ESCA Studies of N,N'-Thiobisamines and of Some of its Chromium Carbonyl Complexes

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The X-ray photoelectron spectra of some N,N'-thiobisamines and of two of its complexes with Cr(CO)₅ have been studied. The S(2p) binding energies are found to correlate with the effective nuclear charge on the sulfur atom as well as with the double bond character of the S–N linkage. The effect of the coordination on the N(1s) and S(2p) binding energies agree with sulfur coordination as well as with a π acceptor behaviour characteristic for thiobisamine ligands.

Introduction

In spite of the presence of electron lone pairs on its sulfur and nitrogen atoms N,N'-thiobisamines, S(NR₂)₂, appear as quite unreactive substances [1]. However, as determined in some recent studies [2, 3], thiobisamines participate in solvolysis reactions as well as in the formation of some coordination compounds. Hydrolysis and alcoholysis reactions, the products of which normally undergo redox processes [4], are catalysed by the presence of Brønsted or Lewis acids. Although this kind of reactivity is certainly related with nucleophilic character of the thiobisamines, stable coordination compounds have been obtained only with metals in low oxidation states [3]. Further, hydrolysis of thiobisamines can also be induced by electrochemical oxidation [5].

Considering that the chemical properties of thiobisamines should be related with the electron density on nitrogen and sulfur atoms, we have studied the X-ray photoelectron spectra of several N,N'-thiobisamines as well as those of two of its complexes with chromium pentacarbonyl.

Results and Discussion

As shown in Fig. 1, for most of the compounds studied the binding energies S(2p) (Table I) correlate with the change of effective charge on the sulfur atoms calculated from the partial ionic character of

the S–N bonds according to the Pauling method [6]. The influence of the substituents was introduced by using the electronegativities of the groups NR₂ [7] reported in Table II. Further, the binding energies

Table I. Binding energies (eV) for N,N'-thiobisamines and some of their chromium pentacarbonyl complexes*.

Compound	S(2p)	N(1s)	Cr2p(3/2)
1-1	167.6	404.0	
1-2	166.2	403.35	
1-3	166.6	403.0	
1-4	166.0	403.0	
1-5	166.1	403.1	
1-6	167.2	404.4	581.3
1-7	165.3	402.4	581.6

* The binding energies are referred to Au 4f(7/2) = 84.0 eV.

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Fig. 1. Experimental S(2p) binding energies (eV) for N,N'-thiobisamines *versus* calculated variation of the effective charge on sulfur atom Δq_s . The changes of q_s were referred to N,N'-thiobisdicyclohexylamine.

Table II. Electronegativity of NR_2 groups*.

Group	X_G
2-1	2.34
2-2	2.34
2-3	2.40
2-4	2.38
2-5	2.32

* Calculated according to Ref. [7].

S(2p) observed for the thiobisamines are in the range expected for sulfur in an oxidation state +2 [8].

Moreover, a similar relationship is observed between the binding energies of the S(2p) electrons and the S–N bond forces or S–N bond orders as calculated from the force constants of the S–N linkages [9]. As shown in Fig. 2, the binding energy of the internal electrons in the sulfur atom of the thiobisamines increases with increasing double bond character of the S–N bond. In general, the S(2p) binding energies for the N,N'-thiobisamines (except for N,N'-thiodibenzylamine) appear to be determined by inductive effects; the electronegativity of the amino group polarizes the S–N bond producing an increase of the effective charge on the sulfur atom and an enhancement of the bond force constant.

Although the correlations (Fig. 1 and 2) are valid for most of the thiobisamines, N,N'-thiodibenzylamine presents an anomalous behaviour. The S(2p)

binding energy in this case reflects an atomic charge lower than that estimated from the electronegativity of the dibenzylamino group; the double bond character of the S–N linkage, however, occurs to a greater extent than that observed for other thiobisamines with the same binding energy (Fig. 2).

The relatively large electron density in the S–N bond reflected in the S(2p) binding energy and in the strength of the S–N bonding should be provided from the aromatic rings on the nitrogen substituents by hyperconjugation.

In the study of the electrooxidation of thiobisamines, N,N'-thiobisdibenzylamine also shows a different behaviour. Normally, the thiobisamines in organic media with small quantities of water undergo an electrooxidation process that is irreversible be-

Fig. 2. Experimental S(2p) binding energies (eV) for N,N'-thiobisamines versus bond orders for the S–N linkage.

Fig. 3. Cyclic voltammogram of (a) N,N'-thiobismorpholine and (b) N,N'-thiobisdibenzylamine in CH_3NO_2 (0.1 M – PTEA).

cause of the hydrolysis of the formed radical cation [5] (Fig. 3a):

In the case of the benzylamino derivative, this radical appears to be stable to a greater extent leading, as shown in Fig. 3b, to a reversible one-electron cyclic voltammogram.

According to a semiempirical MO study done for the N,N'-thiobisdimethylamine and other sulfur (II) compounds, the reactivity of such kind of compounds depends not only on the strength of the S–N bond but also on the positive charge on the sulfur atom and on the presence of orbitals with favourable symmetry for the interaction; in fact, the thiobisdimethylamine with a charge on the sulfur atom of +0.001 is less reactive than SCl_2 with a calculated charge of +0.085 [10, 11].

In Table I the N(1s) and S(2p) binding energies are listed for thiobismorpholine as well as for the thiobisdibenzylamine both coordinated to chromium pentacarbonyl. The effect of the coordination on the binding energies, which are shifted towards lower values, agrees with the coordination *via* the sulfur atom previously proposed by IR, ^1H NMR and UV visible spectral data [3]. In fact, for a coordination through the nitrogen atom larger shifts of the binding energies of the N(1s) electrons should be expected [12]. The shifts of the S(2p) binding energies caused by coordination are similar to those observed for thioethers [13].

The lowering of the binding energies of the internal electrons of sulfur and nitrogen atoms in the ligands can be interpreted as a net charge transfer from the metal to the sulfur atoms caused by a π -back-bonding metal-sulfur interaction. This explanation agrees with the coordinative properties of the N,N'-thiobisamines estimated from their Graham π -parameters [14]. Such estimations indicate that these species behave to some extent as π -acceptor ligands [3].

The energies for the metal core electrons (Table I) are in good agreement with those previously reported [15] for the metals in a formal oxidation state of zero.

Experimental

N,N'-thiobisamines were prepared according to a procedure previously reported [16]. The products were purified by recrystallization from suitable solvents or by distillation under reduced pressure. The synthesis of (N,N'-thiobisamine)-carbonyl complexes was described elsewhere [3].

X-ray photoelectron spectra were recorded with an AEI, ES-200 electron spectrometer. Binding energies were determined using the Au 4f(7/2) peak reference (84.0 eV). Other instrumental details have been described previously [12]. The binding energy values are reliable to ± 0.2 eV. The samples were measured at the indicated temperature; thiobispiperidine -50°C ; N,N'-thiobisdimethylamine -80°C ; N,N'-thiobisdibenzylamine -30°C ; N,N'-thiobisdicyclohexylamine -50°C ; (thiobismorpholine)-pentacarbonyl-chromium(0) -30°C ; (thiobisdibenzylamine)-pentacarbonyl-chromium(0) -30°C .

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