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X-ray Photoelectron Spectroscopy of a Copper(III) Macrocyclic Complex

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We have recently reported chemical and spectroscopic investigations of an intensely colored macrocyclic complex of copper (Figure 1) which appears to be stable in aqueous solutions in its trivalent state.[2] While data from spectrophotometric and EPR titration experiments, NMR spectrometry, and a number of chromatographic techniques (including anion exchange, gel permeation, thin layer, and electrophoresis) were entirely consistent with the proposed Cu(III) formulation, our attempts at obtaining reversible electrochemical behavior from this species have thus far been unsuccessful. In order to further verify the assignment of the oxidation state of copper in this complex and to determine its magnetic properties, we have obtained photoelectron spectra from this compound.

X-ray photoelectron spectroscopy provides valuable information on the electronic properties of transition-metal complexes. For example, it is well-known that core binding energies generally increase with increasing positive oxidation state of the emitting atom. Furthermore, Frost and coworkers[3] have shown that shake-up satellites are present in the spectra of paramagnetic but not diamagnetic copper compounds.

The synthesis and purification of [Cu^{III}–macrocycle] have been reported previously.[2] X-ray photoelectron spectra were obtained with a GCA/McPherson ESCA 36 photoelectron spectrometer employing Al Kα X-ray excitation. Cu^{II}O and [Cu^{III}–macrocycle] samples were analyzed as powders pressed into a gold mesh while Cu^0 data were obtained from a well-cleaned foil. No change in the photoelectron spectrum of the macrocycle was noted during the course of the several experiments performed. The spectra were calibrated using a C(1s) binding energy at 285.0 eV which arises from hydrocarbon present in the sample or from omnipresent surface contamination. The room-temperature magnetic susceptibility of [Cu^{III}–macrocycle] was measured on a PAR vibrating-sample magnetometer.

The Cu(2p$_{1/2}$,2p$_{3/2}$) photoelectron spectra for Cu^0, Cu^{II}O, and [Cu^{III}–macrocycle] are shown in Figure 2. The spectrum of paramagnetic copper in Cu^{II}O (3d^9) shows an intense shake-up satellite at ~942 eV which is clearly not present in the spectrum of diamagnetic copper, Cu^0 (3d^{10}). The spectrum of [Cu^{III}–macrocycle] also shows no such shake-up structure and, therefore, denotes that the copper ions in the macrocyclic complex must be diamagnetic, as is expected from the proposed presence of spin-paired Cu(III) ions (3d^8). This conclusion is further confirmed by magnetic susceptibility measurements which yielded a value of -1.9×10^{-6} emu/g at room temperature, clearly indicating a diamagnetic complex species.

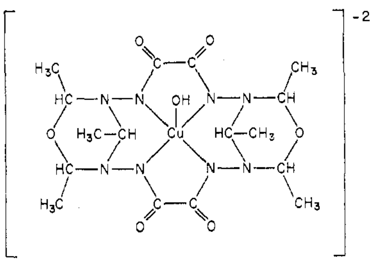

Figure 1. Disodium *bcde*-[7,9,16,18,19,20-hexamethyl-8,17-dioxa-1,2,5,6,10,11,14,15-octaazatricyclo[13.3.1.1^{6,10}]eicosane-3,4,12,13-tetronato(4−)-N^2,N^5,N^{11},N^{14}]-α-hydroxocuprate(III), designated [Cu^{III}–macrocycle].

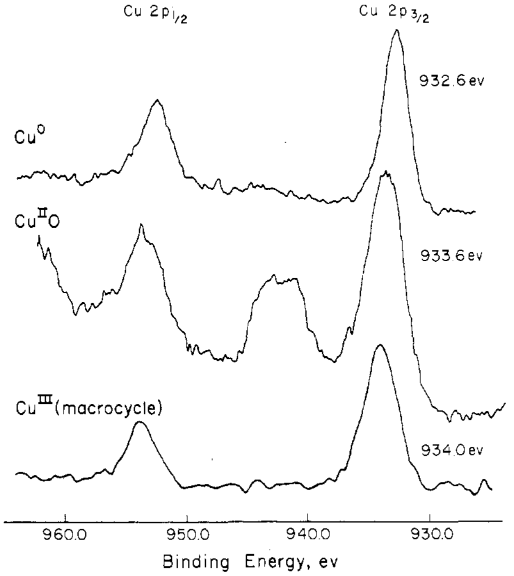

Figure 2. X-ray photoelectron spectra in the Cu(2p$_{1/2}$,2p$_{3/2}$) region of metallic copper foil, Cu^0, cupric oxide, Cu^{II}O, and the proposed trivalent copper complex, [Cu^{III}–macrocycle]. The feature at ~942 eV is a shake-up satellite from paramagnetic copper in Cu^{II}O; see text for a full discussion.

One would also expect to be able to verify the oxidation state of copper in the macrocyclic complex by comparing its Cu(2p$_{3/2}$) binding energy to that of other copper complexes in known oxidation states.[4] To our knowledge there are no available data on the photoelectron spectra of other Cu(III) compounds, and our own attempts to obtain photoelectron spectra of the Cu(III) complexes with biuret and oxamide, K[Cu(C$_2$H$_3$N$_3$O$_2$)$_2$] and Na[Cu(C$_2$H$_2$N$_2$O$_2$)$_2$], respectively, have been unsatisfactory. We must therefore compare our data to those of copper in different oxidation states. The Cu(2p$_{3/2}$) binding energy for [Cu^{III}–macrocycle] is 0.4 eV greater than that for Cu^{II}O, Figure 2. The relatively high chemical shift data for the macrocyclic complex is consistent with the proposed trivalent oxidation state of copper. However, since it has been shown that binding energies for ionic and complexed copper in identical formal oxidation states can vary significantly,[5] some care must be exercised in reaching this conclusion.

Nonetheless, combining the findings of the diamagnetic nature of the copper ion with its relatively high 2p$_{3/2}$ binding energy can only lead to the conclusion that the copper ion in the macrocyclic complex is indeed present as Cu(III), as has been inferred from a variety of physicochemical experiments previously reported.[2]

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Registry No. Cu^0, 7440-50-8; Cu^{II}O, 1317-38-0; [Cu^{III}–macrocycle], 63627-93-0.

References and Notes

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(4) Our observed ΔE_b value for Cu^{II}O vs. Cu^0 is 1.0 eV, in close agreement with the value of 1.2 eV reported by P. E. Larson, *J. Electron Spectrosc.*, **4**, 213 (1974).
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