X-ray Photoelectron Spectra of Copper(I) and Copper(II) Complexes Derived from Macrocyclic Ligands[1]

R. R. Gagné,*[2a] J. L. Allison,[2a] C. A. Koval,[2a] W. S. Mialki,[2b] T. J. Smith,[2a] and R. A. Walton*[2b]

Contribution No. 6050 from the Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, and the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907.

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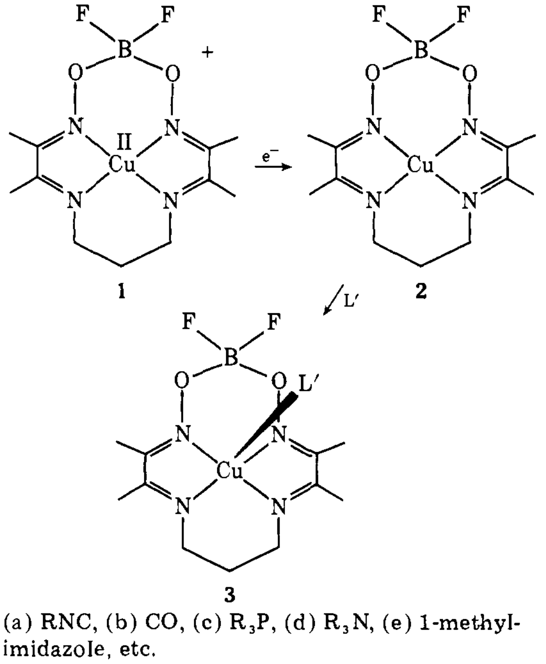
Abstract: The X-ray photoelectron spectra (X-ray PES) of pairs of mononuclear Cu(II) and Cu(I) complexes of several macrocyclic ligands show that there is a chemical shift of ~2.5 eV between the Cu 2p binding energies of these two oxidation states. A comparison of these data with that for mononuclear Cu(III) complexes of biuret and the tetradentate tripeptide ligand derived from α-aminoisobutyric acid shows a shift of ~2 eV between Cu(III) and Cu(II). These X-ray PES measurements do not support the alternative formulation of certain of the Cu(I) complexes as Cu(II) or Cu(III) species with reduced ligands. Thus a previous suggestion that $\mathrm{Cu^{I}(TAAB)(NO_3)}$ is in reality $\mathrm{[Cu^{III}(TAAB^{2-})](NO_3)}$ is not in accord with the present X-ray PES results. The preceding information has been used in the analysis of the X-ray PES of binuclear copper complexes of the macrocycle (L) which is prepared by condensing 1,3-diaminopropane with 5-methyl-2-hydroxyisophthaldehyde. The oxidation-state formalism which has been used to describe the complexes $\mathrm{Cu^{I}Cu^{I}L}$, $\mathrm{[Cu^{II}Cu^{I}L]ClO_4}$, and $\mathrm{[Cu^{II}Cu^{I}(CO)L]ClO_4}$ is consistent with the observed Cu 2p binding energy spectra. However, the $\mathrm{Cu^{II}Cu^{II}}$ complex $\mathrm{[Cu^{II}Cu^{II}L](ClO_4)_2{\cdot}2H_2O}$ reveals some unexpected and novel features in its Cu 2p spectrum. The appearance of two sets of Cu $2p_{1/2,3/2}$ doublets is attributed to the X-ray induced one-electron reduction of ~50% of the Cu(II)-Cu(II) complex to a symmetrical delocalized species Cu(+1.5)-Cu(+1.5) possessing Cu 2p binding energies which are intermediate between those of Cu(II) and Cu(I). This novel species also displays a characteristic satellite structure. Similar behavior is exhibited by the chloride complex $\mathrm{Cu^{II}Cu^{II}LCl_2{\cdot}6H_2O}$, but with the mixed metal complex $\mathrm{[Cu^{II}Zn^{II}L](ClO_4)_2{\cdot}2H_2O}$ the one-electron reduction is believed to produce the d^{10}-d^{10} Cu(I)-Zn(II) species.

Introduction

The four-coordinate copper(I) complex,[3] **2**, has been shown to react with a variety of monodentate ligands (Scheme I, L′ = isonitriles, phosphines, CO, amines, nitriles).[4,5] The resulting diamagnetic adducts, **3**, are five coordinate, an unusual coordination number for copper(I).[4,5] An alternative formulation for both the adducts, **3**, and the four-coordinate precursor, **2**, regards these species as containing Cu(II) or Cu(III) complexed to a reduced macrocyclic ligand. The latter explanation is comparable to that invoked to account for the chemical properties of certain iron and nickel dithiolate complexes.[6]

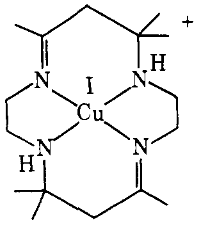
Scheme I



L′ = (a) RNC, (b) CO, (c) $\mathrm{R_3P}$, (d) $\mathrm{R_3N}$, (e) 1-methylimidazole, etc.

Oxidation state formalism questions also exist for the binuclear complex **5** (Scheme II). Prepared by one-electron reduction of the $\mathrm{Cu^{II}Cu^{II}}$ complex **4**, complex **5** is, formally, a mixed-valence, $\mathrm{Cu^{II}Cu^{I}}$ complex.[7] The mixed-valence complex **5** forms a carbonyl adduct **6**, apparently another example of five-coordinate copper(I).[7] The mixed-valence species **5** can also be further reduced, by one electron, to give a black, crystalline, diamagnetic product, **7**, presumably containing two copper(I) ions.[7] Complexes **4–7** have been examined by electron paramagnetic resonance, electronic absorption spectroscopy,[7] and crystallographic methods,[8] but continue to pose intriguing questions of bonding, intramolecular electron transfer, and metal oxidation states.

This paper presents the results of X-ray photoelectron spectral studies on the complexes **1–7**, $\mathrm{Cu^{II}}$(*trans*-diene)$^{2+}$ (**8**) and its copper(I) analogue **9**, and $\mathrm{Cu^{II}(TAAB)^{2+}}$ (**10**) and its copper(I) analogue **11**, along with model complexes, in an attempt to better define the electronic structures of these species.



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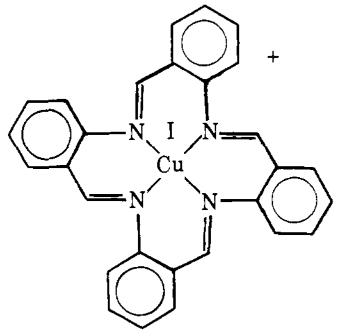

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Experimental Section

The perchlorate salts of complexes **1**,[4] **4**,[9] **5**,[7] **6**,[7] **8**,[10] and **9**,[10] the nitrate salts of **10** and **11**,[11] and the neutral complexes **2**,[4] **3** (L′ =

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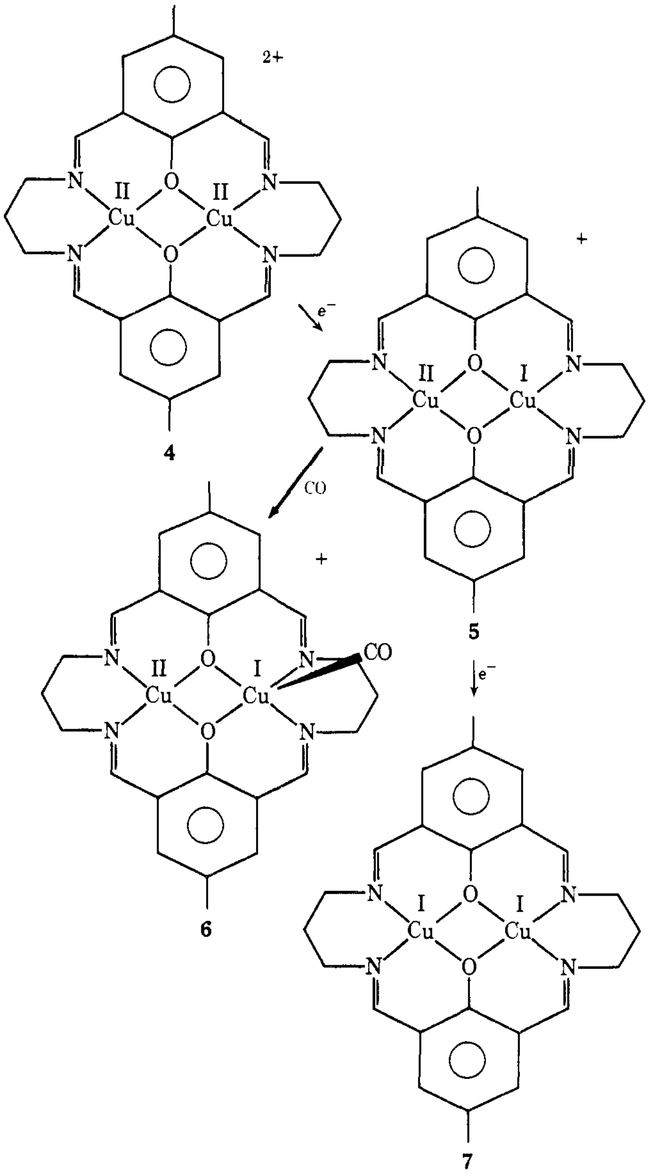
Scheme II



CO),[4] 3 (L′ = 1-MeIm),[4] and 7[7] were prepared by previously reported procedures. All reduced, copper(I) complexes were stored under helium in a Vacuum Atmospheres controlled atmosphere chamber prior to use. Analytically pure samples of the complexes $[Cu(py)_2Cl_2]_n$, $[Cu(bpy)Cl_2]_n$, $[Cu(phen)Cl_2]_n$, $Cu(terpy)Cl_2$, $Cu(trien)(ClO_4)_2 \cdot H_2O$, and $Cu(tren)Cl_2$ were kindly provided by Drs. G. Cayley and D. P. Murtha.

X-ray photoelectron spectra were recorded using a Hewlett-Packard Model 5950A ESCA spectrometer. Monochromatic aluminum $K\alpha_{1,2}$ radiation (1486.6 eV) was used as the X-ray excitation source and the powdered samples were dispersed on a gold-plated copper surface. An electron "floodgun" was used in conjunction with this instrument to eliminate, or at least reduce to a minimum, surface charging effects. Additional experimental details are described fully elsewhere.[12]

Results

The pertinent X-ray PES data for monomeric copper(I) and copper(II) complexes derived from macrocyclic ligands, together with data for several standard copper(II) complexes containing nitrogen ligands, are presented in Table I. Related binding energies for the binuclear copper complexes of a macrocyclic ligand are listed separately in Table II. In the case of complexes **1–3**, LBF_2 is used as the abbreviation for the macrocyclic ligand 1,1-difluoro-4,5,11,12-tetramethyl-1-bora-3,6,10,13-tetraaza-2,14-dioxacyclotetradeca-3,5,10,-12-tetraenato, while L is used for the macrocycle in the binuclear complexes **4–7**, wherein two copper atoms are held in close proximity (these complexes contain the pairs Cu(II)-Cu(II), Cu(II)-Cu(I), or Cu(I)-Cu(I)). The other macrocycles, *trans*-diene and TAAB, are as shown in the Introduction.

The appearance of very weak Cu 2p peaks at ~955 and ~935 eV in the X-ray PES of $Cu(LBF_2)$, $Cu(LBF_2)(L')$, Cu(*trans*-diene)(ClO_4), and Cu(TAAB)(NO_3) arises from small amounts of surface oxidation to copper(II) during our X-ray PES sample preparations. This occurs in spite of our attempts to prevent such a decomposition by resorting to the use of a nitrogen-filled drybox. Upon deliberately exposing these complexes to the air (for periods of up to 30 min) and rerunning their X-ray PES, we observe a dramatic increase in the amount of copper(II) contamination, the intensity of the copper(II) peaks now exceeding that of their lower binding energy counterparts.

Discussion

Copper 2p Binding Energies in Mononuclear Complexes. The Cu 2p binding energies of the copper(II) complexes listed in the top half of Table I and those of complexes **1**, **8**, and **10**, which have been formulated as derivatives of copper(II), are in good agreement with literature X-ray PES data for copper(II) species.[13-17] Furthermore, the occurrence of shake-up satellites[13,18] at ~8–10 eV to the high binding energy side of the primary $2p_{1/2,3/2}$ peaks confirms this conclusion. The chemical shift of approximately −2.5 eV between the Cu 2p peaks of $Cu(LBF_2)(ClO_4)$ (**1**) and $Cu(LBF_2)$ (**2**) (and its derivatives with carbon monoxide (**3b**) and 1-methylimidazole (**3e**), together with the absence of satellites in the Cu 2p spectra of the latter complexes, is characteristic of the difference between structurally related copper(II) and copper(I) species.[13,16,18] Therefore, the formulation[4b] of $Cu(LBF_2)$ and $Cu(LBF_2)(L')$, where L′ = CO or 1-methylimidazole, as copper(I) complexes is fully substantiated. Similarly, the Cu 2p binding energies of the complexes Cu(*trans*-diene)(ClO_4) (**9**) and Cu(TAAB)(NO_3) (**11**) are between 2.5 and 3.0 eV lower than those of the copper(II) species **8** and **10**, consistent with the formulation of the **9** and **11** as complexes of copper(I). This interpretation is further supported by the absence of the characteristic copper(II) shake-up satellite structure.[13,18]

The results of the Cu 2p binding energy measurements on **2**, **3**, and **11** are of further significance insofar as they relate to the question[3,4,11] of whether these complexes are genuine copper(I) species or, alternatively, contain copper(II) or copper(III) bound to a reduced macrocyclic system. Our X-ray PES results clearly favor the former formulation and do not support the contention of Katovic et al.[11] that $[Cu(TAAB)]^+$ (**11**) is in reality $[Cu^{III}(TAAB^{2-})]^+$. In fact, X-ray PES measurements on the genuine copper(III) complex of biuret, $KCu(H_{-2}bi)_2$, shows that its Cu 2p energies (Cu $2p_{3/2}$ at 936.7 eV) are ~2 eV higher than those of its copper(II) analogue, $K_2Cu(H_{-2}bi)_2$ (Cu $2p_{3/2}$ at 934.8 eV).[19] This is supported by measurements on the copper(III) complex $Cu(H_{-2}Aib_3)$, where $H_{-2}Aib_3$ is the tetradentate tripeptide derived from α-aminoisobutyric acid,[20] which has a Cu $2p_{3/2}$ energy of 936.2 eV.[21] Accordingly, there is no X-ray PES evidence for **11** being a derivative of copper(III).[22]

Although it is not our intent to give a detailed consideration to the N 1s spectra of the macrocyclic ligands, a couple of points are worth mentioning at this time. First, in the case of $Cu(TAAB)(NO_3)_2$ (**10**) and Cu(TAAB)(NO_3) (**11**), the N 1s intensity ratios for the two types of nitrogen (NO_3 at ~406 eV, TAAB at ~400 eV) change from 1:2 to 1:4 in accord with the stoichiometry differences between these two complexes, thereby confirming the structural integrity of these complexes during the X-ray PES measurements. Second, in the N 1s spectrum of $Cu(LBF_2)(ClO_4)$ (**1**), two well-resolved peaks of equal intensity, are observed, a gratifying result in view of the

Table I. X-ray Photoelectron Spectra of Copper Complexes of Nitrogen-Containing Ligands

complex[b]		binding energies, eV[a]				
		Cu $2p_{3/2}$	N 1s	C 1s	Cl $2p_{3/2}$	F 1s
$[Cu(py)_2Cl_2]_n$		934.5 (2.0)	399.4 (1.1)	284.5		
$[Cu(bpy)Cl_2]_n$[c]		934.0 (1.7)	399.3 (1.1)	284.5 285.5 sh	197.4	
$[Cu(phen)Cl_2]_n$		934.3 (1.7)	399.4 (1.2)	284.8	197.6	
$Cu(terpy)Cl_2$		934.9 (1.5)	399.9 (1.1)	285.3 286.3 sh		
$Cu(trien)_2(ClO_4)_2 \cdot H_2O$		934.8(1.7)	399.9 (1.3)	~285.0 sh 285.7	207.9	
$Cu(tren)Cl_2$		934.8 (1.8)	400.0 (1.7)	285.9	198.0	
$Cu(LBF_2)(ClO_4)$[e]	**1**	935.4 (1.7)[c]	399.7 (1.4) 401.1 (1.5)	285.4 286.4 sh	207.5	686.1
$Cu(LBF_2)$	**2**	932.9 (1.6)[d]	~399.9 (3.0)	285.1		685.7
$Cu(LBF_2)(CO)$	**3b**	933.1 (1.6)[d]	~400.0 (4.0)	285.1		
$Cu(LBF_2)$(1-MeIm)	**3e**	932.9 (1.8)[d]	400.0 (3.3)	285.2		
Cu(*trans*-diene)$(ClO_4)_2$	**8**	935.2 (1.5)[c]	399.8 (1.5)	285.2	207.5	
Cu(*trans*-diene)(ClO_4)	**9**	932.5 (1.5)[d]	400.0 (1.7)	285.4		
Cu(TAAB)$(NO_3)_2$	**10**	935.4 (2.0)[c]	400.2 (1.3) 406.3 (1.4)	285.1		
Cu(TAAB)(NO_3)	**11**	932.9 (1.8)[d]	399.6 (1.8) 406.2 (1.8)	285.0		

[a] Full width half-maximum values (fwhm) for the Cu $2p_{3/2}$ and N 1s peaks are given in parentheses. The Cu $2p_{1/2}$ component is located at 20.0 ± 0.2 eV above that of the $2p_{3/2}$ peak. [b] Ligand abbreviations: pyridine (py), 2,2′-bipyridyl (bpy), 1,10-phenanthroline (phen), 2,2′,-2″-terpyridyl (terpy), triethylenetetramine (trien), tris(2-aminoethyl)amine (tren). [c] Weak peak located at ~933.0 eV due to small amounts of Cu(I) produced by X-ray photoreduction. The intensity of this peak decreased further upon reduction in the X-ray power from 1 kW to 600 W. [d] A weak peak centered between 934.8 and 935.2 eV arises from trace amounts of surface oxidation of this air-sensitive Cu(I) complex to Cu(II). This occurs during sample preparation (see Discussion). [e] The complex was studied as its dioxane solvate $Cu(LBF_2)(ClO_4) \cdot \frac{1}{2}C_4H_8O_2$.

Table II. X-ray Photoelectron Spectra of Binuclear Copper Complexes of a Nitrogen Macrocycle

complex		binding energies, eV[a]	
		Cu $2p_{3/2}$	N 1s
$[Cu^{II}Cu^{II}L](ClO_4)_2 \cdot 2H_2O$	**4**	935.4 (~2.0) 934.2 (~2.0)	399.4 (1.2)
$[Cu^{II}Cu^{I}L]ClO_4 \cdot 0.5CH_3OH$	**5**	935.3 (2.6) 932.3 (1.9)	399.1 (2.0)
$[Cu^{II}Cu^{I}(CO)L]ClO_4$	**6**	935.5 (2.5) 932.7 (2.0)	399.5 (1.9)
$Cu^{I}Cu^{I}L$	**7**	932.5 (1.6)	399.6 (1.5)

[a] Full width half-maximum values (fwhm) for the Cu $2p_{3/2}$ and N 1s peaks are given in parentheses. The Cu $2p_{1/2}$ component is located at 20.0 ± 0.2 eV above that of the $2p_{3/2}$ peak. In all instances the C 1s peak was close to 285 eV.

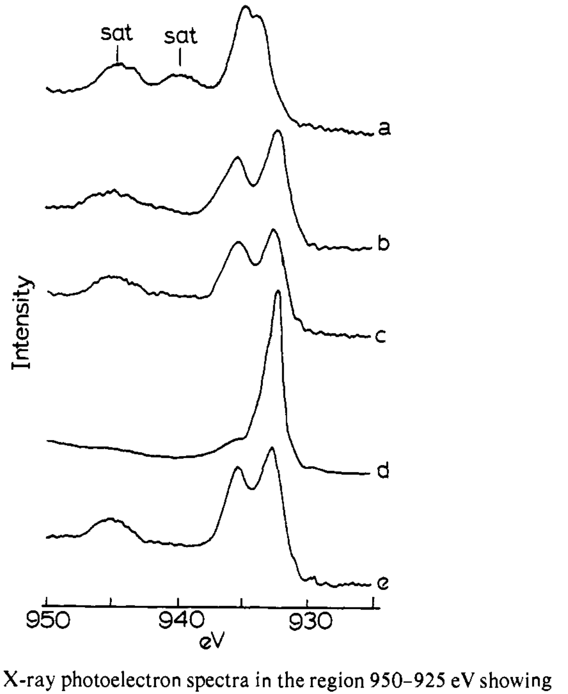


Figure 1. X-ray photoelectron spectra in the region 950–925 eV showing the primary Cu $2p_{3/2}$ photolines and associated satellite structure: (a) $[Cu^{II}Cu^{II}L](ClO_4)_2 \cdot 2H_2O$; (b) $[Cu^{II}Cu^{I}L]ClO_4 \cdot 0.5CH_3OH$; (c) $[Cu^{II}Cu^{I}(CO)L]ClO_4$; (d) $Cu^{I}Cu^{I}L$; (e) spectrum of $Cu^{I}Cu^{I}L$ after exposure to the air for 30 min.

two different nitrogen environments present; we presume that the higher energy peak arises from the nitrogen atoms which are bound to the O atoms of the O_2BF_2 bridging unit. Unfortunately, with $Cu(LBF_2)$ and $Cu(LBF_2)(L')$, the two nitrogen peaks are not resolved. However, the fwhm values (3.0–4.0 eV) of the resulting broad N 1s band (Table I) are comparable to the overall width (2.9 eV) of the resolved doublet in the case of the N 1s spectrum of $Cu(LBF_2)(ClO_4)$.

Copper 2p Binding Energies in Binuclear Complexes. The Cu 2p chemical shift difference of approximately 2.5 eV observed for the pairs of structurally related mononuclear copper(I) and copper(II) complexes in the preceding section provides a basis for considering the related X-ray PES data of the binuclear species $[Cu_2L]^{n+}$ (n = 0, 1, or 2), **4–7**. In the case of the binuclear complex $Cu^{I}Cu^{I}L$ (**7**), a sharp Cu $2p_{3/2}$ peak at 932.5 eV (Table II and Figure 1) is characteristic of the Cu(I) oxidation state in a nitrogen macrocycle. The weak feature close to 935 eV (Figure 1d) is due to a trace of Cu(II) surface contaminant, an interpretation which was confirmed by deliberately exposing this air-sensitive complex to the atmosphere (Figure 1e). The dramatic increase in the intensity of this latter feature, together with the appearance of the attendant characteristic Cu(II) satellite structure at ~945 eV, attests to the rapid surface oxidation of this complex.

The mixed-valence complexes **5** and **6** both contain the expected pair of Cu $2p_{1/2,3/2}$ doublets whose energies closely match those expected for mixed Cu(II)-Cu(I) species (Figures 1b,c). Like the related X-ray PES data for **7**, the spectra of **5** and **6** showed no dependence on X-ray flux (X-ray power

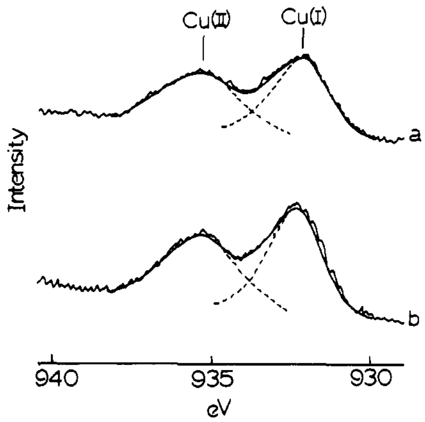


Figure 2. Cu $2p_{3/2}$ primary photolines of $[Cu^{II}Cu^{I}L]ClO_4\cdot0.5CH_3OH$ recorded using different X-ray fluxes: (a) 600 W; (b) 1000 W. Both spectra were recorded for ca. 20 min, and their deconvolution using a Du Pont 310 curve resolver (employing a Gaussian-shape fit) showed that the intensity ratio $I[Cu(II)]/I[Cu(I)]$ was 1.0 ± 0.1. Full width half-maximum values were 2.6 ± 0.1 eV for the Cu(II) component and 1.9 ± 0.1 eV for Cu(I).

varied between 600 W and 1 kW), but unlike **7** these spectra were unaffected by prior exposure of the samples to the atmosphere, an observation which is in keeping with the relative stability of these two complexes to aerial oxidation. Deconvolution of the Cu 2p spectra of mixed-valence **5** and **6** (Figure 2) confirmed (1) that the Cu(I) component peaks were significantly narrower than those due to Cu(II) (this is expected due to the broadening of the latter via multiplet splitting effects)[23] and (2) that the $I[Cu(II)]/I[Cu(I)]$ intensity ratio was 1.0 ± 0.1. The presence of two different copper environments in **5** and **6** is supported by their N 1s binding energy spectra. The N 1s peaks (Table II) are significantly broader than that for the symmetric $[Cu^{I}Cu^{I}L]$ species in which the four nitrogen atoms are indistinguishable.

The similarity of the X-ray PES of **5** and **6** argues that at least on the X-ray PES time scale ($\sim10^{-17}$ s) we are dealing with genuine mixed-valence copper(II)-copper(I) complexes. This is certainly the case with **6**, for which EPR data show[7] that the odd electron is localized on a single copper center. With **5**, electronic and EPR spectra provide evidence[7] of interaction between the Cu(I) and Cu(II) centers, although this is markedly temperature dependent. In the case of the EPR experiments, a seven-line isotropic spectrum (in CH_2Cl_2) at 25 °C arises because of the interaction of the odd electron with both copper centers ($I = ^3/_2$), and the intramolecular electron transfer therefore occurs at a rate which is rapid compared to the relatively slow EPR experiment (10^{-8}–10^{-4} s). However, in frozen solutions the observed four-line ($g_{\parallel}$) anisotropic spectrum shows that, as in **6**, the odd electron is now localized on a single copper center.

Up to this point we have assumed that the appearance of two sets of peaks near the binding energies of isolated Cu(II) and Cu(I) species could be taken as evidence that the compound does not have a delocalized ground state. Such an assumption has been criticized by Hush,[24] who pointed out that a symmetrical delocalized mixed-valence compound will have two accessible unsymmetrical photoionized states, due to electron relaxation in the strong field of the core hole, and these will be localized. Accordingly, the peak separation for a complex with a delocalized ground state could be close to that for isolated Cu(I) and Cu(II). From this theory,[24] the intensity of the peak at low binding energy to that at high binding energy is proportional to the electronic coupling $|J|$, so that for weakly coupled but delocalized metals (i.e., $|J|$ is small) we should observe two peaks of nearly equal intensity. As we have mentioned earlier, the intensities of the two sets of peaks for **5** are within experimental error the same, so that this complex could be an example of a delocalized mixed-valence complex containing very *weakly coupled* metal centers. Consequently, we were left with the problem of distinguishing between a genuine "trapped-valence" mixed oxidation state complex and one which has a delocalized symmetric ground state. Accordingly, we have recently embarked on the solution of the crystal structure of $[Cu^{II}Cu^{I}L]ClO_4$. This structure solution clearly shows[8] that this molecule has an unsymmetrical ground state, in accord with our initial interpretation of the X-ray PES results. This is similar to the crystallographic results for the mixed Co(II)-Co(III) complex $[Co^{II}Co^{III}LBr_2(H_2O)_2]^+Br^-$ which was previously investigated by Hoskins and Williams.[25] Therefore, to our knowledge, there are still no examples of mixed-valence metal complexes which are known to possess a symmetrical delocalized ground state and for which two sets of metal core binding energies have been observed, despite efforts to search for such examples.[26]

The final complex of interest to us in the present study was the binuclear Cu(II) species **4.** To our surprise, rather than the expected single Cu $2p_{1/2,3/2}$ spin-orbit doublet and its associated satellite structure, two sets of primary photolines were observed (Table II and Figure 1a). The higher energy $2p_{1/2,3/2}$ doublet was characteristic of Cu(II) while the lower energy set was intermediate in value between that expected for mononuclear Cu(II) and Cu(I). Deconvolution of the spectrum showed that the two sets of peaks were of similar intensity and possessed very similar fwhm values (1.8–2.0 eV). Furthermore, an additional feature in the X-ray PES of **4** was the presence of a second set of satellite structure (at ~6 eV above the primary Cu 2p photolines). This spectrum was reproducible under a variety of different experimental conditions. These included variations in the probe temperature (from room temperature to −40 °C), the time of irradiation (varied between 5 min and 10 h), and the X-ray power (varied from 400 to 1000 W).[27] The one minor spectral variation was the presence of a weak shoulder at ~932.5 eV in the Cu 2p spectrum of some of the samples. This was due to the formation of small amounts of "normal" Cu(I) species. Different synthetic batches of the complex showed the same spectral features. Monitoring the C 1s, N 1s, O 1s, and Cl 2p spectra provided no evidence for radiation damage involving the ligands. For example, the Cl 2p binding energy spectrum (Cl $2p_{3/2}$ at 207.7 eV) showed that the only chlorine-containing anion present was ClO_4^-.

To check whether the unusual Cu 2p X-ray PES of **4** was specific to this complex or typical of other binuclear Cu(II) species of this same ligand, we investigated the X-ray PES of the analogous chloride complex $Cu^{II}Cu^{II}LCl_2\cdot6H_2O$, a species which contains coordinated chloride and square-pyramidal Cu(II) centers,[28] and of the mixed Cu(II)-Zn(II) complex $[Cu^{II}Zn^{II}L](ClO_4)_2\cdot2H_2O$.[29] The Cu 2p spectrum of $Cu^{II}Cu^{II}LCl_2\cdot6H_2O$ revealed features in common with **4**, although the two sets of Cu 2p doublets were unresolved. However, the overall width of the overlapping Cu $2p_{3/2}$ components (fwhm = 3.8 eV) was identical with that of **4** (Figure 1a). In addition, the lower energy satellite structure ($\Delta E \sim 6$ eV) seen in the spectrum of **4** (Figure 1a) is clearly present in the X-ray PES of $Cu^{II}Cu^{II}LCl_2\cdot6H_2O$. The spectrum of the mixed metal complex $[Cu^{II}Zn^{II}L](ClO_4)_2\cdot2H_2O$ is different from that of the Cu(II)-Cu(II) derivatives in two important respects. First, while two Cu 2p doublets are observed, they are at energies (Cu $2p_{3/2}$ at 934.7 and 932.7 eV) which are typical of mononuclear Cu(II) and Cu(I) species, respectively (Table I). Second, the lower energy satellite structure, which is present in the X-ray PES of **4** and $Cu^{II}Cu^{II}LCl_2\cdot6H_2O$, is absent in the related spectrum of $[Cu^{II}Zn^{II}L](ClO_4)_2\cdot2H_2O$.[30]

While the above observations concerning the X-ray PES of the Cu(II)-Cu(II) and Cu(II)-Zn(II) species can be rationalized in terms of a fairly constant level of X-ray induced reduction of Cu(II) (approximately 50% of the material is reduced), the spectral differences between these two species are best explained in terms of the nature of the molecular orbital which is involved in the reduction. In the case of the two Cu(II)–Cu(II) complexes, the chemical shift of the lower energy set of Cu $2p_{1/2,3/2}$ peaks is intermediate between that of localized Cu(II) and Cu(I), an observation which may be consistent with the electron being delocalized over both metal centers in a genuine Cu(+1.5) dimer. The satellite at $\Delta E \sim +6$ eV would then be associated with this reduced species, while the higher energy satellite structure (that between 8 and 10 eV) is due to that proportion of the Cu(II)–Cu(II) dimers which has not been reduced. The reason that this delocalized reduced binuclear complex can be generated in the solid state whereas solution electrochemical reductions produce localized Cu(II)–Cu(I)[7] is attributed to favorable lattice energy effects. With the heteronuclear complex $[Cu^{II}Zn^{II}L](ClO_4)_2{\cdot}2H_2O$, the one-electron X-ray induced reduction leads to diamagnetic Cu(I)–Zn(II), rather than a paramagnetic delocalized species, a reflection on the difficulty of reducing Zn(II). Such a reduced species, possessing d^{10} metal centers, would not be expected to exhibit any satellite structure and, with the exception of that due to unreduced Cu(II)–Zn(II) which is still present, no additional satellite structure is observed.

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References and Notes

(1) This paper is part 25 in the series "The X-ray Photoelectron Spectra of Inorganic Molecules". For part 24, see P. Brant, W. S. Mialki, and R. A. Walton, *J. Am. Chem. Soc.*, **101**, 5453 (1979).

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(21) Other binding energies for this complex are as follows: C1s, 284.8, ~286.0 sh and 287.4; N 1s, ~399.2 br; O 1s, 531.4 eV.

(22) Since our manuscript was first submitted for publication, Professor Jeremy K. Burdett has kindly informed us of the results of some extended Hückel MO calculations he has carried out on the complexes **1, 2, 3,** and **11** (J. K. Burdett and P. D. Williams, manuscript in preparation). Calculations for $[Cu(TAAB)]^+$ (**11**) are in accord with this complex being a Cu(I) species in which the HOMO is Cu $d_{x^2-y^2}$ and the LUMO is ligand π^*. This result agrees with our Cu 2p X-ray PES results which favor the formulation of this complex as Cu(I). Similarly, agreement is found between the interpretations of the X-ray PES results and the MO calculations for $Cu(LBF_2)(ClO_4)$ (**1**) and $Cu(LBF_2)(CO)$ (**3b**), insofar as the formal description of the copper oxidation states is concerned (Cu(II) and Cu(I) species, respectively). However, for $Cu(LBF_2)$ (**2**), whose Cu 2p spectrum is similar to that observed for other authentic Cu(I) complexes (**3, 9, 11**, etc., in Table I), the MO calculations point to the metal $d_{x^2-y^2}$ orbital lying above that of the normally unoccupied ligand π^* orbital. This would lead to internal electron transfer to the ligand, a situation where the metal is now formally Cu(III). This conclusion is not supported by the results of our X-ray PES studies on **2**, which clearly favor it being an authentic Cu(I) complex.

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(30) Other relevant binding energies of this complex are Zn $2p_{3/2}$ = 1022.2 eV, N 1s = 399.3 eV, Cl $2p_{3/2}$ = 207.7 eV, and C 1s = 285.0 eV. The related binuclear Zn(II) complex $Zn^{II}Zn^{II}LCl_2{\cdot}2H_2O$ has Zn $2p_{3/2}$ = 1022.2 eV, N 1s = 399.1 eV, and C 1s = 285.0 eV.