Department of Chemistry   **Irwin A. Cohen***
City University of New York
Brooklyn College
Brooklyn, New York 11210

Department of Chemistry   **David K. Lavallee**
City University of New York   **Alan B. Kopelove**
Hunter College
New York, New York 10021

Figure 1. Cu 2p binding energy spectra of (a) Cu(en)$_2$(SCN)$_2$ and (b) [Cu(py)$_2$(SCN)$_2$]$_n$. Spectra were recorded on a Hewlett-Packard Model 5950A ESCA spectrometer using Al K$\alpha_{1,2}$ radiation (1486.6 eV). An electron "floodgun", to reduce surface charging effects to a minimum, and an X-ray-beam power of 1000 W were used in recording both spectra. Times for the data accumulation are as follows: (a) 23 min; (b) 4.5 min.

X-ray Photoelectron Spectra of Copper Complexes Considered as Models for Metalloproteins Containing Copper–Sulfur Bonds[1]

Sir:

Recent studies on the X-ray photoelectron spectra (XPS) of metal complexes of the sulfur-containing amino acids cysteine and penicillamine[2,3] have demonstrated that a *negative* chemical shift is characteristic of the binding of the thiol (RSH) group in these ligands to a metal ion. However, one group of metal–thiol (M–SR) complexes which exhibit some unusual XPS properties are the copper complexes of cysteine (I), penicillamine (II), α-mercaptopropionylglycine (III), and N-mercaptoacetylglycyl-L-histidine (IV).[4–8] As a result of XPS investigations on these species, Weser and co-workers[4–6,8] proposed that they contained Cu(I) sites bound to sulfur radicals, i.e., Cu^I(SR).

The purpose of the present communication is both to offer an alternative interpretation of the XPS of these copper complexes and to point out errors in previous analyses of these results.[4–8]

The abbreviations cyst, pen, MPG, and MAGH will be used for the appropriate anionic forms of the complexed ligands I, II, III, and IV, respectively. The copper–cysteine complex was described[4] as being of 1:1 stoichiometry, [Cu(cyst)]$_n$, while the two penicillamine complexes which were studied[4–6] comprised the structurally characterized[9] complex Tl$_5$[Cu$_{14}$-(pen)$_{12}$Cl] and a violet product of poorly defined stoichiometry. The complexes of ligands III and IV, Na[Cu(MPG)]·2H$_2$O and Na$_2$[Cu(MAGH)]·2H$_2$O,[7,8] are believed to contain [NO$_2$S][10] and [N$_3$S][7] donor sets, respectively; in the case of Na[Cu(MPG)·2H$_2$O, one of the oxygens arises from a coordinated water molecule.

The features common to the XPS of the five copper complexes are (1) evidence that the copper is present as Cu(I) rather than Cu(II) and (2) S 2p binding energies in the range 163.0–163.9 eV.[4–8] The XPS evidence in favor of Cu(I) is, with one exception, clear-cut since not only are the Cu 2p binding energies of Cu(I) complexes significantly lower than those of their Cu(II) analogues but satellite structure associated with the primary Cu 2p photolines is observed with Cu(II) species but is absent in the XPS of Cu(I).[11–13] The one exception to this observation concerns some conflicting data[7,8] for the complex Na$_2$[Cu(MAGH)]·2H$_2$O. While the two sources[7,8] agree as to the values of the Cu 2p$_{3/2}$ (932.1 eV) and S 2p (163.0 eV) binding energies, Younes, Pilz, and Weser[8] reported no Cu(II) satellite while Sugiura[7] observed such a feature (albeit weak) at 943.5 eV.[14] The presence of Cu(II) satellite structure requires that a primary Cu 2p$_{3/2}$ photoline due to Cu(II) be present; this peak must therefore be contained within the broad high-energy tail[14] of the much more intense Cu(I) Cu 2p$_{3/2}$ peak which is centered at 932.1 eV.

The almost exclusive detection of Cu(I) in the XPS measurements is somewhat surprising in view of the knowledge that certain of these complexes possess bulk properties which are characteristic of Cu(II), for example, the ESR Cu hyperfine structure associated with the paramagnetic complex Na[Cu(MPG)]·2H$_2$O[10] and the crystal structure of Tl$_5$-[Cu$_{14}$(pen)$_{12}$Cl] which reveals eight Cu(I) and six Cu(II) sites.[9] Nonetheless, Weser and co-workers[4–6,8] excluded the possibility that X-ray-induced reduction from Cu(II) to Cu(I) had occurred within the spectrometer. This conclusion was based principally upon the following three observations: (1) The XPS of the complex Cu(en)$_2$(SCN)$_2$, which contains Cu–S bonds, was purported to show[8] that this complex is not subject to photoreduction under the same experimental conditions as those used in recording the XPS of the other copper complexes. (2) Treatment of the violet copper–penicillamine complex with 3% H$_2$O$_2$ produces a material whose XPS now shows the presence of Cu(II) and oxidized sulfur (S 2p = 169.2 eV).[4,5] (3) If in the preparation of the violet copper–penicillamine complex a threefold excess of Cu(II) is used in the reaction, then the XPS of the resultant brown-green reaction mixture shows the presence of large quantities of Cu(II) in addition to Cu(I).[5,15]

(1) Part 27 of the series "X-Ray Photoelectron Spectra of Inorganic Molecules". Part 26: Brisdon, B. J.; Mialki, W. S.; Walton, R. A., accepted for publication in *J. Organomet. Chem.*
(2) Sokolowski, G.; Pilz, W.; Weser, U. *FEBS Lett.* **1974,** *48,* 222.
(3) Srinivasan, V.; Stiefel, E. I.; Elsberry, A.; Walton, R. A. *J. Am. Chem. Soc.* **1979,** *101,* 2611.
(4) Rupp, H.; Weser, U. *Biochim. Biophys. Acta* **1976,** *446,* 151.
(5) Rupp, H.; Weser, U. *Biochem. Biophys. Res. Commun.* **1976,** *72,* 223.
(6) Younes, M.; Weser, U. *Biochem. Biophys. Res. Commun.* **1977,** *78,* 1247.
(7) Sugiura, Y. *Inorg. Chem.* **1978,** *17,* 2176.
(8) Younes, M.; Pilz, W.; Weser, U. *Inorg. Biochem.* **1979,** *10,* 29.
(9) Birker, P. J. M. W. L.; Freeman, H. C. *J. Chem. Soc., Chem. Commun.* **1976,** 312.
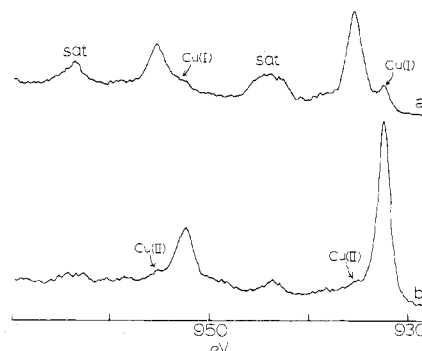(10) Sugiura, Y.; Hirayama, Y.; Tanaka, H.; Ishizu, K. *J. Am. Chem. Soc.* **1975,** *97,* 5577.

(11) Frost, D. C.; Ishitani, A.; McDowell, C. A. *Mol. Phys.* **1972,** *24,* 861.
(12) Kim, K. S. *J. Electron Spectrosc. Relat. Phenom.* **1974,** *3,* 217.
(13) Edwards, D. A. *Inorg. Chim. Acta* **1976,** *18,* 65.
(14) See Figure 4 in ref 7.

In our opinion, these points are not convincing support for the contention[4-6,8] that photoredox behavior can be excluded. First, and perhaps most importantly, the belief of Younes, Pilz, and Weser[8] that the Cu 2p binding energies they observed for $Cu(en)_2(SCN)_2$ are typical of Cu(II) is incorrect. While satellite structure due to Cu(II) is apparently present,[8] the energies of the primary Cu 2p photolines which they report in their paper (Cu $2p_{1/2}$ at 952.0 eV and Cu $2p_{3/2}$ at 932.0 eV)[8] are in fact characteristic of Cu(I). The binding energies of unreduced $Cu(en)_2(SCN)_2$ had been reported earlier by Best and Walton;[16] the resulting Cu 2p spectrum is shown in Figure 1a. The Cu $2p_{1/2}$ and Cu $2p_{3/2}$ primary photolines are located at 955.3 and 935.3 eV, and their associated satellite structure is at ~+8 eV relative to the $2p_{1/2,3/2}$ peaks. A small amount of Cu(I) is clearly present (peaks at ~952.5 and ~932.5 eV), and this must arise from a trace of photoreduction. In the case of the study by Younes, Pilz, and Weser,[8] it is apparent that almost complete reduction to Cu(I) had occurred during the XPS measurements.

The fact that some residual Cu(II) satellite structure can still be observed in the Cu 2p XPS even when most of the Cu(II) originally present has been photoreduced to Cu(I) is a factor which was not apparently taken into account in the interpretations by Younes, Pilz, and Weser.[8] This possiblity is illustrated in Figure 1b in the case of the Cu 2p spectrum of $[Cu(py)_2(SCN)_2]_n$. This complex is subject to a rapid X-ray-induced reduction within the spectrometer.[16] While the Cu $2p_{1/2,3/2}$ peaks of Cu(I) (at 952.5 and 932.5 eV) dominate the spectrum, a small amount of Cu(II) is still present. The latter is characterized by weak Cu $2p_{1/2}$ and Cu $2p_{3/2}$ primary photolines (see Figure 1b) and clearly defined (but weak) Cu $2p_{3/2}$ satellite structure at ~944 eV. Since reduction of $Cu(en)_2(SCN)_2$ occurs under the experimental conditions used by Younes, Pilz, and Weser,[8] it seems likely that this has also occurred with other copper complexes they studied.[4-6,8]

We turn now to the second piece of evidence which was cited (vide supra) in support of the proposal that X-ray-induced reduction of copper had not occurred.[8] Since treatment of the copper–penicillamine complex with H_2O_2 would be expected to destroy the Cu–thiol bonding, and this is indeed what happens, there is no reason to expect that the resulting material will be as photoredox active as the untreated complex. Accordingly, this experimental observation[8] does not bear on the question of whether the untreated samples of the copper–penicillamine complex will be X-ray sensitive or not.

Finally, the third observation can similarly be explained in terms of photoreduction. Thus an alternative interpretation to the one advanced by Younes, Pilz, and Weser[8] is that the excess Cu(II) which is present in the product obtained by mixing Cu(II) with penicillamine in a 3:1 mole ratio[8] is not reduced, while that smaller portion of the Cu(II) which is complexed to the thiol group of penicillamine is converted to Cu(I) upon irradiation.

An additional observation which supports photoreduction of the copper as the most likely explanation of the XPS results is that the S 2p binding energies (163.0–163.9 eV[4-8]) can then be assigned to disulfide sulfur (RSSR) rather than unstable ·SR radical species.[17,18] In this event, the photoredox behavior of these copper(II)–thiol complexes can be represented formally as the internal redox reaction $2Cu^{II}(SR) \rightarrow Cu^I_2(RSSR)$.[19]

Department of Chemistry   **Richard A. Walton**
Purdue University
West Lafayette, Indiana 47907

Geometry of Nickel(II) Complexes Containing a 12-Membered Ring in Solution

Sir:

Martin, DeHayes, Zompa, and Busch[1] have illustrated by means of calculations a relationship between the ring size of a macrocyclic ligand and the amount of strain such ligands would impose on a metal complex on the assumption that the cyclic ligand is bonded in a coplanar manner with the metal ion. If the ring size of the ligand is too small to coordinate with a given metal ion in a coplanar manner without imposing large strain energies, distortion from square-planar coordination will occur. The most common type of distortion involves the macrocyclic ligand folding so as to form either a cis-octahedral[1-5] or a trigonal-bipyramidal structure.[3,5] A square pyramid with the metal ion extruded from the basal plane is another type of distortion from a square-planar geometry which has been observed.[6,7] Calculations of strain energies by Martin et al. suggested that a 12-membered ring, [12]-aneN$_4$, would have difficulty in forming square-planar or trans-octahedral complexes with either cobalt(III) or nickel(II).[1] Although they did not take into account that the nickel–nitrogen bond is smaller in a low-spin complex than in a high-spin complex and as a result [12]aneN$_4$ might be able to assume planar chelation with a metal ion, no such complexes have yet been isolated.

Fabbrizzi[8] recently reported that in an aqueous solution of $[Ni([12]aneN_4)]^{2+}$ at 88 °C (or $[Ni([12]aneN_4)]^{2+}$ dissolved in 6 M $NaClO_4$) there coexisted in equilibrium a square-planar nickel(II) species and a six-coordinate nickel(II) species. An aqueous solution of $[Ni([12]aneN_4)]^{2+}$ at room temperature is purple, a color typically indicative of six-coordinate nickel(II); however, at higher temperatures (or in 6 M $NaClO_4$) the solution was yellow, a color commonly observed for square-planar NiN$_4$ systems. The lower temperature spectra were typical of six-coordinate nickel(II) complexes, but at higher temperatures the spectra appeared to contain bands associated with both a six-coordinate nickel(II) complex and a square-planar nickel(II) complex.[8]

We have observed that the green [Ni(tb[12]aneN$_4$)Cl]Cl (tb[12]aneN$_4$ = 1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane) is a five-coordinate complex (believed to be a

(1) Martin, L. Y.; DeHayes, L. J.; Zompa, L. J.; Busch, D. H. *J. Am. Chem. Soc.* **1974,** *96,* 4046.
(2) Smierciak, R.; Passariello, J.; Blinn, E. L. *Inorg. Chem.* **1977,** *16,* 2646.
(3) Kalligeros, G. A.; Blinn, E. L. *Inorg. Chem.* **1972,** *11,* 1145.
(4) Collman, J. P.; Schneider, P. W. *Inorg. Chem.* **1966,** *5,* 1380.
(5) Sarther, C. M.; Blinn, E. L. *Inorg. Chem.* **1976,** *15,* 3083.
(6) Styka, M. C.; Smierciak, R. C.; Blinn, E. L.; DeSimone, R. E.; Passariello, J. W. *Inorg. Chem.* **1978,** *17,* 82.
(7) Hoard, J. L.; Hamor, M. J.; Hamor, T. A.; Caugley, W. S. *J. Am. Chem. Soc.* **1965,** *87,* 2312.
(8) Fabbrizzi, L. *Inorg. Chem.* **1977,** *16,* 2667.

(15) The presence of Cu(I) can be seen from the asymmetric shape of the Cu $2p_{3/2}$ photoline shown in the figure presented in ref 5.
(16) Best, S. A.; Walton, R. A. *Isr. J. Chem.* **1976,** *15,* 160.
(17) The range of S 2p binding energies of these copper–thiol complexes is typical of disulfide sulfur rather than thiol sulfur,[18] further supporting the notion that reduction of the copper and concomitant oxidation of the sulfur-containing moiety has occurred.
(18) Walton, R. A., accepted for publication in *Coord. Chem. Rev.*