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X-Ray Photoelectron Spectroscopy of Oxine-Metal Chelates

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Synopsis. Photoelectron spectra of oxine-metal chelates were measured. The chemical shifts of the N(1s) electron binding energy were smaller than 0.7 eV. There were nearly linear relations between the chemical shifts and the electronegativities of metals or the partial ionic characters of the nitrogen-metal bonds of chelates.

X-Ray photoelectron spectroscopy (ESCA) is rapidly becoming an established method in chemical research. The technique provides a sensitive probe of the electronic environment of atoms in molecule. A number of studies by ESCA have shown that the inner level electron binding energies (B. E.) of an atom are sensitive to the over-all charge on an atom.

The use of the ESCA to determine the effect of co-ordination on the electron density of a ligand is based on the fact that change in the electron density about an atom is reflected in 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 a metal or the partial ionic character of the bond between a metal and a ligand with the chemical shift of N(1s) binding energy in oxine-metal chelates.

Experimental

The photoelectron spectra were measured using an AEI ES100 electrostatic electron spectrometer under the control of a DS100/32 computer data processing system. The aluminum K_αX-ray line (1486.6 eV) and magnesium K_αX-ray line (1253.6 eV) were used for photoelectron excitation. All the oxine metal chelates, which have 1 : 2 ratio of metal and oxine, were prepared by ordinary procedures. All samples except free oxine were run at room temperature as powder dusted onto double sided adhesive tape under the vacuum of about 10^{-6} Torr. In the case of free oxine a freezing technique was used because of its high volatility.

To compensate for any sample charging effects, the calibration of the spectra was done using the C(1s) electron line from the carbons present in the samples. Its binding energy was taken to be 285.0 eV throughout this study.

Results and Discussion

Figure 1 showed the C(1s) and N(1s) photoelectron spectra of free oxine. The spectra of chelates showed the profiles similar to those of free oxine. All measured binding energy values were given in Table 1. In the table, ΔE is the chemical shift which is the difference between the N(1s) binding energies of free oxine and each chelate compounds, pK the common logarithm of the stability constant of a chelate which is available in the text book,[1)] χ the Pauling electronegativity of a metal, I the partial ionic character ($I=1-\exp\{-0.25(\chi_N-\chi_M)^2\}$) of the bond between nitrogen and metal given by Pauling[2)] in which χ_N and χ_M are the electronegativities of nitrogen and metal.

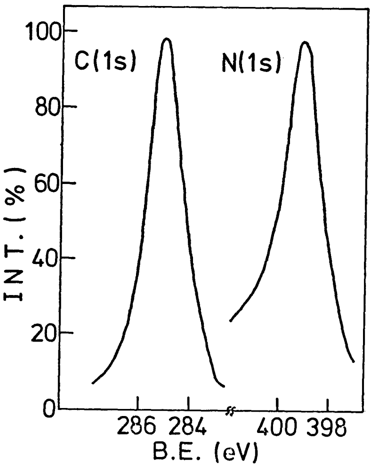

Fig. 1. C(1s) and N(1s) photoelectron spectra of oxine.

Table 1. N(1s) binding energy values

Compound	B.E. of N(1s) (eV)	ΔE[a)] (eV)	pK[b)]	χ[c)]	I[d)] (%)
C_9H_7NO	399.1				
$(C_9H_6NO)_2Ca$	399.1	0	3.2	1.0	63
$(C_9H_6NO)_2Mg$	399.3	0.2	11.7	1.2	55
$(C_9H_6NO)_2Mn$	399.4	0.3	15.3	1.5	43
$(C_9H_6NO)_2Zn$	399.5	0.4	18.8	1.6	39
$(C_9H_6NO)_2Pb$	399.4	0.3	18.7	1.8	30
$(C_9H_6NO)_2Co$	399.5	0.4	19.6	1.8	30
$(C_9H_6NO)_2Ni$	399.5	0.4	21.3	1.8	30
$(C_9H_6NO)_2Cu$	399.7	0.6	26.1	1.9	26

a) The differences between the N(1s) binding energies of chelates ($(C_9H_6NO)_2M$) and the ligand (C_9H_7NO). b) The common logarithms of the stability constants of chelates. c) The electronegativities of metals(M). d) The partial ionic characters in the N-M bond between a metal and a ligand.

Fig. 2 showed the nearly linear relation between the measured chemical shift (ΔE) and the electronegativity (χ). The increase of the N(1s) chemical shift of chelates with the increase of an electronegativity of a metal could be observed. The chemical shifts of the N(1s) binding energy in all chelates on the complex formation were considered to be due to the decrease of the electron density on the nitrogen atoms caused by the co-ordination of lone-pair electrons of the nitrogen atoms to the metal.

In the charge-potential model,[3)] 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. Thus:

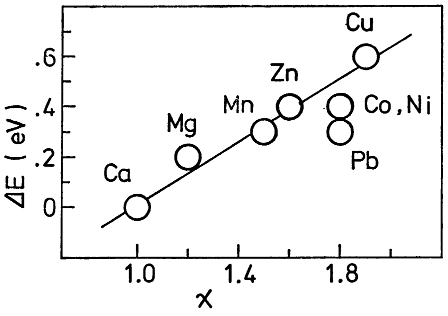

Fig. 2. Relation between the chemical shift of N(1s) binding energy (ΔE) and the electronegativity (χ).

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

In an ionic compound, V includes the contribution from other neighboring ions, that corresponds to a Madelung term. In general, the neglect of V may cause serious error for ionic compounds but for the covalent compound studied here the chemical shift should be dominated by the charge (Q) on the atom concerned.

Here, applying the correlation, $Q = q + \sum I$ (Q; charge on an atom, q; formal charge of a concerned atom, $\sum I$; summation of partial ionic characters of all bonds) proposed by Nordberg *et al.*[4] to the case of oxine chelates, the equation, $Q = I_{\text{C-N}} + I_{\text{C=N}} + I_{\text{N-M}}$, was roughly obtained since q on the nitrogen is zero. Assuming that the summation of the first and second terms of right-hand side in the above equation was constant and V was negligible throughout all the oxine chelates studied here, then the equation, $\Delta E = k_1 I_{\text{N-M}} + K$ (K; constant), could be derived.

In practice, it was observed that this relation approximately held in this study. Figure 3 showed a linear relation between the measured chemical shift (ΔE) of the N(ls) binding energy and the calculated partial ionic character ($I_{\text{N-M}}$) of the bond between nitrogen and metal atoms. This indicated that the increase of the ionic character in the bond, or the decrease of the covalent character leads to the smaller chemical shift.

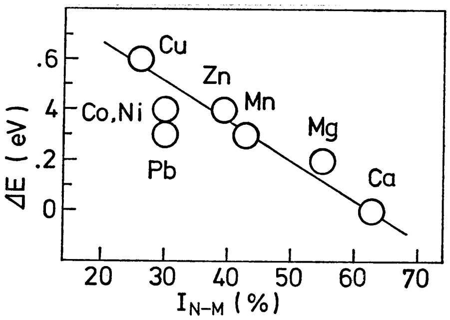

Fig. 3. Relation between the chemical shift of N(1s) binding energy (ΔE) and the partial ionic character ($I = 1 - \exp\{-0.25(\chi_{\text{N}} - \chi_{\text{M}})^2\}$).

Thus it was found that the shift of an inner electron binding energy in ESCA, though it is small, give some important knowledge (ionic or covalent character) for the bonds in co-ordination compounds.

Another point, which may be important in analytical chemistry, obtained in this experiment was that there was some relation between the chemical shift (ΔE) measured in solid state and pK value determined in solution; the higher was the stability of a chelate, the larger was the chemical shift of it.

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