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SYNTHESIS, CHARACTERIZATION AND ANTIBACTERIAL STUDIES OF SOME METAL COMPLEXES WITH THE SCHIFF BASE OF A HETEROCYCLIC ALDEHYDE

Aurora Reiss[1*], Theodor Căproiu[2] and Nicolae Stănică[3]

[1]University of Craiova, Faculty of Chemistry, 107I Calea Bucuresti , Romania
[2]Institute of Organic Chemistry, 202B Spl. Independentei, 77208, Bucharest, Romania
[3]Institute of Physical Chemistry, 202 Spl. Independentei, 77208 Bucharest, Romania

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ABSTRACT. Metal complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with a new Schiff base derived from 3-aminodibenzofuran and 2-furancarboxaldehyde are reported. The complexes have been characterized using chemical analysis, spectroscopic methods (IR, UV-vis, ^{1}H NMR and ESR), conductometric and magnetic data. According to these data, we propose an octahedral geometry for Co(II), Ni(II) and Cu(II) complexes and a tetrahedral geometry for Zn(II), Cd(II) and Hg(II) complexes. Antibacterial activity of the ligand and its complexes were studied against selected bacteria: Escherichia coli, Staphylococcus aureus and Pseudomonas aeruginosa. It has been found that all the complexes are antimicrobially active and show higher activity than the free ligand.

KEY WORDS: Schiff base, Metal complexes, Antibacterial activity

INTRODUCTION

Schiff base complexes have remained an important and popular area of research due to their simple synthesis, versatility and diverse range of applications [1]. Many potent antibacterial and antifungal Schiff base compounds were reported [2-6].

In previous communications, we have reported complexes with a Schiff base derived from 3-aminodibenzofuran and different aldehydes (salicylaldehyde or pyridine aldehyde) [7-11]. In continuation of our work, we present here the synthesis and characterization of the complexes obtained by the reaction of the Schiff base derived from the condensation of 3-aminodibenzofuran with 2-furancarboxaldehyde, with Co(II), Ni(II), Cu(II), Zn(II) Cd(II) and Hg(II). The structure of the new Schiff base and the atom numbering scheme are given in Figure 1.

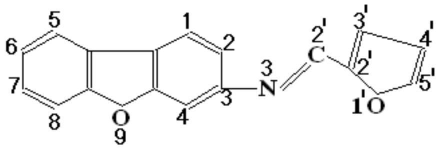

Figure 1. Structure of Schiff base and the atom numbering scheme.

The new Schiff base and its complexes were tested for antibacterial activity against pathogenic bacterial species: *Escherichia coli*, *Staphylococcus aureus* and *Pseudomonas aeruginosa*.

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*Corresponding author. E-mail: reissaurora@yahoo.com

EXPERIMENTAL

Reagents

$CoCl_2{\cdot}6H_2O$ (Merck Germany, analytically pure, a. p.), $NiCl_2{\cdot}6H_2O$ (Merck Germany, a. p.) $CuCl_2{\cdot}2H_2O$ (BDH England, a. p.), $ZnCl_2$ (Aldrich Germany, a.p.), $CdCl_2$ (Aldrich Germany, a. p.), $HgCl_2$ (Merck Germany, a. p.) and 2-furan carboxaldehyde (Merck Germany, 98 %).

Instruments

The IR spectra were recorded on a Perkin Elmer 157 (USA) instrument in anhydrous KBr pellets in the range 400-4000 cm^{-1}. A Unicam UV2-300 (Germany) spectrometer was used to obtain electronic spectra in DMF solutions. The molar conductivities were determined using an OK-102 (Hungary) conductivity meter. The magnetic susceptibility measurement was made on a Faraday balance (Romania) at room temperature. EPR spectra were registered in powder form at room temperature using an Art-5-IFA Bucharest (Romania) spectrometer that operates in the X band, the modulation of the magnetic field being 100 kHz. Mn^{2+} was used as an internal standard. Metal contents were measured by standard methods [12]. C, H and N were analysed using a M.L.W. microelementary CHN analyser (U.K.). The ^1H NMR spectra were recorded on a Varian Gemini 300BB (USA) spectrometer.

Synthesis of Schiff base

Ethanolic solutions of 3-aminodibenzofuran and 2-furan carboxaldehyde in 1:1 molar ratio were mixed and refluxed over a water-bath for 3 hours. The resulting Schiff base that separated out on cooling the mixture was filtered, washed with ethanol and air-dried.

Synthesis of the complexes

The Schiff base dissolved in dioxane and the metal chloride in ethanol were mixed in 2:1 molar ratio and refluxed for 2-4 hours. The complexes that separated out on keeping the solution overnight were filtered, washed with ethanol, ether and then dried under reduced pressure.

RESULTS AND DISCUSSION

The complexes obtained are microcrystalline coloured powders whose melting points are higher then that of the free ligand. They are air-stable, insoluble in common organic solvents but soluble in dimethylformamide (DMF). Based on the elemental analysis data, the formulas ML_2Cl_2 are assigned for all the complexes. The molar electric conductivities showed that the complexes of Co(II), Ni(II) and Cu(II) are non-electrolytes with $\lambda_M = 10.1\text{-}19.7\ \Omega^{-1}cm^2mol^{-1}$ in 10^{-3} M DMF solutions at room temperature, while the complexes of Zn(II), Cd(II) and Hg(II) are electrolytes of 1:2 type with $\lambda_M = 126.9\text{-}139.7\ \Omega^{-1}cm^2mol^{-1}$ in 10^{-3} M DMF solutions at room temperature (Table 1).

Infrared spectra

The IR spectra of the Schiff base ligand (L) and its complexes are listed in Table 2. The IR spectra of the complexes are compared with those of the free ligand in order to determine the coordination sites that may be involved in coordination. Upon comparison it was found that the $\nu_{C=N}$ stretching vibration from the azomethine group is found in the Schiff base at 1635 cm^{-1}.

This band is shifted to lower (10-20 cm^{-1}) wavenumbers in the complexes, indicating the participation of the azomethine nitrogen in coordination [13]. A band due to the $\nu_{C\text{-}O\text{-}C}$ stretching vibration of the furan ring appeared at 1015 cm^{-1} for the Schiff base [14]. This band is shifted to 980-1020 cm^{-1} in the metal complexes, suggesting the involvement of the furan oxygen atom with the central metal ion.

The new bands at 540-525 and 435-425 cm^{-1} in the spectra of the metal complexes were assigned to $\nu_{M\text{-}O}$ and $\nu_{M\text{-}N}$ stretching vibrations [13-15].

Therefore, it is concluded that the Schiff base behaves as a neutral bidentate ligand in all the complexes and that the coordination takes place from the furan oxygen atom and the imino nitrogen atom of the azomethine group.

Table 1. Analytical and physical data of Schiff base and its complexes.

Compound	Colour/ (yield %)	M.p. (°C)	Calcd (found) %				λ_M^* ($\Omega^{1}\cdot cm^{2}\cdot mol^{-1}$)	μ_{eff} (BM)
			C	H	N	M		
Schiff base(L)	Yellow (80)	180	78.14 (78.09)	4.23 (4.20)	5.35 (5.30)	-	-	-
[CoL_2Cl_2]	Brown (80)	225	62.58 (62.55)	3.39 (3.30)	4.29 (4.27)	9.04 (9.00)	10.1	4.88
[NiL_2Cl_2]	Brown (75)	220	62.61 (62.58)	3.39 (3.35)	4.29 (4.20)	9.00 (8.89)	17.5	3.10
[CuL_2Cl_2]	Brown (75)	230	62.14 (62.10)	3.37 (3.35)	4.26 (4.21)	9.67 (9.65)	19.7	1.88
[ZnL_2]Cl_2	Yellow (78)	220	61.97 (61.97)	3.36 (3.35)	4.25 (4.20)	9.92 (9.90)	126.9	-
[CdL_2]Cl_2	Yellow (80)	210	57.84 (57.82)	3.14 (3.11)	3.96 (3.92)	15.92 (15.91)	133.2	-
[HgL_2]Cl_2	Yellow (68)	215	51.42 (51.40)	2.78 (2.76)	3.52 (3.51)	25.25 (25.23)	139.7	-

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

Table 2. IR data (4000-400 cm^{-1}) of Schiff base and its complexes.

Compound	$\nu_{C=N}$	$\nu_{C\text{-}O\text{-}C}$ (furan)	$\nu_{M\text{-}N}$	$\nu_{M\text{-}O}$
Schiff base (L)	1635	1015	-	-
[CoL_2Cl_2]	1625	1020	435	540
[NiL_2Cl_2]	1620	1020	425	535
[CuL_2Cl_2]	1620	1010	425	530
[ZnL_2]Cl_2	1615	980	430	525
[CdL_2]Cl_2	1625	1010	425	525
[HgL_2]Cl_2	1615	1020	435	540

Magnetic moment and UV-visible spectra

Electronic spectra and magnetic measurements were performed in order to obtain information about the geometry of the complexes.

The μ_{eff} values of Co(II), Ni(II) and Cu(II) complexes were found to be 4.88, 3.10 and 1.88 B.M., respectively, indicating an octahedral geometry around the metal ions [16, 17]. The Zn(II), Cd(II) and Hg(II) complexes are diamagnetic (Table 1).

The UV-visible spectrum of the ligand exhibits two bands at 36630 and 29673 cm^{-1}, which are assignable to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively. The electronic spectrum of Co(II) complex showed bands at 9570, 17700 and 21040 cm^{-1}, which are assignable to $^4T_{1g}(F) \rightarrow$

$^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions, respectively, that are characteristic of octahedral configuration [18]. The Ni(II) complex exhibited three spin-allowed transitions at 10776, 15700 and 25560 cm^{-1}, which are assignable to $^3A_{2g} \rightarrow {}^3T_{2g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions, respectively, that are consistent with an octahedral geometry [18]. The Cu(II) complex showed one broad band at 15800 cm^{-1} assignable to the $^2E_g \rightarrow {}^2T_{2g}$ transition that is a characteristic of an octahedral environment [18].

The electronic spectra of Zn(II), Cd(II) and Hg(II) complexes presented two peaks in the UV region due to L → L* transitions, only. As expected, the electronic spectra of these complexes do not furnish any useful information on their stereochemistry. However, on the basis of analytical, conductance and infrared spectral data, a tetrahedral geometry is proposed for the Zn(II), Cd(II) and Hg(II) complexes.

ESR and ^{1}H NMR spectra

The EPR spectrum of the Cu(II) complex shows $g_{II} > g_{\perp} > 2.0023$ and a G value within in the range 2.08 - 4.49. These data are consistent with a $d_{x^2-y^2}$ ground state in an octahedral geometry [19].

Evidence for the bonding mode of the ligand is provided also by the ^{1}H NMR spectra of the Schiff base and the diamagnetic Zn(II) complex which were recorded in $CDCl_3$. Upon examination the signals due to H-2 and H-4 protons (in *para* position of the nitrogen atom) from the dibenzofuranic cycle are found at 7.30 ppm and 7.48 ppm in the ^{1}H NMR spectrum of the ligand. These signals are shifted towards lower field in the Zn(II) complex (at 7.50 ppm and 7.68 ppm, respectively) because of the coordination of the nitrogen atom. The signal due to the H-5 proton of the furan ring is found at 8.31 ppm in the ^{1}H NMR spectrum of the ligand and is shifted to 7.77 ppm because the involvement of oxygen atom of furan ring on coordination to the metallic ion.

Structural interpretation

The structures of the complexes of the Schiff base derived from 3-aminodibenzofuran and 2-furancarboxaldehyde with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) were confirmed by the elemental analyses, IR, UV-vis, ^{1}H NMR, ESR, molar conductance and magnetic data. From the IR spectra it is concluded that the ligand behaves as a neutral bidentate ligand in all the complexes through the azomethine N and furan O. From the molar conductance data, it is found that Co(II), Ni(II), Cu(II) complexes are nonelectrolytes while Zn(II), Cd(II) and Hg(II) complexes are 1:2 electrolytes. The ^{1}H NMR spectra of the free Schiff base and the diamagnetic Zn(II) complex show the coordination of the ligand through the azomethine N and furan O. On the basis of the above observations and from the magnetic measurements, UV-vis and ESR data, the structures for the complexes may be proposed as follows: an octahedral geometry for Co(II), Ni(II), Cu(II) complexes and a tetrahedral geometry for Zn(II), Cd(II) and Hg(II) complexes. The metal complex structures are shown in Figure 2.

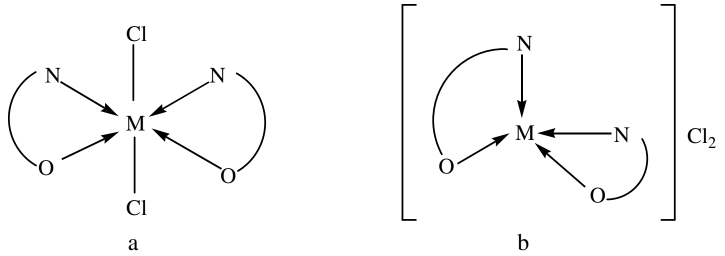

Figure 2. a) [ML_2Cl_2] where M = Co(II), Ni(II) and Cu(II); b) [ML_2]Cl_2 where M = Zn(II), Cd(II) and Hg(II).

Antibacterial studies

The new Schiff base and the complexes were tested for in vitro antibacterial activity against *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa* using the diffusion method [20, 21]. The diffusion method is simple and routinely used in hospital laboratories; it requires commercial disks, the medium used is Mueller-Hinton Agar with 2 % of glucose and the diameter of inhibition zone is visually read at 24 h after incubation at 37 ºC. The antibacterial activity was estimated on the basis of the size of the inhibition zone formed around the paper disks on the seeded agar plates. Streptomycin was used as a standard. The results are presented in Table 3.

Table 3. The antibacterial activity of the ligand and its complexes.

Compound*	E. coli	St. aureus	P. aeruginosa
Schiff base (L)	++	+	+
[CoL_2Cl_2]	++++	+++	+++
[NiL_2Cl_2]	+++	++	++
[CuL_2Cl_2]	+++	++	++
[ZnL_2]Cl_2	+++	++	++
[CdL_2]Cl_2	++	++	++
[HgL_2]Cl_2	++	++	++

*C = 5 mg/L. Inhibition zone diameter mm (% inhibition): +, 6-10 (27-45 %); ++, 10-14 (45-64 %); +++, 14-18 (64-82 %); ++++, 18-22 (82-100 %). Percent inhibition values are relative to the inhibition zone (22 mm) of the most active compound with 100 % inhibition.

The Schiff base and the complexes exhibited varying degrees of inhibitory effects on the growth of the tested bacterial species. The values reveal that the Schiff base became more effective when coordinated to the metal ions. The biological activity of the complexes follow the order: Co(II) > Ni(II) ≈ Cu(II) ≈ Zn(II) > Cd(II) ≈ Hg(II).

Furthermore, the data show that *E. coli* was inhibited to a greater degree by the Co(II) complex. In conclusion, the complexes prepared with the new Schiff base could reasonably be used for the treatment of some common diseases caused by *E. coli*.

CONCLUSION

Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes of the Schiff base derived from 3-aminodibenzofuran and 2-furancarboxaldehyde were prepared and characterized. The study reveals that: (i) Co(II), Ni(II), Cu(II) complexes are non-electrolytes and Zn(II), Cd(II) and Hg(II) complexes are 1:2 electrolytes; (ii) the Schiff base behaves as a neutral bidentate ligand and is coordinated to the central metal ion through the azomethine N and furan O; (iii) Co(II), Ni(II), Cu(II) complexes have octahedral geometry while Zn(II), Cd(II) and Hg(II) complexes have tetrahedral geometry; and (iv) the biological activity of all the complexes is higher that of the free Schiff base ligand and follows the order: Co(II) > Ni(II) ≈ Cu(II) ≈ Zn (II) > Cd(II) ≈ Hg(II). This means that metal chelation significantly affects the antimicrobial behaviour of the organic ligand.

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