Shift of Fe 3d Band due to Chlorine for Fe(III)(salen)

Akio Shigemi,* Tatsunori Tochio,† Manabu Fujiwara,†† Jun Kawai,††† Takayuki Matsushita,†† Yasuhito Isozumi, Takeshi Mukoyama,†††† and Shigero Ikeda,†††††

Radioisotope Research Center, Kyoto University, Kyoto 606-8501

†*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011*

††*Department of Materials Chemistry, Faculty of Science and Technology, Ryukoku University, Seta, Otsu 520-2194*

†††*Department of Materials Science and Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501*

††††*Kansai Gaidai University, 16-1 Kitakatahoko, Hirakata, Osaka 573-1001*

†††††*SR Center, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu, Shiga, 525-8577*

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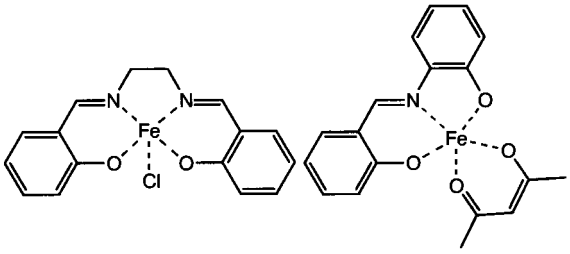
The valence band (VB) spectrum of an iron(III) complex, [Fe(salen)Cl], in X-ray photoelectron spectroscopy (XPS) has been calculated with the DV-Xα molecular-orbital method. The influence of chlorine (Cl) in the VB spectrum is examined. It is found that the shallowest binding energy peak in VB spectrum originates from Cl 3p and Fe 3d, and Fe 3d band is deepened due to chlorine for the Fe(III) Schiff base complex in the XPS VB spectra.

We measured the XPS VB spectra of chloro(*N*,*N'*-ethylenebissalicylideneaminato)iron(III) complex: Fe(salen)Cl and (*N*-hydroxyphenyl-salicylideneaminato)(acetylacetonato)iron(III) complex: Fe(*N*-PhO-sal)(acac). The chemical structures and abbreviations of iron(III) Schiff base complexes were shown as follows:



(1) Fe(salen)Cl (2) Fe(*N*-PhO-sal)(acac)

The XPS VB spectra were studied by Fujimori et al.,[1] Zimmermann et al.,[2] and Ueno et al.[3] In order to interpret the XPS VB spectrum of Fe(salen)Cl, the theoretical calculation of electron distribution of each orbital per one molecule has been carried out. We performed a comparison the theoretical XPS spectrum with photoionization cross-sections and the theoretical XPS spectrum without them, reported by Yamaguchi et al.[4] We adopted the values calculated by Yeh et al.[5] For the value of photoionization cross-sections, in the present letter, we report that 3d band deepens due to chlorine for the Fe(III) Schiff base complex in the XPS VB spectra.

The iron(III) complexes were prepared by a procedure similar to that in the literature.[6] The XPS spectra were measured on a Rigaku XPS-7000 spectrometer. Mg Kα (1253.6 eV) X-ray line was used as the excitation source (10 kV and 30 mA). The step size was 0.1 eV with a dwelling time of 0.5 s. The sample complexes were ground to fine powders form, dusted onto a double-backed adhesive tape with electronic conduction, and set inside the measuring chamber automatically. The measurements were then run at room temperature under vacuum below 10^{-6} Pa. The pass energy of the spherical electron energy analyzer was 15 eV.

We have calculated the electronic structure of the ground state of them using the spin-unrestricted DV-Xα molecular-orbital (MO) method.[7] Therefore, the orbital energy in this paper is different from that of Koopman's theorem, because DV-Xα is one of density functional theory (DFT) method. The model clusters used in the present calculation were each one molecule of Fe(salen)Cl, Fe(salen) and Fe(*N*-PhO-sal)(acac) complexes. The information about the atomic positions was derived from the X-ray crystal structure analysis data. These cluster models have chemical form of [Fe($C_{16}H_{14}N_2O_2$)Cl], [Fe($C_{16}H_{14}N_2O_2$)] and [Fe($C_{12}H_9NO_2$)($C_5H_7O_2$)] and non-symmetry. All theoretically calculated spectra are convoluted by a Gaussian function with a full width at half-maximum (fwhm) of 1.0 eV.

Observed XPS VB spectra, theoretically calculated spectrum

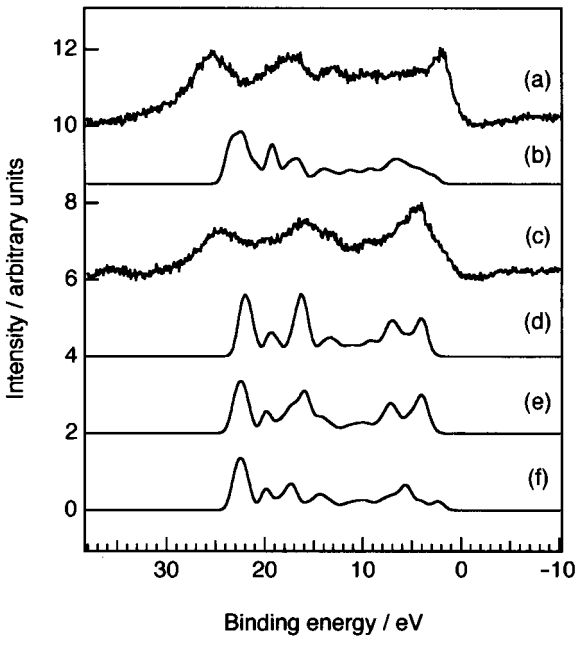


Figure 1. Observed XPS VB spectra (Figure 1 (a) : Fe(*N*-PhO-sal)(acac) and (c) : Fe(salen)Cl), theoretically calculated spectrum (Figure 1 (d)) of Fe(salen)Cl without photoionization cross sections reported by Yamaguchi et al.[4] and our calculated three XPS VB spectra (Figure 1 (b) : Fe(*N*-PhO-sal)(acac), (e) : Fe(salen)Cl and (f) : Fe(salen) model cluster) with photoionization cross sections of Yeh et al.[5] are shown.

of Fe(salen)Cl without photoionization cross sections reported by Yamaguchi et al.[4] and our results of three XPS VB spectra with photoionization cross sections of Yeh et al.[5] are shown in Figure 1. The important difference between (a) and (c) spectrum in Figure 1 is the shape of the peak from 0 to 10 eV. We assumed that this difference was the effect of either chlorine or structure. In order to confirm this, we calculated three kinds of the theoretical XPS spectrum with photoionization cross-sections obtained by Yeh et al.[5] The calculated energy was shifted in such a way that the position of the peak having the shallowest binding energy is to be same as that in the observed spectrum (4.0 eV) for Fe(salen)Cl and the position of the peak having the deepest binding energy is to be same as that in the calculated spectrum (22.4 eV) for Figure 1 (e). The intensity was normalized to make the intensity of the peak having the shallowest binding energy to be 1 in each theoretical spectrum and to be 2 in each experimental spectrum. The theoretically calculated XPS spectra were shown in Figure 1 (b), (d), (e) and (f). Figure 1 (b) was similar to Figure 1 (f). These model clusters did not include chlorine. The important difference between (b), (f) and (d), (e) spectrum in Figure 1 is the number of peaks between 0 and 10 eV. In (b) and (f), there exists only one peak, while two peaks are found in (d) and (e). We consider that this difference is due to the effect of chlorine.

In Figure 2, our calculation indicates that the peak from 0 to 10 eV is mainly composed of Fe 3d + Cl 3p but the C 2p, N 2p and O 2p peaks are not observed as the dominant components. This fact is ascribed to the effect of the photoionization cross-sections. Because the photoionization cross-sections of C 2s, N 2s and O 2s are much larger than those of C 2p, N 2p and O 2p, the transition probabilities from the former three shells are larger than those from the latter three shells (See Table 1).

We have studied for XPS spectrum of 3d transition metal complexes.[8–14] We made an interpretation of XPS VB spectrum of an iron complex by comparing the experimental spectrum with our theoretically calculated spectra using the DV-Xα method. In this work, we neglected the effect of photoelectron interference and scattering, because these effects were small due to the fine powders sample form. Our work indicates that the peak from 0 to 10 eV originates from Fe 3d + Cl 3p. The shallowest binding energy peak in VB spectrum including Fe(III) and Cl^- is determined from Cl^-. In the present work, we showed that 3d band is deepened due to chlorine for the Fe(III) Schiff base complex in the XPS VB spectra.

Table 1. Atomic subshell photoionization cross sections per one electron at Mg Kα (1253.6 eV).

atom orbital	$\sigma(cm^2)$[a]
H 1s	9.2×10^{-6}
C 2s	1.0×10^{-3}
C 2p	5.6×10^{-5}
N 2s	1.9×10^{-3}
N 2p	1.2×10^{-4}
O 2s	2.9×10^{-3}
O 2p	2.5×10^{-4}
Cl 3s	3.6×10^{-3}
Cl 3p	1.3×10^{-3}
Fe 3d	1.5×10^{-3}
Fe 4s	9.1×10^{-4}

[a] $\sigma = \sum \sigma_i \times 2/N_i$, σ: the value of photoionization cross sections per one electron, σ_i: the value of photoionization cross sections by Yeh et al.,[5] N_i: the electron number of ith atomic orbital.

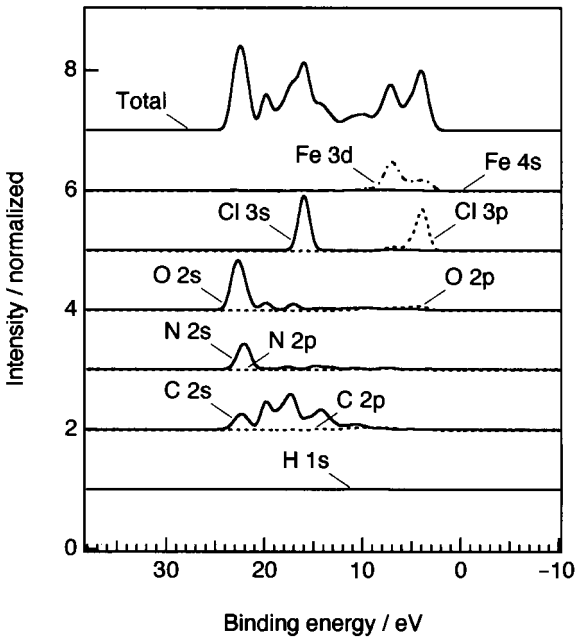


Figure 2. Theoretical XPS VB spectrum and electron distribution of each orbital (Fe 3d, Fe 4s, Cl 3s, Cl 3p, O 2s, O 2p, N 2s, N 2p, C 2s, C 2p, H 1s) per one molecule with photoionization cross-sections obtained by Yeh et al.[5] are shown for Fe(salen)Cl. It can be seen from the figure that the dominant components of the peaks at 22 eV, 19 eV, 17 – 11 eV, 6 eV and 4 eV are O 2s + N 2s + C 2s, C 2s + O 2s, Cl 3s + C 2s + O 2s, Fe 3d + Cl 3p and Cl 3p + Fe 3d, respectively.

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