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Electronic Structure of Transition Metal Complexes II. Trans Influence in Ammine Complexes of the First Transition Metals

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CNDO/2 calculations of pentaammine complexes, $[M(NH_3)_5X]$ (both low and high spin states), where M= Co^{2+}, Co^{3+}, Fe^{2+}, and Fe^{3+}, and X=FH, OH_2, CO, NH_3, pyridine, OH^-, F^-, and CN^-, have been carried out in order to investigate the mutual influence between ligands. The present calculation shows that the σ-type mutual influence is remarkably affected by the oxidation number and the spin state of the metal ion and scarecely affected by the number of d electron (d electron configuration). Furthermore, the calculated results show the metal-ligand bond distance of a complex in the low spin state should be shorter than that in the high spin state.

Many experimental evidences of the trans influences in the transition metal complexes have been found in the field of inorganic chemistry from long time ago. Most of them were found at Pt complexes.[1] Recently, some experimental works have been done about the trans influence in the first transition metal complexes.[2] Shustorovich *et al.* carried out quantum chemical calculations in order to solve this problem.[3] They applied the perturbation theory based on the simple MO method to several types of complexes.

In this paper, we have investigated the trans influences in the various pentaammine complexes, $[M(NH_3)_5X]$ (both low and high spin states) where M=Co^{2+}, Co^{3+}, Fe^{2+}, and Fe^{3+}, and X=FH, OH_2, CO, NH_3, pyridine(py), OH^-, F^-, and CN^-, using CNDO/2 method. We have studied how the trans influence is affected by the oxidation number and the spin state of the metal ion and the kinds of metals and ligands.

Calculations

In the previous paper,[4] we proposed new bonding parameters associated with 4s and 4p AO's of the first transition metals in the CNDO/2 method, which give satisfactory results for the binding energies of coordination bonds of various hexaammine and hexaaqua complexes. In the present study, we have carried out CNDO/2 calculations (unrestricted SCF scheme) of pentaammine complexes (see Fig. 1) using these new parameters.

We take five neutral ligands, FH, OH_2, CO, NH_3, and py, and three ionic ones, OH^-, F^-, and CN^- into consideration. In coordination chemistry, the spin state of the transition metal complex has an important role in its physico chemical properties. Therefore, we have also calculated the electronic structure of the complexes in the low and high spin states.

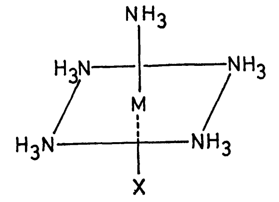


Fig. 1. Pentaammine complexes, where M=Co^{2+}, Co^{3+}, Fe^{2+}, and Fe^{3+}, X=FH, OH_2, CO, NH_3, py, OH^-, F^-, and CN^-.

We used the experimental data for Co–N distances, 2.11 Å(Co^{2+}–N)[5] and 1.97 Å(Co^{3+}–N),[6] and estimated ones for Fe–N distances, 2.15 Å(Fe^{2+}–N)[4] and 2.00 Å (Fe^{3+}–N). We have employed the experimental geometry[7] of the free molecule for that of the ligand. For the simplicity, we have put the distance of M–X bond same as that of M–N bond, that is ,we assumed a regular octahedral geometry for each complex.

Results and Discussion

The mutual influence between the trans ligands is not affected only by the characteristics of the ligand such as the ionization potential, electron affinity *etc.*, but also by the electronic structure of the central metal ion such as the oxidation number, the spin state and the number of d electrons. The mutual influence should be appeared in the charge densities of the central metal ion and the ligands and the bond orders between the metal and the ligands. The charge distribution in the complex reflects sharply the characteristics of the ligand and the central metal ion. However, it is difficult to measure experimentally the change of the charge density on the atom caused by trans influence. Many experimental evidences[2] of the mutual influence have been found by the measurement of bond distances between the metal and the ligands. However, the charge density on the atom is important for the discussion of the reactivity of the complex. Therefore, we will discuss the mutual influence from the standpoint of both the charge density and the bond order.

The most important factors affecting on the mutual

Table 1. Orbital energies of the isolated ligands

$\varepsilon^X_{HOMO}(\sigma)$/a.u.		$\varepsilon^X_{HOMO}(\pi)$/a.u.		$\varepsilon^X_{LUMO}(\pi)$/a.u.	
CN^-	−0.0365	CN^-	−0.2026	CN^-	0.7924
F^-	−0.0651	py	−0.5314	CO	0.1953
OH^-	−0.0941	CO	−0.7736	py	0.1293
py	−0.4773				
NH_3	−0.6022				
CO	−0.6346				
OH_2	−0.7127				
FH	−0.8493				

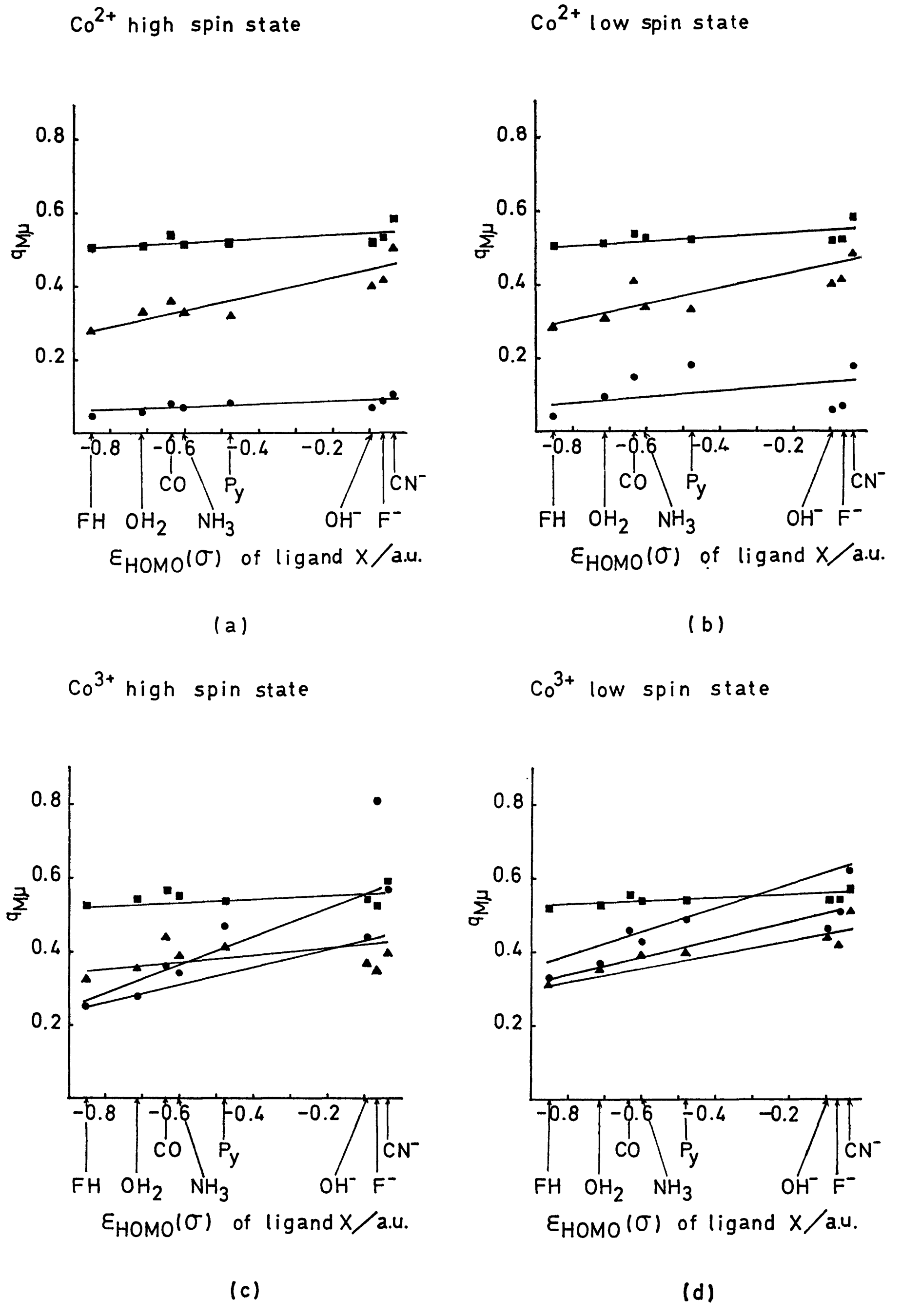


Fig. 2. The charge densities associated with 4s, $4p_z$, and $3d_{z^2}$ orbitals of cobalt.
(a): Co^{2+} (high spin), (b): Co^{2+} (low spin), (c): Co^{3+} (high spin), (d): Co^{3+} (low spin).
Marks; ●: $3d_{z^2}$, ■: 4s, ▲: $4p_z$.

influence are the ionization potential and the electron affinity of the ligand, so that, in Table 1 the highest occupied and the lowest unoccupied orbital energies of isolated ligands calculated by the CNDO/2 method are given as a reference.

Charge Density. From the chemical intuition, we expect the 4s, $4p_z$, $3d_{z^2}$, $3d_{xz}$, and $3d_{yz}$ orbitals of metal ion make the most important contribution to the trans influence. Our results show that only the variations of the charge densities associated with these orbitals are considerably large and others are negligible when ligand X is varied. Figures 2(a)—(d) show the plots of the charge densities associated with 4s, $4p_z$, and $3d_{z^2}$ orbitals of cobalt (Co^{2+} and Co^{3+}) against the highest occupied orbital energy of the ligand X, $\varepsilon^{X}_{HOMO}(\sigma)$.

From these figures, it is found that the charge density associated with $4p_z$ orbital is varied largely at the bivalent metals, while the charge density associated with $3d_{z^2}$ orbital is changed remarkably at the tervalent metals. The reason for this may be due to the following facts. In the bivalent metal, two 4s electrons are removed, so that the electrons come back to 4s and 4p orbitals by the formation of complex. Because the coordination bond is largely polarized, the contribution of $4p_z$ orbital to this bond should be large. This might be the reason why the variation of population of $4p_z$ with respect to the change of the ligand is large. In the tervalent metal, the third electron is removed from 3d orbital. Therefore, by the formation of the complex, an electron comes back at first to 3d orbital. $3d_{z^2}$ orbital contributes largely to the coordination bond, X–M–N, formed by the trans ligands and the metal, but other d orbitals contribute slightly. Consequently, the variation of the population in $3d_{z^2}$ orbital is largely varied by the trans influence.

In tervalent metal complexes, when we plot the charge density associated with $3d_{z^2}$ orbital against $\varepsilon^{X}_{HOMO}(\sigma)$, we obtain two lines. One of them contains py, CO, and CN^-, and another line contains FH, OH_2, NH_3, OH^-, and F^-. The ligands belonging to the former have unoccupied π-orbitals, however, those belonging to the latter no unoccupied π-orbitals. These π-orbitals will affect $3d_{z^2}$ orbital indirectly through the interaction with $3d\pi$ orbital.

The tendency of the charge density variation of the iron (Fe^{2+} or Fe^{3+}) complex (Figs. 3(a)—(d)) is

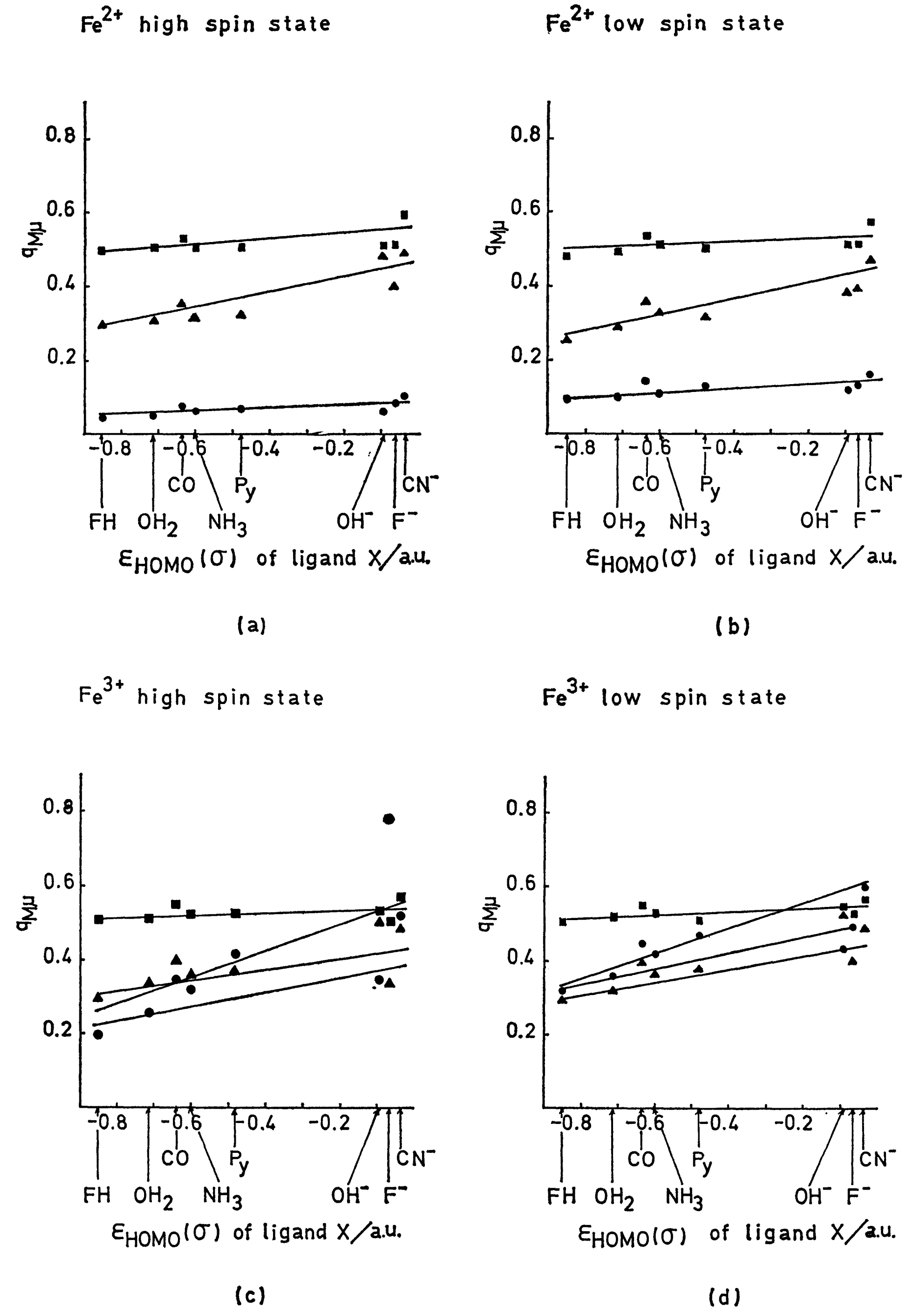


Fig. 3. The charge densities associated with 4s, $4p_z$, and $3d_{z^2}$ orbitals of iron.
(a): Fe^{2+} (high spin), (b): Fe^{2+} (low spin), (c): Fe^{3+} (high spin), (d): Fe^{3+} (low spin). Marks: see Fig. 2.

similar to that of the corresponding cobalt complex.

Comparing the calculated charge densities of Co complex with those of the corresponding Fe complex (*cf.* Figs. 2(a)—(d) and Figs. 3(a)—(d)), we conclude that the charge population at the central metal ion is determined mainly by the oxidation and spin states of the complex.

Bond Order. The total bond order associated with the metal-ligand bond is consisted of the contributions of various orbital pairs. In Table 2, all possible orbital pairs are given. Similar to the results of charge density as mentioned above, the contributions of the particular pairs of orbitals to the trans influence are important, while those associated with other orbital pairs are negligibly small.

First of all, let us investigate about σ-type interac-

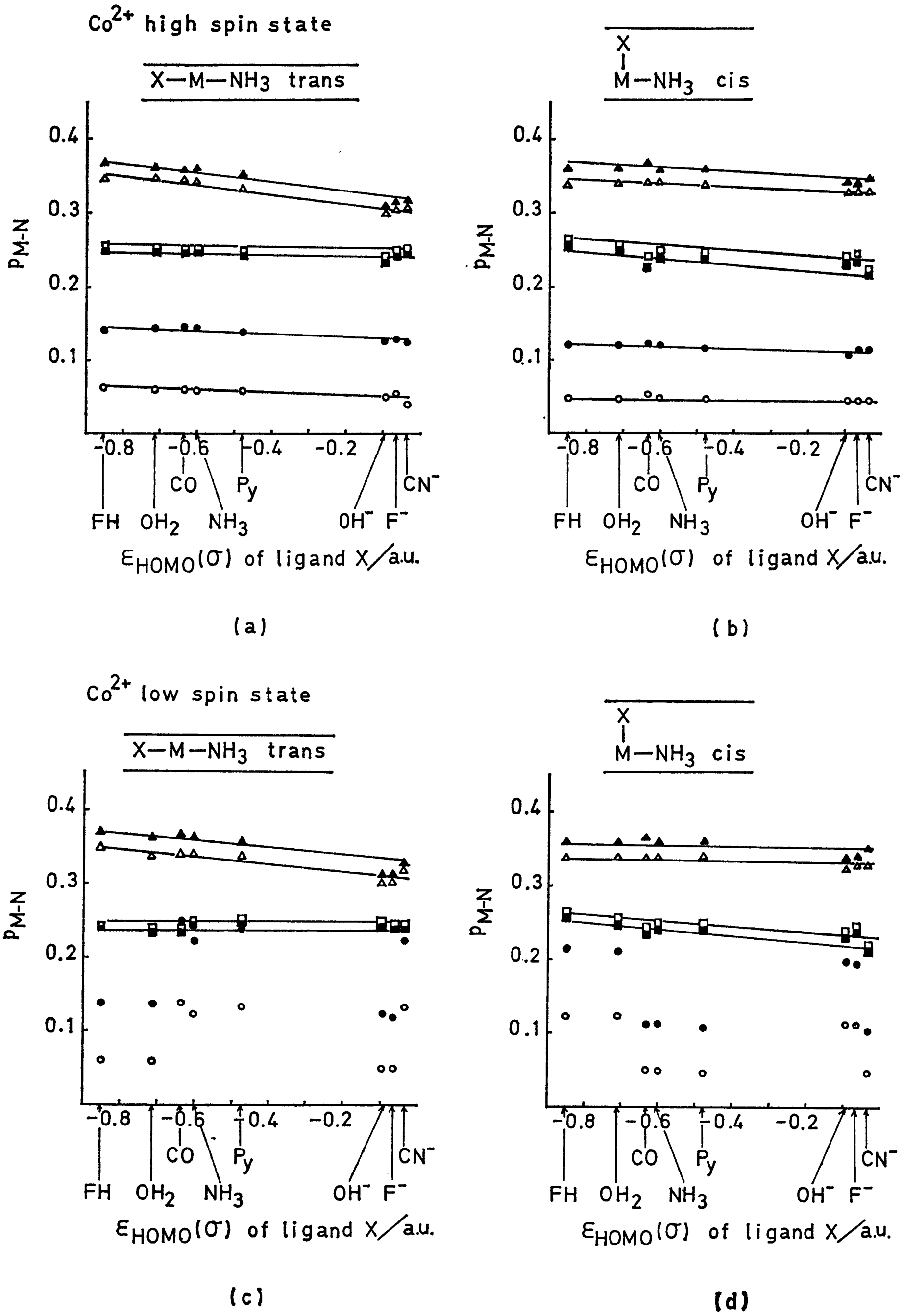


Fig. 4. The bond orders associated with various orbital pairs of M–N bond in bivalent cobalt complex.

(a): Co^{2+}–*trans*N (high spin), (b): Co^{2+}–*cis*N (high spin), (c): Co^{2+}–*trans*N (low spin), (d): Co^{2+}–*cis*N(low spin).

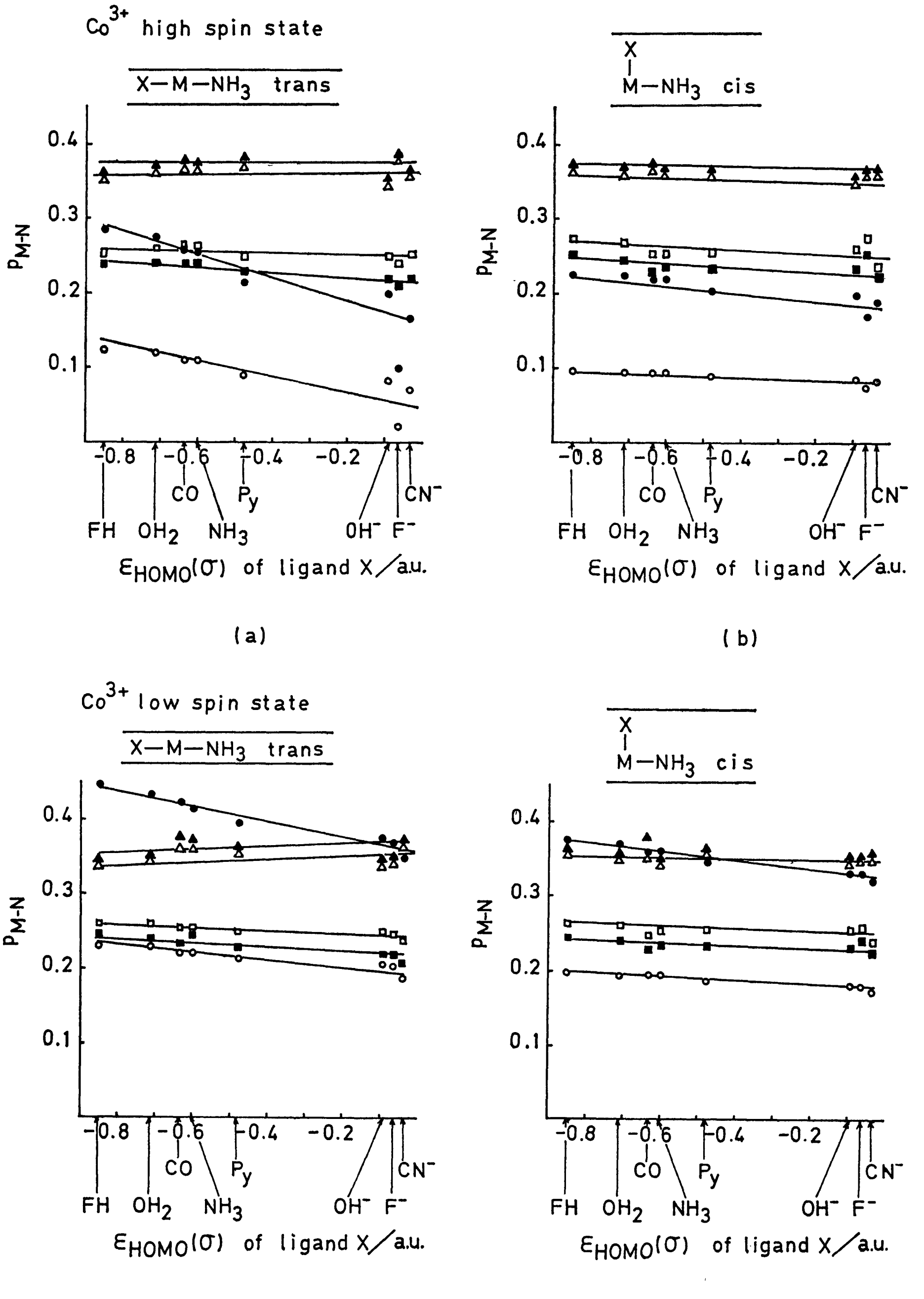
Marks;

M–*trans*N bond—○: $3d_{z^2}$-2s, ●: $3d_{z^2}$-$2p_z$, □: 4s-2s, ■: 4s-$2p_z$, △: $4p_z$-2s, ▲: $4p_z$-$2p_z$.

M–*cis*N bond—○: $3d_{x^2-y^2}$-2s, ●: $3d_{x^2-y^2}$-$2p_x$, □: 4s-2s, ■: 4s-$2p_x$, △: $4p_x$-2s, ▲: $4p_x$-$2p_x$.

tion between the metal and the ligand. In this case, the ligand acts as an electron donor, so that $\varepsilon^{X}_{HOMO}(\sigma)$ plays a key role. Figures 4(a)—7(d) show the plots of the bond orders associated with all possible orbital pairs against $\varepsilon^{X}_{HOMO}(\sigma)$. It is interesting to note that the gross feature of the figure of Co^{n+} at the high spin state or Co^{n+} at the low spin state is very similar to that of the corresponding Fe complex (see *cf.* Figs. 4(a) and 6(a)). Consequently, we can say that in Fe and Co complexes the nature of the coordination bond is determined mainly by the oxidation number and the spin state (low or high), but is not by the number of d electrons of the metal. It is well known that Fe, Co, and Ni form similar complexes, so that they are called a triad. Actually, our calculation shows the electronic states of Fe and Co complexes resemble each other.

In the bivalent metal complexes, the bond orders pertaining to $4p_z$ orbital are prominently varied by the trans ligand X. Figures 4(a)—(d) show that the bond orders associated with $4p_z$-$2p_z$ and $4p_z$-2s pairs are decreased with the increase of $\varepsilon^{X}_{HOMO}(\sigma)$.



(a) (b)

(c) (d)

Fig. 5. The bond orders associated with various orbital pairs of M–N bond in tervalent cobalt complex.

(a): Co^{3+}-*trans*N (high spin), (b): Co^{3+}-*cis*N (high spin), (c): Co^{3+}-*trans*N (low spin), (d): Co^{3+}-*cis*N (low spin).

Marks: see Fig. 4.

This result can be understood from the standpoint of the simple MO theory. Let us consider the coordination bond X–M–N. The orbital energy, α_M, associated with metal's AO increases when $\varepsilon^{X}_{HOMO}(\sigma)$ is increased. Second order perturbation theory calculates this increase, $\Delta\alpha_M$, by the following equation,

$$\Delta\alpha_M = \frac{\beta_{MX}^2}{\alpha_M^0 - \varepsilon^{X}_{HOMO}(\sigma)}$$

where α_M^0 is the orbital energy of metal's AO in the hexaammine complex. The increase of $\Delta\alpha_M$ causes the decrease of bond order, Δp_{MN}, associated with M–N bond in the following manner,

$$\Delta p_{MN} \simeq -p_{MN}^0 \frac{\Delta\alpha_M(\alpha_M^0-\alpha_N^0)}{4\beta_{MN}^2} = k\Delta\alpha_M,$$

where $k = -\frac{p_{MN}^0(\alpha_M^0-\alpha_N^0)}{4\beta_{MN}^2}$ (<0) and α_N^0 is the orbital energy of the lone pair of ligand NH_3. p_{MN}^0 means the bond order of M–N bond in the hexaammine complex. On the other hand, the change of the bond order, Δp_{MX}, associated with M–X bond can be written by

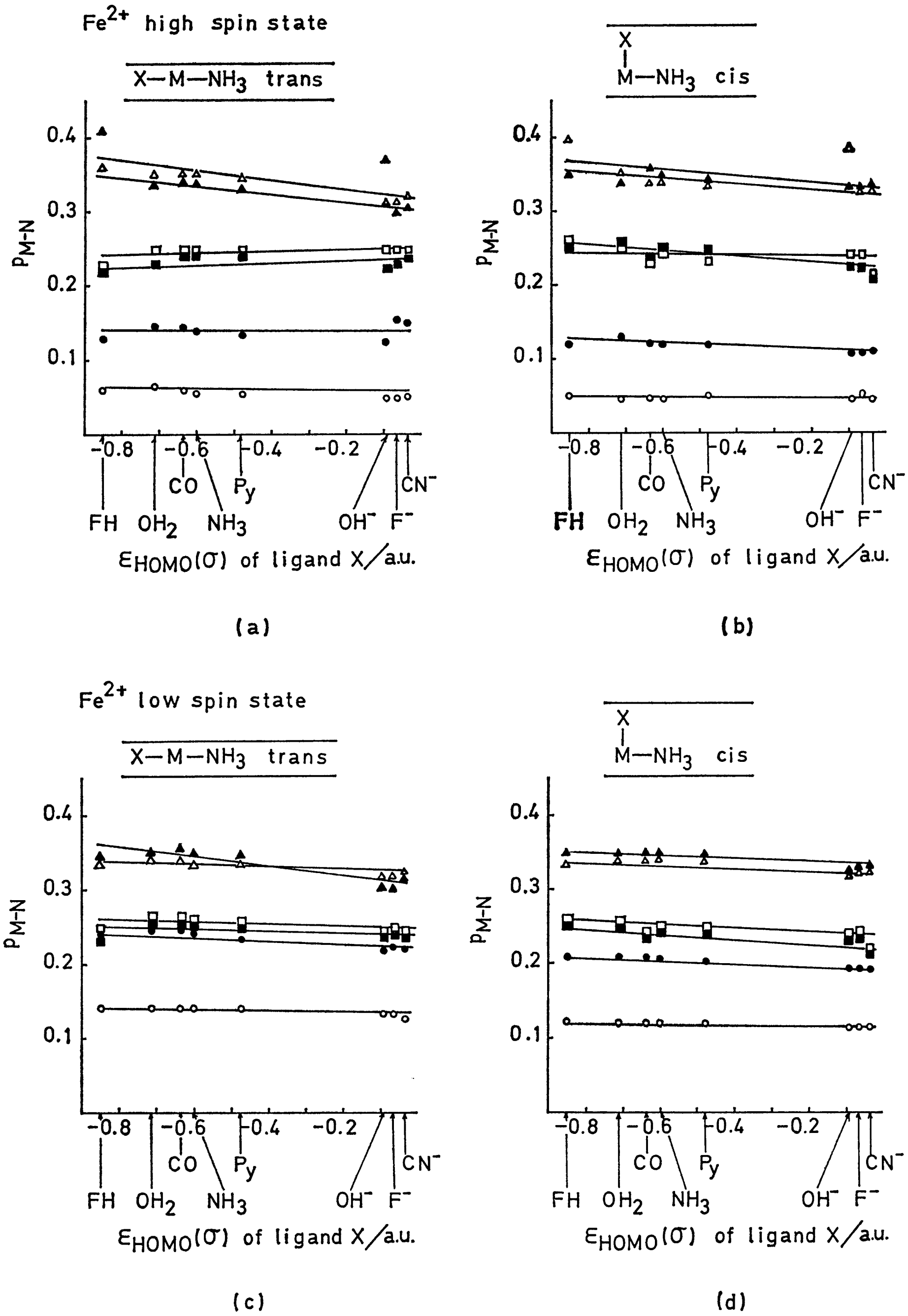


Fig. 6. The bond orders associated with various orbital pairs of M–N bond in bivalent iron complex.

(a): Fe^{2+}–*trans*N (high spin), (b): Fe^{2+}–*cis*N (high spin), (c): Fe^{2+}–*trans*N (low spin), (d): Fe^{2+}–*cis*N (low spin).

Marks: see Fig. 4.

$$\Delta p_{\mathrm{MX}} \simeq p_{\mathrm{MN}}{}^0 \frac{\Delta\alpha_{\mathrm{X}}(\alpha_{\mathrm{M}}{}^0-\varepsilon^{\mathrm{X}}_{\mathrm{HOMO}}(\sigma))}{4\beta_{\mathrm{MX}}{}^2}$$

because of $\Delta\alpha_{\mathrm{X}}=\Delta\varepsilon^{\mathrm{X}}_{\mathrm{HOMO}}(\sigma)=\varepsilon^{\mathrm{X}}_{\mathrm{HOMO}}(\sigma)-\alpha_{\mathrm{N}}{}^0=-\Delta\alpha_{\mathrm{M}}$. Therefore, the bond order associated with M–N bond is decreased, when that associated with M–X bond is increased. In other words, when M–X bond is strengthened, the M–N bond is weakened.

It should be noted that the bond order associated with $3d_{z^2}$-$2p_z$ and $3d_{z^2}$-2s pairs are almost constant against the variation of $\varepsilon^{\mathrm{X}}_{\mathrm{HOMO}}(\sigma)$. This result is consistent with the charge variation of the bivalent metal ion. That is, in the bivalent metal complex, $4p_z$ orbital plays more important role than $3d_{z^2}$ orbital.

It is of interest to consider the effect of the spin state on the trans influence. M–*trans*N bond is greatly affected by the spin state of the metal (see Figs. 6(a) and (c)). Namely, the bond order associated with M–*trans*N bond in the low spin state is much larger than that in the high spin state. In other words, the bond distance of M–*trans*N bond in the low spin state is shorter than that in the high spin state. This

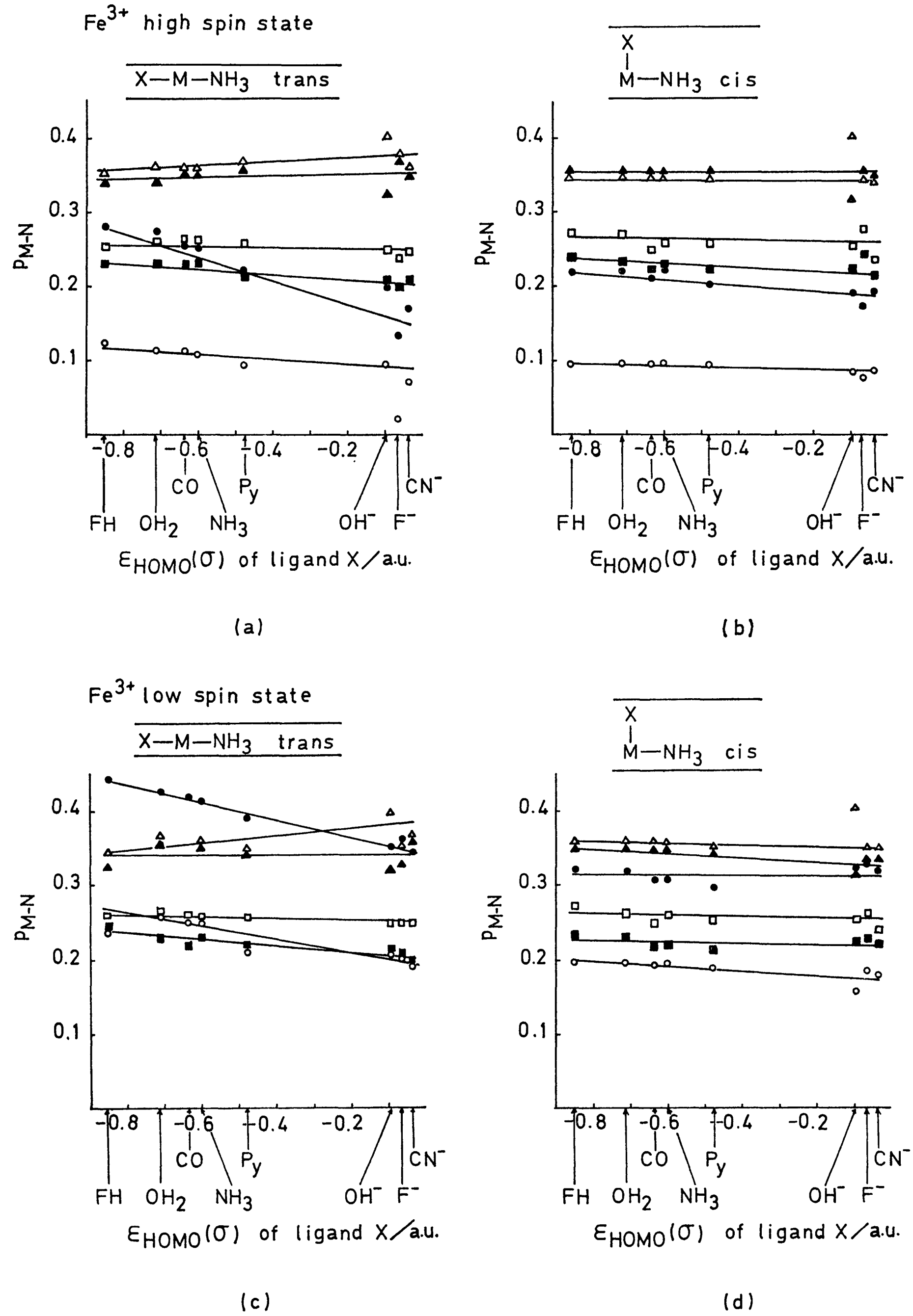
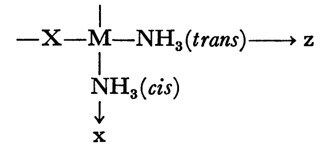


Fig. 7. The bond orders associated with various orbital pairs of M–N bond in tervalent iron complex.
(a): Fe^{3+}–*trans*N (high spin), (v): Fe^{3+}–*cis*N (high spin), (c): Fe^{3+}–*trans*N (low spin), (d): Fe^{3+}–*cis*N (low spin).
Marks: see Fig. 4.

TABLE 2. THE VARIOUS ORBITAL PAIRS CONTRIBUTING TO M-N BOND

σ-Type interaction	
M-*trans*N	M-*cis*N
$4s-2s$	$4s-2s$
$4s-2p_z$	$4s-2p_x$
$4p_z-2s$	$4p_x-2s$
$4p_z-2p_z$	$4p_x-2p_x$
$3p_{z^2}-2s$	$3d_{x^2-y^2}-2s$
$3d_{z^2}-2p_z$	$3d_{x^2-y^2}-2p_x$



$$\begin{array}{l} \qquad\quad | \\ —X—M—NH_3(\mathit{trans}) \longrightarrow z \\ \qquad\quad | \\ \qquad\quad NH_3(\mathit{cis}) \\ \qquad\quad \downarrow \\ \qquad\quad x \end{array}$$

is in accord with the experiment.[8] In M-*cis*N bond, the effect of the ligand X is very small (see Figs. 4(b) and (d)).

In the M-*trans*N bond, the variation of the bond order associated with $4p_z$-2s or $4p_z$-$2p_z$ is large, but that associated with 4s-2s or 4s-$2p_z$ is rather small. Whereas, in the M-*cis*N bond, that associated with 4s-2s or 4s-$2p_x$ is considerably large (see Figs. 4(a) and (b)). From these results, we might conclude that when a p-character of M-*trans* ligand bond increases, that of M-*cis* ligand bond decreases, so that the s-character of M-*cis* ligand bond should increase and *vice versa*. In other word, when the bond distance of M-*trans* ligand bond increases, that of M-*cis* ligand bond becomes to decrease, if the contribution of $3d_{z^2}$ orbital is unchanged. This rule can be applied to the bivalent metal complexes, because the contribution of $3d_{z^2}$ orbital is very small. However, in the tervalent metal complexes, the contribution of $3d_{z^2}$ orbital is rather large, so that this rule may not be applied.

In the tervalent metal complexes, the contribution of each orbital pair to M-*trans*N bond is much complicated (see Figs. 5(a)—(d)). The bond order associated with M-*cis*N bond is also varied considerably by the change of the spin state (see Figs. 5(b) and (d)). An interesting result is that the bond order associated with $3d_{z^2}$-$2p_z$ is increased with the decrease of $\varepsilon^{\mathrm{X}}_{\mathrm{HOMO}}(\sigma)$, while, that associated with $4p_z$-$2p_z$ is decreased. The bond order associated with M-*trans*N bond in the low spin state is larger than that in the high spin state. It is interesting to note that the contribution of $4p_z$-$2p_z$ pair to M-*trans*N bond in the low or the high spin state is almost same, but the contribution of $3d_{z^2}$-$2p_z$ or $3d_{z^2}$-2s in the low spin state is almost double of that in the high spin state. Therefore, we expect that the bond distance of M-*trans*N bond in the low spin state is shorter than that in the high spin state, and also that of M-*cis*N bond in the low spin state is shorter than that in the high spin state.

Let us consider, next, π-type influence in a complex. The ligands FH, OH_2, NH_3, OH^-, and F^- have no unoccupied π-orbitals. On the other hand, CO, py and CN^- have unoccupied π-orbitals which can accept charge from the central metal ion. Therefore, we will find some differences between the bond order p_{MX} associated with the former ligand and that associated with the latter ligand. However, the change of p_{MN} against $\varepsilon^{\mathrm{X}}_{\mathrm{HOMO}}(\pi)$ of the ligand X is very small, because NH_3 has no available π-orbital. Thus, the ligand X having unoccupied π-orbitals has an effect on the charge density variation of the central metal ion, but no effect on the bond order of M-N bond.

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