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ESCA Study of NiLig$_2$ Compounds

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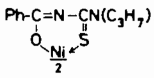
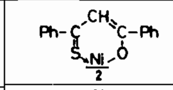
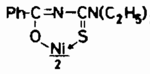
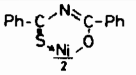
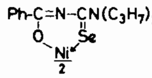
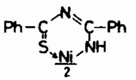
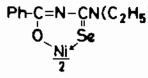
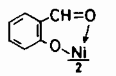
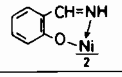
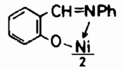
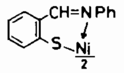
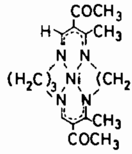
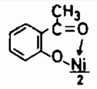
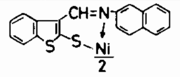
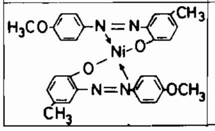
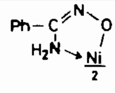
Many works [1–7] devoted to ESCA investigation of Ni compounds have been published recently. In the present work a systematic study of the NiLig$_2$ type of compounds, where Lig is a bidentate ligand, has been carried out.

The spectra were obtained on a VIEE-15 spectrometer. For charge correction the C1s (285 ev) line from the hydrocarbons deposited on the sample was used. Such charge correction [8, 9] gives a good reproducibility of results. The MgKα line was used for spectra excitation. Vacuum in the spectrometer was $\sim 10^{-6}$ torr. To increase the stability of compounds the substances were cooled down to the temperature of liquid nitrogen. When taking the spectra of hygroscopic compounds we used a special chamber which makes it possible to transfer substances from sealed ampoules to the spectrometer avoiding contact with the atmosphere.

The obtained experimental values of binding energy are shown in Table I. To give a complete picture the table also includes the values of Ni binding energy obtained by us [7] under similar experimental conditions. Reproducibility of experimental values is about ±0.1 ev.

TABLE I. Binding Energy Ni2p$_{3/2}$, ev.

Compound	Ni2p$_{3/2}$		Ni2p$_{3/2}$
	855.1		854.7
	854.8		854.7
	854.6		854.9
	854.3		856.2
[(C$_5$H$_{11}$)$_2$NCS$_2$]$_2$Ni	854.4		855.3
[(C$_4$H$_9$O)$_2$PS$_2$]$_2$Ni	854.8		855.4
[(C$_4$H$_9$O)$_2$PSO]$_2$Ni	855.3		854.9
	855.5		856.1
	855.0	Ni(DMG)$_2$	855.2
	855.2	Ni(acac)$_2$	856.1
			855.9

Interesting conclusions on the capability of ligands to withdraw electron density from Ni can be obtained by examining tetracoordinated nickel compounds of the NiLig$_2$ type, where Lig is a bidentate chelate. Analysis of the data in Table I shows that the nature of atoms coordinating the ligand to Ni determines the values of Ni2p$_{3/2}$, *i.e.*, the capability of the ligand to withdraw electron density from Ni is, to a considerable extent, determined by these very atoms. This is especially clear in the case of

TABLE II. Dependence of Ni2p$_{3/2}$ Binding Energy, g_{11} and α^2 on Four Atoms (A) in the First Coordination Sphere in NiLig$_2$ and CuLig$_2$ Compounds.

A	4O	2O, 2N	4N	2O, 2S	2N, 2S	2O, 2Se	4S
Ni2p$_{3/2}$	856.2	855.3	855.2	855.1	855.0	854.6	854.4
	856.1	855.4	855.5	854.8	854.9	854.3	854.8
	856.1	855.2		854.7	854.9		
		855.9		855.3			
				854.7			
g_{11}	2.242	2.216				2.110[a]	2.175
		2.218				2.087[a]	
		2.200					
α^2	0.92	0.85–0.78				0.57[a]	0.74
						0.45[a]	

[a] Data refer to four Se atoms in coordination sphere.

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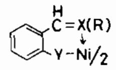

compounds (Table I), where X = O, N; Y = O, S.

Naturally, this result cannot be regarded as a general rule since the structure of the ligand plays a significant role in the electron density redistribution from Ni to the ligand. This rule cannot, *e.g.*, be inferred from the data in ref. 6. Nevertheless, as is shown by the data in Table II compiled on the basis of Table I, the nearest four atoms in $NiLig_2$ compounds in most cases do in fact determine the range of $Ni2p_{3/2}$ values. According to Table II, the capability of atoms to withdraw electron density from Ni is determined by the $O > N > S > Se$ series. This series is in agreement with general considerations and with a number of other experimental studies. *E.g.*, it has been shown [10] that in Cu(II) coordination compounds the value of g_{11} factor also varies in conformity with the atoms located in the first coordination sphere. The same regularity is true for the variation of α^2 value, which characterizes the population of $Cu3d_{x^2-y^2}$ electrons in the compound. The dependence of g_{11} and α^2 values on the closest surrounding atoms in Cu(II) compounds is shown in Table II. As would be expected, the decrease of $Ni2p_{3/2}$ value depending on 4A is reflected in the decrease of α^2 value for a similar environment in Cu(II) compounds.

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