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X-Ray Photoelectron Spectroscopy (ESCA) Investigations in Coordination Chemistry. IV. Study of Transition Metal–Salicylaldoxime Complexes

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ESCA investigations of transition metal complexes of salicylaldoxime and its derivatives were used to demonstrate how the electron binding energies of the donor atoms and central atoms are affected by complex formation, by the stabilities of the resulting complexes, by substituents changing the electron densities of the donor atoms, and by cis–trans isomerism. A qualitative correlation was revealed between the ESCA data and the individual vibrational bands of the complexes, and also the bands of their electronic excitation spectra.

Introduction

The determination of the range of application of X-ray photoelectron spectroscopy (ESCA) in coordination chemistry can be expected from the ESCA investigation of methodically arranged systems which have been comprehensively studied by various different methods. The examination of many types of metal complexes[1–6] has clearly shown that as a result of complex formation, changes take place in the electronic structures of the central atom and the donor atoms (in the electron binding energies of the orbitals) which are sufficiently large to be measurable by this method. It also emerged from our earlier investigations[6–8] that such "weak interactions" as solvation, hydrogen bond formation and coordination in the outer sphere may additionally give rise to changes in the electron binding energies of the atoms involved, which are large enough to be followed by means of ESCA. Relatively few investigations have been reported in which the changes in ESCA data due to complexchemical effects have been compared with data obtained by other methods of structural examination (vibrational spectrum, ultraviolet spectrum, *etc.*)[9].

The aim of the present work is the ESCA study of salicylaldoxime complexes and their derivatives containing electrophilic or nucleophilic substituents (earlier examined in detail by equilibrium measurements[10] and by infrared and ultraviolet spectroscopy[11]), and comparison of the ESCA data with the results of the other investigations.

Equilibrium measurements were earlier used to determine the effects of the substituents on the stabilities of the complexes.[10] The spectroscopic examinations[11] showed the effects on the infrared and ultraviolet spectra of changes in the electronic structure due to the substituents. Infrared spectroscopy and analysis of the complexes also led to the finding that in the nickel(II) and copper(II) complexes of salicylaldoxime and its derivatives the nitrogen and oxygen donor atoms are arranged in a *trans* configuration, whereas in the analogous cobalt(II) and iron(II) complexes they are in a *cis* configuration.

On the above basis the ESCA investigation of these systems was expected to lead to the establishment of the effects exerted on the electron binding energies of the central and donor atoms of the complexes by the substituents, by the resulting complex stability change, and by the *cis–trans* isomerism.

Experimental

The ESCA spectra were recorded with the AEI Scientific Apparatus LTD. ES 100 electron spectrometer as described previously[6,8], with the modification that the complexes were transferred to the surface of the copper sample-holder in acetone solution; after evaporation of the acetone, therefore, the sample was in the form of a thin, smooth film. In this way ESCA bands were obtained with lower half-widths and higher intensities than by means of copper-grid powder photographs. Every recording was repeated 3–4 times. The reproducibility of the measurements was in every case ±0.1 eV or better.

Complex bands arising from non-equivalent atoms were resolved by computer as described in an earlier paper.[6]

Complexes were prepared and analyzed as previously.[11] The analytical results are listed in Table I.

TABLE I. Analytical Data of the Complexes (calculated values in brackets).

Ligand	Metal	N %		C %		Metal %	
Sa[a]	Ni^{2+}	8,45	(8,466)	51,1	(50,81)	17,8	(17,73)
	Cu^{2+}	8,29	(8,343)	49,7	(50,07)	18,9	(18,93)
	Co^{2+}	7,91	(7,933)	46,9	(47,61)	16,6	(16,69)
	Fe^{2+}	7,98	(8,003)	48,0	(48,03)	15,9	(15,95)
CH_3Sa	Ni^{2+}	7,79	(7,805)	52,9	(53,53)	16,3	(16,35)
	Cu^{2+}	7,60	(7,700)	52,0	(52,81)	17,4	(17,45)
ClSa	Ni^{2+}	7,08	(7,008)	42,3	(42,12)	14,6	(14,68)
	Cu^{2+}	6,90	(6,92)	42,0	(41,55)	15,7	(15,71)
NO_2Sa	Ni^{2+}	13,3	(13,31)	39,9	(39,96)	13,7	(13,94)
	Cu^{2+}	13,0	(13,16)	39,4	(39,40)	15,0	(14,92)

[a] Sa = Salicylaldoxime. The substituents are in position 5 of the aromatic ring.

Results and Discussion

The electron binding energies of the 1s orbitals of the nitrogen and oxygen donor atoms in the ligands and their complexes are given in Table II, together with the electron binding energies of the $2p_{3/2}$ orbitals of the central atoms in the nickel and copper complexes, and with the logarithms of the protonation constants of the ligands and the overall stability constants of the complexes.

The electron binding energies are referred to the 1s electron binding energy of the carbon atoms in the aromatic ring of salicylaldoxime. Such a reference was necessary because the charge developing on these insulating samples as a result of the exciting radiation affected the absolute values of the electron binding energy in the various complexes in different ways. This charging gave rise to a particularly large difference between the ESCA data for the electrically neutral *trans* isomers and the *cis* isomers with one negative

TABLE II. The ESCA Data of Salicylaldoxime (Sa), its Derivatives and their Complexes (referred to C 1s[a]), Protonation Constants (K_H) of Ligands, Overall Stability Constants (β) of Complexes and the Frequencies of OH and CN Stretching Vibrations (ν).

Ligand	Central ion	N 1s	O 1s	M $2p_{3/2}$	$\log K_H$	ν_{OH}	ν_{CN}
Sa	H^+	114,7	247,1	–	10,7	3000	1627
CH_3Sa	H^+	114,65	247,1	–	11,06	3180	1625
ClSa	H^+	114,8	247,2	–	10,25	3000	1637
NO_2Sa	H^+	115,1	247,5	–	8,72	2900	1640
					$\log\beta_2$		
Sa	Ni^{2+}	115,3 (114,2)[b]	247,0	569,7	14,3	2950	1650
CH_3Sa	Ni^{2+}	115,25	247,0	569,7	14,7	2950	1652
ClSa	Ni^{2+}	115,4	247,1	569,8	13,7	3000	1649
NO_2Sa	Ni^{2+}	115,7	247,4	570,1	13,8	3100	1633
Sa	Cu^{2+}	115,5	247,0	649,15	21,5	3050	1658
CH_3Sa	Cu^{2+}	115,5	247,0	649,0	22,2	3050	1652
ClSa	Cu^{2+}	115,6	247,1	649,3	21,4	3100	1651
NO_2Sa	Cu^{2+}	115,65	247,35	649,35	–	3240	1648
Sa	Co^{2+}	114,2[b]	246,8	–	13,5	3050	1625
Sa	Fe^{2+}	114,8[b]	247,3	–	16,7	3200	1617

[a] The absolute value of C 1s electron binding energy in salicylaldoxime is 285,7.

[b] *Cis* isomers; all other data refer to *trans* complexes.

charge. However, since exactly the same effects are exerted on the ESCA data for all the atoms within one material sample, the electron binding energies referred to the C 1s can be used unambiguously for the study of the complex correlations.

The following findings arise directly from the data of Table II.

Electrophilic substituents cause the electron binding energy on the donor atoms to increase both in the ligands and in the complexes. In the nickel complexes the electrophilic substituents exert the same effect on the electron binding energy of the central atom as on the donor atoms; in the copper complexes this effect is less pronounced on the central atom.

In the case of the ligands an almost linear correlation is found between the logarithms of the protonation constants and the N 1s electron binding energies. The correlation is less clear-cut between the complex stability constants and the electron binding energies. Comparison of the N 1s electron binding energies of the analogous nickel and copper complexes reveals that the energies are higher for the copper complexes, which have significantly greater stability. An analogous tendency is not exhibited for the oxygen donor atoms.

The above phenomena can be explained in that both the electrophilic substituents and the stronger coordination (more covalent coordinate bond) decrease the electron density on the donor atoms, which appears in the increase of the electron binding energies. It also emerges from the data that the effect of the substituents is considerably greater than the effect of the stability difference due to the different metals in the analogous complexes. This permits the conclusion that the size of the complex stability constants in the given systems is affected not only by the coordinate σ-bond (and the electron densities thus determined), but also by many other factors (π-back-coordination, steric effects, solvation, *etc.*).

The fact that the electron densities on the nitrogen and oxygen donor atoms depend to different extents on the stability change due to the action of the metal clearly shows that the higher stability of the copper complexes can primarily by attributed to the stronger metal–nitrogen interaction.

From a comparison of the N 1s and O 1s electron binding energies of the ligands with those of the complexes, it can be seen that while complex formation increases the electron binding energy on the nitrogen donor atoms, it decreases it on the oxygen donor atoms.

This apparent contradiction can be explained in that complex formation involves the coordination of the originally free electron-pair of the nitrogen to the metal ion, with a resulting decrease of electron density on the nitrogen; the oxygen atoms in the free ligand, however, are protonated and the complex formation means the exchange of the proton for metal. In the given system the central atom of the complexes visibly decreases the electron density on the oxygen to a lower extent than the proton originally on it in the free ligand. An analogous phenomenon was observed by Burness *et al.*[5] in the ESCA investigation of Schiff's base complexes of cobalt(II).

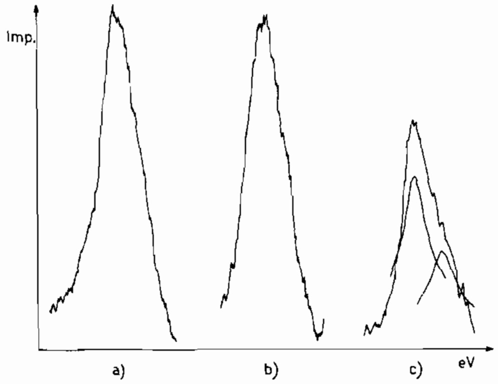

Figure 1. The N 1s ESCA spectra of salicylaldoxime (a), its cobalt (b) and nickel complexes (c).

In all the complexes examined, with the exception of nickel–salicylaldoxime, the N 1s spectra did not indicate the presence of non equivalent nitrogen donor atoms. Figure 1 shows the N 1s spectra of free salicylaldoxime and its cobalt and nickel complexes (in the nitro derivatives the N 1s band of the nitro groups was well separated from the band of the donor nitrogen, and did not interfere with its evaluation, (Figure 2).

The complex N 1s spectrum of nickel–salicylaldoxime was resolved by means of a computer into two lines (Figure 1c) and the values of the electronic bonding energy were determined for these two lines.

It can be seen from the data of Table II that the values of the N 1s electronic bonding energy for all of the copper complexes and for the complexes of nickel with chloro-salicylaldoxime and nitro-salicylaldoxime are considerably higher than those for the

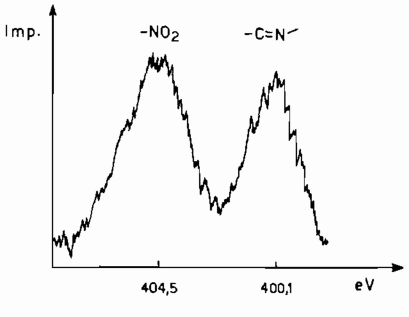

Figure 2. The N 1s ESCA spectrum of nickel-5-nitro-salicylaldoxime.

cobalt and iron complexes. The stability constants in Table II clearly show that this phenomenon cannot be explained on the basis of stability differences.

Since it is known from earlier investigations[11] that the nitrogen donor atoms in the copper and nickel complexes are arranged in a *trans* configuration, while those in the cobalt and iron complexes are in a *cis* configuration, these examinations seem to indicate that the coordination decreases the electron density on the donor atoms to a greater extent in the *trans* complexes than in the *cis* complexes. This is in agreement with the earlier finding from infrared studied that the hydrogen bonds in the salicylaldoxime complexes of nickel and copper, which have *trans* configurations, are significantly weaker than those in the *cis* complexes.[11]

The composite N 1s ESCA bond of nickelsalicylaldoxime seem to indicate the presence of both *cis* and *trans* isomers in this sample.

The investigations reveal that the changes in the electron density of the donor atoms due to the *cis–trans* isomerism may be in some systems sufficiently large to be detectable by ESCA examination of the inner orbitals.

The foregoing clearly shows that by means of X-ray photoelectron spectroscopy it was possible to follow the effects exerted on the electronic structures of the complexes by complex formation, by the ligand substituents, and by *cis–trans* isomerism. Earlier investigations also revealed these effects in the infrared and electronic excitation spectra of the complexes.[11] An examination was subsequently made of what qualitative correlations could be found between the ESCA data and the infrared vibration frequencies, and between the ESCA data and the energies of some absorption maxima of the electronic excitation spectra. Consideration was also given to the extent to which the ESCA data supplement the conclusions drawn from the earlier studies.

Figure 3 shows plots of the O 1s electron binding energies (referred to C 1s) as a function of the OH vibration frequency. It can be seen that for both the copper and the nickel complexes the electron binding energy on the oxygen increases with the increase of ν_{OH}. In both systems the correlation is almost linear. If it is taken into account that the OH vibrations arise from a proton bound in an intramolecular hydrogen bond and the increase of the strength of the hydrogen bond is accompanied by the decrease of ν_{OH}, while in addition the increase of the electron binding energy shows the decrease of the electron density, it can be seen that in these systems the decrease of the electron density on the oxygen atom is associated with the decrease of the strength of the hydrogen bond.

The data for the copper and nickel complexes consist of two independent lines, showing that the strength of the hydrogen bond does not depend exclusively on the size of the electron density on the oxygen pillar atom. It can be seen that in the nickel complexes a hydrogen bond of higher stability relates to the same electron density on the oxygen atom. Compared with the N 1s electron binding energies, this indicates that the cause of the lower stability of the hydrogen bond in the copper complexes is the lower electron density (higher electron binding energy) on the nitrogen pillar atom.

Figure 4 shows a plot of the N 1s electron binding energies (referred to C 1s) as a function of the C=N vibration frequency. Here also two lines were found separately for the data for the copper and the nickel complexes. It can be seen from the Figure that with the decrease of ν_{CN} the electron binding energy on the nitrogen increases. The earlier studies[10, 11] showed that the decrease of the C=N vibration frequency in the chelate ring of salicylaldoxime complexes can be attributed in part to the decrease of the strength of the metal–nitrogen coordinate bond, and in part to the increase of the conjugation in the chelate ring (in the free ligand, where conjugation cannot play a role, the value of ν_{CN} increases on the effect of electrophilic substituents). Since the decrease of the strength of the coordinate bond must result in the increase of the

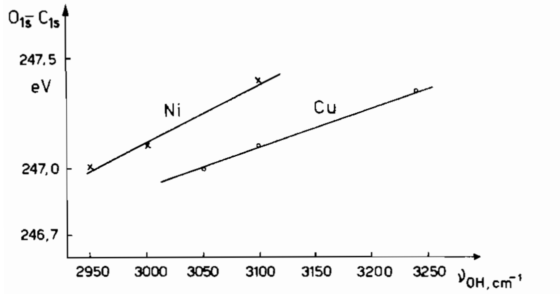

Figure 3. The O 1s electron binding energies (referred to C 1s) of the salicylaldoxime complexes, plotted as a function of the OH stretching vibration frequencies.

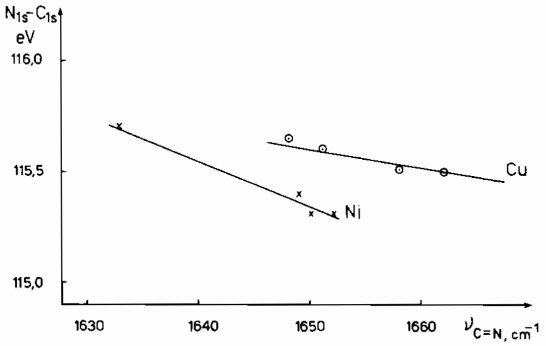

Figure 4. The N 1s electron binding energies (referred to C 1s) of the salicylaldoxime complexes plotted as a function of the frequencies of the CN stretching vibration.

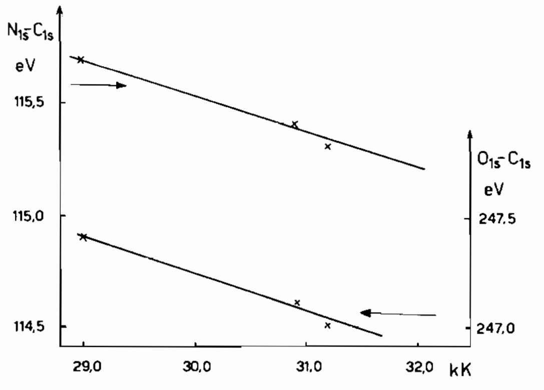

Figure 5. The N 1s and O 1s electron binding energies (referred to C 1s) of the nickel complexes plotted as a function of the frequencies of electron excitation bands.

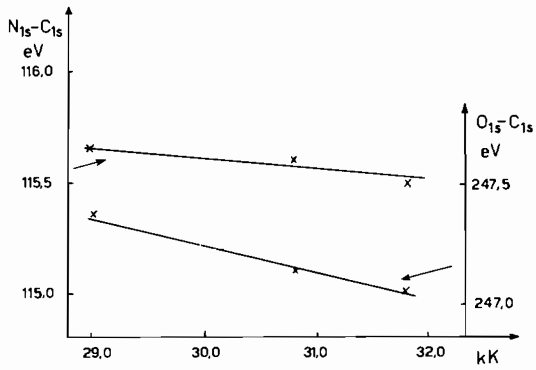

Figure 6. The N 1s and O 1s electron binding energies (referred to C 1s) of the copper complexes plotted as a function of the frequencies of electron excitation bands.

electron density on the nitrogen donor atom, *i.e.* in the decrease of the electron binding energy, the correlation reflected by Figure 4 shows that with the increase of the conjugation of the chelate ring the electron density on the nitrogen atoms decreases. The larger slope of the line through the data for the nickel complexes can be attributed to the fact that in the nickel complexes, with their greater tendency to back-coordination, the electrophilic substituents increase the conjugation of the chelate ring to a greater extent than in the analogous copper complexes.

Figures 5 and 6 show plots of the N 1s and O 1s electron binding energies as functions of the frequencies of individual electronic excitation absorption bands of the nickel and copper complexes. Approximately linear correlations can be observed in both systems. It must be emphasized however that correlation of ESCA data with electron absorption spectra may be less founded than those with IR spectra since former imply excited states of the unionized molecule which have no direct relation to ESCA data. Thus, further investigations are necessary on this field.

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