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An Experimental ESCA Investigation of some Copper Complexes Involving CO

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An ESCA investigation of 7 copper carbonyl complexes is presented to complement a previous theoretical study. The spectra reveal that the copper is essentially in a +1 oxidation state, although for dinuclear complexes there is evidence for slightly lower than a d^{10} electron population on the copper.

Introduction

There is considerable current interest in defining the structural and electronic effects involved in the reversible binding of small molecules to transition metals [1]. The interaction of simple molecules such as carbon monoxide with both simple crystal and polycrystalline metal surfaces has been an extremely active area of research in chemical physics for the past decade [2]. However, comparatively few studies have been made which involve transition metals at the end of the first row series (*e.g.* Cu and Zn) although such elements are of considerable importance in bioinorganic chemistry [3]. The study of the interacton of simple molecules such as CO with transition metals such as copper has, however, received considerable impetus recently from the elegant studies reported by Floriani and co-workers [4] on the reversible binding in homogeneous media of CO involving Cu(I) complexes.

In a previous communication [5] we have considered by means of *ab initio* SCF computations some aspects of the energetics and core ionization phenomena in prototype systems for the 2 main structural types of copper complexes defined by Floriani [4] which reversibly bind CO. In this paper we report experimental ESCA data on a variety of copper complexes involving CO which complements the previous theoretical studies.

The main conclusions of the theoretical study [5] may be summarised as follows:

(i) The SCF computations suggest that in all cases Cu is characterized by an electron population appropriate to Cu(I);

(ii) In complexes containing 2 nitrogens coordinated to the metal, the binding energies (BE) predicted for the Cu core levels are substantially higher by ~2 eV (for the free ions) than for those containing 3 nitrogens to the metal centre;

(iii) The effect of coordination of CO as a ligand to either system is calculated to be a shift in binding energy for the metal of ~0.7 eV to low binding energy the shift being slightly larger for the diamino complex than for the system involving the 3 nitrogens.

(iv) A crude consideration of lattice effects suggests that the shifts predicted for the isolated ions are somewhat larger than those likely to be observed for appropriate model systems in the solid state.

We report here an investigation of the core level spectra for a series of Cu complexes which form a suitable basis for comparison with some of the model systems for which we have presented theoretical predictions.

Experimental

The samples studied, I to VII (Table I), were known to be relatively stable towards disproportionation in the solid state compared to other Cu(I) carbonyls [4].

The compounds are, however, known to be oxygen and moisture sensitive so the samples were prepared for ESCA investigation in a dry nitrogen atmosphere using a glove bag fixed to the insertion lock of the spectrometer. The finely ground samples were attached to the probe tip spread onto double-

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TABLE I. List of compounds studied, N.B. hm = histamine; en = ethylenediamine; diprop = dipropylenetriamine; Tmen = methylethylenediamine.

I	Cu(diprop)BPh_4
II	Cu(diprop)(CO)BPh_4
III	$Cu_2(hm)_3(CO)_2(BPh_4)_2$
IV	$Cu_2(en)_3(CO)_2(BPh_4)_2$
V	$Cu_2(Tmen)_2Cl(CO)_2BPh_4$
VI	$Cu_2(Tmen)_2Br(CO)_2BPh_4$
VII	$Cu_2(Tmen)_2I(CO)_2BPh_4$

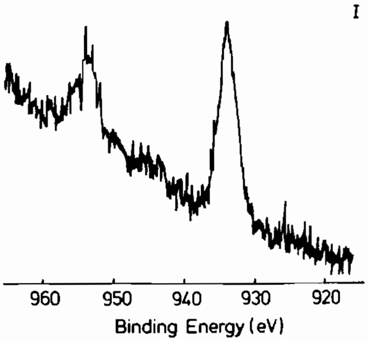

Fig. 1. $Cu_{2p_{1/2}}$ and $Cu_{2p_{3/2}}$ spectra of I (Cu(diprop)BPh_4), with $Mg_{K\alpha_{3,4}}$ peaks subtracted.

sided adhesive tape. To reduce sample degradation the samples were cooled to –80 °C on entry into the UHV region of the spectrometer.

The spectrometer used was a customised Kratos ES300 with the source region being separately pumped from the analyser using electrically driven turbomolecular pumps having nominal pumping speeds of 350 l s^{-1} and 140 l s^{-1} respectively. With sample cooling the base pressure of the system during data acquisition was ~10^{-8} Torr.

Spectra were recorded digitally via a Kratos DS300 data system based on an LSI 11/2 processor, with software enabling data manipulation such as $Mg_{K\alpha_{3,4}}$ satellite subtraction, smoothing etc. Because of sample degradation the most important spectra, the Cu_{2p} levels, were ran first, using FAT* to enhance sensitivity of these low KE peaks. N_{1s} and C_{1s} spectra were then run in FRR** mode. The total acquisition time varied depending on signal to noise ratios but was a maximum of 41 mins. for the Cu_{2p} spectra.

For all spectra a $Mg_{K\alpha_{1,2}}$ X-ray source was used operating at 12 kV and 8 mA.

Results and Discussion

In this paper we consider systems containing 3 nitrogens for which comparison may be drawn with the previously reported theoretical data. For the simplest of these the Cu_{2p}(I) spectra (Fig. 1) reveal the essentially d^{10} nature of the electron configuration around Cu with the absence of any significant satellite structure due to shake-up as would be the case with a Cu(II) d^9 configuration. The $Cu_{2p_{3/2}}$ binding energy (Table II) is 0.8 eV lower than for the Cu(diprop)(CO)BPh_4 (II) which has a somewhat larger shift (0.5 eV) than might have been expected for the free ion [5]. The small difference is probably attributable to the fact that in the CO complex the counterion is somewhat closer to the metal and the lattice potential arising from this will therefore tend to increase the shift.

TABLE II. BE's, shake-up intensities and fwhm of $Cu_{2p_{3/2}}$ peaks studied, and those for CuO and Cu_2O.

	$Cu_{2p_{3/2}}$ Be (eV)	% shake-up	Fwhm $Cu_{2p_{3/2}}$
I	933.8	7	3.00
II	933.0	5	2.6
III	933.4	15	2.8
IV	934.4	17	3.5
V	934.7	21	3.6
VI	933.5	15	3.2
VII	934.7	<1	2.7
Cu_2O	934.7	4^a	2.6
CuO	936.2	37.0^a	3.8

^{a}No $Mg_{K\alpha_{3,4}}$ subtraction.

The Cu_{2p} spectra in each case (I–VII) show that the electron configuration about the Cu is that closely approximated by Cu(I) d^{10}.

The change in nature of the ligand and the difference in lattice potentials on going from the mononuclear to dinuclear complexes makes a straightforward comparison difficult. It is interesting to note, however, that the $Cu_{2p_{3/2}}$ binding energy for the histamine complex (III) which involves one nitrogen in each ligand which is part of a conjugated system is significantly lower (by ~1 eV) than for the corresponding ethylene diamine complex (IV). This difference could conceivably arise from a greater contribution from interatomic relaxation energy contribution. In consequence whilst the Cu_{2p} levels show a shift to lower BE on going from I to III, there is actually a shift to higher BE on going from I to IV.

The effect of replacement of a bridging nitrogen ligand in dinuclear complexes by a bridging halogen is also of interest for the CO complexes. The data divide into 2 sets. The $Cu_{2p_{3/2}}$ binding energies for IV (en), V (Cl) and VII (I) are closely similar whilst those for III (hist) and VI (Br) are also similar but lower in binding energy. The data for the halogen

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*Fixed Analyser Transmission.

**Fixed Retardation Ratio.

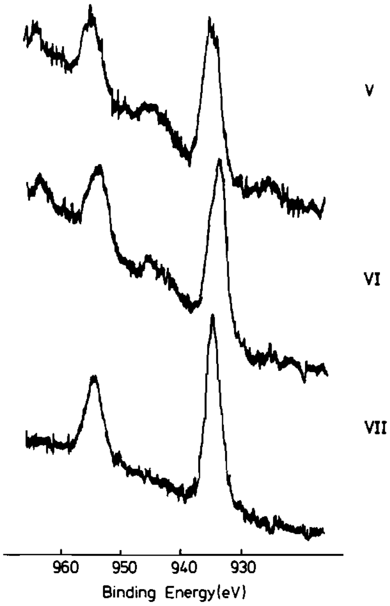

Fig. 2. $Cu_{2p_{1/2}}$ and $Cu_{2p_{3/2}}$ spectra of V ($Cu_2(Tmen)_2Cl(CO)_2(BPh_4)$), VI ($Cu_2(Tmen)_2Br(CO)_2(BPh_4)$) and VII ($Cu_2(Tmen)_2I(CO)_2(BPh_4)$), with $Mg_{K\alpha_{3,4}}$ excited peaks subtracted.

bridged species are particularly interesting since the binding energies fall in the sequence I ≈ Cl > Br which is similar to that observed for the cuprous halides [6]. This may be rationalized on the basis of competing donation and back donation; differences in interatomic relaxations; and differences in lattice potentials.

The N_{1s} binding energies for I and II are closely similar, 400.7 eV and 400.5 eV, as might have been anticipated from the close similarity in calculated charge on nitrogen for the model systems [5] as previously reported. The N_{1s} binding energies for the other systems also fall within a very narrow range of that for I (±0.3 eV).

It is interesting to compare the data for the nitrogen complexes with those recorded in the literature for prototype d^{10} and d^9 systems namely cuprous and cupric oxides [6–8]. The spectra in the literature for Cu_2O indicate a low level of shake-up (~4%) indicative perhaps of surface oxidation. It should be noted that the most common artefact of X-ray bombardment is reduction rather than oxidation, so that low levels of oxidation probably arise prior to introduction of the samples into the spectrometer.

Frost and co-workers [6] have commented on the smaller fwhm for Cu(I) as opposed to Cu(II) complexes for the $Cu_{2p_{3/2}}$ levels. It is clear, however, that even for Cu(I) complexes the fwhm depends on the range of lattice sites within the depth range sampled by ESCA as well as differences in lifetimes for the relevant core hole states. Thus although the fwhm for IV is considerably larger than for III the shake-up intensities are comparable. The data would suggest that for the dinuclear complexes the electron population on copper is slightly less than for a formal d^{10} configuration and in consequence small shake-up satellites are observed.

Comparison of the data for I with Cu_2O shows a substantial shift to lower binding energy for the $Cu_{2p_{3/2}}$ levels indicative of the strong electron donating effect of the N ligands.

The shake-up intensities for both I and II are higher than for Cu_2O but the fwhm are comparable, the transition energy (to the centroid of a broad peak) is comparable for all 3 systems.

For the halogen bridged systems the % shake-up and fwhm decrease in the order Cl ≈ Br > I (*cf.* Fig. 2) whereas the binding energies are in the order I ≈ Cl > Br. This indicates the importance of lattice and relaxation effects in determining overall BE's since the comparison of II with VII shows both to correspond to an electron population on copper close to a d^{10} configuration.

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