (nonstandard No. 14), $a = 8.901$ (2) Å, $b = 12.031$ (3) Å, $c = 19.120$ (5) Å, $\beta = 98.50$ (2)°, $Z = 4$, $R = 0.046$ for 1712 data with $I > 3\sigma(I)$. In octahedral $[NiCl_2(\mathbf{2})]$ the arrangement of the macrocyclic donor atoms around the metal ion is approximately square planar. In $[NiCl_2(\mathbf{4})]\cdot 0.5H_2O$ the *trans*-N_2S_2 ligand adopts a folded conformation with the metal ion situated outside of the binding cavity. These structures suggest that the binding cavity of the *trans*-N_2S_2 macrocycle is smaller than that of the *trans*-N_2O_2 ligands, in contrast to the situation for similar *cis*-N_2X_2 macrocycles.

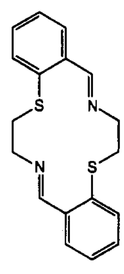
Introduction

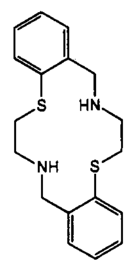
Structural, kinetic, thermodynamic, and spectroscopic studies on a variety of macrocyclic complexes of nickel(II) have shown that there is a correlation between the radius of the binding cavity of the macrocycle and the covalent radius of the metal ion.[1-4] In particular, studies of quadridentate macrocycles with N_2X_2 (X = N, O, S) donor atom sets have demonstrated that high-spin nickel(II) is best accommodated by macrocyclic rings containing 15 or 16 atoms and that 14-membered rings are the minimum size for the ion.[1,2] Those studies estimated the binding cavity radius (R_A in Figure 1) of a macrocycle in its planar chelating conformation by subtracting the mean value of the radii of the donor atoms from the mean of the centroid–donor atom distances (R_H in Figure 1).[5] It is apparent from Figure 1, however, that the binding cavities of *trans*-N_2X_2 macrocycles will be smaller than the cavities of similar *cis*-N_2X_2 macrocycles when the radii of the X donors are larger than the radii of the N donors. A better estimate of R_H in *trans*-N_2X_2 macrocycles would be obtained by considering the centroid–X donor bond distances only. This point has not been adequately investigated hitherto because of the small number of *trans*-N_2X_2 macrocycles available.

We have recently reported the syntheses of 14- and 16-membered dibenzo-substituted *trans*-N_2S_2[6,7] and *trans*-As_2N_2[8] macrocycles. We now describe a convenient synthesis of the corresponding *trans*-N_2O_2 macrocycles **1** and **2** and the crystal and molecular structure of $[NiCl_2(\mathbf{2})]$. For comparison we have also prepared $[NiCl_2(\mathbf{4})]\cdot 0.5H_2O$ and determined its structure. Since the crystal and molecular structures of the dichloronickel(II) complexes of the cis analogues of **2** and **4** are known,[3,9] we were therefore able to compare the relative merits of the two types of chelating agents for the nickel(II) ion.


1


2


3


4

Results and Discussion

Syntheses. The diiodonickel(II) complex of the *trans*-N_2O_2 diimine macrocycle **1** was originally prepared in low yield by prolonged heating of bis((iodoethyl)salicylideneaminato)nickel(II) in boiling acetone.[9] The cyclization of the *iodoethyl complex* also occurred when the solid was heated at 140 °C for 3–16 h in vacuo. The free ligand **1** was subsequently obtained from the complex by displacement with sodium ethylenediaminetetraacetate. We

---

[†] Australian National University.

[‡] Macquarie University.

[§] Present address: School of Physical Sciences, Flinders University of South Australia, Bedford Park, South Australia 5042, Australia.

(1) Goodwin, H. J.; Henrick, K.; Lindoy, L. F.; McPartlin, M.; Tasker, P. A. *Inorg. Chem.* **1982**, *21*, 3261.

(2) Drummond, L. A.; Henrick, K.; Kangasundarum, M. J. L.; Lindoy, L. F.; Tasker, P. A. *Inorg. Chem.* **1982**, *21*, 3923.

(3) Henrick, K.; Lindoy, L. F.; McPartlin, M.; Tasker, P. A.; Wood, M. P. *J. Am. Chem. Soc.* **1984**, *106*, 1641 and references cited therein.

(4) Martin, L. Y.; Sperati, C. R.; Busch, D. H. *J. Am. Chem. Soc.* **1977**, *99*, 2968.

(5) Henrick, K.; Lindoy, L. F.; Tasker, P. A. *Prog. Inorg. Chem.* **1985**, *33*, 1.

(6) Martin, J. W. L.; Wainwright, K. P.; Weerasuria, K. D. V.; Wild, S. B. *Inorg. Chim. Acta* **1985**, *99*, L5.

(7) Martin, J. W. L.; Organ, G. J.; Wainwright, K. P.; Weerasuria, K. D. V.; Willis, A. C.; Wild, S. B. *Inorg. Chem.* **1987**, *26*, 2963.

(8) Martin, J. W. L.; Stephens, F. S.; Weerasuria, K. D. V.; Wild, S. B. *J. Am. Chem. Soc.* **1988**, *110*, 4346.

(9) Kluiber, R. W.; Sasso, G. *Inorg. Chim. Acta* **1970**, *4*, 226.

0020-1669/89/1328-4531$01.50/0 © 1989 American Chemical Society

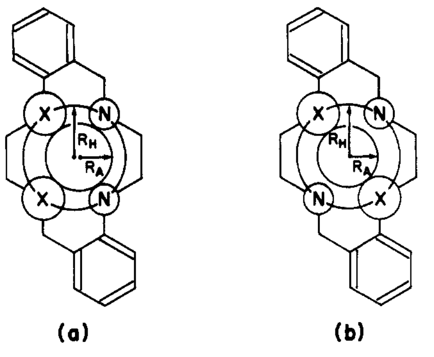
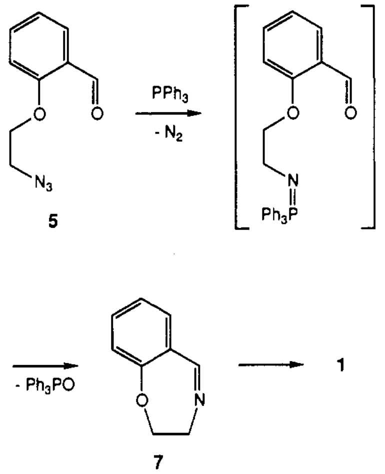
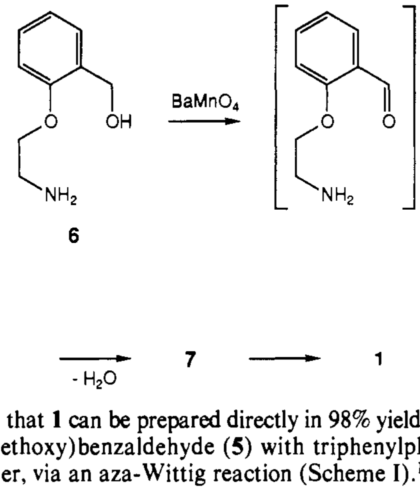


Figure 1. Diagrammatic representations of binding cavities (of radii R_A) in *cis*-N_2X_2 (a) and *trans*-N_2X_2 (b) macrocycles. Note that the center of the binding cavity in (a) is displaced from the centroid toward the N atoms.

Scheme I



Scheme II



have found that **1** can be prepared directly in 98% yield by treating 2-(2-azidoethoxy)benzaldehyde (**5**) with triphenylphosphine in diethyl ether, via an aza-Wittig reaction (Scheme I).[10] Diimine **1** can also be isolated in satisfactory yields (65–70%) by the oxidation of 2-(2-aminoethoxy)benzyl alcohol (**6**) with barium manganate in dichloromethane (Scheme II). The diimine **1** is characterized in the ^1H NMR spectrum ($CDCl_3$) by a low-field signal at δ 8.8 due to the azomethine protons. Over a period of about 12 h in $CDCl_3$, however, the low-field azomethine resonance is replaced by a new signal at δ 8.2; substantial changes also occur in the pattern of the aromatic and the aliphatic resonances in the spectrum. Moreover, it was observed that the *rate* of rearrangement of the macrocycle depended upon the following factors: (i) the polarity of the solvent, (ii) the concentration of the solution, and (iii) the presence of water or acid in the solvent. Thus, the

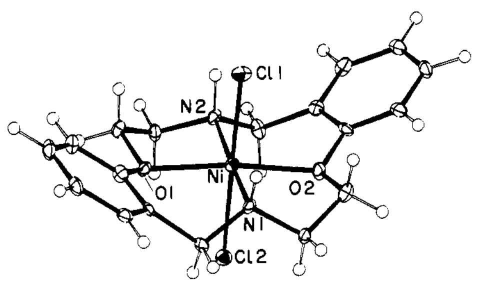
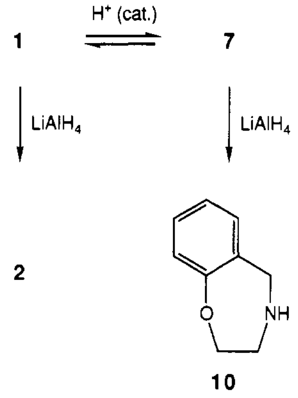


Figure 2. ORTEP view of $[NiCl_2(\mathbf{2})]$ showing the atom-labeling scheme of non-hydrogen atoms. Thermal ellipsoids enclose 35% probability levels.

Scheme III



rearrangement was rapid in nitromethane but slow in toluene or chloroform. The addition of a trace of trifluoroacetic acid to a chloroform solution of **1** resulted in rapid rearrangement. Molecular weight measurements (by vapor pressure osmometry) of **1** in chloroform before and after rearrangement conclusively indicated that a monomer–dimer interconversion was taking place. Indeed, if a solution of **1** is treated with a trace of trifluoroacetic acid, the solvent is evaporated, and the residue is distilled, pure **7** is obtained as a colorless liquid bp 90 °C (0.2 mmHg, Kugelrohr; lit.[9] bp 90 °C, 0.1 mmHg). Alternatively, pure **1**, mp 115–125 °C (lit.[9] mp 73–77 °C), can be converted into **7** by distillation. With time the liquid monomer solidifies as a dimer. Reduction of diimine **1** with lithium aluminum hydride gives the diamine **2**; reduction of the monoimine **7** gives 2,3,4,5-tetrahydro-1,4-benzoxazepine (**10**), bp 100 °C (0.05 mmHg, Kugelrohr; lit.[11] bp 103–105 °C, 4 mmHg) (Scheme III).

We have commented elsewhere on the mechanism of the facile monomer–dimer interconversion.[6,7] The behavior of **1** and **7** parallels that of 4,5-dihydro-3*H*-2-benzazepine and its dimer, for which a stepwise mechanism involving a 1,3-diazetidine intermediate has been proposed.[12] The corresponding unsaturated *trans*-N_2S_2 macrocycle **3** undergoes a similar transformation in the presence of acid, but in this case the monoimine spontaneously dimerizes upon removal of solvent.[6,7] Diamine **4** was obtained by the lithium aluminum hydride reduction of **3** as described previously.[6,7]

Both $[NiCl_2(\mathbf{2})]$ and $[NiCl_2(\mathbf{4})]$ were found to have high-spin pseudooctahedral coordination geometries according to their magnetic and spectroscopic properties. The salt $[Ni(\mathbf{3})](ClO_4)_2$, however, is low spin and square planar. Attempted preparations of similar low-spin complexes with the *trans*-N_2O_2 macrocycles **1** and **2**, and the *trans*-N_2S_2 diamine **4**, gave solutions from which a product could not be isolated. This suggests that only the *trans*-N_2S_2 diimine macrocycle **3** can produce a ligand field strong enough to cause spin pairing of nickel(II), which is consistent with the observation that chelating diimines are stronger donors than

---

(10) Lambert, P. H.; Vaultier, M.; Carrie, R. *J. Chem. Soc., Chem. Commun.* **1982**, 1224.

(11) Kost, A. N.; Stankevicius, A. *Khim. Geterotsikl. Soedin. Sb.* **1971**, *7*, 1288; *Chem. Abstr.* **1972**, *76*, 46063v.

(12) Goldman, I. M.; Larson, J. K.; Tretter, J. R.; Andrews, E. G. *J. Am. Chem. Soc.* **1969**, *91*, 4941.

Table I. Crystal Parameters and Experimental Data for X-ray Diffraction Measurements on [NiCl$_2$(**2**)] and [NiCl$_2$(**4**)]·0.5H$_2$O[a]

	[NiCl$_2$(**2**)]	[NiCl$_2$(**4**)]·0.5H$_2$O
empirical formula	$C_{18}H_{22}Cl_2N_2NiO_2$	$C_{18}H_{23}Cl_2N_2NiO_{0.5}S_2$
fw	428.00	469.14
cryst habit	pinacoids {100}, {010}, {001}	pinacoids {011}, {0$\bar{1}$0}, {$\bar{1}$01}
cryst dimens, mm	0.24 × 0.07 × 0.04	0.11 × 0.08 × 0.23
lattice type	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (nonstd No. 14)
cell dimens		
a, Å	9.092 (4)	8.901 (2)
b, Å	9.803 (4)	12.031 (3)
c, Å	10.431 (4)	19.120 (5)
α, deg	92.34 (3)	
β, deg	104.34 (3)	98.50 (2)
γ, deg	97.31 (3)	
V, Å^3	890.9	2025.0
Z	2	4
d_{calcd}, g cm^{-3}	1.59	1.54
$F(000)$	444	972
μ(Mo Kα), cm^{-1}	14.1	14.4
data collcn instrum	Nicolet XRD P3[17]	Nicolet XRD P3[17]
radiation (graphite monochromated)	Mo Kα	Mo Kα
λ(radiation), Å	0.710 69	0.710 69
temp, °C	−150	−150
2θ range, deg	3–45	3–45
total no. of data	2329	2660
no. of data measd with $I > 3\sigma(I)$	1309	1712
transmissn factors: max, min	0.945, 0.898	0.897, 0.838
R, R'[b]	0.044, 0.038	0.046, 0.043
$(\Delta/\sigma)_{max}$	0.05	0.1

[a] The estimated standard deviation in the least significant digit is shown in parentheses for each entry in this and subsequent tables. [b] $R = \sum|F_o| - |F_c|/\sum|F_o|$; $R' = (\sum w\Delta^2/\sum w|F_o|^2)^{1/2}$.

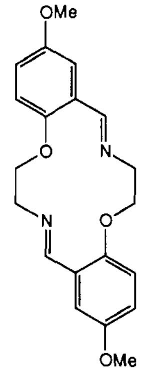
the corresponding diamines.[4] Recrystallization of [NiCl$_2$(**2**)] from an ethanol–methanol mixture gave crystals suitable for X-ray structural analysis; crystals of [NiCl$_2$(**4**)] were obtained as the *hemihydrate* by adding **4** to a hot aqueous solution of nickel(II) chloride and diluting the reaction mixture with 2-propanol. The structure of *cis*-[NiCl$_2$(**3**)] has been reported elsewhere.[6]

Crystal and Molecular Structures. Crystal data, information relating to data collection, and refinement details for [NiCl$_2$(**2**)] and [NiCl$_2$(**4**)]·0.5H$_2$O are given in Table I; atomic coordinates for the two compounds are given in Table III. Important bond distances and angles for the complexes are listed in Table II. Complete data are available as supplementary material.

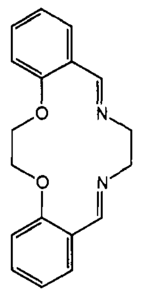
The nickel(II) ion in [NiCl$_2$(**2**)] is located in an octahedral coordination environment consisting of the four donor atoms of the *trans*-N$_2$O$_2$ macrocycle in an approximately square-planar array and the two chloride anions in axial sites (Figure 2). There is a slight tetrahedral distortion of the plane formed by the *trans*-N$_2$O$_2$ donor set and the metal; the oxygen donors O(1) and O(2) each lie 0.11 Å below the plane, and the nitrogen donors N(1) and N(2) lie 0.10 Å above the plane. The nickel ion sits 0.02 Å above the plane, in the direction of Cl(1). Both aromatic rings of the ligand lie on the same side of the N$_2$O$_2$ coordination plane, with the N-bonded H atoms pointing toward Cl(1) and the lone pair on each of the O donors pointing toward Cl(2). Thus, the chiral donor stereocenters O(1), O(2), N(1), and N(2) in the complex have the same relative absolute configurations, viz. R^*,R^*,R^*,R^*.[13] Both oxygen donor atoms in the structure show considerable sp^2 character, however, with C–O–C bond angles approaching 120°. The Ni–O bond lengths (mean 2.065 (4) Å) and Ni–N bond lengths (mean 1.997 (5) Å) are significantly shorter than the "standard" values of 2.15 and 2.11 Å, respectively.[5] The bonding cavity radius of the macrocycle is 1.30 Å, which is close to the value of 1.29 Å found in *trans*-[NiI$_2$(**1**)][14] and the 1.31 Å observed for the radius of the cavity in the dichloronickel(II) complex of the corresponding cis macrocycle.[9] No high-spin nickel(II) complex of a macrocycle has been reported where the binding cavity radius is less than 1.29 Å. The introduction of *p*-methoxy groups onto the benzene rings of **2** is sufficient to cause the macrocycle to adopt a nonplanar mode of coordination about high-spin nickel(II), as found in the structure of the diiodonickel(II) complex of **8**.[15] Thus, a binding cavity of radius 1.29 Å appears to be the lower limit for accommodation of high-spin nickel(II); further reductions in the size of the macrocyclic cavities result in low-spin nickel(II) complexes or complexes where the metal ion is situated outside of the macrocyclic cavity.

Table II. Selected Bond Lengths and Angles

[NiCl$_2$(**2**)]		[NiCl$_2$(**4**)]·0.5H$_2$O	
	Bond Lengths (Å)		
Ni–N(1)	1.989 (6)	Ni–N(1)	2.128 (7)
Ni–N(2)	2.005 (7)	Ni–N(2)	2.108 (6)
Ni–O(1)	2.066 (5)	Ni–S(1)	2.407 (2)
Ni–O(2)	2.064 (5)	Ni–S(2)	2.376 (2)
Ni–Cl(1)	2.430 (3)	Ni–Cl(1)	2.389 (2)
Ni–Cl(2)	2.473 (3)	Ni–Cl(2)	2.472 (2)
	Bond Angles (deg)		
N(1)–Ni–N(2)	175.3 (3)	N(1)–Ni–N(2)	93.7 (2)
O(1)–Ni–O(2)	172.6 (2)	S(1)–Ni–S(2)	178.5 (1)
Cl(1)–Ni–Cl(2)	179.0 (1)	Cl(1)–Ni–Cl(2)	91.7 (1)
N(1)–Ni–O(1)	94.5 (2)	N(1)–Ni–S(1)	93.1 (2)
N(1)–Ni–O(2)	85.1 (2)	N(1)–Ni–S(2)	86.3 (2)
N(1)–Ni–Cl(1)	88.3 (2)	N(1)–Ni–Cl(1)	177.4 (2)
N(1)–Ni–Cl(2)	92.1 (2)	N(1)–Ni–Cl(2)	90.2 (2)
N(2)–Ni–O(1)	85.5 (2)	N(2)–Ni–S(1)	85.9 (2)
N(2)–Ni–O(2)	95.4 (2)	N(2)–Ni–S(2)	92.8 (2)
N(2)–Ni–Cl(1)	87.1 (2)	N(2)–Ni–Cl(1)	84.5 (2)
N(2)–Ni–Cl(2)	92.6 (2)	N(2)–Ni–S(2)	176.0 (2)
O(1)–Ni–Cl(1)	94.3 (2)	S(1)–Ni–Cl(1)	88.7 (1)
O(1)–Ni–Cl(2)	86.7 (2)	S(1)–Ni–Cl(2)	92.9 (1)
O(2)–Ni–Cl(1)	93.1 (2)	S(2)–Ni–Cl(1)	92.0 (1)
O(2)–Ni–Cl(2)	86.0 (2)	S(2)–Ni–Cl(2)	88.4 (1)



8



9

It is noteworthy that the complex [NiCl$_2$(**4**)] adopts a stereochemistry altogether different from the one found for [NiCl$_2$(**2**)]: in [NiCl$_2$(**4**)] (Figure 3) the chloro ligands are cis to one other and the four donor atoms of the *trans*-N$_2$S$_2$ macrocycle occupy the remaining four coordination sites with the two sulfur donors mutually trans to one another. The high-spin nickel(II) cation is situated outside the macrocyclic cavity in this complex (Figure 3). The structure of the complex *cis*-[NiCl$_2$(**3**)] shows that **3** adopts a similar folded conformation with the two imino groups cis to one another and the two sulfur donors trans to one another; the nickel–donor atom bond lengths in the complexes of the diamine **4** and the diimine **3** are remarkably similar. It has been demonstrated previously that the introduction of unsaturation into a macrocyclic ring does not appreciably alter the radius of the

---

(13) The nomenclature adopted here is consistent with recent Chemical Abstracts Service practice; R^* and S^* refer to the relative configurations of the chiral stereocenters in the complex.

(14) Johnston, D. L.; Horrocks, W. D. *Inorg. Chem.* **1971**, *10*, 687.

(15) LaLancette, R. A.; Macchia, D. J.; Furey, W. F. *Inorg. Chem.* **1976**, *15*, 548.

Table III. Final Positional Parameters

	$[NiCl_2(\mathbf{2})]$			$[NiCl_2(4)]\cdot0.5H_2O$		
atom	*x*	*y*	*z*	*x*	*y*	*z*
Ni	2388 (2)	1929 (1)	3754 (1)	1970 (1)	574 (1)	1557 (1)
Cl(1)	2573 (3)	−45 (2)	5090 (2)	1548 (2)	1338 (2)	386 (1)
Cl(2)	2192 (3)	3911 (2)	2359 (2)	3539 (2)	2186 (2)	2012 (1)
X(1)	3627 (6)	3325 (5)	5299 (5)	−349 (2)	1446 (2)	1777 (1)
X(2)	1108 (6)	751 (5)	2068 (5)	4229 (2)	−332 (2)	1343 (1)
N(1)	377 (7)	2082 (6)	4139 (6)	2362 (7)	−176 (5)	2575 (3)
N(2)	4431 (7)	1648 (6)	3463 (7)	575 (7)	−734 (6)	1107 (3)
C(11)	3084 (9)	3556 (8)	6407 (8)	−770 (9)	1128 (7)	2639 (4)
C(12)	4038 (9)	3729 (8)	7656 (9)	−2240 (10)	1373 (7)	2763 (4)
C(13)	3456 (10)	3955 (8)	8754 (8)	−2648 (10)	1226 (8)	3435 (5)
C(14)	1892 (10)	4012 (8)	8559 (8)	−1608 (11)	831 (8)	3979 (5)
C(15)	946 (9)	3834 (8)	7293 (8)	−150 (10)	584 (8)	3850 (4)
C(16)	1511 (9)	3577 (7)	6188 (8)	316 (9)	739 (7)	3196 (4)
C(17)	393 (8)	3433 (7)	4836 (8)	1981 (9)	571 (8)	3154 (4)
C(18)	−767 (8)	1786 (8)	2843 (8)	4004 (9)	−433 (8)	2762 (4)
C(19)	−456 (9)	494 (8)	2166 (8)	4551 (10)	−1150 (8)	2162 (4)
C(21)	1736 (9)	−277 (8)	1505 (8)	3751 (9)	−1380 (7)	683 (4)
C(22)	870 (9)	−1511 (8)	998 (8)	4784 (10)	−1514 (7)	209 (4)
C(23)	1506 (10)	−2514 (8)	416 (8)	4486 (10)	−2261 (7)	−344 (4)
C(24)	3013 (10)	−2278 (8)	410 (8)	3154 (10)	−2897 (7)	−408 (4)
C(25)	3891 (9)	−1013 (9)	956 (8)	2129 (10)	−2746 (8)	62 (5)
C(26)	3290 (9)	12 (8)	1508 (8)	2396 (9)	−1989 (7)	629 (4)
C(27)	4288 (9)	1368 (8)	2018 (8)	1204 (9)	−1872 (7)	1106 (4)
C(28)	5472 (8)	2914 (8)	4091 (8)	−900 (9)	−767 (7)	1372 (4)
C(29)	5247 (9)	3192 (8)	5468 (8)	−1562 (8)	430 (7)	1270 (4)
O(w)				2107 (12)	3756 (9)	609 (5)

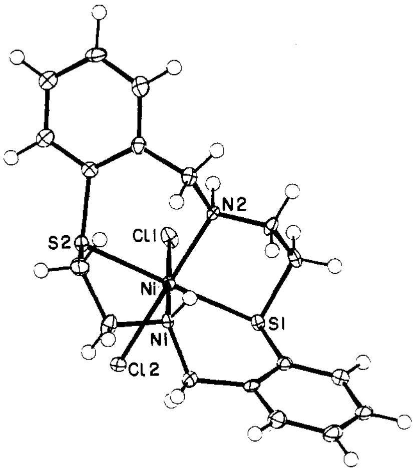


Figure 3. ORTEP view of $[NiCl_2(4)]$ in $[NiCl_2(4)]\cdot0.5H_2O$ showing the atom-labeling scheme of non-hydrogen atoms. Thermal ellipsoids enclose 35% probability levels.

cavity.[3,9] This suggests that the cavities of both **3** and **4** are too small to accommodate high-spin nickel(II), which forces the macrocycles to fold into cis chelating conformations. In $[NiCl_2(4)]$ the relative absolute configurations of S(1), S(2), N(1), and N(2) are *R**, *R**, *R**, and *S**, respectively. The two nitrogen donor atoms form bonds of normal lengths to the nickel ion (mean Ni–N = 2.118 (5) Å). In $[NiCl_2(\mathbf{2})]$, however, where the *trans*-N_2O_2 macrocycle encircles the nickel ion, the Ni–N bonds are significantly shorter (mean 1.997 (5) Å). The complex $[NiCl_2(4)]$ crystallizes as a hemihydrate with the water molecule H-bonded to Cl(1) at a distance of 2.97 Å.

A folded macrocycle, as found in *cis*-$[NiCl_2(4)]$, no longer has a well-defined bonding cavity, and thus it can accommodate a metal ion that is too large for encirclement. The hypothesis that the high-spin nickel(II) ion is too large to fit into the cavity of the *trans*-N_2S_2 macrocycles **3** and **4** in their planar conformations is supported by the observation that **3** reacts with nickel(II) perchlorate to give the *low-spin* square-planar complex $[Ni(\mathbf{3})](ClO_4)_2$. The accepted radius for low-spin nickel(II) is 1.20 Å.[16] For the related *cis*-N_2O_2 macrocycle **9** and its sulfur analogue the longer C–S bonds in the latter more than compensate for the increased radii involved, with the result that the *cis*-N_2S_2 macrocycle has the larger binding cavity of the two.[3] For quadridentate *trans*-N_2X_2 macrocycles containing oxygen or sulfur, the change from an N_2O_2 to an N_2S_2 donor atom set causes a *decrease* in the binding cavity radius because of the large difference between the radii of the two types of donor atoms in the *trans*-N_2S_2 case, as depicted diagrammatically in Figure 1.

Since the cavity radius of the *trans*-N_2O_2 macrocycle in $[NiCl_2(\mathbf{2})]$ (1.30 Å) is already close to the minimum value for high-spin nickel(II), we might expect that the cavities of the *trans*-N_2S_2 macrocycles **3** and **4** would be too small for effective square-planar chelation of the high-spin nickel ion. It is apparent from the structures presented in this work that this is indeed the case. Thus, a modification of the concept of "bonding cavity radius" is required for ligands with *trans*-A_2B_2 donor atom sets where the radii of the larger pair of donor atoms appear to be responsible for determining the effective size of the cavity.

Experimental Section

Proton NMR spectra were recorded at 20 °C with use of a Jeolco FX-200 spectrometer: chemical shifts are quoted as δ values relative to internal Me_4Si. Infrared spectra were recorded on Nujol mulls of the compounds on a Perkin-Elmer Model 257 spectrophotometer. Magnetic susceptibility data were obtained with use of a Newport Gouy balance and are corrected for ligand and inner-core diamagnetism with use of Pascal's constants. The crystal data and refinement details are summarized in Table I. Elemental analyses were performed by staff in the Research School of Chemistry.

The compounds 6,7,15,16-tetrahydrodibenzo[*f*,*m*][1,8,4,11]dithiadiazacyclotetradecine (**3**) and 6,7,8,9,15,16,17,18-octahydrodibenzo[*f*,*m*][1,8,4,11]dithiadiazacyclotetradecine (**4**) were prepared as described in ref 7.

2-(2-Bromoethoxy)benzaldehyde. A solution of sodium hydroxide (54 g, 1.34 mol) in water (375 mL) was slowly added over 30 min to a mixture of salicylaldehyde (150 g, 1.2 mol) and 1,2-dibromoethane (350 g, 1.86 mol) at its boiling point. After an additional 20 h of boiling, the reaction mixture was cooled to room temperature. The organic phase was separated, and the aqueous phase was extracted with dichloromethane (2 × 200 mL). The combined organic fraction was then washed with 10% sodium hydroxide (100 mL), dried ($MgSO_4$), and distilled. The pure product was thus obtained as a colorless oil: yield 80 g (40%); bp 130–145 °C (0.02 mmHg). Anal. Calcd for $C_9H_9BrO_2$: C, 47.2; H, 4.0. Found: C, 47.1; H, 3.8. ^1H NMR ($CDCl_3$): δ 10.45 (s, 1 H, CHO),

---

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

(17) Sheldrick, G. M. *SHELXTL User Manual, Revision 3*; Nicolet XRD Corp.: Cupertino, CA, 1981.

7.80–6.80 (m, 4 H, Ar H), 4.40 (t, 2 H, ^3J = 6.0 Hz, CH_2Br), 3.66 (t, 2 H, ^3J = 6.0 Hz, CH_2O). IR (neat): 1680 cm^{-1} (ν_{CO}).

2-(2-Azidoethoxy)benzaldehyde (5). A solution of sodium azide (18 g, 0.28 mol) in water (150 mL) was slowly added into a stirred solution of 2-(2-bromoethoxy)benzaldehyde (40 g, 0.17 mol) in ethanol (500 mL) with the reaction mixture maintained at 60 °C. After the addition of the azide, stirring of the reaction mixture was continued for a further 3 days at 60 °C (in the dark). At this stage the bulk of the ethanol was removed by distillation and water (500 mL) was added to the residue; this mixture was then extracted with dichloromethane (2 × 200 mL). The combined extracts were dried ($MgSO_4$), and the solvent was removed from the dried solution. The viscous orange oil that remained was dissolved in diethyl ether; the addition of petroleum ether (bp 60–80 °C) to this solution yielded pale yellow needles of the pure product: yield 24 g (71%); mp 43–45 °C. Anal. Calcd for $C_9H_9N_3O_2$: C, 56.5; H, 4.7; N, 22.0. Found: C, 56.6; H, 4.8; N, 21.5. ^1H NMR ($CDCl_3$): δ 10.10 (s, 1 H, CHO), 7.83–6.83 (m, 4 H, Ar H), 4.20 (t, 2 H, ^3J = 6.0 Hz, CH_2N_3), 3.68 (t, 2 H, ^3J = 6.0 Hz, CH_2O). IR (Nujol): 1680 (ν_{CO}), 650 cm^{-1} (ν_{N_3}).

2-(2-Aminoethoxy)benzyl Alcohol (6). A suspension of $LiAlH_4$ (3 g, 79 mmol) in tetrahydrofuran (300 mL) was added over 30 min into a solution of the *azide* (15 g, 78 mmol) in the same solvent (100 mL) at 0 °C. The reaction mixture was then warmed to room temperature with stirring being continued for a further 1 h. The excess $LiAlH_4$ was then decomposed by the sequential addition of water (3 mL), 4 M NaOH (3 mL), and water (9 mL). The colorless precipitate was then separated and thoroughly washed with tetrahydrofuran. The filtrate and washings were combined and dried over $MgSO_4$, and the solvent was distilled off. The residue, a colorless oil, was then dissolved in a small quantity of methanol, and the solution was diluted with diethyl ether. The pure product crystallized from the mixture as colorless needles: yield 12.7 g (97%); mp 64–66 °C. Anal. Calcd for $C_9H_{13}NO_2$: C, 64.7; H, 7.8; N, 8.4. Found: C, 64.9; H, 7.8; N, 8.0. ^1H NMR ($CDCl_3$): δ 7.33–6.66 (m, 4 H, Ar H), 4.66 (s, 2 H, CH_2OH), 4.00 (t, 2 H, ^3J = 6.0 Hz, CH_2O), 3.05 (t, 2 H, ^3J = 6.0 Hz, CH_2N), 2.58 (s, 3 H, NH_2, OH).

6,7,15,16-Tetrahydrodibenzo[*f,m*][1,8,4,11]dioxadiazacyclotetradecine (1). Method 1. Triphenylphosphine (26.3 g, 0.1 mol) was added in small portions to a solution of **5** (19.1 g, 0.1 mol) in diethyl ether (300 mL). The resulting solution was then stirred at room temperature for ca. 1.5 h, by which time dinitrogen evolution had ceased and triphenylphosphine oxide had precipitated. The phosphine oxide was removed by filtration, and the filtrate was evaporated to dryness. The viscous oil that remained was taken up in benzene, and the solution was diluted with *n*-hexane. The pure product crystallized from this mixture as colorless needles: yield 14.4 g (98%); mp 115–125 °C (lit.[9] mp 73–77 °C). Anal. Calcd for $C_{18}H_{18}N_2O_2$: C, 73.5; H, 6.2; N, 9.5. Found: C, 73.1; H, 6.3; N, 9.5. ^1H NMR ($CDCl_3$): δ 8.88 (s, 2 H, CH=N), 7.69 (dd, 2 H, ^3J = 7.6 Hz, ^4J = 1.6 Hz, Ar *o*-H), 7.31–6.81 (m, 6 H, Ar H), 4.21 (t, 4 H, ^3J = 4.3 Hz, CH_2O), 4.02 (t, 4 H, ^3J = 4.3 Hz, CH_2N). ^{13}C NMR ($CDCl_3$): δ 163.0 (C_9, C_{18}), 158.1, 131.9, 127.1, 125.5, 120.9, 110.4 (Ar C), 66.0 (C_6, C_{15}), 59.0 (C_7, C_{16}). IR (Nujol): 1640 cm^{-1} ($\nu_{C=N}$). Mass spectrum: *m/e* 294 ($[M]^+$). Mol wt (osomometry, CH_2Cl_2): 294 (calcd), 292 (found).

Method 2. Freshly prepared barium manganate (15 g, excess) was added to a solution of **6** (15 g, 90 mmol) in dichloromethane (300 mL), and the mixture was stirred for 10 h at room temperature. The solid was then separated by filtration of the reaction mixture through a pad of Celite. The filtrate (and pad washings) was dried ($MgSO_4$) and evaporated to dryness. The residue, after crystallization from benzene–*n*-hexane, gave pure **1**, yield 8.8 g (65%).

6,7,8,9,15,16,17,18-Octahydrodibenzo[*f,m*][1,4,8,11]dioxadiazacyclotetradecine (2). A solution of **1** (5 g, 16 mmol) in tetrahydrofuran (20 mL) was added dropwise into a stirred suspension of $LiAlH_4$ (1.21 g, 32 mmol) in the same solvent (200 mL) at 0 °C. After the reaction mixture had been stirred for 1 h, it was treated sequentially with water (1.2 mL), 4 M NaOH (1.2 mL), and water (3.6 mL) to decompose unreacted hydride. The solid that formed was filtered off and washed with tetrahydrofuran (3 × 50 mL). The combined tetrahydrofuran fraction was then dried ($MgSO_4$) before being evaporated to dryness. The colorless solid was recrystallized from a benzene–*n*-hexane mixture to give the pure product as colorless needles: yield 4.6 g (90%); mp 170–171 °C. Anal. Calcd for $C_{18}H_{22}N_2O_2$: C, 72.5; H, 7.4; N, 9.4. Found: C, 72.4; H, 7.5; N, 9.3. ^1H NMR ($CDCl_3$): δ 7.28–6.82 (m, 8 H, Ar H), 4.16 (t, 4 H, ^3J = 4.6 Hz, CH_2O), 3.83 (s, 4 H, $ArCH_2$), 3.11 (t, 4 H, ^3J = 4.6 Hz, CH_2N). ^{13}C NMR ($CDCl_3$): δ 157.5, 130.9, 129.0, 127.6, 120.8, 110.7 (Ar C), 66.2 (C_6, C_{15}), 51.9, 49.1 (C_7, C_9, C_{16}, C_{18}). IR (Nujol): 3340 cm^{-1} (ν_{NH}). Mass spectrum: *m/e* 298 ($[M]^+$). Mol wt (osmometry, CH_2Cl_2): 298 (calcd), 299 (found).

2,3-Dihydro-1,4-benzoxazepine (7). A solution of diimine **1** (1 g, 3 mmol) in dichloromethane (5 mL) was added into a solution of trifluoroacetic acid (0.05 mL, 0.1 M) in diethyl ether. The mixture was heated under reflux for 1 h; the solvent was then removed, and the residual yellow oil was distilled with use of a Kugelrohr apparatus. The product was obtained as a colorless oil with bp 90 °C (0.2 mmHg, Kugelrohr; lit.[9] bp 90 °C (0.1 mmHg)) and yield 0.86 g (86%). Anal. Calcd for C_9H_9NO: C, 73.5; H, 6.2. Found: C, 73.3; H, 6.2. ^1H NMR ($CDCl_3$): δ 8.21 (s, 1 H, $CH{=}N$), 7.46–6.99 (m, 4 H, Ar H), 4.30 (t, 2 H, ^3J = 5.0 Hz, CH_2O), 4.12 (t, 2 H, ^3J = 5.0 Hz, CH_2N). ^{13}C NMR ($CDCl_3$): δ 161.2 (C_5), 158.6, 135.4, 132.3, 121.5, 119.7 (Ar C), 70.9 (C_2), 57.1 (C_3). IR (neat): 1640 cm^{-1} ($\nu_{C=N}$). Mass spectrum: *m/e* 147 ($[M]^+$). Mol wt (osmometry, CH_2Cl_2): 147 (calcd), 161 (found).

2,3,4,5-Tetrahydro-1,4-benzoxazepine (10). A solution of freshly distilled monoimine **7** (1 g, 6 mmol) in dry tetrahydrofuran (10 mL) was added dropwise into a suspension of $LiAlH_4$ (0.2 g, 5 mmol) in tetrahydrofuran (100 mL) at 0 °C. The resulting mixture was stirred at room temperature for 1 h. The usual workup, followed by distillation of the crude product, afforded **10** as a colorless oil: bp 100 °C (0.05 mmHg, Kugelrohr; lit.[11] bp 103–105 °C (4 mmHg)); yield 0.75 g (74%). Anal. Calcd for $C_9H_{11}NO$: C, 72.4; H, 7.4. Found: C, 72.7; H, 7.5. ^1H NMR ($CDCl_3$): δ 7.27–6.94 (m, 4 H, Ar H), 4.02 (t, 2 H, ^3J = 4.5 Hz, CH_2O), 3.95 (s, 2 H, benzylic CH_2), 3.20 (t, 2 H, ^3J = 4.5 Hz, CH_2N). ^{13}C NMR ($CDCl_3$): δ 159.6, 134.7, 128.9, 127.9, 122.9, 120.6 (Ar C), 74.6 (C_2), 52.7, 51.9 (C_3, C_5). IR (neat): 3320 cm^{-1} (ν_{NH}). Mass spectrum: *m/e* 149 ($[M]^+$).

[*OC*-6-12]-Dichloro(6,7,8,9,15,16,17,18-octahydrodibenzo[*f,m*]-[1,8,4,11]dioxadiazacyclotetradecine-N^8,N^{17},O^5,O^{14})nickel(II) ([$NiCl_2$(2)]. Diamine **2** (0.2 g, 0.67 mmol) was added in small portions into a solution of $[Ni(H_2O)_6]Cl_2$ (0.175 g, 0.74 mmol) in 1-butanol (50 mL) at 80 °C. After ca. 15 min the pale blue microcrystalline precipitate was filtered off and washed with acetone and diethyl ether. Recrystallization of the crude material (0.215 g, 75%) from a methanol–ethanol mixture gave the pure product as blue prisms, mp 290 °C dec. Anal. Calcd for $C_{18}H_{22}Cl_2N_2NiO_2$: C, 50.5; H, 5.2; N, 6.6. Found: C, 51.2; H, 5.5; N, 7.1. IR (Nujol): 3255, 3240 cm^{-1} (ν_{NH}). Magnetic moment: μ_{eff} = 3.18 μ_B (high-spin nickel(II)). Electronic spectrum (solid): 25 200, 16 600, 10 600 cm^{-1}.

[*OC*-6-12]-Dichloro(6,7,8,9,15,16,17,18-octahydrodibenzo[*f,m*]-[1,8,4,11]dithiadiazacyclotetradecine-N^8,N^{17},S^5,S^{14})nickel(II) Hemihydrate ([$NiCl_2$(4)]·0.5H_2O). The diamine (0.26 g, 0.81 mmol) was added in small portions into a stirred solution of $[Ni(H_2O)_6]Cl_2$ (0.20 g, 0.82 mmol) in water (5 mL) over a period of 10 min. The resulting mixture was heated to ca. 70 °C for 30 min and filtered while hot and 2-propanol (1 mL) added. Intensely blue crystals of the *hemihydrate* deposited from the solution over 12 h: yield 0.25 g (67%). Anal. Calcd for $C_{18}H_{23}Cl_2N_2NiO_{0.5}S_2$: C, 46.1; H, 5.0; N, 6.0. Found C, 46.3; H, 4.6; N, 6.0. Magnetic moment: μ_{eff} = 3.18 μ_B (high-spin nickel(II)). Electronic spectrum (solid): 16 400, 10 000 cm^{-1}.

[*SP*-4]-(6,7,15,16-Tetrahydrodibenzo[*f,m*][1,8,4,11]dithiadiazacyclotetradecine-N^8,N^{17},S^5,S^{14})nickel(II) Perchlorate ([Ni(3)](ClO_4)$_2$). The diimine (0.33 g, 1.0 mmol) was suspended in 1-butanol (50 mL), $[Ni(H_2O)_6](ClO_4)_2$ (0.33 g, 1.1 mmol) was added, and the mixture was heated under reflux for 2 h and then cooled. The orange crystalline product was filtered off and washed with ethanol and chloroform; yield 0.54 g (92%). Anal. Calcd for $C_{18}H_{18}Cl_2N_2NiO_8S_2$: C, 37.0; H, 3.1; N, 4.8. Found: C, 37.2; H, 3.0; N, 4.7. Magnetic moment: μ_{eff} = 0.0 μ_B (low-spin nickel(II)). Electronic spectrum (solid): 22 800 cm^{-1}.

Structural Analyses. Single crystals of [$NiCl_2$(**2**)] were grown from an ethanol–methanol mixture and of [$NiCl_2$(**4**)]·0.5H_2O from aqueous propanol. The crystal data, information relating to data collection, and refinement details are summarized in Table I; the final positional parameters are given in Table II.

Computer Programs. The programs used in this work were written by F.S.S.

Acknowledgment. We thank Dr. Ward T. Robinson, University of Canterbury, Christchurch, New Zealand, for recording for us the crystallographic data on [$NiCl_2$(**2**)] and [$NiCl_2$(**4**)]·0.5H_2O.

Registry No. **1**, 28336-11-0; **2**, 96740-35-1; [$NiCl_2$(**2**)], 123642-50-2; [Ni(**3**)], 123642-53-5; [$NiCl_2$(**4**)], 123642-51-3; **5**, 123642-49-9; **6**, 74402-49-6; **7**, 28336-12-1; **10**, 17775-01-8; 2-(2-bromoethoxy)benzaldehyde, 60633-78-5; salicylaldehyde, 90-02-8; 1,2-dibromoethane, 106-93-4.

Supplementary Material Available: For [$NiCl_2$(**2**)] and [$NiCl_2$(**4**)]·0.5H_2O, tables of bond distances and angles, thermal parameters of the non-hydrogen atoms, and calculated hydrogen parameters and drawings giving the labeling scheme for all non-hydrogen atoms (8 pages); tables of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.