2898 © 1981 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 54, 2898—2903 (1981) [Vol. 54, No. 10

# The DV-X$\alpha$ MO Study of the Electronic Structures of $[M(CN)_6]^{3-}$ (M=Cr, Mn, Fe, and Co) and $[Fe(CN)_6]^{4-}$

Mitsuru SANO,** Hirohiko ADACHI,† and Hideo YAMATERA*

*Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464*

*†Department of Nuclear Engineering, Faculty of Engineering, Osaka University, Suita 565*

(Received August 5, 1980)

The discrete-variational X$\alpha$ (DV-X$\alpha$) calculations are used for the hexacyano transition-metal complexes, $[M(CN)_6]^{3-}$ (M=Cr, Mn, Fe, and Co) and $[Fe(CN)_6]^{4-}$. The calculated values of the core- and valence-orbital energies can be correlated with the XPS results. The Mulliken populations are presented. The calculated d-d excitation energies are in good agreement with the $\Delta$ (ligand-field parameter) values obtained from the spectra.

The Hartree-Fock-Slater (HFS) model[1] has recently been applied to the molecular orbital (MO) calculation of the electronic structures of molecules, clusters, and crystals. Three methods have been developed for the application of this model to the MO calculation: the multiple-scattering X$\alpha$ (MS-X$\alpha$) method,[2] the discrete-variational X$\alpha$ (DV-X$\alpha$) method,[3] and the LCAO-X$\alpha$ method.[4] The MS-X$\alpha$ method developed by Johnson and his co-workers seems to be oversimplified for use in the calculation of a metal complex which contains heteropolar covalent bonds. The LCAO-X$\alpha$ method is an attractive approximation,[5] but it does not seem to meet the present purpose because of the incompatibility of a satisfactory basis set and a reasonable computer time. Most suitable to the present case, therefore, is the DV-X$\alpha$ method, which has the following advantages: any type of functions, including numerical functions, can be used as the basis functions and as the potential functions, mathematical difficulties are eliminated, and a large system can be calculated in a relatively short computer time. On the other hand, this method is not suitable for the calculation of accurate total energies. The DV-X$\alpha$ calculations for the ionization and excitation energies have shown an excellent agreement with the experimental results for small molecules[6,7] and metal clusters.[8,9]

However, only a few reports[9,10] have so far appeared concerning the systematical application of the DV-X$\alpha$ method to a series of transition-metal complexes. It still remains uncertain how far the DV-X$\alpha$ method can be relied on for the calculation of the orbital energy, the atomic charge, the bond-overlap population, and the d-d excitation energy of a transition-metal complex.

The present study is concerned with the application of the DV-X$\alpha$ method to a series of hexacyano transition-metal complexes, which have been of special interest for both inorganic and theoretical chemists.[11] Cyanide ions are coordinated to a metal ion with both $\sigma$- and $\pi$-type bondings, and cyano complexes are typical of the complexes in which the $\pi$ back-donation of electrons possibly takes place.

The main purpose of the present study is to obtain a deeper understanding of the coordinate bond by comparing the electronic structures of hexacyano complexes. For this purpose, an HFS MO calculation with the numerical-basis DV-X$\alpha$ method has been made of $[M(CN)_6]^{3-}$ (M=Cr, Mn, Fe, and Co) and $[Fe(CN)_6]^{4-}$. The results are compared with the experimental results in order to confirm their reliability, and comparisons are made between the results for different complexes of the series. A comparison is also made with the recent results of the *ab initio* MO calculation of $[Co(CN)_6]^{3-}$ by Sano *et al.*[12,13]

## Computational Method

The computational details of the spin-polarized DV-X$\alpha$ method and the relation between the DV-X$\alpha$ treatment and ligand-field theory have been sufficiently described elsewhere.[9]

In the HFS model,[1] the exchange-correlation term is given by:

$$V_{xc}{}^{\uparrow}(1) = -3\alpha[(3/4\pi)\rho^{\uparrow}(1)]^{1/3}$$

where $\rho^{\uparrow}(1)$ is the local charge density with up-spin and $\alpha$ is the exchange scaling parameter; $\alpha=0.70$ is used for all atoms throughout the present calculation.[6] The spin-polarized DV-X$\alpha$ self-consistent-charge (SCC) procedure[9] has been performed for both up and down spins, where an approximate self-consistent molecular potential is determined from the Mulliken gross orbital populations. The up- and down-spin numerical basis functions are generated as the solutions of the atomic HFS equations in which an atom-like potential is constructed by spherically averaging the molecular potential around the nucleus for the region inside each atomic sphere.[8] The basis sets including the metal 1s–4p and C and N 1s–2p are utilized for most of the present calculations.

The molecular geometries for the complexes are taken from the experimental results.[14] In the present calculation, the complexes are regarded as having the $O_h$ symmetry.

## Results and Discussion

*The MO's of the Cyanide Ion and Its Coordination to a Metal Ion.* The eigenvalues and charge distributions calculated for free $CN^-$ are tabulated in Table 1.

The $1\sigma$ and $2\sigma$ MO's are N1s and C1s orbitals respectively. On the basis of the orbital components and the bond-overlap populations, each orbital may be characterized as follows: $3\sigma$ is the N2s–C2s bonding

---

** Present address: Laboratory of Inorganic Chemistry, Faculty of General Education, Nagoya University, Chikusa-ku, Nagoya 464.

TABLE 1. ELECTRONIC STRUCTURE OF $CN^-$

| Orbital | Energy/eV | Charge distribution/% C 1s | C 2s | C 2p | N 1s | N 2s | N 2p |
|---|---|---|---|---|---|---|---|
| 5σ | 2.5 | | 23 | 39 | | 6 | 32 |
| 1π | 1.4 | | | 42 | | | 58 |
| 4σ | −0.6 | | 32 | 9 | | 24 | 34 |
| 3σ | −11.9 | | 21 | 12 | | 55 | 11 |
| 2σ | −258.1 | 100 | | | | | |
| 1σ | −368.8 | | | | 100 | | |

| Carbon orbital | Orbital population | Nitrogen orbital | Orbital population |
|---|---|---|---|
| 1s | 2.00 | 1s | 2.00 |
| 2s | 1.52 | 2s | 1.72 |
| 2pσ | 1.21 | 2pσ | 1.55 |
| 2pπ | 1.68 | 2pπ | 2.32 |
| Atomic charge | −0.41 | Atomic charge | −0.59 |

| C–N | Overlap population |
|---|---|
| 5σ | −0.249 |
| 1π | 1.110 |
| 4σ | 0.013 |
| 3σ | 0.397 |

orbital, the major part of the population of nonbonding 4σ and that of antibonding 5σ reside at N and C respectively, and 1 π is bonding. These features are similar to previous results[12,13] derived from the *ab initio* MO calculation. However, the results of the population analysis in the present calculation (−0.59 on N and −0.41 on C) are in contrast with the previous results (−0.454 on N and −0.546 on C).[13] The present results are more reasonable for the reason that they are consistent with the higher electronegativity of the nitrogen atom. The *ab initio* calculation with double-zeta basis functions sometimes gives unreasonable results for Mulliken populations due to a diffuse component of the double-zeta function extending to the neighboring atom.[15] Thus, one of the merits of the DV-Xα SCC method seems to be that it gives reasonable populations.

In spite of the higher negative charge located on the nitrogen atom, the cyanide ion is coordinated to the metal at the carbon atom. This can be expected from the frontier-electron theory,[16] according to which an electrophilic reaction tends to takes place on the atom that has the highest electron density in the highest occupied MO (HOMO) of the ground state of the nucleophile. The HOMO of the free $CN^-$ ion is 5σ, the population of which is greater on the carbon atom (62%) than on the nitrogen atom (38%); this is consistent with the tendency of $CN^-$ to coordinate at the carbon atom.

TABLE 2. ΔE(N1s–C1s) FROM XPS EXPERIMENTS[17] AND DV-Xα MO CALCULATION (eV)

| | $Cr^{3+}$ | $Mn^{3+}$ | $Fe^{3+}$ | $Co^{3+}$ | $Fe^{2+}$ |
|---|---|---|---|---|---|
| DV-Xα | 110.0 | 109.9 | 109.9 | 109.6 | 109.8 |
| Expt | 113.6 | 113.4 | 113.3 | 113.2 | 113.1 |

*Orbital Energies and Ionization Potentials of the Metal Complexes.* The core-electron binding energies for N1s and C1s are first discussed. The orbital-energy values calculated by the Xα method cannot be directly compared with the experimental values obtained from X-ray photoelectron spectroscopy (XPS), since the relaxation effect is disregarded in the calculation. However, the relaxation energies for C and N core orbitals do not change appreciably from one cyano complex to another; thus, the relative changes in core levels may be meaningful. In Table 2, the differences between the N1s and C1s orbital energies of the complexes are compared with the corresponding XPS results. The calculated N1s−C1s difference, ΔE(N1s−C1s), decreases from $[Cr(CN)_6]^{3-}$ (110.0 eV) to $[Co(CN)_6]^{3-}$ (109.6 eV) and from $[Fe(CN)_6]^{3-}$ (109.9 eV) to $[Fe(CN)_6]^{4-}$ (109.8 eV), showing a trend similar

TABLE 3. THE ENERGIES, SYMMETRIES, AND POPULATIONS OF THE FILLED OUTER-SHELL MOLECULAR ORBITALS OF $[Co(CN)_6]^{3-}$

| Symmetry | Energy/eV | Population analysis/% Metal orbital 3d | Metal orbital 4s | Metal orbital 4p | Carbon orbital 2s | Carbon orbital 2p | Nitrogen orbital 2s | Nitrogen orbital 2p |
|---|---|---|---|---|---|---|---|---|
| $2t_{2g}$ | 5.34 | 70.7 | | | | 1.8 | | 27.5 |
| $8t_{1u}$ | 4.07 | | | 1.3 | 8.5 | 33.4 | 3.1 | 53.6 |
| $1t_{1g}$ | 3.99 | | | | | 35.4 | | 64.6 |
| $1t_{2u}$ | 3.61 | | | | | 41.5 | | 58.5 |
| $7t_{1u}$ | 2.96 | | | 0.0 | 0.0 | 22.7 | 19.8 | 57.6 |
| $5e_g$ | 2.83 | 10.8 | | | 0.0 | 6.4 | 27.0 | 55.8 |
| $8a_{1g}$ | 2.82 | | 0.0 | | 0.0 | 8.3 | 30.1 | 61.8 |
| $1t_{2g}$ | 2.26 | 20.5 | | | | 49.9 | | 29.5 |
| $6t_{1u}$ | 0.29 | | | 6.0 | 38.8 | 33.7 | 11.9 | 9.4 |
| $4e_g$ | 0.18 | 36.3 | | | 31.2 | 20.8 | 7.2 | 4.5 |
| $7a_{1g}$ | −2.61 | | 9.9 | | 39.6 | 44.2 | 6.3 | 0.0 |
| $3e_g$ | −10.68 | 0.2 | | | 19.7 | 14.7 | 52.2 | 13.3 |
| $5t_{1u}$ | −10.86 | | | 1.7 | 18.0 | 15.3 | 51.2 | 13.4 |
| $6a_{1g}$ | −11.00 | | 3.1 | | 20.9 | 12.3 | 49.7 | 14.0 |

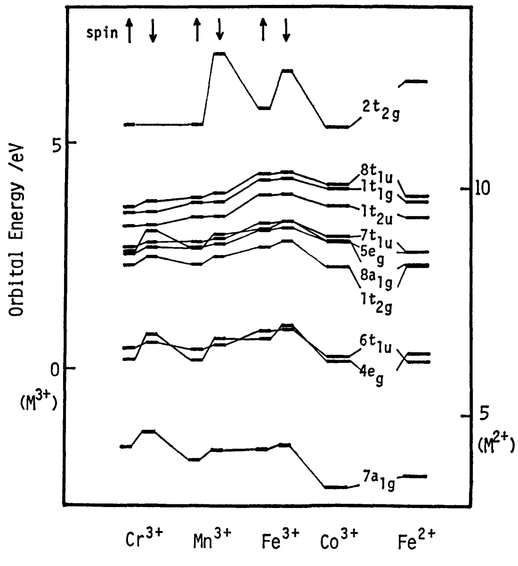

Fig. 1. The occupied valence orbital levels of $[M(CN)_6]^{3-}$ (M=Cr, Mn, Fe, and Co) and $[Fe(CN)_6]^{4-}$.

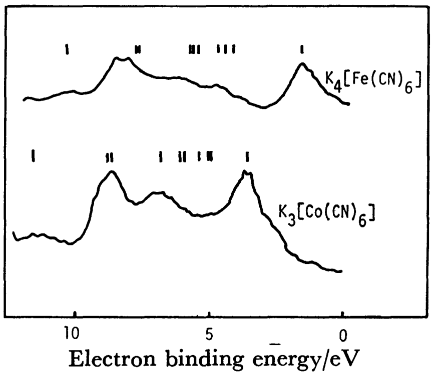

Fig. 2. Valence shell spectra of XPS[20] and orbital energies for $[Fe(CN)_6]^{4-}$ and $[Co(CN)_6]^{3-}$.

to that observed in the XPS data. Detailed discussions of the XPS results have been given elsewhere.[17]

Table 3 shows the energies and symmetries of the filled outer-shell MO's of $[Co(CN)_6]^{3-}$, along with their atomic components. The energies of orbitals with up- and down-spins are schematically shown in Fig. 1 for all the complexes of the series. In all cases, the HOMO is $2t_{2g}$, consisting mainly of metal d$\pi$ with a small contribution of ligand $\pi$ orbitals. This is different from the previous results of a simple Hartree-Fock (HF) calculation,[12] which showed that $2t_{2g}$ consists mainly of ligand orbitals, but it is consistent with the results of the HF calculation with the $\Delta$ SCF procedure,[13] according to which the ionization potential of $2t_{2g}$ (a mainly ligand orbital) is larger than that of $1t_{2g}$ (a mainly metal orbital) and the latter may therefore be regarded as HOMO. The XPS results[19,20] also show that the electron of the smallest binding energy is of a mainly metal-d character, in agreement with the present and the $\Delta$ SCF results. Figure 2 shows a comparison of the calculated orbital-energy levels and the XPS spectra of the valence regions of $[Fe(CN)_6]^{4-}$ and $[Co(CN)_6]^{3-}$.[20] For easy comparison, the position of the calculated energy level of $2t_{2g}$ (d$\pi$, HOMO) was arbitrarily taken as the reference to be fitted to the corresponding XPS peak in Fig. 2. The relative positions of the calculated orbital-energy levels appear to show a good correlation with the spectra, in spite of the fact that the reorganization energy is neglected in the calculation. A more detailed discussion, including the calculation by the transition-state method and an estimation of the relative intensities, will be given elsewhere.[21]

In the valence levels, the $6a_{1g}$, $5t_{1u}$, and $3e_g$ MO's of the complexes are predominantly composed of $CN^-$ $3\sigma$ orbitals (see Tables 1 and 3). The $7a_{1g}$, $4e_g$, and $6t_{1u}$ MO's are $CN^-$ $\sigma$ orbitals mixed with metal $\sigma$ orbitals. The $1t_{2g}$ MO is composed of $CN^-$ $\pi$ and metal d$\pi$. The $8a_{1g}$, $7t_{1u}$, and $5e_g$ MO's are $CN^-$ $\sigma$ orbitals located mainly on N. The $1t_{1g}$ and $1t_{2u}$ MO's are $CN^-$ $\pi$ orbitals, while $8t_{1u}$ MO is predominantly $CN^-$ $\pi$ orbitals slightly mixed with the metal 4p orbital.

We shall compare the orderings of MO's in the free and coordinated $CN^-$ ions. Although the $5\sigma$ orbital

TABLE 4. ATOMIC CHARGES

| Metal | $Cr^{3+}$ |  | $Mn^{3+}$ |  | $Fe^{3+}$ |  | $Fe^{2+}$ | $Co^{3+}$ |
|---|---|---|---|---|---|---|---|---|
|  | up | down | up | down | up | down |  |  |
| 3d$\sigma$ | 0.79 | 0.49 | 0.85 | 0.64 | 0.91 | 0.79 | 1.52 | 1.89 |
| 3d$\pi$ | 2.75 | 0.13 | 2.75 | 0.98 | 2.75 | 1.87 | 4.99 | 5.48 |
| 4s | 0.14 | 0.10 | 0.13 | 0.11 | 0.12 | 0.11 | 0.22 | 0.26 |
| 4p | 0.23 | 0.15 | 0.24 | 0.18 | 0.24 | 0.21 | 0.44 | 0.53 |
| Atomic charge | +1.21 |  | +1.13 |  | +0.98 |  | +0.83 | +0.84 |
| Carbon |  |  |  |  |  |  |  |  |
| 2s | 0.62 | 0.66 | 0.61 | 0.64 | 0.60 | 0.62 | 1.25 | 1.20 |
| 2p$\sigma$ | 0.56 | 0.59 | 0.55 | 0.58 | 0.55 | 0.56 | 1.12 | 1.10 |
| 2p$\pi$ | 0.86 | 0.89 | 0.87 | 0.89 | 0.85 | 0.87 | 1.69 | 1.75 |
| Atomic charge | −0.17 |  | −0.14 |  | −0.05 |  | −0.06 | −0.04 |
| Nitrogen |  |  |  |  |  |  |  |  |
| 2s | 0.86 | 0.86 | 0.86 | 0.86 | 0.86 | 0.86 | 1.72 | 1.72 |
| 2p$\sigma$ | 0.77 | 0.77 | 0.76 | 0.76 | 0.76 | 0.76 | 1.51 | 1.50 |
| 2p$\pi$ | 1.19 | 1.10 | 1.19 | 1.13 | 1.21 | 1.17 | 2.51 | 2.38 |
| Atomic charge | −0.53 |  | −0.55 |  | −0.61 |  | −0.74 | −0.60 |

Table 5. Bond-overlap populations

| | $Cr^{3+}$ | $Mn^{3+}$ | $Fe^{3+}$ | $Co^{3+}$ | $Fe^{2+}$ |
|---|---|---|---|---|---|
| M–Cπ | 0.05 | 0.05 | 0.05 | 0.04 | 0.08 |
| $1t_{2g}$ | 0.05 | 0.06 | 0.07 | 0.08 | 0.06 |
| $2t_{2g}$ | 0.00 | −0.01 | −0.02 | −0.03 | 0.03 |
| M–Cσ | 0.21 | 0.23 | 0.24 | 0.27 | 0.23 |
| $4e_g$ | 0.10 | 0.12 | 0.12 | 0.13 | 0.11 |
| $5e_g$ | 0.05 | 0.04 | 0.04 | 0.03 | 0.06 |
| $a_{1g}$'s<br>$t_{1u}$'s | 0.06 | 0.07 | 0.08 | 0.11 | 0.06 |
| Total M–C | 0.25 | 0.27 | 0.29 | 0.30 | 0.31 |
| C–N σ | 0.42 | 0.43 | 0.44 | 0.45 | 0.43 |
| C–N π | 1.10 | 1.08 | 1.07 | 1.07 | 1.01 |
| Total C–N | 1.51 | 1.50 | 1.50 | 1.51 | 1.44 |

is the HOMO in the free $CN^-$ ion, the ordering of the σ and π orbitals is reversed by the coordination of $CN^-$ with a metal ion. Thus, the ordering is

$$5\sigma > 1\pi > 4\sigma \qquad \text{in the free } CN^- \text{ ion}$$

and;

$$\text{metal } d\pi > \pi(CN^-) > \sigma(CN^-) \quad \text{in the complex ion.}$$

Since the cyanide ion is a good σ-electron donor, the 5σ orbital energy is greatly decreased by the bonding interaction with the metal dσ orbital.

*Bond-overlap Population and Bond Strength.* The calculation has been done by the procedure of SCC. The numerical basis set generated by iterative SCC[8] gave adequate wavefunctions suitable to the Mulliken population analysis. The bond-overlap population and charge distributions thus obtained are given in Tables 4 and 5. The metal-carbon bond strength is related to both the σ- and π-overlap populations for the M–C bond. The σ-bond-overlap populations of the $[M(CN)_6]^{3-}$-type complexes gradually increase with an increase in the atomic number of the metal (from Cr to Co). This is consistent with the tendency for the effective nuclear charge of the metal ion to increase in the order of $Cr^{3+} < Mn^{3+} < Fe^{3+} < Co^{3+}$. The increase in the nuclear charge is only incompletely screened by the increase in the number of metal dπ electrons. Thus, the ligand-to-metal donation of σ electrons is expected to increase with an increase in the atomic number of the metal. On the other hand, the π-bond-overlap population remains almost unchanged, probably because of the counterbalancing effects of the π+dπ bonding and dπ−π antibonding interactions. The total bond-overlap population and, consequently, the M-C-bond strength increase in the order of Cr–C<Mn–C<Fe–C<Co–C. As regards the C–N bond, the bond-overlap population is 1.43 in the free $CN^-$ ion and 1.44—1.51 in the complexes. The C–N-overlap population consists of two components, the σ- and π-overlap populations, which are, respectively, 0.32 and 1.11 in the free $CN^-$ and 0.42—0.45 and 1.07—1.10 in the complexes (except for the $Fe^{2+}$ complex, to be discussed below). The formation of the M–C bond results in a decrease in the antibonding character of 5σ (HOMO) and, consequently, in an increase in the C–N bond-overlap population from 0.32 to 0.42—0.45. This suggests that a stronger metal–carbon σ bond is associated with a stronger C–N σ bond. On the other hand, the formation of metal–ligand π bonds with π back-donation slightly weakens the C–N bond, as is shown by the descrease in the C–N π-overlap population from 1.11 to 1.07—1.10. The σ and π effects partially compensate for each other, resulting in a slight increase in the C–N bond strength. When $Fe^{3+}$ in the hexacyano complex is reduced to $Fe^{2+}$, an electron is added to the dπ orbital. Thus, in $[Fe(CN)_6]^{4-}$ the π back-donation of iron dπ electrons to the cyanide antibonding π orbitals occurs to a greater extent, resulting in a weakening of the C–N π bond. The increase in the number of dπ electrons will only indirectly affect the Fe–C σ bonding and the C–N σ bonding. Consistent with this argument, Table 5 shows that the π-overlap population decreases from 1.07 to 1.01 and that the σ-overlap population changes very little in going from the $Fe^{3+}$ to the $Fe^{2+}$ complex.

*Charge Distribution.* The differences in the charge distribution between the free $CN^-$ ion and the $CN^-$ ligand in the complexes are seen mainly in the carbon charges as a result of the σ donation to metal. A fraction (0.3—0.4) of electron flows into the metal ion from each carbon atom, partially neutralizing the positive charge of the metal ion. The 3dσ population increases from 1.28 to 1.89 with the increase in the carbon-to-metal σ donation in going from $Cr^{3+}$ to $Co^{3+}$. The 3dπ population, of course, increases with the increase in the atomic number. The net population of 3dπ, however, is lower than the formal population, and the deficiency increases from 0.12 to 0.52, showing an increase in the π back-donation with an increase in the atomic number. The population of 4s changes only slightly, while that of 4p increases from 0.38 to 0.53 across the series (due to ligand-to-metal donation). The metal positive charge thus decreases with the increase in the 3dσ population in going from $Cr^{3+}$ to $Co^{3+}$. On carbon, the C2s and C2pσ populations decrease from 1.28 and 1.15 for $[Cr(CN)_6]^{3-}$ to 1.20 and 1.10 for $[Co(CN)_6]^{3-}$ respectively with an increase in the σ donation from carbon to metal, while the C2pπ population remains approximately constant. As for the nitrogen charge, the population remains unchanged for 2s, slightly decreases for 2pσ, and increases for 2pπ, in going from $Cr^{3+}$ to $Co^{3+}$. As a result, the negative charge of nitrogen increases from −0.53 to −0.60, in contrast to the

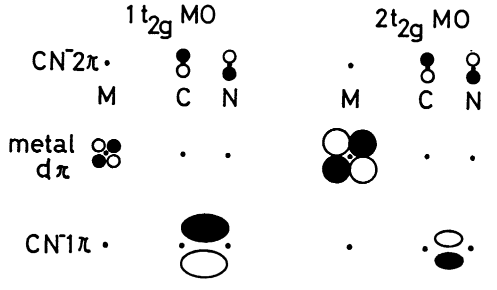

Fig. 3. Orbital interaction of metal dπ and cyanide π orbitals of $T_{2g}$ symmetry. Sizes of circles and ellipses roughly indicate the magnitudes of orbital components. Signs of orbital wavefunctions, namely positive or negative, are shown by white and black area.

decrease in that of carbon from −0.17 to −0.04.

The changes in the cyanide $\pi$ populations will now be briefly discussed. According to the orbital-mixing rule,[22] the $1t_{2g}$ and $2t_{2g}$ MO's consist of linear combinations of the $(1\pi+2\pi+d\pi)$- and $(d\pi-1\pi+2\pi)$-types respectively. These combinations are schematically summarized in Fig. 3. In the formation of the bonding $1t_{2g}$ MO, the $CN^-$ $1\pi$ and $2\pi$ amplitudes intensify each other at the carbon atom and compensate for each other at the nitrogen atom to result in increased and decreased populations on the carbon and nitrogen atoms respectively. On the other hand, in the $2t_{2g}$ MO, a compensation and an intensification of the amplitudes occur at the carbon and nitrogen atoms respectively. The mixing of $2\pi$ (antibonding cyanide orbital) into $d\pi$ with bonding combination strengthens the M–C bond, but weakens the C–N bond.

In the cyano complexes of $Fe^{2+}$ and $Fe^{3+}$, the metal charges are +0.83 and +0.98, respectively, and the difference results mainly from different 3d populations. The $3d\sigma$ population for $Fe^{3+}$ (1.70) is greater than that for $Fe^{2+}$ (1.52) in agreement with a greater $\sigma$ donation to $Fe^{3+}$, while the difference in the $3d\pi$ population between $Fe^{2+}$ (4.99) and $Fe^{3+}$ (4.62) is much less than unity (or the difference in the formal charge) indicating a greater $\pi$ back-donation from $Fe^{2+}$. The charges on the two kinds of iron atoms differ from each other only by 0.15, which is much smaller than the difference in the oxidation number.

As has been shown in previous papers,[12,15] the charge distribution derived from the Mulliken population analysis strongly depends on the basis set of orbitals used in the calculation. Thus, the cobalt charge in $[Co(CN)_6]^{3-}$ was estimated to be +3.138 and +1.301 by two *ab initio* MO calculations with only slightly different basis sets. On the other hand, the atomic charge derived from the analysis of the spatial charge distribution naturally depends on the atomic radius assumed. Our previous analysis[13] gave +0.3 or +2.3 for the cobalt charge in the same complex, depending on the radius: 1.22 Å, in accordance with the results of an X-ray analysis,[23] or 0.95 Å, which is the distance of minimum electron density on the calculated distribution curve. As has previously been discussed,[12,15] the diversity of the calculated charges results from the fact that the allocation of charge to each atom is artificial. Nevertheless, the atomic charges are one of the important clues for elucidating the electronic structure of metal complexes, provided that an appropriate method is used consistently to calculate the charge distributions for the complexes to be compared. In this sense, the present results for charge distribution give useful information on the electronic state of the complexes. The resonable numerical values obtained for atomic charges may indicate that the iterative SCC procedure would give suitable wavefunctions for the purpose of population analysis.

*The Excitation Energies.* One of the main purposes of the present work is to examine the extent to which the experimental values of the ligand field parameter, $\Delta$, can be reproduced by the DV-Xα SCC scheme. The theory has been thoroughly described by Adachi *et al.*[9] The $\Delta$ values are obtained as the weighted averages of the energy differences between the vacant $6e_g$ and occupied $2t_{2g}$ orbitals with the same spin:

$$\Delta = [n^{\uparrow}\{E(6e_g{}^{\uparrow})-E(2t_{2g}{}^{\uparrow})\}+n^{\downarrow}\{E(6e_g{}^{\downarrow})-E(2t_{2g}{}^{\downarrow})\}]/(n^{\uparrow}+n^{\downarrow}),$$

where the superscripts ↑ and ↓ indicate the up- and down-spins, and $n$, the occupation number of the $2t_{2g}$ orbital with the designated spin. In Table 6, the calculated $\Delta$ values are compared with the experimental values reported by Alexander and Gray.[24]

The agreement is reasonably good if the difficulties associated with the estimation of the experimental $\Delta$ values are taken into consideration. For some complexes such as $[Fe(CN)_6]^{3-}$, the d-d bands are not clearly observed due to the overlap of strong charge-transfer bands. The estimation of the $\Delta$ values from the observed wavenumbers of the absorption bands may be more or less dependent on the values assumed for Racah's $B$ and $C$ parameters. A good agreement between the calculated and experimental values of $\Delta$ for metal fluorides has been reported by Larsson and Connolly,[25] who used the SW-Xα method to obtain the $\Delta$ values as the difference between the two d-orbital energies. More careful DV-Xα treatments of the same compounds made by Adachi *et al.*[9] gave an excellent agreement. Along with their results, our present results illustrate the usefulness of the Xα method for the estimation of the $\Delta$ values.

The $\Delta$ values calculated for the $[M(CN)_6]^{3-}$-type complexes increase with the increase in the atomic number of the metal. Though not fully consistent with the existing experimental data, this trend can be expected from the following reasoning: in going from $Cr^{3+}$ to $Co^{3+}$, the effective charge of the metal ion increases, the $\sigma$ donation from $CN^-$ $\sigma$ to metal $d\sigma$

Table 6. Calculated values of the ligand-field parameter, $\Delta$, and the experimental values[24]

| Orbital | $Cr^{3+}$ | $Mn^{3+}$ | $Fe^{3+}$ | $Co^{3+}$ | $Fe^{2+}$ | |
|---|---|---|---|---|---|---|
| $6e_g{}^{\downarrow}$ | 11.11 | 10.61 | 10.43 | 9.46 | 16.50 | (eV) |
| $6e_g{}^{\uparrow}$ | 8.89 | 9.17 | 9.73 | 9.46 | 16.50 | (eV) |
| $2t_{2g}{}^{\downarrow}$ | 7.71 | 6.95 | 6.57 | 5.35 | 12.35 | (eV) |
| $2t_{2g}{}^{\uparrow}$ | 5.42 | 5.40 | 5.76 | 5.35 | 12.35 | (eV) |
| $\Delta$ (calcd) | 28000 | 30200 | 31600 | 33200 | 33500 | ($cm^{-1}$) |
| $\Delta$ (exptl) | 26600 | 34000[a] | 34950 | 34500 | 33800 | ($cm^{-1}$) |

a) 30000 $cm^{-1}$ in Ref. 26.

occurs to a greater extent, and metal d$\sigma$ is more strongly destabilized by the increased antibonding interaction. The $\pi$ back-donation is small in these complexes; thus, the change in $\pi$ back-donation makes a minor contribution to the change in the $\Delta$ values.

The calculated $\Delta$ value for $[Fe(CN)_6]^{4-}$ is greater than that for $[Fe(CN)_6]^{3-}$. This is contrary to the above reasoning, according to which $[Fe(CN)_6]^{4-}$ with $Fe^{2+}$, with a lower effective charge, would have a lower $\Delta$ value. In this case, however, a change in the $\pi$ back-donation makes a significant contribution to the change of the $\Delta$ value. The increase in the stabilization of Fe d$\pi$ due to the stronger $\pi$-bonding effect overbalances the decrease in the destabilization of Fe d$\sigma$ due to the weaker $\sigma$-antibonding effect in going from the $Fe^{3+}$ to the $Fe^{2+}$ complex. Calculation showed that the $\sigma$ donation decreased from 42.3% to 37.7%, while the $\pi$ back-donation increased from 8.5% to 16.8% correspondingly.

## Conclusions

The spin-polarized DV-X$\alpha$ method has been applied to the calculation of the electronic structures of transition-metal cyano complexes. This leads to the following conclusions:

(1) The calculated orbital energies give a good correlation with the XPS results.

(2) The calculated atomic charges and bond-overlap populations due to Mulliken population analysis show a trend that can be satisfactorily elucidated by a qualitative molecular-orbital consideration using the orbital mixing rule.

(3) The $\Delta$ value, as expressed by the difference between d$\sigma$ ($6e_g$) and d$\pi$ ($2t_{2g}$) orbital energies, shows a good agreement with the spectroscopic $\Delta$ values.

(4) The conclusions described under (1)—(3) suggest that the DV-X$\alpha$ MO method gives an adequate description of the electronic structures of transition-metal complexes.

The numerical calculations were performed with a HITAC M-180 system at the Computer Center of the Institute for Molecular Science and a FACOM 230-75 system at the Nagoya University Computation Center. The authors are grateful to the staffs of the computer centers for their assistance in the calculation.

### References

1) For a review of the Hartree-Fock-Slater model, see J.C. Slater, "Quantum Theory of Molecules and Solids," McGraw-Hill, New York (1974), Vol. 4.

2) K. H. Johnson and F. C. Smith, Jr., "Computational Methods in Band Theory," ed by P. M. Marcus, J. F. Janak, and A. R. Williams, Plenum, New York (1971), p. 337; K, H. Johnson, J. G. Norman, Jr., and J. E. D. Connolly, "Computational Methods for Large Molecules and Localized States in Solids," ed by F. Herman, A. D. McLean, and R. K. Nesbet, Plenum, New York (1973), p. 161; J. C. Slater and K. H. Hohnson, *Phys. Rev. B*, **5**, 844 (1979).

3) D. E. Ellis and G. S. Painter, *Phys. Rev. B*, **2**, 2887 (1970); E. J. Baerends, D. E. Ellis, and P. Ros, *Chem. Phys.*, **2**, 41 (1973).

4) H. Sambe and R. H. Felton, *J. Chem. Phys.*, **62**, 1122 (1975).

5) T. Ziegler and A. Rauk, *Inorg. Chem.*, **18**, 1558 (1979).

6) E. J. Baerends and P. Ros *Chem. Phys.*, **2**, 52 (1973); **8**, 412 (1975).

7) A. Rosen, D. E. Ellis, H. Adachi, and F. W. Averill, *J. Chem. Phys.*, **65**, 3629 (1976).

8) H. Adachi, M. Tsukada, and C. Satoko, *J. Phys. Soc. Jpn.*, **45**, 875 (1978).

9) H. Adachi, S. Shiokawa, M. Tsukada, C. Satoko, and S. Sugano, *J. Phys. Soc. Jpn.*, **47**, 1528 (1979).

10) E. J. Baerends and P. Ros, *Mol. Phys.*, **30**, 1735 (1975).

11) A. G. Sharpe, "The Chemistry of Cyano Complexes of the Transition Metals," Academic Press, London (1976).

12) M. Sano, Y. Hatano, and H. Yamatera, *Chem. Phys. Lett.*, **60**, 257 (1979).

13) M. Sano, Y. Hatano, H. Kashiwagi, and H. Yamatera, *Bull. Chem. Soc. Jpn.*, **54**, 1523 (1981).

14) S. Jagner, *Acta Chem. Scand.*, *A*, **29**, 255 (1975).

15) M. Sano, Y. Hatano, and H. Yamatera, *Chem. Lett.*, **1979**, 789.

16) H. Fujimoto and K. Fukui, "Chemical Reactivity and Reaction Paths," ed by G. Klopman, John Wiley and Sons, New York (1974), p. 23.

17) M. Sano and H. Yamatera, *Bull. Chem. Soc. Jpn.*, **54**, 2023 (1981).

18) The N1s and C1s binding energies obtained from XPS are influenced by the charging and the Madelung potential. However, these effects are canceled in their difference, $E$(N1s−C1s), so that a comparison between the experimental and calculated values of $\Delta E$ (N1s−C1s) becomes possible.

19) A. Calabrese and R. G. Hayes, *J. Am. Chem. Soc.*, **96**, 5054 (1974).

20) N. G. Vannerberg, *Chem, Scrip.*, **9**, 122 (1976).

21) M. Sano, H. Adachi, and H. Yamatera, to be published.

22) S. Inagaki and K. Fukui, *Chem. Lett.*, **1974**, 509; S. Inagaki, H. Fujimoto, and K. Fukui, *J. Am. Chem. Soc.*, **98**, 4504 (1976).

23) M. Iwata and Y. Saito, *Acta Crystallogr.*, *Sect.B*, **29**, 822 (1973).

24) J. J. Alexander and H. B. Gray, *J. Am. Chem. Soc.*, **90**, 4260 (1968).

25) S. Larson and L. W. D. Connolly, *Chem. Phys. Lett.*, **20**, 323 (1973).

26) I. D. Chawla and M. J. Frank, *J. Inorg. Nucl. Chem.*, **32**, 555 (1970).