XPS Study of Low-Spin Cobalt(III) Mixed Ligand Complexes

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The low-spin transition metal complexes of great equilibrium stability are in general kinetically inert. Thus their stability and the covalency of their metal donor atom bonds cannot be characterized by formation equilibrium constants or other thermodynamic data. Therefore, X-ray or neutron diffraction measurements, force constants obtained from vibrational spectra, Mössbauer, UVPS, XPS or other data describing the electron structure of the atoms involved in the coordination process are used.

For diffraction measurements of this purpose the sample to be examined must be prepared as a monocrystal; in the vibrational spectrum the assignment of the coordinative bond is made difficult by different deformation vibrations in the corresponding far infrared or Raman range; the number of Mössbauer nuclei is limited and for the evaluation of UVPS data quantum chemical calculations are necesary. Therefore, the XPS measurements [1–4] characterizing the central and donor atoms have an increasing importance in coordination chemistry. The electron binding energy values of the core electrons can be unambiguously assigned to the appropriate orbitals. Their changes give direct (but mainly qualitative) information about the changes in the electron density on atoms involved in the coordination.

In our present work the XPS electron binding energy (e.b.e.) values of low-spin cobalt(III) mixed ligand complexes of square-bipyramidal coordination sphere have been compared. The composition of the complexes is shown in Table I. The two axial coordination sites of the examined complexes are occupied by various monodentate nitrogen donor ligands (except complex I in which NO_3^-, and complexes VI–VIII in which NO_2^- is one of the axial ligands). On the four equatorial coordination sites are situated the donor atoms of chelate-forming ligands, in complex I sulphur atoms, in complexes II–V oxim-nitrogens and in complexes VI–XV carbonyl-oxygens.

TABLE I. The Investigated Cobalt(III) Mixed Ligand Complexes.

Number	Composition[a]
I.	$[Co(tsc)_2(NO_3)_2]NO_3$
II.	$H[Co(heptox)_2(N_3)_2]$
III.	$H[Co(dmg)_2(N_3)_2]$
IV.	$H[Co(benzyldiox)_2(N_3)_2]$
V.	$H[Co(niox)_2(N_3)_2]$
VI.	$[Co(acac)_2(NO_2)(benzylamine)]$
VII.	$[Co(acac)_2(NO_2)(p\text{-ethylaniline})]$
VIII.	$[Co(acac)_2(NO_2)(imidazole)]$
IX.	$[Co(ec)(\alpha\text{-naphtylamine})_2]BF_4$
X.	$[Co(ec)(\beta\text{-naphtylamine})_2]BF_4$
XI.	$[Co(ec)(benzylamine)_2]I$
XII.	$[Co(ec)(imidazole)_2]I$
XIII.	$[Co(ec)(m\text{-xylidine})_2]I$
XIV.	$[Co(ec)(p\text{-phenetidine})_2]I$
XV.	$[Co(ec)(m\text{-Cl-aniline})_2]I$

[a] tsc = thiosemicarbazide, heptox = cycloheptanedionedioxime, dmg = dimethylglyoxime, benzyldiox = benzyldioxime, niox = cyclohexanedione-dioxime, acac = acetylacetone and ec = ethylenediimino-bis(acetyl-acetone).

Experimental

The preparation of the complexes was carried out according to methods published earlier [5–7]. Their composition was checked by elemental analysis of cobalt, carbon, nitrogen and oxygen contents. The experimental analytical results were in good agreement with the calculated data, within the limits of experimental error.

The XPS measurements were performed on a Kratos XSAM 800 device with a Mg $K\alpha_{1,2}$ radiation source. The experimental electron binding energy values were corrected for the charging effect on the basis of the C 1s binding energy (285.0 eV) of the surface hydrocarbon. The reproducibility of the e.b.e. values was ±0.15 eV.

Results and Discussion

The experimental electron binding energy (e.b.e.) values are summarized in Table II. It can be seen that

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TABLE II. The XPS Electron Binding Energy Values of the Investigated Complexes and Free Ligands, eV.

Complexes	Co $2p_{3/2}$	Co 3p	N 1s	O 1s
I.	781.0	62.1	400.9 406.9[a]	532.5
II.	781.3	62.3	401.1	532.7
III.	781.3	62.3	400.9	532.5
IV.	781.2	62.4	401.1	532.8
V.	781.3	62.4	400.8	532.4
VI.	781.5	62.5	403.2[b] 399.9[c]	531.8
VII.	781.8	62.4	403.6[b] 400.3[c]	531.9
VIII.	781.7	62.5	403.5[b] 400.2[c]	531.9
IX.	781.8	62.4	399.5	531.8
X.	781.5	62.3	399.7	531.3
XI.	781.6	62.4	399.6	531.4
XII.	781.6	62.4	399.5	531.8
XIII.	782.0	62.8	399.4	532.2
XIV.	781.6	62.5	399.4	532.2
XV.	781.4	62.7	399.2	532.2
Free ligands				
oxim-N			399.9	
azide-N			398.4 404.9	
amine-N			398.3	
carbonyl-O				530.9
nitrite-O				530.2

[a] Nitrate-N 1s e.b.e. value.

[b] Nitrite-N 1s e.b.e. values.

[c] Amine-N 1s e.b.e. values.

the e.b.e. values of the cobalt(III) central atom are determined by the quality of the donor atoms of the equatorially situated chelate-forming ligands. Both the Co $2p_{3/2}$ and Co 3p e.b.e values increase in the $S < N < O$ order of these donor atoms. This corresponds to the decreasing order of the covalency of the cobalt donor atom bonds, which goes with a decrease in the electron density on cobalt in the above order reflected in the increase of the e.b.e values.

The e.b.e. values of cobalt have proved to be just as insensitive to the substituents situated on the equatorial ligands as to the quality of the axial ligands. In oxim complexes the substitution of dimethylglyoxim by cyclohexanedione-dioxim, cycloheptanedione-dioxim or benzyldioxim changes the e.b.e. values of cobalt only, within the limits of experimental error. Similarly, the linkage of two acetyl-acetone ligands through an ethylene diamine moiety to one ethylene-diiminobis(acetyl-acetone) (compare complexes VI–VIII with complexes IX–XV) or the exchange of various axial nitrogen donor bases in complexes IX–XV does not cause significant changes in the cobalt e.b.e. values. The coordination sphere and the nature of the donor atoms around cobalt remain unchanged.

The above phenomena suggest the idea that the position of the equatorial chelate-forming ligands (the distance between cobalt and the donor atom) is determined by the quality of the donor atom (S, N or O). The coordination of the axial monodentate ligands (*e.g.* its distance from cobalt) however can vary, depending on the equatorial part of the coordination sphere, determined by the chelate-forming ligands.

The XPS spectra of oxim complexes II–V show only the presence of one type of nitrogen. This indicates that the e.b.e values of the axial azide nitrogens are almost the same as that of the equatorial oxim nitrogens in the complexes. In the free ligands the N 1s e.b.e. values show significant differences. Sodium azide itself contains two types of nitrogen atoms, each differing in e.b.e. from oxim-nitrogens (See Table II). Coordination resulted in the equalization of the nitrogen atoms in the low-spin cobalt(III) complex. The most surprising phenomenon is the disappearance of the two N lines of the azide ligand, indicating that azide has to be coordinated by its middle nitrogen.

The interaction of equatorial and axial donor atoms due to their coordination is reflected by the O 1s and N 1s e.b.e. values of complexes IX–XV.

By the decrease of the O 1s e.b.e. values the N 1s e.b.e. values are increasing, which indicates that by the decrease in the covalency of the equatorial Co–O bonds the covalency of the axial Co–N bonds increases.

It is known that nitrite ions can be coordinated either as oxygen or as nitrogen donors. In the first case a nitrito-complex and in the second one a nitro-complex, are formed [8]. The two kinds of coordination can be distinguished on the basis of the infrared spectrum. The characteristics of the nitrito cobalt(III) complexes are the ONO stretching vibrations appearing at 1460 cm^{-1} and 1065 cm^{-1}, while those of the corresponding nitro-complexes are stretching vibrations at 1430 cm^{-1} and 1315 cm^{-1} and a deformation vibration at 825 cm^{-1} [8]. Therefore, the infrared study of complexes VI–VIII, each containing a nitrite ion as an axial ligand, has been made. The appearance of the stretching vibrations at 1460 cm^{-1} (symmetrical) and at 1065 cm^{-1} (asymmetrical) and the lack of IR bands characterizing nitrocomplexes indicates the presence of a nitrite ion coordinated on oxygen.

The O 1s XP lines of the complexes do not show the presence of oxygens of two different e.b.e. values, in spite of the significant difference in the O 1s e.b.e. values of the corresponding free ligands. This agrees with the above conclusion drawn from the infrared measurements. In the complex the electron structure of the axial nitrite-oxygen donor atom becomes similar to that of the equatorially-situated carbonyl oxygen donors under the influence of coordination. The same phenomenon is emphasized by the fact that the e.b.e. energies of the axial and equatorial nitrogen donor atoms are the same in spite of their different chemical nature in oxim complexes.

Conclusions

The XPS electron binding energy values of complexes containing a low-spin cobalt(III) central atom of closed spherical electronic shell indicate that – in spite of the different nature of the equatorial and axial donor atoms (oxim-N and azide-N or carbonyl-O and nitrito-O) – they take up such position in the complexes, which results in their similar net charges. It can be supposed that this tendency results in the coordination of nitrite through its oxygen in complexes VI–VIII, and probably in that of azide through its middle nitrogen in complexes II–V.

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