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Comparison between the chemical behaviors of different complex compounds formed by divalent transition metal ions with a heterocyclic ligand, leading to different structures

Research article

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Abstract

The main purpose of the present paper is to identify the structures for the complexes formed by six divalent transitional metal ions (namely Ni(II), Pd(II), Pt(II), Zn(II), Cd(II) and Hg(II)) with the same heterocyclic ligand, that is able to change the coordination manner, consequently affecting the structure of the respective complex compound.

The heterocyclic ligand is 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* (zusammen) or to the *E* (entgegen) isomer.

More specifically, interacting with a metal chloride MCl_2 – 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 stereochemistry in each case.

Keywords: complex compounds, divalent transition metal ions, heterocyclic ligands

1. INTRODUCTION

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

The present paper deals with such an organic compound, obtained by the condensation of 2,3-indolinedione heterocycle with hydrazinecarbothioamide, namely 2-(2-oxoindolin-3-ylidene)-hydrazine-carbothioamide (denoted as L in the paper), which is coordinated to six divalent transitional metal ions: Ni(II), Pd(II), Pt(II), Zn(II), Cd(II) and Hg(II).

As far as this particular ligand is concerned, the synthetic usefulness of 2,3-indolinedione has led to an extensive use in organic synthesis [1-6].

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 the coordination manner 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.

2. MATERIALS AND METHODS

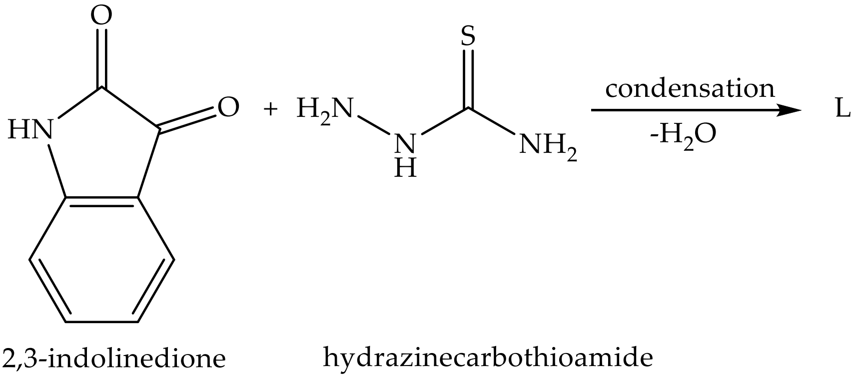
2.1. Synthesis of the free ligand

The synthesis of the free ligand, L, 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 a mixture ethanol-water in the presence of a few drops of acetic acid.

The mixture was refluxed in a water bath for one hour.

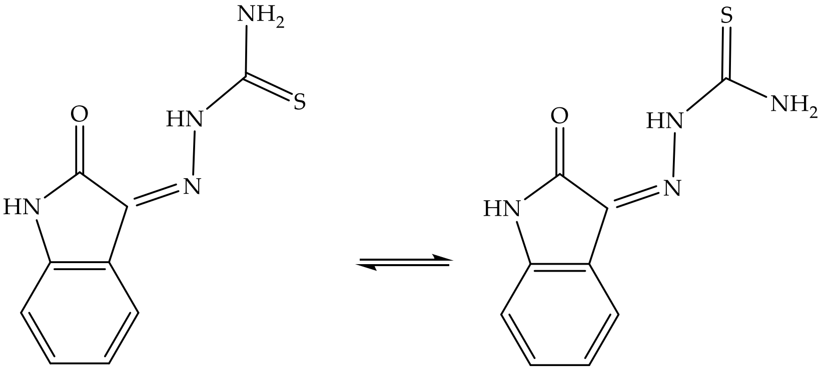
After cooling at room temperature, a yellow microcrystalline solid was separated, washed with ethanol, diethylether and dried over silica-gel.

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 below (Scheme 1).

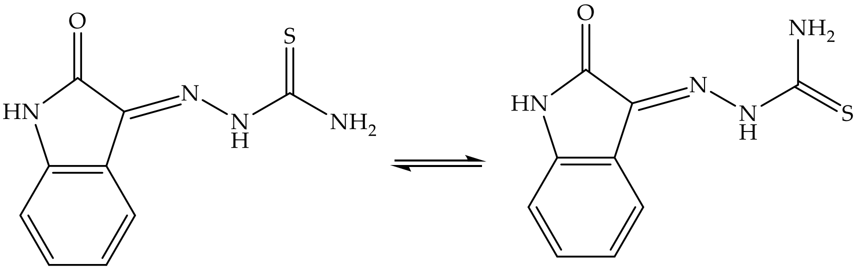


Scheme 1. *Synthesis of 2-(2-oxoindolin-3-ylidene)-hydrazinecarbothioamide (L)*

The structure of the ligand which resulted by condensation is shown in Schemes 2 and 3 for the two possible geometric isomers exhibit by it (for each of them, actually, the structure cannot be exactly described, as they both might undergo free rotation inside the thioamidic group):



Scheme 2. L = 2-(2-oxoindolin-3-ylidene)-hydrazinecarbothioamide – *Z* isomer undergoing free rotation inside the thioamidic group



Scheme 3. L = 2-(2-oxoindolin-3-ylidene)-hydrazinecarbothioamide – *E* isomer undergoing free rotation inside the thioamidic group

Moreover, like all the thiosemicarbazones, the ligand L might exhibit thione-thiol tautomerism, since it contains a thioamide functional group.

2.2. Synthesis of the complex compounds

In order to synthesize the complex of Ni(II) with the ligand whose preparation was described above, to the hot ethanol solution of the ligand (40 mL, $8 \cdot 10^{-4}$ mol) a solution of nickel chloride (10 mL, $4 \cdot 10^{-4}$ mol) was added; the solution thus obtained was refluxed for five hours, then a microcrystalline powder was isolated and washed with 95% ethanol.

In order to obtain all the other complex compounds with the same ligand, a solution of equimolar amount of metal chloride was added to its hot ethanolic solution; 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.

2.3. Instruments

Elemental analysis was performed on a Perkin Elmer 2380 analyzer.

The magnetic susceptibility measurements were performed on a Gouy balance, at 25°C.

The molar conductivities were determined in DMF by using an OK-102 conductivity-meter, at 25°C as well.

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 ^{1}H-NMR data were obtained on a Varian Gemini 300 BB (at 300 MHz) using DMF as a solvent.

The UV-Vis spectra were performed in 10^{-3} M DMF solutions, with an Ocean Optics spectrophotometer.

3. RESULTS

3.1. Research strategy

The structural formulas are going to be deducted from the studies on the elemental analysis and the behaviors exhibited by the ligand and the complex compounds formed by it with the chosen divalent transition metal ions [1-6], namely: Ni(II), Pd(II), Pt(II), Zn(II), Cd(II) and Hg(II).

Spectroscopic properties of the compounds will be corroborated with the magnetic and electric ones, as to be interpreted in order to draw a conclusion regarding the actual coordination manner for each of them.

3.2. Appearance and physical properties

The complexes obtained are all microcrystalline powders, which exhibit melting points higher than the one of the free ligand.

They are all stable at room temperature both in solid state and in solution.

3.3. Elemental analysis, magnetic and electric properties

Elemental analysis for the complex formed with Ni(II) shows that 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) the M:L ratio is proved to be 1:1 (as labeled in Table 1).

Table 1. Elemental analysis, magnetic and electric properties of the chemical compounds

Comp.	μ_{eff}* (BM)	Molar conductance* ($\Omega^{-1}cm^2mol^{-1}$)	Analysis (%): calcd./found				
			C	H	N	Cl	M
L	-	12	48.33/	3.97/	25.78/	-	-
			49.28	3.54	24.83		
$[NiL_2]Cl_2$	4.2	129	53.07/	2.87/	19.26/	12.45/	10.57/
			37.92	2.84	19.74	12.88	10.23
$[PdL_2Cl_2]$	0	14	28.07/	1.97/	14.26/	18.45/	17.57/
			28.32	2.04	14.74	18.88	17.23
$[PtL_2Cl_2]$	0	10	13.07/	1.07/	11.26/	12.45/	24.57/
			12.92	1.04	11.74	12.88	24.23
$[ZnL_2Cl_2]$	0	20	30.27/	2.60/	15.31/	19.57/	18.89/
			30.51	2.35	15.81	19.93	18.46
$[CdL_2Cl_2]$	0	18	22.49/	1.51/	12.19/	15.53/	23.38/
			22.41	1.76	11.80	15.04	23.02
$[HgL_2Cl_2]$	0	16	17.04/	0.98/	7.85/	12.98/	29.57/
			17.25	0.95	7.82	12.34	29.23

*10^{-3} M DMF solutions, at room temperature

3.4. Spectroscopic properties – IR spectra

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 bond stretching vibrations are located on top of the 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 ν_{C-H} vibrations expected between 3100 and 3000 cm^{-1}.

At 1700 cm^{-1}, bands assigned to $\nu_{C=O}$ mode were observed at similar positions in the spectra of all complexes except the Ni(II) one, suggesting the noninvolvement of carbonyl oxygen in all complex formation except this one.

The absorption bands $\nu_{C=N}$ are shifted to lower frequencies (51 and 62 cm^{-1} respectively) in the spectrum of the complexes, indicating that this group is always involved in the coordination.

It also can be seen that absorption bands of $\nu_{C=S}$ stretching vibrations in the spectrum of coordination compounds are also shifted to lower frequencies (35 and 42 cm^{-1} respectively) upon coordination, also indicating that this group is always involved in the coordination process.

Furthermore (as it was previously stated), like all the thiosemicarbazones, the ligand L might exhibit thione-thiol tautomerism, since it contains a thioamide functional group. However, an IR band at 2500-2600 cm^{-1} occurs neither in the spectrum of the free ligand nor in the ones of the complexes, indicating the absence of S-H group in the ligand, so that the ligand L acts as a thione.

3.5. Spectroscopic properties – ^{1}H NMR spectra

The previous statement is supported by the ^{1}H NMR spectra, which does not show any peak at 4 ppm, attributable to the S-H proton. The resonance at 11.2 ppm 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 attributed to the difference between the *E* and *Z* isomers, suggesting that the ligand appears as the *E* isomer within the first complex and as the *Z* isomer within all the other ones.

The fact that the two peaks in the spectra of the complexes keep the same separation between them (0.31 ppm), quite the same as in the free ligand (0.35 ppm) indicates no change in the bond order for the C-N bond when the ligand coordinates to the metal ion (it also may be due to some electron density changes caused by formation of the M-S bond within the S-C-NH_2 substructure).

3.6. Spectroscopic properties - UV-Vis spectra

All the complex compounds except for the Ni(II) one exhibit spectral properties within the UV-Vis range that are very similar to the ones presented by the literature for tetra-coordination.

More precisely, the electronic spectra of Pd(II) and Pt(II) complexes exhibit bands at 16.700/17.050 cm^{-1} and 19.500/20.100 cm^{-1}, assigned to charge transfer and *d-d* transitions, respectively, which suggests a square-planar stereochemistry, whereas the electronic spectra of Zn(II), Cd(II) and Hg(II) complexes exhibit two bands assigned to charge transfer transitions, the assumption for them being that they have a tetrahedral stereochemistry.

As far as the Ni(II) complex is concerned, it shows three distinct bands (at 13.500, 18.700 and 22.200 cm^{-1}), which are attributable to hexa-coordination.

4. DISCUSSION

4.1. Corroborating information gathered from chemical behaviors of the complexes

The chemical compound obtained by the condensation of the two reagents mentioned above, 2,3-indolinedione and hydrazinecarbothioamide, namely 2-(2-oxoindolin-3-ylidene)-hydrazinecarbothioamide (denoted as L within the paper) is obviously able to act as a ligand; it is interesting to note that it might change the coordination manner, *i. e.*, it might act either as a bidentate ligand or as a tridentate one, as the condensation might lead either to the *Z* or to the *E* isomer (as shown above), so it is essential to find out which of these appears in each of the investigated complex compounds, in order to establish the structures.

It can be seen that the ligand might theoretically generate either four-coordinate or six-coordinate complex compounds, interacting with a metal chloride, MCl_2 (M standing for one of the mentioned metal ions) following one of the five reaction schemes below:

(I) $L+MCl_2 \rightarrow [MLCl_2]$ (four-coordinate complex where L acts as a bidentate ligand);

(II) $2L+MCl_2 \rightarrow [ML_2]\,Cl_2$ (four-coordinate complex where L acts as a bidentate ligand);

(III) $2L+MCl_2 \rightarrow [ML_2]\,Cl_2$ (six-coordinate complex where L acts as a tridentate ligand);

(IV) $2L+MCl_2 \rightarrow [ML_2Cl_2]$ (six-coordinate complex where L acts as a bidentate ligand);

(V) $3L+MCl_2 \rightarrow [ML_3]\,Cl_2$ (six-coordinate complex where L acts as a bidentate ligand).

As it was previously stated, elemental analysis for the complex formed with Ni(II) shows that the M:L ratio is 1:2, whereas ~~the one~~ for the complexes formed with Pd(II), Pt(II), Zn(II), Cd(II) and Hg(II) is 1:1, showing that only in the first complex compound the ligand appears twice in the molecule, so the chemical formulas should be: $[ML_2]Cl_2$ if M stands for Ni(II) and $[ML_2Cl_2]$ if M(II) stands for Pd(II), Pt(II), Zn(II), Cd(II) and Hg(II).

The magnetic behaviors (the complex compound with Ni(II) being the only paramagnetic one, all the others being diamagnetic) suggest that, in the first case, a high-spin configuration of Ni(II) with two unpaired electrons can be assumed, which indicates a pseudo-octahedral environment around the metal ion, whereas, for all the other ones, hexa-coordination is not assumable.

The electric behaviours suggest that all the complexes appearing to be non-electrolytes, with molar conductivity values between 10 and 20 $\Omega^{-1}\,cm^2\,mol^{-1}$ in 10^{-3} M DMF solutions, except for the one with Ni(II), which exhibits a molar conductivity value of 129 $\Omega^{-1}\cdot cm^{2}\cdot mol^{-1}$ in 10^{-3} M DMF solution.

The non-electrolyte behavior 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 behavior of the one Ni(II) indicates one of the three remaining variants.

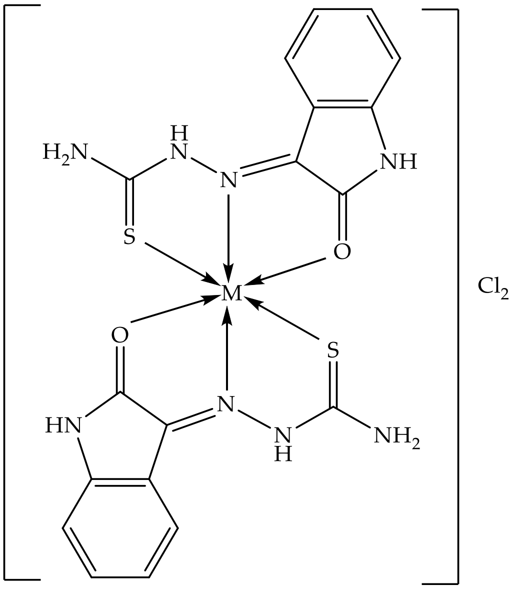
In addition, the M:L ratio helps us to decide which is the real case for each complex. So, the study shows that all the mentioned metal ions generate complexes with coordination number 4, except for Ni(II), which generates a complex with coordination number 6.

The spectroscopic behaviors (which were in detail presented above) reinforce the same assumption.

4.2. Proposed structural formulas

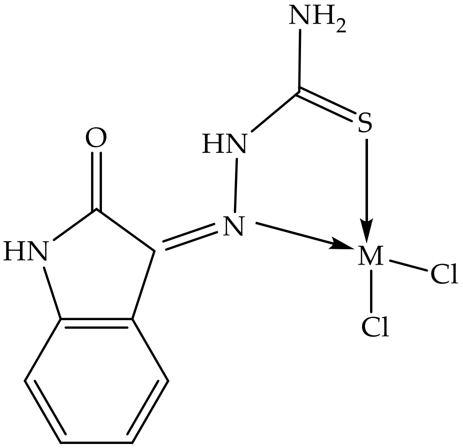
In accordance with all the above, the structural formulas should be proposed as shown below.

If M stands for Ni(II), the compound, which chemical formula is $[ML_2]Cl_2$, appears to be hexa-coordinated (exhibiting an octahedral stereochemistry).



$[ML_2]Cl_2$ (hexa-coordination); M = Ni(II)

If M stands for Pd(II), Pt(II), Zn(II), Cd(II) or Hg(II), the compound, which chemical formula is [ML_2Cl_2], appears to be tetra-coordinated (exhibiting a square-planar stereochemistry in the first two cases and a tetrahedral stereochemistry in the last three ones).



[ML_2Cl_2] (tetra-coordination); M = Pd(II), Pt(II), Zn(II), Cd(II), Hg(II)

5. 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 [ML_2]Cl_2 if M stands for Ni(II) and [ML_2Cl_2] if M(II) 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, showing 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 (being involved in the coordination); therefore, in all these cases, the ligand appears as the *Z* isomer.

All the data recorded from the IR, ^{1}H NMR and electronic spectra helped us to establish the coordination number and the corresponding stereochemistry.

Thus, it was shown that only one of the six investigated complex compounds has a coordination number of 6 (and therefore an octahedral stereochemistry), whereas all the other ones have a coordination number of 4 (two of them exhibiting a square-planar stereochemistry and the other three exhibiting a tetrahedral stereochemistry).

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