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X-Ray Structural Study on Molecular Stereochemistries of Six-coordinate Zn(II) Complexes of *trans*-ZnX_2N_4 Type. Out-of-plane Displacement of Zn(II) from a Plane Formed by In-plane Four Nitrogens

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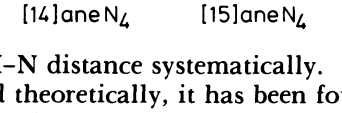
Molecular structures of *trans*-bis(isothiocyanato)(1,4,8,11-tetraazacyclotetradecane and 1,4,8,12-tetraazacyclopentadecane)zinc(II) complexes, $[Zn(NCS)_2(C_{10}H_{24}N_4)]$ (**1**) and $[Zn(NCS)_2(C_{11}H_{26}N_4)]$ (**2**), have been determined by X-ray analyses. Crystal data are: for **1**, orthorhombic, space group $P2_1nb$, a=14.502(2), b=18.163(2), c=6.552(1) Å, V=1718.0(4) Å^3, Z=4; for **2**, monoclinic, space group $P2_1/a$, a=14.453(2), b=14.436(1), c=9.213(1) Å, β=104.82(1)°, V=1858.3(4) Å^3, Z=4. Coordination geometries about Zn(II) in **1** and **2** are of the pseudo-octahedral type with two NCS groups at the trans positions, but the Zn(II) ion in each compound deviates from a plane defined by the four nitrogens of the macrocyclic ligand by 0.179 Å on the average in **1** and 0.193 Å in **2**. Structural features of **1** and **2** suggest, complemented with data reported previously for out-of-plane Zn(II) structures, that potential surface regarding the out-of-plane displacement is very flat. The Zn–NCS distance has been found to decrease as an in-plane Zn–N length (or cavity size of the ligand) increases. The observed negative correlation is substantially stronger than those for Ni(II) and Co(III) complexes and discloses the softness of a Zn(II) ion.

This paper is one of a series of investigations on metal ion characteristics viewed from the correlation between axial and in-plane coordination bond lengths of tetragonal six-coordinate complexes. The aim and method of the studies have been described elsewhere along with a historical review.[1] In order to visualize metal ion characteristics from this point of view, we have carried out *ab initio* MO calculations and X-ray analyses for a series of complexes which have the same or very similar coordination environments. In the theoretical approach, we have discussed the metal ion characteristics on the basis of potential energy surfaces of *trans*-$[MCl_2(NH_3)_4]$ ($M=Co^{3+}$, Fe^{2+}, Ni^{2+}, and Zn^{2+}) along the axial and in-plane coordination bonds.[1] In the experimental approach, we have determined the structures of a series of complexes of *trans*-MX_2N_4 type ($M=Ni^{2+}$, Zn^{2+}, and Co^{3+}). Tetraazacycloalkanes with different ring sizes, 1,4,8,11-tetraazacyclotetradecane ([14]aneN$_4$), 1,4,8,12-tetraazacyclopentadecane ([15]aneN$_4$), and 1,5,9,13-tetraazacyclohexadecane ([16]aneN$_4$), were used as in-plane ligands, so as



[14]aneN$_4$ [15]aneN$_4$

to vary an M–N distance systematically. Both experimentally and theoretically, it has been found that the axial coordination bond length decreases as the in-plane distance increases and the degree of the negative correlation is strongly metal ion dependent (Zn^{2+}> Ni^{2+}>Co^{3+}). A summary of the studies[1] and structural details of the Ni(II) complexes[2] have been described elsewhere.

The present paper reports structural details of the compounds, $[Zn(NCS)_2([14]aneN_4)]$ (**1**) and $[Zn(NCS)_2([15]aneN_4)]$ (**2**). We have tried to synthesize *trans*-dichloro- and *trans*-bis(isothiocyanato)zinc(II) complexes with the tetraazacycloalkanes. We succeeded in the isolation of single crystals suitable for X-ray work only for **1** and **2**. Other combinations of in-plane and axial ligands did not afford single crystals of the desired six-coordinate Zn(II) complexes, but gave mostly five-coordinate complexes.

As will be discussed later, the most characteristic feature in molecular stereochemistries of **1** and **2** is the out-of-plane displacement of Zn from the plane formed by four nitrogens of the in-plane ligand (hereafter abbreviated as the N_4 plane). It is well characterized that Zn(II) complexes with porphine or its analogs, $[Zn(H_2O)(tpp)]$ (tpp=5,10,15,20-tetraphenylporphine),[3a] [(Zn(py)(tpyp)] (tpyp=5,10,15,20-tetra(4-pyridyl)porphine),[3b] and Zn(hexylamine)(pc) (pc=phthalocyanine)[3c], are five-coordinate complex with the square pyramidal geometry. It had been suspected that the Zn(II) atom is too large to fit into the cavities of the porphinato or phthalocyanato ligands, though examples of the in-plane structure were recently found for [Zn(pc)][4] and $[Zn(tpp)]\cdot(toluene)_2$.[5] The results of X-ray analyses of **1** and **2** have shown that the cavity sizes of the present macrocyclic ligands are somewhat larger than those of the porphinato or phthalocyanato complexes. Therefore, it seems that whether Zn(II) in six-coordinate complexes of the *trans*-ZnX_2N_4 type takes an out-of-plane position or an in-plane position is not solely determined by the relative sizes of a hole of a macrocyclic ligand and a Zn(II) ion.

Experimental

Materials. The tetraazacycloalkanes, [14]aneN$_4$ and [15]aneN$_4$, were purchased from Strem Chemical Inc.

Preparation of [Zn(NCS)$_2$([14]aneN$_4$)] (1). $ZnCl_2$ was allowed to react with an equimolar amount of [14]aneN$_4$ in

H_2O at 50 °C for 1 h. To the filtered solution was added two equivalents of KSCN at room temperature. Immediate complexation occurred to yield a white precipitate. The product was dissolved in $CHCl_3$ and the filtered solution was evaporated to dryness. The residue was recrystallized from nitromethane. Anal. Calcd for $[Zn(NCS)_2([14]aneN_4)]=ZnS_2C_{12}H_{24}N_6$: C, 37.74; H, 6.34; N, 22.01%. Found: C, 37.65; H, 6.42; N, 21.94%. IR (Nujol mull): 3210(NH), 2025(CN) cm^{-1}.

Preparation of [Zn(NCS)$_2$([15]aneN$_4$)] (2). This compound was synthesized in a similar way using [15]aneN$_4$ in place of [14]aneN$_4$. The crude product was recrystallized from acetonitrile. Anal. Calcd for $[Zn(NCS)_2([15]aneN_4)]=ZnS_2N_6C_{13}H_{26}$: C, 39.44; H, 6.62; N, 21.23%. Found: C, 39.70; H, 6.71; N, 21.50%. IR (Nujol mull): 3180(NH), 2050(CN) cm^{-1}.

Measurements. IR spectra were recorded on a HITACHI 295 spectrophotometer.

Collection and Reduction of X-ray Diffraction Data. Diffraction data were obtained on a Rigaku AFC-5 four-circle diffractometer with use of graphite-monochromatized Mo $K\alpha$ radiation. The intensity data were corrected for Lorentz-polarization effects. Absorption corrections were applied with a numerical integration procedure with a Gaussian grid (6X6X6). The procedures used for data collection were standard and have been described previously.[6] Pertinent crystallographic data for the compounds are summarized in Table 1.

Solution and Refinement of the Structures. Both the structures were solved and refined by standard Patterson, Fourier, and block-diagonal least-squares techniques. The atomic scattering factors for non-hydrogen atoms were taken from Ref. 7 and those for hydrogen from Stewart, Davidson, and Simpson.[8] The effects of anomalous dispersion for non-hydrogen atoms were corrected in structure factor calculations. The weights (w) were taken as $w=[\sigma_c^2+(0.015|F_o|^2)]^{-1}$. Non-hydrogen and hydrogen atoms were refined anisotropically and isotropically, respectively.

Calculations of the refinements for both the compounds converged nicely. However, we noticed in the structure of compound **1** thus obtained that a thermal ellipsoid of the Zn atom is extraordinarily elongated along the normal to the N_4 plane of the [14]aneN$_4$ ligand. The Zn atom in **1** was found to take an out-of-plane position and thus the two axial coordination bond distances differed substantially from each other. Even the shorter axial coordination bond length [Zn–N(5)=2.247(6) Å] was somewhat longer than normal Zn(II)–NCS bond lengths.[9] Then we collected intensity data for another crystal of **1** grown from a chloroform–methanol mixture and solved the structure. The resultant structural features were essentially the same. The situation seemed to be similar to that reported in the erroneous structure analysis

Table 1. Crystallographic parameters

	1	2
Formula	$ZnS_2N_6C_{12}H_{24}$	$ZnS_2N_6C_{13}H_{26}$
Fw	381.86	395.90
Crystal system	orthorhombic	monoclinic
Space group	$P2_1nb$	$P2_1/a$
a/Å	14.502(2)	14.453(2)
b/Å	18.163(2)	14.436(1)
c/Å	6.522(1)	9.213(1)
β/deg	—	104.823(9)
V/Å^3	1718.0(4)	1858.3(4)
Z	4	4
D_x/g cm^{-3}	1.476	1.415
D_m/g cm^{-3}	1.472	1.419
μ/mm^{-1}	1.17	1.58
2θ limits/deg	2—65	2—60
Unique data[a]	1598	2533
R	0.042	0.052
R_w	0.045	0.062

a) $|F_o|>3\sigma(|F_o|)$.

Table 2. Atomic parameters for $[Zn(NCS)_2([14]aneN_4)]$ (**1**)[a]

Atom	x	y	z
Zn[b]	0	1231(4)	273(18)
Zn'[c]	-184(9)	1244(7)	-111(18)
S(1)	2956(6)	904(2)	2903(4)
S(2)	-3088(6)	1526(2)	-2511(4)
N(1)	-551(7)	159(3)	143(10)
N(2)	-1030(8)	1440(4)	2421(10)
N(3)	422(7)	2324(3)	-55(9)
N(4)	875(8)	1052(4)	-2318(11)
N(5)	1031(8)	998(6)	2586(10)
N(6)	-1186(8)	1488(5)	-2579(10)
C(1)	-1073(9)	76(5)	2040(15)
C(2)	-1633(8)	787(6)	2390(13)
C(3)	-1484(9)	2165(6)	2365(12)
C(4)	-807(9)	2807(5)	2271(13)
C(5)	-307(7)	2897(4)	276(14)
C(6)	910(9)	2361(5)	-2046(14)
C(7)	1497(9)	1708(6)	-2357(13)
C(8)	1365(9)	337(5)	-2257(14)
C(9)	681(10)	-294(6)	-2182(15)
C(10)	133(9)	-415(3)	-178(13)
C(11)	1863(9)	956(5)	2696(11)
C(12)	-1950(11)	1511(6)	-2568(12)

a) Parameters are multiplied by 10^4. b) Occupancy factor=0.64. c) Occupancy factor=0.36.

Table 3. Atomic parameters for $[Zn(NCS)_2([15]aneN_4)]$ (**2**)[a]

Atom	x	y	z
Zn	2387(1)	825(1)	2414(1)
S(1)	3995(1)	2738(1)	6470(2)
S(2)	1353(1)	-1371(1)	-1508(2)
N(1)	2295(4)	1649(4)	393(5)
N(2)	3428(4)	65(4)	1596(7)
N(3)	2395(4)	-159(3)	4133(5)
N(4)	1137(3)	1533(3)	2615(6)
N(5)	3369(3)	1699(4)	3843(5)
N(6)	1248(5)	-327(4)	957(7)
C(1)	2760(8)	1133(6)	-686(8)
C(2)	3782(6)	680(6)	486(12)
C(3)	4175(6)	-412(6)	2693(10)
C(4)	3743(7)	-1052(6)	3572(11)
C(5)	3334(6)	-627(5)	4749(9)
C(6)	2046(6)	201(6)	5394(7)
C(7)	1065(6)	639(6)	4875(9)
C(8)	1037(5)	1600(6)	4135(8)
C(9)	1117(6)	2480(6)	2067(9)
C(10)	882(7)	2519(7)	516(15)
C(11)	1309(6)	1895(6)	-402(10)
C(12)	3627(4)	2133(4)	4911(6)
C(13)	1298(4)	-773(4)	-71(6)

a) Parameters are multiplied by 10^4.

on an aqua(tetraphenylporphinato)zinc(II) complex, [Zn(H_2O)(tpp)],[10] the structure of which was later redetermined by taking disorder in the Zn atom location into consideration.[3a] Then the structure of **1** was solved in a similar way with the Zn atom in two disordered positions.[11] The Zn atom was located at two positions, equidistantly above (Zn) and below (Zn') the N_4 plane. Full-matrix least squares calculations were carried out under the restricted condition that the sum of occupancy factors (P) of Zn and Zn' equals one. Final P_{Zn} and $P_{Zn'}$ values were 0.64 and 0.36. In the converged structure, geometries of [Zn(NCS)$_2$([14]aneN$_4$)] and [Zn'(NCS)$_2$([14]aneN$_4$)] are related approximately to each other by inversion at the center of the N_4 basal plane (Ct).

For **1**, all the hydrogen atoms were located by the difference syntheses and their positional and isotropic thermal parameters were refined. However, for **2**, 19 hydrogens out of 26 were found and included in the calculations.

The final R indices are listed in Table 1. Positional parameters for non-hydrogen atoms are given in Tables 2 and 3.[12] All the calculations were carried out on the HITAC M-200H computer at the Computer Center of the Institute for Molecular Science with the Universal Crystallographic Computation Program System UNICS III.[13]

Description of the Structure

Figure 1 shows perspective views of the complexes **1** and **2**. As shown in Fig. 1, the geometry about the Zn in each compound is of the pseudo octahedral type with NCS^- groups at the trans positions. Table 4 lists relevant bond lengths and angles. Deviations of atoms included in the first coordination sphere from the N_4 best plane are given in Table 5. Figure 2 represents perspective diagrams of the coordination environments of the Zn atoms in **1** and **2**.

[Zn(NCS)$_2$([14]aneN$_4$)] (1). The structure of this compound was solved assuming that the Zn atom is disordered above and below the N_4 plane. The Zn and Zn' atoms are displaced by 0.177(3) and 0.184(4) Å from the N_4 plane toward the N(5) and N(6) atoms of the NCS^- ligands, respectively. The overall stereochemistry of the macrocyclic ligand is essentially the same as that found for Ni(II),[2] Zn(II),[15,16] Pd(II),[16] Pd(IV),[16] and Ag(II)[16] complexes with [14]aneN$_4$. The alternating six- and five-membered chelate rings are in the stable chair and gauche conformations, respectively. Intermolecular hydrogen-bonds operate between sulfur atoms and secondary amine groups of the neighbouring complexes.[17] If the complex with the ring conformations assumes a structure with high symmetry such as C_{2h} or C_i, the occupancy factors of the Zn and Zn' atoms should be 0.5 each. However, intramolecular and packing interactions including the hydrogen

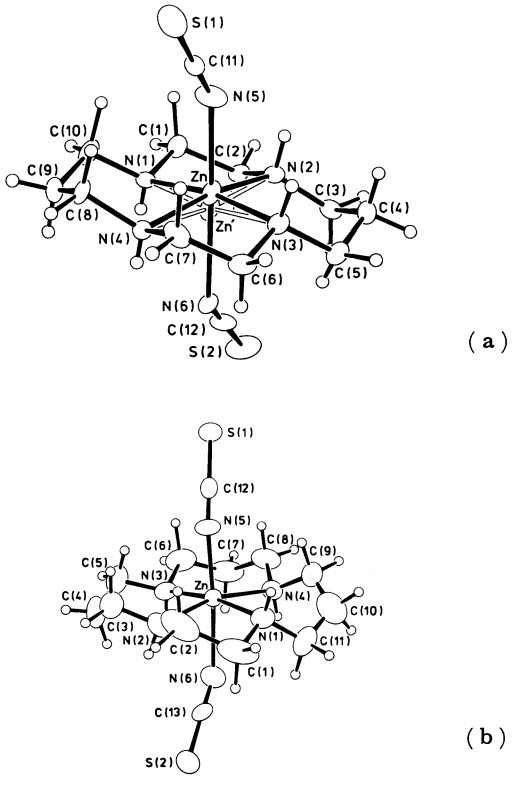


Fig. 1. Molecular structures: (a) [Zn(NCS)$_2$([14]aneN$_4$)] (**1**), the disordered Zn atom with a minor occupancy factor is shown with open bonds; (b) [Zn(NCS)$_2$([15]aneN$_4$)] (**2**), seven hydrogens are located at the calculated positions (see text).

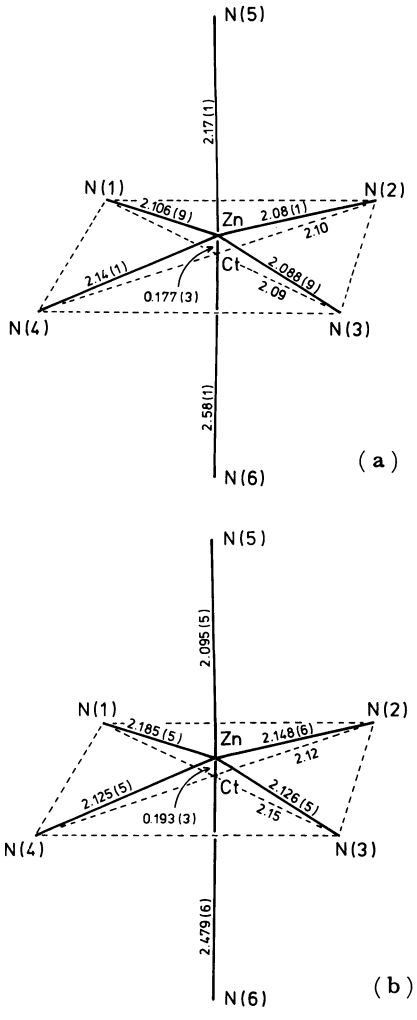


Fig. 2. Coordination geometries about the Zn atoms: (a) [Zn(NCS)$_2$([14]aneN$_4$)] (**1**), the geometry about the Zn atom with a major occupancy factor is shown; (b) [Zn(NCS)$_2$([15]aneN$_4$)] (**2**). Ct represents a center of donor atoms of the macrocyclic ligand.

TABLE 4. RELEVANT BOND DISTANCES (Å) AND ANGLES (DEG) FOR $[Zn(NCS)_2([14]aneN_4)]$ AND $[Zn(NCS)_2([15]aneN_4)]$

$[Zn(NCS)_2([14]aneN_4)]$ (**1**)

Zn	-N(1)	2.106(9)		Zn'	-N(3)	2.151(14)	
Zn	-N(2)	2.083(13)		Zn'	-N(4)	2.133(16)	
Zn	-N(3)	2.088(9)		Zn'	-N(5)	2.529(16)	
Zn	-N(4)	2.138(13)		Zn'	-N(6)	2.214(15)	
Zn	-N(5)	2.166(13)		S(1)	-C(11)	1.594(16)	
Zn	-N(6)	2.576(13)		S(2)	-C(12)	1.651(18)	
Zn'	-N(1)	2.046(14)		N(5)	-C(11)	1.211(18)	
Zn'	-N(2)	2.089(15)		N(6)	-C(12)	1.108(20)	
N(1)	-Zn	-N(2)	85.6(4)	N(1)	-Zn'	-N(2)	87.0(6)
N(1)	-Zn	-N(3)	170.3(3)	N(1)	-Zn'	-N(3)	169.4(7)
N(1)	-Zn	-N(4)	93.0(5)	N(1)	-Zn'	-N(4)	94.9(6)
N(1)	-Zn	-N(5)	96.2(5)	N(1)	-Zn'	-N(5)	87.4(5)
N(1)	-Zn	-N(6)	83.4(4)	N(1)	-Zn'	-N(6)	94.7(6)
N(2)	-Zn	-N(3)	96.1(4)	N(2)	-Zn'	-N(3)	94.1(6)
N(2)	-Zn	-N(4)	170.1(6)	N(2)	-Zn'	-N(4)	169.9(8)
N(2)	-Zn	-N(5)	93.6(6)	N(2)	-Zn'	-N(5)	83.7(5)
N(2)	-Zn	-N(6)	88.5(4)	N(2)	-Zn'	-N(6)	98.9(6)
N(3)	-Zn	-N(4)	83.7(4)	N(3)	-Zn'	-N(4)	82.3(5)
N(3)	-Zn	-N(5)	93.2(4)	N(3)	-Zn'	-N(5)	82.2(5)
N(3)	-Zn	-N(6)	87.1(4)	N(3)	-Zn'	-N(6)	95.6(6)
N(4)	-Zn	-N(5)	96.4(4)	N(4)	-Zn'	-N(5)	86.5(6)
N(4)	-Zn	-N(6)	81.5(5)	N(4)	-Zn'	-N(6)	90.8(6)
N(5)	-Zn	-N(6)	177.9(6)	N(5)	-Zn'	-N(6)	176.8(7)
Zn	-N(5)	-C(11)	137.8(9)	S(1)	-C(11)	-N(5)	178.5(13)
Zn	-N(6)	-C(12)	132.0(10)	S(2)	-C(12)	-N(6)	178.5(15)

$[Zn(NCS)_2([15]aneN_4)]$ (**2**)

Zn	-N(1)	2.185(5)		S(1)	-C(12)	1.648(6)	
Zn	-N(2)	2.148(6)		S(2)	-C(13)	1.599(6)	
Zn	-N(3)	2.126(5)		N(5)	-C(12)	1.145(7)	
Zn	-N(4)	2.125(5)		N(6)	-C(13)	1.163(9)	
Zn	-N(5)	2.095(5)					
Zn	-N(6)	2.479(6)					
N(1)	-Zn	-N(2)	82.8(2)	N(3)	-Zn	-N(5)	93.5(2)
N(1)	-Zn	-N(3)	170.6(2)	N(3)	-Zn	-N(6)	80.3(2)
N(1)	-Zn	-N(4)	86.8(2)	N(4)	-Zn	-N(5)	96.3(2)
N(1)	-Zn	-N(5)	95.2(2)	N(4)	-Zn	-N(6)	84.7(2)
N(1)	-Zn	-N(6)	91.0(2)	N(5)	-Zn	-N(6)	173.8(2)
N(2)	-Zn	-N(3)	92.8(2)	Zn	-N(5)	-C(12)	152.7(5)
N(2)	-Zn	-N(4)	164.5(2)	Zn	-N(6)	-C(13)	129.9(6)
N(2)	-Zn	-N(5)	96.0(2)	S(1)	-C(12)	-N(5)	178.8(5)
N(2)	-Zn	-N(6)	84.0(2)	S(2)	-C(13)	-N(6)	178.8(6)
N(3)	-Zn	-N(4)	95.7(2)				

TABLE 5. DEVIATIONS (Å) OF ATOMS FROM A PLANE DEFINED BY FOUR IN-PLANE NITROGENS OF THE MACROCYCLIC LIGAND

	1	2
N(1)[a]	0.006(7)	0.032(7)
N(2)[a]	−0.006(7)	−0.040(8)
N(3)[a]	0.006(7)	0.028(7)
N(4)[a]	−0.006(6)	−0.027(7)
N(5)	2.341(7)	2.288(6)
N(6)	−2.392(6)	−2.276(8)
Zn	0.177(3)	0.193(3)
Zn'	−0.184(4)	—

a) Atoms used in the calculation of the best plane.

bonds lower more or less the symmetry of the skeletal structure of the macrocyclic ligand to cause the difference in the occupancy factors.

$[Zn(NCS)_2([15]aneN_4)]$ (2). Three six-membered and one five-membered chelate rings adopt a chair-chair-skew-gauche conformational sequence. The ring conformation of this type has been found for $[Ni(NCS)_2([15]aneN_4)]$.[2] But the $[15]aneN_4$ ligand in $[NiCl_2([15]aneN_4)]$[2] and $[\{Zn([15]aneN_4)\}_3(O_2COCH_3)_2](ClO_4)_4$,[15] and that in $[CoCl_2([15]aneN_4)](ClO_4)$ (green form)[18] have been reported to take chair-skew-chair-gauche and skew-skew-skew-gauche conformations, respectively.

The Zn atom in this compound also takes an out-of-plane position and is displaced by 0.193(3) Å from the N_4 best plane toward the N(5) atom. The Zn-N(6)

distance lengthens to 2.479(6) Å, while the Zn–N(5) distance of 2.095(5) Å is within the normal range. Sulfur atoms are again involved in intermolecular hydrogen-bonds with secondary amine groups of the neighbouring complexes.[17]

It has been reported that, in metal complexes with the [15]aneN$_4$ ligand in the chair-chair-skew-gauche conformation, notable structural distortions arise at the periphery of the N(1) atom, which links a gauche five-membered and a skew six-membered chelate ring.[2] Typical distortions in such compounds are lengthening of an M–N(1) bond and deviation of the N(1) atom from the N$_4$ best plane. But, in compound **2**, such strains are relieved to some extent by the displacement of the Zn atom from the N$_4$ plane. This is evidenced by comparison of bond distances and angles associated with the N(1) atom of the present compound and those for [Ni(NCS)$_2$([15]aneN$_4$)].[2]

Discussion

There are two distinct features in the coordination geometries of compounds **1** and **2**: (i) the Zn atom is displaced *ca.* 0.2 Å from the mean plane formed by the four nitrogens of the macrocyclic ligand; (ii) there is a negative correlation between in-plane and axial coordination bond lengths. The out-of-plane displacement of the Zn causes, in each compound, rather large inequalities in two axial coordination bond lengths. The differences amount to 0.38 Å on the average for both **1** and **2**. The distances between the Zn atoms and the weakly bonded NCS$^-$ groups [Zn–N(6)=2.58(1) Å and Zn′–N(5)=2.53(1) Å for **1**, and Zn–N(6)=2.479(6) Å for **2**] appear to be rather long as coordination bond distances. However, the Zn atoms in these compounds should be described as six-coordinate, since deviations of Zn(II) from basal plane reported for the five-coordinate Zn(II) complexes with the square-pyramidal geometry are much larger. It is interesting to note that, in each compound, the nitrogens of the weakly bonded and the strongly bonded NCS$^-$ groups are nearly equidistant from the mean N$_4$ plane: for **1**, Ct–N(5)=2.35, Ct–N(6)=2.40 Å; for **2**, Ct–N(5)=2.29, Ct–N(6)=2.29 Å (see Fig. 2).

The hole sizes found for the present tetraazacycloalkane complexes (Ct–N distance) are 2.10 Å for **1** and 2.13 Å for **2**, and are larger than those of the Zn(II) porphinato or phthalocyanato complexes (1.98—2.07 Å). In spite of this, the Zn atoms in the present compounds take out-of-plane positions. Table 6 collates bond lengths and angles within the [M([14]aneN$_4$)] moieties of various metal complexes containing the [14]aneN$_4$ ligand. In all the compounds, the [14]aneN$_4$ ligand adopts the same overall stereochemistry with the most stable chelate ring conformations. The values in Table 6 are averaged assuming C_{2h} symmetry for the [M([14]aneN$_4$)] moiety. The compounds are listed in increasing order of the Ct–N distance. Some important facts are noted in Table 6 relative to the observed out-of-plane structures. Except for Zn(II) complexes, all the compounds in Table 6 take the in-plane structures. Interestingly, the largest cation, Ag(II), the ionic radius of which is much larger than a Zn(II) ion, sits precisely in the N$_4$ plane [Ag–N=2.158(2) Å].[19] Furthermore, half of Zn(II) atoms in the crystal structure of [Zn(O_2C-OCH_3)([14]aneN$_4$)](ClO_4) take the in-plane position.[15] These observations suggest that simple argument, such that Zn(II) is too large to be accomodated into the cavity in a planar fashion to result in the out-of-plane structure,[3a] must be changed. In Table 6, various bond lengths and angles increase or decrease smoothly, or remain unchanged on going from shorter to longer Ct–N structures, in general. However, it can be seen that some structural parameters such as bond angles of N–M–N(6*) and C–C–C (see footnotes of Table 6 for notations) deviate from the trend in the out-of-plane Zn structures and return to the original tendency in the Ag(II) complex. There is no doubt that cumulative bond length and angle strain is relieved by taking the out-of-plane structure in the Zn(II) complexes. It is also certain from Table 6 that sizes of Ag(II) and Zn(II) ions are larger than a natural cavity size of the [14]aneN$_4$ ligand. In the case of the Ag(II) complex, much larger electronic strain would be introduced if the Ag(II) took an out-of-plane position.

A Zn(II) ion has an electronic configuration of $(3d)^{10}$ and thus no ligand field stabilization due to 3d electrons takes place for a Zn(II) complex. *Ab initio* MO calculations for *trans*-[$ZnCl_2(NH_3)_4$] show that the potential surface along the direction of the out-of-plane displacement of Zn is very flat.[20] It is likely that very similar situations exist for the Zn(II) complexes with the out-of-plane structures. Since the potential surface along the direction in an isolated complex is very flat, it would be affected easily in its crystalline state by the potential from surrounding ions and packing forces. Subtle intra- or intermolecular forces including the intermolecular hydrogen bonds seem to be responsible for the out-of-plane structures. Conversely, it follows that a Zn(II) ion might take the in-plane position if the situation were otherwise. In fact, such examples have been found for [Zn(O_2COCH_3)([14]aneN$_4$)](ClO_4), and [{Zn([15]aneN$_4$)}$_3$(O_2COCH_3)$_2$](ClO_4)$_4$.[15] The out-of plane structures found for the present Zn(II) complexes are associated not only with the relative size between Zn(II) and the cavity but also with the flatness of the potential surface along the normal to the N$_4$ plane.

The $^{13}C\{^1H\}$ NMR spectrum of compound **1** in $CDCl_3$ shows only four signals, which are assignd to C–$\underline{C}H_2$–C (δ, 28.6), two N–$\underline{C}H_2$ carbons (δ, 47.9 and 49.4), and N$\underline{C}$S (δ, 133.9). The observed spectral pattern indicates that compound **1** has C_{2h} symmetry in solution. Such symmetry can be expected when the Zn atom sits precisely in the N$_4$ plane and the [14]aneN$_4$ ligand takes a chair-gauche-chair-gauche conformation, or when the Zn atom moves up and down passing through the N$_4$ hole at a faster rate than an NMR time scale. We failed to answer this question.[21] As for compound **2** in solution, whether the Zn takes the in-plane position or the out-of-plane position was not clear from the NMR study, because **2** has no symmetry element even if Zn were in the in-plane position.

On going from the fourteen-membered to the fifteen membered rings, average in-plane Zn–N or Ct–N distances increased by *ca.* 0.04 Å. The amount of the increase is slightly smaller than those in the Ni–N dis-

Table 6. Mean bond lengths (Å) and angles (deg) of metal complexes with 1,4,8,11-tetraazacyclotetradecane(L)[a,b,c]

	Ni^{II} (low spin)	Ni^{III} (low spin)	Pd^{II}	Pd^{II}-Pd^{IV}	Pd^{IV}	Ni^{II} (high spin)		Zn^{II} (in-plane)	Zn^{II} (out-of-plane)		Ag^{II}
Compound	$[NiL](PF_6)_2$[d]	$[NiCl_2L](ClO_4)$[e]	$[PdL](ClO_4)_2$[f]	$PdClL(ClO_4)_2$[f,g]	$PdCl_2L(NO_3)_2$[f]	$NiCl_2L$[h,i]	$Ni(NCS)_2L$[i]	$ZnL(O_2CCH_3)(ClO_4)$[j]	$Zn(NCS)_2L$[k]	$ZnL(O_2CCH_3)(ClO_4)$[j]	$[AgL](ClO_4)_2$[l]
M-N	1.945(8)	1.970(7)	2.051(4)	2.054(13)	2.062(3)	2.067(1)	2.074(7)	2.100(16)	2.105(31)	2.117(68)	2.158(4)
N-C(5*)	1.480(8)	1.489(13)	1.465(45)	1.478(11)	1.488(3)	1.477(6)	1.477(6)	1.470(6)	1.480(17)	1.473(9)	1.472(3)
N-C(6*)	1.489(12)	1.489(3)	1.460(10)	1.488(20)	1.484(1)	1.483(2)	1.477(4)	1.481(6)	1.480(26)	1.469(12)	1.486(1)
C-C(5*)	1.505(6)	1.493(2)	1.510(18)	1.491(13)	1.514(2)	1.514(3)	1.510(12)	1.514(6)	1.520(10)	1.501(7)	1.531(4)
C-C(6*)	1.508(13)	1.503(6)	1.560(1)	1.517(8)	1.516(3)	1.527(6)	1.516(7)	1.521(1)	1.521(10)	1.510(7)	1.518(3)
N-M-N(5*)	86.7(1)	86.2(4)	83.1(3)	84.4(3)	84.7(1)	85.3(1)	85.3(2)	84.8(1)	84.8(25)	83.4(2)	84.0(1)
N-M-N(6*)	93.3(1)	93.8(8)	96.9(3)	95.6(3)	95.3(1)	94.7(1)	94.7(2)	95.2(1)	94.4(21)	90.9(2)	96.0(1)
M-N-C(5*)	108.4(1)	107.8(11)	108.1(20)	107.6(13)	106.7(0)	106.3(1)	105.7(4)	105.4(8)	106.7(5)	106.0(47)	104.5(3)
M-N-C(6*)	119.6(8)	119.2(2)	115.6(1)	115.8(1)	115.8(0)	116.3(1)	116.2(6)	115.1(1)	115.1(3)	114.0(60)	111.5(3)
N-C-C(5*)	106.8(1)	107.1(11)	106.3(18)	109.4(10)	107.2(7)	109.3(7)	109.0(1)	109.4(8)	109.2(3)	110.0(5)	109.7(1)
N-C-C(6*)	112.2(8)	111.7(7)	112.9(14)	112.1(5)	112.0(3)	111.9(1)	112.3(2)	112.1(1)	111.8(1)	113.5(7)	112.6(3)
C-C-C	112.3(3)	113.6(6)	116.5(9)	117.7(7)	115.1(2)	115.8(1)	116.5(5)	117.1(4)	115.8(1)	115.4(4)	117.5(2)
C-N-C	110.1(1)	111.8(8)		113.1(3)	114.2(2)	113.7(5)	114.6(5)	115.0(7)	114.9(2)	114.3(1)	115.1(5)

a) Values are averaged assuming that each compound has C_{2h} symmetry. b) Abbreviations: 5*, five-membered ring; 6*, six-membered ring. c) Crystal radii (Å) are 0.70 (low spin Ni^{3+}), 0.78 (Pd^{2+}), 0.76 (Pd^{4+}), 0.84 (high spin Ni^{2+}), and 0.89 (Zn^{2+}) (R. D. Shannon, C. T. Prewitt, *Acta Crystallogr., Sect. B*, **25**, 925 (1969)). Ionic radius of Ag^{2+} is 1.01 Å ("Kagaku Benran," Maruzen, Tokyo (1975)). d) Ref. 14. e) T. Ito, M. Sugimoto, K. Toriumi, H. Ito, *Chem. Lett.*, **1981**, 1477. f) M. Yamashita, H. Ito, K. Toriumi, T. Ito, *Inorg. Chem.*, **22**, 1566 (1983). g) A mixed valence complex, $[Pd^{II}L][Pd^{IV}Cl_2L](ClO_4)_4$. h) B. Bosnich, R. Mason, P. T. Pauling, G. B. Robertson, M. L. Tobe, *Chem. Commun.*, **1965**, 97. i) Ref. 2. j) Ref. 15. k) The present study. l) PI form. T. Ito, H. Ito, K. Toriumi, *Chem. Lett.*, **1961**, 1101.

tances (0.05—0.06 Å) for one ring member added similarly in Ni(II) complexes with the same tetraazacycloalkanes.[2] The increases are not as large as expected from calculations of strain energy minimizations for free ligand molecules (0.10—0.15 Å).[22] The shorter axial coordination bond length (Zn–N(5)) in **1** is longer than the corresponding distance (Zn–N(5)) in **2**. The longer one (Zn–N(6)) in **1** is also longer than the corresponding distance (Zn–N(6)) in **2**. That is, the axial coordination bond length decreases as the in-plane distance increases. The same relationship also holds when the mean distance of Zn–N(5) and Zn–N(6) or an average Ct–NCS^- distance is taken as the "axial bond length".

It is most reasonable to consider the observed correlation to be a result of the electronically controlled cis effect, since the crystal structures of **1** and **2** show no significant steric effects that would cause the correlation. The degree of the correlation found for the Zn complexes is substantially stronger than those reported for a series of similar Ni(II) and Co(III) complexes.[1]

We have previously discussed the electronic origin that gives rise to the correlations between intramolecular coordination bond lengths from the viewpoint of the potential energy surface.[1] A section of the potential surface along the in-plane and axial coordination bond axes is an ellipse which is elongated in the M–X directon and has a tilt with respect to the coordination bond axes. Such features of the potential surface are primarily responsible for the experimentally observed correlations. Furthermore, the shape of the potential surface, *i.e.*, the degree of the correlation is closely related to softness or hardness in the HSAB concept[23] for metal ions.[1] The present result indicates that a Zn(II) ion is much softer than a Ni(II) ion, though Pearson classifies both of these ions into borderline between soft and hard metal ions.[23]

In structures containing the thiocyanate ion bonded to a metal atom through nitrogen, a wide range of metal-isothiocyanate bond angles have been obtained, though the majority of examples fall in the range 150—180°.[24] It has also been suggested that inter- and intra-molecular forces affect this angle though such effects are often difficult to prove.[24] The angles found for the present complexes are somewhat smaller than the normal values. The values for **1** range from 132.0(10)° to 137.8(9)°. For **2**, one of the angles [Zn–N(6)–C(13)] narrows down to 129.9(6)°, which is comparable to the smallest value so far reported, 129°, for bis(isothiocyanato)- bis(*N*,*N*′-dimethylethylenediamine)-copper(II).[24]

References

1) T. Ito, M. Kato, and H. Ito, *Bull. Chem. Soc. Jpn.*, **57**, 1556 (1984).

2) T. Ito, M. Kato, and H. Ito, *Bull. Chem. Soc. Jpn.*, **57**, 2641 (1984).

3) a) M. D. Glick, G. H. Cohen, and J. L. Hoard, *J. Am. Chem. Soc.*, **89**, 1966 (1967); b) D. M. Collins and J. L. Hoard, *ibid.*, **92**, 3761 (1970); c) T. Kobayashi, T. Ashida, N. Uyeda, E. Suito, and M. Kakudo, *Bull. Chem. Soc. Jpn.*, **44**, 2095 (1971).

4) W. R. Scheidt, M. E. Kastner, and K. Hatano, *Inorg. Chem.*, **17**, 706 (1978).

5) W. R. Scheidt and W. Dow, *J. Am. Chem. Soc.*, **99**, 1101 (1977).

6) M. Sugimoto, J. Fujita, K. Toriumi, H. Ito, and T. Ito, *Inorg. Chem.*, **22**, 955 (1983).

7) "International Tables for X-ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV.

8) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

9) A Zn(II)–NCS bond length in [Zn(NCS)(tren)](SCN) has been reported to be 2.03 Å [P. C. Jain, E. C. Lingafeltrer, and P. Paoletli, *J. Am. Chem. Soc.*, **90**, 519 (1968)].

10) E. B. Fleischer, C. K. Miller, and L. E. Webb, *J. Am. Chem. Soc.*, **86**, 2342 (1964).

11) A difference Fourier map calculated without the Zn atom contribution showed only a broad peak elongated perpendicularly to the N_4 plane at a distance of 0.097(3) Å from it.

12) Hydrogen atomic coordinates, thermal parameters of non-hydrogen atoms, lists of observed and calculated structure factors, and tables of full bond lengths and angles are kept in the Office of the Chemical Society of Japan (Document No. 8442).

13) T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku*, **55**, 69 (1979).

14) H. Ito and T. Ito, unpublished study.

15) M. Kato and T. Ito, submitted for publication.

16) See Table 6.

17) The hydrogen-bond parameters are as follows.

$[Zn(NCS)_2([14]aneN_4]$ (**1**)		$[Zn(NCS)_2([15]aneN_4)]$ (**2**)	
$S(1)\cdots N(1)^{i}$	3.52(1) Å	$S(1)\cdots N(3)^{i}$	3.604(5) Å
$S(2)\cdots N(3)^{ii}$	3.42(1)	$S(2)\cdots N(4)^{ii}$	3.487(5)
		$S(2)\cdots N(1)^{iii}$	3.467(5)

Key to symmetry operations

(i)	$0.5+x$	$-y$	$-z$	(i)	$0.5-x$	$0.5+y$	$1-z$
(ii)	$0.5+x$	$0.5-y$	$0.5+z$	(ii)	$-x$	$-y$	$-z$
				(iii)	$0.5-x$	$-0.5+y$	z

18) H. Ito, M. Kato, and T. Ito, unpublished study.

19) T. Ito, H. Ito, and K. Toriumi, *Chem. Lett.*, **1981**, 1104.

20) The calculations were carried out by using a double ζ quality basis set for metal 3d orbitals and minimal basis set for the others as in Ref. 1. Details will be reported elsewhere.

21) The spectral pattern was essentially the same in a more polar solvent such as CD_3OD, where the out-of-plane structure may be more stabilized. And the spectrum remained unchanged when the temperature was lowered down to −87.5 °C in CD_2Cl_2.

22) L. Y. Martin, L. J. DeHayes, L. J. Zompa, and D. H. Busch, *J. Am. Chem. Soc.*, **96**, 4046 (1974).

23) R. G. Pearson, *J. Chem. Educ.*, **45**, 581, 643 (1968).

24) M. B. B. Drew, and A. H. B. Othman, *Acta Crystallogr., Sect., B*, **31**, 613 (1975), and references cited therein.