Comparative Studies on Periodatocuprate(II, III) and Telluratocuprate(II, III)

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The crystal structures, electronic spectra, and Cu2p XPS of Cu(III) complexes $Na_4H[Cu(H_2TeO_6)_2] \cdot 17H_2O$ and $Na_4K[Cu(HIO_6)_2] \cdot 12H_2O$ have been described. The characterizations of a Cu(III) atom in a complex are as follows: (i) In a square-planar coordination, the average bond length of Cu–O is 0.183 nm, shorter than the 0.190–0.200 nm found for a Cu(II) complex. (2) The "blue shift" occurs for d–d transitions in the electronic spectrum of the Cu(III) complex compared to those of its related Cu(II) complex, resulting from the higher valence state. (3) Cu(III) compounds with CuO_4 square-planar coordination are expected to be diamagnetic whereas Cu(II) compounds to be paramagnetic. (4) Comprehensive investigations on Cu2p XPS show that the binding energy of Cu2$p_{3/2}$ of a pure Cu(III) compound is about 2.0 eV higher than that of its corresponding Cu(II) compound: the shake-up satellites do not appear in the Cu2p XPS for a pure diamagnetic Cu(III) compound, the same as found for a diamagnetic Ni(II) compound: the FWHM of the signal of Cu2p XPS may become broader for Cu(III) compound because its core hole's lifetime shortens due to the higher valence state of copper. © 1995 Academic Press, Inc.

INTRODUCTION

For years, many chemists have been paying considerable attention to the synthesis and properties of compounds with unusual valence states. Compounds of Cu(III) chelated by periodate and tellurate were prepared in the early years of this century (1, 2), and the chemical formulae of the complex anion $[Cu(H_2TeO_6)_2]^{5-}$ and $[Cu(HIO_6)_2]^{5-}$ were determined by Balikungeri and his co-workers in 1977 (3). The following year, the absorption spectra of the Cu(III) complexes were published and the strong absorptions were assigned to ligand-to-metal charge transfer transitions in D_{2h} symmetry (4); however, the d–d transitions were not described in detail. With the discovery of high Tc oxide superconductors of cuprates

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and the discussion of their superconductivity, the preparations and properties of Cu(III) compounds have been of more and more interest recently (5–8). The electronic spectra of periodatocuprate(II, III) were reported by Adler et al. but the d–d transitions were not given in detailed description (5). The Cu2p XPS of the diamagnetic Cu(III) complex periodatocuprate(III) reported by Schlögl et al. (6) showed no satellites with the main peak of Cu2$p_{3/2}$ at 935.8 eV, while that of the paramagnetic Cu(III) compound $LaCuO_3$ showed strong shake-up satellites with the main peak of Cu2$p_{3/2}$ 2.5 eV higher than that of La_2CuO_4 (7). However, there were weak satellites in the Cu2p XPS of $NaCuO_2$, a diamagnetic Cu(III) compound (8). Where the satellites of a diamagnetic Cu(III) compound come from and how much greater the main peak of Cu2$p_{3/2}$ of a pure Cu(III) compound is than that of its related Cu(II) compound have not been stated clearly. The properties of another Cu(III) complex, telluratocuprate(III), have not been studied as yet. Here the coordination of the Cu–O bond, the electronic spectra, and the Cu2p XPS of bisperiodatocuprate(III) and bistelluratocuprate(III) complexes will be investigated compared with those of their related Cu(II) complexes.

EXPERIMENTAL

Preparation of Samples

Red-brown and dark-brown single crystals of $Na_4K[Cu(HIO_6)_2] \cdot 12H_2O$ (NC(III)I) and $Na_4H[Cu(H_2TeO_6)_2] \cdot 17H_2O$ (NC(III)T) were prepared by methods reported in the literature (4, 9–12); and a blue powder sample of $Na_6[Cu(HIO_6)_2] \cdot 13H_2O$ (NC(II)I) was synthesized as described by Adler et al. (5). Chemical analyses found the atom ratio Cu : I : Na : K to be 1.1 : 1.8 : 5.8 : 0.1 and H_2O 13.2. A greenish sample was obtained by heating $Na_4H[Cu(H_2TeO_6)_2] \cdot 17H_2O$ at 200°C for 1.0 hr to lose water and reduce to a Cu(II) compound, whose chemical formula was $Na_4H_2[Cu(H_2TeO_6)_2]$ (NC(II)T). All the agents used in this work were AR grade except KOH which was GR grade.

Physical Measurements

Diffuse reflectance spectra of the complexes were recorded on a VSU-2P spectrophotometer; absorption spectra of aqueous solution were performed on a UR-3000 spectrophotometer with a 1-cm thick quartz cell. The magnetic susceptibilities were determined on a Model MB-2 Faraday magnetic balance. The XPS experiments were carried out in a vacuum generator ESCA LAB MK II system with X-rays from AlKα ($h\nu$ = 1486.6 eV) and a vacuum pressure of about 2 × 10^{-7} Pa. The C_{1s} signal with binding energy (BE) at 284.6 eV was taken as a correction of charging effect. The resolution for the Ag$3d_{5/2}$ peak was 1.2 eV of full width at half maximum (FWHM) under the experimental condition in this work.

RESULTS AND DISCUSSION

Description for Structures

NC(III)T crystallizes in the triclinic system, space group $P\bar{1}$ with a = 0.594 nm, b = 0.896 nm, c = 1.256 nm, α = 98.5°, β = 99.0°, γ = 93.9°, and Z = 1 (9, 10). The complex anion $[Cu(H_2TeO_6)_2]^{5-}$ network, in which the square-planar near D_{4h} symmetry of CuO_4 is formed with a mean Cu–O bond length ($d_\perp$) of 0.184 nm, is shown in Fig. 1a. NC(III)I belongs to the monoclinic system, space group $P2_1/C$ with a = 0.611 nm, b = 2.506 nm, c = 1.472 nm, β = 97.8°, and Z = 4 (11, 12). The complex
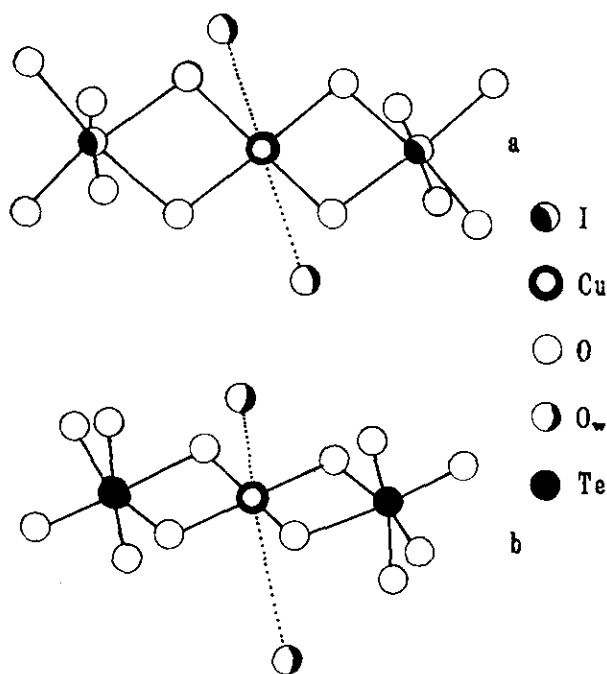

FIG. 1. The complex anion networks of (a) $[Cu(H_2TeO_6)_2]^{5-}$ and (b) $[Cu(HIO_6)_2]^{5-}$
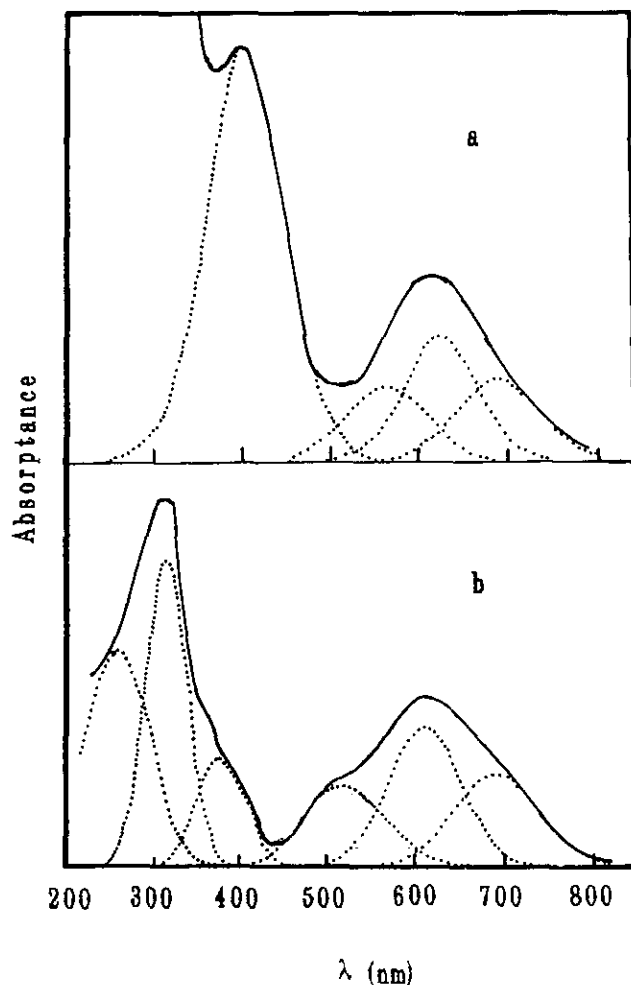

FIG. 2. Electronic spectra of Cu(II) complex of periodate; (a) ASS of KC(II)I, (b) DRS of NC(II)I.

anion $[Cu(HIO_6)_2]^{5-}$ network includes a copper(III) atom chelated by two groups of distorted octahedral $IO_5(OH)$ to configure an approximate square-planar CuO_4 unit, almost in D_{4h} symmetry, with a Cu–O distance ($d_\perp$) of about 0.183 nm. The mean Cu–O bond length ($d_\perp$) in the planar units is similar to those of $NaCuO_2$ (13), 0.184 nm, and of $K_4H_4Cu(IO_6)_2O_2 \cdot 6H_2O$ (14), 0.182 nm. The Cu–O bond length in a square-planar unit of a Cu(II) compound is between 0.190 and 0.200 nm, in agreement with the result of the effective ion radii of Cu^{2+} (0.071 nm) and O^{2-} (0.124 nm) (15). In turn, the effective ion radius of Cu^{3+} is about 0.060 nm.

Electronic Spectra

Cu(II, III) complexes of periodate. The absorption spectrum for the aqueous solution (ASS) with original composition 0.01 mol dm^{-3} Cu(NO$_3$)$_2$, 0.2 mol dm^{-3} KIO$_4$, and 1.0 mol dm^{-3} KOH (KC(II)I) is illustrated in Fig. 2a (1.0 mol dm^{-3} KOH aqueous solution is used as
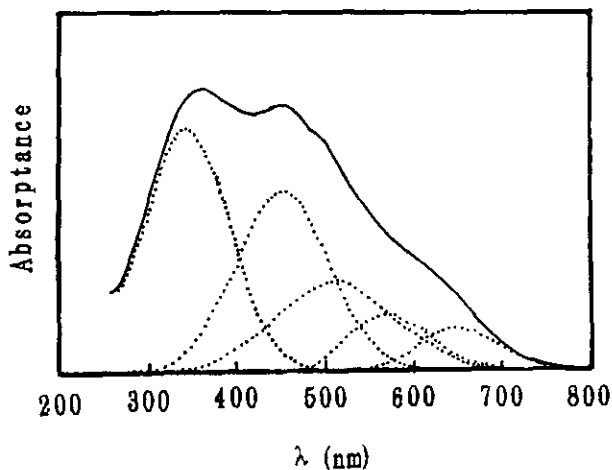
FIG. 3. Diffuse reflectance spectrum of Cu(III) complex of periodate.

reference solution), with bands at 405 and 615 nm whose molar extinction coefficients (ε) are 112 dm^3 mol^{-1} cm^{-1} and 49 dm^3 mol^{-1} cm^{-1}. Following the expression $\varepsilon = \varepsilon_{max}\, 2^{1-(\nu-\nu_0)/\sigma]^2}$ (ε, molar extinction coefficient, ν, wavelength, σ, half width of a band at half the peak height) (4, 16), the band at 615 nm can be analyzed into three Gaussian curves at 562 nm (17800 cm^{-1}), 621 nm (16100 cm^{-1}), and 686 nm (14600 cm^{-1}) (Fig. 2a, dotted lines). They belong to d–d transitions (5, 17). Three Gaussian curves (Fig. 2b, dotted lines) assigned to d–d transitions are also obtained at 520 nm (19,200 cm^{-1}), 610 nm (16,400 cm^{-1}) and 689 nm (14,500 cm^{-1}) in the diffuse reflectance spectrum (DRS) of NC(II)I. The spectra are similar to those of Cu(II) compounds containing elongating octahedral coordination (17). The polarity of solvent and the state of a sample will have an effect on the d_{z^2} level and less effect on the d_{xz} and d_{yz} levels (18). The shift between 562 and 520 nm is greater than that between 621 and 610 nm, while the position at 686 nm is almost the same as that at 689 nm, as seen in comparing Figs. 2a with 2b. This implies that the order of d-orbitals is $d_{x^2-y^2} > d_{xy} > d_{xz}, d_{yz} > d_{z^2}$ in KC(II)I and NC(II)I. The average value of orbital energy splitting (Δ) between $d_{x^2-y^2}$ and d_{xy} is estimated at 14,500 cm^{-1} in the periodatocuprate(II) complex.

For a diamagnetic trivalent copper compound, such as NC(III)I, the ground state is $^1A_{1g}$ in D_{4h} symmetry, arising from a ^1G excited state of the free ion Cu^{3+} with a d^8 configuration. According to the molecular orbital theory for D_{4h} symmetry complexes with d^8 system (19), the maximum at 342 nm (29200 cm^{-1}) and 449 nm (22300 cm^{-1}) in DRS of NC(III)I (Fig. 3) are assigned to dipole-allowed ligand to metal ($L \rightarrow M$) charge transfer transitions, or $^1A_{1g} \rightarrow {}^1E_u$ and $^1A_{2u}$, not dipole-forbidden $^1A_{1g} \rightarrow {}^1E_g$ and $^1A_{2g}$ transitions as described in Ref. (5).

Two strong absorptions at 266 and 415 nm due to $L \rightarrow M$ charge transfer transitions are also measured for $[Cu(HIO_6)_2]^{5-}$ complex solution, as reported in Refs. (4, 5). In NC(III)I, the Cu(III) atom is surrounded by four oxygen atoms in nearly square-planar configuration, and two oxygen atoms at distances ($d_{\parallel}$) of 0.27 and 0.36 nm above and below the planar (Fig. 1b). On the view of the distinction of copper coordination and the θ value ($\theta = d_{\parallel}/d_{\perp}$ (20)), the $3d$ levels could be expected to be $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz}, d_{yz}$, as in Ref. (5). The 510 nm (19,000 cm^{-1}), 572 nm (17,500 cm^{-1}), and 682 nm (14,700 cm^{-1}) are three spin-allowed d–d type transitions; they are $^1A_{1g} \rightarrow {}^1E_g$, $^1A_{1g} \rightarrow {}^1A_{2g}$, and $^1A_{1g} \rightarrow {}^1B_{1g}$, respectively. The above differences between various items do not reconcile with the diagram calculated by Konig and Klemer when the Racah parameters are $C = 4B = 3620$ cm^{-1} (21). According to the Racah terms (19), the Δ for periodate cuprate(III) is calculated to be 21,100 cm^{-1} when B and C are assumed to be 905 and 3620 cm^{-1}. The Δ for Cu(III) complex of periodate increases 1.6 times as much as that of its related Cu(II) complex of periodate.

Cu(II, III) complexes of tellurate. The ASS of 0.0015 mol dm^{-3} $Cu(NO_3)_2$, 0.3 mol dm^{-3} H_6TeO_6, and 1.5 mol dm^{-3} KOH (KC(II)T) is shown in Fig. 4a (1.5 mol dm^{-3} KOH aqueous solution is taken as the reference solution).
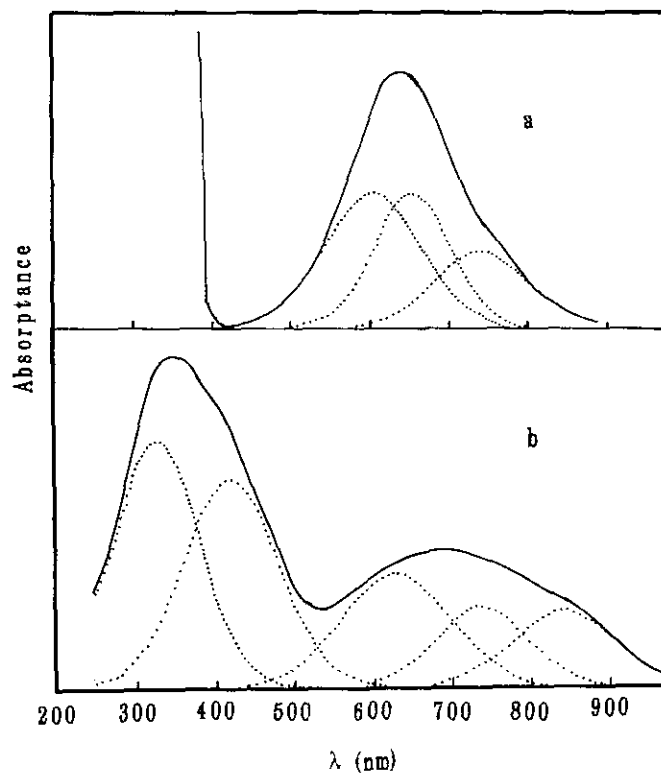

FIG. 4. Electronic spectra of Cu(II) complex of tellurate (a) ASS of KC(II)T, (b) DRS of NC(II)T.
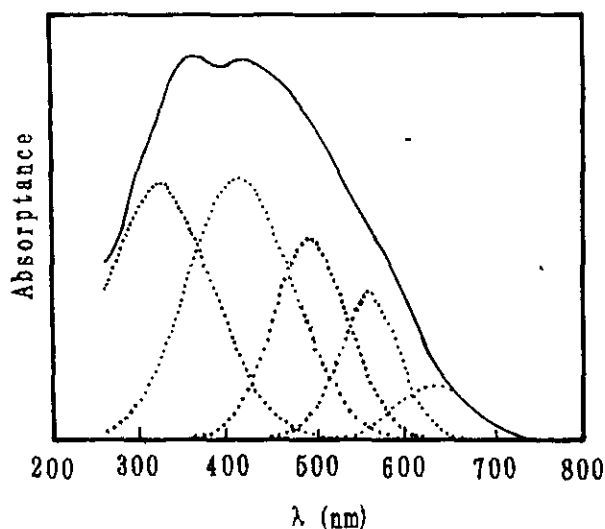
FIG. 5.   Diffuse reflectance spectrum of Cu(III) complex of tellurate.

The ε at 650 nm is 33 dm^3 mol^{-1} cm^{-1}, which is weaker than that of KC(II)I at 615 nm. The band at 650 nm is the superposition of d–d transitions (17), which can be analyzed into three Gaussian curves (Fig. 4a, dotted lines) at 605 nm (16,500 cm^{-1}), 653 nm (15,300 cm^{-1}) and 740 nm (13,500 cm^{-1}). The DRS of NC(II)T is illustrated in Fig. 4b with three Gaussian curves (dotted lines) at 628 nm (15,900 cm^{-1}), 737 nm (13,600 cm^{-1}), and 840 nm (11,900 cm^{-1}). The curves at 737 and 628 nm in DRS (Fig. 4b) correspond to the curves at 740 and 605 nm in ASS (Fig. 4a), while the difference between 840 nm (Fig. 4b) and 653 nm (Fig. 4a) is so significant that the former can be taken as the red shift band of the later. The Cu3d levels can be considered as $d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{xz}, d_{yz}$ for KC(II)T, the aqueous complex, and as $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz}, d_{yz}$ for NC(II)T, the solid state sample, and the Δ value is obtained as about 13,500 cm^{-1} for Cu(II) tellurate complex.

There are two apical atoms with Cu $\cdots$ O$_w$ distances ($d_\parallel$) of 0.35 nm above and below the CuO$_4$ plane respectively, in NC(III)T (Fig. 1a) (9, 10), and the coordination is similar to that of NC(III)I. Thus the Cu3d orbital order could be expected to be $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz}, d_{yz}$, the same as that of NC(III)I. In DRS of NC(III)T (Fig. 5), the two stronger Gaussian curves at 324 nm (30,900 cm^{-1}) and 415 nm (24,100 cm^{-1}) belong to dipole-allowed $L \rightarrow M$ charge transfer transitions, while two significant bands are observed at 270 and 405 nm in the ASS of [Cu(H$_2$TeO$_6$)$_2$]$^{5-}$ complex (9), analogous to those of Balikungeri *et al.* (3, 4). The Gaussian curves centered at 492 nm (20,300 cm^{-1}), 567 nm (17,700 cm^{-1}), and 630 nm (15,900 cm^{-1}) (Fig. 5, dotted lines) are of $^1A_{1g} \rightarrow ^1E_g$, $^1A_{1g} \rightarrow ^1A_{2g}$, and $^1A_{1g} \rightarrow ^1B_{1g}$, respectively, the spin-allowed d–d transitions. By taking the Racah parameters $C = 4B =$

3620 cm^{-1}, the Δ value is calculated to be 21,300 cm^{-1}, which is 1.6 times higher than that of its related Cu(II) tellurate complex.

Here it is easy for us to understand that the higher the valence state of copper, the stronger the ligand field of the complex, and a blue shift would be expected to take place in the d–d transitions. The Δ values are 21,100 and 21,300 cm^{-1} for periodatocuprate(III) and telluratocuprate(III) complexes, respectively.

Cu2p XPS

The Cu2p XPS of NC(III)I (Fig. 6a) is similar to that reported by Schlogl *et al.* (6). The B.E. of Cu2$p_{3/2}$ is 935.7 eV, 1.8 eV higher than the 933.9 eV value for NC(II)I (Fig. 6b), while the B.E. of Cu2$p_{3/2}$ of LaCuO$_3$ is 2.5 eV higher than that of La$_2$CuO$_4$ (7) and the B.E. of BaCuO$_{2.5}$ is 1.5 eV higher than that of BaCuO$_{2.0}$ (22). It can be considered that the B.E. of Cu2$p_{3/2}$ of a pure Cu(III) compound is about 2.0 eV higher than that of its related Cu(II) compound. For a Cu(II) compound, the Cu2$p_{3/2}$ or Cu2$p_{1/2}$ XPS consists of a main $(3d^{10}L)$ and a satellite (d^9L) peak (23), however, for the diamagnetic Cu(III) compound, NC(III)I, whose molar diamagnetic susceptibility is about -962×10^{-6} emu/mole; the Cu2p XPS only contains main lines. The phenomenon for Cu2p XPS of NC(III)I is the same as that of a diamagnetic Ni(II)
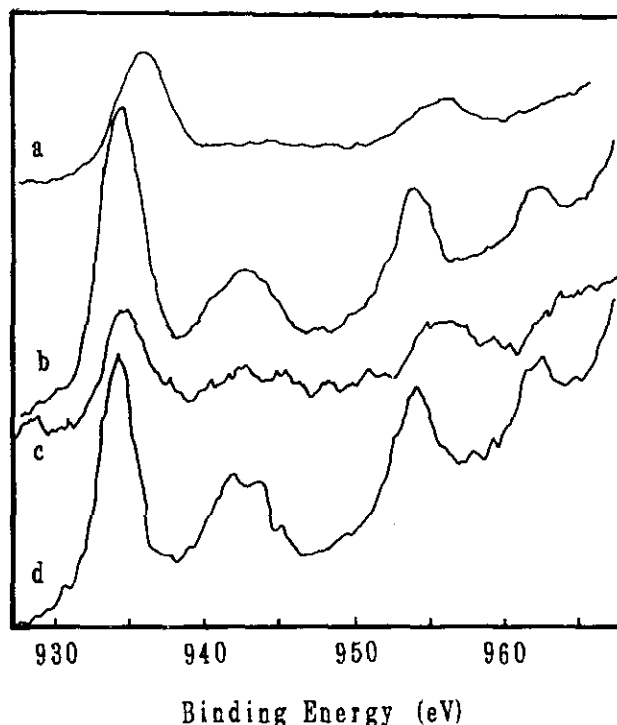

FIG. 6.   Cu2p XPS of (a) NC(III)I, (b) NC(II)I, (c) NC(III)T, and (d) NC(II)T.

compound whose Ni2p XPS shows no satellites (22). In accordance with the selection rule for the shake-up transitions associated with the 2p photoelectron lines of transition metal compounds (24), it is certain that the Cu2p XPS of a diamagnetic Cu(III) compound involves only main lines ($3d^{10}L^2$, (8)).

The weak satellite with a ratio of the satellite to the main peak (I_s/I_m) about 0.33 for NC(II)I, much weaker than those with I_s/I_m about 0.50 for most of other Cu(II) compounds (25), indicates that the Cu–OI bond is a strong covalent bond in NC(II)I.

The FWHM of $Cu2p_{3/2}$ for NC(III)I is 3.6 eV, about 0.2 eV wider than that for NC(II)I. For Ni(II) compounds with d^8 configuration, the FWHM of Ni2p XPS for a diamagnetic compound is narrower than that for its intimate paramagnetic compound (26). For a paramagnetic Cu(II) compound, at its final state with a Cu2p core hole, the spin–spin coupling of the 2p hole and 3d elections gives two different values of $2S + 1$, 1 and 3; for a diamagnetic Cu(III) compound, the value of $2S + 1$ is only equal to 2. Hence, the FWHM of the diamagnetic Cu(III) compound should be narrower than that of its corresponding paramagnetic Cu(II) compound. On the other hand, however, according to the uncertainty principle, the FWHM will widen with the shortening of the lifetime of the core hole, resulting from the increase of the copper valence state. Another convincing instance is that the FWHM of $BaCuO_{2.5}$ (p-type semiconductor) is about 0.4 eV wider than the FWHM of $BaCuO_{2.0}$ (p-type semiconductor) (22).

The I_s/I_m of Cu2p for NC(II)T with the $Cu2p_{3/2}$ main position at 934.0 eV is 0.53 (Fig. 6d), stronger than that of NC(II)I. This indicates that the covalence of the Cu–OI bond is stronger than that of the Cu–OTe bond, and the periodate radical is a more excellent chelating agent, in agreement with the bond parameters from electronic spectra and ESR of the Cu(II) probe in periodate and tellurate (27).

The Cu2p XPS of the sample NC(III)T exhibits satellites of I_s/I_m about 0.33 with the main position at about 934.6 eV (for $Cu2p_{3/2}$), 0.6 eV higher than that of NC(II)T. We failed to obtain a Cu2p XPS without satellites for NC(III)T samples. The molar diamagnetic susceptibility of NC(III)T is about -484×10^{-6} emu/mole, much weaker than that of NC(III)I. Each of the NC(III)T samples prepared during each separate period has satellites in its Cu2p XPS which derive from the contaminants of Cu(II) compounds on the surface of each sample, because the tellurate radical is a weaker ligand than the periodate radical, and the Cu(III) on the surface of NC(III)T is easier to reduce to Cu(II) than that of NC(III)I. The opinion that the shake-up satellite resulting from Cu(II) is agreement with the description of Herzog et al. for the satellites of Cu2p XPS of $NaCuO_2$ (28). The presence of Cu(II) on the

surface, makes the BE lower, for example, than the BE for NC(III)T is 1.0 eV lower than that for NC(III)I. The FWHM of NC(III)T is 3.4 eV, which is wider than that 3.0 eV of NC(II)T.

Now the conclusion could be drawn that a pure diamagnetic Cu(III) compound shows no shake-up satellites in its Cu2p XPS with the BE of $Cu2p_{3/2}$ about 2.0 eV higher than that of its related Cu(II) compound, which can be used as reference value to elucidate whether the surface of a Cu(III) compound is pure, and the FWHM may be wider than that of the Cu(II) compound, for the reason that the higher valence state shortens the lifetime of the photoelectron hole.

ACKNOWLEDGMENTS

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