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Synthesis, Characterization and Antibacterial Studies of Transition Metal Complexes with 2-Thiophenecarboxaldehyde Derived Schiff Base

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Transition metal complexes of Schiff base derived from the condensation of 3-aminodibenzofuran with 2-thiophencarboxaldehyde, are reported and characterized. 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 are proposed. Antibacterial activity of the ligand and its complexes were studied against selected bacteria.

Key Words: Synthesis, Transition metal complexes, 2-Thiophenecarboxaldehyde, Schiff base, Antibacterial activity.

INTRODUCTION

Schiff bases and their metal complexes 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 compounds were reported by condensation of aldehydes with heterocyclic compounds[2-4]. We have reported complexes with Schiff bases derived from 3-aminodibenzofuran and different aldehydes[5-9]. In continuation of our work, the synthesis and characterization of the complexes obtained by the reaction of the Schiff base derived from the condensation of 3-aminodibenzofuran (ADBF) with 2-thiophencarboxaldehyde (TFCA), with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) are reported.

EXPERIMENTAL

All chemicals used were of analytical purity: $CoCl_2\cdot6H_2O$ (Merck, p.a.), $NiCl_2\cdot6H_2O$ (Merck, p.a.) and $CuCl_2\cdot2H_2O$ (BDH England, p.a.), $ZnCl_2$ (Aldrich, p.a.), $CdCl_2$ (Aldrich, p.a.), $HgCl_2$ (Aldrich, p.a.), 2-thiophencarboxaldehyde (Merck, 98 %). The IR spectra were recorded on a Perkin-Elmer 157 instrument in anhydrous KBr pellets in the range 4000-400 cm^{-1}. A Unicam UV2-300 spectrometer was used to obtain electronic spectra in DMF solutions. The molar conductivities were determined by using OK-102 conductivity meter. The magnetic susceptibility measurement was made on a Faraday balance at room temperature. EPR spectrum was registered

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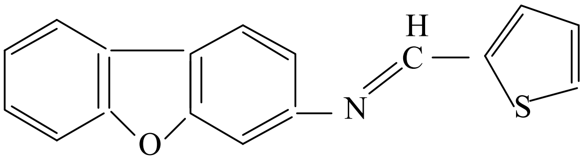
in powder at room temperature using an Art-5-IFA Bucharest spectrometer, that operates in X band, the modulation of magnetic field being 100 kHz and Mn^{2+} was used as an internal standard. Metal contents were estimated by standard methods[10]. C, H and N were analyzed using M.L.W. microelementary CHN analyzer. The ^1H NMR spectra were recorded on a Varian Gemini 300BB.

Synthesis of Schiff base: An ethanolic solution of 3-aminodibenzofuran (ADBF) (0.001 mol, 25 mL) was added to an ethanolic solution of 2-thiophencarboxaldehyde (TFCA) (0.001 mol, 25 mL) and refluxed over a water-bath for 4 h. After concentration of the solution, the precipitate was separated, filtered, washed with ethanol and dried over $CaCl_2$ in vacuum. The structure of the Schiff base is:



Synthesis of the complexes: A mixture of TFCA (0.002 mol, 50 mL) and ADBF (0.002 mol, 50 mL) in ethanol was added to an ethanolic solution of metal chlorides (0.001 mol, 50 mL) at pH 7-7.5. The mixture was refluxed for 6-8 h and then the excess of solvent was distilled. The precipitated compounds were filtered, washed with ethanol and dried over $CaCl_2$ in vacuum. The complexes obtained are microcrystalline coloured powders, whose melting points are higher then that of the free ligand (Table-1). They are air-stable, insoluble in common organic solvents but soluble in dimethyl formamide. Based on the elemental analysis data the formulas ML_2Cl_2 was suggested for all the complexes. The molar electric conductivities showed that the complexes of Co(II), Ni(II) and Cu(II) are non-electrolytes with λ_M = 10.1-21.7 Ω^{-1} cm^2 mol^{-1} while the complexes of Zn(II), Cd(II) and Hg(II) are electrolytes of 1:2 type with λ_M = 126.9-133.8 Ω^{-1} cm^2 mol^{-1} in 10^{-3} DMF solutions at room temperature.

RESULTS AND DISCUSSION

Infrared spectra of all the metal complexes are compared with those of the free ligand in order to determine the coordination sites that may get involved in coordination. Upon comparison it was found that the ν(C=N) stretching vibration from the azomethinic group is found in the Schiff base at 1675 cm^{-1}. This band is shifted to lower (30-50 cm^{-1}) wave numbers in the complexes indicating the participation of azomethine nitrogen in coordination[11]. The medium intensity band at 920 cm^{-1} in the free ligand, which is attributed to ν(C-S-C) (ring) stretching vibration[12] shifted to lower values (60-85 cm^{-1}) for all complexes, suggesting the involvement of the sulfur atom in the bonding with central metallic ion. The band assigned to the asymmetric ν(C-S) is similarly shifted and confirms the participation of sulfur atom in the complex formation[13]. The new bands at 435-425 cm^{-1} in the spectra of metal

TABLE-1
ANALYTICAL, PHYSICAL, IR AND ELECTRONIC SPECTRAL DATA OF SCHIFF BASE (L) AND ITS METAL COMPLEXES

Compd. / Colour / Yield (%)	m.p. (ºC) / μ_{eff} (BM)	ν(C=N) / ν(M-N)	ν(C-S-C) / ν(C-$S_{asym.}$)	Bands (cm^{-1})	Transitions	Geometry of the complexes
Schiff base Orange (80)	180 / –	1675	920/ 673	36630 29673	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	–
[CoL_2Cl_2] Brown (68)	235 / 4.88	1635/ 435	843/ 640	9570 17700 21040	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	Octahedral
[NiL_2Cl_2] Brown (73)	220 / 3.12	1625/ 425	841/ 654	10776 15700 25560	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$ $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ $^3A_{2g} \rightarrow {}^3T_{1g}(P)$	Octahedral
[CuL_2Cl_2] Black (65)	240 / 1.89	1630/ 425	859/ 650	15800	$^2E_g \rightarrow {}^2T_{2g}$	Octahedral
[ZnL_2]Cl_2 Yellow (72)	215 / Diamag.	1625/ 430	851/ 654	26000	L → L*	Tetrahedral
[CdL_2]Cl_2 Yellow (75)	210 / Diamag.	1645/ 425	860/ 635	24500	L → L*	Tetrahedral
[HgL_2]Cl_2 Yellow (77)	225 / Diamag.	1630/ 435	835/ 630	26500	L → L*	Tetrahedral

complexes were assigned to ν(M-N) stretching vibrations[11,14]. It is suggested that the Schiff base behaves as a neutral bidentate ligand in all the complexes and the coordination takes place from thiophene sulphur and imino nitrogen of azomethine link.

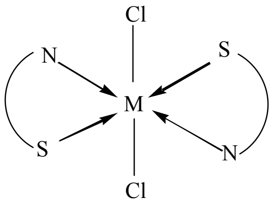
The μ_{eff} values of Co(II), Ni(II) and Cu(II) complexes are presented in Table-1, indicating an octahedral geometry around the metal ions[15,16]. The electronic spectral data of Co(II), Ni(II) and Cu(II) complexes (Table-1) and the transitions of each complex are characteristic to an octahedral configuration[17]. EPR spectrum of the Cu(II) complex shows $g_{II} > g_{\perp} > 2.0023$ and G value within in the range 2.08-4.49 which are consistent with $d_{x^2-y^2}$ ground state in an octahedral geometry[18].

Zn(II), Cd(II) and Hg(II) complexes are diamagnetic. The electronic spectra of Zn(II), Cd(II) and Hg(II) complexes present peaks in UV domain due to L → L* transitions, only. As expected the electronic spectra of these complexes do not furnish any relevant informations towards stereochemistry, but on the basis of analytical, conductance and infrared spectral data, a tetrahedral geometry is proposed for Zn(II), Cd(II) and Hg(II) complexes.

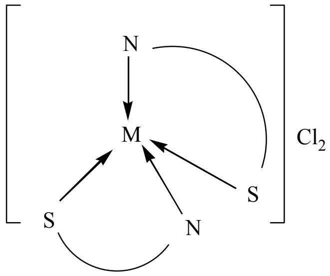
^{1}H NMR spectra of the Schiff base and the diamagnetic Zn(II) complex were recorded in the same solvent $CDCl_3$. Upon examination the signals due to H-2 and

H-4 protons (in *para* position of the nitrogen atom) from the dibenzofuranic cycle are found at δ 7.30 and 7.48 ppm in the ^{1}H NMR spectrum of the ligand. These signals are shifted towards lower field in complex at δ 7.50 and 7.68 ppm, respectively, because of the coordination of the nitrogen atom. The signal due to H-5 proton of the thiophene ring is found at δ 8.31 ppm in the ^{1}H NMR spectrum of the ligand and is shifted to δ 7.77 ppm because the involvement of sulphur atom of thiophene ring in coordination to the metallic ion.

On the basis of the above observations the structures for the complexes may be proposed as follows:



M = Co(II), Ni(II), Cu(II)



M = Zn(II), Cd(II), Hg(II)

The new Schiff base and the complexes were tested for the *in vitro* antibacterial activity using the diffusion method against *Escherichia coli, Staphylococcus aureus, Pseudomonas aeruginosa*[19,20]. The antibacterial activity was estimated on the basis of the size of inhibition zone formed around the paper disks on the seeded agar plates. The streptomycin was used as a standard. 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 pronounced when it is 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*.

REFERENCES

1. S. Yamada, *Coord. Chem. Rev.*, **192**, 537 (1999).
2. Z.H. Chohan, A. Rauf and C.T. Supuran, *Metal-Based Drugs*, **8**, 287 (2002).
3. G.G. Mohamed, M.M. Omar and A.M.M. Hindy, *Spectrochim. Acta*, **62A**, 1140 (2005).
4. A. Scozzafava, L. Menabuoni, F. Mincione, G. Mincione and C.T. Supuran, *Bioorg. Med. Chem. Lett.*, **11**, 575 (2001).
5. A. Kriza, A. Reiss, S. Florea and T. Caproiu, *J. Indian. Chem. Soc.*, **77**, 207 (2000).
6. A. Kriza, A. Reiss, S. Florea and A. Meghea, *Polish J. Chem.*, **74**, 585 (2000).
7. A. Reiss, A. Kriza, S. Florea, T. Caproiu and N. Stanica, *Rev. Roum. Chim.*, **50**, 445 (2005).
8. A. Reiss, S. Florea and J. Neamtu, Annals of the University of Craiova, The Chemistry Series, Vol. 32, p. 9 (2003).

9. A. Reiss, S. Florea, A. Ganescu and El. Calin, Annals of the University of Craiova, The Chemistry Series, Vol. 33, 21 (2004).
10. C. Gh. Macarovici, Analiza Chimica Cantitativa Anorganica, Ed. Academiei R.S.R., Bucuresti, p. 30 (1979).
11. M.M. Omar, G.G. Mohamed and A.M.M. Hindy, *J. Therm. Anal. Cal.*, **86**, 315 (2006).
12. S.C. Mohapatra and D.V.D. Rao, *J. Indian Chem. Soc.*, **57**, 262 (1980).
13. S. Burman, D.N. Sathyanarayana, *J. Inorg. Nucl. Chem.*, **43**, 1940 (1981).
14. B.K. Patel and S.C. Chaudhury, *J. Indian Chem. Soc.*, **65**, 661 (1988).
15. R.L. Orlin, *Transition Met. Chem.*, **1**, 3 (1976).
16. B.P. Figgins, Introduction to Ligand Fields John Wiley, New York, p. 56 (1976).
17. B.P. Lever, Inorganic Electronic Spectra, Elsevier, New York, p. 68 (1984).
18. B.J. Hathaway and D.E. Billing, *Coord. Chem. Rev.*, **5**, 143 (1970).
19. E. Duca, M. Duca, Microbiologie Medicala, Ed. Did. si Ped. Buc., p. 45 (1979).
20. V. Zotta, Chimie farmaceutica, Ed. Medicala, Bucuresti, p. 65 (1985).

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