



Research on three complex compounds of divalent first-row transition metal ions having the Schiff base derived from sulfanilamide and N-acetylisatin as bidentate ligand

Research article

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Received: 15.09.2022 / Accepted: 20.10.2022 / Published: 20.12.2022

Abstract

The present paper aims to describe the research performed on three complex compounds formed by divalent first-row transition metal ions – namely M = Co(II), Ni(II) and Zn(II) (representing the complex kernels) with the Schiff base derived from the condensation of sulfanilamide with N-acetylisatin (which proved itself to be able to act as a bidentate ligand in all these cases).

This Schiff base is N-(1-acetyl-2-oxoindolin-3-ylidene)-4-aminobenzenesulfonamide, which appears twice in each complex, but is not the only ligand in the structure, as two water molecules are also part of the coordination sphere; there also is an ionization sphere, represented by two chloride ions whose role is to equilibrate the electrical charge of the complex kernel (all the ligands being charge-free) – the general molecular formula of the complexes being thus: $[ML_2(H_2O)_2]Cl_2$.

From the electrical point of view, we dealt with three complex compounds that all showed themselves to be electrolytes. As far as magnetic properties are concerned, two of them proved themselves to be paramagnetic, whereas the last one was found to be diamagnetic. After adding different spectral data, corroborating them with the prior information and with the elemental analysis – we have drawn the conclusion that the complexes are six-coordinated, so they all will tend to adopt an octahedral geometry.

Keywords: complexes, first-row transition metal ions, Schiff bases

1. INTRODUCTION

Along the last decades, Schiff bases have altogether been proved to be valuable resources for the coordination chemistry, as they can easily act as ligands.

Moreover, frequently, biologically active compounds, including sulfanilamide-derived and isatin-derived ones, demonstrate enhanced activity upon chelation with transitional metals.

Indeed, it was proved that, in particular, on one side, sulfanilamide-derived compounds (also known as sulfa-drugs) have been used [1, 2], as potential therapeutic agents with different purposes, correlated to their biological properties [1]. Their action mechanism is hindering the synthesis of folic acid in bacteria causing death of undesired cells. From the time of their discovery, sulfa-drugs attracted an outstanding attention as antiviral, antibacterial or antifungal agents.

On the other side, isatin-derived compounds are also known to be able to act as ligands [3 - 7] and to display a wide range of biological and pharmacological activities [3, 4].

Multipurpose medicinal importance of sulfanilamide-derivates and isatin-derivates gave us a plausible reason for combining these types of molecules, by synthesizing a Schiff base which derivatives both from sulfanilamide and isatin.

Consequently, the Schiff base that the current paper deals with is the one obtained by the condensation of sulfanilamide with N-acetylisatin, which seems to exhibit a remarkable biological activity (a study regarding this matter is in progress and will be described elsewhere, constituting the object of a future paper of ours).

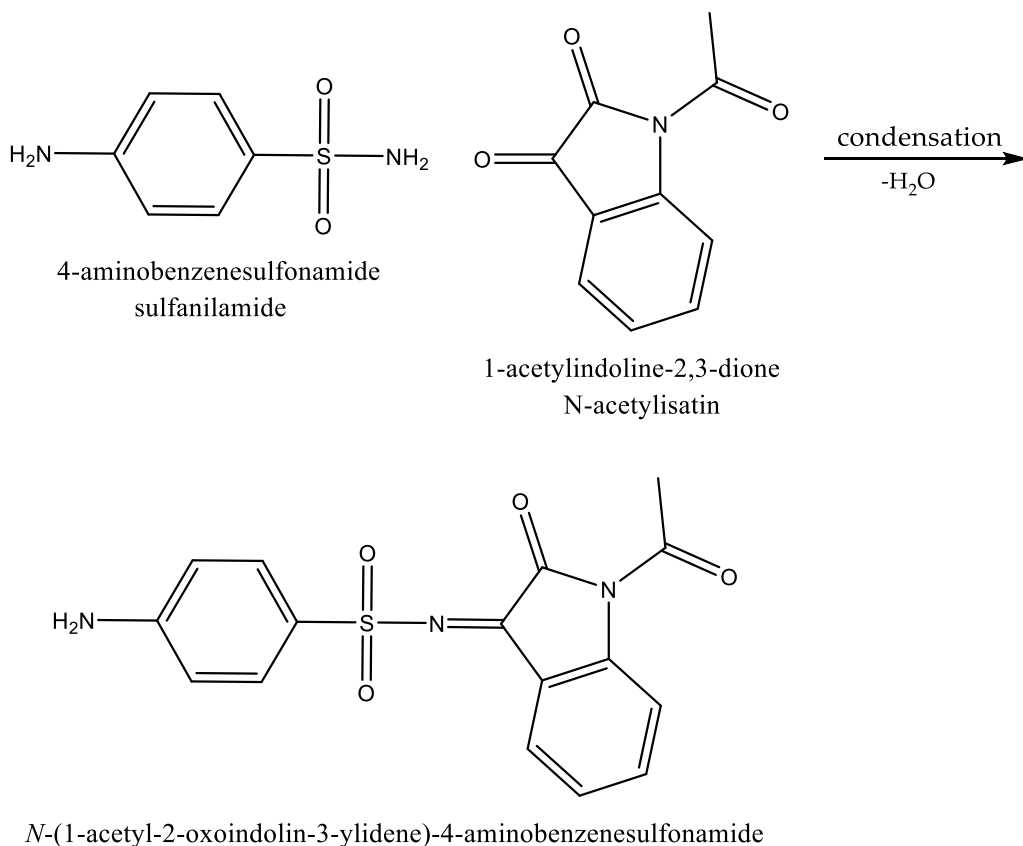
2. MATERIALS AND METHODS

2.1. Synthesis of the ligand

The Schiff base presented within the present paper is the one obtained by the condensation of sulfanilamide (4-aminobenzene-sulfonamide) with N-acetylisatin (1-acetylidoline-2,3-dione).

The IUPAC name of the resulted compound is N-(1-acetyl-2-oxoindolin-3-ylidene)-4-aminobenzene-sulfonamide and will be simply denoted by L in what follows.

The synthesis of the ligand, L (N-(1-acetyl-2-oxoindolin-3-ylidene)-4-aminobenzene-sulfonamide), was carried out by combining the two reagents, i.e. sulfanilamide (4-aminobenzene-sulfonamide) and N-acetylisatin (1-acetylintoline-2,3-dione), in a 1:1 molar ratio (following Scheme 1).

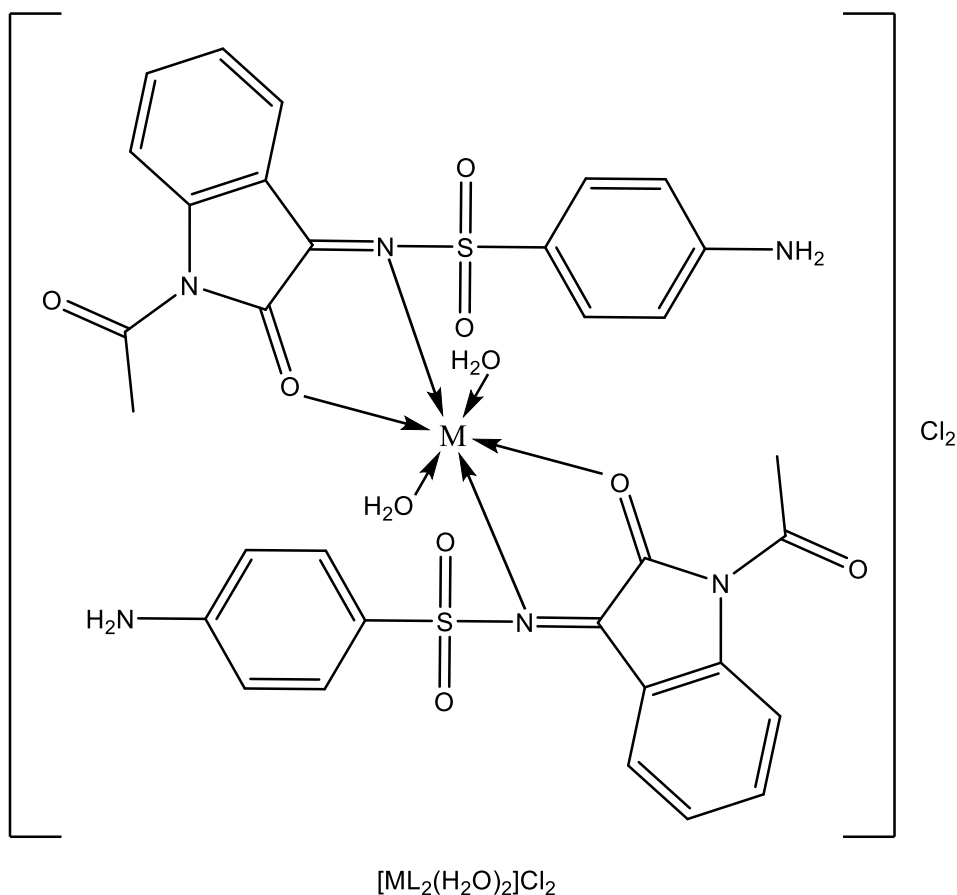


Scheme 1. Synthesis of the Schiff base acting as a bidentate ligand, denoted by L (N-(1-acetyl-2-oxoindolin-3-ylidene)-4-aminobenzene-sulfonamide)

The Schiff base was an air and moisture stable reddish-brown coloured microcrystalline compound (m.p. 200 °C), soluble in DMSO and DMF at room temperature and in ethanol upon heating.

2.2. Synthesis of the complex compounds

As previously stated, it acted as a bidentate ligand, readily reacting with Co(II), Ni(II) and Zn(II) chlorides, within ethanol solutions, to form the corresponding complex compounds (whose proposed structure is showed in Scheme 2).



Scheme 2. The structure proposed for the complexes, $[ML_2(H_2O)_2]Cl_2$ where M stands for: Co(II)/Ni(II)/Zn(II) and L denotes N-(1-acetyl-2-oxindolin-3-ylidene)-4-aminobenzene-sulfonamide

As to synthesize the complexes described above, to the hot ethanol solution of the ligand (40 mL, $8 \cdot 10^{-4}$ mol) a solution of cobalt/nickel/zinc 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. All the reagents used were of A.R. grade. The complex compounds thus obtained were all coloured microcrystalline compounds (m.p. 231/219/242 °C), soluble in DMSO and DMF at room temperature and in ethanol upon heating.

2.3. Instruments

A Perkin Elmer 2380 analyser was used to perform the elemental analysis. Molar conductivity was determined in DMF by using an OK-102 conductivity-meter, at room temperature. Magnetic susceptibility was measured by means of a Gouy balance, also at room temperature. IR analysis was carried out within the 4000 – 400 cm⁻¹ range on a Perkin Elmer FTIR 1600 Hewlett Packard spectrophotometer, with anhydrous KBr pellets, whereas UV-Vis analysis was performed on an Ocean Optics spectrophotometer, in 10⁻³ M DMF solutions. Finally, ¹H-NMR analysis was realised on a Varian Gemini 300 BB, by using DMF as a solvent, at 300 MHz.

3. RESULTS AND DISCUSSION

3.1. Elemental analysis

The first results obtained in the research were gathered in Table 1.

Table 1. Yield, molecular formula, molar mass and elemental analysis of complexes

Complex compound	Yield/%	Molar mass/g·mol ⁻¹	Molecular formula	Calculated/found, %			
				C	H	N	M
[CoL ₂ (H ₂ O) ₂]Cl ₂	71	852.58	CoC ₃₂ H ₃₀ N ₆ O ₁₀ S ₂ Cl ₂	45.08/ 45.03	3.55/ 3.57	9.86/ 9.89	6.91/ 6.86
[NiL ₂ (H ₂ O) ₂]Cl ₂	76	852.34	NiC ₃₂ H ₃₀ N ₆ O ₁₀ S ₂ Cl ₂	45.09/ 45.04	3.55/ 3.54	9.86/ 9.84	6.89/ 6.94
[ZnL ₂ (H ₂ O) ₂]Cl ₂	74	859.04	ZnC ₃₂ H ₃₀ N ₆ O ₁₀ S ₂ Cl ₂	44.74/ 44.73	3.52/ 3.47	9.78/ 9.82	7.61/ 7.64

Elemental analysis for all the complexes formed by the ligand L (N-(1-acetyl-2-oxoindolin-3-ylidene)-4-aminobenzene-sulfonamide) with

Ni(II)/Co(II)/Zn(II) shows that the M:L ratio is invariantly 1:2 (two ligand molecules are coordinated to the central divalent transition metal ion).

3.2. Magnetic and electrical properties

Molar conductivities and magnetic susceptibilities, measured at room temperature, are presented in Table 2.

Table 2. Molar conductivities and magnetic susceptibilities of complexes

Complex compound	$\Omega_M/\Omega^{-1}\text{cm}^2\text{mol}^{-1}$	$\mu_{\text{eff}}/\text{BM}$
$[\text{CoL}_2(\text{H}_2\text{O})_2]\text{Cl}_2$	142.2	4.6
$[\text{NiL}_2(\text{H}_2\text{O})_2]\text{Cl}_2$	137.4	3.5
$[\text{ZnL}_2(\text{H}_2\text{O})_2]\text{Cl}_2$	140.2	0

These results show that, from the electrical point of view, we dealt with three complex compounds that all showed themselves to be electrolytes. As far as magnetic susceptibilities are concerned, two of them exhibited paramagnetic properties, whereas the last one appeared to be diamagnetic.

3.3. IR spectral data

IR analysis shows that, on one side, one NH_2 band characteristic for sulfanilamide and, on the other side, one $\text{C}=\text{O}$ band characteristic for N-acetylisatin is affected as the Schiff base is formed.

A new band appeared at $1645\text{--}1648\text{ cm}^{-1}$, due to azomethine ($\text{C}=\text{N}$) linkage from this Schiff base. Other characteristic bands also appear as a consequence of the formation of the complex compounds.

A comparison between the IR spectra of the ligand and the ones of the three complexes enhances the idea that the ligands coordinate in a bidentate manner to the metals.

Azomethine vibrations of all metal complexes were shifted to lower frequency, indicating the involvement in the coordination of the nitrogen atom from the $\text{C}=\text{N}$ group.

New weaker bands appeared in the IR spectra of the metal complexes within the following wavenumber ranges: 3477–3485, 550–555 and 433–446 cm^{-1} , thus confirming the coordination of the ligand to the metal ion via N-acetylisatin-O and sulfanilamide-N atoms.

The results are summarized in Table 3.

Table 3. IR spectral data recorded for complexes

Complex compound	IR wavenumbers/ cm^{-1}
$[\text{CoL}_2(\text{H}_2\text{O})_2]\text{Cl}_2$	3477 (H ₂ O), 1712 (C=O), 1645 (C=N), 555 (M–N), 436 (M–O)
$[\text{NiL}_2(\text{H}_2\text{O})_2]\text{Cl}_2$	3485 (H ₂ O), 1715 (C=O), 1646 (C=N), 550 (M–N), 433 (M–O)
$[\text{ZnL}_2(\text{H}_2\text{O})_2]\text{Cl}_2$	3480 (H ₂ O), 1711 (C=O), 1648 (C=N), 551 (M–N), 435 (M–O)

3.4. UV-Vis spectral data

The electronic spectra of the Co(II) complex displayed three medium intensity transition bands at 7409, 17451 and 20589 cm^{-1} , attributable, respectively, to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{P})$ transitions in an octahedral environment. Also, a high intensity band was recorded, at 29321 cm^{-1} , which can be attributed to a M \rightarrow L charge transfer.

Similarly, the electronic spectra of the Ni(II) complex displayed three medium intensity transition bands at 10398, 15709 and 26457 cm^{-1} , due, respectively, to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{P})$ transitions in an octahedral environment. Again, a strong band is attributable to a M \rightarrow L charge transfer, which appears at 29878 cm^{-1} .

As the Zn(II) complex proved itself to be diamagnetic, it did not exhibit any $d-d$ transition, in its spectrum only a strong band of high intensity appearing at 28939 cm^{-1} , due to a M \rightarrow L charge transfer.

The results are summarized in Table 4.

Table 4. UV-Vis spectral data recorded for complexes

Complex compound	UV-Vis wavelengths/nm
$[\text{CoL}_2(\text{H}_2\text{O})_2]\text{Cl}_2$	7409, 17451, 20589, 29321
$[\text{NiL}_2(\text{H}_2\text{O})_2]\text{Cl}_2$	10398, 15709, 26457, 29878
$[\text{ZnL}_2(\text{H}_2\text{O})_2]\text{Cl}_2$	28939

3.5. ¹H NMR spectral data

The ¹H NMR spectrum of the ligand L (N-(1-acetyl-2-oxoindolin-3-ylidene)-4-aminobenzene-sulfonamide) was compared to that of its Zn(II) complex.

They both presented distinctive amino (NH₂) proton signals at 9.10 ppm as a singlet, which provided evidence for condensation of only one amino group of sulfanilamide.

Coordination of the amino protons was evident by downfield shifting of all proton signals of Zn(II) complex, which was attributed to the attraction of electronic density by the central metal ion.

All the other protons underwent downfield shifts by 0.5–1.1 ppm, due to the increased conjugation upon coordination with Zn(II).

The discussion for the other two complex compounds was carried out in a similar manner.

4. CONCLUSION

Being known that Co(II), Ni(II) and Zn(II) can adopt either an octahedral or a tetrahedral geometry, depending on the type of the ligand, the gathering of all spectral data (IR, UV-Vis and ¹H NMR) and also data regarding magnetic and electrical properties led us to the conclusion that, for all the investigated complex compounds formed by the Schiff base derived from the condensation of sulfanilamide with N-acetylisatin, whose IUPAC name is N-(1-acetyl-2-oxoindolin-3-ylidene)-4-aminobenzenesulfonamide (which proved itself to be able to act as a bidentate ligand), by coordination to divalent first-row transition metal ions – namely M = Co(II), Ni(II) and Zn(II) (representing the complex kernels) – shows that the M:L ratio is invariantly 1:2 (two ligand molecules being coordinated to the central divalent transition metal ion), but L is not the only ligand in the structure, as two water molecules are also part of the coordination sphere; there also is an ionization sphere, represented by two chloride ions whose role is to equilibrate the electrical charge of the complex kernel (all the ligands being charge-free).

Thus, the general molecular formula of the complexes is: [ZnL₂(H₂O)₂]Cl₂.

Therefore, the coordination number is six and the corresponding geometry is the octahedral one.

As formerly stated, a study about the biological activity of the ligand N-(1-acetyl-2-oxoindolin-3-yliden)-4-amino-benzenesulfonamide and its complexes formed with Co(II), Ni(II) and Zn(II) is in progress and will be further reported.

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