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XPS study of metal complexes with an unsymmetrical tetradentate Schiff base

Václav Haber*
Department of Inorganic Chemistry, Charles University, 128 40 Prague (Czechoslovakia)

and **Pavel Ptáček**
ESCA Centre, J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovakian Academy of Science 182 23 Prague (Czechoslovakia)

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Abstract

Complexes of several 3d transition metals (Mn(II)–Zn(II)) with 2-(2,5,8-triaza-1-octenyl)phenol (Hsaden), [Msaden]ClO_4, have been studied using X-ray photoelectron spectroscopy (XPS). The N 1s peak is asymmetric and is an envelope of two components. A weaker component at a lower binding energy (*BE*) is attributed to the azomethine nitrogen atom, the other one to the nitrogens in the two amino groups. The assignment is supported by spectra of diethylenetriamine complexes in which the N 1s peak is sharper and its *BE* value is similar to that of the second component. The N 1s electron BE increases from Mn to Cu, in accordance with the Irving–Williams series; planar [Nisaden]ClO_4 complex is the only exception.

Introduction

A large number of Schiff bases and their complexes have been studied for their interesting and important properties, e.g. their ability to reversibly bind oxygen [1], catalytic activity in hydrogenations of olefins [2] and transfer of an amino group [3], photochromic and thermochromic properties [4], complexing ability towards some toxic metals [5] etc.

However, only a few compounds of this type have been studied by XPS, namely the symmetric tetradentate Schiff bases, such as H_2salen, H_2salphen (H_2salen = bis(salicylidene)ethylenediamine, H_2salphen = bis(salicylidene)phenylenediamine) and related metal complexes [6–8]. The main results have been obtained by comparing the spectra of different ligands of this type among themselves and with spectra of complexes containing the same cation. The variation of the nitrogen and oxygen 1s electron *BE*s can be rationalized by considering the reduction of the electron density on the donor atoms after complexation. Protonation is accompanied by an even greater decrease in their electron density; consequently, the *BE*s increase in the order: non-complexed atom < complexed atom < protonated atom.

The comparison of 2p electron *BE*s of cations in a series of complexes with different ligands makes it possible to estimate the donor abilities of the ligands. However, the differences are rather small and may be affected by charging of samples during the measurement.

Most studies were restricted to a few metals, namely cobalt, nickel and copper, so that information on the role of the central atom is very limited. Our studies are aimed at bridging this gap. To avoid the problems connected with charging of the samples, we use ionic compounds containing perchlorate anion whose Cl 2p electron *BE* is used as an internal standard. The present paper describes the XPS spectra of a set of complexes [Msaden]ClO_4 [9], where M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II); Hsaden denotes an asymmetrical Schiff base. The spectra of amine complexes with the same metals, $[M(den)_2](ClO_4)_2$, are also presented for comparison.

Experimental

All the compounds were prepared from the free ligands and the appropriate perchlorates in water–methanol solution as described earlier [9]. To prevent oxidation, compounds containing Mn(II),

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*Author to whom correspondence should be addressed.

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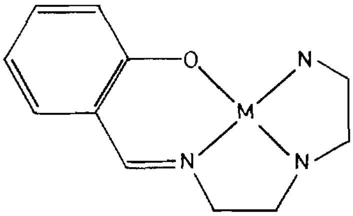
Fe(II) and Co(II) were prepared in a nitrogen atmosphere. The Schiff base complexes, which usually crystallize as hydrates, were dried *in vacuo* for several hours at 100 °C to obtain anhydrous samples [10]. The structures of several compounds were confirmed by X-ray diffraction studies [11–13]. The shape of the complex cation in all these compounds is as follows:



According to magnetic susceptibility measurements all the Mn(II), Fe(II) and Co(II) complexes are high spin ones [10]. The vibrational spectra indicate that perchlorate ions are not coordinated in the compounds studied.

The X-ray photoelectron spectra were measured on a VG 3 ESCA MkII spectrometer using Al Kα radiation ($h\nu = 1486.6$ eV). The samples were finely pulverized and spread on a gold holder as thin films. This arrangement cannot completely eliminate charging of the sample. For this reason, Cl 2p electron *BE* in perchlorate was used as an internal standard, $BE = 208.7$ eV [14]. This value of *BE* is virtually identical in different compounds, because of negligible tendency to complexation and protonation. Unfortunately, the presence of perchlorate ions made it impossible to determine O 1s electron *BE* of oxygen in the phenolic group.

The background pressure of residual gases during the measurements was lower than 10^{-6} Pa. The hemispherical electrostatic analyzator was operated in the retarding mode with a pass energy of 20 eV. The accuracy of the measured *BE* values is $+0.2$ eV. The peak areas for semiquantitative analyses were determined using a linear background. The relative empirical sensitivity factors published by Wagner [15] were used for calculation of the sample composition.

Results and discussion

The results of the XPS semiquantitative analyses of the surface layers are in agreement with the sample compositions. The only exceptions is the Cl:M ratio which decreases during irradiation of the sample. A new peak simultaneously appears with a Cl 2p electron *BE* about 10 eV smaller, indicating decay of perchlorate anions. No other change, either in positions or intensities of the other peaks, was observed during the measurements.

The 2p electron *BE*s of the metals and the values for the N 1s electron *BE*s are given in Table 1. Although the M 2p electron *BE* is closely related to the central atom charge and therefore to its valency, it is difficult to determine the valency only on the basis of this criterion, since the intervals for various oxidation states may overlap. Nevertheless, the values for M 2p electron *BE* in $[M(den)_2]^{2+}$ and $[Msaden]^+$ are approximately the same and support the oxidation number 2+. The similarity in the Ni $2p_{3/2}$ electron *BE*s for $[Ni(den)_2]^{2+}$ and $[Nisaden]^+$ is rather surprising in view of the different stereochemistry and electron arrangement: nevertheless the charges on the nickel atoms in the two complexes are similar.

The difference between M $2p_{3/2}$ and $2p_{1/2}$ electron *BE*s for $[Cosaden]ClO_4$ is substantially higher (15.7 eV) than for similar Schiff base complexes, e.g. [Cosalen] (14.9 eV) and [Cosalphen] (15.1 eV) [6]. This is in agreement [17, 18] with the high spin arrangement of the first complex and the low spin arrangement of the others. The same reason explains the different values for $[Nisaden]ClO_4$ (17.3 eV) and $[Ni(den)_2](ClO_4)_2$ (18.15 eV). The spin paired configuration of the central atom in $[Nisaden]ClO_4$ is also supported by the shape of the Ni 2p spectrum, especially because of the absence of satellite peaks. The difference between M $2p_{3/2}$ and $2p_{1/2}$ electron *BE*s for the amine complexes is somehow higher, see Table 1, which may reflect a weaker donor ability [19] of amines compared with $(saden)^-$.

As can be seen in Fig. 1, the N 1s electron *BE*s in amine complexes increase in the sequence: $Mn < Fe < Co < Ni < Cu > Zn$ which is exactly the same order as in the Irving–Williams [20] series of stability constants. These energies reflect the amount of electron density transferred from nitrogen atoms to a metal ion via coordination bonds and, as expected, correlate with the sum of the metal ionization potentials [21].

The N 1s electron spectra of the Schiff base complexes are asymmetric and their deconvolution yields two components with an intensity ratio 1:2. The more intense component with a higher *BE* value belongs to the amine nitrogens. The *BE* values are only slightly higher than those of the amine complexes. Substantially higher *BE* values for the nickel complex is in accordance with shorter coordination bonds in $[Nisaden]ClO_4$ (about 193 pm), in comparison with those in octahedral complexes, e.g. 212 pm in $[Ni(en)_3](NO_3)_2$ [22].

The weaker component of the N 1s peaks belongs to the imine nitrogen. The assignment is supported

TABLE 1. The binding energy values of the M $2p_{3/2}$ and N 1s electrons and the difference d = M $2p_{1/2}$ − M $2p_{3/2}$ in [Msaden]ClO$_4$ and [M(den)$_2$](ClO$_4$)$_2$ (eV)

Ligand	Core level	Metal					
		Mn	Fe	Co	Ni	Cu	Zn
Saden	M $2p_{3/2}$	641.8	712.1	781.8	856.2	935.5	1023.1
	d	11.7	13.6	15.7	17.4	20.0	23.1
	N 1s imine	399.6	399.5	399.7	399.9	399.7	399.4
	amine	400.5	400.55	400.7	401.15	400.85	400.5
den	M $2p_{3/2}$	642.1	709.7	781.8	855.95	935.6	1022.5
	d	12.4	14.1	15.7	18.15	20.2	n.m.
	N 1s	400.25	400.3	400.45	400.5	400.6	400.35

[a] n.m. = not measured. Complex with ethylenediamine [Cu(en)$_2$](ClO$_4$)$_2$ was measured instead of [Cu(den)$_2$](ClO$_4$)$_2$, because of different coordination bonds in the latter complex [16].

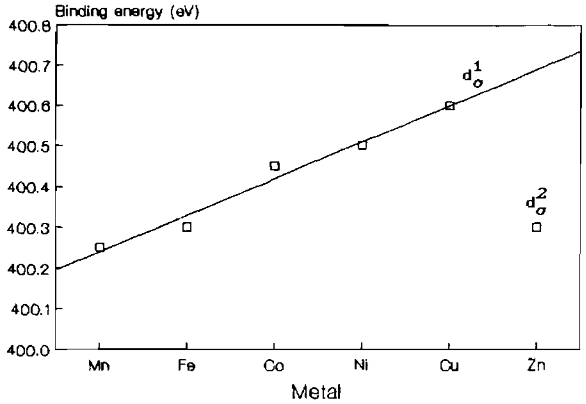


Fig. 1. The N 1s electron binding energies in [M(den)$_2$](ClO$_4$)$_2$ complexes.

not only by the intensity ratio, but also by comparison with N 1s electron *BE* in complexes with H$_2$salen and similar ligands. The values given in the literature are not directly comparable due to different charging of solids. We prefer therefore the difference between M $2p_{3/2}$ and N 1s electron *BE*s, as given in Table 2.

The dependence of the N 1s electron *BE* values on the central atoms is shown in Fig. 2. Only half-filled d_σ orbitals are suitable for the coordination bonds in the high spin complexes of Mn, Fe, Co and [Cusaden]ClO$_4$. The vacant $d_{x^2-y^2}$ orbital in the planar nickel complex allows electron density transfer to a much greater extent. The zinc complex with filled d orbitals exhibits the opposite behaviour, as seen from the lowest value of the corresponding *BE*.

The smaller *BE* values of the imine nitrogen are somewhat surprising, because M–N (imine) bonds are usually shorter than M–N (amine) ones; the differences are about 10 pm. There are two ways of accumulation of electron density on the imine nitrogen. The electronegativity of the sp^2 hybrid orbitals is higher than that of the sp^3 ones and thus imine nitrogen should withdraw more electron density from neighbouring atoms. Backdonation from metal to π^*(N=C) orbital can also be considered in transition metal complexes, even though this interaction is certainly weaker than in the case of N$_2$ or even NO complexes. The second mechanism is ineffective in zinc complexes, because of low lying 3d orbitals.

TABLE 2. The difference between M $2p_{3/2}$ and N 1s electron binding energies in given complexes (eV)

Metal	Complex			
	[Msalen]	[Msaden]ClO		[M(den)$_2$](ClO$_4$)$_2$
		imine	amine	
Co	381.0[a] low spin	382.1 high spin	381.1 high spin	381.35 high spin
Ni	456.1[b] planar	456.3 planar	455.05 planar	455.5 octahedral
Cu	535.6[b]	535.8	534.65	534.8[c]

[a] From ref. 6. [b] From ref. 7. [c] [Cu(en)$_2$](ClO$_4$)$_2$.

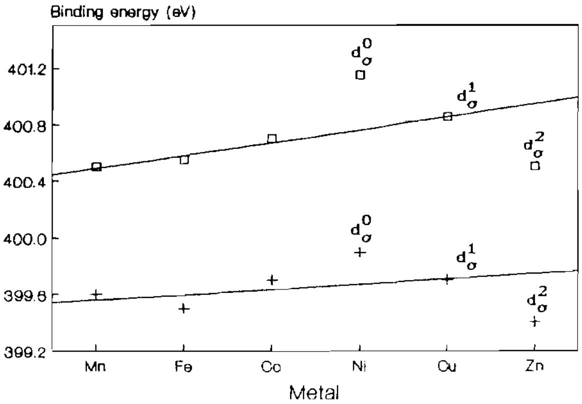


Fig. 2. The N 1s electron binding energies in [Msaden]ClO$_4$ complexes (+denotes values for imine nitrogen, □ values for amine one).

The differences between N 1s electron *BE*s for amine and imine nitrogen are similar in all the complexes, see Fig. 2 and, unfortunately, the changes are within experimental error. However, the slope of the line connecting the imine N 1s electron *BE* values, seems to be smaller than those for the amine nitrogens. This difference can only be probably explained by an increase in the π interaction from manganese to nickel complex, since the stronger $\sigma(L \rightarrow M)$ donation should have the opposite effect. Nevertheless, data with a better precision are required for making an unambiguous conclusion.

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