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Der Pharma Chemica, 2012, 4(6):2385-2388

(<http://derpharmachemica.com/archive.html>)



ISSN 0975-413X
CODEN (USA): PCHHAX

Studies on the metal complexes of N'-(thiophen-2-yl-methylidene)- pyridine-4-carbohydrazide

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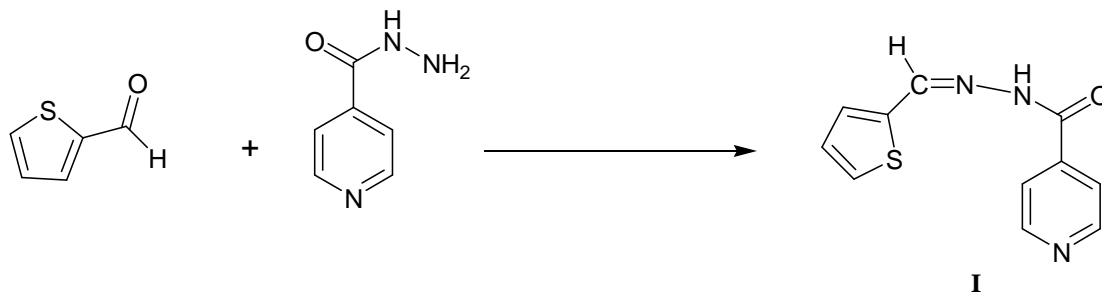
ABSTRACT

Fe(III), Ru(III), Co(II), Ni(II), Cu(II), Pd(II), Zn(II), Cd(II) and Hg(II) complexes of a hydrazone derived from thiophene-2-carbaldehyde and pyridine-4-carbohydrazide have been synthesized and structurally characterized by various physico-chemical data. The ligand acts towards the metal ions, as a neutral, bidentate one coordinating through azomethine nitrogen and thiophene sulphur. Fe, Ru, Co, Ni, and Cu Complexes are paramagnetic while the remaining are diamagnetic. Consolidating all the data obtained, the Fe, Ru, Co, Ni, and Cu complexes have been assigned an octahedral geometry, Pd complex, a square planar geometry and the Zn, Cd and Hg complexes, a tetrahedral geometry.

Key words: N'-(thiophen-2-yl-methylidene)-pyridine-4-carbohydrazide complexes, Synthesis, characterization.

INTRODUCTION

Hydrazones, simple as well as substituted ones, command for themselves, a special status amongst organic compounds because of their coordinating capability, analytical and industrial potentiality and biological activity. The coordination chemistry of these compounds has assumed, over the years, new dimensions owing to the fact that they exhibit varied ligational behaviour towards different metal ions and manifest novel structural features in the metal complexes [1-3]. In biological front, many of the hydrazones are reported to be physiologically active and find application in the treatment of several dreadful diseases [4]. The biological activity of these compounds has often been attributed to their ability to form complexes with the metals present in biosystem [5]. In many cases, the metal ion association exerts a synergistic effect on the activity of the free ligand [6]. In an effort to gain more insight into these aspects, coordination chemists have been evincing greater interest in the synthesis and structural characterization of metal complexes formed of these ligands, for these studies would throw light on the properties which the ligands are known for. Partaking the interest in this regard, the present paper describes the synthesis of Fe(III), Ru(III), Co(II), Ni(II), Cu(II), Pd(II), Zn(II), Cd(II) and Hg(II) Complexes of N'-(thiophen-2-yl-methylidene)-pyridine-4-carbohydrazide (TMPCH; I) derived from thiophene-2-carbaldehyde and pyridine-4-carbohydrazide and their structural characterization by elemental analysis, conductance, magnetic and infrared, electronic and ESR spectral data.

TMPCH:**MATERIALS AND METHODS**

All the chemicals used were of AR or BDH grade. The ligand TMPCH was prepared by refluxing an equimolar mixture of thiophene-2-carbaldehyde and pyridine-4-carbohydrazide in methanol in presence of a few drops of acetic acid for about 3 hrs. The solid that separated was filtered, washed with water and recrystallized from methanol. The colour, yield (%), m.p.(^oC) and C, H, N analysis (%) of TMPCH are respectively, light yellow, 86, 130 and 56.83, 3.66, 17.82.

The Fe(III), Ru(III), Co(II), Cu(II), Pd(II), and Hg(II) complexes of the ligand were prepared taking metal chlorides, and Ni(II), Zn(II) and Cd(II) complexes taking respective metal acetates. In the preparation metal complexes, the metal and the ligand were combined in 1:2 mole ratio in the case of Fe(III), Ru(III), and Cu(II) and in 1:1 ratio in the case of Co(II), Ni(II), Pd(II), Zn(II), Cd(II) and Hg(II) using required quantities of methanol so as to effect the solubility of the metal salts and ligand. The contents were refluxed on a hot water bath for 2-3 hrs and the solid that separated was filtered, washed with water, hot methanol and ether and was vacuum dried over fused CaCl₂.

The elemental analysis (C,H,N) for the ligand and the complexes were carried out at CDRI, Lucknow. Conductance measurements on the complexes were made in DMF at 10⁻³ M concentration on a Digisun digital conductivity meter. Gouy balance calibrated with Hg[Co(NCS)₄] was used to measure the magnetic susceptibility of metal complexes at room temperature. The IR spectra of the ligand and its metal complexes in KBr were recorded in the range 4000-450 cm⁻¹ using Perkin Elmer FT-IR spectrophotometer. The electronic spectra of the metal complexes were recorded on Perkin Elmer UV-Vis spectrophotometer. WIN-EPR (BRUKER) spectrophotometer operating in the frequency range 8.8-9.6 GHz was employed in recording the ESR spectrum of Cu(II) complex in DMF at LNT.

RESULTS AND DISCUSSION

All the complexes are coloured, stable at room temperature and are non-hygroscopic. The ligand and its metal complexes are mostly insoluble in water, very slightly soluble in hot methanol and fairly soluble in dimethylformamide. The analytical and physical data of the metal complexes are given in table-1.

The per cent values of the elements : carbon, hydrogen and nitrogen in the complexes have been calculated as per the composition given. It may be seen from the table that there is a fair agreement between the experimental and calculated values suggesting the composition as given. The molar conductance values indicate that the Fe(III), and Ru(III) complexes are 1:1 electrolytes while all others are non-electrolytes [7]. The magnetic studies reveal that the Fe(III), Ru(III), Co(II) and Cu(II) complexes are paramagnetic to the extent of respectively five, one, three and one unpaired electrons while others are diamagnetic.

The ligand exhibits a broad band at 3390 cm⁻¹ due to ν N-H which appears higher shifted in the spectra of its complexes. This indicates that the nitrogen of this group is not involved in coordination. A low intensity band that appears around 1660 cm⁻¹ in the ligand as well as its complexes has been assigned to ν C=O. The ν C=N (pyridine cyclic) band makes its presence at 1417 cm⁻¹ as a medium intensity band and this remains unshifted in the complexes. Another medium intensity band, the ligand shows at 1594 cm⁻¹ due to azomethine ν C=N has been found lower shifted by 15-30 cm⁻¹ in the complexes suggesting that the nitrogen of this group is coordinated to the metals. Further, the ligand shows up a sharp band at 788 cm⁻¹ due to ν C-S (thiophene cyclic) which undergoes a downward

shift by about 30 cm^{-1} in the complexes indicating the participation of the sulphur of this entity in bonding with the metals. Thus, the ligand acts towards the metals studied as a neutral, bidentate one coordinating through the nitrogen of azomethine group and sulphur of thiophene [8,9].

The electronic spectral data of the Ru(III), Co(II), Ni(II), Cu(II) and Pd(II) complexes along with the assignment are given here under.

Complex	Frequency (cm^{-1})	Assignment
Ru-TMPCH	16840	${}^2T_{2g} \rightarrow {}^4T_{1g}$
	18380	${}^2T_{2g} \rightarrow {}^4T_{2g}$
	22730	${}^2T_{2g} \rightarrow {}^2A_{2g}$
Co-TMPCH	15150	${}^4A_2(F) \rightarrow {}^4T_1(P)$
	16670	${}^1A_{1g}(D) \rightarrow {}^1A_{2g}(G)$
Ni-TMPCH	22730	${}^1A_{1g}(D) \rightarrow {}^1B_{1g}(G)$
	24510	${}^1A_{1g}(D) \rightarrow {}^1E_g(G)$
Cu-TMPCH	21200	${}^2B_{1g} \rightarrow {}^2E_g$
	14660	${}^1A_{1g} \rightarrow {}^1A_{2g}$
Pd-TMPCH	20000	${}^1A_{1g} \rightarrow {}^1B_{1g}$
	24690	${}^1A_{1g} \rightarrow {}^1E_g$

The transitions assigned are characteristic of octahedral geometry for Ru (III) (low spin) and Cu(II) complexes, tetrahedral for Co(II) complex and square planar for Ni(II) and Pd(II) complexes [10-14].

The Fe(III), Zn(II), Cd(II) and Hg(II) complexes reveal no d-d bands owing to spin forbidden nature in the former and to the filled d configuration in the latter three. On the basis of other data obtained for them, the Fe(III) complex has been assigned high spin octahedral geometry and the Zn(II), Cd(II), and Hg(II) complexes, tetrahedral geometry.

The ESR spectrum of Cu(II) complex is isotropic with no hyperfine splitting, the g value being 2.28. The isotropic nature of the spectrum is an additional evidence for octahedral symmetry of the complex.

Table-1: Analytical and physical data of metal complexes

Metal complex	Colour	Percent			Molar Conductance $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$	μ_{eff} B.M.
		C	H	N		
[Fe (C ₁₁ H ₉ N ₃ OS) ₂ Cl ₂]Cl	Brown	41.78(42.29)	2.82(2.90)	13.16(13.45)	66	5.70
[Ru (C ₁₁ H ₉ N ₃ OS) ₂ Cl ₂]Cl	Brown	39.07(39.44)	2.65(2.71)	12.18(12.54)	63	1.83
[Co (C ₁₁ H ₉ N ₃ OS) Cl ₂]	Dark Red	36.10(36.59)	2.46(2.51)	11.40(11.64)	12	4.42
[Ni (C ₁₁ H ₉ N ₃ OS)(OAc) ₂]	Light Green	43.68(44.15)	3.65(3.71)	10.16(10.30)	10	-
[Cu (C ₁₁ H ₉ N ₃ OS) ₂ Cl ₂]	Green	43.70(44.26)	2.98(3.04)	13.81(14.08)	12	1.83
[Pd (C ₁₁ H ₉ N ₃ OS)Cl ₂]	Light Green	31.56(32.33)	2.16(2.22)	10.00(10.28)	11	-
[Zn (C ₁₁ H ₉ N ₃ OS)(OAc) ₂]	Light Yellow	43.00(43.44)	3.60(3.65)	9.68(10.13)	14	-
[Cd (C ₁₁ H ₉ N ₃ OS)(OAc) ₂]	Yellow	38.38(39.01)	3.20(3.27)	9.03(9.10)	12	-
[Hg (C ₁₁ H ₉ N ₃ OS)Cl ₂]	Yellow	25.60(26.28)	1.75(1.80)	8.20(8.36)	10	-

Values in parentheses are the calculated ones.

CONCLUSION

Based on the foregoing data, it may be concluded that the ligand acts as a neutral, bidentate one coordinating to the metals through nitrogen of azomethine group and sulphur of thiophene. Fe(III), Ru(III) and Cu(II) complexes are octahedral, Co(II), Zn(II), Cd(II) and Hg(II) complexes are tetrahedral and Ni(II) and Pd(II) complexes are square planar in geometry.

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