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# Electronic Structures of Tris(2,2′-bipyridyl) Complexes of Transition Metals in Lower Oxidation States

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The electronic structures of various transition metal complexes with 2,2′-bipyridyl in low oxidation states are studied theoretically by the composite system method. The results show that the excess electrons are not localized on the metal ion but are transferred to some extent to the ligand antibonding $\pi$-molecular orbitals with the lower oxidation states of complex ions. The present theory can explain reasonably and systematically the observed magnetic moments and ESR spectra of the complexes, the simple one-electron treatment being inappropriate for a theoretical explanation of their magnetic properties. According to the present treatment, their electronic absorption spectra can be explained satisfactorily from a qualitative point of view as the overlapping of the $\pi$–$\pi^*$ transition bands in the ligands with the metal-ligand charge-transfer transition bands.

A number of transition metal complexes in low oxidation states have been synthesized. In particular, the tris(2,2′-bipyridyl) complexes in various oxidation states have been synthesized for the iron-series transition metals and their magnetic properties have been investigated.[1–10] König studied their ESR spectra,[11] assuming that the excess electrons are localized completely on the metal ion. Hall and Reynolds explained the $g$ value obtained by the ESR measurement for [Fe(bip)$_3$]$^0$ [12] on the same assumption. However, in view of the metal-ligand interaction, this assumption may not always be appropriate. In fact, their measurement of the electronic absorption spectrum[9,10] of [Fe(bip)$_3$]$^0$ indicates that most of the excess electrons delocalize to the bipyridyl $\pi$-electron systems, and their ESR and electronic absorption studies give different conclusions on the excess electron distribution of the same complex. This contradiction must be solved.

The present study has been undertaken to understand more extensively the electronic structures of tris(2,2′-dipyridyl) complexes in low oxidation states and to solve several problems on their magnetic and optical properties from the theoretical point of view. In particular, the distribution of "excess electrons" in the ground states of these complexes seems to be interesting in connection with their magnetic properties and with their oxidation-reduction abilities.

## General Background of the Present Theoretical Consideration

The metal complexes in lower oxidation states treated in the present study are summarized in Table 1 together with those in ordinary oxidation states. We have adopted the two quantities to characterize the isoelectronic series;[13] namely, $N_\pi$, the total numbers of the metal $3d\pi$ electrons plus the $\pi$ electrons in ligand

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[1] S. Herzog and R. Table, *Z. Anorg. Allg. Chem.*, **306**, 159 (1960); *Angew. Chem.*, **70**, 469 (1958); S. Herzog and H. Zuhlke, *Z. Chem.*, **6**, 434 (1966).

[2] S. Herzog, *Naturwiss.*, **43**, 35 (1956); S. Herzog and U. Grimm, *Z. Chem.*, **6**, 380 (1966).

[3] S. Herzog and M. Schmidt, *ibid.*, **3**, 392 (1963); **2**, 24 (1962).

[4] a) S. Herzog, *Z. Anorg. Allg. Chem.*, **267**, 337 (1952); b) S. Herzog, U. Grimm, and W. Waicenbauer, *Z. Chem.*, **7**, 355 (1967).

[5] S. Herzog. R. Klausch, and J. Lautos, *ibid.*, **4**, 150 (1964); G. M. Waind and B. Martin, *J. Inorg. Nucl. Chem.*, **8**, 551 (1958).

[6] S. Herzog and H. Praekel, *Z. Chem.*, **5**, 469 (1965).

[7] S. Herzog, *J. Inorg. Nucl. Chem.*, **8**, 557 (1958); *Z. Chem.*, **2**, 225, 208 (1962).

[8] S. Herzog, G. Byhan, and P. Wulfert, *ibid.*, **1**, 370 (1961).

[9] F. S. Hall and W. L. Reynolds, *Inorg. Chem.*, **5**, 931 (1966).

[10] C. Mahon and W. L. Reynolds, *ibid.*, **6**, 1927 (1967).

[11] E. König, *Z. Naturforsch.*, **19a**, 1139 (1964).

[12] The tris-(2,2′-bipyridyl) complex is abbreviated to [Me(bip)$_3$]$^Q$, where Me=metal and $Q$ is the charge on the complex.

[13] The ligand-to-metal $\pi$-electron transfer is not taken into account in the present treatment. Therefore, $N_\pi$ may be considered as the number of metal $3d\pi$ electrons when there is no $\pi$-electron transfer from the metal to ligands.

Table 1. $[Me(bip)_3]^Q$ Complexs in various oxidation states[a,b)]

| $Q$ | $N$[c)] | | | | | | |
|---|---|---|---|---|---|---|---|
| | 15 | 16 | 17 | 18 | 19 | 20 | 21 |
| −2 | | | | Ti<br>0 | | Cr<br>2 | |
| −1 | | | Ti<br>1 | V<br>0 | Cr<br>1 | Mn<br>3 | Fe<br>p |
| 0 | Sc<br>1 | Ti<br>0 | V<br>1 | Cr<br>0 | Mn<br>3 | Fe<br>p | Co<br>1 |
| 1 | | V<br>2 | Cr<br>1 | | | Co | |
| 2 | V<br>3 | Cr<br>2 | Mn<br>5 | Fe<br>0 | Co<br>4 | Ni<br>2 | |
| 3 | Cr<br>3 | Mn | Fe<br>1 | Co<br>0 | | | |

a) The synthesis and magnetic moment are described in Refs. 1—10.

b) The number in each site indicates the number of unpaired electrons deduced from the observed magnetic moment. The notation "p" denotes that the complex is paramagnetic but its magnetic moment has not been measured.

c) $N=N_\pi+N_\sigma$, where $N_\pi$ is the total number of electrons in the $3d\pi$ and ligand antibonding $\pi$-orbitals and $N_\sigma$ is the total number of electrons in the metal $\sigma$ ($3d\sigma$, $4s$, $4p\sigma$) and ligand $\sigma$ lone-pair orbitals

antibonding MO's, and $Q$, the charge of the complex as a whole.

The theoretical method is similar to that developed previously for the metal chelate compounds containing organic unsaturated molecules as ligands.[14–17)] It is based on the composite-system method in which the $\pi$-electron system of the complex is divided into the metal and three ligand molecules. Thereafter, the interaction among the four components is considered by the configuration interaction among the ground, locally-excited and charge-transfer (CT) configurations. The $\pi$-electron wavefunctions and energy integrals for the ligand molecule were obtained previously by use of the SCFMO-CI method considering the effect of electrostatic potential field caused by the metal ion.[15)] The metal-ligand resonance integral $\beta$ necessary for the configuration interaction calculations is determined by the equation

$$\beta = -S_{MN}(I_M+I_N)/2 \qquad (1)$$

where $I_M$ and $I_N$ are the ionization potentials of the metal $3d\pi$ AO and the nitrogen $2p\pi$ AO, respectively, and $S_{MN}$ is the overlap integral between these two AO's.

We assume that the complex has a $D_3$ symmetry as illustrated in Fig. 1. This geometrical configuration has been established for the ordinary tris-complexes[18,19)] and also for some complexes in lower oxidation states.[20)]

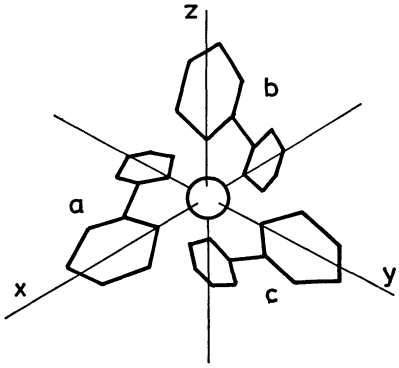

Fig. 1. The geometrical structure of tris-(2,2'-bipyridyl) complexes.

## The $\pi$-Electron Distribution

First of all, we examine the magnetic properties of a series of complexes of $N_\pi=4$ on the assumption that the excess electrons are localized completely on the metal $3d\pi$ AO's. The calculation has been made by taking the ground configuration and the CT configurations in which a metal $3d\pi$ electron is moved to $\varphi_7$, the lowest vacant MO of a ligand, and by constructing spin-orbitals.[15)] The result shows[21)] that the lowest state is commonly $^3E$ for $[Cr(bip)_3]^{2+}$, $[V(bip)_3]^+$ and $[Ti(dip)_3]^0$. The result is independent of the metal-to-

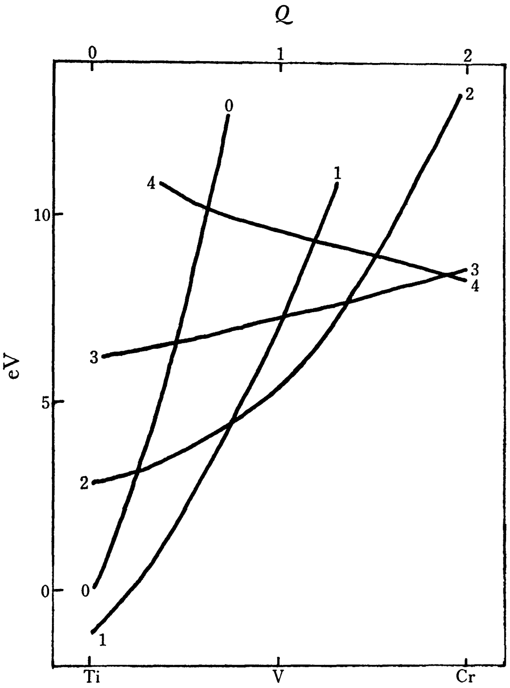

Fig. 2. Energies of the $N_\pi=4$ series of complexes with $N_{3d\sigma}=2$. The numbers in the figure represent the $N_{3d\pi}$ values.

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[14)] I. Hanazaki, F. Hanazaki, and S. Nagakura, *J. Chem. Phys.*, **50**, 265, 276 (1969).

[15)] I. Hanazaki and S. Nagakura, *Inorg. Chem.*, **8**, 648, 654 (1969).

[16)] T. Itoh, N. Tanaka, I. Hanazaki, and S. Nagakura, This Bulletin, **41**, 365 (1968).

[17)] T. Itoh, N. Tanaka, I. Hanazaki, and S. Nagakura, *ibid.*, **42**, 702 (1969).

[18)] D. H. Templeton, A. Zalkin, and T. Ueki, *Acta Cryst.*, **21A**, 154 (Suppl.) (1966).

[19)] B. Morosin and J. R. Brathovde, *Acta Cryst.*, **17**, 705 (1964); b) B. Morosin, *ibid.*, **19**, 131 (1965); c) U. M. Padmanabhan, *Proc. Indian Acad. Sci.*, **47a**, 329 (1958); d) R. B. Roof, Jr., *Acta Cryst.*, **9**, 781 (1956).

[20)] G. Albrecht, *Z. Chem.*, **3**, 182 (1963).

[21)] The numerical calculation was performed by use of OKITAC 5090H and FACOM 270-30 electronic computers at the Institute of Physical and Chemical Research.

ligand CT energy which is taken as a parameter. Thus the theory can not explain the observed magnetic susceptibilities which indicate spin-triplet and -singlet states for the chromium and titanium complexes, respectively.[22]

Similarly, for the $N_\pi=3$ series, the theory predicts the $^4A_2$ ground state commonly for $[V(bip)_3]^{2+}$, $[Ti(bip)_3]^+$ and $[Sc(bip)_3]^0$, whereas the experimental results indicate quartet and doublet states for the ground states of the vanadium and scandium complexes, respectively[8,23] Hence, the assumption that the excess electrons are localized in the metal $3d\pi$ AO's seems inappropriate.

In connection with the above-mentioned discussion, we examine in detail the distribution of excess electrons for the isoelectronic series of $N_\pi=4$,5, and 8. Details of the calculation are summarized in the Appendix.

The calculated energies of various electron distributions for the $N_\pi=4$ series are shown in Fig. 2 for $N_{3d\sigma}=2$ as the function of $Q$[24]. Here $N_{3d\sigma}$ represents the number of electrons on the metal $3d\sigma$ AO's donated from $\chi_{N\sigma}$'s, the nitrogen lone pair AO's, through the $\sigma$-type dative bonds. Hence, each $\chi_{N\sigma}$ possesses $+N_{3d\sigma}/6$ positive hole. The figure does not show absolute values of energies, but relative ones taking the $N_{3d\pi}=4$ case as the standard. Here $N_{3d\pi}$ denotes the number electrons on the $3d\pi$ AO's; *i.e.*, $N_\pi-N_{3d\pi}$ electrons are on the ligand antibonding MO's. Although the estimated energy values are rough (probably with errors of a few eV's; see Appendix I for the detail), Fig. 2 clearly shows that most of the excess electrons are transferred to the ligand antibonding MO's for the lower $Q$ values and that they are gradually concentrated to the metal $3d\pi$ AO's as $Q$ increases. For instance, as shown in Fig. 2, three of the excess electrons in $[Ti(bip)_3]^0$ are in the ligand antibonding MO's so that this substance may be thought to be the complex of bipyridyl anion radicals with $Ti^{3+}[(3d\pi)^1]$. The net charge on the metal is $+1$ since $N_{3d\sigma}=2$. On the other hand, the excess electrons in the chromium complex are almost completely localized in the metal $3d\pi$ AO's so that it seems to be an ordinary complex of neutral bipyridyl molecules with $Cr^{2+}[(3d\pi)^4]$ ion, the net charge on the metal being 0 since $N_{3d\sigma}=2$. Similarly, $[V(bip)_3]^+$ can be regarded as the metal complex with a neutral bipyridyl molecule and the two anion radicals.

Similar results are obtained for the isoelectronic series of $N_\pi=5$ and 8. The former is illustrated in Fig. 3. In contrast to the other complexes of the $N_\pi=5$ series,[1,2,4a,25] $[Mn(bip)_3]^{2+}$ has a high spin ground state with five unpaired electrons, two of them occupying probably the $3d\sigma$ orbitals.[26] As can be seen in Fig. 3, the lowest energy for the low spin configuration is relatively higher for this complex than for the others. Hence, stabilization through the exchange interaction may predominate, making the high spin state lower than the low spin state with $N_\pi=5$.

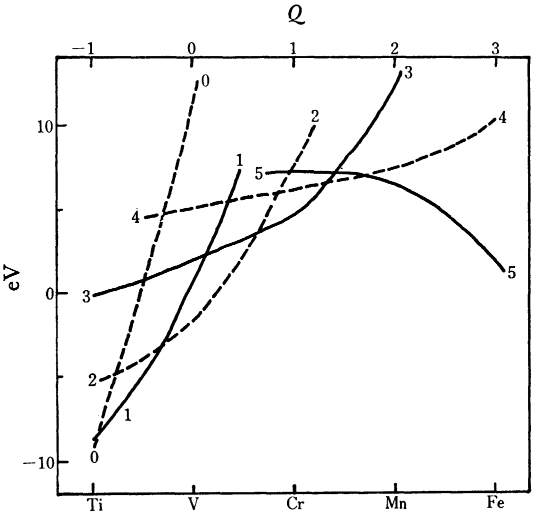

Fig. 3. Energies of the $N_\pi=5$ series of complexes with $N_{3d\sigma}=2$. The numbers in the figure represent the $N_{3d\pi}$ values.

In the case of the isoelectronic series of $[Fe(bip)_3]^0$ corresponding to $N_\pi=8$, if the excess electrons are localized on the metal, two of them should occupy the $3d\sigma$ AO's since the $3d\pi$ AO's can receive at most six electrons (case I). On the other hand, if we put all 8 electrons in the $\pi$-electron system, at least two of them should occupy the ligand antibonding MO's (case II). In the former case, the $6-N_{3d\pi}$ electrons occupy the antibonding $\pi$ MO's and $N_{3d\sigma}=2+n$, where $n$ is the number of electrons transferred from $\chi_{N\sigma}$'s. In the latter case, the $8-N_{3d\pi}$ electrons are in the ligand antibonding MO's and $N_{3d\sigma}$ is just the electron number transferred from $\chi_{N\sigma}$'s. At the present stage, we can not conclude which case takes place actually for $[Fe(bip)_3]^0$ since we can not know the relative energies among the states with different $N_{3d\sigma}$ values. This problem is discussed later.

## The Nature of the Ground State

Now we examine the nature of the ground states of the complexes in more detail on the basis of electron distribution. In the following calculation, the exchange interaction between $3d\pi$ AO's and the interaction with the lowest CT configurations are taken into account strictly.

$N_\pi=4$ *Series*. Assuming $N_{3d\sigma}=2$, the lowest enregy (ground) configuration of $[Ti(bip)_3]^0$ is that with $N_{3d\pi}=1$ as shown in Fig. 2. The second lowest is that with $N_{3d\pi}=0$. The configuration-interaction calculation is performed by considering eight triplet and six singlet ground configutations with $N_{3d\pi}=1$ and four triplet and three singlet CT configurations with

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[22] A. Earnshow, L. F. Larkworthy, K. C. Patel, K. S. Patel, R. C. Carlin, and E. G. Terezakis, *J. Chem. Soc.*, **A**, **1966**, 511.

[23] N. Elliott, *J. Chem. Phys.*, **46**, 1006 (1967).

[24] We do not treat explicitly the $\sigma$-electron system. However, the previous study[15] on $[Fe(bip)_3]^{2+}$ indicates that the $N_{3d\sigma}$ value of $\sim 2$ is appropriate for explaining the observed electronic absorption spectrum. For instance, the lowest configuration of $[Ti(bip)_3]^0$ is that with $N_{3d\pi}=2$ if we assume $N_{3d\sigma}=0$. This indicates that the net charge on the metal is $+2$. By an analogy with $[Fe(bip)_3]^{2+}$, at least two electrons should be transferred from $\chi_{N\sigma}$ to the $3d\sigma$ AO's. From this point of view, we adopt tentatively $N_{3d\sigma}=2$.

[25] B. N. Figgis, J. Lewis, F. E. Mabbs, and G. A. Webb, *J. Chem. Soc.* **A**, **1966**, 422.

[26] F. H. Burstull and R. S. Nyholm, *J. Chem. Soc.*, **1952**, 3570.

$N_{3d\pi}=0$. The energies of all the ground configurations which are equal to one another are taken as reference. The energies for all the CT configurations are commonly equal to $E_{\mathrm{CT}}$, the CT energy from the $3d\pi$ AO to $\varphi_7$, and are taken as a parameter. All the off-diagonal matrix elements are determined by the quantity $B=C_{7\mathrm{N}}\beta_{\mathrm{MN}}$. The core resonance integral $\beta_{\mathrm{MN}}$ is given by the aid of Eq. (1) to be $-1.87$ eV by assuming the electron configuration of $[(3d\pi)^1(3d\sigma)^2]$ for $\mathrm{Ti}^+$. $C_{\mathrm{MN}}$ is the coefficient of the $2p\pi$ AO of nitrogen in $\varphi_7$ and is determined to be $-0.3886$ by the previous calculation.[15,27]

The lowest state is shown in Fig. 4a for each spin and symmetry species of $[\mathrm{Ti(bip)_3}]^0$. The ground state is $^1A_1$, being about 0.1 eV lower than the second lowest state, $^3E$, within the reasonable range of $E_{\mathrm{CT}}$. This result can explain the observed magnetic susceptibility.[1]

By taking three triplet and six singlet ground configurations with $N_{3d\pi}=4$ and twenty seven triplet and twenty four singlet CT configurations with $N_{3d\pi}=3$, a similar calculation has been made for $[\mathrm{Cr(bip)_3}]^{2+}$. The oxidation state of the metal is assumed to be $\mathrm{Cr}^0[(3d\pi)^4(3d\sigma)^2]$ and $\beta$ is estimated to be $-1.26$ eV. In addition, a new quantity $K$, the exchange integral between the two $3d\pi$ AO's, appears in the matrix elements[28] and is estimated to be 0.41 eV. The theoretical result predicts that the ground state $^3E$ is lower by ~1 eV than the second lowest one. This is coincident with the observation.[22]

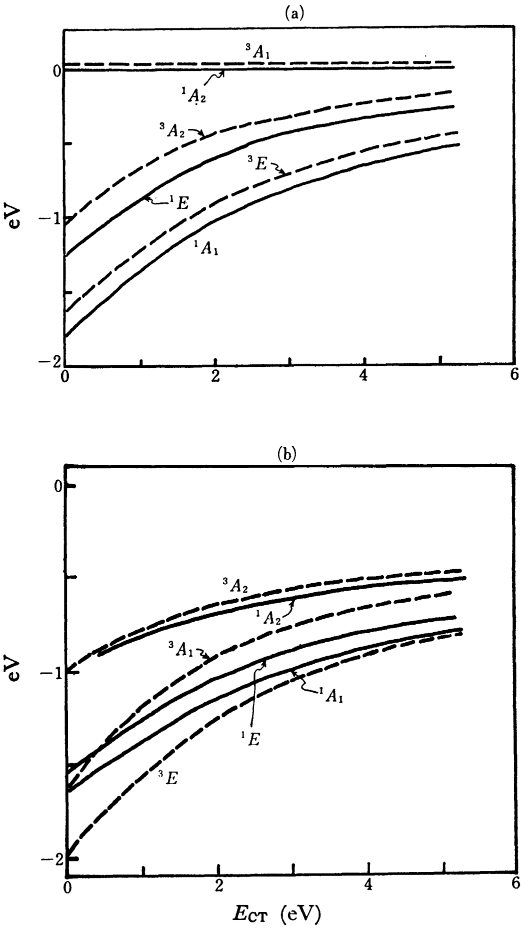

Fig. 4. Lower electronic states of the $N_\pi=4$ series of complexes. (a) $[\mathrm{Ti(bip)_3}]^0$ and (b) $[\mathrm{V(bip)_3}]^+$.

The ground state of $[\mathrm{V(bip)_3}]^+$ is calculated by considering the fifty one ground and forty five CT configurations for $N_{3d\pi}=2$ and 3, respectively. Assuming the electron configuration of $[(3d\pi)^2(3d\sigma)^2]$ for $\mathrm{V}^+$, we estimate $\beta$ and $K$ to be $-1.63$ and 0.513 eV, respectively. The lowest state is $^3E$, as is shown in Fig. 4b. Perthel[29] obtained the effective magnetic moment of 2.80 Bohr magneton for $\mathrm{V(bip)_3I\cdot(1/2)py}$, where py=pyridine. This value is close to that due to two unpaired electron spins, indicating the triplet ground state. On the other hand, König *et al.* could not observed the ESR signal of this substance in solution.[30,31] The reason why the ESR signal can not be observe at room temperature may probably be due to the fact that the orbitally degenerate ground state $^3E$ causes a large anisotropy in the $g$ value and the hyperfine splitting, giving rise to a fairly short relaxation time.[32]

$N_\pi=5$ *Series*. A similar calculation has been made for $[\mathrm{Ti(bip)_3}]^-$ by taking the ground and CT

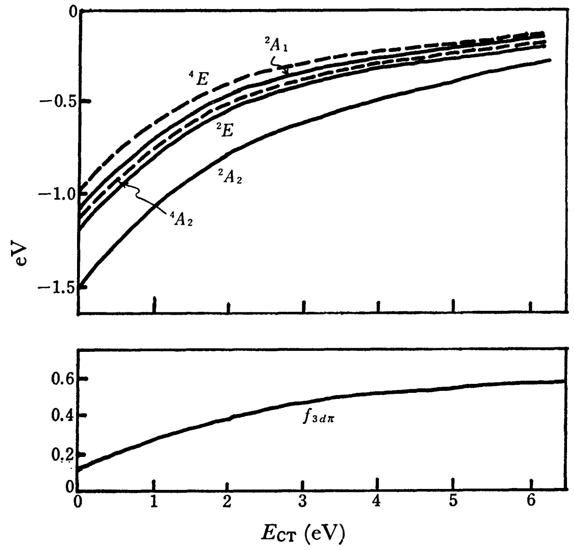

Fig. 5. Lower electronic states and spin densities on the $3d\pi$ AO's for $[\mathrm{V(bip)_3}]^0$.

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[27] This is the value determined for the free bipyridyl molecule.[15] It varies with the change in the electron distribution, but the effect is not large: for instance, $C_{7\mathrm{N}}=-0.3185$ if the potential field of the dipositive metal ion is taken into account.[15] The change in the $\beta$ value is also not large because of the mutual cancellation of the changes in $S_{\mathrm{MN}}$ and $I_{\mathrm{Me}}$; for instance, $\beta=-1.69$ eV if we assume $\mathrm{Ti}^0[(3d\pi)^4]$.

28) The $E_{\mathrm{CT}}$ value contains only the averaged spin interaction as is mentioned above. The $3d\pi$ exchange intergral $K$ brings about the actual spin interaction in a rigorous manner.

29) R. Perthel, *Z. Phys. Chem.*, **211**, 74 (1959).

30) E. König, H. Fischer, and S. Herzog, *Z. Naturforsch.*, **18b**, 432 (1963).

31) S. Herzog, *Z. anorg. allg. Chem.*, **294**, 155 (1958).

32) König *et al.* suggested that the spin-orbit interaction gives a singlet ground state on the assumption that the excess electrons are localized on the metal. Hence, the ESR signal can not be observed if the substance is completely in the singlet ground state. This may hold as very low temperatures but not at room temperature. For, if the lowest state is singlet as they pointed out, a triplet state lies a little higher. The splitting is probably comparable to or smaller than the thermal energy at room temperature.

configurations with $N_{3d\pi}=0$ and 1, respectively. The result shows that the lowest state is $^2A_2$, being lower by about 0.3 eV than the second lowest one, $^2E$. The $[\mathrm{V(bip)_3}]^0$ complex is calculated to be also in the $^2A_2$ ground state by considering the ground and CT configurations with $N_{3d\pi}=2$ and 1, respectively. By assuming the electron configuration of $[(3d\pi)^2(3d\sigma)^2]$ for $\mathrm{V}^+$, $\beta$ and $K$ are estimated to be $-1.50$ and 0.51 eV, respectively. The $[\mathrm{Cr(bip)_3}]^+$ complex is shown to be in a $^2A_1$ ground state by the calculation taking into account the ground and CT configurations with $N_{3d\pi}=$ 3 and 4, respectively. The electron configuration of $\mathrm{Cr}^+$ is assumed to be $[(3d\pi)^3(3d\sigma)^2]$ and the $\beta$ and $K$ values are evaluated to be $-1.36$ and 0.58 eV, respectively. All these results can explain the observed magnetic properties[1,2,4a] which indicate commonly the doublet ground state for the three substances. The lowest state for each spin and symmetry species is shown for the vanadium complex in Fig. 5.

## Analysis of the ESR Data for the $N\pi=5$ Series

Let us examine the ESR data observed by König[11] on the basis of our theoretical results. The bonding and antibonding MO's constructed from the 4*s* AO ($\chi_{4s}$) and the ligand $\sigma$ AO's can be written as follows:[33]

$$\varphi = C_1\chi_{4s} + C_2\sum l \tag{2}$$

$$\varphi^* = C_1'\chi_{4s} - C_2'\sum l, \tag{3}$$

where $\sum l$ is the symmetric linear combination of the nitrogen $\sigma$ lone-pair AO's. The hyperfine coupling constant $A_{\mathrm{Me}}$ due to the metal nucleus can be represented approximately as

$$A_{\mathrm{Me}} = A_{\mathrm{Me}}^p + A_{4s}, \tag{4}$$

where

$$A_{\mathrm{Me}}^p = [A_0^p + (\rho_{4s}^0/2)A_{4s}^p]f_{3d\pi} \tag{5}$$

and

$$A_{4s} = A_{4s}^0 f_{4s}. \tag{6}$$

Here $A_0^p$ represents the hyperfine interaction due to the spin polarization of 1*s*, 2*s*, and 3*s* electrons produced by an unpaired electron on the $3d\pi$ AO's. $A_{4s}^p$ is a similar constant for a pair of 4*s* electrons. $A_{4s}^0$ represents the hyperfine interaction caused by an unpaired electron on $\chi_{4s}$. The quantities $f_{3d\pi}$ and $f_{4s}$ represent the spin densities on the $3d\pi$ AO's and $\chi_{4s}$, respectively. The latter represents only the electron spin transferred from the $3d\pi$ AO's; that is, it does not include the 4*s* spin produced by exchange polarization.[34] The quantity $\rho_{4s}^0$ is written approximately as[35]

$$\rho_{4s}^0 = 2C_1^2 \tag{7}$$

Similarly, the hyperfine coupling constant due to the nitrogen nucleus can be written as

$$A_{\mathrm{N}} = A_{\mathrm{N}}^p + A_{2s} \tag{8}$$

where

$$A_{\mathrm{N}}^p = A_{\mathrm{NO}}^p f_{\mathrm{N}\pi} \tag{9}$$

and

$$A_{2s} = A_{2s}^0 f_{2s}^{\mathrm{N}} \tag{10}$$

$A_{\mathrm{NO}}^{\mathrm{p}}$ represents the hyperfine coupling due to the spin polarization of nitrogen 1*s* and 2*s* electrons caused by an unpaired electron on the $2p\pi$ AO. $A_{2s}^0$ represents the hyperfine coupling due to a spin on the 2*s* AO transferred from the metal $3d\pi$ AO's. The quantities $f_{\mathrm{N}\pi}$ and $f_{2s}^{\mathrm{N}}$ are the spin densities on the nitrogen $2p\pi$ and 2*s* AO's respectively. The latter does not contain the electron spin induced through spin polarization.

By a combination of the above-mentioned relations with the expressions for spin densities given in Appendix II and with the observed coupling constants $|A_{\mathrm{Me}}|=83.5$ and $|A_{\mathrm{N}}|=2.3$ Gauss,[11] we can calculate the spin and electron densities in $[\mathrm{V(bip)_3}]^0$ for a given value of $E_{\mathrm{CT}}$.[36] The results are summarized in Table 2.

We can obtain solutions only for positive $A_{\mathrm{Me}}$ and $A_{\mathrm{N}}$.

TABLE 2. RESULTS OF ANALYSIS OF ESR DATA FOR $[\mathrm{V(bip)_3}]^0$ AND $[\mathrm{Cr(bip)_3}]^+$ [a]

| | $[\mathrm{V(bip)_3}]^0$ | | $[\mathrm{Cr(bip)_3}]^+$ | |
|---|---|---|---|---|
| | $E_{\mathrm{CT}}=$ 0(eV) | $E_{\mathrm{CT}}=$ 5(eV) | $E_{\mathrm{CT}}=$ 0(eV) | $E_{\mathrm{CT}}=$ 1.3(eV) |
| $f_{4s}$ | 0.11 | 0.16 | 0.14 | 0.15 |
| $f_{3d\pi}$ | 0.19 | 0.63 | 1.61 | 1.69 |
| $f_{\mathrm{L}\pi}$ | 0.85 | 0.41 | −0.56 | −0.64 |
| $f_{2s}^N$ | 0.0057 | 0.0049 | 0.0046 | 0.0045 |
| $f_{\mathrm{N}\pi}$ | 0.033 | 0.016 | −0.022 | −0.025 |
| $\rho_{3d\pi}$ | 1.49 | 1.93 | 3.51 | 3.29 |
| $\rho_{4s}^{\mathrm{b}}$ | 0.93 | 0.15 | 0.08 | 0.00 |
| $\rho_{4s}^{\mathrm{a}}$ | 0.086 | 0.99 | 0.23 | 0.17 |
| $A_0^P f_{3d\pi}$ | −20.2 | −67.3 | 38.3 | 40.2 |
| $A_{4s}^P(\rho_{4s}^0/2)f_{3d\pi}$ | 4.6 | 0.6 | −0.1 | 0.0 |
| $A_{4s}$ | 99.1 | 150.1 | −60.3 | −62.6 |
| $A_{\mathrm{N}}^P$ | −0.8 | −0.4 | 0.5 | 0.6 |
| $A_{2s}$ | 3.1 | 2.7 | 2.5 | 2.5 |

a) The quantities in the first column are defined in the text and Appendix. The coupling constants are all given in the Gauss unit.

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[33] The following orthonormality conditions hold;

$$C_1^2 + C_2^2 + 2C_1C_2S = 1,$$
$$C_1'^2 + C_2'^2 - 2C_1'C_2'S = 1$$

and

$$C_1C_1' - C_2C_2' - (C_1C_2' - C_1'C_2)S = 0,$$

where $S$ is the overlap integral between $\chi_{4s}$ and $\sum l$, and is calculated to be 0.685 by use of the Slater AO for the nitrogen and four-terms function for $\chi_{4s}$[J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962)].

[34] It is possible at least to a first-order approximation to divide the 4*s* spin density into $f_{4s}$ and the spin density produced by the spin polarization effect.

[35] The quantity $\rho_{4s}^0$ is the spin-paired electron density when we disregard the effect of the unpaired electrons of the $3d\pi$ AO's. We ignore the contribution to $\rho_{4s}^0$ from the antibonding MO $\varphi^*$. It is also to be noted that this quantity differs in the definition from the density $\rho_{4s}^b$ defined in Eq. (11). The former is the net atomic population whereas the latter is the gross population.

[36] The following values are adopted for the basic coupling constants (in Gauss);

$$A_0^p = -106.6, \qquad A_{4s}^p = 91.57,$$
$$A_{4s}^0 = 923.1, \qquad A_{\mathrm{NO}}^p = -25,$$
$$A_{2s}^0 = 546.1$$

The $A_{4s}^0$, $A_{\mathrm{NO}}^{\mathrm{P}}$ and $A_{2s}^0$ values are taken from Ref. 11. The others are newly estimated by extrapolations from the theoretical results of Watson and Freeman [*Phys. Rev.*, **123**, 2027 (1961)].

In this table, the 4*s* electron densities due to the electrons in $\varphi$ and $\varphi^*$ are defined as

$$\rho_{4s}^{b} = 2(C_1{}^2 + C_1C_2S) \tag{11}$$

and

$$\rho_{4s}^{a} = \gamma^2(C_1{}'^2 - C_1{}'C_2{}'S) \tag{12}$$

respectively, where $\gamma$ is defined by Eq. (A9) in Appendix. The spin and electron densities thus determined seem to be reasonable for the $E_{\mathrm{CT}}$ values of 0 to 5 eV.

As can be seen from Table 2, $A_{\mathrm{Me}}$ is determined predominantly by the spin density on the 4*s* AO. Spin polarization causes only a minor effect. $A_{\mathrm{N}}$ is determined by the spin density on the 2*s* AO which transferred from the $3d\pi$ AO's through the trigonal field mixing. The spin polarization caused by the odd electron on the nitrogen $2p\pi$ AO also brings about a minor effect.

A similar analysis can be applied to $[\mathrm{Cr(bip)_3}]^+$. By use of the value $S=0.736$ and of the observed coupling constants[11] $|A_{\mathrm{Me}}|=21.8$ and $|A_{\mathrm{N}}|=3.05$ Gauss, we can obtain the spin and electron distributions as functions of $E_{\mathrm{CT}}$. The solution can be obtained only for $A_{\mathrm{Me}}<0$ and $A_{\mathrm{N}}>0$ and $\mathrm{E_{CT}} \leq 1.3$ ev. The results of $[\mathrm{Cr(bip)_3}]^+$ are also summarized in Table 2, and show some new aspects differing from those of the vanadium complex. The spin density on the $3d\pi$ AO's amounts to 1.6 in line with the fact that the spin density on the ligand $\pi$-electron systems is negative. This may be a little striking but is not an unexpected result. It can also be seen that the contribution of the 4*s* AO to the dative bonding is smaller than that of the vanadium complex.

$[\mathrm{Ti(bip)_3}]^-$ gives no hyperfine structure.[11] This can be explained on the basis of the present theoretical result that the metal has almost no $3d\pi$ electron. The spin density $f_{2s}$ also vanishes since $f_{3d\pi} \simeq 0$. $A_{\mathrm{N}}^{p}$ is non-vanishing but is probably very small as is observed for the vanadium and chromium complexes. In fact, it should not exceed 1/3 of the nitrogen hyperfine coupling constant of the bipyridyl anion radical,[37–39] since an unpaired electron is distributed on these ligand molecules. Therefore, it seems to be reasonable that the titanium complex exhibits no hyperfine structure.[40]

## Electronic Absorption Spectra

Few experimental studies on electronic absorption spectra of metal complexes in lower oxidation state have been made, except for those $[\mathrm{Fe(bip)_3}]^0$ and $[\mathrm{Fe(bip)_3}]^-$ reported by Reynolds and co-workers.[9,10] Recently, however, Torii, Kobayashi, and their co-workers studied the electronic absorption spectra of a number of complexes in low oxidation states.[41,42] König and Herzog have also studied the electronic absorption spectra of the titanium, vanadium, and chromium complexes in various oxidation states.[43]

As was already mentioned, some ligands of the lower oxidation state complexes can be seen as the bipyridyl anion radicals or its dinegative ions. From this point of view, the $\pi$-electron structures of the anion radical and the dinegative ion of 2,2′-bipyridyl are examined theoretically in addition to that of the neutral bipyridyl studied previously.[15] The $\pi$-electron structure of the anion radical in the cis form was calculated by the SCFMO-CI method for the open shell system,[44] by taking a hundred singly and doubly excited configurations in the configuration interaction calculation.[45] The results are summarized in Table 3, showing a fairly good agreement with the observation for Na(bip) (sodium bipyridyl) in tetrahydrofuran.[10,39]

Table 3. Lower excited states of 2,2′-bipyridyl anion radical

| | Calculated | | | Observed[a] | |
|---|---|---|---|---|---|
| | Transition energy (kK) | Oscillator strength | Symmetry[b] | Transition energy (kK) | Molar extinction coefficient |
| $V_1$ | 5.92 | 0.047 | L | 10.6<br>11.8<br>13.1 | 1300<br>1400<br>1100 |
| $V_2$ | 8.20 | 0.002 | S | | |
| $V_3$ | 16.55 | 0.189 | L | 17.8<br>18.6 | 6600<br>6300 |
| $V_4$ | 24.98 | 0.000 | S | | |
| $V_5$ | 26.70 | 0.085 | L | 24.2 | shoulder |
| $V_6$ | 30.47 | 0.213 | L | 25.8 | 31600 |
| $V_7$ | 33.36 | 0.022 | S | | |
| $V_8$ | 37.82 | 0.020 | L | | |
| $V_9$ | 37.88 | 0.023 | S | | |
| $V_{10}$ | 39.25 | 0.018 | L | | |
| $V_{11}$ | 39.93 | 0.060 | S | | |
| $V_{12}$ | 42.80 | 0.071 | L | 35 | shoulder? |
| $V_{13}$ | 43.74 | 0.165 | S | 37.5 | 9400 |
| $V_{14}$ | 47.43 | 0.027 | S | | |
| $V_{15}$ | 48.05 | 0.063 | L | | |
| $V_{16}$ | 48.86 | 0.001 | S | | |
| $V_{17}$ | 49.90 | 0.055 | L | | |

a) Na(bip) in tetrahydrofuran.[39]
b) L and S denote the long- and short-axes polarized transitions, respectively.

The $\pi$-electron structure of the 2,2′-bipyridyl dinegative ion in the cis form was also calculated by the Pariser-Parr-Pople SCFMO-CI method, considering the electrostatic potential field caused by the metal charge (the metal charge was assumed to be +2).[14,15] The

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[37] E. König and H. Fischer, *Z. Naturforsch.*, **17a**, 1063 (1962).

[38] J. dos Santos Veiga, W. L. Reynolds, and J. R. Bolton, *J. Chem. Phys.*, **44**, 2214 (1966).

[39] Y. Torii, T. Yazaki, Y. Kaizu, S. Murasato, and H. Kobayashi, This Bulletin, **42**, 2264 (1969).

[40] König attributed this to the smaller natural abundance of the titanium isotopes with nuclear spins. However, this seems to be unreasonable since the natural abundances do not differ so much between the titanium and chromium isotopes, the hyperfine structure due to the metal being observed for the latter. It is also not reasonable to attribute it to the short relaxation time since the ground state of $[\mathrm{Ti(bip)_3}]^-$ is not degenerate and the separation from the lowest excited state is almost the same as that of $[\mathrm{V(bip)_3}]^0$.

[41] Y. Kaizu, T. Yazaki, Y. Torii, and H. Kobayashi, This Bulletin, **43**, 2068 (1970).

[42] H. Kobayashi and Y. Torii, private communication.

[43] E. König and S. Herzog, *J. Inorg. Nucl. Chem.*, **32**, 585, 601, 613 (1970).

[44] H. C. Logguet-Higgins and J. A. Pople, *Proc. Phys. Soc.*, **A68**, 591 (1955).

[45] This calculation has been performed by use of the program written by Dr. S. Iwata and Mr. H. Katsumata.

Table 4. Lower excited states of 2,2′-bipyridyl dinegative ion

| Calculated[a)] | | Observed[b)] transition energy (kK) |
|---|---|---|
| Transition energy (kK) | Oscillator strength | |
| 17.40 | 0.115 | 15—17 |
| 20.72 | 0.531 | |
| 21.26 | 0.010 | 26.2 |
| 24.35 | 0.049 | |
| 33.79 | 0.546 | |
| 37.79 | 0.205 | |
| 43.42 | 0.008 | |
| 45.38 | 0.078 | |
| 48.67 | 0.010 | |
| 51.27 | 0.247 | |

a) The configuration interaction was considered among the 22 singly excited configurations for the cis form ion.

b) $Li_2$(bip) in tetrahydrofuran.[42)] The absolute intensities are uncertain but the peak molar extinction coefficient of the first band, with a vibrational structure, is about 1/10 of that of the second band.

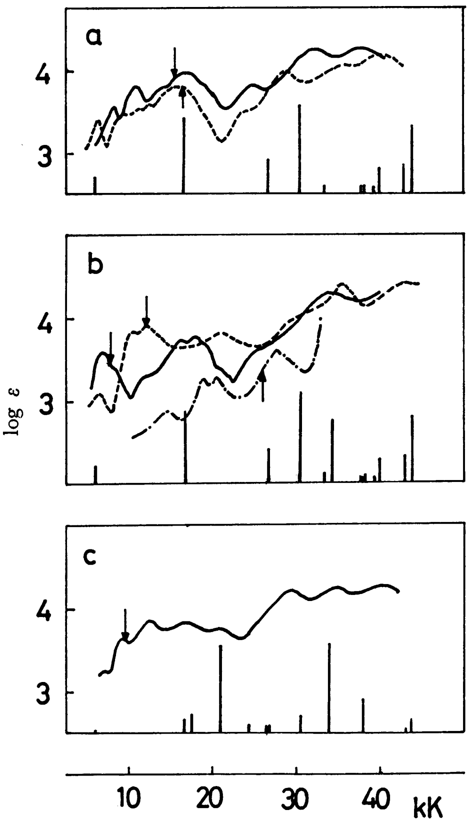

Fig. 6. The electronic absorption spectra of some complexes in lower oxidation states. The theoretical prediction is shown by the vertical lines. The length indicates the oscillator strength value in an arbitrary scale. The band position predicted for the CT transition is indicated by an arrow for each substance. (a) —$[V(bip)_3]^0$ and ---$[Ti(bip)_3]^0$. The theoretical result is that of $bip^-$. (b) —$[Cr(bip)_3]^+$, ---$[V(bip)_3]^+$ and -·-$[Fe(bip)_3]^0$. The theoretical result is the weighted average of the calculations for $bip^0$ and $bip^-$. (c) $[Ti(bip)_3]^-$. The theoretical result is the 1:2 average of the calculations for $bip^-$ and $bip^{2-}$.

result is shown in Table 4, together with the transition energies measured with $Li_2$(bip) (dilithium bipyridyl) in tetrahydrofuran[42)]

The electronic absorption spectra[41,43)] of $[V(bip)_3]^0$ and $[Ti(bip)_3]^0$, which can be considered as the metal complex with three $bip^-$, are shown in Fig. 6a together with the theoretical result for $bip^-$. The position of the lowest CT transition band predicted theoretically is indicated by an arrow. In the present theoretical study, we ignore the dipole interaction between the $\pi$–$\pi^*$ transitions in different ligands and also the interaction of CT transition with the ligand $\pi$-$\pi^*$ transition. This means that we disregard the splitting of each band due to the above-mentioned interactions. Therefore we confine ourselves to a qualitative comparison of the theoretical and observed results.

As is shown in Fig. 6a, the electronic absorption spectra of $[V(bip)_3]^0$ and $[Ti(bip)_3]^0$ are at least qualitatively explained by the overlapping of the $\pi$–$\pi^*$ transition bands of $bip^-$ and the metal-ligand $\pi$-electron transfer ones. The observed bands in the energy region lower than 10 kK are ascribed to the ligand $\pi$–$\pi^*$ transitions (to $V_1$ and $V_2$ of Table 3). The bands in 10—20kK region can be due to the mixture of the CT transition and the ligand $\pi$–$\pi^*$ transition to $V_3$. The 26 kK and 30 kK bands of titanium and vanadium complexes, respectively, are due to the ligand $\pi$–$\pi^*$ transition to $V_0$ corresponding to the strong 26 kK band observed for Na(dip).[39)]

In Fig. 6b are shown the electronic absorption spectra[30,41–43)] of $[Cr(bip)_3]^+$, $[V(bip)_3]^+$,and $[Fe(bip)_3]^0$ which can approximately be considered to be the metal complex with a $dip^0$ and two $dip^-$. The corresponding theoretical prediction shown in Fig. 6b is the weighted average of the calculated band intensites for $dip^0$ and $dip^-$. The absorption bands of $[V(bip)_3]^+$ are well interpreted as the 1:2 mixture of the $bip^0$ and $bip^-$ spectra except for the 10—12 kK band which can be ascribed to the metal-ligand CT transition on the basis of the present theoretical study. In the spectrum of $[Cr(bip)_3]^+$, the 6—8 kK band may be due to two transitions; the CT transition from $\varphi_7$ of $bip^-$ to the $3d\pi$ AO's and the lowest $\pi$–$\pi^*$ transition of $bip^-$. The other transitions can be well interpreted as the overlapping of the local excitations in $bip^0$ and $bip^-$.

Concerning $[Fe(bip)_3]^0$ there are two possibilities, cases I and II, as already mentioned. If we assume $N_{3d\sigma}=2$, both cases give the ground state in which two excess electrons are located on the ligands and the CT state about 3 eV about it. The CT directions differ for cases I and II; namely, from $\varphi_7$ to $3d\pi$ for the former and from $3d\pi$ to $\varphi_7$ for the latter. The absorption spectra of this complex and free $bip^-$ are somewhat similar to each other, but differ significantly in their relative intensity ratios. This indicates a fairly strong perturbation affecting the $bip^-$ electronic structure. In case II, the CT from $3d\pi$ to $\varphi_7$ can interact with the $\pi$–$\pi^*$ transitions in $bip^0$ but not with those in $bip^-$. On the other hand, the CT transition predicted for case I can interact only with the $\pi$–$\pi^*$ transitions of $bip^-$. Hence, the latter case seems to be more suitable to explain the relative intensities of the bands below 30 kK. It is difficult to determine the $bip^-/bip^0$ ratio in the complex because of a strong disturbance by the absorption band of the dissociated free bip in the region above 30 kK. The absorption spectrum of the complex strongly perturbed by the CT interaction, however, may be explained by the overlapping of the absorption spectra of $\mathrm{bip}^-$ and $\mathrm{bip}^0$ in a 2:1 ratio. This is because, according to a rough estimate of the ground state energy, the electron configuration in this ratio is most stable.

The absorption spectrum[42] of $[\mathrm{Ti(bip)_3}]^-$ is shown in Fig. 6c, together with the theoretical prediction of the weighted average of the calculated intensities for $\mathrm{bip}^-$ and $\mathrm{bip}^{2-}$ in the 1:2 ratio. The correspondence seems to be fairly good if the 12 kK band is ascribed to the transition to the CT state which is predicted to lie about 1 eV above the ground state.

## Discussion

The electron distribution of the ground state determined above indicates that excess electrons are localized on the metal for the complexes with a large $Q$ value and are gradually transferred to the ligand $\pi$-electron systems as $Q$ decreases. Hence, we can not distinguish the complexes in lower oxidation states clearly from those in normal oxidation states. Moreover, the term "oxidation state" should be considered as the charge on the complex as a whole and should not be directly related to the oxidation state of the metal ion only.

In this connection, it seems to be interesting to examine how many electrons move when an electron is added to the normal complex. For instance, adding an electron to the $\pi$-electron system of $[\mathrm{Cr(bip)_3}]^{2+}$ in which four $\pi$ electrons are localized on the metal, we find about two electrons in the ligand antibonding MO's; that is to say, the addition of an electron induces not only its delocalization to the ligands but also the transfer of another electron which is originally in the metal. A similar tendency can be found for the vanadium complex. Adding an electron to $[\mathrm{V(bip)_3}]^{2+}$ in which three electrons are localized in the metal, we find two electrons in the $3d\pi$ AO's and the other two in the ligands. Adding another electron, we find two electrons in the metal and the other three in the ligands. This general tendency can be understood as follows; an electron in $\varphi_7$ repels the $3d\pi$ electron resulting in the reduction of the metal ionization potential whereas it lifts the orbital energies of the ligands to reduce their electron affinities. The former effect is fairly larger since the metal-ligand average distance is shorter than the interligand average distance. Hence, the addition of an electron makes the transfer of metal $3d\pi$ electron easier. For lower $Q$ values, this tendency reaches a saturation since the metal ionization potential decreases rapidly with the decreasing net charge on the metal.

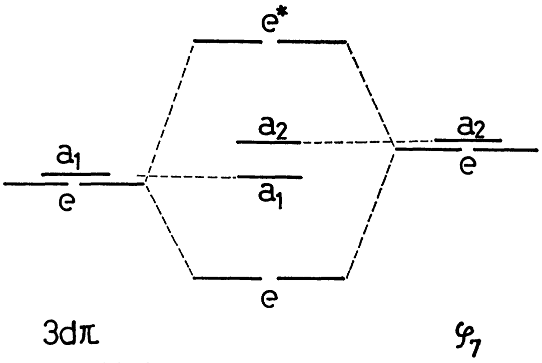

Fig. 7. The energy level diagram.

The magnetic behaviour of the ground state seems to be interpreted by the composite-system treatment adopted in the present work. The one-electron-orbital model adopted so far to the interpretation of the ESR result seems to be inappropriate for the low oxidation metal complexes under consideration. According to this model illustrated in Fig. 7, an unpaired electron of the $N_{3d\pi}=5$ complex should occupy the $a_1$ or $a_2$ orbital and should be localized completely on the metal or ligand, respectively. This is in serious disagreement with the present result which indicates an extensive delocalization of the unpaired electron both on the metal and ligands. The contradiction can be ascribed to the fact that the simple one-electron-orbital model completely ignores the strong exchange polarization of the $e$-orbital electrons due to the unpaired electron in the $a_1$ or $a_2$ orbital.

Tetrazakis and Carlin[46] explained the magnetism of $[\mathrm{Cr(bip)_3}]^{2+}$ on the basis of the theory[47] presented by Figgis *et al.*, giving the trigonal splitting $\Delta \sim 630\ \mathrm{cm}^{-1}$ ($^3A_2$ is lower) and the orbital delocalization factor $k \sim 0.6$. Although the $k$ value seems to be consistent with the present result in which the metal-ligand CT configurations lie very close to the ground configurations, the $\Delta$ value is in serious disagreement with ours: $\Delta \sim -10^4\ \mathrm{cm}^{-1}$ ($^3E$ is lower). Since $\varphi_7$ is symmetric with respect to the bipyridyl molecule, it can not interact with the $3d\pi$ orbitals, whereas the $e$-symmetry orbital can interact with them. Hence, the result of Figgis *et al.* that $\Delta$ is positive (that is, the $a_1$ orbital is lower) is incorrect.

Next, we examine the magnetic property of $[\mathrm{Fe(bip)_3}]^0$ qualitatively on the basis of Fig. 7. Although the one-electron-orbital model is inappropriate for quantitative treatment, it may be useful for the qualitative discussion of the spin state. By an analogy with the results for the $N_{3d\pi}=4$ and 5 series, the metal-ligand CT interaction is probably strong for this case with a low $Q$ value. Hence the $e^*$ orbital should lie far apart from the $a_1$ and $a_2$ orbitals, so that, in case II, the eight $\pi$ electrons occupy the $e$, $a_1$, and $a_2$ orbitals, resulting in a spin singlet ground state. This is in contradiction to the observation. On the other hand, in case I, the six $\pi$ electrons may occupy the $e$, $a_1$, and $a_2$ orbitals if the $3d\pi$ AO and ligand antibonding MO of the $a_1$ and $a_2$ symmetry, respectively, are close to each other. We have four unpaired electrons, two in the $a_1$ and $a_2$ orbitals and two in the $\sigma$ orbitals of the $e$ symmetry, with a spin quintet ground state. Thus examination of both the magnetism and the electronic absorption spectrum supports case I. Another supporting fact is that the substance readily decomposes to bipyridyl and iron on heating.[6] This can be understood as due to the weak $\sigma$-dative bonding caused by partial occupation of

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[46] E. G. Tetrazakis and R. L. Carlin, *Inorg. Chem.*, **6**, 2125 (1967).

[47] B. N. Figgis, J. Lewis, F. E. Mabbs, and G. A. Webb, *J. Chem. Soc.*, **A**, **1966**, 1411.

the $\sigma$-antibonding MO's.

[Mn(bip)$_3$]$^-$ which is isoelectronic with [Fe(bip)$_3$]$^0$ shows a magnetic moment of 3.71 Bohr magneton.[3] This can not be explained on the basis of the even number of unpaired electrons. The substance should be considered as a mixture of the spin quintet and triplet species. The situation can be understood by the energy level scheme shown in Fig. 7. If the $a_1$ and $a_2$ orbitals are close to each other as for the iron complex, we have four unpaired electrons, and thus a spin quintet ground state. If a stronger metal-ligand interaction makes the $a_1$ and $a_2$ orbitals split, all the $\pi$ electrons should be paired and we have the spin triplet ground state because of the unpaired electrons in the $\sigma$-antibonding orbitals. We have a mixture of the two species if the separation between the $a_1$ and $a_2$ orbitals is comparable with the exchange integral between the two $3d\pi$ AO's. The electron distribution in case II gives no reasonable explanation also for this complex.

[Cr(bip)$_3$]$^{2-}$ has two unpaired electrons.[4b] This is understood as predominance of the triplet state because of the large $a_1$–$a_2$ separation. Thus, for this isoelectronic series, the iron, manganese and chromium complexes, together with well-known [Ni(bip)$_3$]$^{2+}$, have two unpaired electrons in the $\sigma$-antibonding orbitals, in addition to those in the $\pi$-electron system.

The authors are deeply indebted to Prof. Hiroshi Kobayashi and Dr. Yasuo Torii of the Tokyo Institute of Technology for valuable discussion and for use of the spectral data before publication.

## Appendix I

Here we will show the method calculating the energies for various $\pi$-electron distributions given in Figs. 2 and 3. Let us take [Ti(bip)$_3$]$^0$, $N_\pi=4$, as an example.

If we take the energy of the electron configuration $N_{3d\pi}=4$ and $N_{3d\sigma}=0$ as a reference, the energy of the configuration $N_{3d\pi}=3$ and $N_{3d\sigma}=0$ is just the CT energy to remove an $3d\pi$ electron to the lowest vacant MO $\varphi_7$ of one of the ligands (say, ligand a);

$$E(3,\ 0) = I_{\mathrm{Me}} - A_{\mathrm{L}} - 3V_{\mathrm{MQ}} + 2V_{\mathrm{OQ}} - V_{\mathrm{MO}} \qquad \text{(A1)}$$

where the configurational energy is represented as $E(N_{3d\pi}, N_{3d\sigma})$. $I_{\mathrm{Me}}$ and $A_{\mathrm{L}}$ are the valence state ionization potentials corresponding to the ionization process Ti$^0$[$(3d\pi)^4$]$\rightarrow$Ti$^+$-[$(3d\pi)^3$] and the electron affinity of the ligand, respectively. $V_{\mathrm{MQ}}$, $V_{\mathrm{OQ}}$, and $V_{\mathrm{MO}}$ are, respectively, the electrostatic interaction energies between a $3d\pi$ electron and the formal charges due to $\pi$ electrons on each ligand, between an electron in $\varphi_7$ of a ligand and the formal charges on one of the other ligands, and between $3d\pi$ electron and an electron in $\varphi_7$ of a ligand. $I_{\mathrm{Me}}$ is estimated to be 3.01 eV from the observed atomic term values by averaging all spin interactions. By the aid of SCF calculation for the free 2,2′-bipyridyl molecule, the following results are obtained: $A_{\mathrm{L}}=0.02$,[48] $V_{\mathrm{MQ}}=1.00$, $V_{\mathrm{OQ}}=0.25$ and $V_{\mathrm{MO}}=4.98$ (all in eV), and, therefore, $E(3{,}0)=-4.51$ eV. $A_{\mathrm{L}}$ is evaluated from the calculated $\varphi_7$ orbital energy ($\varepsilon_7=-1.72$ eV) of the ligand by the following equation;[48]

$$A_{\mathrm{L}} = -\varepsilon_7 - 1.7 \qquad \text{(A2)}$$

Next, we evaluate the energy of the configuration $N_{3d\pi}=2$ and $N_{3d\sigma}=0$. By considering the process to remove an electron from the ligand antibonding MO of the configurations $N_{3d\pi}=2$ to the $3d\pi$ AO, we have

$$\begin{aligned} E(3,\ 0) = E(2,\ 0) + I_{\mathrm{L}} - A^{\pi}_{\mathrm{Me}}(2,\ 0) \\ - V_{\mathrm{OO}} + V_{\mathrm{MO}} + 3V_{\mathrm{MQ}} \end{aligned} \qquad \text{(A3)}$$

where $I_{\mathrm{L}}$ is the ionization potential necessary for removing a ligand antibonding-orbital electron, being equivalent to $A_{\mathrm{L}}$ defined above. In this case, $A_{\mathrm{L}}$ is evaluated to be 7.26 eV by Eq. (A2), since $\varepsilon_7$ is calculated to be $-8.955$ eV by the SCF MO calculation including the potential field caused by the metal charge (the net charge on the metal is $+2$ for $N_{3d\pi}=2$ and $N_{3d\sigma}=0$).[15] $A_{\mathrm{Me}}{}^{\pi}$ $(m,n)$ is the electron affinity of metal corresponding to the process Ti$^{Q}$[$(3d\pi)^m(3d\sigma)^n$]$\rightarrow$Ti$^{Q-1}$-[$(3d\pi)^{m+1}(3d\pi\sigma)^n$] where $Q=4-(m+n)$. $A_{\mathrm{Me}}(m,n)$ is also defined in a similar manner. $V_{00}$ is the interaction between electrons in the lowest vacant MO′s of different ligands and calculated to be 2.87 eV. $V_{\mathrm{MO}}$ and $V_{\mathrm{MQ}}$ have the same meanings as before and are calculated by use of the SCF MO′s obtained by taking into account the potential field of the metal ion. Hence,[49]

$$E(2,\ 0) = E(3,\ 0) - 6.21 = -\ 10.63\text{eV}. \qquad \text{(A4)}$$

The configuration $N_{3d\sigma}=2$ and $N_{3d\sigma}=1$ can be produced from $N_{3d\pi}=2$ and $N_{3d\pi}=0$ by removing an electron from one of the MO′s $\varphi_{\mathrm{N}\sigma}$ constructed from the $\sigma$-lone pair AO's of nitrogens to the metal $3d\pi$ AO′s.

$$\begin{aligned} E(2,\ 1) = E(2,\ 0) + I_\sigma - A^{\sigma}_{Me}(2.0) \\ + V_{\mathrm{SQ}} - 2V_{\mathrm{SO}} + V_{\mathrm{MS}} + 2V_{\mathrm{MO}} - 3V_{\mathrm{MQ}} \end{aligned} \qquad \text{(A5)}$$

where $I_\sigma$ is the ionization potential to remove an electron from $\varphi_{\mathrm{N}\sigma}$ and is taken to be 10.35 eV from the corresponding ionization potential of pyridine.[50] $A_{\mathrm{Me}}{}^{\sigma}(2{,}0)$ is estimated to be 3.04 eV. $V_{\mathrm{SQ}}$, $V_{\mathrm{SO}}$, and $V_{\mathrm{MS}}$ are the interaction of an electron in $\varphi_{\mathrm{N}\sigma}$ with the formal charge distributions in the $\pi$ electron systems of three ligands with an electron in $\varphi_7$ and with a $3d\pi$ electron, respectively. They are estimated to be $-8.35$, 4.41, and 8.46 eV, respectively, by use of the SCF MO obtained by taking into account the potential field of the metal ion.[15] The interatomic interaction within a ligand molecule is calculated by use of the Slater AO's, whereas the interactions between different ligands and between the metal and ligand are calculated by use of the point-charge approximation. By use of these quantities, $E(2{,}1)$ is evaluated to be $-2.17$ eV.

The configuration with $N_{3d\pi}=2$ and $N_{3d\sigma}=2$ is produced from that with $N_{3d\pi}=2$ and $N_{3a\sigma}=1$ by removing another electron from $\varphi_{\mathrm{N}\sigma}$ to $3d\sigma$ AO;

$$\begin{aligned} E(2,\ 2) = E(2,\ 1) + I_\sigma{}^{+} + V_{\mathrm{SQ}} - 2V_{\mathrm{SO}} - A^{\sigma}_{\mathrm{Me}}(2,\ 1) \\ - V_{\mathrm{MS}} + 2V_{\mathrm{MO}} - 3V_{\mathrm{MQ}} \end{aligned} \qquad \text{(A6)}$$

where $I\sigma^{+}$ is the second ionization potential of $\varphi_{\mathrm{N}\sigma}$ and estimated to be 15.87 eV correcting $I\sigma$ with respect to the electrostatic interaction between the nitrogen $\sigma$ lone-pair AO's. The other quantities have the same meanings as before, and are calculated by use of the SCF MO's obtained putting a

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[48] We employ the correction of 1.7 eV.[16,17]

[49] The energy $E(2{,}0)$ may be obtained by considering the process removing $3d\pi$ electron in the configuration $N_{3d\pi}=3$ to the ligand vacant MO. We employ here, however, the reverse CT process in order to utilize the previously obtained MO's for, ligand under the influence of dipositive metal ion.

[50] M. I. Al-Jaboury and D. W. Turner, *J. Chem. Soc.*, **1964**, 4438; E. Clementi, *J. Chem. Phys.*, **46**, 4731, 4737 (1967); J. L. Whitten *et al.*, *ibid.*, **48**, 953 (1968); J. Del Benne and H. H. Jaffe, *ibid.*, **48**, 1811 (1968); M. A. El-bayoumi and O. S. Khalil, *ibid.*, **47**, 4863 (1967).

positive charge on the metal and +1/6 hole on each nitrogen $\sigma$ AO. $E(2,2)$ is thus estimated to be 4.04 eV.

The estimated energy of each electron configuration should not be considered to be the energy of the actual state for the following reasons: (i) The energy change due to resonance interaction is not taken into account, (ii) the spin interaction is averaged out, and (iii) the stabilization due to electron rearrangement accompanied by electron transfer is not taken into account. Although the resonance and spin interactions are ignored in the estimation of electron distribution, they are taken into account in the calculation of the magnetic property of the ground state. Hence, we discuss here the third point. We evaluate the energy of the $N_{3d\pi}=3$ and $N_{3d\sigma}=0$ distribution to be 4.51 eV below the reference state with $N_{3d\pi}=4$. This is just the CT energy including no electron rearrangement effect. If we denote the stabilization due to the effect as $\Delta_1$ (taken as positive), the absolute energy should be $-4.51-\Delta_1$ as illustrated in Fig. 8a. Similarly, the CT energy from the $N_{3d\pi}=3$ system to the $N_{3d\pi}=2$ system is calculated to be $-3.62$ eV on the basis of the electron distribution of the $N_{3d\pi}=3$ system. If we put the rearrangement energy of the $N_{3d\pi}=2$ system as $\Delta_2$, the absolute energy of this system is $-(4.51+\Delta_1+3.62+\Delta_2)$. If we start from the $N_{3d\pi}=2$ system, we obtain the absolute energy of the $N_{3d\pi}=4$ system as $(6.12-\Delta_3+7.22-\Delta_4)$ above the former, as is illustrated in Fig. 8b. Since the relation

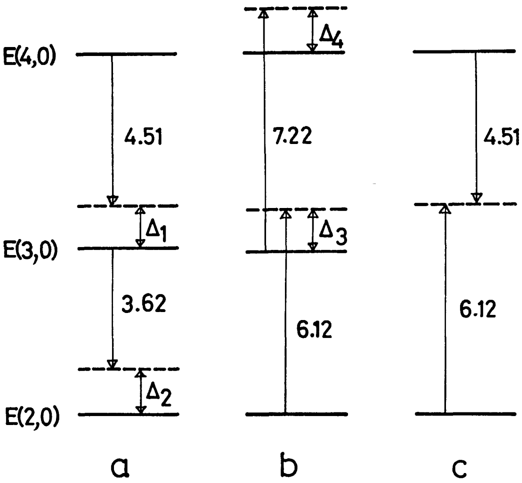

Fig. 8. The energy estimation for some electron distributions of $[\mathrm{Ti(bip)_3}]^0$.

$$(4.51+\Delta_1+3.62+\Delta_2) = (6.12-\Delta_3+7.22-\Delta_4)$$

should hold, we obtain

$$\Delta_1+\Delta_2+\Delta_3+\Delta_4 = 5.21 \text{ eV}.$$

Assuming $\Delta_1\simeq\Delta_2\simeq\Delta_3\simeq\Delta_4=\Delta$, the absolute value of the $N_{3d\pi}=2$ system is estimated to be $-4.51-3.62-2\Delta=-10.74$ eV. As illustrated in Fig. 8c, the corresponding energy can be evaluated by adding the energy of the $N_{3d\pi}=3$ distribution based on the $N_{3d\pi}=4$ to that based on the $N_{3d\pi}=2$. The sum $4.51+6.12=10.63$ eV, is very close to the estimated absolute energy given above. The energy of the $N_{3d\pi}=3$ system is obtained as $-4.51$ and $-7.22$ eV by calculations based on the distributions $N_{3d\pi}=4$ and 3, respectively. The absolute value can be estimated as $-4.51-\Delta=-5.8$ eV. Thus the electron rearrangement effect amounts to ±1.3 eV for this state.

## Appendix II

The ground state of $[\mathrm{V(bip)_3}]^0$ is represented by the wavefunction

$$\Psi(^2\mathrm{A}_2) = A_1\Psi_1 + A_2\Psi_2 + A_3\Psi_3 + B_1\Psi_1' + B_2\Psi_2' + B_3\Psi_3' \qquad \text{(A7)}$$

where $\Psi_1$, $\Psi_2$, and $\Psi_3$ are the configurational wavefunctions with $N_{3d\pi}=2$ and $\Psi_1'$, $\Psi_2'$ and $\Psi_3'$ are those of the CT configurations with $N_{3d\pi}=1$. The coefficients $A_i$'s and $B_i$'s have been determined by the calculation described in Appendix I.

Considering the mixing of the $3d\pi$ and $4s$ orbitals due to the trigonal field we have

$$\Psi'(^2\mathrm{A}_2) = \Psi(^2\mathrm{A}_2) - \gamma[A_1\Sigma_2 + (3)^{-1/2}A_2(\Sigma_1-(2)^{1/2}\Sigma_4) - (2/3)^{1/2}A_3(\Sigma_1-(2)^{1/2}\Sigma_3) \qquad \text{(A8)}$$

where $\Sigma_1$ to $\Sigma_4$ are the wavefunctions of the CT ($4s\rightarrow\varphi^*$) configurations belonging to the $^2A_2$ symmetry.(51) The coefficient $\gamma$ determines the extent of mixing and may be expressed as

$$\gamma = (C_1'/\Delta E)\langle\chi_{3d\pi}|\mathbf{V}_{tr}|\chi_{4s}\rangle \qquad \text{(A9)}$$

where $\Delta E$ is the energy of electron transfer from $3d\pi$ to $4s$ and $\mathbf{V}_{tr}$ is the trigonal electrostatic field.

By use of this wavefunction, the spin densities can be expressed by their definitions as follows.

$$\begin{aligned}
f_{4s} &= (2/3)\gamma^2C_1'^2(A_2^2+2A_3^2)\\
f_{3d\pi} &= (2/3)A_2^2 + (14/27)A_3^2 - (1/3)B_1^2 + B_2^2\\
&\quad - (1/3)B_3^2 + (2/3)\gamma^2(A_2^2+2A_3^2)\\
f_{2s} &= (1/27)\gamma^2C_2'^2(A_2^2+2A_3^2) \qquad \text{(A10)}\\
f_{\mathrm{L}\pi} &= A_1^2 + (1/3)A_2^2 + (13/27)A_3^2 + (4/3)(B_1^2+B_3^2)\\
&\quad + \gamma^2[A_1^2-(1/3)A_2^2-(2/3)A_3^2]\\
f_{\mathrm{N}\pi} &= (1/3)(C_{7\mathrm{N}})^2f_{\mathrm{L}\pi}
\end{aligned}$$

where $f_{\mathrm{L}\pi}$ represents the sum of the spin densities in the $\pi$-electron systems of three ligands.

The ground state wavefunction $\Psi$ for $[\mathrm{Cr(bip)_3}]^+$ can also be represented by Eq. (A7) except that the configurational wavefunctions $\Psi_1$ to $\Psi_3$ are those of $^2A_1$ with $N_{3d\pi}=3$ and $\Psi_1'$ to $\Psi_3'$ are those of $^2A_1$ with $N_{3d\pi}=4$. The interaction with the $4s$ AO can be written as

$$\Psi'(^2A_1) = \Psi(^2A_1) + (3)^{1/2}\gamma[A_1\Sigma_1'+A_2\Sigma_2'-A_3\Sigma_3'] \qquad \text{(A11)}$$

where $\Sigma_1'$ to $\Sigma_3'$ are the wavefunctions for the CT configurations corresponding to the electron transfer from the $3d\pi$ AO's to $\varphi^*$. The spin densities are expressed as

$$\begin{aligned}
f_{4s} &= (1/3)(A_1^2+A_2^2+5A_3^2)\gamma^2C_1'^2,\\
f_{3d\pi} &= (1/3)[A_1^2+A_2^2+5A_3^2+4(B_1^2+B_3^2)]\\
&\quad +(2/3)\gamma^2[A_1^2+A_2^2+5A_3^2],\\
f_{2s} &= (1/54)(A_1^2+A_2^2+5A_3^2)\gamma^2C_2'^2, \qquad \text{(A12)}\\
f_{\mathrm{L}\pi} &= (1/3)[2(A_1^2+A_2^2-A_3^2)-(B_1^2-3B_2^2+B_3^2)\\
&\quad +2(A_1^2+A_2^2-A_3^2)\gamma^2],\\
f_{\mathrm{N}\pi} &= (1/3)(C_{7\mathrm{N}})^2f_{\mathrm{L}\pi}
\end{aligned}$$

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(51) The electron transfers from $\varphi$ to $3d\pi$ and to the vacant MO of ligand are ignored since their energies lie probably fairly higher than that of the electron transfer $3d\pi\rightarrow\varphi^*$.