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An XPS and Auger Study of some Polynuclear Copper Compounds

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Abstract

An XPS and Auger characterization of the electronic structure of some polynuclear copper compounds is reported. The core level photoelectron spectra, the Cu(L_3VV) Auger lines and the Auger parameters are discussed in terms of both the different coordination environments in the studied copper compounds and of the polarizability of the ligands.

Introduction

The analysis of the structural features and the reactivities of molecular metal clusters is of great interest in organometallic and coordination chemistry, since these polynuclear compounds can be considered as models of metal surfaces involved in catalytic processes [1–3], and are therefore of fundamental importance for understanding catalytic systems.

We have already studied [4–6] some 'centered' and 'non-centered' gold cluster compounds by XPS with the aim of obtaining information about their electronic structure and coordination environment. In this paper we present the results of an XPS study of some polynuclear copper compounds.

It is well known from the literature [7] that the structural chemistry of copper is different from that of gold compounds. Cu(I), indeed, forms only small clusters with three to eight metal atoms and Cu(I) halide complexes show 'cubane-like' structures without direct metal–metal bonds. In the present paper we compare the XPS spectra of $(LCuCl)_4$, $(LCuC{\equiv}CPh)_4$, $(LCu{\equiv}CPh)_n$ (L = triphenylphosphine) with the spectra of other copper compounds chosen as references.

$(LCuX)_4$ (X = Cl, Br, I) [7] compounds cannot be strictly considered as clusters; notwithstanding, they still represent an area of considerable interest because of their polynuclear structure. The X-ray structural data for these compounds show a distorted 'cubane-like' framework, which can better be described as a tetragonal polyhedron with the X unit bonded to the metal atoms via a tricentric bond.

X-ray structural data for $(LCuC{\equiv}CPh)_4$ compound [8] show Cu–Cu bond distances shorter than those in $(LCuCl)_4$. No structural data are presently available for the compound $(LCuC{\equiv}CPh)_n$.

Experimental

The investigated compounds were prepared and characterized according to literature methods [8, 9]. Photoelectron spectra were recorded using a VG ESCA 3 MKII spectrometer with $AlK_{\alpha_{1,2}}$ radiation (1486.6 eV).

The samples were dusted as thin film on to double-sided tape and were sufficiently stable under X-rays in the experimental conditions adopted. The absence of radiation damages in the sample was monitored by repeated scans.

The C1s line (b.e. = 285.0 eV) from residual pump-oil contamination was used as an internal standard for spectral calibration. The reported binding energies were measured at half widths of the maxima of the bands.

Results and Discussion

Table I presents the Cu2p3/2, P2p and Cl2p b.e. values for the studied compounds, together with the K.E. values of the CuL_3VV Auger line.

All the Cu2p3/2 b.e. values lie in the range 932.5–933.1eV, typical of Cu(0) or Cu(I) compounds. The presence of copper in oxidation state Cu(II) can also be excluded by the absence of the satellite structure characteristic of Cu(II) paramagnetic compounds [10].

It is well known from the literature [11] that it is not possible to distinguish between Cu(0) and Cu(I) compounds by means of b.e. values only. The Auger data, however, show a considerable shift (~3 ev) between Cu and the other listed compounds, indi-

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TABLE I. Cu2p(3/2), P2p and Cl2p Binding Energies (eV) and Cu(L_3VV) Kinetic Energies (eV) for the Copper(I) Compounds.

Compound	Cu2p3/2	Cu(L_3VV)K.E.	P2p	Cl2p
Cu	932.9	918.3		
CuCl	932.4	915.5		199.7
L_3CuCl	933.0	915.0	131.4	198.7
$(LCuCl)_4$	933.0	914.8	131.5	198.9
$CuC\equiv CPh$	932.5	915.9		
$(LCuC\equiv CPh)_4$	932.6	915.9	131.5	
$(LCuC\equiv CPh)_n$	933.0	915.7	131.5	
L = triphenylphosphine			131.1	

cating that in all the compounds studied the copper atoms have a +1 oxidation state.

All the P atoms have the same b.e. values (within experimental error): 131.4–131.5 eV. The values are higher than that for the free phosphine ligand (131.1 eV), as expected as a consequence of the decrease of the electronic charge density over the phosphorus atom after coordination. On the other hand, the values are smaller than those of other similar compounds (131.7–132.1 eV) [4–6], indicating a higher degree of M → L back-donation in the compounds under study.

CuCl and L_3CuCl were chosen as reference compounds for $(LCuCl)_4$ and a comparison of the b.e. values shows similar results for the Cu and Cl atoms of both the phosphine complexes. On the other hand, b.e. values for Cl in CuCl are significantly higher (~1 eV) than for the former two compounds, and the b.e. for Cu is lower by about 1 eV. Cu–Cl bond distances in L_3CuCl and $(LCuCl)_4$ (2.336 and 2.438 Å, respectively) [9, 12] are of the same order of magnitude, despite the different structural framework of the two compounds, and are considerably longer than that of CuCl (2.050 Å) [13].

The decrease of the Cl b.e. in the phosphine complexes with respect to CuCl can therefore be viewed as a consequence of an increased Cu–Cl charge separation in these molecules, also reflected in a higher Cu b.e. value.

X-ray structural data for the compound $(LCuC\equiv CPh)_4$ [8] describe it as an essentially tetrahedral metal skeleton bearing four terminally-bonded triphenylphosphine molecules and four triply-bridging phenilacetylide ligands with very short $C\equiv C$ distances, indicative of the absence of M → L π back-donation. Cu2p b.e. values for both ($CuC\equiv CPh$) and $(LCuC\equiv CPh)_4$ are very similar and are smaller than those for L_3CuCl and $(LCuCl)_4$. This b.e. difference can be accounted for by considering the different donor power of Cl and $-C\equiv CPh$ ligands, the latter being a stronger σ – donor.

$(LCuC\equiv CPh)_n$ has been described as a polymeric compound which, on the basis of IR and structural considerations [8, 14], is believed to contain differently bonded (*i.e.* π and σ bonded) phenilacetylide ligands. The slight increase in the Cu2p3/2 b.e. value for this compound, indeed, seems to reflect a net decrease of electronic charge over the Cu(I) atoms, probably as a consequence of (i) the lower donor power of the π acetylide bond with respect to the σ bond, and (ii) the possibility of M → L back-donation, which is known to take place in M–acetylide π-complexes and which is also reflected in a lower $C\equiv C$ stretching frequency [15].

It is well known from the literature that the Auger chemical shifts and their directions can be correlated with the polarizability of the ligands to which the metal atom is bonded. This effect is particularly critical for atoms such as Zn, Cd, In and, among others, Cu [16].

The concept of the Auger parameter, α, was first developed by Wagner [17, 18] and defined as the K.E. of the sharpest Auger line minus that of the most intense photoelectron line. This quantity is characteristic of a molecular or solid state, and it can be demonstrated that chemical shifts in these quantities can be correlated to differences in extra-atomic relaxation energies, and hence to polarization energies in the final states.

Table II shows Auger parameters α and chemical shifts, referred to Cu metal, of the Auger parameters of the compounds under study. B.E. chemical shifts are also reported for comparison.

A more usual way of presenting the same data is the display of photoelectron and Auger data in the form of plots, such as that shown in Fig. 1, in which

TABLE II. Auger Parameters and Chemical Shifts (eV) for the Copper(I) Compounds.

Compound	α	$\Delta\alpha^a$	Δ Eb
Cu	364.6		
CuCl	361.1	3.5	−0.5
L_3CuCl	361.2	3.4	+0.1
$(LCuCl)_4$	361.1	3.5	+0.1
($CuC\equiv CPh$)	361.9	2.8	−0.5
$(LCuC\equiv CPh)_4$	362.0	2.6	−0.3
$(LCuC\equiv CPh)_n$	362.1	2.5	+0.1

^{a}Chemical shifts referred to Cu metal.

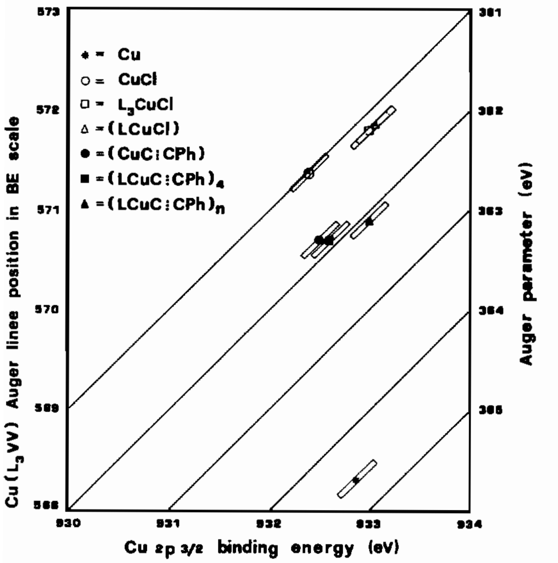

Fig. 1. Auger parameter plot for the copper(I) compounds.

atoms having the same oxidation state and the same chemical environment are expected to lie on the same 45° lines.

In the present case there is indeed a noticeable separation between Cu(0) and Cu(I) compounds. Among these, however, it is possible to clearly distinguish two sets of Auger parameters for chloride and acetylide compounds. Again, the lower-lying acetylide compound line is indicative of a higher polarizability of the ligand and of a stronger σ and π M → ligand bond than in the chloride compounds.

The combined use of XPS and Auger spectroscopy is confirmed, therefore, to be a useful tool in the study of Cu compounds, being capable of giving additional information about the electronic structure of the M–L bonds.

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