

## X-Ray Photoelectron Spectroscopy of Copper(II), Copper(I), and Mixed Valence Systems

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### ABSTRACT

X-ray photoelectron spectroscopy using copper(II), copper(I) and the mixed valence Cu(II)/Cu(I) compounds was employed as a means of studying electron transfer reactions in copper proteins. The X-ray photoelectron spectra of copper(II) compounds display characteristic satellites of both variable size and resolution. Some of these satellites could be assigned to specific ligand interactions. Unlike electron paramagnetic resonance spectroscopy, the X-ray photoelectron spectroscopic measurements of copper(I) compounds allowed the unequivocal assignment of this oxidation state. No satellites at all could be detected in the Cu(I) spectra. Furthermore, established mixed valence Cu(II)/Cu(I) complexes including  $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 \cdot 2\text{H}_2\text{O}$  and  $\text{Cu}_4\text{Cl}_5$  (ethylenediamine)<sub>2</sub>, proved essentially a mixture of distinct portions of Cu(I) and Cu(II). This indicates that both oxidation states of copper survive in such complexes. In contrast, all Cu X-ray photoelectron signals of the more tentatively described mixed valence complexes  $\text{Na}_2\text{Cu}_3\text{S}_3$  and the mineral covellite,  $\text{Cu}^{\text{I}}_4\text{Cu}^{\text{II}}_2(\text{S}_2)_2\text{S}_2$ , could be attributed exclusively to Cu(I). In view of the known binding of copper with sulfur in many copper proteins, it was of utmost importance to study the copper-sulfur interactions. We have demonstrated the absence of Cu(II) in CuS. This indicates strong metal-induced polarization of sulfur resulting in electron transfer to copper to yield Cu(I).

### INTRODUCTION

The prominent role of copper in cellular biochemistry is widely recognized [1,2]. The active sites of many redox systems are attributed to this metal ion. Apart from its strong involvement in bioenergetics, it may act as an allosteric component on a great number of biopolymers including proteins, polysaccharides, and polynucleotides. Copper is found coordinated with sulfur, oxygen, and nitrogen and has proved most versatile in its complex geometry. Valuable structural information comprising larger sections of a copper complex has been inferred from chiroptical measurements and nuclear magnetic resonance spectroscopy. Conclusions have been drawn from electron spectra and electron

paramagnetic resonance measurements regarding its complex geometry. Unfortunately, we do not know the molecular mechanism of electron transport on copper. A promising approach for the study of the electron density around copper nuclei and the evaluation of the genuine oxidation state is the application of XPS. With this method, the binding energy values of the core electrons can be determined and conclusions drawn regarding the chemical environment [3,4]. In the present study, XPS spectra were recorded using 29 copper compounds whose structures had been determined by X-ray diffraction. Valuable information about the effect of the known complex geometry on the electron density around the copper was obtained.

Special emphasis was placed on the problem generally described as mixed valence states. Because of their intensive absorption in the visible region, many copper proteins were considered to contain the metal in both valence states, i.e., Cu(I) and Cu(II) [5-8]. Direct spectroscopic evidence for the presence of a mixed valence state of the iron in iron-sulfur proteins was obtained from Mössbauer spectroscopy [9-11]. However, this method is restricted to very few elements and is certainly not applicable to copper. XPS proved most advantageous for this kind of study owing to the convenient assignment of Cu(II) and Cu(I).

## EXPERIMENTAL

### X-ray Photoelectron Spectroscopy

The samples were irradiated primarily with X-rays originating from Mg  $K_{\alpha 1,2}$  having an energy of 1253.6 eV. The emitted photoelectrons were analyzed for their kinetic energy in a Varian V-IEE 15 high-resolution electron spectrometer equipped with an on-line 620L computer (8K). The binding energy of the electrons,  $E_b$ , is obtained from the relation:  $E_b = E_{X-ray} - E_{kin}$ .

As the Mg  $K_{\alpha}$  X-radiation is not monochromatic, satellites arising from the Mg  $K_{\alpha 3,4}$  doublet for every main signal with a constant distance of 8.5 eV at lower binding energies were seen. Photoelectron peaks due to these satellites are indicated as  $\alpha_{3,4}$  [12]. During the irradiation, the probes were maintained at approximately  $-100^\circ$  by cooling the sample holder with liquid nitrogen. This precaution was required to avoid possible photoreduction reactions [13]. The samples were run as powders dusted onto the backing of a one-sided adhesive Cellotape (Scotch Tape, 3M Company). Standardization of the spectra was performed employing the C 1s electron line at 284.0 eV obtained from the aliphatic hydrocarbons on the adhesive side of the Cellotape. Thus, charging effects of the sample were compensated [14]. The standard deviation of the respective energy values was  $\pm 0.1$  eV. The reference line was recorded immediately after the line of interest. The spectra were time-averaged and smoothed. The energy regions of Cu  $2p_{1/2}$ , Cu  $2p_{3/2}$ , S  $2p$ , N  $1s$ , O  $1s$  were scanned sequentially for the respective compound. The areas of the XPS signals were calculated using a planimeter (type 34051) from A. Ott, Kempten.

## Chemicals

$\text{CuF}_2$ ,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $(\text{NH}_4)_2[\text{CuCl}_4] \cdot 2\text{H}_2\text{O}$ ,  $(\text{Cu}(\text{cyclohexanebutyric acid})_2$ ,  $\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{H}_2\text{O}$  were from Merck, Darmstadt.  $\text{CuBr}_2$  and  $\text{Cu}(\text{acetylacetonate})_2$  were purchased from Baker, Phillipsburg.  $\text{Cu}(\text{C}_2\text{O}_4)$  from Roth, Karlsruhe. Chalcocite ( $\text{Cu}_2\text{S}$ ), S. W. Africa, and covellite ( $\text{CuS}$ ), Alghero, Sardinia, were gifts from Dr. Pichler and Prof. Weiskirchner, Mineralogisches Institut, Tübingen.

$\text{CuI}$  was prepared after the method given in [15]. The royal-blue modification of  $\text{Cu}(\text{HCOO})_2$  was synthesized according to [16].  $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$  was prepared from  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and concentrated aqueous  $\text{NH}_3$ . Crystalline amino acid  $\text{Cu}(\text{II})$  complexes of Gly, Ala, Ser, Lys, Asp, and Glu were prepared by adding excessive  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$  to hot aqueous solutions of the respective amino acids. Upon cooling crystals started to appear. They were washed several times with water and ethanol and were dried over  $\text{P}_4\text{O}_{10}$ .  $\text{Cu}(\text{His})_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  was prepared by the method of [17].  $\text{K}_2[\text{Cu}(\text{biuret})_2] \cdot 4\text{H}_2\text{O}$  was prepared according to [18]. Crystalline copper sulfur compounds were prepared essentially as given in the literature:  $\text{CuS}$  [19],  $\text{NH}_4\text{CuS}_4$  [20],  $\text{Cu}_2\text{S}_2\text{O}_3 \cdot \text{Na}_2\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  [21],  $\text{Na}_2\text{Cu}_3\text{S}_3$  [22] and  $\text{CuSCN}$  [23]. Mixed valence compounds:  $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 \cdot 2\text{H}_2\text{O}$  [24],  $\text{Cu}_4\text{Cl}_5(\text{ethylenediamine})_2$  [25], and  $\text{Na}_4[\text{Cu}(\text{NH}_3)_4][\text{Cu}(\text{S}_2\text{O}_3)_2]_2$  [26]. The purity and stoichiometry of the compounds were monitored by elementary analysis and atomic absorption spectroscopy.

## RESULTS AND DISCUSSION

In preliminary studies carried out in the author's laboratory [27-38], XPS developed into a powerful tool for examining molecular bonding in many bioinorganic compounds. The core electrons are located essentially in atomic orbitals and their binding energies are characteristic of the respective atoms. However, measurable deviations are known for the inner shell binding energies depending on the nature of the chemical environment. These distinct differences in the core electron binding energies or chemical shifts can be assigned to alterations in the **electron density of the valence shell**. For example, in oxidized species higher binding energies are detected, while upon progressive reduction the opposite effect is seen. XPS spectra of **transition metal compounds** can yield information on bonding from the examination of the **satellites** accompanying the main peaks. It was particularly interesting that the XPS spectra of many elements showed characteristic satellites of variable resolution and magnitude. In the case of copper, the satellites proved very distinct and a definite differentiation between  $\text{Cu}(\text{I})$  and  $\text{Cu}(\text{II})$  could be made. Novakov detected rather unusual satellites accompanying the  $\text{Cu } 2p_{1/2}$ ,  $\text{Cu } 2p_{3/2}$  signals of many copper compounds including  $\text{Cu}(\text{I})$  species [39]. In subsequent studies it was shown that the satellite spectra of the cuprous compounds arose from surface oxidation of the cuprous species. **It is now firmly established that these satellites occur in**

**Cu(II) only and not in the closed shell Cu(I) [13,40-43].** It is noteworthy in this respect that Zn(II), isoelectronic with Cu(I), shows no satellites on the 2 p levels (44). Thus, the presence or absence of satellites must be attributed to differences in the electron configurations of Cu(I),  $[\text{Ar}] 3d^{10}$  and of Cu(II),  $[\text{Ar}] 3d^9$ . At present the origin of the Cu(II) satellites has not been completely elucidated.

**There appears general agreement that the Cu(II) satellites are not due to multiplet coupling.** With the progressive decrease of unpaired electrons, the magnitude of the satellite splitting is considerably higher [13,44]. Moreover, to attribute the presence of satellites to the loss of energy after the photoelectron process must be excluded. The photoelectron satellite may be better explained by multielectron excitation as proposed by Novakov [39] and Rosencwaig [44]. In this so-called shake-up process, part of the energy of the emitted photoelectron is used to promote a valence electron to unoccupied states in the **conduction band**. These excitations accompanying the primary photoionization process are probably 3d to 4s or 4p. Kim suggested that the shake-up satellites may be attributed to monopole charge transfer transitions (ligand  $\rightarrow$  Cu 3d), using the sudden approximation and the **ligand field theory** whereby the position and the fine structure of the satellite depend on the nature of the ligands [43]. At the moment no final decision regarding the origin of the satellites can be made. Nevertheless, considerable knowledge is derived from the affect of either crystal or ligand fields on the exposed metal ion. In the following XPS spectra, the effect of ligands on both the shape and magnitude of the Cu  $2p_{1/2}$  and Cu  $2p_{3/2}$  satellite levels was investigated.

### Cu(II)Halides

The Cu  $2p_{1/2}$  and Cu  $2p_{3/2}$  energy levels of different Cu(II)halides show one main signal and very distinct satellites (Fig. 1). For comparative reasons the position of the main peak was adjusted to zero, although the 2 p levels of the  $\text{CuF}_2$  main peak signal were shifted by 4.4 eV to a higher binding energy relative to  $\text{CuBr}_2$ . The absolute energy values are summarized in Table 1. All spectra were of good quality and resolution. As in earlier published work [13], two satellites could be **monitored in the Cu  $2p_{3/2}$  XPS spectra**. A convenient approach for the evaluation of multisatellites which are split or overlap is by utilizing the numerical ratio of the full width at half maximum of both the satellite and the main peak [13]. A ratio near 1.5 indicates the presence of split satellites. **Below 1.0, one single satellite can be seen** (Table 2). The strong interaction of the highly electronegative fluorine has its counterpart in the shifting of either satellite to lower binding energy values and the absence of a second satellite in the Cu  $2p_{3/2}$  region. It is, however, unclear whether or not the first or the second satellite peak was levelled off.

The above cupric halides belong to the class of compounds with a (4+2) Jahn-Teller distorted octahedral coordination [45]. In these structures, the unpaired electron is considered to be the  $3d_{x^2-y^2}$  orbital. It is noteworthy that there is a definite trend in the series  $\text{CuF}_2$  to  $\text{CuBr}_2$  for the satellite splitting to

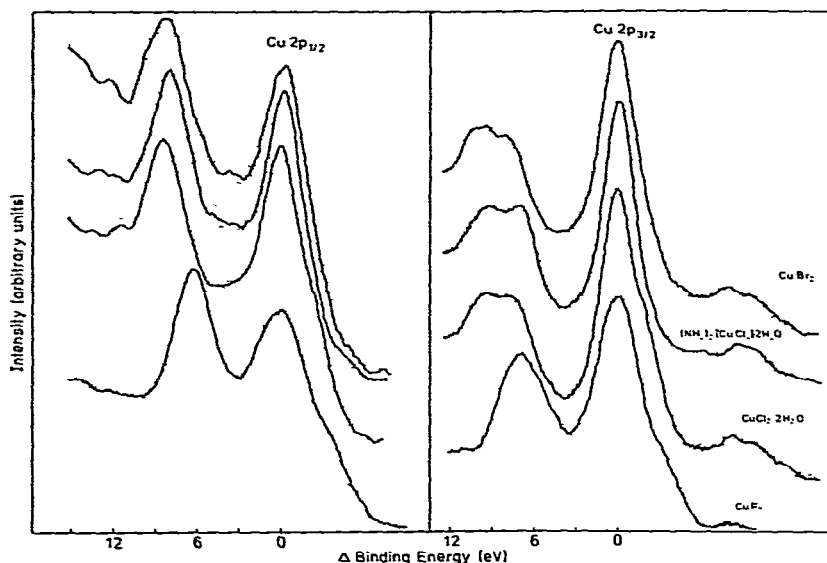


FIG. 1. XPS spectra of the Cu  $2p_{1/2}$  and Cu  $2p_{3/2}$  levels. Recording conditions: work function 6.0 eV; analyzer energy 100 eV; sweep width 30 eV; sweep time 20 sec; number of channels 200; pressure range 1-2  $\mu$ Torr; number of scans 9,  $\text{CuF}_2$ ; 5,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ; 10,  $(\text{NH}_4)_2[\text{CuCl}_4] \cdot 2\text{H}_2\text{O}$ ; 9,  $\text{CuBr}_2$ .

become larger as the compound becomes more strongly covalent. This ordering can be described in terms of the nephelauxetic or "cloud-expanding" sequence [46].

### Cu(II)Carboxylates and Cu(II)Amino Acids

According to Jørgensen (4), there is one rather unique property of Cu(II), the single  $\sigma$  antibonding electron in a  $(x^2-y^2)$ -type orbital delocalized to a large extent on the ligands. Provided the ligands bound to Cu(II) are exclusively the electronegative oxygen species as found in the Cu(II)carboxylate complexes (Fig. 2), the delocalization of the unpaired electron is expected to be rather distinct. The probability of shake-up processes may be enhanced by this delocalization. The complete separation of the satellite peaks into two components as seen for Cu(II) acetylacetonate and Cu(II)formate may be an example of this. Surprisingly, different intensities for the two satellites were seen. The intensity of the first satellite at a lower binding energy was remarkably reduced; both satellites were further apart. The highest separation (5.0 eV) was observed for Cu(II)acetylacetonate. Regarding the XPS spectra of the Cu  $2p_{1/2}$  level, a distinct broadening of the satellite was noticed which was assigned to an overlapping second satellite. In the case of Cu(II)acetylacetonate, the separation

TABLE 1  
Electron Binding Energies and Satellite Splittings

Compound	Cu 2p <sub>1/2</sub>		Cu 2p <sub>3/2</sub>		N 1s (eV)	O 1s (eV)	S 2p (eV)
	Satellite	Main Peak (eV)	Satellite	Main Peak (eV)			
CuF <sub>2</sub>	965.0	958.8	945.4	938.5			
CuCl <sub>2</sub> · 2H <sub>2</sub> O	963.4	955.0	944.5, 942.4	935.1			
(NH <sub>4</sub> ) <sub>2</sub> [CuCl <sub>4</sub> ] · 2H <sub>2</sub> O	962.4	954.1	943.7, 941.1	934.2	401.1		
CuBr <sub>2</sub>	963.0	954.4	944.1, 942.0	934.2			
CuI	—	953.6	—	933.7			
Cu(HCOO) <sub>2</sub> , royal-blue	963.6, 960.7	955.9	944.6, 940.7	935.9		532.5	
Cu <sub>2</sub> (CH <sub>3</sub> COO) <sub>4</sub> · 2H <sub>2</sub> O	961.3	954.7	944.1, 940.0	934.5		531.9	
Cu(C <sub>2</sub> O <sub>4</sub> )	962.2	955.6	944.3, 941.1	935.4		532.6	
Cu(cyclohexanecarboxylic acid) <sub>2</sub>	962.6, 959.6	954.3	943.8, 940.0	934.3		531.5	
Cu(acetylacetonate) <sub>2</sub>	962.9, 959.0	953.9	943.8, 938.7	933.9		530.9	
Cu(NH <sub>3</sub> ) <sub>4</sub> SO <sub>4</sub> · H <sub>2</sub> O	963.0	955.3	943.8	935.1	400.2	531.8	168.6
Cu(Gly) <sub>2</sub>	963.2	954.8	942.8	934.8	399.9	531.6	
Cu(Ala) <sub>2</sub>	963.1	955.1	942.9	934.9	400.2	532.2	
Cu(Ser) <sub>2</sub>	963.6	955.4	943.8	934.7	399.9	531.8	
Cu(Lys) <sub>2</sub>	962.8	953.8	942.4	933.8	400.4	531.2	
Cu(Asp) <sub>2</sub>	963.3	954.9	942.8	934.9	400.3	532.1	
Cu(Glu) <sub>2</sub>	963.3	954.9	942.5	934.6	399.9	531.9	
Cu(His) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> · 2H <sub>2</sub> O	962.9	954.5	942.4	934.3	400.2, 406.1	531.6	
K <sub>2</sub> [Cu(NHCONHCONH) <sub>2</sub> ] · 4H <sub>2</sub> O	963.3	954.9	943.3	934.8	398.9	531.5	
CuSCN	—	953.3	—	933.1	399.1		164.3
Cu <sub>2</sub> S <sub>2</sub> O <sub>3</sub> · Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> · 2H <sub>2</sub> O	—	952.8	—	933.1		531.3	162.5, 167.3
NH <sub>4</sub> CuS <sub>4</sub>	—	951.7	—	931.5	400.6		162.1
Chalcocite (Cu <sub>2</sub> S)	—	954.2	—	934.3			163.2
CuS	—	952.2	—	932.3			162.1
Covellite (CuS)	—	953.0	—	932.8			162.4
Na <sub>2</sub> Cu <sub>3</sub> S <sub>3</sub>	—	952.4	—	932.4			161.8
Cu <sub>2</sub> SO <sub>3</sub> · CuSO <sub>3</sub> · 2H <sub>2</sub> O	963.3	955.2, 953.6	944.2	936.4, 933.2		532.0	167.8
Cu <sub>4</sub> Cl <sub>5</sub> (ethylenediamine) <sub>2</sub>	962.9	954.6, 952.7	943.7	934.6, 932.6	399.6		
Na <sub>4</sub> [Cu(NH <sub>3</sub> ) <sub>4</sub> ] [Cu(S <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	963.2	955.5, 953.5	944.1	935.3, 933.3	400.0	532.1	163.3, 168.8

Abbreviations for TABLE 2: FWHM=Full Width at Half Maximum; SP=Satellite Peak; MP=Main Peak

TABLE 2  
Satellite Splitting and Satellite Ratios

	Cu 2p <sub>1/2</sub>		Cu 2p <sub>3/2</sub>	
	Satellite Splitting (eV)	FWHM <sub>SP</sub> FWHM <sub>MP</sub>	Satellite Splitting (eV)	FWHM <sub>SP</sub> FWHM <sub>MP</sub>
CuF <sub>2</sub>	6.2	0.70	6.9	1.10
CuCl <sub>2</sub> · 2H <sub>2</sub> O	8.4	0.86	9.4, 7.3	1.67
(NH <sub>4</sub> ) <sub>2</sub> [CuCl <sub>4</sub> ] · 2H <sub>2</sub> O	8.3	1.08	9.5, 6.9	1.89
CuBr <sub>2</sub>	8.6	1.00	9.9, 7.8	1.52
Cu(HCOO) <sub>2</sub> , royal-blue	7.7, 4.8	1.72	8.7, 4.8	2.22
Cu <sub>2</sub> (CH <sub>3</sub> COO) <sub>4</sub> · 2H <sub>2</sub> O	6.6	1.72	9.6, 5.5	2.07
Cu(C <sub>2</sub> O <sub>4</sub> )	6.6	1.41	8.9, 5.7	1.76
Cu(cyclohexanecarboxylic acid) <sub>2</sub>	8.3, 5.3	1.70	9.5, 5.7	2.33
Cu(acetylacetonate) <sub>2</sub>	9.0, 5.1	3.15	9.9, 4.8	3.25
Cu(NH <sub>3</sub> ) <sub>4</sub> SO <sub>4</sub> · H <sub>2</sub> O	7.7	1.02	8.7	1.54
Cu(Gly) <sub>2</sub>	8.4	1.23	8.0	1.48
Cu(Ala) <sub>2</sub>	8.0	1.23	8.0	2.00
Cu(Ser) <sub>2</sub>	8.2	1.10	9.1	1.48
Cu(Lys) <sub>2</sub>	9.0	1.15	8.6	1.20
Cu(Asp)	8.4	1.41	7.9	1.69
Cu(Glu)	8.4	1.39	7.9	1.53
Cu(His) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> · 2H <sub>2</sub> O	8.4	1.54	8.1	1.61
K <sub>2</sub> [Cu(NHCONHCONH) <sub>2</sub> ] · 4H <sub>2</sub> O	8.4	0.93	8.5	1.44
Cu <sub>2</sub> SO <sub>3</sub> · CuSO <sub>3</sub> · 2H <sub>2</sub> O	8.1		7.8	
Cu <sub>4</sub> Cl <sub>5</sub> (ethylenediamine) <sub>2</sub>	8.3		9.1	
Na <sub>4</sub> [Cu(NH <sub>3</sub> ) <sub>4</sub> ] [Cu(S <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	7.7		8.8	

of these satellites was high enough. Cu(II)acetate was a good example for a compound of a direct antiferromagnetic exchange interaction between neighboring copper atoms [47]. In dimeric cupric acetate the two copper atoms are bridged by four acetate groups; the copper-copper distance of 2.61 Å is only slightly larger than that found in metallic copper (2.55 Å) [48]. The low magnetic moment of 1.4 Bohr magnetons is ascribed to a direct magnetic exchange. Figgis [49] suggested that the antiferromagnetic behaviour could be attributed to the direct but very weak interaction between the unpaired electrons in the two 3 d<sub>x<sub>2-y<sup>2</sup></sub></sub> energy levels. It was of interest to observe that regardless of the above antiferromagnetic interaction the satellite splitting was maintained in the XPS spectrum of Cu 2p<sub>3/2</sub> level of Cu(II)acetate. In the case of the exclusive coordination of Cu(II) to nitrogen atoms, only one homogeneous satellite is seen in the XPS spectrum of Cu(II)biuret (Fig. 3).

As deduced from X-ray crystallographic data [18], the copper in the violet-pink potassium *bis*(biureto)cuprate tetrahydrate is square-coordinated to

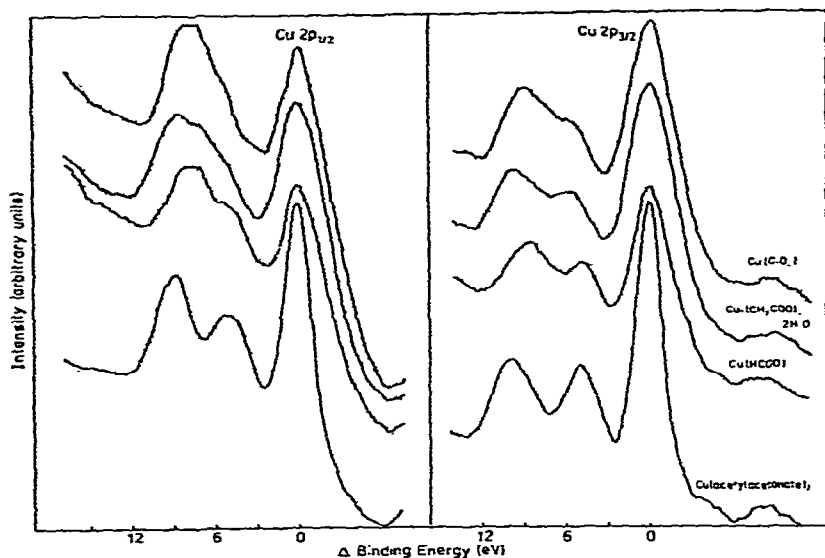


FIG. 2. XPS spectra of the Cu 2p<sub>1/2</sub> and Cu 2p<sub>3/2</sub> levels. Recording conditions: number of scans 13, Cu(HCOO)<sub>2</sub>, royal-blue; 15, Cu<sub>2</sub>(CH<sub>3</sub>COO)<sub>4</sub> · 2H<sub>2</sub>O; 10, Cu(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>; 10, Cu(acetylacetonate)<sub>2</sub>; further details as in Fig. 1.

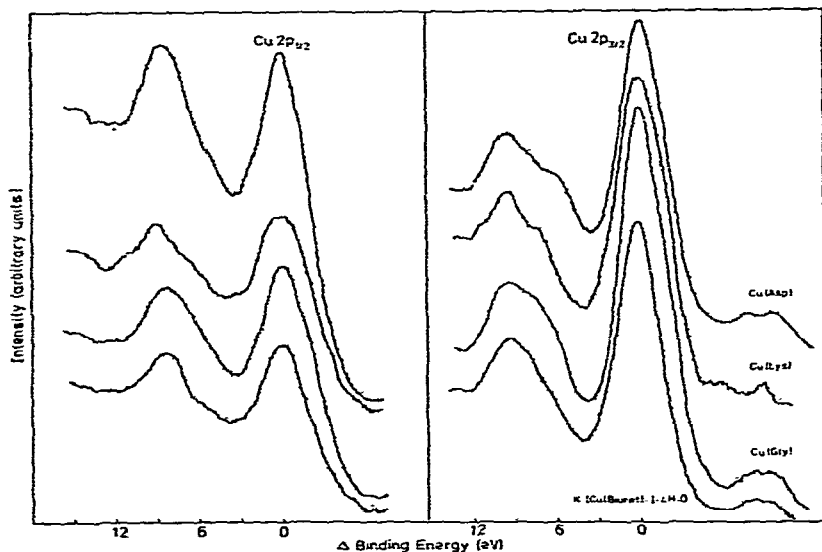


FIG. 3. XPS spectra of the Cu 2p<sub>1/2</sub> and Cu 2p<sub>3/2</sub> levels. Recording conditions: number of scans 15, K<sub>2</sub>[Cu(NHCONHCONH)<sub>2</sub>] · 4H<sub>2</sub>O; 10, Cu(Gly)<sub>2</sub>; 12, Cu(Lys)<sub>2</sub>; 6, Cu(Asp)<sub>2</sub>; further details as in Fig. 1.



four amide nitrogen atoms belonging to two (biuret)<sup>2-</sup> residues. Furthermore, the binding energy of N 1s (398.9 eV, Table 1) is low. It may be concluded that each biuret molecule is acting as a dianion attributable to the ionization of two hydrogen atoms.

In those Cu(II) complexes where both oxygen and nitrogen serve as the direct ligands, a gradual splitting of the Cu 2p<sub>3/2</sub> satellite was observed. The splitting was similar to that seen for the Cu(II)carboxylate complexes. It might be tempting to draw conclusions about the molecular architecture of the respective Cu(II)compounds from the shape and character of the satellite. However, much more work remains to be done.

### Copper(I)Compounds

In contrast to the inability of electron paramagnetic resonance measurements to detect Cu(I), XPS proved a powerful means to demonstrate this oxidation state, using Cu<sup>II</sup>O and Cu<sup>I</sup><sub>2</sub>O [40-42]. After the recent discovery of copper-sulfur proteins in our laboratory [32,37,38,50], the reaction of differently oxidized copper with sulphides prompted us to carry out a comprehensive XPS study. Regarding the copper sulphides, there is likely to be extreme metal-ligand covalency. In these compounds electron delocalization can occur with a very small expenditure of energy, resulting in a high electronic conductivity. It was expected that the less electronegative sulfur would be unable to locate both electrons at the sulphur atom. In other words at least one electron would be used to fill up the 3d shell of copper. This phenomenon was already inferred from X-ray emission spectroscopic measurements [51,52]. Unfortunately, no final decision was possible. As in the case of Cu<sub>2</sub>O, the sulfur species Cu<sub>2</sub>S (chalcocite) displayed one single homogeneous XPS signal in either the Cu 2p<sub>1/2</sub> or the Cu 2p<sub>3/2</sub> level (Fig. 4).

No satellites characteristic for Cu(II) were observed. Moreover, it was shown that in the course of the XPS measurements no detectable photochemical reduction of Cu(II) to Cu(I) occurred (see Figs. 1-3). The same XPS spectra were obtained when an established source for Cu(I), the NH<sub>4</sub>CuS<sub>4</sub> complex, was employed. Upon examining CuS, all satellites were levelled off and no sign whatsoever of the presence of Cu(II) could be seen. This result was very intriguing and supported the above assumptions. From X-ray diffraction studies using the mineral covellite (CuS) and Na<sub>2</sub>S<sub>3</sub>Cu<sub>3</sub>, it was presumed that mixed valences of Cu(I)/Cu(II) species do exist. However, it was shown unequivocally that exclusively Cu(I) is bound to sulfur in these copper compounds (Figs. 4 and 5).

### Mixed Valence Cu(II)/Cu(I) Complexes

Chemical systems containing ions of the same element in two different formal states of oxidation are called "mixed valence" compounds. Mixed valence systems are of considerable interest because their properties are rarely just the

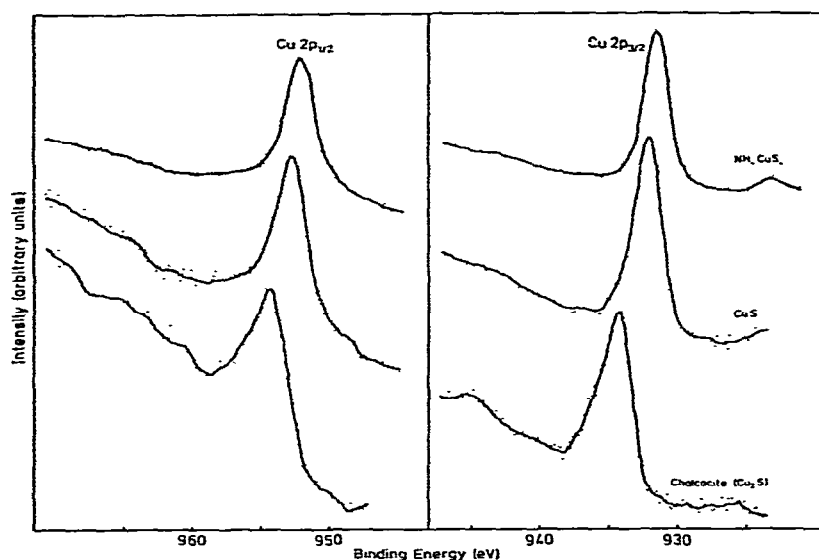


FIG. 4. XPS spectra of the Cu 2p<sub>1/2</sub> and Cu 2p<sub>3/2</sub> levels. Recording conditions: number of scans 10, chalcocite (Cu<sub>2</sub>S); 10, CuS; 10, NH<sub>4</sub>CuS<sub>4</sub>; further details as in Fig. 1.

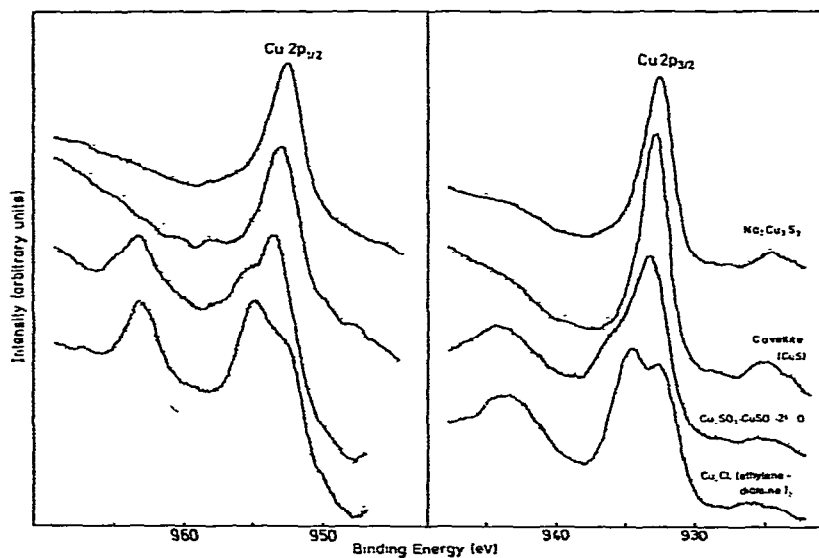
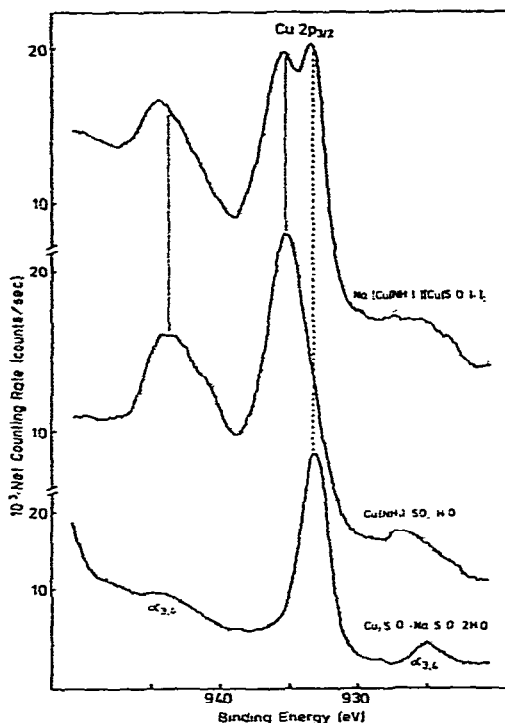


FIG. 5. XPS spectra of the Cu 2p<sub>1/2</sub> and Cu 2p<sub>3/2</sub> levels. Recording conditions: number of scans 10, Cu<sub>4</sub>Cl<sub>2</sub>(ethylenediamine)<sub>2</sub>; 9, Cu<sub>2</sub>SO<sub>3</sub>·CuSO<sub>3</sub>·2H<sub>2</sub>O; 17, Covellite (CuS); 8, Na<sub>2</sub>Cu<sub>3</sub>S<sub>3</sub>; further details as in Fig. 1.

sum of the two metal ions taken separately. XPS spectroscopy promised to be a powerful tool in the study of this phenomenon. The primary processes leading to ionized atoms proceed extremely fast and would conveniently allow the detection of "electronic ordering." We used the mixed valence classification scheme of Robin and Day, which is based essentially upon the strength and symmetry of the ligand fields about the metal ions [53]: A metalloprotein belongs to class I if the metal ions of differing valence are sufficiently separated from each other with the consequence that no detectable interaction in either the ground or the excited state can occur. In such a system, where the ions are in sites of different symmetry and ligand field strength, XPS should clearly show spectra of the constituent ions. The complex  $\text{Na}_4[\text{Cu}^{\text{II}}(\text{NH}_3)_4][\text{Cu}^{\text{I}}(\text{S}_2\text{O}_3)_2]_2$  was chosen since from X-ray diffraction data and magnetic measurements [26] it was concluded that the copper must be in a mixed valence state. In this complex, square-planar  $[\text{Cu}^{\text{II}}(\text{NH}_3)_4]^{2+}$  ions are well separated from  $[\text{Cu}^{\text{I}}_n(\text{S}_2\text{O}_3)_{2n}]^{3n-}$  polyanions. Each Cu(I) is surrounded by four thiosulphate groups while each thiosulphate is bound with two Cu(I) (Fig. 6 A, B).

One homogeneous XPS  $\text{Cu } 2p_{3/2}$  signal using  $\text{Cu}_2\text{S}_2\text{O}_3 \cdot \text{Na}_2\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  was recorded. The two adjacent minor peaks were attributed to Mg  $K_{\alpha 3,4}$  X-ray satellites and not to contaminating Cu(II). For comparative reasons the  $\text{Cu}^{\text{II}}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$  was recorded showing the typical Cu(II) spectrum. The fact that the spectrum of the mixed valence copper complex was essentially a mixture of the two lower Cu(I) and Cu(II) XPS spectra aroused considerable interest. This indicates that in this mixed valence complex distinct portions of Cu(I) and Cu(II) exist. Occasionally limited space for presentation of all XPS spectra in full is available. In this case it will be of help to know at least the ratio of the integrated areas between both the main peak and the satellite peak. The ratio for Cu(I) was 15.9 (the Mg  $K_{\alpha 3,4}$  satellite included), while 1.6 was calculated for the respective Cu(II) compound. The ratio for the mixed valence Cu(II)/Cu(I) was 2.8. Two further examples for mixed valence complexes are depicted in Fig. 5.

The classical  $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 \cdot 2\text{H}_2\text{O}$  [24] and, to a greater degree,  $\text{Cu}_4\text{Cl}_5(\text{ethylenediamine})_2$  [25] both show a splitting of the main copper signal in either the  $\text{Cu } 2p_{1/2}$  or the  $\text{Cu } 2p_{3/2}$  level. Of high importance are those model systems in which the metal ions are found in close proximity when strong metal interactions are expected. According to the preceding classification these model systems are listed as class III metal complexes. Class III mixed valence systems have metal ions situated in exactly equivalent sites and are therefore indistinguishable. Class III can be further subdivided into classes III-A and III-B depending upon whether or not discrete polynuclear ions can be distinguished in the crystal [53]. In many class III copper complexes, the metal is frequently found associated with sulfur ligands. On the other hand, sulfur is known to be an active constituent in many redox enzymes where it is frequently bound to iron or copper. The already mentioned copper sulfur complexes covellite and  $\text{Na}_2\text{Cu}_3\text{S}_3$  [22] are known in the literature as classical III-B mixed valence complexes. For example, covellite was described as  $\text{Cu}^{\text{I}}_4\text{Cu}^{\text{II}}_2(\text{S}_2)_2\text{S}_2$  [53]. It may be concluded that in both copper complexes the metal is in the oxidation state I and surrounded by sulfur of equivalent ligand fields.

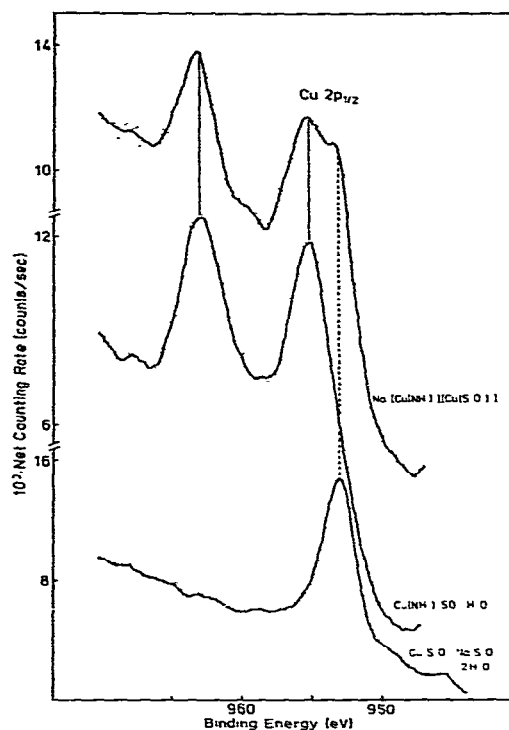


(A)

FIG. 6. (A, B) XPS spectra of the Cu  $2p_{1/2}$  level (A) and the Cu  $2p_{3/2}$  level (B). Recording conditions: number of scans 10,  $\text{Cu}_2\text{S}_2\text{O}_8 \cdot \text{Na}_2\text{S}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ ; 10,  $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$ ; 10,  $\text{Na}_4[\text{Cu}(\text{NH}_3)_4][\text{Cu}(\text{S}_2\text{O}_3)_2]_2$ ; further details as in Fig. 1.

## CONCLUSION

One important aspect of XPS should be pointed out. Established physico-chemical procedures including visible and ultraviolet spectroscopy, in general, produce a picture of the absorbing molecule within the order of  $10^{-13}$ - $10^{-14}$  sec. In contrast, only  $10^{-17}$  sec is required for the primary ionization process generated during XPS [4]. Needless to say that this new method is the most rapid technique available for examining electronic structure at present. The long-lasting discussion regarding intermediate or monomeric redox states in mixed valence complexes can now be ended. The earlier physico-chemical methods did not permit definite conclusions for such complexes attributable to the relatively great amount of time required for tracing a molecular picture. Furthermore, results obtained from the mixed valence copper complexes were very encouraging for other studies in bioenergetic systems. Perhaps, it will be



(B)

possible to find a way for detecting the different intermediate oxygen species which are postulated during the electron transfer to molecular oxygen [54,55].

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