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The Electronic Structure of $RN_2S_2^-$ Ligands from XPS (ESCA) Spectra of Some Nickel(II) Complexes

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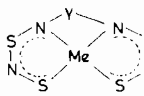
As a part of a systematic investigation of correlation between XPS and structural data for transition metal complexes (mainly Ni(II) with sulfur-containing ligands, we report an XPS study of quadratic nickel(II) complexes with the ligand $N_2S_2H_2$ and two of N-substituted derivatives. Previous investigations were concerned with complexes containing $[Ni(II)S_4]$ chromophores [1, 3] (Nickelphenyldithiocarbazato and Nickeldithiocarboxylato complexes) and $[Ni(II)\text{-}S_2N_2]$ chromophores (Nickeldithiocarbazato complexes) [1, 2] usually associated with relatively complex organic ligands such as substituted dithiocarbazates $R_1R_2N(R_3N)CSS^-$, dithiocarboxylates $R\text{-}CSS^-$ and perthiocarboxylates $RCS(S)S^-$.

The present compounds are instead examples of very simple ligand structures formed essentially only by N and S atoms belonging to the chelate rings, where a fairly simple analysis of the charge distribution effects along the chelate rings should be possible, so as to allow easy direct correlation with theoretical computations of charge distributions, as well as with experimental values of chemical shifts in the b.e. of core orbitals of the involved atoms.

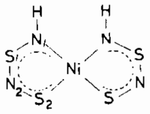
The ligand systems themselves can be regarded as fragmentation and reduction products of nitrogen sulfide, and their investigation by XPS is a contribution to the elucidation of the electronic structure of inorganic nitrogen–sulfur systems by this technique; in fact, the electronic structure of several such compounds is currently being investigated at our Laboratory also by other techniques besides XPS.

The simplest compound in the $Ni(N_2S_2R)_2$ series (I; X = H) was prepared by Goehring [4] and correctly characterized as a dihydro-derivative by Piper [5] although some doubts persisted as to whether its structure was *cis* or *trans*-planar. Several other complexes of the same kind were synthesized later by other authors, *e.g.* Thewalt and Weiss [6] who prepared also bridged derivatives of type

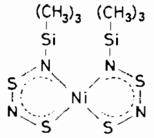


(Y = $-CH_2-O-CH_2-$, $-CH_2-NCH_3-CH_2-$, $-CHOH-CHOH-$)

thus proving the *cis* structure. There are anyway ample possibilities of varying the nature of the R group, so as to produce possible substituent effects on the electronic structure of the metal–chelate ring. We measured in ESCA the trimethylsilyl derivative (II), and the bridged condensation product of I with methylglyoxal (III), quite analogous to the previously prepared glyoxal derivative [6]:



I



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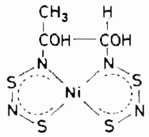


III

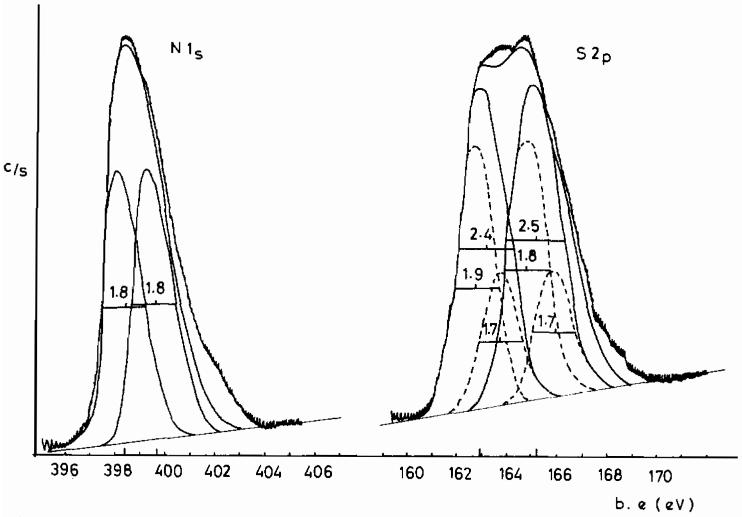


Figure 1. XP spectra of N_{1s} and S_{2p} after deconvolution.

TABLE I. Bonding Energies of Ni(II) Compounds.

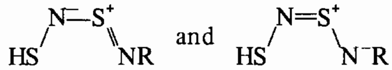
	N_{1s}		S_{2p}		$Ni_{2p\,3/2}$
	N(I)	N(2)	S(1)	S(2)	
$Ni(S_2N_2H)_2$	399.7	398.4	165.1	162.9	854.3
$Ni[S_2N_2Si(CH_3)_2]_2$	399.0	398.0	165.1	162.9	854.1
$Ni(S_2N_2)_2(\overset{CH_3}{C}(OH){-}\overset{H}{C}(OH))$	399.1	398.1	165.2	163.0	854.1

TABLE II. Atomic Charge (CNDO/2).

	N(1)	N(2)	S(1)	S(2)
$S_2N_2H_2$	5.30	5.22	6.01	5.33
$S_2N_2HCH_3$	5.24	5.23	6.02	5.56

XPS spectra (VG ESCA-3 spectrometer, $AlK_{\alpha 1,2}$ source, calibration against Au $4f_{7/2}$ taken at 84.0 eV) were taken of the S_{2p}, N_{1s} and $Ni_{2p\,3/2}$ peaks, and showed in all cases broad bands for N and S, clearly indicating the presence of two inequivalent species of atoms in 1:1 ratio (see Fig. 1). Deconvolutions, carried out on a Dupont 310 Curve Resolver, yielded the b.e. values for the single components reported in Table I. In order to get clues to the possible assignment, calculations of the predicted gross atomic charge distribution along model molecules of the free ligands N_2S_2HR (R = H, CH_3) in the same conformation as in the crystal structure of the d^8 metal complexes [7] were carried out in the CNDO/2 formalism (Table II).

Experimental b.e. data indicate only a small difference between the two types of inequivalent nitrogens, in agreement with the substantially equal predicted atomic charge in the free ligand moiety, which suggests dominant contributions from structure



The difference (~1 eV) in the complexed ligands arises probably from the donor effect of N(1) towards Ni. Much larger is the difference between both types of sulfur, in agreement with a substantial positive charge (~+0.5) expected on S(1), against practical neutrality of S(2). This situation is not qualitatively changed when S(2) becomes an anionic donor in the metal complex.

The b.e. values for $Ni_{2p\,3/2}$ fall in the common range observed for low-spin Ni(II) complexes, and the average b.e. of N 1s are in the range of most nitrogen compounds containing neutral or slightly negative N atoms. As for sulfur, S(1) is closer to the range of b.e. values for tetravalent S, while S(2) corresponds to most other cases of bivalent anionic sulfur. We can compare the difference N1s – S2p [8] which is about 234 eV for S(1) (with respect to the average b.e. of N1s), and 236 eV for S(2), with that observed in metal dithiocarbazates [1, 2] amounting to an average of 238 eV. The b.e. difference between pairs of unequivalent sulfurs (here of the order of 2 eV, for a predicted charge difference of about 0.5 *e*) has been reported as ~1.7 in methyldithiocarbazate esters [3] (computed charge difference ~0.25 *e*), and ~1.8 eV for metal perthiobenzoates [3] (estimated charge difference ~0.4 *e*).

The effect of R substituents is not large and is noticeable, as expected, only on the nitrogen b.e.. Both the C-alkyl and the substituted silyl group are expected to exert, with respect to the unsubstituted H-ligand, a more marked inductive donor effect, particularly on N(1). This is not borne out by theoretical calculations (actually, CNDO/2 methods often fail in reproducing some well established semiempirical trends such as the present one), but corresponds clearly to the experimentally observed decrease of N(1) b.e. from 399.7 in the complex of the unsubstituted ligand to 399.0 ∓ .1 in the C- and Si-derivatives.

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