COVALENCY OF COPPER COMPLEXES DETERMINED BY Cu 2p X-RAY PHOTOELECTRON SPECTROMETRY

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Abstract Copper 2p X-ray photoelectron spectra of divalent copper complexes, the structures of which have been well characterized, are measured. The intensity of so-called 'shake-up' satellite relative to the main line is measured for the cupric complexes and cupric oxide. It is found that the satellite intensity decreases as the copper(II) compound becomes covalent. A method to determine the covalency of copper(II) compounds are presented.

Key words copper, x-ray photoelectron spectra, covalency, ionicity

Copper 2p X-ray photoelectron spectra (XPS) of cupric [copper(II)] compounds have a high energy satellite at 940-945 eV in binding energy. This satellite is called 'shake-up' satellite. This satellite is, however, not due to the electron shake-up, but due to a dynamical electron transfer from one of the ligands to the central copper ion at the instance of the 2p electron photoionization. That is to say, the main line is assigned to the final state of $2p^{-1}3d^{10}L^{-1}$ electron configuration, i.e. charge-transfer peak, whereas the so-called 'shake-up' satellite is assigned to the $2p^{-1}3d^9$ configuration after van der Laan *et al.*[1], where L denotes ligands. The valence electron configuration of cupric compounds is nominally $3d^9$, thus the valence electron configuration of the final state of the so-called 'shake-up' satellite is similar to that of the ground state. The ground state total wave function of a cupric compound is,

$$\Phi_G \sim \Phi(\text{Cu}^{2+}\text{L}^{2-}) \cos\theta + \Phi(\text{Cu}^+\text{L}^-) \sin\theta$$

where $\text{Cu}^{2+}\text{L}^{2-}$ is the ionic state and Cu^+L^- the covalent state. That is to say, the electronic state of a divalent copper compound is expressed by a resonance of ionic and covalent states. After the creation of the $2p^{-1}$ hole by X-ray photoionization, the wave function becomes

$$\Phi_{2p} \sim \Phi(\text{Cu}^{2+}\text{L}^{2-}) \cos\theta + \Phi(\text{Cu}^+\text{L}^-) \sin\theta$$

According to the charge-transfer theory [1-3], the intensity ratio of the $2p_{3/2}$ main line (I_m) relative to the so-called 'shake-up' satellite (I_s) is,

$$\frac{I_m}{I_s} = \tan^2(\theta - \theta')$$

The dynamical charge transfer from ligand to the copper is larger for covalent cupric compounds than for ionic compounds, since an electron is easily transferred from one of the ligands to the copper 3d half filled orbital through the covalent bondings between the ligand and copper due to a large Coulomb attraction potential of the $2p^{-1}$ hole. Consequently, $\sqrt{I_m/I_s}$ is a measure of covalency, or a measure of the mixing of covalent state with ionic state. That is to say, the satellite intensity I_s/I_m is small for covalent cupric compounds and large for ionic cupric compounds. Though these have been well established for simple solids such as CuF_2 , CuCl_2 , CuBr_2 , and CuO [1-2], it is not clarified whether this holds for cupric complexes, since the above

formulation is based on a very simple model. To clarify the relation between the covalency determined by XPS and the real covalency of the complex, we have measured the satellite intensity of cupric complexes. According to the above formulation, we use a measure of covalency as

$$\text{covalency} \sim \sqrt{\frac{I_m}{I_s}}$$

Four cupric complexes, the crystal structures of which have been well characterized, were selected for XPS spectral measurements as shown in Fig.1: complex **I** is the same as that shown in Fig.4 of Ref.[4], complex **II** as Fig.7 of Ref.[5], complex **III** is a monomer of complex **I**, and complex **IV** as Fig.4 of Ref.[5]. The local coordination states of the copper ion are shown in Fig.2.

Fig.1 Perspective view of complexes I-IV. Green: Cu, red: O, blue: N, black: C, yellow: Cl, and brown: Br.

Fig.2 Local structure of complexes I-IV.

Copper $2p_{3/2}$ XPS spectra of the four cupric complexes and cupric oxide were measured by a VG ESCA LAB MK-II spectrometer equipped with Al anode X-ray source (applied power was typically 14 kV and 34 mA). The samples were powder form and spread on 3M adhesive tape attached to the sample holder. The pass energy of the spherical electron energy analyzer was 50 eV. Step size was 0.35 eV with dwelling time of 100 ms from 920 eV to 980 eV by binding energy. The spectra were accumulated 10 times, thus it took about 3 min to obtain one spectrum. Measurements were at least three times to check the reproducibility. The samples were damaged easily by X-irradiation and/or thermal radiation from the X-ray tube as shown in Fig.3. Therefore each spectrum was measured within 3 min. The vacuum chamber was $\sim 10^{-8}$ Torr during the measurements. The measured spectra were smoothed by Savitzky-Golay method [6] with 5 points 2-20 iterations (depending on S/N). This smoothing is essential to reduce the χ^2 at the peak separation procedure. After smoothed, an inelastic background was subtracted from the spectra by Shirley's method [6]. The processed spectra are shown in Fig.4. These spectra were then separated into several Gaussian-Lorentzian mixing functions to evaluate I_S/I_m (TABLE 1). All the spectral processing was done by VGS 5000/5250 Enhanced Data Processing System on a DEC micro PDP 11/73 computer.

TABLE 1. Measured satellite intensity I_S/I_m and covalency of the cupric compounds.

Compound	CuO	I	II	III	IV
I_S/I_m	0.54(1)	0.49(2)	0.40(2)	0.38(2)	0.27(2)
Covalency	1.36	1.43	1.58	1.62	1.92

Fig.3 Reduction of Cu in complex II during measurement. (a) After 3 min, (b) after 30 min, and (c) after 50 min of X-irradiation. Arrows indicate Cu^+ in the sample.

The ordering of the covalency of the four complexes and cupric oxide is,

since the ordering of the electronegativity [7] is $\text{O} (3.44) > \text{Cl} (3.16) > \text{N} (3.04) > \text{Br} (2.96)$. (Though it seems that Cu-N is more ionic than Cu-Br from the electronegativity difference, the square planar CuN_4 provides π electrons which are very delocalized, thus complex IV is more covalent than complex II.) The agreement between this ordering and that determined from XPS (TABLE 1) is satisfactory.

Fig.4 Measured Cu $2p_{3/2}$ X-ray photoelectron spectra of cupric compounds after smoothed and background subtracted. The spectra are shifted to compare the profile.

In summary, we have determined from XPS the covalency of the four complexes, resulting satisfactory agreement between the covalency determined from XPS and determined from chemical intuition. This shows that the relative satellite intensity of the X-ray photoelectron spectra is a measure of covalency of cupric compounds.

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