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ESCA Spectra of Ni(II) Methyl Esters Dithiocarbazato Complexes

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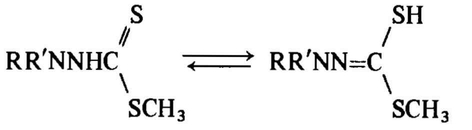
N_{1s}, S_{2p} binding energies for the methyl esters of dithiocarbazato complexes and N_{1s} and S_{2p} binding energies for the methyl esters of dithiocarbazic acids were measured. It was found that on going from the free esters to the corresponding complex, after band deconvolution, there was a significant b.e. decrease for one of the two N peaks, whilst the other peak was not greatly shifted. Since in these complexes deprotonation can only take place on N(2), we attribute the lower b.e. value to this atom.

Introduction

Methyl esters of dithiocarbazic acids, RR′NNR″-CS_2CH_3, can exist in the tautomeric forms [1]



(in the case in which R″ = H) being capable of giving complexes in both the neutral and the acid form.

In a previous work [2] we have studied the Ni(II) complexes of dithiocarbazic acids with the aim of correlating binding energy variations of the ligand atoms with the nature of the chromophore present as assigned using other techniques. Continuing this study we have examined the compounds obtained by reacting Ni(II) salts with the methyl esters in the acid forms [1]. Structural studies are in progress in our Laboratory on the same compounds [3].

Experimental

Spectra were run on an AEI ES 100 spectrometer using $AlK_{\alpha 1,2}$ radiation (1486.6 eV). Samples were deposited as thin films onto a gold plate so as to minimize charging effects. The Au $4f_{7/2}$ level at 84.0 eV from the sample holder was used as reference.

Results and Discussion

Table I shows binding energy values and corresponding FWHH for the N_{1s} and S_{2p} peaks of the free ligands and the corresponding Ni(II) complexes. In the same Table binding energy values are shown for the two N and S atoms as obtained by deconvolution of the above peaks, Δ being the chemical shift of the same atom in going from the free ligand to the corresponding complex. The assignments of these values to the two N and S atoms of the free ligands were supported by theoretical calculations by the CNDO/2 and EHT methods. It may be noticed that the binding energy values for N(2) in the free esters are roughly constant and always at higher energy than those for N(3). This result may be understood in terms of the influence of the electron-withdrawing group $-CS_2CH_3$ on N(2), whilst N(3) binding energies follow the inductive effect of the substituents (for the discussion see ref. 2). Band deconvolution for the two sulphur atoms in the ligand molecules gave two peaks, of about the same width and

TABLE I. N_{1s} and S_{2p} Binding Energies of Esters of Dithiocarbazic Acids and Corresponding Complexes.[a]

Complexes	N_{1s}	N(2)	ΔN(2)	N(3)	ΔN(3)	S_{2p}	=S	Δ(=S)	$-SCH_3$	Δ($-SCH_3$)	Suggested Chromophore
1) $Ni[NH_2NCS_2CH_3]_2$	399.2(2.8)	398.6	2.3	400.0	−0.4	162.8(3.0)	163.5	0.8	161.8	0.6	$(3)N_2S_2$
2) $Ni[NHN(CH_3)CS_2CH_3]_2$	401.1(1.7) 399.0(1.6)	401.1	–	399.0	0.6	163.7(2.8)	164.5	−0.1	162.8	−0.4	$(3)N_2S_2$
3) $Ni[(CH_3)_2NNCS_2CH_3]_2$	399.8(2.5)	398.6	2.4	400.2	−0.9	162.4(2.8)	163.0	0.9	163.4	1.1	$(3)N_2S_2$
4) $Ni[C_6H_5NHNCS_2CH_3]_2$	399.6(2.8)	398.7	2.3	400.1	−0.1	162.9(2.9)	163.8	0.1	161.1	1.0	$(2)N_2S_2$
5) $Ni[(C_6H_5)_2NNCS_2CH_3]_2$	399.6(3.3)	398.9	2.0	400.3	—	162.7(3.2)	163.5	0.4	161.7	0.4	$(2)N_2S_2$
Ligands[b]											
6) $NH_2NHCS_2CH_3$	400.1(2.8)	400.9		399.6		163.6(3.2)	164.3		162.4		
7) $NH_2N(CH_3)CS_2CH_3$	400.3(2.5)	401.1		399.6		163.3(3.1)	164.4		162.4		
8) $(CH_3)_2NNHCS_2CH_3$	400.1(3.3)	401.0		399.3		163.0(2.9)	163.9		162.5		
9) $C_6H_5NHNHCS_2CH_3$	400.7(1.9)	401.0		400.0		163.0(3.2)	163.9		162.1		
10) $(C_6H_5)_2NNHCS_2CH_3$	400.6(1.6)	400.9		400.3		163.2(3.1)	163.9		162.1		

[a] FWHH in parenthesis; Δ: chemical shift between the free ligands and the corresponding compounds. [b] Values quoted in ref. 2.

separated by about two eV. Again with the help of the same theoretical calculations, we attributed the peak at lower b.e. to the $-SCH_3$ sulphur and the higher b.e. one to the sulphur in the C=S group.

On going from the free esters to the corresponding complexes it may be noticed that, after band deconvolution, there is a significant b.e. decrease for one of the two N peaks of compounds 3 and 5, whilst the other peak does not give evidence of a great shift. Since in these complexes deprotonation can only take place on N(2), we attributed the lower b.e. value to this atom. In compounds 1 and 4 there is a b.e. decrease for one of the two N atoms that is similar to that of compounds 3 and 5, so we are inclined to believe, by analogy, that this effect is again due to a deprotonation of N(2).

If N(3) b.e. are taken into account it may be shown that there is a significant b.e. increase for complexes 1 and 3. It has been already pointed out that a b.e. increase on an atom should be correlated with an electronic charge decrease on the atom itself, so we might explain this effect in compounds 1 and 3 as being a consequence of coordination. This may be confirmed by observing that N(3) b.e.'s for complexes 4 and 5 are equal to those for the free esters, since N(3) cannot coordinate, probably owing to steric hindrance effects and low basicity.

Values for compound 2 are completely different when compared with the others of the Table. There is no b.e. difference for N(2) between the ester and the complex, indicating that this atom is not affected by coordination nor by deprotonation taking place on N(3). Coordination of $-NH_2$ allows this group to lose one hydrogen, and the small net decrease in b.e. of 0.6 eV for this atom may be viewed as a balance between deprotonation and coordination effects. The above results may be confirmed by taking into account the fifth and sixth columns of Table I, which show b.e. differences between the two S atoms of the free ligands and the parent complexes. B e.'s for both S atoms decrease in complexes 1 and 3, probably owing to conjugation between –N(2)– and the $-CS_2CH_3$ group, whilst for compounds 4 and 5 this decrease in b.e. is much lower. We tentatively explain this difference in behaviour as caused by coordination of N(2) in complexes 4 and 5, which would decrease availability of electronic delocalization between N(2) and the $-CS_2CH_3$ group. These conclusions are also supported by unpublished I.R. and electronic spectral data. Finally, it is interesting to note that whilst N(2) is roughly constant (with the obvious exception of compound 2) a b.e. increase of N(3) is generally balanced by a decrease of sulphur b.e. and *vice versa.* Again, this might be interpreted as a consequence of charge delocalization along the whole molecule of the ligand, which seems to occur both when N(2) or N(3) are coordinated.

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