The Structures of *trans*-Dichloro- and *trans*-Bis(isothiocyanato)nickel(II) Complexes with 1,4,8,11-Tetraazacyclotetradecane, 1,4,8,12-Tetraazacyclopentadecane, and 1,5,9,13-Tetraazacyclohexadecane. The Negative Correlation between the Axial and In-plane Coordination Bond Lengths in Tetragonal Ni(II) Complexes of the *trans*-NiX_2N_4 Type

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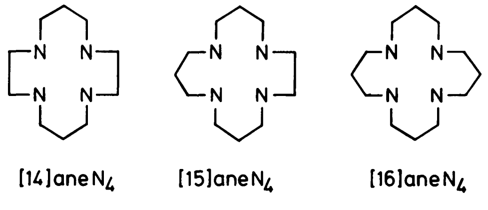
The molecular structures of the six titled compounds, which contain 14-membered, 15-membered, or 16-membered tetraazamacrocyclic ligands, have been determined by single crystal X-ray analyses. On going from smaller to larger rings, the average in-plane Ni–N distance increased by 0.05—0.06 Å for each ring member added. For a series of complexes with given axial ligands (X), the mean axial coordination bond length (Ni–X) was found to decrease as the average in-plane distance (Ni–N) increased. The degree of the negative correlation was stronger for complexes with weaker axial ligands (Cl^-) than for those having stronger axial ligands (NCS^-). Similar negative interrelationships between the Ni–X and Ni–N distances have been found for complexes which have the same in-plane macrocyclic ligand, but different axial ligands. The molecular stereochemistries of the complexes have been discussed. For all the complexes with the 1,4,8,12-tetraazacyclopentadecane ligand, a structural disorder of the same type has been found: gauche five-membered and skew six-membered chelate rings are randomly interchanged in the crystal. This arises mainly from the similarity of the bite angles of the five- and six-membered chelate rings in the gauche and the skew conformations respectively.

This paper is one of a series of investigations of metal-ion characteristics viewed from the correlation between the axial and in-plane coordination bond lengths in tetragonal six-coordinate complexes of the *trans*-MX_2N_4 type (M=Ni^{2+}, Zn^{2+}, and Co^{3+}). The aim and method of the studies have been described in a previous paper along with a historical review.[1] In this series of investigations, 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. Both experimentally and theoretically, it has been found that the axial M-X distance decreases as the in-plane M–N distance increases. The degree of the negative correlation is strongly metal ion dependent and varies in the order: $Zn^{2+} > Ni^{2+} > Co^{3+}$. A summary of the studies[1] and the structures of the Zn complexes[2] have been described elsewhere. The present paper reports the structural details and the correlation observed for the titled Ni(II) complexes: $[NiCl_2([14]aneN_4)]$ (**1**), $[NiCl_2([15]aneN_4)]$ (**2**), $[NiCl_2([16]aneN_4)]$ (**3**), $[Ni(NCS)_2([14]aneN_4)]$ (**4**), $[Ni(NCS)_2([15]aneN_4)]$ (**5**), and $[Ni(NCS)_2([16]aneN_4)]$ (**6**).



As in-plane ligands, the tetraazacycloalkanes shown above were employed. On going from smaller to larger rings, the average M–N bond lengths can be varied systematically.[3,4] As axial ligands (X), we chose Cl^- and NCS^-, which have a relatively weak and a strong ligand field strength respectively, so that it was possible to investigate the effect of the ligand field strength on the correlation.

The structure of **1** was reported previously by Bosnich *et al.*[5] We have now redetermined the structure, aiming at an improvement in the accuracy of the structure analysis, and also because the atomic parameters for this compound have not been reported.

In this study, we have also measured the far-infrared spectra of a series of complexes of this type in order to see if the electronic interaction between the in-plane and axial ligands is manifested in the stretching vibrations of the coordination bonds.

Experimental

Materials. All the compounds **1**—**6** were prepared according to the reported synthetic procedures.[3] Blue violet column crystals of **2**, violet block crystals of **5**, and blue block crystals of **6** were grown slowly from a methanol solution. Pink prismatic crystals of **1**, green polyhedral crystals of **3**, and red violet plates of **4** were obtained by recrystallization from a methanol-chloroform mixed solvent, nitromethane, and acetonitrile, respectively.

Measurement. The far-infrared spectra were recorded as nujol mull on polyethylene film with a Nicolet FT-IR 7199A spectrometer.

Collection and Reduction of X-ray Diffraction Data. The diffraction data were obtained on a Rigaku AFC-5 four-circle diffractometer by the use of graphite-monochromatized Mo $K\alpha$ radiation. The lattice parameters were obtained from the least-squares fit of 40—50 2θ values with $26° < 2\theta < 30°$. The θ–2θ scan mode was used at a scan rate of 3° min^{-1} to record the intensities. The intensities of three standard reflections were monitored for each crystal at 100-

Table 1. Crystallographic parameters

Compound	**1**	**2**	**3**	**4**	**5**	**6**
Formula	$NiCl_2N_4C_{10}H_{24}$	$NiCl_2N_4C_{11}H_{26}$	$NiCl_2N_4C_{12}H_{28}$	$NiS_2N_6C_{12}H_{24}$	$NiS_2N_6C_{13}H_{26}$	$NiS_2N_6C_{14}H_{28}$
Fw	329.93	343.96	357.98	357.19	389.22	403.24
Crystal system	monoclinic	monoclinic	triclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/a$	$P\bar{1}$	$P\bar{1}$	$P2_1/a$	$P2_1/a$
a/Å	13.607(1)	14.504(1)	10.169(2)	14.172(1)	14.653(3)	14.822(3)
b/Å	8.3685(9)	8.3019(8)	11.530(2)	15.201(1)	14.386(2)	14.522(2)
c/Å	6.6207(8)	6.6771(6)	9.639(1)	8.394(1)	9.151(2)	14.522(3)
α/deg	90	90	65.17(1)	79.80(1)	90	90
β/deg	103.585(8)	100.24(1)	115.57(1)	102.94(1)	105.92(2)	106.00(1)
γ/deg	90	90	120.76(1)	90.17(1)	90	90
V/Å^3	732.8(1)	791.2(1)	846.5(3)	1733.3(3)	1854.9(6)	1909.0(5)
Z	2	2	2	4	4	4
D_x/g cm^{-3}	1.495	1.444	1.404	1.438	1.394	1.403
D_m/g cm^{-3}	1.495	1.448	1.415	1.437	1.391	1.407
μ/mm^{-1}	1.667	1.547	1.450	1.350	1.265	1.231
2θ limits/deg	2—60	2—65	2—60	2—60	2—60	2—60
Unique data[a]	5374	1980	2801	5374	2236	2801
R	0.027	0.059	0.032	0.033	0.055	0.039
R_w	0.036	0.076	0.046	0.038	0.076	0.039

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

reflection intervals. The fluctuations of their F_o values were within experimental error. The intensity data were corrected for the Lorentz-polarization effects and for the absorption. The pertinent crystallographic data for the compounds are summarized in Table 1.

Solution and Refinement of the Structures. All 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. 6, and those for hydrogen, from Stewart, Davidson, and Simpson.[7] The effect of anomalous dispersion for non-hydrogen atoms was corrected in the structure factor calculations. The weight (w) was taken as $w=[\sigma_c^2+(0.015|F_o|)^2]^{-1}$, where σ_c denotes a standard deviation of F_o as calculated from the counting statistics.

In the cases of Compounds **2** and **5**, each of which has the [15]aneN_4 ligand with a six-membered chelate ring and a five-membered chelate ring in the skew and gauche conformations respectively, significant disorder was found in the crystal structure. The disorder occurs in such a way that the gauche five-membered chelate ring and the skew six-membered chelate ring are randomly interchanged in the crystal. The general structural features found for the moiety are depicted in Fig. 1. For the disordered chelate rings, Fourier maps showed relatively sharp peaks for nitrogens, but very broad peaks for carbon atoms. The central carbon (C_b) was generally not found clearly in a Fourier map, and so it was located by a difference synthesis. The carbon atom adjacent to the nitrogen (C_a or C_c) appeared as a broad single peak, but was not observed as two peaks corresponding to the five- and six-membered chelate rings. Therefore, the structures were refined assuming occupancy factors of 1.0 for C_a and C_c, and 0.5 for C_b.

Except for Compounds **2** and **5** which involve disorder, the difference syntheses permitted the location of all the hydrogen atoms, and their positional and isotropic thermal parameters were refined. The final R indices are listed in Table 1, while the positional parameters for non-hydrogen atoms are given in Table 2.[8]

All the calculations were carried out on the HITAC M-200H computer at the Computer Center of the Institute for Molecular Science using the Universal Crystallographic Computation Program System UNICS III.[9]

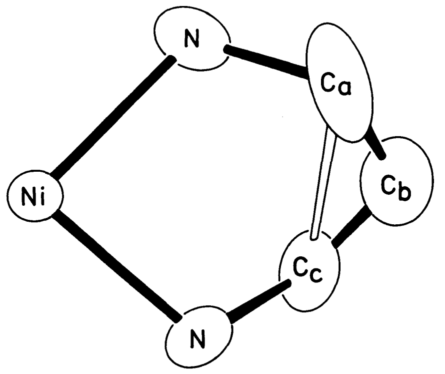


Fig. 1. Disorder of the gauche five-membered and skew six-membered chelate rings in [15]aneN_4 complexes.

Description of the Structures

Figure 2 shows the perspective views of Complexes **1**—**6**. As shown in Fig. 2, the geometries about Ni in all the compounds are of the *trans*-NiX_2N_4 type. The coordination bond distances and angles are given in Table 3. Table 4 lists the deviations of the atoms in a first coordination sphere from a NiN_4 best plane formed with Ni and the in-plane four nitrogens for Complexes **3**, **5**, and **6**. The data for **1**, **2**, and **4** are not given, since in these compounds the Ni atom lies at a center of symmetry.

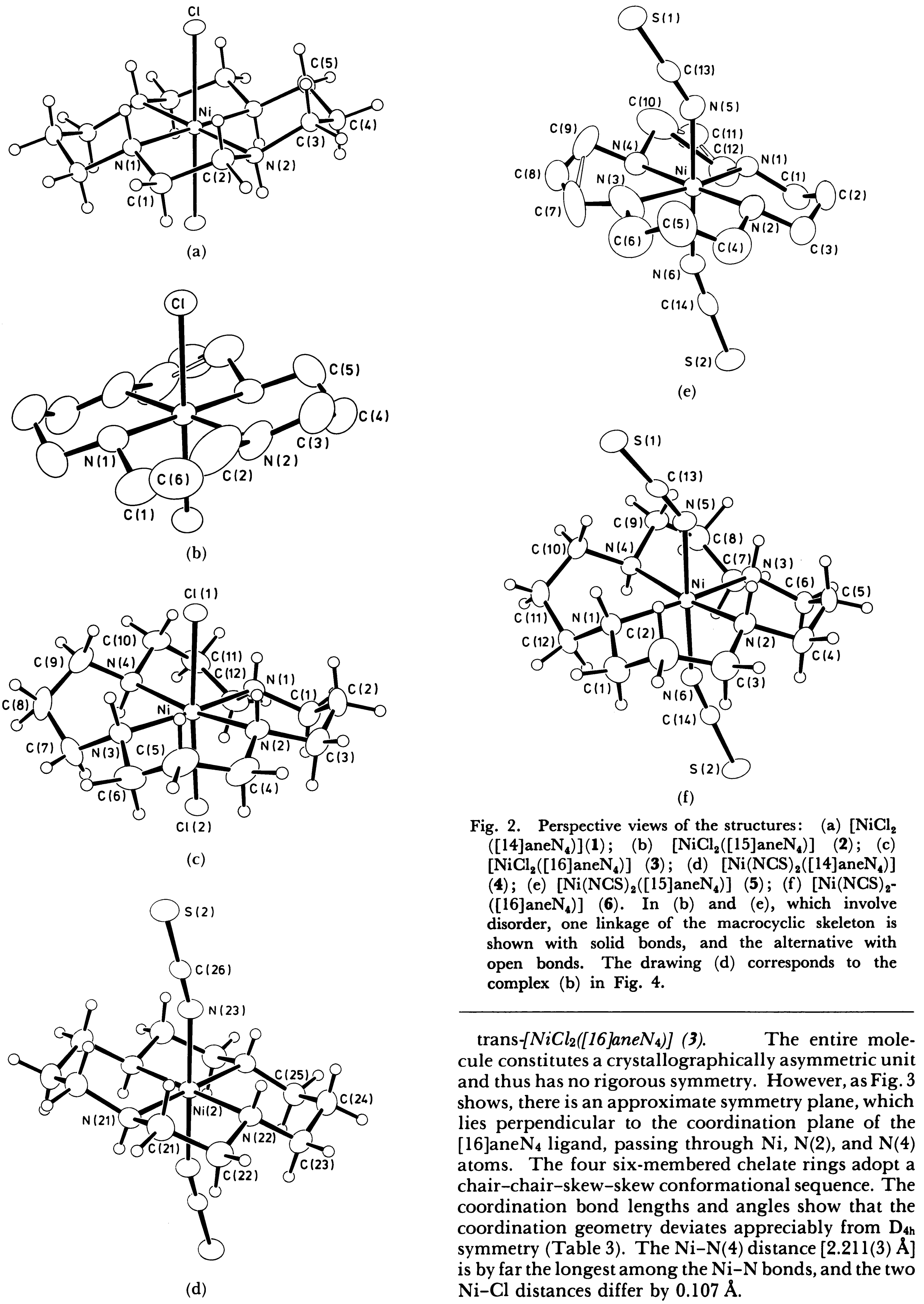
trans-[$NiCl_2$([14]aneN_4)] (1). The total stereochemistry is the same as that reported previously.[5] The accuracy of the bond lengths and angles is raised approximately one order of magnitude, as evidenced by their esd values. The alternating two six- and two five-membered chelate rings are in the stable chair and gauche conformations, respectively.

trans-[NiCl$_2$([15]aneN$_4$)] (2). The structure of this compound was solved under the crystallographic requirement that the Ni atom lies at a center of symmetry, even though the entire molecule cannot have such a symmetry element. This is because of the structural disorder described in the previous section. As is shown in Fig. 2(b), the three six-membered and one five-membered chelate rings are in a chair–skew–chair–gauche conformational sequence.

Table 2. Atomic coordinates and their standard deviations

Atom	x	y	z
[NiCl$_2$([14]aneN$_4$)] (1)[a]			
Ni	0	0	0
Cl	7629(3)	16244(5)	31674(6)
N(1)	13211(10)	-13193(17)	6691(21)
N(2)	7095(10)	13642(16)	-18392(19)
C(1)	18934(14)	-8404(24)	-8794(29)
C(2)	17896(13)	9445(24)	-12353(27)
C(3)	5227(14)	31122(21)	-18496(27)
C(4)	-6021(15)	35000(22)	-24576(30)
C(5)	-12048(14)	30698(21)	-8507(28)
[NiCl$_2$([15]aneN$_4$)] (2)[b]			
Ni	0	0	0
Cl	797(1)	1500(1)	-2413(1)
N(1)	-706(2)	-1350(4)	-2478(4)
N(2)	-1165(3)	1599(5)	-512(5)
C(1)	-1724(4)	-1030(8)	-2813(6)
C(2)	-1800(4)	1092(10)	-2823(8)
C(3)	-1079(5)	3212(8)	-60(8)
C(4)	-579(5)	3401(7)	2086(9)
C(5)	478(5)	3076(6)	2392(7)
C(6)	2144(9)	-116(16)	3526(16)
[NiCl$_2$([16]aneN$_4$)] (3)[a]			
Ni	13077(4)	25507(3)	18912(7)
Cl(1)	2724(8)	-902(6)	28217(9)
Cl(2)	26146(8)	50780(6)	10687(11)
N(1)	14128(27)	26683(23)	40998(13)
N(2)	35887(24)	23578(22)	28833(15)
N(3)	9671(30)	24151(23)	-3981(17)
N(4)	-11650(25)	23875(22)	10233(19)
C(1)	30206(39)	32448(39)	51664(21)
C(2)	39953(41)	24328(44)	55832(23)
C(3)	47440(36)	28527(41)	43002(25)
C(4)	45024(38)	27838(40)	17768(27)
C(5)	35394(45)	22569(42)	2900(29)
C(6)	24183(47)	29401(38)	-8690(31)
C(7)	-792(50)	31203(36)	-16593(33)
C(8)	-18183(48)	22739(39)	-17352(35)
C(9)	-21717(38)	15496(35)	-1367(37)
C(10)	-18658(35)	17629(33)	23760(39)
C(11)	-12313(41)	27088(35)	34032(41)
C(12)	5604(41)	35037(32)	38202(43)
[Ni(NCS)$_2$([14]aneN$_4$)] (4)[a]			
Ni(1)	0	0	0
S(1)	20054(6)	19516(6)	-30031(9)
N(11)	11599(16)	249(15)	19868(11)
N(12)	7960(16)	-10087(13)	-5057(13)
N(13)	6881(16)	9782(14)	-14560(15)
C(11)	17393(22)	-8047(22)	21568(17)
C(12)	17867(21)	-9580(19)	4660(19)
C(13)	7225(25)	-10392(22)	-22785(21)
C(14)	-3137(27)	-10476(23)	-32436(23)
C(15)	-9162(25)	-1946(24)	-35262(25)
C(16)	12341(18)	13854(15)	-20901(27)
Ni(2)	0	50000	0
S(2)	19578(6)	67676(5)	-33479(31)
N(21)	-8647(15)	61578(13)	-7459(33)
N(22)	6671(15)	55724(13)	20144(35)
N(23)	10354(16)	55869(15)	-13113(37)
C(21)	-3772(21)	68034(17)	2621(39)
C(22)	95(22)	63235(18)	20254(41)
C(23)	9585(21)	49521(18)	36173(43)
C(24)	16169(21)	41953(20)	35244(45)
C(25)	11471(20)	34948(18)	25421(47)
C(26)	14204(17)	60810(16)	-21442(49)
Ni(3)	50000	0	0
S(3)	29223(5)	16029(5)	23623(53)
			(continued)
N(31)	55613(14)	12721(13)	-1864(55)
N(32)	41450(14)	4712(13)	-23555(57)
N(33)	38945(15)	4244(14)	10366(59)
C(31)	51279(20)	-18320(16)	15966(61)
C(32)	45857(21)	13050(17)	-29852(63)
C(33)	39815(20)	-1825(18)	-35026(65)
C(34)	35461(20)	-10326(18)	-27792(67)
C(35)	42003(20)	-16602(16)	-13445(69)
C(36)	34837(17)	9118(15)	15737(71)
Ni(4)	50000	50000	0
S(4)	71684(5)	32421(5)	-21026(75)
N(41)	42765(14)	39038(13)	9345(77)
N(42)	38727(14)	51301(13)	-20945(79)
N(43)	58169(15)	41442(13)	-9647(81)
C(41)	32924(19)	39822(17)	-1577(83)
C(42)	33592(19)	42890(17)	-19562(85)
C(43)	41418(21)	54018(18)	-37076(87)
C(44)	46790(22)	62677(19)	-37881(89)
C(45)	57068(21)	62138(18)	-27215(91)
C(46)	63902(17)	37741(14)	-14113(93)
[Ni(NCS)$_2$([15]aneN$_4$)] (5)[b]			
Ni	2387(1)	763(1)	2414(1)
S(1)	1260(2)	-1380(2)	-1547(2)
S(2)	4058(2)	2734(2)	6489(2)
N(1)	1192(4)	1499(4)	2635(6)
N(2)	2409(5)	-172(4)	4203(6)
N(3)	3576(5)	76(5)	1910(10)
N(4)	2338(5)	1642(4)	511(7)
N(5)	1521(5)	-204(4)	952(7)
N(6)	3293(4)	1655(4)	3885(7)
C(1)	1100(6)	1582(6)	4216(10)
C(2)	1123(7)	635(8)	4973(11)
C(3)	2091(7)	172(7)	5479(9)
C(4)	3340(8)	-636(7)	4843(11)
C(5)	3705(9)	-1031(8)	3594(15)
C(6)	4166(11)	-400(10)	2896(15)
C(7)	3965(8)	618(12)	817(14)
C(8)	3609(14)	987(11)	-319(20)
C(9)	2694(9)	1262(8)	-732(10)
C(10)	1335(8)	1974(9)	-214(14)
C(11)	925(14)	2531(12)	493(21)
C(12)	1181(7)	2456(6)	1997(11)
C(13)	1408(4)	-701(5)	-71(8)
C(14)	3607(5)	2106(5)	4948(8)
[Ni(NCS)$_2$([16]aneN$_4$)] (6)[a]			
Ni	23499(3)	7171(3)	22249(7)
S(1)	12844(7)	-15384(7)	-14539(9)
S(2)	40274(8)	26506(7)	62474(11)
N(1)	35235(19)	513(19)	16597(13)
N(2)	23532(20)	-2442(20)	40182(15)
N(3)	12003(18)	15062(19)	25784(17)
N(4)	22061(18)	15497(18)	1502(19)
N(5)	14515(20)	-2497(20)	8504(21)
N(6)	32624(19)	15730(19)	36962(23
C(1)	41773(27)	-4823(28)	28802(25)
C(2)	36748(32)	-11814(30)	35710(27)
C(3)	32161(31)	-7785(31)	46972(29)
C(4)	19904(29)	761(28)	52728(31)
C(5)	10556(28)	5621(31)	47529(33)
C(6)	11001(25)	15206(28)	41293(35)
C(7)	12217(26)	24721(25)	20548(37)
C(8)	8968(28)	25745(28)	3523(39)
C(9)	12084(25)	18127(26)	-5116(41)
C(10)	25439(26)	10788(26)	-10204(43)
C(11)	35950(28)	9459(29)	-6124(45)
C(12)	40535(23)	7309(26)	10199(47)
C(13)	13665(21)	-7977(23)	-885(49)
C(14)	35837(21)	20231(22)	47489(51)

a) Parameters are multiplied by 10^5. b) Parameters are multiplied by 10^4.



(a)

(b)

(c)

(d)

(e)

(f)

Fig. 2. Perspective views of the structures: (a) [$NiCl_2$([14]aneN_4)](**1**); (b) [$NiCl_2$([15]aneN_4)] (**2**); (c) [$NiCl_2$([16]aneN_4)] (**3**); (d) [Ni$(NCS)_2$([14]aneN_4)] (**4**); (e) [Ni$(NCS)_2$([15]aneN_4)] (**5**); (f) [Ni$(NCS)_2$-([16]aneN_4)] (**6**). In (b) and (e), which involve disorder, one linkage of the macrocyclic skeleton is shown with solid bonds, and the alternative with open bonds. The drawing (d) corresponds to the complex (b) in Fig. 4.

trans-*[$NiCl_2$([16]aneN_4)] (3).* The entire molecule constitutes a crystallographically asymmetric unit and thus has no rigorous symmetry. However, as Fig. 3 shows, there is an approximate symmetry plane, which lies perpendicular to the coordination plane of the [16]aneN_4 ligand, passing through Ni, N(2), and N(4) atoms. The four six-membered chelate rings adopt a chair–chair–skew–skew conformational sequence. The coordination bond lengths and angles show that the coordination geometry deviates appreciably from D_{4h} symmetry (Table 3). The Ni–N(4) distance [2.211(3) Å] is by far the longest among the Ni–N bonds, and the two Ni–Cl distances differ by 0.107 Å.

trans-[Ni(NCS)$_2$([14]aneN$_4$)] (4) There are four crystallographically independent [Ni(NCS)$_2$([14]aneN$_4$)] complexes, in each of which Ni resides at a center of symmetry. The total stereochemistries of the [14]aneN$_4$ ligands in these complexes are essentially the same and are very similar to that found for **1**. The coordination bond lengths are slightly different in the four complexes. The in-plane Ni–N distances range from 2.064(2) to 2.082(2) Å, while the corresponding axial Ni–N (NCS) distances vary from 2.130 (2) to 2.075(6) Å. Though the ranges of the in-plane or axial bond lengths are very limited, a negative correlation is noted between them (*vide infra*).

Of particular interest is the wide variety of orientation modes of the NCS$^-$ groups (Fig. 4). The tilts of the Ni–N (NCS) bonds from the normal to the NiN$_4$ best planes range from 1.3° to 1.9°. The Ni–N–C and N–C–S angles within the NCS$^-$ groups range from 156.2(2) to

Table 3. Bond lengths (l/Å) and angles (ϕ/°)

[NiCl$_2$([14]aneN$_4$)] (1)							
Ni	-Cl		2.5101(4)	Cl	-Ni	-N(1)	86.68(4)
Ni	-N(1)		2.067(1)	Cl	-Ni	-N(2)	91.97(4)
Ni	-N(2)		2.066(1)	N(1)	-Ni	-N(2)	85.3(1)
[NiCl([15]aneN$_4$)] (2)							
Ni	-Cl		2.497(1)	Cl	-Ni	-N(1)	88.5(1)
Ni	-N(1)		2.104(3)	Cl	-Ni	-N(2)	91.8(1)
Ni	-N(2)		2.124(4)	N(1)	-Ni	-N(2)	87.2(1)
[NiCl([16]aneN$_4$)] (3)							
Ni	-Cl(1)		2.535(1)	Cl(1)	-Ni	-N(4)	89.5(1)
Ni	-Cl(2)		2.428(1)	Cl(2)	-Ni	-N(1)	0.3(1)
Ni	-N(1)		2.143(2)	Cl(2)	-Ni	-N(2)	91.5(1)
Ni	-N(2)		2.186(3)	Cl(2)	-Ni	-N(3)	90.5(1)
Ni	-N(3)		2.142(2)	Cl(2)	-Ni	-N(4)	97.4(1)
Ni	-N(4)		2.211(3)	N(1)	-Ni	-N(2)	92.6(1)
Cl(1)	-Ni	-Cl(2)	172.93(4)	N(1)	-Ni	-N(3)	174.4(1)
Cl(1)	-Ni	-N(1)	91.3(1)	N(1)	-Ni	-N(4)	87.1(1)
Cl(1)	-Ni	-N(2)	81.5(1)	N(2)	-Ni	-N(3)	92.9(1)
Cl(1)	-Ni	-N(3)	88.6(1)	N(2)	-Ni	-N(4)	171.1(1)
				N(3)	-Ni	-N(4)	87.3(1)
[NI(NCS)$_2$([14]aneN$_4$)] (4)							
Ni(1)	-N(11)		2.069(2)	N(11)	-Ni(1)	-N(12)	85.0(1)
Ni(1)	-N(12)		2.064(2)	N(11)	-Ni(1)	-N(13)	88.3(1)
Ni(1)	-N(13)		2.130(2)	N(12)	-Ni(1)	-N(13)	90.5(1)
Ni(2)	-N(21)		2.066(2)	N(21)	-Ni(2)	-N(22)	85.5(1)
Ni(2)	-N(22)		2.076(3)	N(21)	-Ni(2)	-N(23)	91.1(1)
Ni(2)	-N(23)		2.128(3)	N(22)	-Ni(2)	-N(23)	89.1(1)
Ni(3)	-N(31)		2.082(2)	N(31)	-Ni(3)	-N(32)	85.4(1)
Ni(3)	-N(32)		2.079(5)	N(31)	-Ni(3)	-N(33)	90.7(1)
Ni(3)	-N(33)		2.108(5)	N(32)	-Ni(3)	-N(33)	89.1(1)
Ni(4)	-N(41)		2.081(4)	N(41)	-Ni(4)	-N(42)	85.4(2)
Ni(4)	-N(42)		2.075(6)	N(41)	-Ni(4)	-N(43)	89.8(2)
Ni(4)	-N(43)		2.119(6)	N(42)	-Ni(4)	-N(43)	91.9(3)
[NI(NCS)$_2$([15]aneN$_4$)] (5)							
Ni	-N(1)		2.102(6)	N(1)	-Ni	-N(6)	91.6(2)
Ni	-N(2)		2.122(6)	N(2)	-Ni	-N(3)	91.8(3)
Ni	-N(3)		2.161(9)	N(2)	-Ni	-N(4)	176.6(2)
Ni	-N(4)		2.137(6)	N(2)	-Ni	-N(5)	87.1(2)
Ni	-N(5)		2.099(6)	N(2)	-Ni	-N(6)	91.2(2)
Ni	-N(6)		2.059(5)	N(3)	-Ni	-N(4)	86.9(3)
N(1)	-Ni	-N(2)	94.7(3)	N(3)	-Ni	-N(5)	86.7(3)
N(1)	-Ni	-N(3)	173.0(3)	N(3)	-Ni	-N(6)	90.7(3)
N(1)	-Ni	-N(4)	86.4(3)	N(4)	-Ni	-N(5)	89.6(2)
N(1)	-Ni	-N(5)	91.2(2)	N(4)	-Ni	-N(6)	92.0(2)
				N(5)	-Ni	-N(6)	176.8(2)
[Ni(NCS)$_2$([16]aneN$_4$)] (6)							
Ni	-N(1)		2.175(3)	N(1)	-Ni	-N(6)	90.2(1)
Ni	-N(2)		2.164(2)	N(2)	-Ni	-N(3)	93.6(1)
Ni	-N(3)		2.152(3)	N(2)	-Ni	-N(4)	171.2(1)
Ni	-N(4)		2.224(2)	N(2)	-Ni	-N(5)	84.1(1)
Ni	-N(5)		2.103(3)	N(2)	-Ni	-N(6)	91.3(1)
Ni	-N(6)		2.051(2)	N(3)	-Ni	-N(4)	87.1(1)
N(1)	-Ni	-N(2)	93.6(1)	N(3)	-Ni	-N(5)	92.9(1)
N(1)	-Ni	-N(3)	172.8(1)	N(3)	-Ni	-N(6)	89.0(1)
N(1)	-Ni	-N(4)	85.9(1)	N(4)	-Ni	-N(6)	87.1(1)
N(1)	-Ni	-N(5)	88.5(1)	N(4)	-Ni	-N(6)	97.4(1)
				N(5)	-Ni	-N(6)	175.2(1)

168.2(2)° and from 177.8(5) to 179.2(2)°, respectively. All the NCS$^-$ groups are involved in intermolecular hydrogen-bonds between the sulfur atoms and the secondary amine groups of the neighboring complexes,[10] forming a linear chain along the a-axis. The orientations of the NCS$^-$ groups are mainly determined by these hydrogen-bonds.

trans-[Ni(NCS)$_2$([15]aneN$_4$)] (5) In this compound, the three six-membered rings and one five-membered ring are in a chair-chair-skew-gauche conformational sequence. Although the total stereochemistry of the [15]aneN$_4$ ligand differs from that in **2**, a similar structural disorder was observed for the gauche five-membered and the skew six-membered chelate rings (Fig. 2(e)). The combination of the chiral configurations of the four nitrogen donors are the same

Table 4. Deviations (d/Å) of nickel and donor atoms from a NiN$_4$ plane defined by nickel and four in-plane nitrogens for complexes **3**, **5**, and **6**

3		**5**		**6**	
Ni	0.072	Ni	0.040	Ni	0.058
N (1)	0.063	N (1)	0.002	N (1)	0.081
N (2)	−0.096	N (2)	−0.020	N (2)	−0.106
N (3)	0.063	N (3)	−0.001	N (3)	0.081
N (4)	−0.101	N (4)	−0.019	N (4)	−0.113
Cl (1)	−2.456	N (5)	−2.057	N (5)	−2.043
Cl (2)	2.497	N (6)	2.099	N (6)	2.105

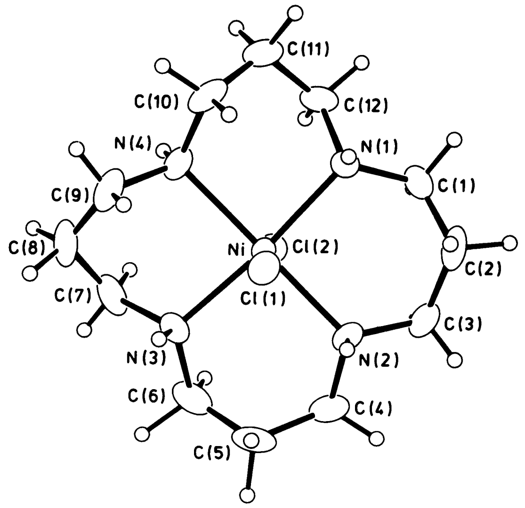


Fig. 3. Structure of [NiCl$_2$([16]aneN$_4$)] (**3**) as viewed along the normal to the NiN$_4$ plane.

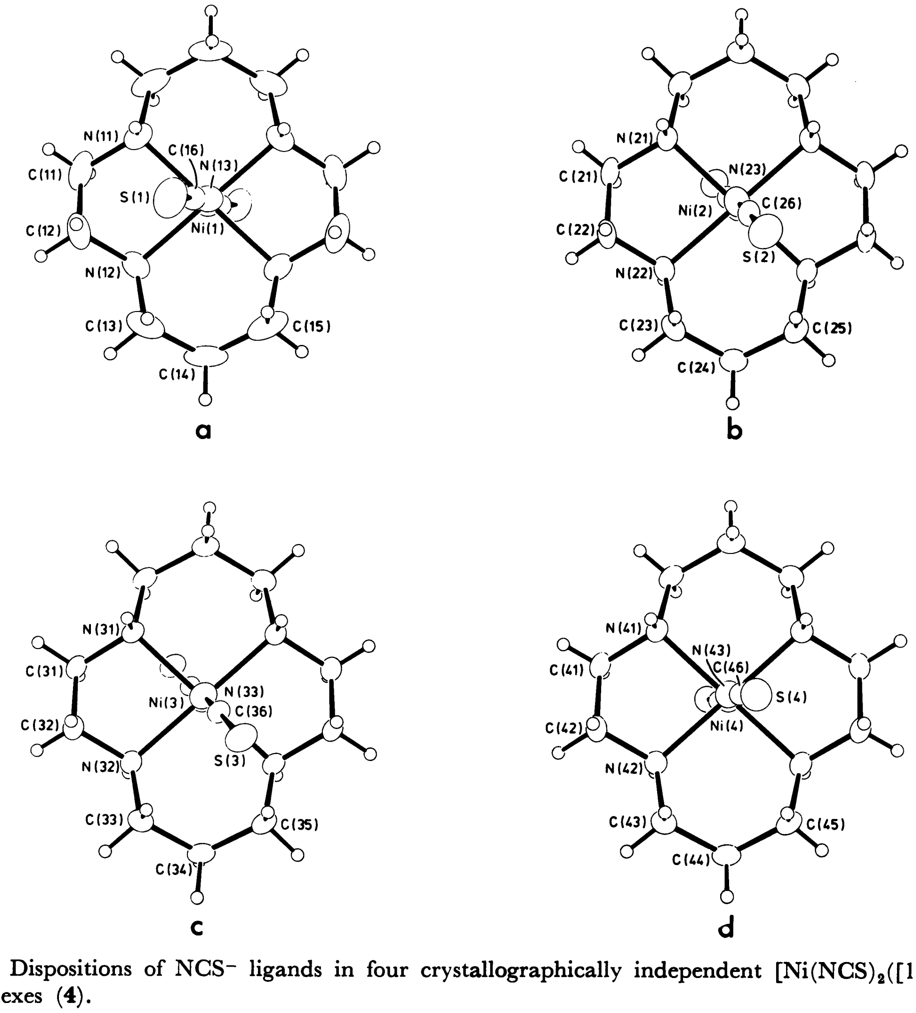


Fig. 4. Dispositions of NCS$^-$ ligands in four crystallographically independent [Ni(NCS)$_2$([14]aneN$_4$)] complexes (**4**).

as those in **3**. The structural distortions characteristic of the nitrogen configurations will be discussed later.

*trans-[Ni(NCS)$_2$([16]aneN$_4$)] (**6**)* Four six-membered chelate rings adopt chair–chair–skew–skew conformations, as in the *trans*-dichloro analogue **3**. The nitrogen configurations are the same as those in **3** and **5**. The distortions arising from the nitrogen configuration will be discussed in a subsequent section. The orientation of the NCS$^-$ ligands is, again, caused by intermolecular hydrogen-bonds between the sulfur atoms and the amine nitrogens of the neighboring complexes.[10]

Discussion

Stereochemistries of Coordinated Macrocyclic Ligands. It has been known that the cyclic nature of the tetraazacycloalkane ligand gives rise to isomerism as a result of the difference in the combination of the chiralities of the four coordinated secondary amine nitrogens.[11] In all the present complexes having the [14]aneN$_4$ ligand, the macrocyclic ligands adopt the same nitrogen configurations, and thereby have the same overall skeletal structure. Alternating two six- and two five-membered chelate rings are in the chair and gauche conformations, respectively. This ring conformation has been known to be the most strain free among the five possible isomers when the [14]aneN$_4$ ligand is coordinated in a planar fashion.[11] The same stereochemistry of the [14]aneN$_4$ ligand has been found in the crystal structures of $[Ni([14]aneN_4)](PF_6)_2$,[12a] $[Ni([14]aneN_4)I]I$,[12b] $[NiCl_2([14]aneN_4)](ClO_4)$,[13] $[Pd([14]aneN_4)](ClO_4)_2$,[14] $[PdCl_2([14]aneN_4)](NO_3)_2$,[14] $[Pd([14]aneN_4)][PdCl_2([14]aneN_4)](ClO_4)_4$,[14] $[Zn(O_2COCH_3)([14]aneN_4)](ClO_4)$,[15] and $[Ag([14]aneN_4)](ClO_4)_2$ ($P\bar{1}$-form)[16].

Busch and his associates separated two configurational isomers each for *trans*-$[CoCl_2([15]aneN_4)]^+$ and *trans*-$[CoCl_2([16]aneN_4)]^+$ and discussed the stereochemical stabilities of the isomers and other possible configurational isomers on the basis of strain energy calculations, the ^{13}C NMR spectra, and the chemical properties.[4] The overall stereochemistry of the macrocyclic skeleton found for **5** is the same as that reported for the most stable brown isomer of $[CoCl_2([15]aneN_4)]^+$ (Isomer I in their notation). However, the overall structure of **2** is the type of neither the Isomer I nor the Isomer II of $[CoCl_2([15]aneN_4)]^+$. The latter was found to be a skew-skew-skew-gauche form.[4,17] The calculations of strain-energy minimization for *trans*-$[CoCl_2([15]aneN_4)]^+$ show that the conformational structure of **2** is the second least strained among six possible configurational isomers.[4] We did not obtain in the synthetic and X-ray studies any indication of the presence of isomers for the trans-dichloro Ni(II) complex of [15]aneN$_4$. The skeletal structures of [16]aneN$_4$ found in **3** and **6** are the same as that reported for the green isomer of $[CoCl_2([16]aneN_4)]^+$ (Isomer II).[4]

It is known that the cyclic nature of tetraaza macrocyclic ligands in a planar coordination introduces strain in the metal-donor atom distance, the chelate (bite) angle subtended at the central metal atom, and so on.[11] Such strain is generally relieved by relaxing the coplanarity of the metal-donor atom set. Except for **1**, **2**, and **4**, in which Ni atoms reside at the inversion center, all the structures show a distortion of the NiN$_4$ set toward the tetrahedral character (Table 4).

The combinations of the nitrogen configurations in complexes **3**, **5**, and **6** are all of the same type : three NH protons are above, and the remaining one below, the NiN$_4$ plane. The former ones are bound to three nitrogens, N(1), N(2), and N(3), which are involved in two adjacent six-membered chelate rings in the chair form, while the latter is bound to N(4), which links two skew rings or a skew and a gauche ring. The following structural distortions are commonly noted in these compounds and are likely to be characteristic of the skeletal structure arising from the configuration : inequality in the in-plane Ni–N distances, inequality in the two axial bond lengths, distortion of the in-plane donor atom set of a tetrahedral character, and a fairly large deviation of the Ni atom from the mean NiN$_4$ plane. Among the complexes, the distortion of the in-plane donor atom set toward the tetrahedral character becomes larger in this order: **6**>**3**>**5**. This is ascribed to the suitability of size between the hole of the macrocycle and the high-spin octahedral Ni^{2+}: (i) the 16-membered macrocycle is less fit for Ni^{2+} than the 15-membered one, and (ii) the cavity size of the [16]aneN$_4$ ligand in **6** enlarges as compared with that of **3**, because of the cis effect (see below).

When the cavity size is larger than the natural or the best fit size for Ni^{2+}, the deviations of carbon atoms adjacent to donor nitrogens from the mean plane of the chelate ring generally become larger. As a result, in Complexes **3** and **6**, which have [16]aneN$_4$, C(9) and C(10) atoms are disposed so close to one of the axial coordination sites as to exert a steric effect, and the resulting steric hindrance causes the lengthening of the axial bond [Ni–Cl(1) in **3** and Ni–N(5) in **6**].

Correlation between Axial and In-plane Coordination Bond Lengths. As expected, the in-plane Ni–N distance increases with an increase in the number of ring members of the macrocyclic ligand. This increase in the Ni–N distance amounts to 0.05—0.06 Å for each ring member added. The increase is not, however, as large as expected from calculations of the strain energy minimization for free ligand molecules (0.10—0.15 Å).[18] The observed correlations between the average Ni–N and Ni–X distances are shown in Fig. 5. The data reported previously for the same types of complexes with similar tetraazamacrocyclic or diamine ligands are also included: *trans*-$[NiCl_2(N_47)]$,[20] *trans*-$[NiCl_2(N_49)]$,[20] *trans*-$[Ni(NCS)_2(NH_3)_4]$,[21] and *trans*-$[Ni(NCS)_2(en)_2]$.[22] As is seen in Fig. 5, there exists a negative correlation for each series of complexes with given axial ligands: the axial coordination bond length decreases as the in-plane distance increases. Similar observations have also been reported for some other systems.[23–25] The results in Fig. 5 were obtained assuming that each metal-donor atom set (*trans*-NiX$_2$N$_4$) has D$_{4h}$ symmetry. Although some Ni–X and Ni–N distances in Fig. 5 show quite a large standard deviation because of distortion from the D$_{4h}$ symmetry, there is no doubt that the negative

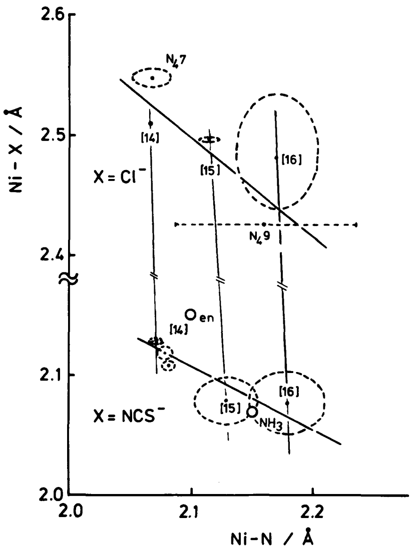


Fig. 5. Correlation between axial and in-plane coordination bond lengths in Ni(II) complexes of the *trans*-NiX_2N_4 type. Size of a dashed ellipse or line illustrate an esd obtained upon averaging chemically or crystallographically nonequivalent distances,[19] while that of a full-line figure within the dashed one shows an arithmetic mean of esd's for individual metal-ligand distances. Ligand abbreviations: [14]=[14]aneN_4, [15]=[15]aneN_4, [16]=[16]aneN_4, en=ethylenediamine, and $N_4$7 and $N_4$9 see Ref. 20. For NH_3 and en complexes, no esd values were reported.

interrelationship holds. The data points for Complexes **3** and **6** deviate from the smoothed lines in Fig. 5. In these complexes, there exists an obvious steric effect that causes a lengthening of the M–X bond, as described previously. Unless the steric constraint were present, the mean M–X bond distances in these complexes would be somewhat shorter and the data points would approach the smoothed lines.

It is interesting to note that the data for the four crystallographically inequivalent molecules of *trans*-[Ni(NCS)$_2$([14]aneN_4)] show a clear trend for the negative correlation within a very limited range of metal-ligand distances (see Fig. 5).

When the $NiCl_2N_4$ and $Ni(NCS)_2N_4$ systems are compared, the slope for the chloro complexes is steeper than that for the isothiocyanato complexes. This indicates that the weaker the axial ligand field is, the stronger the correlation. The effect of the ligand field strength of the axial ligand upon the correlation has been explained theoretically on the basis of the features of the potential energy surface.[1]

From the data given in Fig. 5, it is possible to see changes in the M–N distances of complexes with the same in-plane ligand upon alterations in the axial ligand. Although the number of data for such comparisons are very limited and the changes in the M–N distances are very small, the thin lines in Fig. 5 likely show the presence of a negative dependence of the in-plane Ni–N lengths on the axial Ni–X bond distances.

Coordination geometries found for Ni(II) complexes with 1,4,7,10-tetraazacyclotetradecane ($N_4$7) may provide further evidence for the occurrence of such an electronic interaction between the axial and in-plane ligands. Interestingly, the structural analyses reveal that coordination geometries of [$NiCl_2$($N_4$7)][25] and [Ni(NCS)$_2$($N_4$7)][26] are of the trans-type and of the cis-type with the macrocycle folded, respectively. It is most reasonable to consider the observed cis and trans stereochemistries to be a result of the electronically controlled cis effect. If strong axial ligands such as NCS^- are to coordinate at the axial positions, the Ni–N (in-plane) distance must be elongated. However, it is impossible with this macrocycle, since the hole size of this particular macrocycle is equal to or slightly smaller than necessary to accommodate a high-spin octahedral Ni^{2+}.[27]

Busch and his coworkers observed a very similar phenomenon in a ligand field electronic spectral study of a series of the same type of Ni(II) complexes.[3] They found that the ligand field strength of an axial ligand (Dq^z) decreases as the in-plane ligand field strength (Dq^{xy}) increases, and they termed this the *"electronic cis effect"*. The correlation found in the electronic spectral study and that observed in the present study seem to have the same electronic origin.

We have previously discussed the electronic origin that brings about the correlations in Fig. 5 from the standpoint 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 has a tilt with respect to the coordination bond axes. When the ligand field strength of the axial ligand is weaker than the in-plane ligand field, the ellipse is elongated in the Ni–X direction. Such features of the potential surface are primarily responsible for the observed correlation of the coordination bond lengths.[1] It has also been shown that the slope of the line showing the interrelationship in Fig. 5 discloses the degree of softness[28] of a Ni(II) ion semiquantitatively.[1]

Figure 6 shows plots of the Ni–Cl stretching frequencies [ν(Ni–Cl)] *vs.* the Ni–Cl and Ni–N bond distances. Band assignments to the Ni–Cl stretching vibrations were made by a comparison of the spectra of *trans*-dichloro, *trans*-dibromo, and *trans*-bis(isothiocyanato) complexes with a series of macrocyclic ligands. It was impossible from only such simple comparisons to assign bands due to Ni–N stretching vibrations. As a result, we failed to figure a plot of ν(Ni–Cl) *vs.* ν(Ni–N), but the following discussion is possible on the basis of the IR data in Fig. 6. Under rigorous D_{4h} symmetry, a single band due to the antisymmetric Ni–Cl stretching vibration (ν_a) is expected to appear. When the complex has lower symmetry, two bands due to antisymmetric and symmetric vibrations (ν_a and ν_s) will appear. Single bands were observed at 198 cm^{-1} for **1**, at 223 cm^{-1} (very broad) for **2**, at 225 cm^{-1} for [$NiCl_2$($N_4$9)], and at 187 cm^{-1} for [$NiCl_2$($N_4$7)]. On the other hand, Compound **3** showed two clearly separated sharp bands at 216 (ν_a) and 178 cm^{-1} (ν_s). This result corresponds to the relatively large difference in the two Ni–Cl distances in **3**. As shown in Fig. 6(a), the antisymmetric band ν_a(Ni–Cl) shifts to higher frequencies as the Ni–Cl distance decreases. When the ν_a(Ni–Cl) band posi-

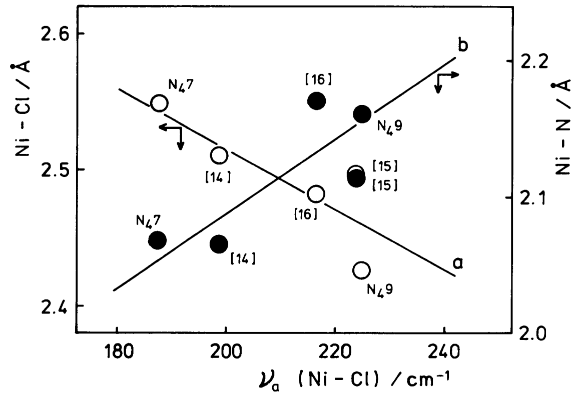


Fig. 6. Plots of antisymmetric Ni–Cl stretching frequencies (ν_a(Ni–Cl))/cm^{-1}) *vs.* mean Ni–Cl distances (a) and *vs.* average Ni–N distances (b). See the caption of Fig. 5 for the ligand abbreviations.

tions are plotted against the Ni–N distance, a reversed relationship is obtained (Fig. 6(b)). This result suggests, though indirectly, that the electronic cis effect is manifested in the far infrared spectra due to coordination bond stretching vibrations.

Structural Disorder Characteristic of [15]aneN$_4$ Complexes. We have thus far determined five structures of metal complexes containing the [15]aneN$_4$ ligand : the present two complexes, **2** and **5**, *trans*-[CoCl$_2$([15]aneN$_4$)](ClO$_4$) (green form),[17] [Zn(NCS)$_2$([15]aneN$_4$)],[2] and [{Zn([15]aneN$_4$)}$_3$(O$_2$COCH$_3$)$_2$](ClO$_4$)$_4$.[29] All the compounds have a gauche five-membered and a skew six-membered chelate ring in a pair. We found the same type of disorder common to all these structures. The general features are shown in Fig. 1. Because of this disorder, the bond distances of C$_a$–C$_b$ and C$_b$–C$_c$ appear somewhat shorter, whereas the C$_a$–C$_c$ distance is longer, than the normal value. It is worth noting that, in spite of the presence of the significant disorder, the positional parameters of the nitrogens involved in the disordered chelate rings were refined to have reasonably small esd values. This indicates that the nitrogens for the five- and six-membered rings are at nearly the same position in the crystal structure; therefore, the bite angles of the gauche five- and skew six-membered chelate rings must be very similar. In fact, the bite angles found for the skew six-membered rings which are not involved in the disorder (87.3(1)° and 87.1(1)° for **3**, and 87.1(1)° and 85.9(1)° for **6**) are close to the normal value of the gauche chelate rings (~86°).[11] Concomitantly, the bite angles found for the disordered ring average 87.2(1)° for **2** and 86.7(3)° for **5**. The disorder in the crystals of the [15]aneN$_4$ complexes is considered to arise mainly from such a situation.

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10) The hydrogen-bond parameters are as follows:

[Ni(NCS)$_2$([14]aneN$_4$)] (**4**)		[Ni(NCS)$_2$([16]aneN$_4$)] (**6**)	
S(1)···N(32)^{i}	3.664(2) Å	S(1)···N(3)^{i}	3.541(3) Å
S(2)···N(42)^{i}	3.536(2)	S(1)···N(4)^{ii}	3.561(3)
S(3)···N(11)^{i}	3.460(2)	S(2)···N(2)^{iii}	3.649(3)
S(4)···N(22)^{ii}	3.546(2)		

Key to symmetry operations:

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

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