# NOTES

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## X-Ray Photoelectron Spectroscopy of EDTA-Metal Chelates

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**Synopsis.** Photoelectron spectra of metal chelates of ethylenediaminetetraacetic acid (EDTA) were measured. A nearly linear relationship holds between the chemical shifts of the N(1s) electron binding energies and the charge on the nitrogen atoms of the chelates, calculated by means of Pauling's electronegativity concept.

A technique for studying X-ray photoelectron spectroscopy (ESCA) and the results for EDTA were previously reported.[1] The use of ESCA to determine the effect of coordination on the electron density of a ligand is based on the fact that changes in the electron density about an atom are reflected on changes in the binding energies of the core electrons. It is the aim of this study to determine whether it will be possible to correlate the electronegativity of the metal or the calculated charge on the nitrogen atom with the chemical shift of N(1s) binding energy in the EDTA-metal chelates. The chelate compounds studied (commercial products, analytical grade) are given in Table 1. Al*K*α X-ray was used as an excitation source.

The C(1s), N(1s), and O(1s) electron spectra of the EDTA-Zn chelate are shown in Fig. 1. The spectra of all the other compounds show profiles similar to those of the EDTA-Zn chelate. Two peaks in the C(1s) electron spectrum correspond to the carbon atoms of a methylene group and a carbonyl group, respectively. The peak with the lower binding energy (the carbon of the methylene group) was used as an energy standard, its binding energy being taken to be 285.0 eV throughout this experiment. The N(1s) and O(1s) electron spectra of all compounds were single peaks with full-width at half-height (FWHH) of 2.0—2.2 eV and 2.1—2.3 eV, respectively. The measured N(1s) electron binding energies are given in Table 1. The chemical shifts $\Delta E$ are the differences between the N(1s) electron binding energies of free EDTA (the type of $(\text{-CH}_2)_3\text{N}$) and the chelates. The value of free EDTA was 399.1 eV.[1] The chemical shifts in all chelates are considered to be due to the decrease in the electron density on the nitrogen atoms caused by the coordination of lone-pair electrons of the nitrogen atoms to the metal.

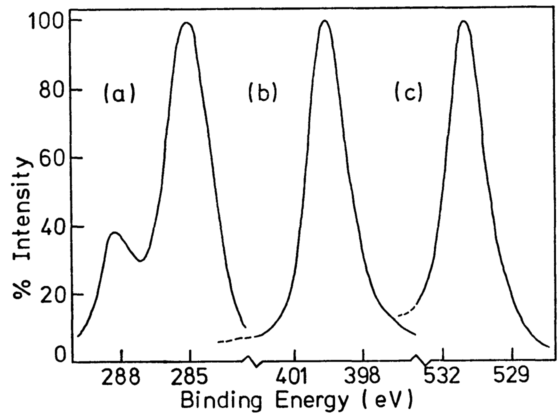

Fig. 1. (a) C(1s), (b) N(1s) and (c) O(1s) photoelectron spectra of the EDTA–Zn chelate.

In the charge-potential model[2] the chemical shift can be expressed in terms of the charge on the atom $Q$ and the Coulomb potential energy $V$ of an electron due to the other atoms of the molecule:

$$\Delta E = k_1 Q + V + k_2 \quad (k_1, k_2;\ \text{constants})$$

In an ionic compound, $V$ includes the contribution

TABLE 1. N(1s) BINDING ENERGY VALUES

| Compounds | M | B.E. of N(1s)[a] (eV) | $\Delta E$[b] (eV) | $\chi$[c] | $Q$[d] | p$K$[e] |
|---|---|---|---|---|---|---|
| EDTA,NaM(II) | Ba | 399.1 | 0 | 0.9 | −0.21 | 7.7 |
| | Ca | 399.2 | +0.1 | 1.0 | −0.18 | 10.7 |
| | Mg | 399.3 | +0.2 | 1.2 | −0.12 | 8.6 |
| | Mn | 399.3 | +0.2 | 1.5 | −0.01 | 13.9 |
| | Zn | 399.5 | +0.4 | 1.6 | +0.04 | 16.5 |
| | Pb | 399.6 | +0.5 | 1.8 | +0.12 | 18.0 |
| | Ni | 399.6 | +0.5 | 1.8 | +0.12 | 18.5 |
| | Co | 399.6 | +0.5 | 1.8 | +0.12 | 16.2 |
| | Cu | 399.5 | +0.4 | 1.9 | +0.16 | 18.8 |
| EDTA, NaM(III) | Fe | 399.2 | +0.1 | 1.8 | +0.12 | 25.1 |
| | Bi | 399.2 | +0.1 | 1.9 | +0.16 | — |

a) Uncertainties are less than or equal to ±0.1 eV. b) Chemical shift of the N(1s) electron binding energy. c) Pauling's electronegativity of the metal. d) Calculated charge on the nitrogen atom. e) The common logarithm of the stability constant of a chelate.

from other ions and is thus a Madelung term. $V$ may play a very important role in ionic compounds. However, for the covalent species the chemical shift should be dominated by the charge $Q$ on the atom concerned.

The charge $Q$ was calculated by means of the correlation $Q=q+\sum I$, proposed by Nordberg *et al.*,[3] where $Q$ is the charge on an atom, $q$ the formal charge of a concerned atom and $\sum I$ the summation of partial ionic characters of various bonds in which the atom is involved. The partial ionic character $I$ was estimated by the relationship $I=1-\exp\{-0.25(\chi_A-\chi_B)^2\}$ derived by Pauling,[4a] in which $\chi_A$ and $\chi_B$ are the electronegativities of A and B atoms, respectively, in the A–B bond concerned.

In the case of EDTA chelates, the relation $Q=1+3I_{N^+-C}+I_{N^+-M}$ was obtained for the charge on the nitrogen atom since $q$ is $+1$. $I_{N^+-C}$ and $I_{N^+-M}$ are the partial ionic characters in the nitrogen-carbon and nitrogen-metal bonds, respectively. The calculated charges using the value 3.3 as the electronegativity of $N^+$ [4b] are listed in Table 1.

On the other hand, the charge calculated in this way on the nitrogen atom of the type of $(-CH_2)_3N$ in free EDTA was $-0.18$. This value corresponds to the charge ($-0.20$) on the nitrogen atom in $(CH_3)_3N$ calculated by del Re,[5] by a semiempirical LCAO-MO method.

A nearly linear relation holds between the chemical shift of the N(1s) electron binding energy ($\Delta E$) and the charge $Q$ on the nitrogen atom in the bivalent metal chelates (Fig. 2). The chemical shifts of the N(1s) in Ba and Ca chelates are very small as expected from their calculated charges.

There are certain trends in the bivalent metal chelates between the chemical shift and the electronegativity of the metal, and between the chemical shift and the common logarithm of the stability constant[6] of the chelate. The chemical shift becomes larger as the electronegativity becomes larger, and the stability of chelates becomes greater.

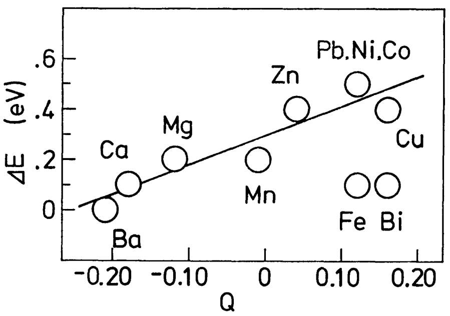

Fig. 2. Relationship between the chemical shift of N(1s) electron binding energy ($\Delta E$) and the charge($Q$) on the nitrogen atom.

In the case of Fe(III) and Bi(III), their chemical shifts are small as compared to those expected from their calculated charges.

There is no appreciable difference in the O(1s) electron binding energy over all the chelates, values being 531.0—531.2 eV.

## References

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