*Bull. Chem. Soc. Jpn.*, *57*, *1556—1561 (1984)* [Vol. 57, No. 6

# Correlation between Axial and In-Plane Coordination Bond Lengths in Tetragonal Six-coordinate Complexes of the *trans*-$MX_2N_4$ Type ($M=Co^{3+}$, $Ni^{2+}$, and $Zn^{2+}$). X-Ray Structural and *ab initio* Molecular Orbital Studies

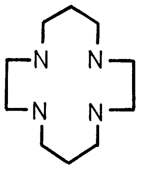
Tasuku Ito,* Masako Kato, and Haruko Ito
*Department of Applied Molecular Science, Institute for Molecular Science, Okazaki National Research Institutes, Okazaki 444*

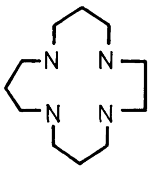
(Received December 16, 1983)

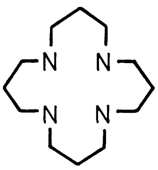
X-Ray data of 16 structures having coordination geometry of the *trans*-$MX_2N_4$ type show that (i) an out-of-plane coordination bond length decreases as an in-plane distance increases, (ii) the degree of the correlation is metal ion dependent and varies in the order, $Zn^{2+}>Ni^{2+}>Co^{3+}$. In the Ni(II) systems, complexes having stronger ligands ($X=NCS^-$) at axial positions show the weaker correlation as compared with complexes with weaker axial ligands ($Cl^-$). Electronic origin that causes such negative correlations has been investigated in terms of the potential energy surfaces obtained from *ab initio* MO calculations for model compounds, *trans*-$[MCl_2(NH_3)_4]$. A section of the potential surface along the M-Cl and M-N bond axes is an ellipse and the ellipse has a tilt with respect to the metal-ligand bond axes. The dependence of the M-Cl distances on the M-N distances becomes stronger, as the tilt of the ellipse increases, and/or as the ratio of the length of long to short axes of the ellipse is increased. The degree of correlation expected from the potential energy surfaces are consistent, in all respect, with experimentally observed results. The interrelationships, found both experimentally and theoretically, are associated with softness of metal ions. Among the metal ions studied, Co(III) is the hardest, Zn(II) is the softest, and Ni(II) is intermediate.

Earlier studies of tetragonally distorted octahedral metal complexes suggest that, in complexes of this type, there exists an interaction between in-plane and out-of-plane ligands through a metal ion.[1] Hathaway[2] and Gažo[1] demonstrated, on the basis of available X-ray data of metal ion salts and simple coordination compounds, correlations between in-plane and out-of-plane coordination bond lengths for some Cu(II) and Ni(II) complexes of this type. Generally, an in-plane bond distance increases as an out-of-plane distance decreases. In our recent structural study of a series of Ni(II) complexes, a similar negative correlation of the coordination bond lengths was observed.[3] It has been also noted, in solution chemistry of some Co(III) complexes of this type, that equatorial ligands affect rates of hydrolyses of the axial ligands.[4] In an NMR spectral study of five-coordinate Cd(II) porphyrin complexes with substituted pyridines at the axial position, coupling constant between $^{111}Cd$ and porphyrin nitrogen($^{15}N$) has been found to decrease with an increase in basicity of substituted pyridine.[5] Busch and coworkers observed a similar phenomenon in ligand field electronic spectra.[6] They showed that, in Ni(II) complexes of *trans*-$NiX_2N_4$ type, ligand field strength of an axial ligand ($Dq^z$) decreases as an in-plane ligand field ($Dq^{xy}$) increases, and they termed it the "electronic cis effect".[6] They also reported that a series of Co(III) complexes of the same type do not show a correlation between $Dq^z$ and $Dq^{xy}$.[7]

These seem to arise from the same electronic origin. The occurrence of such an interaction between in-plane and out-of-plane ligands through a metal ion, as well as the degree of the interaction, should be metal ion dependent. The present series of the studies were undertaken in order to investigate the electronic effect in more systematic and quantitative way to elucidate the role and function of the metal ion in the observed phenomenon. We have carried out X-ray analyses and *ab initio* MO calculations for a series of complexes which have the same or very similar coordination environments. As metal ions, we chose Co(III), Ni(II), and Zn(II) because of the following reasons: (i) these metal ions form tetragonal octahedral complexes of this type; (ii) routine application of an *ab initio* MO method is in hand in this laboratory for complexes of first row transition metal ions. In the experimental approach, we have determined the structures of a series of complexes of *trans*-$MX_2N_4$ type, where X is halide or pseudo-halide ion. Tetraazacycloalkanes with different ring sizes, 1,4,8,11-tetraazacyclotetradecane ([14]ane$N_4$), 1,4,8,12-tetraazacyclopentadecane ([15]ane$N_4$), and 1,5,9,13-tetraazacyclohexadecane ([16]ane$N_4$), were used as in-plane ligands so as to vary the M-N distance systematically.


[14]ane$N_4$


[15]ane$N_4$


[16]ane$N_4$

As axial ligands (X), we chose $Cl^-$ and $NCS^-$, which have relatively weak and strong ligand field strengths, respectively, so that it is possible to investigate the effect of ligand field strength on the correlation between M-X and M-N distances. In the present paper, we summarize and discuss the experimental data on the coordination bond distances found in the series of studies. Structural details of Ni(II)[8] and Zn(II)[9] complexes have been described elsewhere. In the theoretical approach, we have carried out *ab initio* MO calculations on model systems, *trans*-$MCl_2(NH_3)_4$ ($M=Co^{3+}$, $Fe^{2+}$, $Ni^{2+}$, and $Zn^{2+}$).[10] We discuss electronic factors, or metal ion characteristics, which bring about the experimentally observed correlation of intramolecular coordination bond lengths in terms of potential energy surfaces along M–N and M–Cl bond axes.

We also showed, for the Ni(II) complexes, that the electronic cis effect is manifested in far infrared spectra due to coordination bond stretching vibrations.[8]

## Results and Discussion

*Correlation between Axial and In-plane Coordination Bond Lengths in* trans-*$MX_2N_4$ Type Complexes.* Table 1 collates the average in-plane (M–N) and axial (M–X) coordination bond lengths of the complexes studied. As expected, with an increase in the number of ring members in macrocyclic ligands, the in-plane M–N distance increases. This increase amounts to 0.04—0.06 Å for each ring member added. They are not as large as expected from calculations of strain energy minimizations for free ligand molecules (0.10—0.15 Å).[11] Data reported previously for the same type of complexes with other similar tetraazamacrocyclic or diamine ligands are also included in Table 1. The correlations are shown in Fig. 1, in which the M–X distances are plotted on the vertical axis and the M–N distances horizontally. As is seen in Fig. 1, there exists a negative correlation between M–X and M–N distances for complexes of each metal ion with given axial ligands: axial coordination bond length decreases as in-plane distance increases, generally. Although there exist steric effects in the molecular and crystal structures of the compounds, that cause the large standard deviations in the average coordination bond lengths,[8,9] they are characteristic of each system and should not give rise to the correlation shown in Fig. 1. Thus, the nature of the phenomenon depicted in Fig. 1 must be electronic in origin.

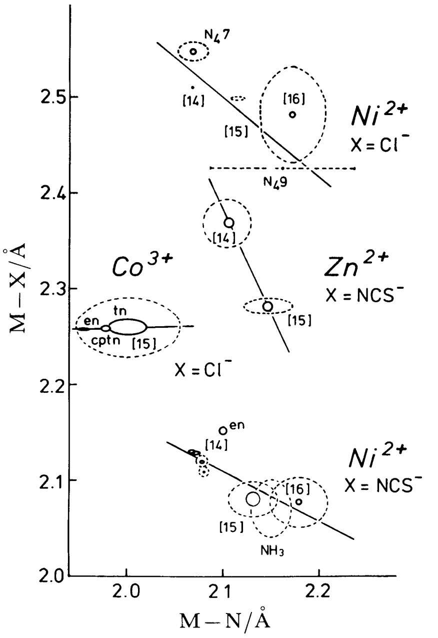


Fig. 1. Correlation between axial and in-plane coordination bond lengths in complexes of the *trans*-$MX_2N_4$ type. Size of a dashed ellipse or line illustrate an esd obtained upon averaging chemically or crystallographically inequivalent distances, while that of a full-line figure within the dashed one shows an arithmetic mean of esd's for individual metal-ligand distances (see footnote a) in Table 1). Ligand abbreviations: [14]=[14]aneN$_4$, [15]=[15]aneN$_4$, [16]=[16]aneN$_4$. See footnotes of Table 1 for others. For the en complex, no esd values were reported.

TABLE 1. AVERAGE IN-PLANE AND AXIAL COORDINATION BOND LENGTHS IN COMPLEXES OF *trans*-$MX_2N_4$ TYPE[a)]

| Compound | M–X/Å | M–N/Å | Ref. No. |
|---|---|---|---|
| $[NiCl_2([14]aneN_4)]$ | 2.5101(4) | 2.067(1) | 8, 12 |
| $[NiCl_2([15]aneN_4)]$ | 2.497(1) | 2.114(10) | 8 |
| $[NiCl_2([16]aneN_4)]$ | 2.482(54) | 2.171(34) | 8 |
| $[NiCl_2(N_47)]$[b)] | 2.548(8) | 2.068(16) | 3 |
| $[NiCl_2(N_49)]$[c)] | 2.426(1) | 2.161(75) | 3 |
| $[Ni(NCS)_2([14]aneN_4)]$[d)] | 2.130(2) | 2.067(3) | 8 |
| | 2.128(2) | 2.071(5) | 8 |
| | 2.108(2) | 2.081(5) | 8 |
| | 2.119(6) | 2.078(6) | 8 |
| $[Ni(NCS)_2([15]aneN_4)]$ | 2.079(20) | 2.131(25) | 8 |
| $[Ni(NCS)_2([16]aneN_4)]$ | 2.077(26) | 2.179(32) | 8 |
| $[Ni(NCS)_2(NH_3)_4]$ | 2.07(3) | 2.15(2) | 13 |
| $[Ni(NCS)_2(en)_2]$ | 2.15 | 2.10 | 14 |
| $[Zn(NCS)_2([14]aneN_4)]$ | 2.367(25)[h)] | 2.104(25) | 9 |
| $[Zn(NCS)_2([15]aneN_4)]$ | 2.282(8)[h)] | 2.146(28) | 9 |
| $[CoCl_2([15]aneN_4)]$[e)] | 2.259(31) | 2.001(56) | 15 |
| $[CoCl_2(en)_2]^+$ | 2.257(1) | 1.955(4) | 16 |
| $[CoCl_2(tn)_2]^+$[f)] | 2.26 | 2.00 | 17 |
| $[CoCl_2(cptn)_2]^+$[g)] | 2.258(3) | 1.978(5) | 18 |

a) A number in parentheses is an esd for a mean value of more than two chemically or crystallographically inequivalent bond lengths and is equal to $[\Sigma\Delta_i^2/(n-1)]^{1/2}$, where $\Delta_i$ is the deviation of $i$-th value in a set of $n$ such values from arithmetic mean of the $n$ values. In case of $n=2$, it is taken to be the largest of three values: the esd for one parameter ($q_1$), the esd for the other ($q_2$), or $|q_1-q_2|/2$. b) $N_47$=1,4,7,10-tetraazacyclotetradecane. c) $N_49$=1,4,7,10-tetraazacyclohexadecane. d) There are four crystallographically independent complexes in the unit cell.[8] e) Green form isomer. f) tn=1,3-Propanediamine. g) cptn=1,2-cyclopentanediamine. h) An average value of $C_t$–NCS distances, where $C_t$ denotes a center of the cavity formed with four in-plane nitrogens(see Ref. 9).

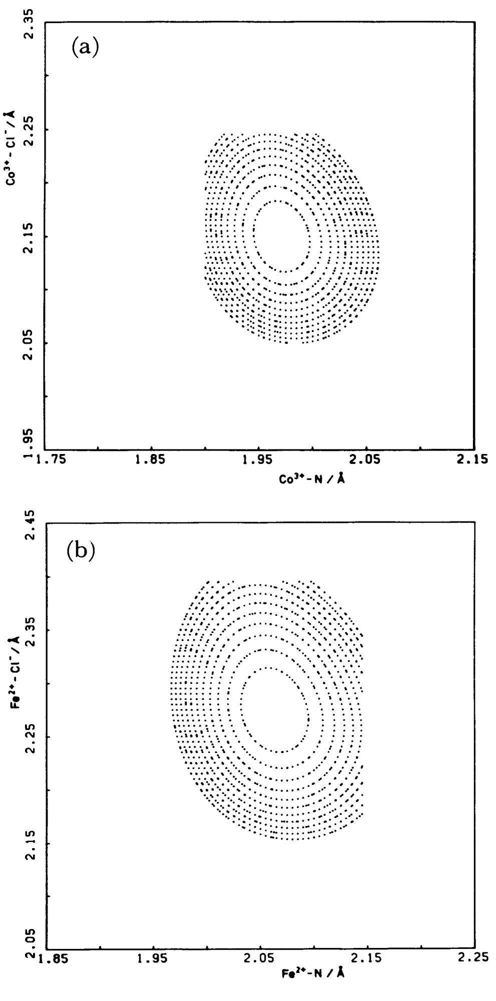
In the crystal structure of *trans*-[Ni(NCS)$_2$([14]aneN$_4$)], there are four crystallographically nonequivalent molecules.[8] Interestingly, data for these four molecules show clearly a trend for the negative correlation within the very limited range of metal-ligand distances (see Fig. 1).

Among the present three metal ions, the Zn$^{2+}$ system shows the strongest correlation, the Co$^{3+}$ system almost no correlation, and the Ni$^{2+}$ system is intermediate.

When the NiCl$_2$N$_4$ and Ni(NCS)$_2$N$_4$ 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 is the correlation (*vide infra*). It should be noted that the Zn system has a steep slope in spite of the fact that the data have been obtained with complexes with strong axial ligands NCS$^-$.[19]

For the Ni(II) system, it is possible to observe changes in the M–N distances of complexes having the same in-plane ligand by altering 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, it is likely that there exist negative correlations between M–X and M–N distances in each of [NiX$_2$([14]aneN$_4$)], [NiX$_2$([15]aneN$_4$)], and [NiX$_2$([16]aneN$_4$)].

Coordination geometries found for Ni(II) complexes with the N$_4$7 ligand may provide further evidence for the occurrence of such an electronic cis effect. The structures of [NiCl$_2$(N$_4$7)][3] and [Ni(NCS)$_2$(N$_4$7)][20] have been found to be of trans and cis types, respectively. It is most reasonable to consider the observed cis and trans stereochemistries to be a result of the electronically controlled cis effect in view of the relative size between the cavity of the N$_4$7 ligand and a high spin octahedral Ni$^{2+}$, and the relative ligand field strength between Cl$^-$ and NCS$^-$ ligands.[8,20]



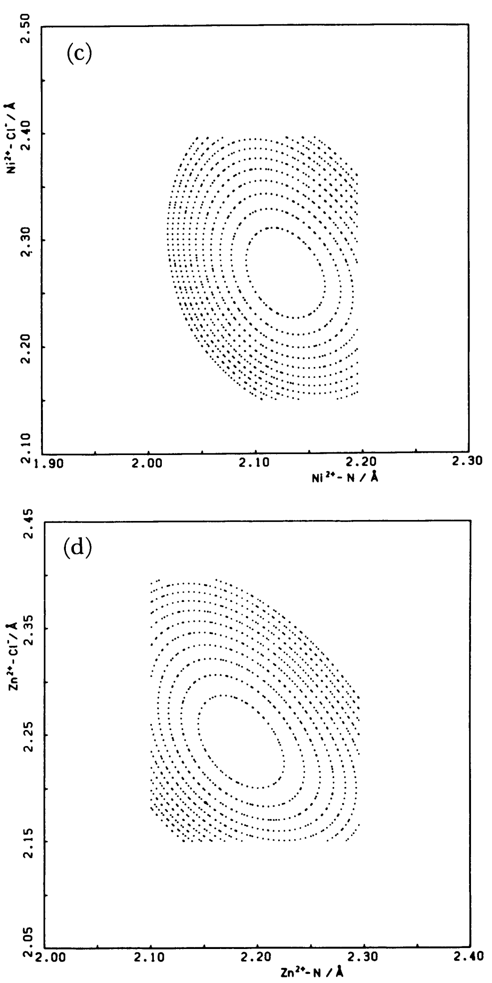
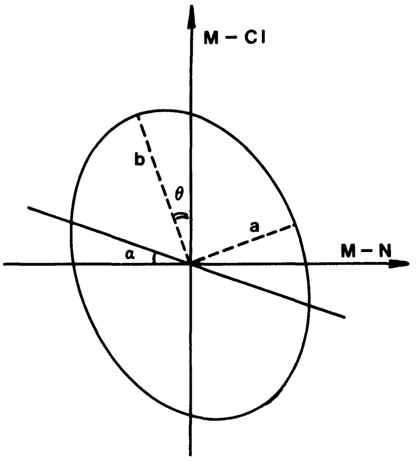


Fig. 2. Potential energy surfaces of *trans*-[MCl$_2$(NH$_3$)$_4$] along the M–Cl (vertical axis) and M–N (horizontal axis) coordination bonds: (a) *trans*-[CoCl$_2$(NH$_3$)$_4$]$^+$; (b) *trans*-[FeCl$_2$(NH$_3$)$_4$]; (c) *trans*-[NiCl$_2$(NH$_3$)$_4$]; (d) *trans*-[ZnCl$_2$(NH$_3$)$_4$]. Contours are at intervals of 0.5 kcal mol$^{-1}$.

*Potential Energy Surfaces of* trans-*[MCl$_2$(NH$_3$)$_4$] (M= Co$^{3+}$, Fe$^{2+}$, Ni$^{2+}$, and Zn$^{2+}$) along Coordination Bond Axes.* Figure 2 shows the calculated potential energy surfaces for the Co$^{3+}$, Fe$^{2+}$, Ni$^{2+}$, and Zn$^{2+}$ complexes, M–Cl distances being plotted on the vertical axis and M–N distances horizontally. The MO calculations for a hypothetical low spin Fe(II) complex, *trans*-[FeCl$_2$(NH$_3$)$_4$], have been carried out in order to investigate the effect of electric charge, since experimental data have been obtained with complexes of divalent metal ions except for the Co(III) system. The Fe(II) complex is isoelectronic with the Co(III) complex and its ground state was assumed to be closed-shell singlet.[21]

The calculated maps of the potential surfaces have the following common features: (i) each contour is an ellipse elongated in the M–Cl direction; (ii) each ellipse has an anticlockwise tilt. When the maps shown in Fig. 2 are compared, the ellipse for $Co^{3+}$ is the closest to a circle, the axis ratio of the $Zn^{2+}$ ellipse is the largest, and the $Ni^{2+}$ system is intermediate. The tilt of the ellipse is the smallest for $Co^{3+}$, intermediate for $Ni^{2+}$, and the largest for $Zn^{2+}$. Contour lines are the most congested for $Co^{3+}$, while they are the farthest apart for $Zn^{2+}$. These features are very important in the interpretation of the experimentally observed correlation between the axial and in-plane coordination bond distances.

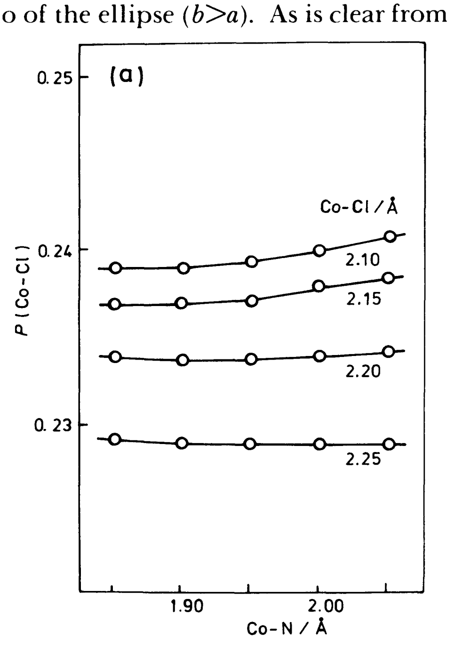
On the basis of the section map, we will discuss the case where the M–N distance is varied, as was done experimentally by use of the macrocyclic ligands with different ring sizes.



When energy minimum points at various M–N distances are connected, a line with a slope ($\alpha$) is obtained. This line shows the interrelationship between the M–Cl and M–N distances under the electronically most stable circumstances. Thus, the larger the slope ($\alpha$) is, the stronger is the correlation. Assuming that each contour is a perfect ellipse, $\alpha$ is given by the following equation,

$$\tan^{-1}\alpha=[\{1-(a/b)^2\}\sin\theta\cos\theta]/[\sin^2\theta+(a/b)^2\cos^2\theta], \quad (1)$$

where $\theta$ denotes a tilt of the ellipse and $a/b$ represents an axis ratio of the ellipse ($b>a$). As is clear from Eq. 1, if the contour is not an ellipse but a circle ($a=b$), or if the longer axis of the ellipse is parallel to the vertical axis ($\theta=0$), $\alpha$ equals zero. Under such circumstances, the M–Cl distance does not change at all, even though the M–N distance is varied. The larger $\alpha$ value would be expected when the ellipse has a larger tilt[23] and the axis ratio of the ellipse is smaller.[24]



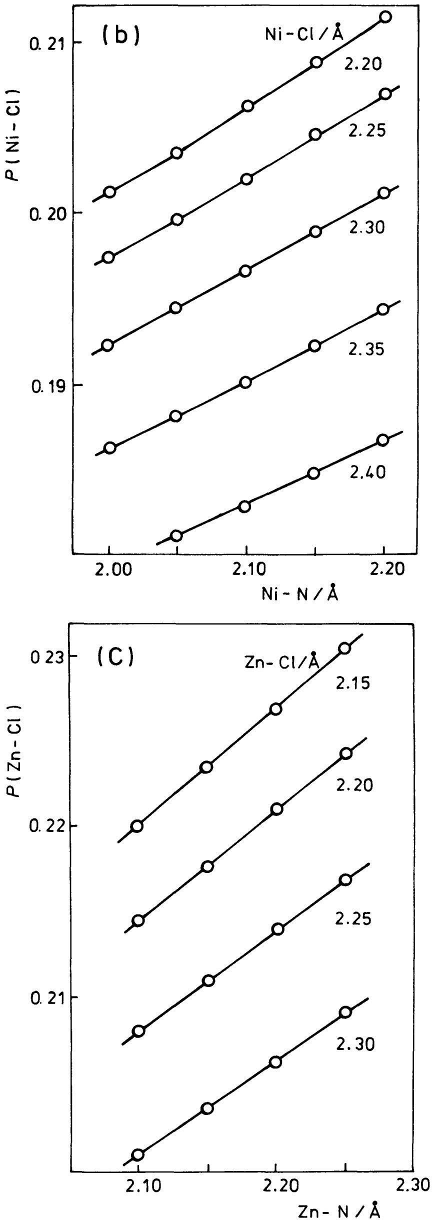


Fig. 3. M–Cl overlap population ($P$) as a function of M–N distances: (a) *trans*-$[CoCl_2(NH_3)_4]^+$; (b) *trans*-$[NiCl_2(NH_3)_4]$; (c) *trans*-$[ZnCl_2(NH_3)_4]$.

As the difference in the ligand field strengths between axial and in-plane ligands becomes larger, the ellipticity ($a/b$) decreases to give larger $\alpha$. This is exemplified by the difference in the slopes for the chloro and isothiocyanato Ni(II) complexes, shown in Fig. 1 (*vide supra*). In the present systems, the ellipse becomes more nearly circular with an increase in the axial ligand field strength. The closer the ellipse is to a circle, the weaker is the correlation. The Co(III) system demonstrates such a situation (see Figs. 1 and 2(a)).

The tilt of the ellipse in Fig. 2 is 14° for Co(III), 18° for Fe(II), 31° for Ni(II), and 41° for Zn(II). The tilt reflects ease with which electrons move when the coordination bond lengths are forced to be varied. Thus, it seems that the tilt is associated with polarizability of the complex. Figure 3 shows overlap population on an M–Cl bond as a function of M–N distances. Generally, the M–Cl overlap population increases as the M–N distance increases. This arises from the fact that each metal atom tends to keep the electric charge neutral. In fact, within the computed range of M–N and M–Cl distances (the optimized distance ± *ca.* 0.25 Å, see Computational Procedures), total electron population on the metal atoms (Mulliken population) was constant within 2% for each metal atom. The values were 26.4 for Co(III), 25.5 for Fe(II), 27.5 for Ni(II), and 29.4 for Zn(II). The interrelationships depicted in Fig. 3, which are strongly metal ion dependent, are deeply related to the tilts of the ellipses of Fig. 2.

The congestion of the contour lines, *i.e.*, the slope of the potential surface, is also an important factor. If contour lines were less congested, the electronic cis effect would occur more easily. On the other hand, coordination bond lengths would not vary widely, if the slope of the potential surface were steep. It is manifested in the Co(III) system (see Figs. 1 and 2(a)). The most apparent difference in the feature of the potential surfaces between the Co(III) and Fe(II) complexes is the slopes. There is no doubt that the Co(III) surface becomes steeper by the effect of the electric charge. Higher electric charge on the metal brings about more congested contour lines.

The conclusions obtained from the features of the potential surfaces, such as the axis ratio, the tilt of the ellipse and the degree of the congestion of the contour lines, agree very well with the experimentally observed results shown in Fig. 1.

Pearson made the following statement in his paper describing the concept of Hard and Soft Acids and Bases: Softness in both the acid and base means that the repulsive part of the potential energy curve rises less sharply than for hard acids and bases.[25] According to this, it follows that the degree of the congestion of the contour lines in Fig. 2 shows hardness of the metal ions. Furthermore, softness (or hardness) is known to be directly associated with the polarizability,[25] which is correlated with the tilt of the ellipse in Fig. 2. In view of these, it is clear from Figs. 1 and 2 that, among the metal ions studied, Co(III) is the hardest, Zn(II) is the softest, and Ni(II) is intermediate. Although Pearson classifies both of $Ni^{2+}$ and $Zn^{2+}$ into borderline Lewis acids,[25] there is a clear difference in softness between them.

In the present MO calculations, we used a double $\zeta$ quality basis set for metal 3d orbitals and minimal basis sets for the others. The approximation might not be sufficient to describe detailed electronic structures and molecular dimensions. For example, M–Cl bond distances in the optimized structures (see below (Table 2)) are evidently shorter than the normal values.[26] However, we believe that the present calculations give sufficiently reliable results concerning the relative differences of the potential surfaces.

Both theoretically and experimentally, it has been found that the degree of correlation increases in the order, $Co^{3+} < Ni^{2+} < Zn^{2+}$. It should be pointed out that the number of d-electrons in $e_g$ orbital in $O_h$ symmetry increases in the same order: 0 for $Co^{3+}$, 2 for $Ni^{2+}$, and 4 for $Zn^{2+}$.

## Computational Procedures

*Geometries and Basis Set.* Each ammonia ligand was assumed to have the N–H bond length of 1.00 Å and tetrahedral bond angles with its $C_3$ axis lying on the M–N bond. The ammonia molecules were arranged in such a manner that the entire molecule of *trans*-$[MCl_2(NH_3)_4]$ has $D_{2d}$ symmetry.

The basis sets used were the STO-3G set for ligand atoms and the [4s3p2d] contracted set for central metal atoms, respectively.[27] For $M = Co^{3+}$, $Fe^{2+}$, and $Zn^{2+}$, the ground states are assumed to be closed-shell singlet, whereas, for $M = Ni^{2+}$, it is assumed to be triplet, and the restricted Hartree-Fock method was used in the SCF–MO calculations.

*Section Maps of the Potential Surfaces along M-Cl and M-N Bond axes.* In order to draw section maps of the potential energy surfaces along the coordination bond axes, we have calculated SCF MO's on 20—30 geometries for each model compound, M–N and M–Cl distances being varied by 0.05 Å near the minimized structures. Contours were drawn by means of two-dimensional spline fitting program at intervals of 0.5 kcal $mol^{-1}$. Coordinates for the optimum structure of each compound were obtained by smooth interpolation from the section map (Table 2).

TABLE 2. OPTIMIZED COORDINATION GEOMETRIES FOR *trans*-$[MCl_2(NH_3)_4]$.

| M | M–N/Å | M–Cl/Å |
|---|---|---|
| $Co^{3+,a)}$ | 1.97 | 2.15 |
| $Fe^{2+}$ | 2.06 | 2.27 |
| $Ni^{2+}$ | 2.13 | 2.27 |
| $Zn^{2+}$ | 2.18 | 2.25 |

a) For Co(III) complexes of *trans*-$CoCl_2N_4$ type, Co–N and Co–Cl distances have been found to be ≈1.98 Å and ≈2.26 Å, respectively.[18]

All the calculations were carried out by using the IMSPACK program system[28] on a HITAC M-200H computer at the Computer Center of IMS.

### References

1) J. Găzo, R. Bŏca, E. Jóna, M. Kabešová, Ľ. Macášková, and J. Šima, *J. Coord. Chem. Rev.*, **43**, 87 (1982), and references cited therein.

2) B. J. Hathaway and A. A. G. Tomlinson, *Coord. Chem. Rev.*, **5**, 1 (1970).

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

4) J. F. Endicott and B. Durham, "Coordination Chemistry of Macrocyclic Compounds," ed by G. A. Melson, Plenum Press, New York, N. Y. (1979), Chap. 6.

5) D. D. Domoinguez, M. M. King, and H. J. Yeh, *J. Magn. Reson.*, **32**, 161 (1978).

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

7) Y. Hung, L. Y. Martin, S. C. Jackels, A. M. Tait, and D. H. Busch, *J. Am. Chem. Soc.*, **99**, 4029 (1977).

8) T. Ito, M. Kato, and H. Ito, *Bull. Chem. Soc. Jpn.*, in press and presented at XXII International Conference on Coordination Chemistry, Budapest, Hungary, August 1982, Abstract P. TuB14.

9) T. Ito, M. Kato, and H. Ito, *Bull. Chem. Soc. Jpn.*, in press.

10) Except for Co(III), such complexes are hypothetical.

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

12) B. Bosnich, R. Mason, P. T. Pauling, G. B. Robertson, and M. L. Tobe, *J. Chem. Soc., Chem. Commun.*, **1965**, 97.

13) E. K. Yukhno and M. A. Poraj-Košic, *Kristallografiya*, **2**, 239 (1957); Struc. Rep. **22**, 407.

14) B. W. Brown, and E. L. Lingafelter, *Acta Crystallogr.*, **16**, 753 (1963).

15) H. Ito, M. Kato, and T. Ito, unpublished result.

16) A. Nakahara, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Jpn.*, **25**, 331 (1952).

17) K. Matsumoto, S. Ooi, and H. Kuroya, *Bull. Chem. Soc. Jpn.*, **43**, 1903 (1970).

18) M. Goto, K. Ohta, K. Toriumi, and T. Ito, *Acta Crystallogr., Sect. B*, **37**, 1189 (1981).

19) So far we have not succeeded in the sysnthesis of *trans*-[Zn(NCS)$_2$([16]aneN$_4$)]. The [14]aneN$_4$, [15]aneN$_4$, and [16]aneN$_4$ ligands did not afford single crystals of six-coordinate Zn(II) complexes with Cl$^-$ ligands at the axial positions.

20) M. Sugimoto, H. Ito, K. Toriumi, T. Ito, *Acta Crystallogr., Sect. B*, **38**, 2453 (1982).

21) It has been shown that [Fe$^{II}$Cl$_2$([14]aneN$_4$)] is a high-spin complex.[22]

22) D. D. Watkins, Jr., D. P. Reiley, J. A. Stone, and D. H. Busch, *Inorg. Chem.*, **15**, 387 (1976).

23) This holds mathematically until $\theta$ reaches $\tan^{-1}(a/b)$, where $\alpha$ adopts the maximum value. When $\theta$ exceeds $\tan^{-1}(a/b)$, $\alpha$ gets smaller with an increase in $\theta$.

24) This holds always irrespective of the value of $\theta$.

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

26) This arises from the use of STO-3G basis set for the chlorine atom, contribution of 3d orbitals being not taken into account at all.

27) The basis sets used in this study for metal atoms were similar to those used in an *ab initio* MO study on simple nickel–phosphine complexes by Morokuma *et al.*[29] The [4s3p2d] set was contracted from the (11s7p5d) primitive Gaussian set, which was modified from (12s6p4d)[30] by deleting the two most diffuse an s-type, a p-type, and a d-type functions and adding an s-type, a p-type, and a d-type functions with the exponents 0.2, 0.25, and 0.2, respectively. The 3s-type functions arising from the totally symmetric linear combination of d-type functions were removed from the basis set.

28) K. Morokuma, S. Kato, K. Kitaura, I. Ohmine, S. Sakai, and S. Obara, IMS Computer Center Library, Institute for Molecular Science, No. 0372 (1980).

29) K. Kitaura, S. Sakaki, and K. Morokuma, *Inorg. Chem.* **20**, 2292 (1981).

30) B. Roos, A. Veillard, and G. Vinot, *Theor. Chim. Acta*, **20**, 1 (1971).