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The Study of Transition-metal Complexes with Ethylenediamine and Cyano Ligands by Means of the X-Ray Photoelectron Spectra

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The X-ray photoelectron spectra (XPS) were measured in order to obtain the N1s and C1s core-orbital energies of ten ethylenediamine and 21 cyano complexes of transition metals. The difference between the N1s and C1s energies, ΔE, which was found to be hardly affected by the counter ion or by charging, was accurately determined for each complex. The trends observed in the ΔE values for these series of complexes are correlated with the electronic structures of the complexes by the use of Siegbahn's equation. For the ethylenediamine complexes, the ΔE values are shown to be related to the σ donation. For the cyano complexes, the ΔE values are mainly controlled by the nitrogen charge, which is itself closely connected with the π back-donation. Demonstrative of the importance of the π back-donation are the cases of $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$, where the decrease in the negative charge from the former to the latter is found to occur dominantly (76%) in the nitrogen atoms. Molecular orbital (MO) calculations in the discrete variational Xα (DV-Xα) scheme were performed for a few series of the cyano complexes, giving results consistent with the XPS results.

The X-ray photoelectron spectrum (XPS) gives information about the charge distribution in a molecule and, accordingly, can be expected to provide a clue to clarifying the electronic structure. However, the chemical shifts of the inner-shell electrons of the metal and ligand atoms of transition-metal complexes have not been well related to the electronic structures because of several difficulties. One is the phenomenon of sample charging, which is serious for insulators. This phenomenon hinders one from making accurate measurements of electron binding energies. In order to overcome this difficulty, the 4f peaks of sputtered gold are usually used as a reference. This is not satisfactory, however, for measuring small chemical-shift differences, since the Au4f levels are influenced by the quantity of the gold and sometimes also by the chemical reaction of the gold with the sample, as is the case with cyanides. Another problem is that the electron binding energies of a complex ion to be measured may be influenced by the counter ion. These difficulties can be removed by the use of an internal reference or by the observation of the difference between the binding energies of different electrons in the same complex.

We investigated how the difference between two core binding energies of ligand atoms is related to the electronic structure of the complex. Transition-metal complexes coordinated with ethylenediamine and cyano ligands were selected for the investigation for the following reasons. Firstly, they are stable enough under a high vacuum and against X-ray irradiation to show reproducible results at −50 °C or below. Secondly, they contain carbon and nitrogen atoms in the ligand, and their coordination bonds show a striking contrast between the mainly σ character in the ethylenediamine complexes and both σ and π characters in the cyano complexes.

The XPS studies of some cyano complexes have been reported on the valence-region spectra by Calabrase and Hayes[1)] and on the chemical shifts of the ligand core orbital by Vannerberg.[2)]

In this paper, the XPS experimental results are presented for the N1s and C1s binding energies in ethylenediamine and cyano complexes of various transition-metal ions, and trends observed for the differences between the N1s and C1s energies are discussed in relation to the electronic structures of the complexes.

Experimental

The spectra were recorded on a JEOL Model JESCA-3A spectrometer. Aluminium $K\alpha_{1,2}$ radiation (1486.6 eV) was used as the X-ray excitation source, and the measurements were carried out at 5×10^{-8} Torr (1 Torr = 133.3 Pa) or below. For the calibration of the electron binding energies, we used both Au4f$_{7/2}$ (83.8 eV) and Ag3d$_{5/2}$ (368.2 eV) peaks[3)] from a thin layer of gold and/or silver deposited onto an aluminium plate. Commercially available potassium salts of cyanide complexes, $K_3[Mn(CN)_6]$, $K_3[Fe(CN)_6]$, $K_3[Co(CN)_6]$, $K[Cu(CN)_2]$, $K[Ag(CN)_2]$, and $K[Au(CN)_2]$, were used without further purification. Other compounds were prepared according to standard methods. A small amount of each sample was ground in ethanol, and a droplet of this ethanolic suspension was placed on a gold plate and dried, or the crystals were ground without solvent and were deposited on an adhesive tape. Care was taken to make sure that the spectra did not contain any features due to contaminants. Carbon contaiminations were examined by comparing the integrated intensities of the carbon 1s and nitrogen 1s peaks. All the spectra reported here were proved to be free from any appreciable contamination. In order to avoid any significant decomposition of the sample by high-vacuum and X-ray irradiation, the sample was cooled at about −50 °C or below. We obtained the difference between the C1s and N1s binding energies by measuring them at the same time. This procedure was repeated several times for each sample, yielding consistent results. The average binding-energy difference was determined with an accuracy of about ±0.1 eV in several runs on a given compound.

We tried to obtain the absolute binding energies by calibrating the nitrogen 1s and carbon 1s peaks against the 4f$_{7/2}$ peak of the gold sputtered onto the sample. This method was not, however, satisfactory for giving the absolute values of the binding energies, because the measured chemical shifts of the N1s and C1s binding energies were dependent upon the quantity of the sputtered gold[4)] and it is not certain that the Fermi level in the gold should coincide with that in the sample. However, the uncertainty associated with the binding energies can, for the most part, be eliminated

Table 1. The electron binding energies of N1s and C1s and their differences for various tris(ethylenediamine)cobalt(III) salts ($Au4f_{7/2}=83.8$ eV)

Compound $[Co(en)_3]X_3$	Binding energy/eV		
	N1s	C1s	ΔE(N1s−C1s)
X = Cl	399.4	285.3	114.1
Br	399.5	285.4	114.1
NO_3	399.6	285.5	114.1
ClO_4	399.7	285.5	114.2

Table 2. The electron binding energies of N1s and C1s and their differences for various ethylenediamine complexes ($Au4f_{7/2}=83.8$ eV)

Compound	Binding energy/eV		
	N1s	C1s	ΔE(N1s−C1s)
$[Cr(en)_3]Cl_3$	400.4	286.5	113.9
$[Co(en)_3]Cl_3$	399.4	285.3	114.1
$[Ni(en)_3]Cl_2$	399.4	285.7	113.7
$[Cu(en)_3]SO_4$	399.4	285.4	114.0
$[Zn(en)_3]Cl_2$	400.0	285.9	114.1
$[Pd(en)_2]Cl_2$	399.7	285.7	114.0
$[Pt(en)_2]Cl_2$	400.2	285.9	114.4

by making use of their difference. For the convenience of comparison, the binding energies in ethylenediamine complexes were standardized against the sputtered-gold $4f_{7/2}$ peak (83.8 eV), and those in cyanide complexes, against the internal-potassium $2p_{3/2}$ peak (293.5 eV).[2)]

Results

In order for us to correlate the chemical shift of the electron binding energy from XPS with the electronic structure of the complex, an accurate determination of the chemical shift is needed. The chemical shift is, however, influenced considerably by the charging effect and also by the counter-ion effect. We first investigated these two effects on the chemical shift using Λ-$[Co(en)_3]X_3$ ($X=Cl^-$, Br^-, NO_3^-, and ClO_4^-) as the samples. The C1s and N1s electron binding energies, as measured for the complex salts, are shown in Table 1, along with the energy difference (ΔE) between N1s and C1s. Both the N1s and C1s energies increase in the order of Cl^-, Br^-, NO_3^-, and ClO_4^- salts, but the ΔE value remains almost unchanged (114.1—114.2 eV), suggesting that ΔE is hardly affected by the counter ion. In addition, the ΔE value is not influenced by sample charging. Thus, the ΔE values can be used with advantage for the discussion of the electronic structures of the metal complexes. The C1s and N1s energies were measured on various ethylenediamine complexes; the meaningful and reproducible data are listed in Table 2 in the order of the increasing atomic number of the metal. The N1s and C1s binding energies listed in Columns 2 and 3 of this table show scattered values, without any apparent trend, but their differences, ΔE, given in Column 4, clearly show the following trends:

Table 3. The electron binding energies of N1s and C1s and their differences for various cyano complexes ($K2p_{3/2}=293.5$ eV)

Compound	Binding energy/eV		
	N1s	C1s	ΔE(N1s−C1s)
$K_3[Cr(CN)_6]$	399.1	285.5	113.6
$K_3[Mn(CN)_6]$	399.1	285.7	113.4
$K_3[Fe(CN)_6]$	399.0	285.7	113.3
$K_3[Co(CN)_6]$	398.9	285.7	113.2
$K_3[Rh(CN)_6]$	399.0	285.8	113.2
$K_4[Mn(CN)_6]$	398.4	285.2	113.2
$K_4[Fe(CN)_6]$	398.4	285.3	113.1
$K_4[Os(CN)_6]$	398.1	285.4	112.7
$K_2[Ni(CN)_4]$	399.0	285.6	113.4
$Ni(CN)_2$	405.1[a)]	291.6[a)]	113.5
$K_2[Pd(CN)_4]$	399.0	285.7	113.3
$K_2[Pt(CN)_4]$	398.9	285.7	113.2
$K[Cu(CN)_2]$	398.8	285.3	113.5
AgCN	405.5[a)]	291.8[a)]	113.7
$K[Ag(CN)_2]$	399.1	285.7	113.4
$K_3[Ag(CN)_4]$	398.9	285.6	113.3
$K[Au(CN)_2]$	399.2	286.0	113.2
$K_2[Zn(CN)_4]$	399.4	285.7	113.7
$K_2[Cd(CN)_4]$	399.3	285.7	113.6
$K_2[Hg(CN)_4]$	399.1	285.6	113.5
$Hg(CN)_2$	406.7[a)]	293.2[a)]	113.5
KCN	399.0	285.4	113.6

a) Uncalibrated value.

(1) The ΔE value increases in going from left to right, or from top to bottom, of the periodic table in each series of bi- and tervalent metal complexes: 113.9→114.1 eV for $Cr^{3+}\rightarrow Co^{3+}$, 113.7→114.1 eV for $Ni^{2+}\rightarrow Zn^{2+}$, and 113.7→114.4 eV for $Ni^{2+}\rightarrow Pt^{2+}$.

(2) The ΔE value is larger for tervalent metal complexes than for bivalent ones if a comparison is made between complexes of the metals near to each other in the periodic table: $Ni^{2+}<Cr^{3+}<Cu^{2+}<Co^{3+}$, Zn^{2+}.

Measurements were also made of various cyanide complexes, for which the N1s and C1s binding energies and the ΔE values are given in Table 3. The following trends are observed:

(3) The ΔE values for $[M(CN)_6]^{3-}$ and $[M(CN)_6]^{4-}$ decrease with an increase in the atomic number of the metal of the first transition series: 113.6→113.2 eV for $Cr^{3+}\rightarrow Co^{3+}$ and 113.2→113.1 eV for $Mn^{2+}\rightarrow Fe^{2+}$.

(4) The ΔE value is greater for a tervalent-metal complex than for the complex of the same metal of a bivalent state: Fe^{3+} (113.3)>Fe^{2+} (113.1), and Mn^{3+} (113.4)>Mn^{2+}(113.2).

(5) The ΔE value is also greater for the higher oxidation number of the metal if a comparison is made between complexes of different metals with the same structure and the same electronic configuration: Hg^{2+}(113.5)>Au^{+}(113.2) for $[M(CN)_2]^{(2-n)-}$, and Co^{3+}(113.2)>Fe^{2+}(113.1) and Fe^{3+}(113.3)>Mn^{2+} (113.2) for $[M(CN)_6]^{(6-n)-}$.

(6) The ΔE value decreases with an increase in the atomic number of the metal in the same family: $Fe^{2+}(113.1) > Os^{2+}(112.7)$, $Ni^{2+}(113.4) > Pd^{2+}(113.3) > Pt^{2+}(113.2)$, $Ag^{+}(113.4) > Au^{+}(113.2)$, and $Zn^{2+}(113.7) > Cd^{2+}(113.6) > Hg^{2+}(113.5)$.

(7) In contradistinction to the trend described under (3), ΔE shows an increase with an increase in the atomic number in the series: $[Fe(CN)_6]^{4-}(113.1) < [Ni(CN)_4]^{2-}(113.4) < [Zn(CN)_4]^{2-}(113.7)$, $[Pd(CN)_4]^{2-}(113.3) < [Cd(CN)_4]^{2-}(113.6)$, and $[Os(CN)_6]^{4-}(112.7) < [Pt(CN)_4]^{2-}(113.2) < [Hg(CN)_4]^{2-}(113.5)$. This may be due to different symmetries of the complexes. The order of increasing ΔE is $O_h < D_{4h} < T_d$.

(8) The ΔE values for cyanide complexes are smaller than that for KCN; AgCN and $K_2[Zn(CN)_4]$ are exceptions, however.

These trends (1)—(8) will be discussed in more detail in the following section.

Discussion

The trends observed for ethylenediamine and cyanide complexes will be discussed in order to correlate them with the electronic structure. The charge-potential model developed by Siegbahn and his co-workers[5] is used to relate the shift in the core-electron binding energy to the charge distribution in a molecule. According to the model, the binding energy of the relevant electron of the i atom can be given by:

$$E_{\mathrm{i}} = E_{\mathrm{i}}^{\circ} + k_{\mathrm{i}}q_{\mathrm{i}} + \sum_{\mathrm{j}\neq \mathrm{i}} q_{\mathrm{j}}/r_{\mathrm{ij}}. \tag{1}$$

In this equation, E_{i}° is the energy of a reference level; q_{i} and q_{j}, the charges on the i and j atoms respectively, and r_{ij}, the internuclear distance between the i and j atoms. The last term of Eq. 1 represents an intramolecular Madelung-type potential. The value of the k parameter depends on the atomic species and can be obtained experimentally from the chemical-shift data in small molecules. Using Eq. 1, the difference between N1s and C1s can be expressed as follows:

$$\Delta E = k_{\mathrm{N}}q_{\mathrm{N}^*} - k_{\mathrm{C}}q_{\mathrm{C}^*} + \Big(\sum_{\mathrm{i}\neq \mathrm{N}^*} q_{\mathrm{i}}/r_{\mathrm{iN}^*} - \sum_{\mathrm{j}\neq \mathrm{C}^*} q_{\mathrm{j}}/r_{\mathrm{jC}^*}\Big) + E_{\mathrm{N}^*}^{\circ} - E_{\mathrm{C}^*}^{\circ}, \tag{2}$$

where the subscripts, N* and C*, denote, respectively, the particular nitrogen and carbon atoms under consideration and where r_{iN^*} and r_{jC^*} are the distances of the i and j atoms from the particular nitrogen and carbon atoms. The k_{N} and k_{C} values are taken as 21.5 and 21.9 for N1s and C1s respectively. (The units of the charge and the potential are e and V respectively.)[5]

The Trends (1) and (2) Observed for Ethylenediamine Complexes. The trends will be discussed by using Eq. 2. For the sake of simplicity, all the bond lengths and the charges on the carbon and hydrogen atoms are assumed to remain unchanged when the central metal is changed. Then, the difference in ΔE between two complexes can be obtained as follows:

$$\Delta(\Delta E) = \Delta E' - \Delta E = k_{\mathrm{N}}(q_{\mathrm{N}^*}' - q_{\mathrm{N}^*}) + (q_{\mathrm{M}}' - q_{\mathrm{M}})/r_{\mathrm{MN}^*} + (q_{\mathrm{N}}' - q_{\mathrm{N}})(1 + 4\sqrt{2})/2r_{\mathrm{MN}^*}, \tag{3}$$

where M refers to metal atoms, and N to nitrogen atoms different from N*, although $q_{\mathrm{N}} = q_{\mathrm{N}^*}$, $q_{\mathrm{N}}' = q_{\mathrm{N}^*}'$, and $r_{\mathrm{MN}} = r_{\mathrm{MN}^*}$. In this and the following equations, the primed symbols refer to the complex containing the metal of higher atomic number. From the conservation of the charge, one obtains:

$$q_{\mathrm{M}}' - q_{\mathrm{M}} = -6(q_{\mathrm{N}}' - q_{\mathrm{N}}). \tag{4}$$

By substituting Eq. 4 in Eq. 3, one obtains:

$$\Delta(\Delta E) = (q_{\mathrm{N}}' - q_{\mathrm{N}})(k_{\mathrm{N}} - 6/r_{\mathrm{MN}} + (1 + 4\sqrt{2})/2r_{\mathrm{MN}}). \tag{5}$$

If the bond length, r_{MN}, is taken to be 2.0 Å, then the term, $(k_{\mathrm{N}} - 6/r_{\mathrm{MN}} + (1 + 4\sqrt{2})/2r_{\mathrm{MN}})$, has a positive value of 2.3 V.

The trend (1) shows that the $\Delta(\Delta E)$ values are positive for the sequence of Cr^{3+} and Co^{3+} ($\Delta E_{\mathrm{Co}} - \Delta E_{\mathrm{Cr}} = 0.2$ eV) and for Ni^{2+} and Zn^{2+} ($\Delta E_{\mathrm{Zn}} - \Delta E_{\mathrm{Ni}} = 0.4$ eV). Therefore, the term of $(q_{\mathrm{N}}' - q_{\mathrm{N}})$ is positive and the negative nitrogen charge decreases in going from Cr^{3+} to Co^{3+} and from Ni^{2+} to Zn^{2+}. This change in the nitrogen charge results from an increase in the nitrogen-to-metal σ donation with an increase in the atomic number, that is, with an increase in the effective nuclear charge.

For square-planar bis ethylenediamine complexes of Pd^{2+} and Pt^{2+}, Eq. 2 leads to the following equation instead of Eq. 5:

$$\Delta(\Delta E) = (q_{\mathrm{N}}' - q_{\mathrm{N}})(k_{\mathrm{N}} - 4/r_{\mathrm{MN}} + (1 + 2\sqrt{2})/2r_{\mathrm{MN}}). \tag{5'}$$

The substitution of parameter values in Eq. 5′ gives:

$$\Delta E_{\mathrm{Pt}} - \Delta E_{\mathrm{Pd}} = 6.5(q_{\mathrm{N}}' - q_{\mathrm{N}}).$$

The corresponding experimental $\Delta(\Delta E)$ value is 0.4 eV; thus, $(q_{\mathrm{N}}' - q_{\mathrm{N}})$ is positive. This means a greater σ donation in the Pt^{2+} complex, which is consistent with the general tendency for the electronegativity to increase in going down the periodic table in its middle part, where the noble metals appear.

The same argument applies to the trend described under (2) for a tervalent-metal complex to show a larger ΔE value when compared with the complex of a bivalent metal of a similar atomic number. A metal ion of a higher oxidation state is usually more electronegative and usually accepts a larger amount of negative charge from the coordinated nitrogen atoms. Thus, the trends observed in the ΔE values of ethylenediamine complexes can be well explained on the basis of Eq. 3 and correlated with the extent of the σ donation.

The Trends (3) Observed for the Octahedral Cyanide Complexes. Now, we shall turn to the cyanide complexes, $[M(CN)_6]^{3-}$ (M=Cr, Mn, Fe, and Co) and $[M(CN)_6]^{4-}$ (M=Mn and Fe). For these complexes, Eq. 2 leads to:

$$\begin{aligned}\Delta E = {} & k_{\mathrm{N}}q_{\mathrm{N}} + q_{\mathrm{C}}/r_{\mathrm{CN}} + q_{\mathrm{M}}/r_{\mathrm{MN}} + 4q_{\mathrm{C}}/\sqrt{r_{\mathrm{MC}}^2 + r_{\mathrm{MN}}^2} \\ & + 4q_{\mathrm{N}}/\sqrt{2}\,r_{\mathrm{MN}} + q_{\mathrm{C}}/(r_{\mathrm{MN}} + r_{\mathrm{MC}}) + q_{\mathrm{N}}/2r_{\mathrm{MN}} \\ & - (k_{\mathrm{C}}q_{\mathrm{C}} + q_{\mathrm{N}}/r_{\mathrm{NC}} + q_{\mathrm{M}}/r_{\mathrm{MC}} + 4q_{\mathrm{C}}/\sqrt{2}\,r_{\mathrm{MC}} \\ & + 4q_{\mathrm{N}}/\sqrt{r_{\mathrm{MC}}^2 + r_{\mathrm{MN}}^2} + q_{\mathrm{C}}/2r_{\mathrm{MC}} + q_{\mathrm{N}}/(r_{\mathrm{MN}} + r_{\mathrm{MC}})),\end{aligned}$$

which gives the following equation for $\Delta(\Delta E)$ with the metal–carbon and carbon–nitrogen bond lengths of 2.0 and 1.15 Å respectively:

$$\Delta(\Delta E) = \Delta E' - \Delta E = 6.0(q_{\mathrm{N}}' - q_{\mathrm{N}}) - 15.1(q_{\mathrm{C}}' - q_{\mathrm{C}}) - 2.6(q_{\mathrm{M}}' - q_{\mathrm{M}}). \tag{6}$$

TABLE 4. THE MULLIKEN CHARGES (IN e) AND CORE-ORBITAL ENERGY DIFFERENCES (IN eV) FOR $[M(CN)_6]^{3-}$ (M=Cr, Mn, Fe, AND Co) AND $[Fe(CN)_6]^{4-}$, AS ESTIMATED BY DV-Xα MO CALCULATIONS

	Cr^{3+}	Mn^{3+}	Fe^{3+}	Fe^{2+}	Co^{3+}
Metal	+1.21	+1.13	+0.98	+0.83	+0.84
Carbon	−0.17	−0.14	−0.05	−0.06	−0.04
Nitrogen	−0.53	−0.55	−0.61	−0.74	−0.60
ΔE(N1s−C1s)	110.0	109.9	109.9	109.8	109.6

With the relation between the charges given by:

$$6(q_N'-q_N) + 6(q_C'-q_C) = -(q_M'-q_M), \qquad (7)$$

Eq. 6 can be written as:

$$\Delta(\Delta E) = 21.6(q_N'-q_N) + 0.5(q_C'-q_C). \qquad (8)$$

On the basis of this equation, the relation between the atomic charges and $\Delta(\Delta E)$ will be discussed in this and the following sections.

Since the coefficient of $(q_C'-q_C)$ is much smaller than that of $(q_N'-q_N)$ in Eq. 8, we shall, for the present, ignore the $(q_C'-q_C)$ term. With the XPS result, $\Delta(\Delta E)=-0.4$ eV, for Cr^{3+} and Co^{3+}, Eq. 8 gives $q_N'-q_N=-0.02$. The negative value is to be expected from the qualitative consideration that the cobalt complex with a larger number of dπ electrons will show a greater π back-donation, which increases the electron density at the nitrogen atom; this tendency is, however, partially compensated for by the greater effective nuclear charge of Co^{3+}. This may explain why the charge on nitrogen is slightly more negative in the cobalt complex than in the chromium complex. Consistent results are obtained from the infrared spectroscopy, which shows that the force constant of the M–C vibration is greater for Co^{3+} than for Cr^{3+}, while that of C–N remains nearly constant.[6] Table 4 shows the results of our DV-Xα MO calculation,[7] which are in qualitative agreement with the above findings, although the $(q_N'-q_N)$ value (−0.07) and the $\Delta(\Delta E)$ value (1.5 eV) derived from the calculated atomic charges are greater (in absolute values) than those obtained from the experimental results. The $(q_C'-q_C)$ value is positive and greater than $-(q_N'-q_N)$, showing that the σ donation increases in going from the Cr^{3+} to the Co^{3+} complex by a larger amount than the increase in the π back-donation. The $\Delta(\Delta E)$ value (0.4 eV) obtained as the difference of calculated N1s and C1s energies showed a good agreement with the XPS result (0.4 eV).

The Trend (4) Observed between $[M(CN)_6]^{4-}$ and $[M(CN)_6]^{3-}$ (M=Mn and Fe). The relation of the charges between bivalent and tervalent complexes is:

$$q_M' + 6q_C' + 6q_N' = q_M + 6q_C + 6q_N + 1.0, \qquad (9)$$

where the prime refers to the tervalent complexes. If the geometry of complexes is the same as has been described above, the equation for $\Delta(\Delta E)$ can be obtained as follows:

$$\begin{aligned}\Delta(\Delta E) &= \Delta E(M^{3+}) - \Delta E(M^{2+})\\ &= 21.6(q_N'-q_N) + 0.5(q_C'-q_C) - 2.6. \qquad (10)\end{aligned}$$

Experimentally, the $\Delta(\Delta E)$ value was found to be about 0.2 eV, so that we may write;

$$0.2 + 2.6 = 21.6(q_N'-q_N) + 0.5(q_C'-q_C). \qquad (11)$$

Disregarding $0.5(q_C'-q_C)$, we obtain $q_N'-q_N=0.13$. According to the orbital mixing rule,[8,9] a π back-donation from metal to ligand will result in an increased population at the nitrogen atom, but in an almost unchanged or even decreased population at the carbon atom. Thus, the XPS result can be taken as showing the effect of π back-donation; the extent of π back-donation is greater in the Fe^{2+} than in the Fe^{3+} complex. This is also shown by the force constants reported for the M–C and C–N vibrations. Thus, the M–C force constant is greater for Fe^{2+} than for Fe^{3+}, while the C–N force constant is smaller for the Fe^{2+} complex.[10] The results of our MO calculations (given in Table 4) are also in good agreement with the XPS results. Thus, the charges at the nitrogen atom of the complexes are −0.74 (Fe^{2+}) and −0.61 (Fe^{3+}), which give $q_N'-q_N=0.13$. This agrees excellently with the result (0.13) derived from the XPS data by disregarding the $q_C'-q_C$ term. Therefore, $q_C'-q_C$ can be expected to be small, and a consistent result of $q_C'-q_C=0.01$ is shown by the MO calculation. Thus, the positive $\Delta(\Delta E)$ shows that the major part (more than 72%) of the decreased negative charge of the complex has been lost from the nitrogen atoms; for $\Delta(\Delta E)=0.2$ in the case under consideration, the loss from the nitrogen atoms amounts to 76%. This means that the π back-donation greatly decreases in going from the Fe^{2+} to the Fe^{3+} complex.

The Trend (5) Observed for the Isoelectronic Cyanide Complexes. The trend (5) will be discussed in the case of the octahedral complexes, *e.g.*, $[Fe(CN)_6]^{4-}$ and $[Co(CN)_6]^{3-}$. If $0.5(q_C'-q_C)$ is ignored in comparison with $21.6(q_N'-q_N)$ in Eq. 8, we obtain:

$$0.1 + 2.6 = 21.6(q_N'-q_N), \qquad (12)$$

where the prime refers to tervalent complexes. Equation 12 gives 0.13 for the value of $(q_N'-q_N)$, which is in good agreement with the value of 0.14 obtained from the DV-Xα MO calculation for the Fe^{2+} and Co^{3+} complexes.[10] The above argument on the basis of XPS results is also supported by the small value of $(q_C'-q_C)$ (=0.02) from DV-Xα.

In the cases of $[Au(CN)_2]^-$ and $[Hg(CN)_2]$ with $D_{\infty h}$ symmetry (N–C–M–C–N), the metal–carbon and carbon–nitrogen bond lengths are taken to be 2.0 and 1.15 Å respectively, and the relation between the charges is given by:

$$2q_N' + 2q_C' + q_M' = 2q_N + 2q_C + q_M + 1.0, \qquad (13)$$

where the prime refers to $[Hg(CN)_2]$. Then, the following equation can be obtained:

$$\Delta(\Delta E) = 13.7(q_N'-q_N) - 4.9(q_C'-q_C) - 2.6. \qquad (14)$$

As a first approximation, $(q_C'-q_C)$ is disregarded, as

Table 5. The Mulliken charges (in e) and core-orbital energy differences (in eV) for $D_{\infty h}$ symmetry complexes, as estimated by DV-Xα MO calculation

	$[Ag(CN)_2]^-$	$[Au(CN)_2]^-$	$[Hg(CN)_2]$
Metal	+0.42	+0.33	+1.11
Carbon	−0.22	−0.17	−0.26
Nitrogen	−0.50	−0.49	−0.30
ΔE(N1s−C1s)	110.2	109.7	110.5

in the above cases. Then, with the observed $\Delta(\Delta E)$ value of 0.3 eV, we obtain $q_N' - q_N = 0.21$, which means a smaller π back-donation in $[Hg(CN)_2]$ than in $[Au(CN)_2]^-$. This can be expected from the higher nuclear charge of the central ion for the former. The MO calculation gave a consistent result, $q_N' - q_N = 0.19$.[11] However, the MO calculation showed that $(q_C' - q_C)$ $(= -0.09)$ is not so small (in absolute value) as to be neglected.[12] The negative value means that the carbon atom has a more negative charge when it is coordinated to Hg^{2+} than when linked to Au^+. This might seem to contradict the higher electronegativity of Hg^{2+}; however, it can be understood electrostatically by considering the higher polarizing power of Hg^{2+}. It is also consistent with the molecular orbital consideration that the greater π back-donation in the Au^+ complex will cause a more extensive mixing of the antibonding CN^- π orbital into the bonding CN^- π, in-phase at N and out-of-phase at C. The importance of the change in π back-donation has also been demonstrated in this case. Calculating $\Delta(\Delta E)$ with the atomic charges from the MO calculation, we obtain 0.4 eV for $\Delta(\Delta E)$, which is nearly equal to the XPS result (0.3 eV). (The ΔE(N1s−C1s) values directly obtained from the MO calculation (Table 5) also show a consistent trend, although the $\Delta(\Delta E)$ value is twice as large.)

The Trend (6) Observed for Complexes of the Metals of the Same Family. The ΔE value slightly decreased in going down the periodic table in each family. A discussion of $\Delta(\Delta E)$ similar to those made above cannot be made here, because the differences in the M–C distance are appreciable in the present case. With the calculated atomic charges for the Ag^+ and Au^+ complexes (Table 5), however, Siegbahn's equation gave a $\Delta(\Delta E)$ value (−0.1 eV) consistent with the XPS result (−0.2 eV).

The Trend (7) Observed between Complexes of Different Symmetries. The coordination of cyanide ions to a metal ion results in a shift of the negative charge from the ligands to the metal ion. When the oxidation number of the metal ion remains the same, the total charge received by the metal ion will not remarkably change from one metal ion to another. Thus, the donation per ligand will be less in $[Fe(CN)_6]^{4-}$ than in $[Ni(CN)_4]^{2-}$, for example. The smaller net donation can be attributed to a smaller σ donation or to a larger π back-donation; the former leaves more negative charge on C, and the latter increases the electronic density on N. The observed tendency for the ΔE value to be smaller for a hexacyano than for a tetracyano complex implies the importance of the effect of the π back-donation. Among the tetracyano complexes, the observed ΔE value is smaller for a planar than for a tetrahedral coordination. This may also indicate a greater π back-donation in the planar complexes.

The Trend (8) Observed for Most of the Cyano Complexes. As has been described above, the electronic density of the cyanide ion is decreased on C, and increased on N, by the ligation of the cyanide ion to a metal ion. Thus, compared with the free cyanide ion, the ΔE value can be expected to be smaller in a complex. This is demonstrated by the XPS results (Table 3). The exceptionally high ΔE value for $[Zn(CN)_4]^{2-}$ may be attributed to the poor π back-donation and/or the polarization of the CN^- ligand. Though less pronounced, a similar situation is also found in other tetrahedral complexes. The Cr^{3+} ion is the hardest of the metal ions listed in Table 3 and has only three dπ electrons. Thus, a large ΔE value can be expected for $[Cr(CN)_6]^{3-}$, in agreement with the XPS results.

Conclusion

The ΔE value, the difference between the N1s and C1s orbital energies, was measured for various ethylenediamine complexes and cyano complexes. The following trends were observed.

1) The ΔE value was not influenced by the counter ion or by the charging-up of the sample, and the observed trends could be related to the trends in the charge distribution of the complex and the character of the coordinate bond by making use of Siegbahn's equation and also by means of the DV-Xα MO calculation.

2) For ethylenediamine complexes, the ΔE value increased in the following orders: $Cr^{3+} < Co^{3+}$, $Ni^{2+} < Cu^{2+} < Zn^{2+}$, and $Ni^{2+} < Pd^{2+} < Pt^{2+}$. These indicate the sequences of the decreasing negative charge of the nitrogen atom or the increasing donation of electrons from ligand to metal.

3) For cyanide complexes, the following trends are found and explained. The ΔE value increased in the following orders: $Cr^{3+} < Mn^{3+} < Fe^{3+} < Co^{3+}$, $Mn^{2+} < Fe^{2+}$, $Mn^{2+} < Mn^{3+}$, $Fe^{2+} < Fe^{3+}$, $Mn^{2+} < Fe^{3+}$, $Fe^{2+} < Co^{3+}$, $Au^+ < Hg^{2+}$, $Os^{2+} < Fe^{2+}$, $Pt^{2+} < Pd^{2+} < Ni^{2+}$, $Au^+ < Ag^+$, $Hg^{2+} < Cd^{2+} < Zn^{2+}$ (for complexes of the same symmetries), and $O_h < D_{4h} < T_d$ (for those of different symmetries). In the $[M(CN)_6]^{3-}$ (M: Cr→Co) and $[M(CN)_6]^{4-}$ (M: Mn→Fe) series, Siegbahn's equation shows that the tendency observed in ΔE reflects mainly the change in the nitrogen charge. The greater change in the carbon charge, as shown by the DV-Xα calculation, has a minor effect on the ΔE value. In $[M(CN)_6]^{n-}$ (M=Mn and Fe), the nitrogen charge becomes less negative by about 0.1 in going from the M^{2+} to the M^{3+} complex with a decreasing π back-donation, whereas the carbon charge remains almost unchanged. For complexes of different metal ions with the same electronic configuration, the ΔE value is controlled by the nitrogen charge, whose difference is about 0.2 between Hg^{2+} and Au^+ and 0.13 between Mn^{2+} and Fe^{3+} and between Fe^{2+}

and Co^{3+}. The π back-donation is shown to be also important in accounting for the trend observed in the ΔE values of complexes of different geometries and of free CN^-.

4) The DV-Xα MO calculation gave results consistent with the XPS results, thus showing its usefulness for the interpretation of the XPS results.

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