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An XPS Investigation of Pentatomic Heterocyclic Ligands Containing N, O and S and their Cu Complexes

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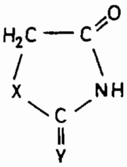
Abstract

A series of heterocyclic pentatomic rings containing N, O and S has been studied by X-ray photoelectron spectroscopy together with some of their Cu complexes. Core line binding energy shifts for N and S atoms are shown to correlate satisfactorily with CNDO/2 fractional atomic charges, after correction for intramolecular Madelung potential terms. Structural electronic effects of various substituent atoms or groups (NH, O, S) both in endo- and in exocyclic position have been rationalized in terms of different contributions to resonance forms implying conjugation within molecular skeleton moieties.

The corresponding complexes have been confirmed to contain Cu(I) central metal atoms; the coordinated ligands have been shown to act as bidentate species, through the thionic S and the endocyclic NH (neutral or deprotonated) group. Structural hypotheses have been formulated for some complexes also on the basis of semiquantitative XPS measurements.

Introduction

In preceding papers [1, 2] we investigated the structural electronic properties and donor ability towards copper of some members of a class of pentatomic heterocyclic ligands, with general formula



where X = S, NH and Y = O, S, NH.

The techniques employed in refs. 1 and 2 were UV Photoelectron Spectroscopy and IR; magnetic susceptibility and reflectance measurements were also reported.

On the basis of the experimental data we characterized the Cu complexes with X = Y = S; X = NH, Y = S; and X = S, Y = O ligands as Cu(I) species in which partial deprotonation of a NH group occurs. The structures proposed for the complexes imply particular arrangements of Cu and ligand donor atoms, resulting in oligomeric units containing four copper atoms in the oxidation state +1 [1]. On the basis of IR findings we assumed that the ligands act as bidentate through N and S when deprotonated and as monodentate through NH in the neutral form. This implies the occurrence of a direct Cu–Cu bond.

To further investigate the effective coordination modes of the above reported ligands, we have undertaken an XPS investigation on both free ligands and Cu complexes.

The specific points of interest are: (a) a better knowledge of the structural electronic effects of the replacement of X or Y groups in the rings, to be correlated with our previous UPS study; (b) a more detailed identification of donor atoms from the ligands in Cu complexes; (c) possible evidence from XPS of a direct Cu–Cu bond; (d) a confirmation or new proposals for coordination structures in Cu complexes.

Experimental

All the ligands (Fluka and B.H.S.) were of reagent grade and were purified before use. Details of the preparation of all Cu complexes have already been published elsewhere [1].

XPS measurements were carried out on a VG-ESCA 3 photoelectron spectrometer, employing an Al Kα Source ($h\nu = 1486.6$ eV). Samples were dusted on metal tips and measured at liquid nitrogen temperature or at room temperature. All results are considered accurate to ±0.2 eV. Semiquantitative measurements were obtained from peak area ratios, assuming Scofield's atomic cross-section values [3]. A dependence of mean free-path values with $E_k^{1/2}$ was assumed. Curve-fittings of composite peaks in gaussian components were obtained by use of a conventional computer program.

The dependence of binding energies (*b.e.*) on the chemical environment of the ionized atom may be

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TABLE I. Corrected Binding Energies (eV) and Fractional Computed Atomic Charges q (CNDO/2) for $\overline{\text{HN(1)–CH}_2\text{–}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{–X–C}}\text{=Y}$

	Binding energies				q		
	N1s		S2p		N	X	Y
Y = O							
X = N(2)H	N(1)	393.7			−0.247	−0.218	−0.38
	N(2)	394.4					
S	N(1)	394.3		162.3	−0.197	−0.099	−0.28
Y = S							
X = N(2)H	N(1)	394.9		159.4	−0.18	−0.13	−0.375
	N(2)	395.8					
S	N(1)	395.8	=S	160.4	−0.11	−0.03	−0.246
			S	163.2			
Y = NH							
X = S	N(1)	394.9		163.0	−0.18	−0.07	−0.26
	=NH	395.2					

approximately described by the equation: *b.e.* = $(b.e.)_0 + kq + V$, where q is the atomic charge and V the intramolecular potential. In a point-charge model [4], $V = \Sigma_{j \neq i} q_j / r_{ij}$, where q_j is the net atomic charge on each j atom in the molecule and r_{ij} are the interatomic distances. Corrected *b.e.* values are obtained by subtracting the Madelung potential term V from measured values. The q_j values were derived from CNDO/2 calculations [2]; the r_{ij} values were taken from crystal structure determinations or estimated from known geometries [2 and refs. therein].

Results and Discussion

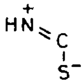
Free Ligands

XPS results and computed fractional atomic charges q for atoms of interest in free ligands are collected in Table I and reported in Figs. 1 and 2.

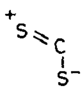
The observed trend of corrected *b.e.* values *versus* q is plotted in Figs. 1 and 2. Corrected *b.e.* values show a clear correlation with charges for both S and atoms. In the case of sulphur atoms, the value of the correlation coefficient r equals 0.99 and the extrapolated value of S2p *b.e.* at $q = 0$ is 163.6 eV, a value well comparable with literature reports [4, 5]. The slope of this correlation is 11.6 eV/q, which is in the range of previously reported values 9.7 [5], 14.0 [4], 14.1 [6] and 16.8 [7]. The chemical nature of S atoms in our molecules is clearly reflected, in the plot, in a separation among points relative to thionic and thiolic sulphur, as expected. The particular situation represented by 2,4 thiazolidinedione will be discussed in a subsequent paragraph.

Within each of the two groups some effects are observed

(i) The replacement of an NH group by a ring S atom on passing from thiohydantoin to rhodanine has a strong effect on both *b.e.* (+1.0 eV) and q (+0.13 a.u.) values of the thionic sulphur. This effect can be related to the extension of π-conjugation which is expected to be higher for the



form with respect to the



form [8].

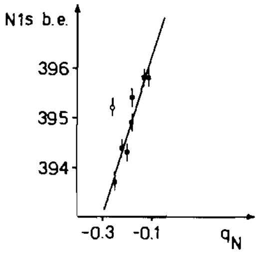


Fig. 1. Corrected *b.e.* values for N1s level *vs.* computed (CNDO/2) net atomic charge on nitrogen. The value for the correlation coefficient r is 0.94. The nitrogen atom of the structurally unique Y = NH insaturation in pseudothiohydantoin molecule was not included in the fit.

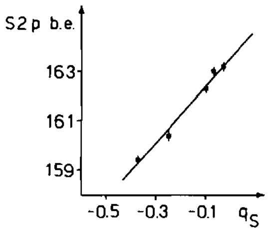
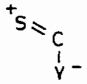


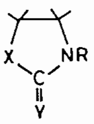
Fig. 2. Corrected *b.e.* values for S2p level *vs.* computed (CNDO/2) net atomic charge on sulphur (r = 0.99).

(ii) The sequence of S2p *b.e.* and q values for the ring S atom present in 2,4-thiazolidinedione, pseudothiohydantoin anr rhodanine reveals a clear separation between the first molecule and the others. This result reflects the scarce involvement of the ring heteroatom S in the resonant form



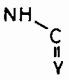
when Y = 0, as already observed by us for closely related molecules [8, 9] in a comparison among Y = O, S, Se insaturations.

(iii) We can compare the present result with our previous data on S heteroatoms in closely related molecules [8], with the same general molecular skeleton



but one insaturation only, in the Y position.
(Y = O, S; X = NR′, O, S, CH_2; R, R′ = H, alkyl)
The effect of a second insaturation (>C=O) results in an increase in both S2p *b.e.* (+0.3 $\div$ 0.5 eV) and q_s (+1.2 $\div$ +1.0 a.u.) for thionic sulphur.

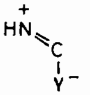
The electron-withdrawing effect of >C=O group thus reduces the extent of charge delocalization in the



moiety towards the Y atom or group. A more complete description of this effect will be given after the subsequent discussion of results for N atoms.

The plot of corrected N1s *b.e.* values *versus* q_N values shows a correlation coefficient $r = 0.94$, with an extrapolated N1s *b.e.* value at $q = 0$ of 397.8 eV. The slope of the line is 15.97, quite close to the already reported values of 14.4 and 18.5 ± 2.5 [5, 10]. The poorest correlation is found for the N atom in the structurally unique Y = NH group in pseudothiohydantoin; the other N heteroatom present in the ring shows a much better correlation and is included in the plot.

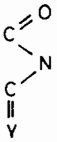
Corrected N1s *b.e.* values reported in Table I may be divided into two groups, the first one for the molecule with Y = O, the other one collecting results for Y = NH, S. Mean N1s corrected *b.e.* values are in the range of 394 ± 0.4 eV and 395.4 ± 0.5 eV, respectively. This separation is a further evidence of a much more limited involvement of N donor functions in conjugation forms



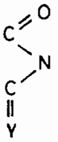
when Y = O, a result already discussed above for S atoms.

An interesting point to stress here is that the lowest N1s *b.e.* values are presented by the only two ligands which do not react, in our experimental conditions, with a Cu(II) salt to give Cu(I) complexes [1]. In particular, the Cu complex with 2,4 thiazolidinedione was obtained by reaction of a Cu(II) salt with pseudothiohydantoin, a species with a much more positive N ring atom. Thus, it seems that the coordination ability of the NH ring group may be correlated with the extent of conjugation of NH with the exo-groups, *i.e.* with the nature of the Y insaturation.

As in the case of S atoms, a comparison of present results with those already reported by us for related molecules reflects the influence of a second insaturation (C=O) in the ring. We found a systematic decrease in N1s corrected *b.e.* values and a parallel increase in negative q_N values for the N atoms in the

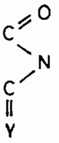


moiety. Thus, a second insaturation makes the Y atom more positive and the NH group more negative. The overall picture emerging is that of an enlarged conjugation among the atoms in the



moiety, since the charge withdrawal exerted by the amidic O involves also the Y function through four bonds. This is consistent with the increase in ionization energies of all the valence orbitals (including those localized on Y) upon substitution of the CH_2 with the CO group, already observed by gas-phase UV photoelectron spectroscopy [2].

Among some minor effects which may be revealed by an analysis of N data, we wish to discuss the behaviour of a second NH group in a ring. If we compare results for molecules with Y = O, S and X = NH with those presented by Y = O, S and X = S species, we find a positive shift in N1s *b.e.* of 0.6 eV when Y = O and 0.9 eV when Y = S for the N atom in the



frame, with a q_N of +0.05 and +0.07 a.u.

These results quantitatively reflect the different ability in charge delocalization of a ring NH or S

TABLE II. Binding Energies (eV) and modified Auger Parameters α′ (eV) for Cu Species

	$Cu2p_{3/2}$	N1s	S2p	Cu LVV	α′
Cu–rhodanine	933.1	399.4 400.9	163.0 164.7 168.5	916.0	1849.1
Cu–thiohydantoin	933.1	399.0 400.6	163.2 168.5	915.6	1848.7
Cu–2,4 thiazolidinedione	933.1	399.9	163.6 168.9		
Cu	932.7			918.4	1851.1
Cu–(*p*-toluensulphonate)$_2$	936.3		168.9	915.1	1851.4

function [8], and afford evidence for the particular situation represented by two NH groups in the same ring, *i.e.* the lowering of individual N1s *b.e.* This effect is also accompanied by the most negative *b.e.* value for the Y atom in each series, as already observed in related molecules [8, 9].

Copper Complexes

The XPS results for Cu complexes are collected in Table II, together with *b.e.* values for pure Cu and Cu(*p*-toluensulphonate)$_2$, reported for comparison.

We will refer first to Cu–rhodanine and Cu–thiohydantoin complexes. $Cu2p_{3/2}$ *b.e.* and FWHM values and the complete absence of satellite structures which accompany Cu $2p_{3/2}$ and 1/2 peaks in Cu(II) (paramagnetic) compounds, confirm that Cu is present as Cu(I). Reported $CuL_3M_{4.5}M_{4.5}$ Auger transitions and modified Auger parameters α′ values are further evidence for the correctness of this assignment.

Semiquantitative XPS analysis gave the following atomic ratios:

Cu–thiohydantoin: $Cu_{2.0}N_{3.9}S_{2.1}S(A^-)_{0.65}$

Cu–rhodanine: $Cu_{2.0}N_{2.0}S_{4.5}S(A^-)_{1.3}$

(where A^- is the *p*-toluensulphonate anion).

These results are in good agreement with our previous reports [1], based on ponderal ratios and respectively equal to $Cu_{2.0}N_{4.0}S_{3.0}$ and $Cu_{2.0}N_{2.0}S_{5.0}$. The poorest agreement is with total percentages for S (2.75 and 5.8 against 3.0 and 5.0) but the results are still close to the error of ±10%, usually accepted in XPS quantitative measurements [11].

Thus, the overall accordance of ponderal and XPS-based atomic ratios allow us to confirm our previously proposed formulas for the two complexes, *i.e.* $[Cu_2(L)(LH)]^+A^-$, where L and LH are the deprotonated or neutral ligands rhodanine and thiohydantoin. Passing to a comparison of α′ parameters, we recall that the relationship between difference in α′ and in extra-atomic relaxation energy (or polarization energy) in the final state, proposed by Wagner [12] is strictly valid only for core-type Auger lines. When considering CVV transitions, as in our case, a comparison of α′ values may still give some useful information in comparing strictly related structures [11a], such as complexes with similar ligands. In our case, the close proximity of α′ values suggests similar Cu environments and ligand polarizabilities in the two complexes.

We turn now to an analysis of S2p and N1s peaks. The two S2p components present in free rhodanine are positively shifted in the complexes by different amounts: +0.9 eV for thionic S and +0.6 eV for the S in the ring. While the first Δ*b.e.* is a clear indication of the involvement of the $>C=S$ function in the coordinative bond with Cu, as may be inferred from a comparison of literature reports for substituted thioureas and similar molecules [7, 8], much fewer literature reports concern the coordination of thioether S. Δ*b.e.* values of +0.3 ÷ +1.2 eV have been associated to the formation of a thioether sulphur–metal coordinative bond [13]. However, we cannot exclude the observed Δ*b.e.* on rhodanine ring S atom to be the effect of charge withdrawing from different groups in this conjugated rings, after coordination. A second effect which should be operating here is a modification in the Madelung potential terms after complexation. The potential term q_j/r_{ij} generated by the negative charge donated to the central atom tends to decrease the *b.e.* shift observed on the donor atom (it amounts to a negative term to be subtracted from observed *b.e.*), while it tends to increase the *b.e.* shift for non-coordinated atoms, since these last become generally more positive on complexation.

The S2p results for Cu–thiohydantoin (in which only C=S functions are present) show a Δ*b.e.* on complexation of +1.1 eV, a value which is almost twice that reported for the ring S in Cu–rhodanine. The FWHM of this peak (2.5 eV) which is typical, in our experimental conditions, of single S species, clearly confirms that all thionic S are coordinated to Cu in this molecule. In conclusion while there is a clear indication of a Cu–S coordination through a thioketonic function, S2p *b.e.* values neither confirm nor exclude the involvement of a thioether S function in the Cu–rhodanine complex. Since, however, it will be pointed out later on in this paper that nitrogen (either as a N or NH group) is always coordinated to Cu, the coordination of a thioether S would result in thiohydantoin acting as a tridentate ligand.

The N1s peak in both complexes is split into two components at lower and higher values with respect to free ligands. We assign these two components to deprotonated and amidic NH groups, both coordinated to Cu. The following experimental findings and literature results support our assignment.

(a) The observed negative shift in N1s *b.e.* for a NH group cannot be the consequence of a coordinative bond which does not involve directly that group, since the N1s $\Delta b.e.$ is expected to be positive even in this case (see above);

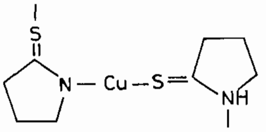
(b) The absolute *b.e.* values of the lower-lying N1s peak component are well comparable with that reported for a deprotonated amide group coordinated to Cu (398.9 eV) [14]. A deprotonated amide group not involved in a coordinative bond shows a N1s *b.e.* of 398.3 eV [7], which is 0.7 ÷ 1.1 eV lower than the experimentally found values for our species.

(c) The N1s peak component around 401.0 eV presents a positive *b.e.* shift from the free ligand of 0.7 ÷ 0.9 eV in the two complexes; the relatively high *b.e.* and the amount of the shift are much in favour of a coordinative bond to the central metal atom. An interesting difference between Cu(I) complexes with rhodanine and thiohydantoin is the presence of, respectively, one and two NH functions in the free ligands. The splitting of the N1s peak upon complexation necessarily implies that the rhodanine ligands are only partly coordinatively bound to a deprotonated amido group and partly through an NH function. From a curve fitting of the corresponding N1s peak, the ratio between these two components is 1:1. In the case of thiohydantoin, the presence of two NH groups leads to a more ambiguous case, since it is rather difficult to determine if both N atoms in a molecule are bound to different Cu atoms or if the splitting has the same meaning discussed for Cu–rhodanine. Since, however, in the case of Cu–thiohydantoin we have clearly determined that thioketonic S atoms are all bound to Cu, if both N atoms from a single molecule were effectively coordinated, the result would be a triple coordination for this ligand. We recall again that the only clearly incompatible situation for N donor functions in our rings is the contemporary presence of an NH group coordinated to Cu and a 'free' second NH group (see above).

With reference to our preliminary investigation on the same Cu complexes [1], XPS results have confirmed the Cu +1 oxidation state in the two complexes, the atomic ratios of complexes and a partial (~50%) deprotonation of the ligands upon complexation. No clear evidence for different Cu species has been obtained by XPS, to be related with a Cu–Cu direct bond [1].

XPS has revealed that thionic sulphur atoms are always bonded to Cu, and that Cu is coordinatively bonded to NH and =S, or N and =S atoms, in partial disagreement with previous results. In fact, the presence of two types of thionic S atoms (free and coordinated) was inferred in ref. 1 on the basis of a splitting of ν(C=S) bands in the complex. This splitting may now be tentatively ascribed to the partial deprotonation of the NH group in the complexes.

The resulting structure of these Cu complexes may be described, on the basis of present results, either as a polymeric chain of



units or as a complex oligomeric unit containing four Cu and four ligand molecules in a quadrangular arrangement. The existence of polymeric structure of the first type was already reported in the literature for Ag(I) complexes with ligands quite similar to the present ones [7]. Also the high insolubility of the present complexes is in agreement with the existence of a polymeric structure.

We pass now to consider the Cu–2,4 thiazolidinedione complex. The product obtained from the reaction of Cu(II) (toluensulphonate)$_2$ and pseudothiohydantoin produced a complex Cu2p spectrum, with a clear presence of either satellites accompanying main 2p peaks and a second component on the higher *b.e.* side of the 2p peak. However, a strict comparison with the Cu2p spectrum of Cu(toluenesulphonate)$_2$ revealed that a residual presence (~20% of the total) of Cu(II) in this insoluble complex accounts for the complicating features in the Cu2p spectrum. After subtracting these components (both Cu(II) 2p peak component and accompanying satellites), the presence of another Cu species is clearly suggested by the *b.e.* value of 933.1 eV. This value coincides with those reported for the other two complexes, and allows, together with the measured FWHM value and the lack of satellites, to assign the species to a Cu(I) complex. Only one N1s peak component is present in the spectrum of the Cu(I) complex, even if the pseudothiohydantoin ligand contains two NH functions. This result is in complete agreement with our previous assignment, mainly based on IR findings [1], to a Cu-2,4 thiazolidinedione complex. The *b.e.* value for the N1s peak is quite different from those here reported for pseudothiohydantoin, being positively shifted by 0.3 eV with respect to 2,4 thiazolidinedione.

It is to be recalled that in this case no thioketonic S function is present in the ligand, thus preventing a comparison with the other two complexes based on absolute *b.e.* values. In fact, the presence of a thioketonic S bound to Cu should increase the observed *b.e.* shift on the N atom, because of positive Madelung potential terms (see above).

Thus, we expect that, upon coordination to Cu, the observed $\Delta b.e.$ for N1s should decrease with respect to the other two complexes, and actually it is +0.3 eV against +0.6 ÷ 0.9 eV. The S2p *b.e.* is practically coincident with that found for 2,4 thiazolidinedione, a further support to the proposed assignment. $\Delta b.e.$ values close to 0 eV have already been reported in the literature for coordinatively bound thioether S [13]; thus, XPS data alone are again insufficient to remove ambiguity as to the coordinative situation in this species.

In conclusion, the Cu complex obtained from a Cu(II) salt and pseudothiohydantoin is a Cu(I) complex species bound to 2,4 thiazolidinedione ligands through N atoms; a possible involvement of thioether S functions cannot be *a priori* excluded [13]. The actual value of N1s *b.e.* does not distinguish clearly whether NH or deprotonated amido group is actually coordinatively bonded.

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