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An XPS Investigation on some Selenium-containing Ligands: Azolidine Derivatives

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An XPS study of the effects of selenium donor atom in azolidine-type ligands is reported. The binding energy values and the atomic charges computed in the CNDO/2 scheme are presented for atoms of interest within the investigated compounds and discussed particularly in terms of the relative ability in charge delocalization presented by single atoms or atomic groups in the ring.

Introduction

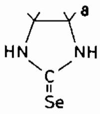
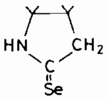
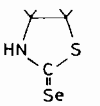
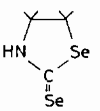
The electronic structure of relatively simple organic molecules containing some potential donor functions, and of the corresponding transition metal complexes has raised considerable interest in recent times, particularly by the use of new spectroscopic techniques such as XPS and UPS, which have been applied recently to the investigation of organic ligands with structures based on the azolidine type, and of their transition metal complexes [1–4]. A particular effect in the general problem is the replacement of the less common donor selenium by oxygen or sulphur, both in *exo*- and *endo*cyclic position, in substituted derivatives of the above type, and we report in this paper on the XPS characterization of this effect. Previous investigations have shown that general properties of selenoamido compounds are remarkably close to those of the corresponding thioamides, while differing markedly from the corresponding amides [5–7]. It is indeed known that replacement of S by Se ('selenation') in IR spectroscopic reports [8, 9] can be used as an assignment criterium for thioamides IR bands; such a replacement, in fact, is almost equivalent to an isotopic substitution, since it leaves vibrational and structural properties of the HN–C=S moiety practically unchanged. We should, however, expect selenoamides to exhibit some minor differences in coordinative ability towards metal centers with respect to thioamides; indeed selenium can be regarded as the most likely donor function in complex selenoamides since the higher availability of donor charge may represent a quantitative variation with respect to the corresponding sulphur derivatives. We report in this paper on XPS data regarding some selenium-substituted azolidine-type ligands (the oxygen and sulphur analoga of which have been previously subject to XPS investigation [3]), in order to give evidence of a systematic evaluation of the selenium effects.

Experimental

All compounds were prepared and purified according to literature [5, 8–10]. XPS measurements were made on a VG ESCA 3 photoelectron spectrometer, employing AlK$\alpha_{1,2}$ radiation (1486.6 eV). Samples were dusted onto a gold tip and measured at room temperature. No sign of damage was evident during each run. The Au 4$f_{7/2}$ peak (b.e. 84.0 eV) was measured to calibrate the spectra; the O1s line (532.0 eV) and C1s line (285.0 eV) were taken as references to compensate for possible charging effects.

Uncertainty corresponds to a standard deviation of ∓0.2 eV, except for Se 3$p_{3/2}$ and S 2p in compounds X = S, Y = Se, where slightly higher uncertainty is expected, because of overlapping of both signals, and consequent application of deconvolution procedures. Deconvolution was accomplished by use of a DuPont 310 Curve Resolver, assuming a gaussian profile for each peak, a FWHM of 3.3 ∓ 0.2 eV for Se 2$p_{3/2}$ and 2.5 ∓ 0.2 eV for S 2p (in agreement with previous reports of ours for single S- or Se-containing compounds), and a separation between the spin–orbit components of Se 3p line of 5.5 ∓ 0.2 eV [7]. Calculations were performed in a CNDO/2 scheme, modified [12] to extend to the second row elements. Geometries were estimated on the ground of known interatomic distances

TABLE I. Measured and Corrected Binding Energies (eV) and Fractional Computed Atomic Charges (a.u.) for the Reported Compounds.

	measured b.e.			corrected b.e.	q_x
 [a]	N1s		400.1	396.2	−0.14
	$Se3p_{3/2}$		161.2	158.3	−0.52
	Se3d		55.0	52.1	
	N1s		400.5	397.1	−0.09
	$Se3p_{3/2}$		161.8	159.3	−0.45
	Se3d		55.4	52.9	
	N1s		400.0	397.0	−0.03
	$Se3p_{3/2}$		161.9	159.7	−0.42
	Se3d		55.5	53.3	
	S2p		164.2	163.5	−0.03
	N1s		400.0	397.3	−0.01
	$Se3p_{3/2}$	= Se	161.8	159.4	−0.45
			164.0	163.5	+0.003
	Se3d	= Se	55.4	53.0	−0.45
			57.6	57.1	+0.003

[a] See ref. 2.

for similar compounds [2, 3]. Corrected b.e. values for atom i were obtained by subtracting from the measured b.e. values the intramolecular potential terms

$$V_i = \sum_{i \neq j} \frac{q_j}{r_{ij}} \quad [13].$$

Results and Discussion

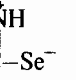
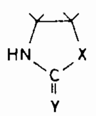
We discuss first the compounds reported in Table I. N1s b.e. values, corrected for intramolecular Madelung terms, increase from X = NH to X = CH_2, S, Se; in the three latter cases differences are quite small, practically inside the experimental error (∓0.2 eV). Such trend is qualitatively confirmed by computed q_N values. The binding energy for $3p_{3/2}$ and 3d levels of exocyclic Se increases in the same order and about in the same sequence of difference as N1s, in agreement with computed q_{Se} values. The above data are consistent with charge delocalization according to resonance forms of type  $\overset{+}{N}H{=}C{-}Se^-$ from the nitrogens onto the external Se atom; the effect is obviously larger with X = NH, when it is produced by two nitrogens, and it is substantially similar in the remaining three cases, where the overall negative charge on the exocyclic Se atom is smaller, even if the individual effect of the single N atom is larger. Therefore, the nature of the ring member X shows quite similar effects to that observed and discussed in previous works [2, 3] for analogous systems containing exocyclic O or S atoms instead of Se. The effect of replacing S by Se in the unsaturated group $\rangle C{=}Y$ results mainly in a small but reproducible increase in the 1s b.e. of the ring nitrogen, parallelled by a decrease of the negative charge on N. This is clearly confirmed by the results collected in Table II, where changes in b.e. and in atomic charges for couples of S- and Se-containing compounds are of the same magnitude (0.3–0.5 eV; 0.1–0.2 a.u. respectively). The effect of the presence of a Se atom in place of S *within the ring* is exemplified by the compound X = Y = Se with respect to X = S, Y = Se. The changes in N1s b.e. (+0.3 eV) and q_N (+0.02 a.u.) suggests that endocyclic replacement of S by Se results in a small decrease of the negative charge on N. Correspondingly, there is a slight increase of negative charge on the external heteroatom, as shown by the variations in b.e. of Se $3p_{3/2}$ and Se 3d (−0.3 eV) and in q_{Se} (−0.03 a.u.). Larger differences are evident from the comparison between Se- and O-

TABLE II. Corrected N1s Binding Energies (eV) and Fractional Computed Atomic Charges (a.u.) on N for Compounds with General formula:



	Y = O[a]		Y = S[a]		Y = Se	
	corrected b.e.	q_N	corrected b.e.	q_N	corrected b.e.	q_N
X = NH	393.9	−0.225	395.9	−0.15	396.2	−0.14
X = CH_2	395.3	−0.21	396.8	−0.11	397.1	−0.09
X = O	394.7	−0.22	395.1	−0.15		
X = S	395.4	−0.185	396.5	−0.05	397.0	−0.03
X = Se					397.3	−0.01

[a] For Y = O, S series of compounds, see ref. 2.

containing compounds (Table II), where the variations in b.e. of N1s and in q_N are larger than +1.5 eV, respectively +0.10 a.u. and confirm the much larger ability of Se to draw electronic charge from N, if compared to O in the same chemical environment. Further evidence for the peculiar behaviour of Se if compared to S or O comes from a comparison among the compounds in the sequence X = Y = S; X = S, Y = Se; and X = Y = Se. While, in fact, Δ b.e. of N1s is 0.5 eV and Δq_N is 0.02 a.u. on passing from X = Y = S to X = S, Y = Se, as already discussed above, the complete replacement of both S atoms through Se atoms results in variations as large as 0.8 eV, respectively 0.04 a.u. Furthermore, data concerning the three compounds X = Y = O, S, Se yield quantitative evidence for the combined effects of two Se atoms with respect to two O atoms in the same heterocyclic framework: Δ b.e. for N1s and Δq_N are respectively 2.6 eV and 0.21 a.u. on passing from X = Y = O to X = Y = Se, whereas they amount to 1.8 eV and 0.17 a.u. respectively from X = Y = O to X = Y = Se. This latter series supports the conclusion that the extent of double-bond formation decreases in the order $\rangle C{=}O > \rangle C{=}S > \rangle C{=}Se$; besides, the X heteroatom becomes closer to neutrality on going from X = O to S and Se, thereby releasing less electronic charge to the ring. In the same sequence ring-nitrogen becomes increasingly positive because of two converging effects: a larger tendency of the Se heteroatom to draw electronic charge from the ring nitrogen, and a smaller ability to release negative charge by conjugative mechanism from ring Se.

The existence of well-defined trends in the electronic structure of azolidine systems caused by the presence of one or two Se atoms, which can receive quantitative evidence from a comparative survey of XPS data, suggests the possibility of discussing some implications on the electronic structure, and particularly on N1s b.e. and q_N values for the members of the series of Se-substituted azolidines which are still unknown owing to unsuccessful attempts to their synthesis. Thus, let us consider *e.g.* the series X = O, Y = Se; X = Se, Y = O and X = Se, Y = S. We recall that the variations in N1s b.e. and q_N on passing from Y = S to Y = Se are in the range 0.3–0.5 eV, respectively 0.01–0.02 a.u. for the experimentally known cases where X = NH, CH_2, S (Table II); if we assume that the same differences hold for X = O, we expect for the compound X = O, Y = Se, N1s b.e. at approximately 395.5 eV and $q_N \cong -0.13$ a.u., from a comparison with the corresponding values for the compound X = O, Y = S.

As for the two unknown compounds X = Se, Y = O, S, a convenient criterion for comparison is suggested by the couple of compounds with X = S, Y = Se and X = Y = Se with N1s Δ b.e. of 0.3 eV and Δq_N of 0.02 a.u. If we assume variations of the same amount on passing from X = Y = S to X = S, Y = Se, we can extrapolate for the latter compound a corrected N1s b.e. value of 396.8 eV together with $q_N \cong -0.03$ a.u. By an analogous procedure, starting from the XPS data for X = S, Y = O we can furthermore expect for the compound X = Se, Y = O the N1s b.e. values of 395.7 eV and a q_N of −0.16 a.u.

In conclusion, XPS data can afford a reasonable picture together with a quantitative description of the substituent effects induced by the presence of Se atoms in azolidine-type molecules both in endocyclic and exocyclic positions.

References

1 F. A. Devillanova, C. Furlani, G. Mattogno, G. Verani and R. Zanoni, *Gazz. Chim. Ital., 110* (1), 19 (1980).

2 M. V. Andreocci, M. Bossa, F. A. Devillanova, C. Furlani, G. Mattogno, G. Verani and R. Zanoni, *J. Mol. Struct.,* (1980) in press.

3 M. V. Andreocci, F. A. Devillanova, C. Furlani, G. Mattogno, G. Verani and R. Zanoni, *J. Mol. Struct., (1980) in press.*

4 M. Bossa, C. Furlani, G. Mattogno and R. Zanoni, *Gazz. Chim. Ital,* (1981) in press.

5 F. Cristiani, F. A. Devillanova and G. Verani, *J. Chem. Soc. Perkin Trans., II,* 324 (1977).

6 E. Shefter, M. N. G. James and H. G. Mautner, *J. Pharm. Sci., 55,* 643 (1966).

7 H. Rupp and U. Weser, *Bioinorg. Chem., 5,* 21 (1975).

8 F. A. Devillanova and G. Verani, *J.Chem. Soc. Perkin Trans., II,* 1529 (1977).

9 F. A. Devillanova and G. Verani, *Aust. J. Chem., 31,* 2609 (1978).

10 F. A. Devillanovaa and G. Verani, *Transition Met. Chem., 2,* 9 (1977).

11 K. A. Jensen and P. H. Nielsen, *Acta Chem. Scand., 20,* 597 (1966).

12 QCPE program 261.

13 K. Siegbahn *et al.,* 'ESCA Applied to Free Molecules' North Holland (1971).