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X-Ray Photoelectron Spectroscopy of EDTA

Tooru Yoshida and Shigemasa Sawada
Osaka Prefectural Industrial Research Institute, Enokojima, Nishi-ku, Osaka 550

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The binding energies of N(1s) in ethylenediaminetetraacetic acid (EDTA) and its related compounds were measured by means of a photoelectron spectrometer, and the molecular structures of EDTA were discussed. Two kinds of peaks were observed in the N(1s) spectra of EDTA and its related compounds, with binding energies of about 401 and 399 eV. In EDTA-4H, the heights of the two peaks were almost equal, while in its sodium salts the peak height with the higher binding energy decreased as the number of carboxylate groups in the molecule increased. In EDTA-4Na, only a single peak with a low binding energy was observed. In EDTP-4H and GEDTA-4H, the spectra showed two peaks with different heights. The binding energy values of the main peaks of simple amino acids, such as glycine and alanine, were about 401 eV. From the above results, it can be deduced that there are two kinds of N atoms, =N$^+$H– and =N– types, in an EDTA molecule.

Ethylenediaminetetraacetic acid (EDTA) is widely used as a chemical reagent because of its ability to form stable and soluble chelate complexes with metal ions. Since the complex stability is partly related to the proton affinity of the acid, a clear idea of the structure of the acid could lead to a better understanding of the metal-complex formation.

EDTA is a compound belonging to the group of amino acids including glycine or alanine, and it may take a zwitterion structure even in the solid state. However, the results obtained from the IR spectra do not always give the obvious conclusion. Chapman1) concluded that the tendency to form a zwitterion in both EDTA-4H and EDTA-2Na·$2H_2O$ is less than in simple mono-amino acid, while Nakamoto *et al.*2) reported that EDTA-2Na·$2H_2O$ is almost zwitterionic.

The exact crystal structure of EDTA-4H was determined by Cotrait3) by X-ray analysis. According to his conclusions, two of the four carboxyl groups are used to make intermolecular hydrogen bonds with neighboring molecules, while the remaining two are bonded to the nitrogen atoms intramolecularly.

Recently a new technique of X-ray photoelectron spectroscopy called ESCA has been developed; this method is a very useful tool for learning new aspects of the natures of chemical bonds. A detailed description of the ESCA method has been published by Siegbahn *et al.*4)

Experimental

The X-ray photoelectron spectra were measured on an AEI ES100 spectrometer under the control of a DS100/32 computer data processing system. Al-Kα (1486.6 eV) and Mg-Kα (1253.6 eV) X-ray lines were used as the excitation sources. The abscissa of the chart is the binding energy (BE), while the ordinate is the relative intensity of each peak.

All the compounds measured are given in Table 1. They were all commercially available, were of an analytical grade, and were used without further purification. The samples were ground to powder, dusted onto a double-backed adhesive tape or pressed on a copper mesh, and set inside the measuring chamber. The measurements were then run at room temperature under a vacuum of about 10^{-6} Torr.

Results

1s Spectra of Carbon. Figure 1 shows the spectrum of the C(1s) of EDTA-4H. Two peaks with the different binding energies shown by the broken lines in the figure were obtained by a curve resolution. The

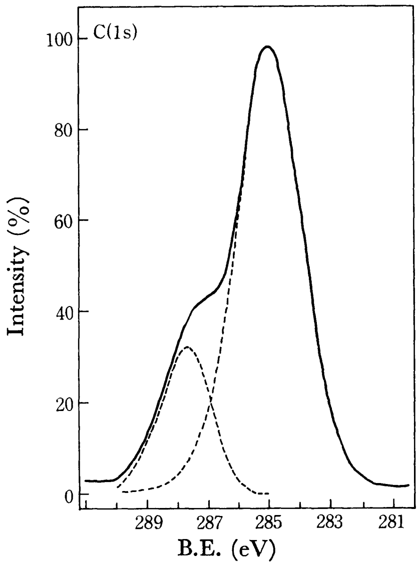

Fig. 1. C(1s) electron spectrum of EDTA-4H.

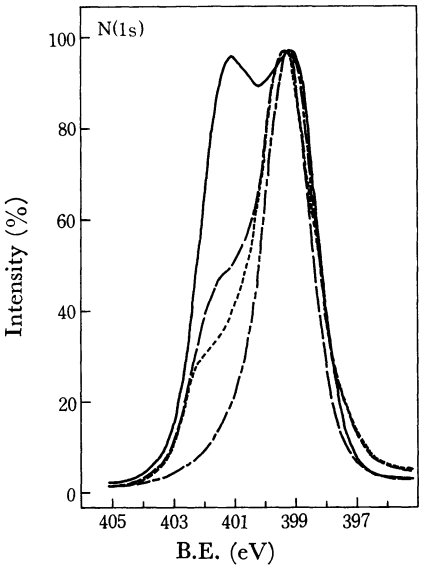

Fig. 2. N(1s) electron spectra
——: EDTA-4H, ----: EDTA-2Na
------: EDTA-3Na, ———: EDTA-4Na

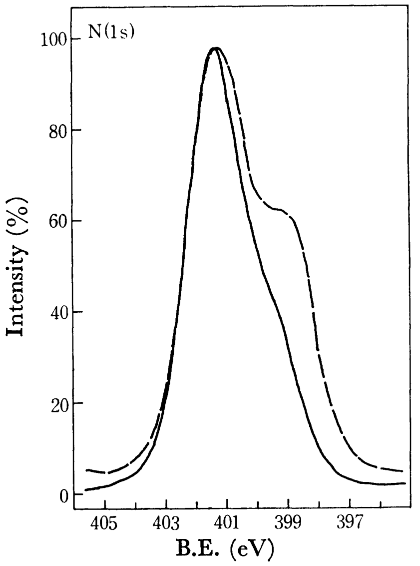

Fig. 3. N(1s) electron spectra.
——: EDTP-4H, ——: GEDTA-4H

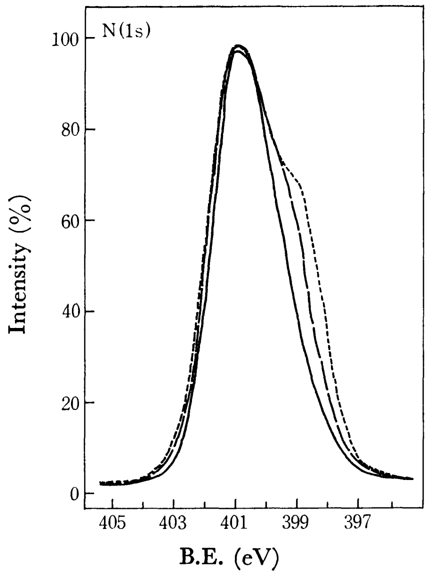

Fig. 4. N(1s) electron spectra.
——: AA, ——: γ-AB, ----: NTA

C(1s) spectra of the other compounds also give profiles similar to that of EDTA-4H. The taller peak (the right-hand one of the two) was used as the energy standard throughout the present experiments.

The differences in binding energy between the two peaks of EDTA-4H and EDTA-4Na were 2.7 and 3.1 eV respectively.

1s Spectra of Nitrogen. In Figs. 2, 3, 4, and 5, the N(1s) spectra of some EDTA derivatives and mono-amino acids are given. EDTA-4H and EDTA-2Na·2H$_2$O show two peaks very clearly, while EDTA-4Na shows a well-defined single peak. The other compounds show spectra with a shoulder or an asymmetric broad profile which suggests the existence of two peaks.

TABLE 1. N(1s) BINDING ENERGY VALUFS

Compounds		N(1s) B.E. (eV)	
Ethylenediaminetetraacetic acid (EDTA-4H) HOOCH$_2$C\ /CH$_2$COOH N(CH$_2$)$_2$N HOOCH$_2$C/ \CH$_2$COOH		401.3 (1)	399.1 (1)
Disodium ethylenediaminetetraacetate (EDTA-2Na)		401.4 (2)	399.3 (5)
Trisodium ethylenediaminetetraacetate (EDTA-3Na)		401.4 (1)	399.3 (3)
Tetrasodium ethylenediaminetetraacetate (EDTA-4Na)			399.2
Ethylenediaminetetrapropionic acid (EDTP-4H) HOOC(H$_2$C)$_2$\ /(CH$_2$)$_2$COOH N(CH$_2$)$_2$N HOOC(H$_2$C)$_2$/ \(CH$_2$)$_2$COOH		401.4 (3)	399.3 (1)
Glycoletherdiaminetetraacetic acid (GEDTA-4H) HOOCH$_2$C\ /CH$_2$COOH N(CH$_2$)$_2$O(CH$_2$)$_2$O(CH$_2$)$_2$N HOOCH$_2$C/ \CH$_2$COOH		401.3 (2)	399.1 (1)
Disodium ethylenediaminetetraacetate dihydrate (EDTA-2Na·2H$_2$O)		401.4 (2)	399.3 (3)
Tetrasodium ethylenediaminetetraacetate dihydrate (EDTA-4Na·2H$_2$O)			399.2
Zinc disodium ethylenediaminetetraacetate (EDTA-Zn)			399.5
Aminoacetic acid (AA)	H$_2$NCH$_2$COOH	400.8 (5)	398.9 (1)
Iminodiacetic acid (IDA)	HN/CH$_2$COOH \CH$_2$COOH	400.9 (3)	399.1 (1)
Nitrilotriacetic acid (NTA)	/CH$_2$COOH N-CH$_2$COOH \CH$_2$COOH	400.9 (2)	398.9 (1)
β-Aminopropionic acid (β-AP)	H$_2$N(CH$_2$)$_2$COOH	400.9 (4)	399.1 (1)
γ-Aminobutyric acid (γ-AB)	H$_2$N(CH$_2$)$_3$COOH	401.0 (3)	399.0 (1)

The numbers in parentheses are the relative intensities roughly determined from the two peaks.

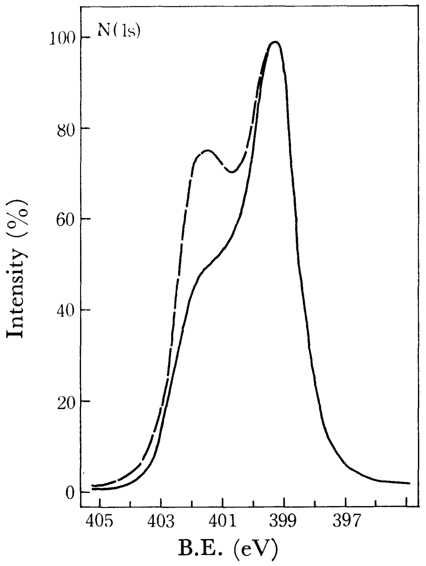

Fig. 5. N(1s) electron spectra.
——: EDTA-2Na, ——: EDTA-2Na·$2H_2O$

The measured values for the N(1s) binding energy are listed in Table 1. The numbers in parentheses indicate the relative intensities roughly determined from the two peaks.

Discussion

C(1s) Signal. There are two kinds of carbons, $-CH_2-$ and –CO–, in EDTA distinguishable by the ESCA method. As the O atom has a higher electronegativity than the H atom, the electron density on the C atom in –CO– is lower than that in $-CH_2-$. Accordingly, the C(1s) signal of –CO– must have a higher binding energy than that of the $-CH_2-$. The fact that the binding-energy difference between these two kinds of carbons in EDTA-4H is about 0.4 eV lower than that in EDTA-4Na may be explained as follows; the electron density on the C atom in –CO– in the former is higher than that in the latter because of the presence of an intermolecular hydrogen bond in the former, so the binding energy of the C atom in –CO– in the former is lower than that in the latter.

As many precise discussions[5] based on some theoretical calculations have been reported with regard to this difference in binding energy, which is called a chemical shift, no further discussion will be given here. The binding energy value of C(1s) of $-CH_2-$ is taken to be 285.0 eV.

N(1s) Signals. Figure 2 shows the existence of two different states of the nitrogen atom in EDTA. From the binding energy values of the major peaks of N(1s) observed in simple amino acids, such as AA, IDA, NTA, β-AP, and γ-AB, it may be concluded that the higher binding energy peak of the two in EDTA can be assigned to the N atom with the $-\overset{+}{N}H-$ structure. The value of this binding energy is about 401 eV. Hence, the remaining peak, with a lower binding energy, can be assigned to the ordinary N atom, which has the =N– structure. The binding energy value of the remaining peak is about 399 eV, almost coincident with that of the single peak of EDTA-4Na, in which the zwitterion structure can not exist.

According to the analysis of the X-ray diffraction patterns, EDTA-4H belongs to the $C_{2/c}$ space group and has a symmetry center at the middle point of $=NCH_2CH_2N=$. Two of the four carboxylic H atoms have a shorter distance to the N atom than the other two, suggesting protonation or hydrogen bonding. On the contrary, the ESCA spectrum shows that, in a crystalline state, the two N atoms in an EDTA-4H molecule are not equivalent in electronic charge.

As for the series of the Na salts of EDTA, the spectra also show the existence of two kinds of nitrogen and a trend for the peak height of the protonated $=\overset{+}{N}H-$ group to decrease as the number of the carboxylate group in the molecule increases. The decrease in the number of carboxyl groups in a molecule will reduce the possibility of protonation to the N atom.

As is shown in Fig. 5, crystal water in EDTA-2Na seems to have a particular effect on the ESCA spectrum of N(1s), but it does not in EDTA-4Na. Assuming that the hydrated Na salt conforms the same spatial molecular arrangement as that[6] of the hydrated K or Rb salt, it may be considered that H atoms from crystal water are preferably used to make an intermolecular hydrogen bond, while the two H atoms of the carboxyl group serve to make an intramolecular hydrogen bond with their own nitrogen atom. Therefore, in EDTA-2Na·$2H_2O$ the opportunity to make a charged amino group will increase.

EDTP-4H and GEDTA-4H have chemical structures similar to that of EDTA-4H, but give different ESCA spectra; that is, the $=\overset{+}{N}H-$ peak is dominant over the =N– peak. This may be explained as follows: in EDTP-4H, the distance between the two N atoms is the same as in EDTA-4H, but the side-chain is longer. Therefore, ring formation is easier than in EDTA-4H. In GEDTA-4H, the side-chain is the same as in EDTA-4H, but the N-to-N distance is longer, so the repulsion of the developed positive charge on each nitrogen atom is less than in EDTA-4H.

On the basis of the results obtained here, it may be considered that there are at least two factors affecting the appearance of two peaks on the ESCA spectrum of EDTA-4H. One is steric hindrance, which makes it hard to build up a five-membered ring, and the other is charge repulsion, which prevents too much density of the positive charge at the center of a molecule.

The N(1s) spectrum of the EDTA-Zn chelate showed a single peak with a binding energy falling between those of the protonated and the unprotonated N(1s) of EDTA-4H. Detailed discussions of this and other EDTA-metal chelates will be published elesewhere.

All of the N(1s) spectra in the simple amino acids examined are more or less doublets. Although no clear explanation of this can be given here, it may be conceived that the steric environment around the N atom in AA, IDA, and NTA will reduce the chance for the H atom to attach to the N atom.

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