



STEREOCHEMISTRY OF VARIOUS COMPLEXES CONTAINING A BIDENTATE SCHIFF BASE THAT IS ABLE TO CHANGE DENTICITY

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The goal of this paper is to investigate the stereochemistry for the complexes formed by several transitional metal ions (namely Ni(II), Pd(II), Pt(II), Zn(II), Cd(II) and Hg(II)) with a Schiff base that can change denticity, consequently changing the structure of the respective chelate compound. The chemical compound 2-(2-oxoindolin-3-ylidene)-hydrazinecarbothioamide, which is obtained by condensation of 2,3-indolinedione with hydrazinecarbothioamide, is obviously able to act as a ligand; it is interesting to note that it might change denticity, *i. e.* it might be a bidentate or a tridentate ligand, as the condensation might lead either to the “Z” (zussamen) or to the “E” (entgegen) isomer. More specifically, interacting with a metal chloride MCl₂ – M standing for a transitional metal – it might theoretically generate either four-coordinate or six-coordinate complex compounds. By interpreting the experimental data (elemental analysis, spectral analysis, molecular conductance and magnetic moment measurements), one may draw a conclusion regarding the coordination geometry in each case.

INTRODUCTION

During the last years, the coordination chemistry has been considerably enriched due to the synthesis and characterization of a large number of six- and four-coordinate square-planar complexes of transitional metal ions.¹⁻³

As far as the ligands are concerned, the synthetic usefulness of 2,3-indolinedione has led to an extensive use in organic synthesis. The chemical compounds obtained from it by condensation with various aldehydes and ketones occupy a special place among organic ligands, since they contain various donor atoms and are able to change denticity depending on the starting reagents and their reaction conditions. In this context, experimental data on synthesis, physicochemical properties, composition and structure of these compounds are interesting both from scientific and practical points of view.

The present paper deals with such an organic compound, obtained by condensation of 2,3-indolinedione with hydrazinecarbothioamide,

namely 2-(2-oxoindolin-3-ylidene)-hydrazinecarbothioamide (denoted as “L” in the paper), which is coordinated to the d^8 and d^{10} transitional metal ions.

RESULTS

Elemental analysis for the complex formed with Ni(II) the M:L ratio appears to be 1:2, whereas for the complexes formed with Pd(II), Pt(II), Zn(II), Cd(II) and Hg(II) it was proved that the M:L ratio is 1:1 (Table 1).

The complexes obtained are microcrystalline powders, which exhibit melting points are higher than the one of the free ligand. They are all stable at room temperature both in solid state and in solution. The first complex compound (the one with (Ni(II)) is brown and it has $\mu_{\text{eff}} = 4.2$ BM, all the others being diamagnetic. Their molar electric conductivities showed that all the complexes are non-electrolytes, with molar conductivity values between 10 and 20 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ in 10^{-3} M DMF solutions at room temperature, except for the one

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of Ni(II), which exhibits a molar conductivity value of $129 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ in 10^{-3} M DMF solution (as presented in Table 1).

The results of the spectroscopic study will be given in the next section, so as to be interpreted in

order to draw a conclusion regarding the actual coordination manner and consequently the actual denticity of the ligand in each case.

Table 1

Analytical and physicochemical data of the investigated compounds

Compound	m.p (°C)	Molar conductance ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)	Analysis (%): calcd./found				
			C	H	N	Cl	M
L	232	12	48.33/ 49.28	3.97/ 3.54	25.78/ 24.83	-	-
[NiL ₂]Cl ₂	300	129	53.07/ 37.92	2.87/ 2.84	19.26/ 19.74	12.45/ 12.88	10.57/ 10.23
[PdL ₂]Cl ₂	275	14	28.07/ 28.32	1.97/ 2.04	14.26/ 14.74	18.45/ 18.88	17.57/ 17.23
[PtL ₂]Cl ₂	268	10	13.07/ 12.92	1.07/ 1.04	11.26/ 11.74	12.45/ 12.88	24.57/ 24.23
[ZnL ₂]Cl ₂	282	20	30.27/ 30.51	2.60/ 2.35	15.31/ 15.81	19.57/ 19.93	18.89/ 18.46
[CdL ₂]Cl ₂	270	18	22.49/ 22.41	1.51/ 1.76	12.19/ 11.80	15.53/ 15.04	23.38/ 23.02
[HgL ₂]Cl ₂	265	16	17.04/ 17.25	0.98/ 0.95	7.85/ 7.82	12.98/ 12.34	29.57/ 29.23

DISCUSSION

The reaction scheme corresponding to the formation of the free organic ligand which we deal with, by the condensation of the two reagents mentioned above, 2,3-indolinedione and hydrazinecarbothioamide, is presented in Fig. 1.

The chemical compound thus obtained, (denoted as “L” from now on) is obviously able to act as a ligand; it is interesting to note that it might change denticity, *i.e.* it might be a bidentate or a tridentate ligand, as the

condensation might lead either to the “Z” or to the “E” (entgegen) isomer (as shown in Fig. 2), so we have to find out which of its geometrical isomers appears in each of the investigated complex compounds.

Therefore, the ligand might theoretically generate either four-coordinate or six-coordinate complex compounds, by interacting with a metal chloride $\text{MCl}_2 - \text{M}$ standing for one of the metal ions mentioned above – following one of the five reaction schemes below:

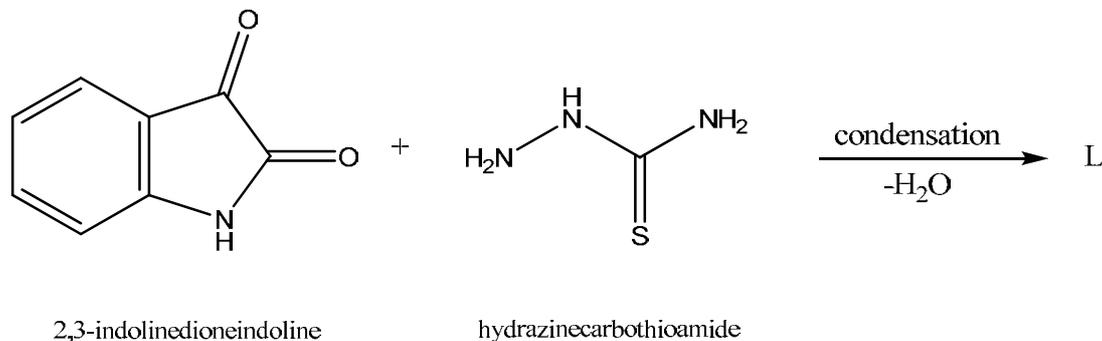
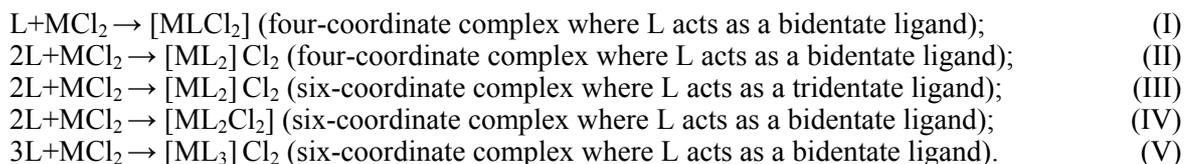


Fig. 1 – Reaction scheme of the ligand formation.

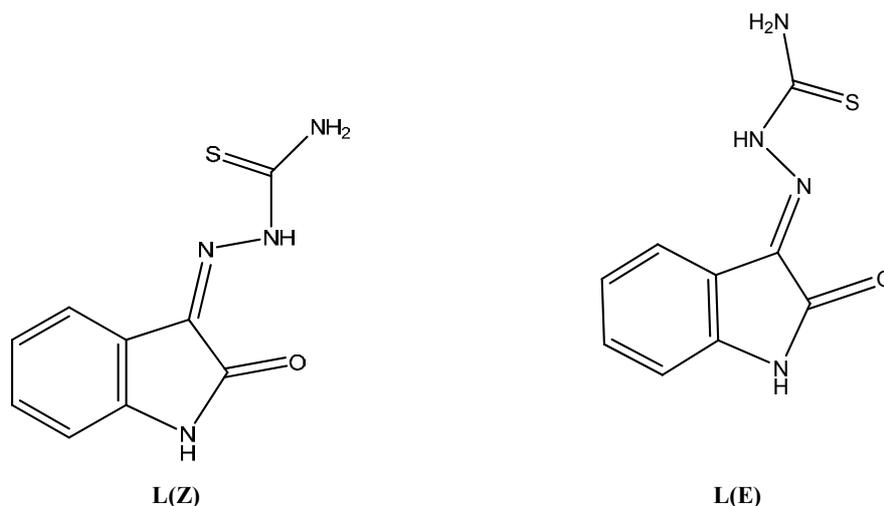


Fig. 2 – The two geometrical isomers of the ligand: “zusammen” L(Z) and “entgegen” L(E).

Which of these cases is the real one for each complex remains for us to establish, using all the experimental results obtained for these coordination compounds and the free ligand, *i. e.* by gathering the physicochemical data and the spectral properties.

The present study aims to show that all the mentioned metal ions will generate complexes according to the first reaction scheme (Fig. 3), except for Ni(II), which will act according to the third one (Fig. 4).

The non-electrolyte behaviour of the complex compounds formed by Pd(II), Pt(II), Zn(II), Cd(II) and Hg(II) indicates either case (I) or case (IV), whereas the electrolyte behaviour of the one Ni(II) indicates one of the remaining three cases. In addition, the M:L ratio helps us to decide which is the real case for each complex.

The spectral data support the assumption that we have already made regarding the structure of the complexes with Pd(II), Pt(II), Zn(II), Cd(II) and Hg(II) with this Schiff base, also clarifying the structure for the one with Ni(II), as it will be explained below.

As far as the IR spectra are concerned, one may note that, in the 3500-3000 cm^{-1} region of these

spectra, the bands attributable to the NH_2 and NH stretching vibrations are always present.

All bands generated by nitrogen-hydrogen stretching vibrations are located on top of broad absorption starting at about 3500 cm^{-1} and covering approximately 700 cm^{-1} range. This phenomenon, typical for hydrogen bonded systems, also strongly overlaps the $\nu_{\text{C-H}}$ vibrations expected between 3100 and 3000 cm^{-1} . At 1700 cm^{-1} , bands assigned to $\nu_{\text{C=O}}$ mode were observed at similar positions in the ligand and the complex spectra, suggesting the noninvolvement of carbonyl oxygen in complex formation, except for the Ni(II) one in which case the $\nu_{\text{C=O}}$ value undergoes a negative shift (44 cm^{-1}) upon coordination. The absorption bands $\nu_{\text{C=N}}$ are shifted to lower frequencies (51 and 62 cm^{-1} respectively) in the spectrum of the complexes, indicating that this group is involved in the coordination. It also can be seen that absorption bands of C=S stretching vibrations in the spectrum of coordination compounds are also shifted to lower frequencies (35 and 42 cm^{-1} respectively) upon coordination.

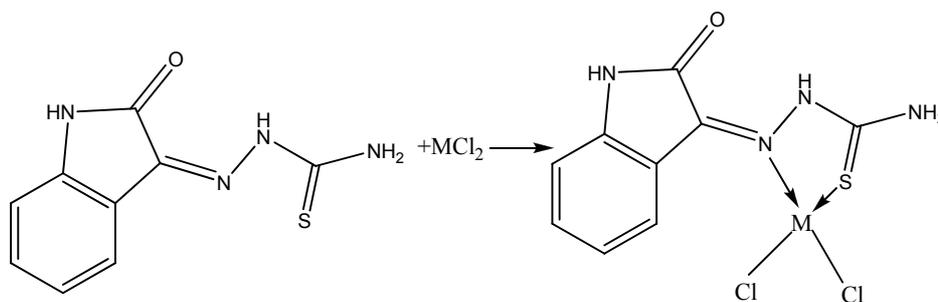


Fig. 3 – Reaction scheme for the formation of the four-coordinate complexes (M=Pd(II), Pt(II), Zn(II), Cd(II) and Hg(II)).

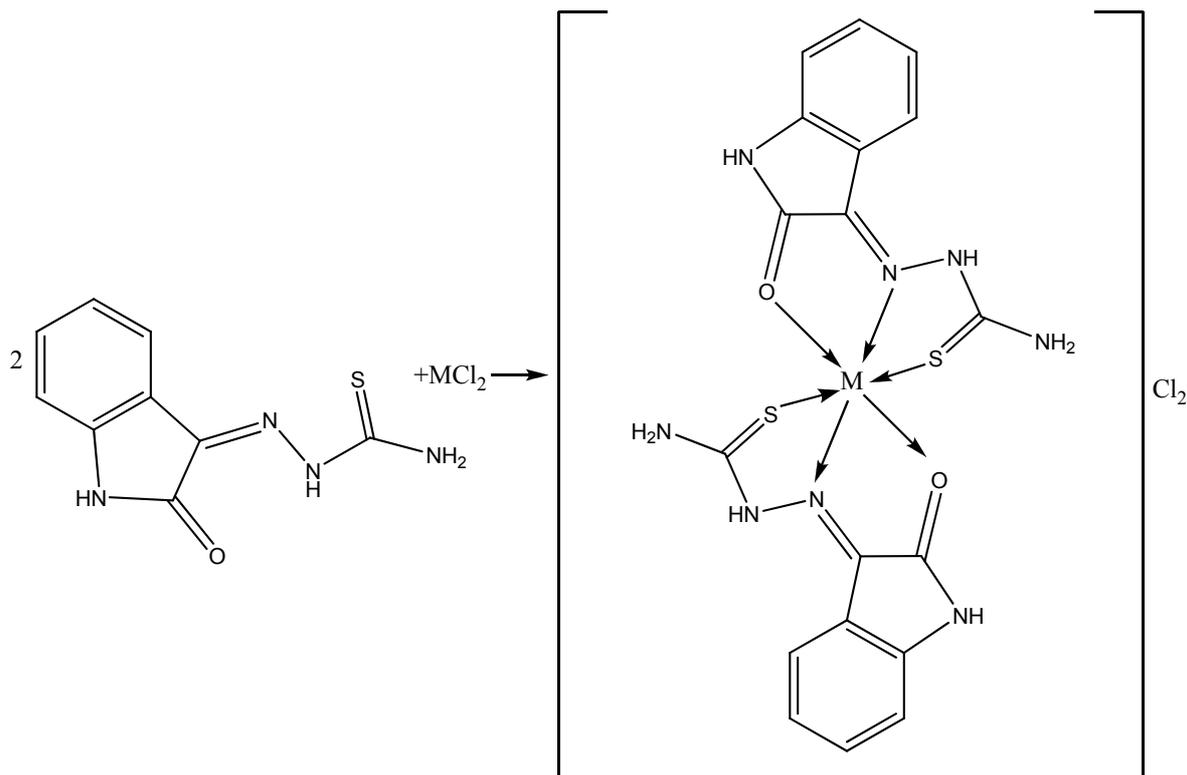


Fig. 4 – Reaction scheme for the formation of the six-coordinate complex (M=Ni(II)).

As all thiosemicarbazones, the ligand L might exhibit thione-thiol tautomerism, since it contains a thioamide functional group. An IR band at $2500\text{--}2600\text{ cm}^{-1}$ -NH-C=S occurs neither in the spectrum of the free ligand nor in the ones of the complexes, and this indicates the absence of S-H group in the ligand, showing that L acts as a thione.

This is supported by the ^1H NMR spectrum, which does not show any peak at 4 p.p.m., attributable to the S-H proton. The resonance at 11.2 p.p.m. in the spectrum of L was assigned to the N-NH proton and it also appears in the spectrum of the complexes. The deshielding of NH_2 protons upon complexation – that occurs for the last five complex compounds – can be related to the change from an E to a Z conformation of the ligand for all of them, while the E form is confirmed for the one with Ni(II). The fact that the two peaks in the spectra of the complexes keep almost the same separation between them (0.31 p.p.m.) as in the free ligand (0.35 p.p.m.) indicates no change in the bond order for the carbon-nitrogen bond when coordinating to the metal ion.

The electronic spectrum of the Ni(II) complex shows three distinct bands which are characteristic for hexa-coordinated Ni(II). The first band, that is found at 13.500 cm^{-1} , is due to the $^3\text{A}_{2g} \rightarrow ^3\text{T}_{2g}$ (F) electronic transition, whereas the second one, which is present in the electronic

spectrum at 18.700 cm^{-1} , is attributable to the $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}$ (F) transition, and the third one, appearing at 22.200 cm^{-1} , may be assigned to the $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}$ (P) transition.⁴

Since the value of the magnetic moment is 4.2 BM, a high-spin configuration of Ni(II) can be assumed. It indicates a pseudo-octahedral environment around the Ni(II) ion.

The electronic spectra of Pd(II) and Pt(II) complexes exhibit bands at $16.700/17.050\text{ cm}^{-1}$ and $19.500/20.100\text{ cm}^{-1}$, assigned to charge transfer and *d-d* transitions, respectively.⁵ The comparison of similar Pd(II) and Pt(II) compounds suggests a square-planar stereochemistry. The spectra of diamagnetic Zn(II), Cd(II) and Hg(II) complexes exhibit two bands assigned to charge transfer transitions. The assumption for these complexes is that they have a tetrahedral geometry.

EXPERIMENTAL

The preparation of the ligand, 2-(2-oxoindolin-3-ylidene)hydrazinecarbothioamide was carried out as follows: the two reagents, *i.e.* 2,3-indolinedione and hydrazinecarbothioamide, taken in a 1:1 molar ratio, were dissolved in aqueous ethanol in presence of a few drops of acetic acid. The mixture was refluxed over water bath for one hour. After cooling at room temperature, a yellow microcrystalline solid was separated, washed with ethanol, diethylether and dried over silica-gel.

In order to obtain the complex of Ni(II) with the ligand whose preparation was described above, to the hot ethanol solution of the ligand (40 cm³, 8·10⁻⁴ mol) a solution of nickel chloride (10 cm³, 4·10⁻⁴ mol) was added; the solution thus obtained was refluxed for five hours, then a microcrystalline powder was isolated and washed with 95% ethanol.

To obtain the other complex compounds with the same ligand, to its hot ethanol solution a solution of equimolar amount of metal chloride was added; the solution obtained was also refluxed for five hours, then microcrystalline powders were isolated and washed with 95% ethanol.

All the reagents used were of A.R. grade.

Instruments

The elemental analysis was performed on a Perkin Elmer 2380 analyzer. The molar conductivities were determined in DMF by using an OK-102 conductivity-meter at 25°C. The magnetic susceptibility measurements were performed on a Gouy balance, at 25°C as well. The ¹H-NMR data were obtained on a Varian Gemini 300 BB (at 300 MHz) using DMF as a solvent. The IR spectra were recorded in the 4000 – 400 cm⁻¹ range on a Perkin Elmer FTIR 1600 Hewlett Packard instrument, using anhydrous KBr pellets. The electronic spectra were performed in 10⁻³ M DMF solutions, with an Ocean Optics spectrophotometer.

CONCLUSION

Taking into account all these results, a conclusion can be drawn about the investigated complex compounds: the whole study is consistent with the proposed structures of the complexes,

namely [ML₂]Cl₂ if M stands for Ni(II) and [ML₂Cl₂] if M stands for Pd(II), Pt(II), Zn(II), Cd(II) and Hg(II).

The fact that the Ni(II) complex behaves as an electrolyte indicates that the chloride ions are present in the outer space of the compound, indicating that the ligand appears as the “E” isomer.

On the other hand, the fact that the other complexes behave as non-electrolytes indicates that chloride ions are contained in the inner space of the compound (they are involved in the coordination); therefore, the ligand appears as the “Z” isomer. The IR, ¹H NMR and electronic spectra support these assumptions.

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