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Synthesis and characterization of N-(2-thienylmethylidene)-1-propanamine and its metal complexes

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ABSTRACT

Rhodium(I), palladium(II), zinc(II) and cadmium (II) complexes of type ML_2Cl_2 , where M is Rh(I), Pd(II), Zn(II) and Cd(II) and L is Schiff base N-(2-thienylmethylidene)-1-propanamine (TNAP), formed by condensation of 2-thiophenecarboxaldehyde (2-TFCA) and propylamine (PA) have been synthesized. The Schiff base ligand and metal complexes were characterized by elemental analysis, magnetic and spectroscopic measurement. Formula determination by continuous variation method suggested the stoichiometry of 1:2 (metal: ligand). Infrared and NMR spectra of the complexes suggested coordination to the metal atom through the nitrogen and sulphur atoms. Conductance measurement suggested the non-electrolytic nature of the complexes.

Keywords: N-(2-thienylmethylidene)-1-propanamine, Schiff base, octahedral structure, complexes.

INTRODUCTION

Coordination compounds have been a challenge to inorganic chemist since they were identified in the 19th century. They defy the usual rules of valence at that time and hence were called complexes. They play vital role in our lives. Transition metal complexes with soft or hard donor groups have been used extensively in coordination and organometallic chemistr [1,2]. Coordination compounds have been used as antimalarial, antileukemic and antitumor agents[3-5]. Metal complexes of Schiff base are studied extensively due to synthetic flexibility of these compounds and their selectivity as well as sensitivity towards the central metal atom [6]. In

previous works [7] complexes with Schiff bases have been prepared and used for extracting some metal ions. Schiff base complex compounds played important roles in the development of inorganic chemistry, biochemistry and environmental chemistry. These types of complexes with transition and heavy metals are used in organic synthesis, medicine and agriculture as analytical reagent and metal ion catalyst [8-12]. It has been shown that coordination of biologically active organic ligands to metal ions increases their biological activity [13-15]. In this present study, we present the synthesis and characterization of the N-(2-thienylmethylidene)-1-propanamine ligand and of its Rh^+ , Pd^{2+} , Zn^{2+} , and Cd^{2+} complexes.

EXPERIMENTAL SECTION

Reagents: $RhCl_2 \cdot 6H_2O$ (Merck, 99.99%), $PdCl_2 \cdot 6H_2O$ (Merck, 99.99%), $ZnCl_2 \cdot H_2O$ (Merck, 99.99%), $CdCl_2 \cdot 2H_2O$ (Merck, 99.99%), 2-thiophenecarboxaldehyde (2-TFCA) (Merck, 98%), and propylamine (PA) (Merck, 99.99%).

Synthesis of bidentate Schiff base: An ethanolic solution of 2-TFCA (0.002 mol, 25 ml) was added with an ethanolic solution of PA (0.002 mol, 25 ml) and refluxed for 12 hours on a water bath. After the concentration of the solution, the precipitate was separated, filtered, washed with ethanol and dried over $CaCl_2$ in a vacuum. Equation of reaction is shown in Scheme 1.

Synthesis of the ML_2Cl_2 complexes: A mixture of 2-thiophenecarboxaldehyde (0.004 mol, 50 ml) and propylamine (0.004 mol, 50 ml) in ethanol was added to an ethanol solution of metal chlorides (0.002 mol, 50 ml). The mixture was refluxed on a water bath for 16-18 hours. The excess solvent was then evaporated. The compounds separated were filtered, washed, with ethanol and dried over $CaCl_2$ in a vacuum.

Instruments: The ligand and complexes were analyzed for M, S and Cl by conventional method [16] while C, H and N by micro analytical methods. The IR spectra were obtained in KBr disc using a BIO-RAD FTS 135 spectrophotometer. The UV-VIS spectra were recorded on a UNICAM UV-VIS UV-4 spectrophotometer in DMF solution. The 1H NMR spectra (in $CDCl_3$) were recorded on a Varian T60 and the ^{13}C NMR spectra were obtained using a Bruker WH 270 spectrophotometer. The magnetic moments have been determined by the Faraday method. A digital conductivity meter K 612 was used to measure the molar conductivity in DMF.

RESULTS AND DISCUSSION

The synthesis of the novel ligand, N-(2-thienylmethylidene)-1-propanamine (TNAP) (Scheme 1) appeared as a powder with high melting points. They are not soluble in ethanol, ethyl ether, and chloroform but soluble in acetone and more soluble in DMF. In the elemental analysis result (Table 1), the experimental values are in agreement with the calculated values. The molar conductance of the complexes (Table 2) in DMF ($10^{-3}M$) are in the range $10.6-12.9 \Omega^{-1}cm^2mol^{-1}$ indicating their non-electrolytic nature. The coloured nature of the complexes showed that they absorb in the ultraviolet/visible region.

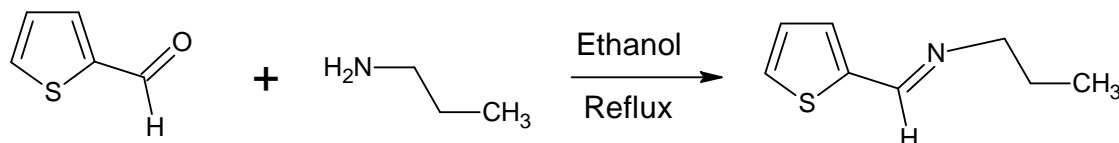
Table 1: Elemental analysis of ligand and complexes

Compound	M %		C %		H %		N %		S %	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
TNAP	----		62.74	66.77	7.19	7.21	9.15	9.16	20.19	20.15
Rh(TNAP)Cl ₂	21.43	21.45	40.02	40.04	4.59	4.57	5.83	5.86	13.35	13.36
Pd(TNAP)Cl ₂	22.00	22.02	39.73	39.72	4.56	4.58	5.79	5.74	13.25	13.27
Zn(TNAP)Cl ₂	14.68	14.63	43.41	43.44	4.98	5.00	6.32	6.30	14.50	14.48
Cd(TNAP)Cl ₂	22.95	22.94	39.24	39.24	4.23	4.22	5.72	5.70	13.09	13.12

Table 2: Analytical and physical data of the complexes

Compound	M.P (°C)	Colour	Meff (MB)	$\Omega^{-1}\text{cm}^2\text{mol}^{-1}$
Rh(TNAP)Cl ₂	230	Purple	4.65	12.9
Pd(TNAP)Cl ₂	156	Blue	3.55	12.2
Zn(TNAP)Cl ₂	138	Green	1.97	10.8
Cd(TNAP)Cl ₂	136	Pink	1.94	10.6

Formula determination using method of continuous variation showed the stoichiometry of the metal:ligand ratio. A graph of absorbance against mole fraction of ligand was plotted. The legs of the “triangle” were extrapolated until they crossed. The mole fraction at the point of intersection was noted. Metal:ligand ratio of 1:2 was obtained.

**Scheme 1: Synthesis of N-(2-thienylmethylidene)-1-propanamine**

IR spectra: The IR spectra (Table 3) of the ligands exhibits a band at 1671 cm⁻¹ assignable to $\nu\text{C}=\text{N}$ of the azomethyne group. This band shifted to lower frequency by about 38-55 cm⁻¹ in the complexes, suggesting coordination through N atom of the azomethyne group. The medium intensity band at 850 cm⁻¹ observed in free ligand ascribed to νCSC (ring) stretching vibration is shifted to lower frequencies with 28-30 cm⁻¹ for all the complexes, suggesting the involvement of sulphur atom in the bonding with the metal ions. The band assigned to the νCSasym is shifted to lower frequency after complexation and the νCSSym . Completely disappears in all the complexes. This also confirms that the sulphur atom is taking part in the complex formation. The proof of nitrogen coordination to the metal atom is provided by the occurrence of the bands from 410 -415 cm⁻¹ in the IR spectra of the complexes.

Table 3: Characteristic infrared absorption frequencies in (cm⁻¹) of ligand and complexes

Compound	$\nu_{\text{C=N}}$	ν_{CSC}	$\nu_{\text{CHtiophen}}$	$\nu_{\text{C-Ctiophen}}$	ν_{CSsym}	ν_{CSasym}	$\nu_{\text{M-N}}$
TNAP	1671	850	3071	1522	693	642	-----
Rh(TNAP)Cl ₂	1633	820	3069	1510	-----	621	412
Pd(TNAP)Cl ₂	1616	832	3072	1517	-----	618	415
Zn(TNAP)Cl ₂	1621	824	3062	1520	-----	627	410
Cd(TNAP)Cl ₂	1622	825	3064	1520	-----	626	410

The ¹HNMR spectra of the complexes and ligand is presented in Table 4. In the ¹HNMR spectra of the ligand, the formation of Schiff base is supported by the presence of a singlet at δ 9.54 and 9.72 ppm respectively, corresponding to the azomethyne proton (CH=N). This peak is shifted downfield in the spectra of the complexes. This suggests coordination through the nitrogen atom of the azomethyne.

In the ¹³CNMR spectra (Table 4), a peak at δ 159.7 and 162.3 ppm corresponding to the carbon atom of the azomethyne (CH=N) is shifted downfield in the spectra of the complexes. This suggest coordination through the nitrogen atom of the azomethyne.

Table 4: NMR spectra data δ (ppm)of the ligands and complexes

Compound	¹ HNMR				¹³ CNMR		
	δ	δ	δ	δ	δ	δ	δ
TNAP	9.54	9.72	6.74	6.94	159.7	162.3	112.9
Rh(TNAP)Cl ₂	8.25	8.52	6.73	6.91	155.5	160.8	112.9
Pd(TNAP)Cl ₂	8.28	8.51	6.76	6.93	155.8	160.7	112.7
Zn(TNAP)Cl ₂	8.24	9.56	6.74	6.94	155.6	160.3	112.6
Cd(TNAP)Cl ₂	8.21	8.58	6.77	6.92	155.1	160.5	112.9

Electronic spectra: Electronic spectra data is shown in Table 5. Within the UV spectrum of the ligand the absorption band at 41070 cm⁻¹ have been assigned n \rightarrow π transition. These transitions are also found in the spectra of the complexes, but are shifted to lower frequencies $\Delta\nu = 1100$ -2870 cm⁻¹. confirming the coordination of the ligand to the metal ions. These bands are assigned intraligand transition. The absorption bands of [Rh(TNAP)Cl₂] at 19970, 19030 and 15800 have been assigned ³T₂(F) \rightarrow ³A₂, ³T₁(F) \rightarrow ³A₂ and ³T₁(P) \rightarrow ³A₂ electronic stste [17]. The absorption bands at 36030 – 39870 cm⁻¹ are assigned the charge transfer transition. These bands are absent in the absorption spectrum of the ligand.

Table 5: Electronic spectra of the ligand and complexes

Compound	Absorption maxima (cm ⁻¹)				
TNAP	41070				
Rh(TNAP)Cl ₂	39970	36030	19970	19030	15800
Pd(TNAP)Cl ₂	38200	37890			
Zn(TNAP)Cl ₂	38560	37430			
Cd(TNAP)Cl ₂	38769	39870			

The formula [ML₂Cl₂] where M is Rh(I), Pd(II), Zn(II) and Cd(II) and L is Schiff base N-(2-thienylmethylidene)-1-propana mine (TNAP) have been proposed for the complexes. The proposed structural formulas for the complexes are shown in Figure 2.

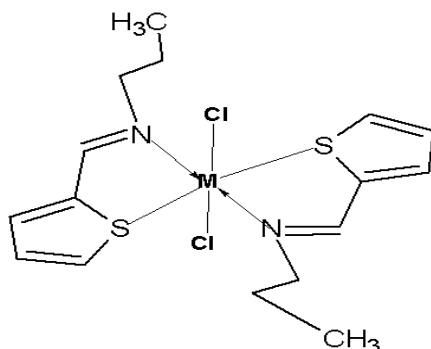


Figure 2: Suggested structures for the complexes $[ML_2Cl_2]$, $M = Rh^I, Pd^{II}, Zn^{II}, Cd^{II}$, $L = N-(2\text{-thienylmethylidene})\text{-}1\text{-propanamine}$

CONCLUSION

New bidentate Schiff base ligand *N*-(2-thienylmethylidene)-1-propanamine (TNAP), derived from 2-thiophenecarboxaldehyde and propylamine and their complexes with Rh(I), Pd(II), Zn(II) and Cd(II) have been synthesized and characterized. The products were characterized by elemental analysis, magnetic and spectroscopic measurements. Formula determination by continuous variation suggested that the complexes have 1:2 (metal:ligand) stoichiometry. The formula $[ML_2Cl_2]$ where M is Rh(I), Pd(II), Zn(II) and Cd(II) and L is Schiff base *N*-(2-thienylmethylidene)-1-propanamine (TNAP) have been proposed for the complexes.

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