



## Case study showing how electric and magnetic properties can be used as first key-leads in identifying a ligand denticity and ultimately a complex compound's structural formula

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### **Abstract:**

The purpose of this work is to present a concrete example of using electric and magnetic investigations on a coordinative compound as first leads for determining which is the denticity of the ligand involved in it and therefore what is the structural formula of the respective complex. As a concrete example, the present paper presents a series of complex compounds formed by different divalent transitional metal ions with a Schiff base, (2Z/E)-2-(2-oxo-1,2-dihydro-3H-indol-3-ylidene)hydrazine-1-carbothioamide, which is able to change its denticity depending on the influence of the metal ion. Within this paper, we will present results of a research that has been done as to elucidate the ligand denticity and therefore the complex compound's structural formula, where the ligand is the above mentioned Schiff base and the four central metal ions belong to the *3d* series: Fe(II), Fe(III), Co(II), Co(III). From the first place, elemental analysis was performed. Molar conductivity, together with magnetic susceptibility, were used as key-clues in determining the denticity of the ligand in each case, which finally led to establishing the structural formulae of all complex compounds.

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**Keywords:** complex compounds, Schiff bases, molar conductivity, magnetic susceptibility, ligand denticity

## 1. INTRODUCTION

As it is important to understand the chemical structure of molecules in order to explain and even to predict their properties, it obviously becomes necessary to identify the actual manner of coordination of any ligand to the metal ion within a mononuclear complex compound. In order to achieve this, after carrying out the elemental analysis of such compounds, their structure is examined through a complex study [1-8], beginning with electrical and magnetic behavior investigation, followed by a detailed spectral analysis (involving mass spectroscopy, atomic emission/absorption spectroscopy, UV-Vis, IR and Raman spectroscopy, NMR-<sup>1</sup>H/NMR-<sup>13</sup>C spectroscopy and RES spectroscopy, X-ray diffraction on pure crystals) and ending with a computational modeling, in terms of quantum mechanics.

Nevertheless, there are some situations in which, after performing the elemental analysis, molar conductivity and magnetic susceptibility can be used as key-clues in obtaining valuable structural information.

In what follows, we aim to present such a case study, namely the research that has been done as to elucidate the ligand denticity and therefore the complex compound's structural formula, where the ligand is a particular Schiff base and the central metal ion (either divalent or trivalent) belongs to the *3d* series – more exactly: Fe(II), Fe(III), Co(II), Co(III).

## 2. MATERIALS AND METHODS

### 2.1. Synthesis

The ligand's synthesis, as well as an example of complex compound's synthesis were already presented elsewhere [9]. All reagents were of A.R. grade. The solutions of all complexes obtained were refluxed for five hours, then microcrystalline powders were isolated and washed with 95% ethanol.

### 2.2. Instruments

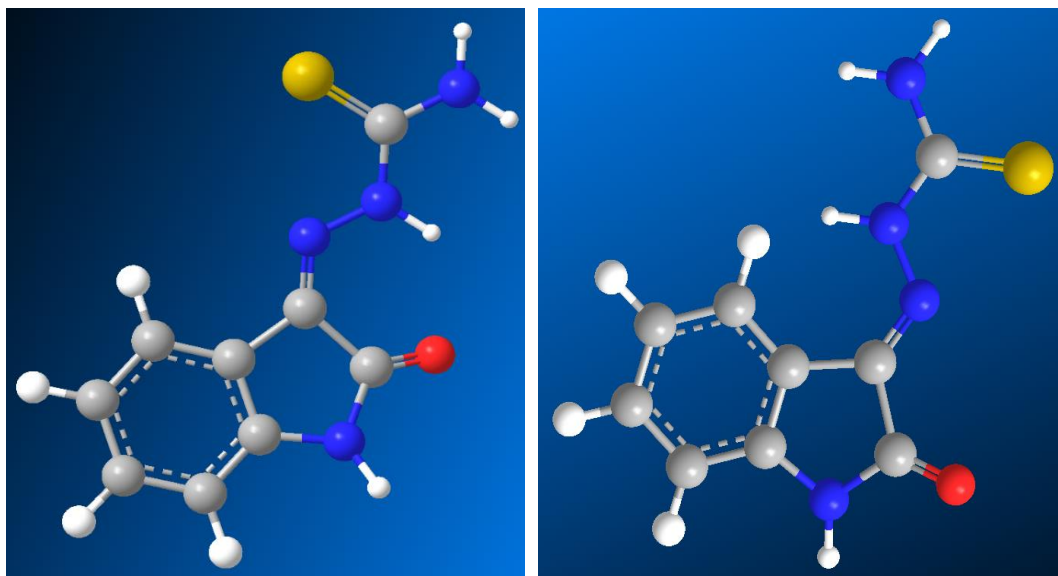
A Perkin Elmer 2380 analyzer has been used as to realize the elemental analysis.

An OK-102 conductivity-meter was chosen in order to perform the molar conductivity measurements in 10<sup>-3</sup> M DMF solutions (all at 25 °C), whereas a Gouy balance was used to execute the magnetic susceptibility measurements (also all at 25 °C).

### 3. RESULTS AND DISCUSSION

#### 3.1. Structure and fluctuant denticity of the ligand

The structure of the ligand (L) is shown below, in Figures 1 and 2, as its both possible geometric isomers, *zusammen* (Z) and *entgegen* (E).



**Figure 1.** Ligand's (L) *zusammen* (Z) isomer **Figure 2.** Ligand's (L) *entgegen* (E) isomer

As it can be easily seen, the geometric isomerism can lead to fluctuant denticity of this ligand, *i.e.*, it could act as either bidentate or tridentate ligand, depending on the central metallic ion. By coordination to metal ions, it might generate complex combinations which could differ as far as stereochemistry is concerned, so we have to explore the possibilities and decide in each case.

#### 3.2 Electric and magnetic properties – first key-leads in identifying ligand denticity

After performing the elemental analysis, we obtain the metal : ligand ratio in each situation. Then, electric and magnetic properties can be used as first key-leads in identifying the ligand denticity, by helping us to decide between the following five possible chemical equations [9]:

- (I)  $L + MCl_2 \rightarrow [MLCl_2]$  (four-coordinate complex in which L acts as a bidentate ligand);
- (II)  $2L + MCl_2 \rightarrow [ML_2]Cl_2$  (four-coordinate complex in which L acts as a bidentate ligand);
- (III)  $3L + MCl_2 \rightarrow [ML_3]Cl_2$  (six-coordinate complex in which L acts as a bidentate ligand).
- (IV)  $2L + MCl_2 \rightarrow [ML_2Cl_2]$  (six-coordinate complex in which L acts as a bidentate ligand);
- (V)  $2L + MCl_2 \rightarrow [ML_2]Cl_2$  (six-coordinate complex in which L acts as a tridentate ligand).

We shall now briefly present the way that we dealt with each case.

As the metal : ligand ratio for all situations was found to be 1 : 2, the first and third chemical equations were out of the question.

For the compounds formed with Fe(II) and Co(III) ions, electrolytic behavior has been observed (the molar conductance recorded for them being 131 and 127  $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ , respectively), whereas for the other two ions, Fe(III) and Co(II), the behavior was non-electrolytic (with recorded molar conductance of 10 and 20  $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ , respectively).

Thus, from the three remaining chemical equations, we can exclude the fourth for the compounds formed with Fe(II) and Co(III) and – at contrary – indicate the fourth for the compounds formed with Fe(III) and Co(II).

Furthermore, as the two complex ions – *i.e.*, the ones in which the central metal ions were Fe(II) and Co(III) – exhibit diamagnetic behavior, we were led to the last chemical equation for both of them, and as the two neutral complex compounds – *i.e.*, the ones in which the central metal ions were Fe(III) and Co(II) – exhibit paramagnetic behavior (with  $\mu_{\text{eff}} = 4.4$  and 4.2 BM, respectively), the previous statement was confirmed for these two.

#### 4. CONCLUSION

For two of the studied complex compounds – the ones formed with Fe(II) and Co(III), with electrolytic and diamagnetic behaviors, the chemical formula that we identified is  $[\text{ML}_2]\text{Cl}_2$  (six-coordinate complexes in which L acts as a tridentate ligand), whereas for the other two complex compounds – the ones formed with Fe(III) and Co(II), which exhibited non-electrolytic and paramagnetic behaviors, the chemical formula that we identified is  $[\text{ML}_2\text{Cl}_2]$  (six-coordinate complexes in which L acts as a bidentate ligand).

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