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An X-Ray Photoelectron Spectroscopic Study of Several Ligands in Coordination Compounds

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The N(1s) electron binding energies were measured by means of X-ray photoelectron spectroscopy for the complexes of 2-pyridinecarboxylic acid, 8-quinolinol, and anthranilic acid with a variety of bivalent metal ions. The correlations of their binding energies with the electronegativity and the ionic potential (Z/r) of the metal ion and the charge on the nitrogen atom, and the covalent character of the nitrogen-metal bond calculated on the basis of Pauling's concept were examined. The chemical shift in the N(1 s) binding energy was about 1 eV at most. However, it was suggested that it is possible to use the chemical shift to determine the nature and strength of the nitrogen-metal bond in a series of complexes of the same ligand.

X-Ray photoelectron spectroscopy (XPS) is now extensively used to study the electronic and geometric structures of coordination compounds. There have been many studies of the determinations of the oxidation state of elements, the donor-acceptor capacity of ligands, the mode of ligand coordination, the structure of valence levels, *etc.* However, there have been few studies in which the effect of a variety of metal ions of both transition and typical elements on the binding energy of inner-shell electrons of a ligand in a series of complexes of the ligand has been systematically examined.[1)]

The purpose of the present study is to determine the N(1s) electron binding energies of the complexes of the three bidentate ligands involving nitrogen and oxygen donor atoms—2-pyridinecarboxylic acid, 8-quinolinol, anthranilic acid, with various bivalent metal ions, and to examine the correlations of their binding energies with the electronegativity and the ionic potential of the metal ion and the charge on the nitrogen atom and the covalent character of the nitrogen–metal bond calculated based upon Pauling's concept.[2)]

Experimental

The X-ray photoelectron spectra were measured on an AEI ES200 spectrometer. Al k_α (1486.6 eV) and Mg k_α (1253.6 eV) X-ray radiations were used as the excitation sources. Samples were ground to powder and then dusted onto a double-backed adhesive tape. The measurements were run at room temperature under a vacuum of about 10^{-7} Torr. However, a freezing technique was used for a few volatile samples. All the free ligands (abbreviated as LH) were commercially available and of an analytical grade, and they were used after recrystallization from ethanol. The metal salts used were acetates except for the following salts: K_2PtCl_4, $PdCl_2$, $Fe(NH_4)_2(SO_4)_2$, $SnCl_2$, $BeSO_4$, and $Sr(NO_3)_2$. The complexes were prepared based upon the literature methods.[3)] In outline, the methods consisted of the addition of an ethanol or acetic acid solution of ligands to an aqueous solution of metal salts, in some cases followed by neutralization by an aqueous NaOH or ammonia. The ligand-metal ratios were 2:1 for all the complexes except for the beryllium complex of 2-pyridinecarboxylic acid. The composition of the beryllium complex of 2-pyridinecarboxylic acid was $Be_2OL_2\cdot 2H_2O$, as was the case with its 8-quinolinol complex.[4)] Instead of the beryllium complex of 8-quinolinol, that of 2-methyl-8-quinolinol was used; its composition was BeL_2.[5)] The sodium and perchlorate salts of each LH were obtained by treating LH with NaOH and $HClO_4$ in ethanol respectively. All the compounds were checked by elemental analysis. It is reasonable to assume that the C(1s) binding energy is nearly constant within the complexes of the same ligand. Furthermore, as only the relative energies were considered in the present study, the binding energy of the C(1s) electron peak was used as the energy standard throughout the present experiments; it was taken to be 285.0 eV. The reproducibilities of the values thus obtained were within ±0.1 eV.

Binding-energy Correlations

It has been shown that, in the point-charge model, the core-electron binding energy (abbreviated as BE) can be expressed as follows in terms of the charge density, q_A, on the A atom of interest:[6)]

$$BE = k_A q_A + V + E_R + l_A, \tag{1}$$

where V denotes the electrostatic potential at the nucleus caused by the surrounding atoms, where E_R gives the relaxation energy attributable to photoionization, and where k_A and l_A are constants to be decided from experiments. Here, V is given by the equation: $V = \sum_{A \neq B} q_B/R_{A-B}$, where q_B is the charge on the surrounding atom, B, and where R_{A-B} is the interatomic distance from the B atom to the A atom. For the covalent compound, the summation may be restricted to atomic charges within one molecule. E_R can be expected to be almost constant as long as molecules in similar environments are being compared.[7)]

In this study, the structures of the compounds to be compared are so similar that the N(1s) binding energy may be approximately written as follows:

$$BE = k_N q_N + q_M/R_{M-N} + K \tag{2}$$

where q_N and q_M are the charges on the nitrogen and the metal respectively, where R_{M-N} is the interatomic distance of the metal and the nitrogen atoms, and where K is a constant. Here, all the other terms except for q_M/R_{M-N} in V were regarded as constants.

To a very rough approximation, the N(1s) binding energy is linearly related to the charge of the nitrogen atom.[6)] That is,

$$BE = k'_N q_N + l'_N \tag{3}$$

where k'_N and l'_N are constants.

Results and Discussion

All the compounds used and their N(1s) binding energies are given in Table 1. The electronegativities[8)]

TABLE 1. MEASURED N(1s) BINDING ENERGIES

Sample No.	Compound[a]	*BE*/eV		
		2-Pyridinecarboxylic acid	8-Quinolinol	Anthranilic acid
1	PtL_2	400.4	400.3	400.5
2	PdL_2	400.2	400.1	400.3
3	CuL_2	399.8	399.8	399.9
4	NiL_2	399.5	399.5	399.9
5	CoL_2	399.4	399.5	399.7
6	FeL_2	399.6	—	399.9
7	MnL_2	399.4	399.5	399.7
8	ZnL_2	399.4	399.6	399.8
9	CdL_2	399.5	399.5	399.8
10	HgL_2	400.0	—	400.1
11	SnL_2	399.5	—	399.8
12	PbL_2	399.3	399.5	399.6
13	BeL_2 or Be_2OL_2[b]	399.6	399.6	399.8
14	MgL_2	399.3	399.4	399.7
15	CaL_2	399.1	399.1	399.8
16	SrL_2	399.1	399.1	399.6
17	BaL_2	399.0	399.1	399.6
18	LNa	399.0	398.9	399.3
19	LH	399.2	399.1	399.6
20	LH_2ClO_4	401.4	401.5	402.0

a) Crystal waters in the structural formula were omitted because of the negligible effect of crystal water on the N(1s) binding energy. b) The formula corresponds to the complex of 2-pyridinecarboxylic acid.

and ionic[9] and atomic[10] radii adopted in this study are given in Table 2, along with the calculated charges and covalent characters.

All the N(1s) binding energies of the complexes of the three ligands were equal to, or higher than, those of the corresponding sodium salts, while they were lower than those of the corresponding perchlorates. The changes in the binding energy, the chemical shifts, were about 1 eV at most. These chemical shifts were considered to be attributable to the decreases in the electron density on the nitrogen atoms caused by the coordination of the lone-pair electrons of the nitrogen atoms to the metal.

In this study, the O(1s) binding energies were not discussed because of their small chemical shifts compared with those of the N(1s) binding energies.

Correlations between N(1s) Binding Energies and Electronegativities. Qualitatively, the electronegativity of an element is considered to be a measure of its ability to attract electrons. Therefore, it can be expected that, within the complexes of the same ligand, the binding energy of the donor atom of the ligand increases with the electronegativities of the metal ions involved.

The correlation between the N(1s) binding energy and the electronegativity in the complexes of 2-pyridinecarboxylic acid is shown in Fig. 1. An increase in the binding energy with the increase in the electronegativity could be observed, although the trend was weak. The correlations in the complexes of 8-

TABLE 2. SEVERAL PHYSICAL CONSTANTS AND CALCULATED CHARGES

Element	Electronegativity[a] (χ)	Ionic radius r/Å	Atomic radius/Å	C(%)[b]	q_N[c]	q_M[c]	q_M/R_{M-N}
Pt	2.28	0.80	1.32	76.7	0.364	−0.963	−0.5
Pd	2.20	0.80	1.37	73.5	0.331	−0.831	−0.4
Cu	2.10	0.72	1.28	69.3	0.290	−0.663	−0.3
Ni	1.91	0.69	1.24	61.3	0.209	−0.339	−0.2
Co	1.88	0.72	1.25	60.0	0.196	−0.288	−0.1
Fe	1.83	0.74	1.35	57.8	0.175	−0.203	−0.1
Mn	1.55	0.80	1.36	46.1	0.057	0.259	0.1
Zn	1.65	0.74	1.37	50.2	0.099	0.098	0.0
Cd	1.69	0.97	1.52	51.9	0.115	0.032	0.0
Hg	2.00	1.10	1.55	65.1	0.248	−0.493	−0.2
Sn	1.80	0.93	1.58	56.5	0.162	−0.152	−0.1
Pb	1.87	1.21	1.74	59.5	0.192	−0.271	−0.1
Be	1.57	0.35	1.12	46.9	0.066	0.228 0.408[d]	0.1 0.2[d]
Mg	1.31	0.66	1.60	36.8	−0.036	0.621	0.3
Ca	1.00	0.99	1.96	26.3	−0.140	1.022	0.4
Sr	0.95	1.12	2.15	24.9	−0.155	1.079	0.4
Ba	0.89	1.34	2.24	23.1	−0.172	1.144	0.4
C	2.55						
N	3.04(3.31)[e]		0.74[f]				
O	3.44(3.80)[e]						
H	2.20						

a) Pauling's electronegativities. The values for the metal atom correspond to the +2 oxidation state. b) The covalent characters of the nitrogen-metal bonds estimated on the basis of Pauling's partial ionic character. c) The charges on the nitrogen and the metal atoms calculated based upon the Pauling's concept. d) The values correspond to the $Be_2OL_2 \cdot 2H_2O$ structure. e) The electronegativities of N^+ and O^+ estimated by Pauling's method. f) The covalent radius of the nitrogen atom.

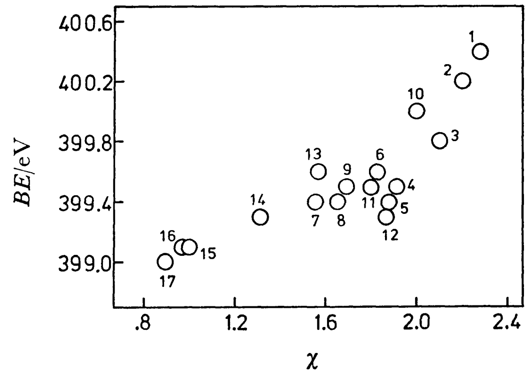

Fig. 1. Correlation between the N(ls) binding energies and the electronegativities of metals. Numbers refer to Table 1.

quinolinol and anthranilic acid were similar.

Correlations between N(1s) Binding Energies and Charges. The charges, q_N and q_M, in Eq. 2 were calculated by a method[11] utilizing Pauling's partial ionic character. That is, in general, the q_A on the A atom can be expressed as follows: $q_A = Q_A + \sum_{A \neq B} I_{AB}$, where Q_A is the formal charge on the A atom, and where I_{AB} is the partial ionic character of the A–B bond. Here, I_{AB} is given by the equation: $I_{AB} = 1 - \exp\{-0.25(\chi_A - \chi_B)^2\}$, where χ_A and χ_B are the electronegativities of the A and B atoms. In spite of a great deal of arbitrariness involved in obtaining the charge in this way, many good correlations have been reported between such a charge and the core-binding energy.[12] Because the bond length data for most of the compounds in Table 1 were not known, R_{M-N} in Eq. 2 was replaced for convenience by the sum of the atomic radius of the metal atom and the covalent radius of the nitrogen atom.

The values of q_N, q_M, and q_M/R_{M-N} thus obtained are given in Table 2. Here, the values of q_N in the table are for the complexes of 2-pyridinecarboxylic acid and 8-quinolinol; those for anthranilic acid are omitted.

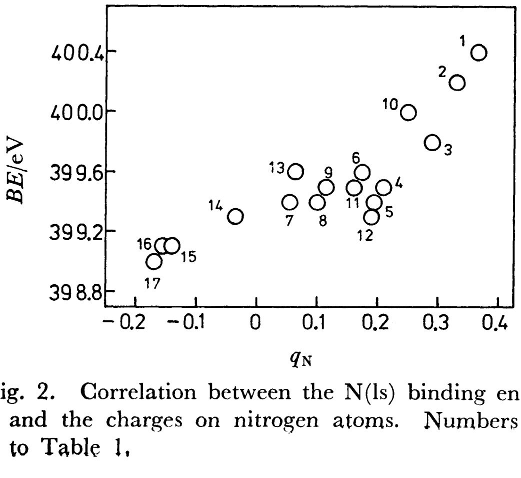

Fig. 2. Correlation between the N(ls) binding energies and the charges on nitrogen atoms. Numbers refer to Table 1.

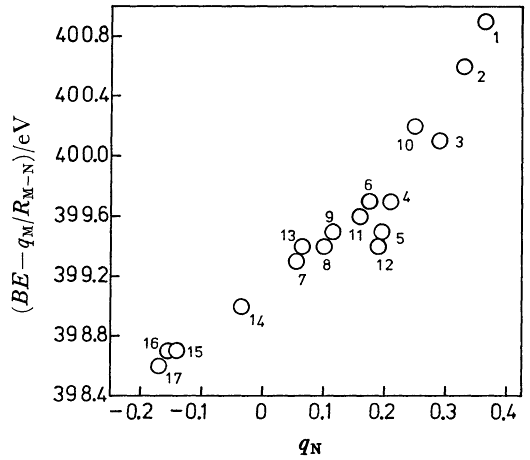

Fig. 3. Correlation between the corrected N(ls) binding energies and the charges on nitrogen atoms. Numbers refer to Table 1.

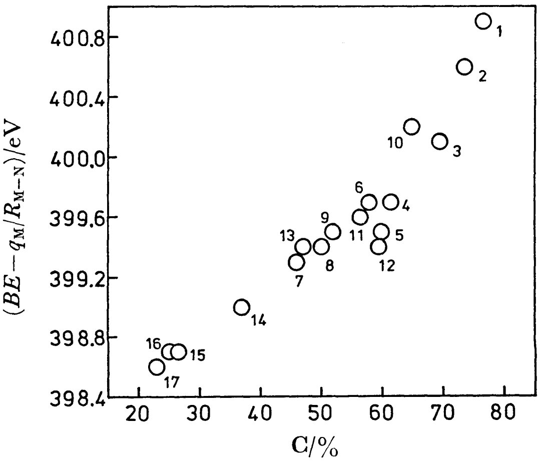

Fig. 4. Correlation between the corrected N(ls) binding energies and the covalent characters of the nitrogen–metal bonds. Numbers refer to Table 1.

For the complexes of 2-pyridinecarboxylic acid, the correlations of q_N with the binding energy and the corrected binding energy $(BE - q_M/R_{M-N})$ are shown in Figs. 2 and 3. In both figures, an increase in the binding energy with an increase in the charge was observed, although its trend was not linear. As can be seen in Fig. 3, the inclusion of the correction term, q_M/R_{M-N}, slightly improves the correlation. For the complexes of 8-quinolinol and anthranilic acid also, similar correlations were observed.

Correlations between N(1s) Binding Energies and Covalent Characters. The covalent characters (abbreviated as C (%)) of the nitrogen–metal bonds, estimated on the basis of Pauling's partial ionic character,[2] are given in Table 2. That is, the covalent character corresponds to $100(1 - I_{MN})$, where I_{MN} is the partial ionic character of the bond. For the complexes of 2-pyridinecarboxylic acid, the correlation between the corrected binding energy $(BE - q_M/R_{M-N})$ and the covalent character is shown in Fig. 4. An increase in the binding energy with the increase in the covalent character was observed. For the complexes of 8-quinolinol and anthranilic acid also, similar correlations were observed.

Considering the $\Delta H - T\Delta S = -RT\ln K$ relationship, it is seen that the stability constants of complexes, K, are functions of both the enthalpy change, ΔH, and the entropy change, ΔS. However, if the ligand is the same, and there is also no significant difference in the size or structure of the complexes (*i.e.*, if ΔS is practically constant), the variation in their stabilities is primarily attributable to the difference in the strength of the metal-to-donor bond represented by ΔH. Therefore, in a bond in which pi bonding is not involved or in which sigma bonding is dominant, the stronger this bond is, that is, the more the covalent character of the bond, the more is the electron deficiency around the nitrogen atom, resulting in a corresponding increase in the N(ls) binding energy.

The higher binding energies of the complexes of the Pd and Pt of transition metal ions (Nos. 1—7 in the figure), of the Hg of zinc family ions (Nos. 8—10), and of the Be of alkaline earth ions (Nos. 13—17) compared with the other metal ions of each group seem to be consistent with the general trend that the above four metal ions form the more stable complexes in each group.

Correlations between N(1s) Binding Energies and Ionic Potentials. For the complexes of 2-pyridinecarboxylic acid, the correlation between the corrected binding energy and Z/r is shown in Fig. 5. The correlations for the complexes of 8-quinolinol and anthranilic acid were similar to Fig. 5. From the figure, the following facts were observed. In the group of alkaline earth ions, the binding energy increases linearly with Z/r. In the group of transition metal ions and zinc family ions, however, such no trend is observed at all. Furthermore, the binding energies of the latter group were considerably higher than those of the former metal ions with similar ionic potentials.

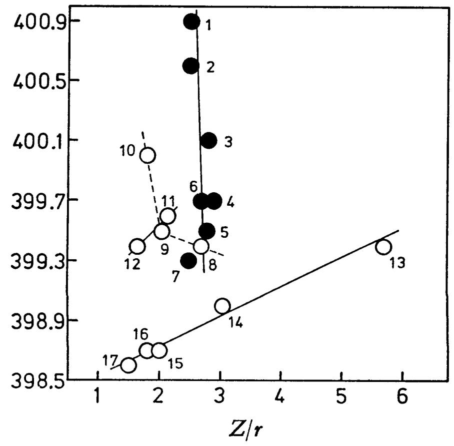

Fig. 5. Correlation between the corrected N(ls) binding energies and ionic potentials. Numbers refer to Table 1.
●: Complexes of transition elements, ○: complexes of typical elements.

These facts clearly suggest the difference in bonding type between the two groups. That is, the bonding type is ionic for the former metal ions and covalent for the latter.

The results of this study seem to support the conclusion that it is possible to use the chemical shift in the N(1s) binding energy by means of XPS, even if it is small, to determine the nature and strength of the nitrogen–metal bond in a group of carefully selected compounds.

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References

1) V. I. Nefedov, *J. Mol. Structure*, **46**, 251 (1978).

2) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y. (1960), p. 98.

3) a) A. Kleinstein and G. A. Webb, *J. Inorg. Nucl. Chem.*, **33**, 405 (1971); b) A. G. Hill and C. Curran, *J. Phys. Chem.*, **64**, 1519 (1960); c) Y. Kidani, R. Saito, and H. Koike, *Yakugaku Zasshi*, **92**, 1063 (1972); d) L. Sacconi and R. Cini, *Chem. Abstr.*, **47**, 11835 h (1953).

4) K. Motojima, *Nippon Kagaku Zasshi*, **77**, 95 (1956).

5) K. Motojima, *Bull. Chem. Soc. Jpn.*, **29**, 29 (1956).

6) K. Siegbahn *et al.*, "ESCA Applied to Free Molecules," North-Holland Pub. Co., Amsterdam (1969), p. 108.

7) D. W. Davis and D. A. Shirley, *J. Electron Spectrosc. Relat. Phenom.*, **3**, 137 (1974).

8) A. L. Allred, *J. Inorg. Nucl. Chem.*, **17**, 215 (1961).

9) L. H. Ahrens, *Geochim. Cosmochim. Acta*, **2**, 155 (1952).

10) H. Strunz, "Mineralogisch Tabellen," Akademisch Verlagesgesellschaft (1970).

11) R. Nordberg, R. G. Albridge, T. Bergmark, U. Ericson, J. Hedman, C. Nordling, K. Siegbahn, and B. J. Lindberg, *Ark. Kemi*, **28**, 257 (1967).

12) K. Siegbahn *et al.*, "ESCA Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Almqvist and Wiksells AB, Uppsala (1967).