

Preparation and Spectroscopic Study of New NS Ligand and its Cd(II) and Zn(II) Metal Complexes

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Abstract

A new nitrogen sulphur Schiff base has been prepared from the condensation 1-(pyridin-4-yl) ethanone with 3-methylbenzyl hydrazinecarbodithioate leading the formation of new ligand 3-methylbenzyl (2Z)-2-[1-(pyridin-4-yl)ethylidene]hydrazine carbodithioate (PE3MBC). The ligand was reacted with Cd(II) and Zn(II) metal salts to form new coordinated complexes. The new ligand and its metal complexes were characterized *via* various physico-chemical and spectroscopic techniques and conductivity, magnetic susceptibility of metal complexes based on the data analysis the metal complexes are expected to be tetrahedral in geometry.

Keywords: Schiff base, Pyridine, Zinc (II), Cadmium (II).

Introduction

Ligands and its transition metal complexes has been of great interest to research workers since seventies of the last century. At that time it was found that pyridine complexes show activity against leukemia. These compounds warrant further study because they provide an interesting series of ligands whose properties can be greatly modified by introducing different organic substituents, thereby giving variation in donor properties and they are often biologically active^[1-4]. Metal complexes and ligands contain pyridine have also been known to possess a wide range of anticancer, antibacterial, antifungal, antiamebic and insecticidal activities^[5-9].

The Schiff base new ligand 3-methylbenzyl (2Z)-2-[1-(pyridin-4-yl)ethylidene] hydrazinecarbodithioate (PE3MBC) was synthesized by the condensation reaction of 3-methylbenzyl hydrazinecarbodithioate (3MBC) with 1-(pyridin-4-yl) ethanone (PE), two new metal complexes were synthesized using their metal salts in order to evaluate their coordination chemistry.

Experimental

Preparation of 3-methylbenzyl hydrazinecarbodithioate

Potassium hydroxide (0.2 mol) was dissolved in absolute ethanol (70 ml). To this solution, hydrazine hydrate (0.2 mol) was added and the mixture was cooled in an ice-salt bath to 0°C. Carbon disulphide (0.2 mol) was added dropwise with constant stirring over

a period of one hour. The two layers that subsequently formed were separated using a separating funnel. The light-brown lower layer was dissolved in 40% ethanol (60 ml) below 5°C. The mixture was kept in an ice-bath and to it, 3-methylbenzyl chloride (0.2 mol) was added dropwise with vigorous stirring of the mixture. The sticky white product, (S3MBDTC), which formed was filtered and left to dry overnight in a desiccator over anhydrous silica gel. (Yield: 75%, m.p. 130°C).

Preparation of 3-methylbenzyl (2Z)-2-[1-(pyridin-4-yl) ethylidene] hydrazinecarbodithioate (PE3MBC)

3-methylbenzyl hydrazinecarbodithioate (0.01 mol) was dissolved in hot acetonitrile (100 ml). This was added to an equimolar solution of 1-(pyridin-4-yl) ethanone in ethanol (10 ml). The mixture was heated and stirred for 30 minutes and then allowed to stand for a few hours, after which yellow crystals formed, which were filtered off and recrystallised from acetonitrile. Yields were fairly high, ca. 85%, C: 59.23(60.29), H: 5.54(5.43), N: 12.65(13.32) and S: 22.03(20.33).

General method of synthesis for Zinc and Cadmium metal complexes

The transition metal salts used were the acetate salts of Cd(II) and Zn(II) acetate (0.001 mol) which was dissolved in hot ethanol (10 ml) and was mixed with a solution of the ligand (0.001mol) in acetonitrile (80 ml)

and the resulting mixture was heated for 30 minutes. On standing overnight, the mixture yielded crystalline complexes which were filtered off and dried in a desiccator over anhydrous silica gel, overnight. Yield: *ca.* 70%. Some analytical, physical and spectral data on the complexes can be found in Tables (1).

Physical measurements

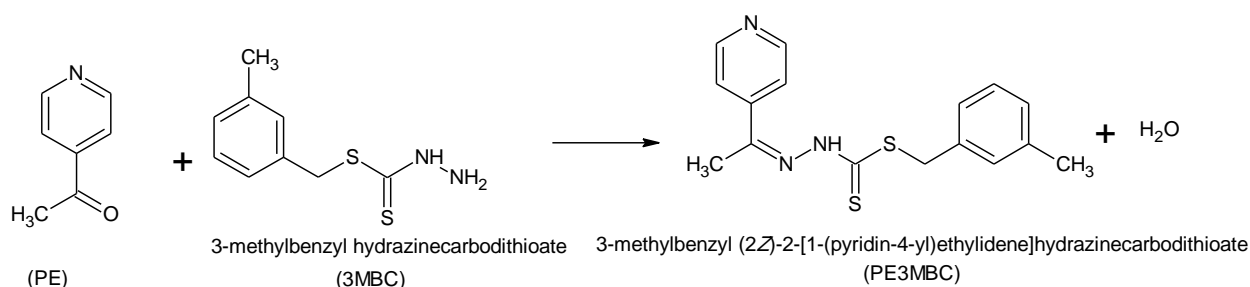
The analyses for carbon, hydrogen, nitrogen and sulphur were carried out using a LECO CHNS-932 instrument. The IR spectra in KBr pellets were recorded on a Perkin-Elmer FT IR 1750X spectrophotometer ($4000\text{--}400\text{ cm}^{-1}$). Metal determinations were carried out using a Perkin-Elmer Plasma 1000 Emission Spectrometer. The molar conductance of 10^{-3} M solutions of the metal

complexes in DMSO were measured at 29°C using a Jenway 4310 conductivity meter and a dip-type cell with a platinized electrode.

Magnetic susceptibilities at room temperature were measured using a Sherwood Scientific MSB-AUTO magnetic susceptibility balance. The UV-VIS spectra were run on a Shimadzu UV- 2501 PC/ Shimadzu UV-Vis-1650 recording Spectrophotometer (1000- 200 nm).

Results and Discussion

Scheme (1) shows the condensation reaction to prepare the new ligand, while the physical and analytical data of the complexes are shown in Table (1). The analytical data agree well with the proposed formulations of the complexes.



Scheme (1) The synthesis equation of the new ligand.

*Table (1)
physical properties and CHNS of the synthesized compounds.*

Compound	Colure	Melting point ($^{\circ}\text{C}$)	% Found(calculated)				
			%C	%H	%N	%S	%M
3MBC	Beige	130	50.14 (50.91)	5.47 (5.70)	13.39 (13.19)	30.97 (30.20)	-
PE3MBC	Yellow	208	62.24 (60.92)	6.02 (5.43)	13.11 (13.32)	19.68 (20.33)	-
$\text{Zn}(\text{PE3MBC})_2$	Golden Yellow	189	56.76 (55.36)	4.49 (4.65)	12.56 (12.10)	18.57 (18.47)	9.38 (9.42)
$\text{Cd}(\text{PE3MBC})_2$	Yellow	203	50.82 (51.85)	4.29 (4.35)	11.59 (11.34)	18.53 (17.30)	15.01 (15.16)

Infrared Spectroscopy (FTIR)

The IR spectral data for the Schiff bases and their metal (II) complexes are shown in Table (2). Four key functional group bands were selected to provide a comparative analysis, as these bands shift to higher or lower wave numbers upon complexation with the metal(II) complexes. The $\nu(\text{C}=\text{N})$, $\nu(\text{N}-\text{N})$, $\nu(\text{CSS})$ and $\nu(\text{NH})$ bands arise from the HNNS/ HNS Schiff base. The presence of the $\nu(\text{C}=\text{N})$, $\nu(\text{N}-\text{N})$ and $\nu(\text{CSS})$ bands at $1608\text{-}1588\text{ cm}^{-1}$, $1046\text{-}1088\text{ cm}^{-1}$ and $824\text{-}972\text{ cm}^{-1}$ respectively indicates that the coordination of the Schiff base to the central metal(II) ion is *via* the pyridyl nitrogen-if sterically unhindered, due to resonance effect, the azomethine nitrogen and the thiolate sulphur atom. From the observation, the free benzyl hydrazinecarbodithioate ligand does not display band at $\nu(\text{S}-\text{H})$, because the Schiff base lies in thione tautomer. A very strong intensity at ν (1048 cm^{-1} , bending) which represent as $\text{C}=\text{S}$ which clearly indicates it remains in the thione form in the solid state. In the Schiff base, there is no peak assigned to $\text{C}=\text{S}$ indicating that the Schiff bases appear in thiole form. There is peak at (1608 cm^{-1}) which

attribute to $\text{C}=\text{N}$, from this observation, it is concluded that the Schiff bases are formed via condensation reaction with condensation 1-(pyridin-4-yl)ethanonein which the primary amine reacted with the carbonyl group to form the new ligand. For complexes of cadmium(II) and zinc there is peaks assigned at (876 cm^{-1} and 821 cm^{-1}) which attribute to CSS which indicate the shifting of this band to higher frequency due to coordination of thiole sulphur with central metal ion. This only can happen if ligand in thiole form, which indicates that the ligand were undergoes deprotonated and behave as tridentate uni-negative chelating agents. $\text{C}=\text{N}$ showed at peak (1588 cm^{-1}) but as we can see that in the metal complexes, it is shift to the lower frequency to $1589\text{-}1601\text{ cm}^{-1}$) this shows that the metal bonded through azomethine nitrogen atom. A strong band at 1060 cm^{-1} in the IR spectrum of the Schiff base is assigned to the hydrazinic $\nu(\text{NN})$ band. Its shift to lower wave numbers in spectra of all the metal complexes ($1088\text{-}1077\text{ cm}^{-1}$) reflects reduction in the repulsion between the lone pairs of electrons on the nitrogen atoms conforming the coordination *via* the azomethine nitrogen atom.^[10-14]

Table (2)
Fourier Transform Infrared Spectroscopy (FT IR) data.

Ligand/ Complex	$\nu(\text{C}=\text{N})$	$\nu(\text{N}-\text{N})$	$\nu(\text{CSS})$	$\nu(\text{NH}) / \text{NH}_2$
3MBC	1608	1046	972	3399
PE3MBC	1588	1060	824	3082
Zn(PE3MBC)₂	1589	1088	876	-
Cd(PE3MBC)₂	1601	1077	821	-

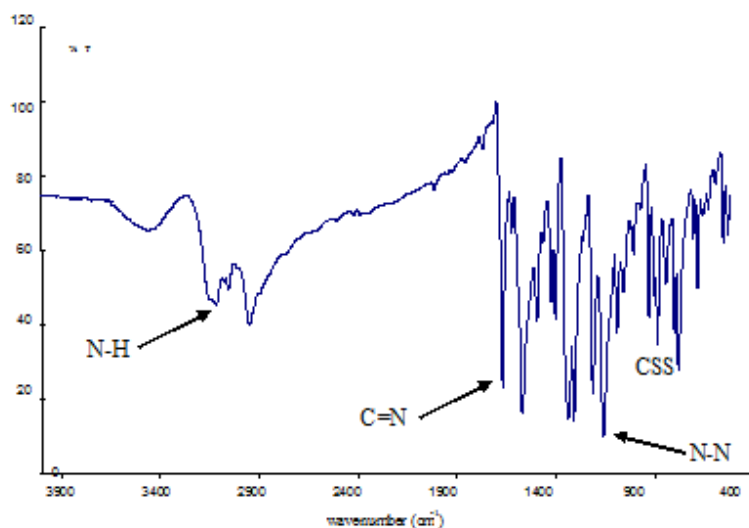


Fig. (1) IR Spectrum of PE3MBC Ligand.

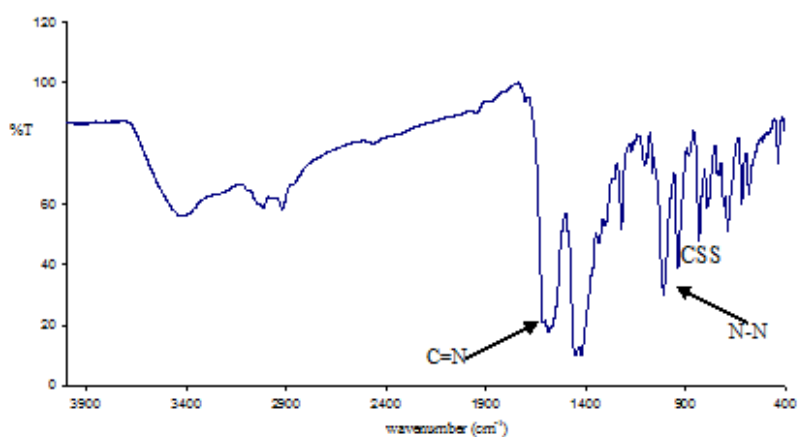


Fig. (2) IR Spectrum of Zn(PE3MBC)₂.

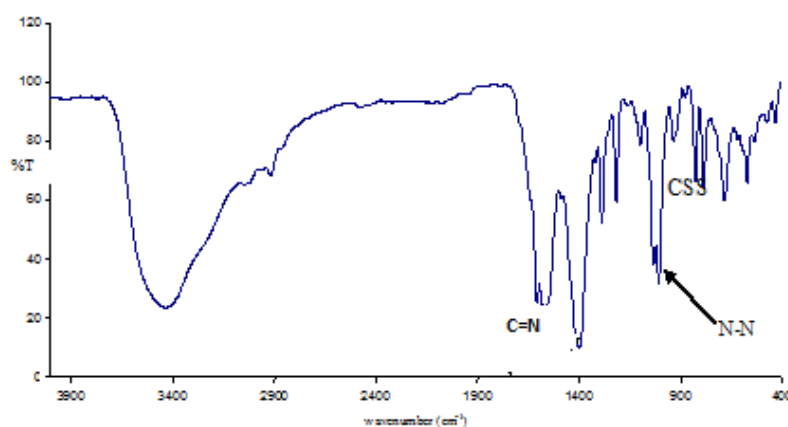


Fig. (3) IR Spectrum of Cd(PE3MBC)₂.

Molar conductivity, Magnetic Susceptibility and UV-Spectroscopy

Table (3) shows the molar conductance data, all the complexes were nonelectrolytes, representing that the ligand is coordinated to

the metal ions as a uninegatively charged tridentate species. The molar conductance values of the complexes in DMSO fall in the range of 1.43 to 4.39 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ in DMSO.

Although some dissociation of the complexes seems to occur, the conductance values are much lower than that expected for a 1:1 electrolyte in this solvent ^[15].

Table (3) shows also the magnetic susceptibility data and as it is observed, all the complexes has diamagnetic natures. The coordinated is suggested tetrahedral for

Cd(II) and Zn(II) complexes ^[16]. The electronic spectra of the complexes in DMSO (Table (3)) exhibits intra-ligands $n \rightarrow \pi^*$ band at 326 nm. Both the Cd(II) and Zn(II) complexes do not exhibit any d-d transition as they are d^{10} system.

Table (3)
Molar conductivity, Magnetic Susceptibility of metal complexes.

Complex	Λ ($S\ cm^2\ mol^{-1}$)	μ_{eff} (BM)	λ_{max} (Log ϵ) (nm)
PE3MBC	-	-	326 (2.91)
Zn(PE3MBC) ₂	1.43	diamagnetic	258 (3.39), 292 (3.09)
Cd(PE3MBC) ₂	4.39	diamagnetic	299 (2.99)

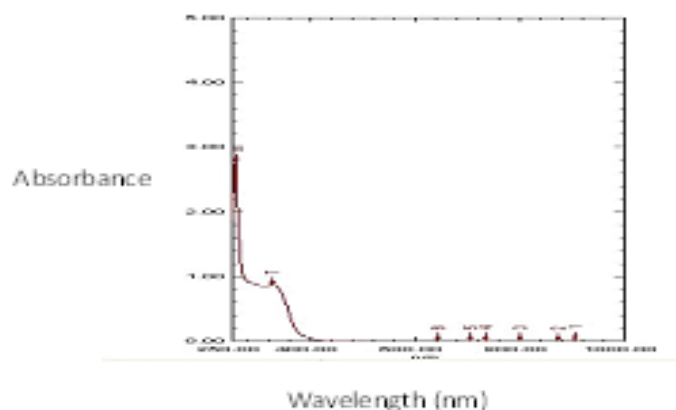


Fig.(4) UV/Vis Spectrum of PE3MBC($10^{-4}M$).

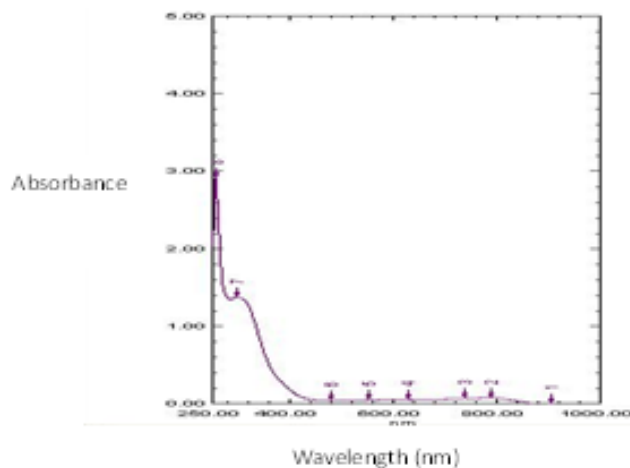


Fig. (5) UV/Vis Spectrum of Zn (PE3MBC)₂($10^{-4} M$).

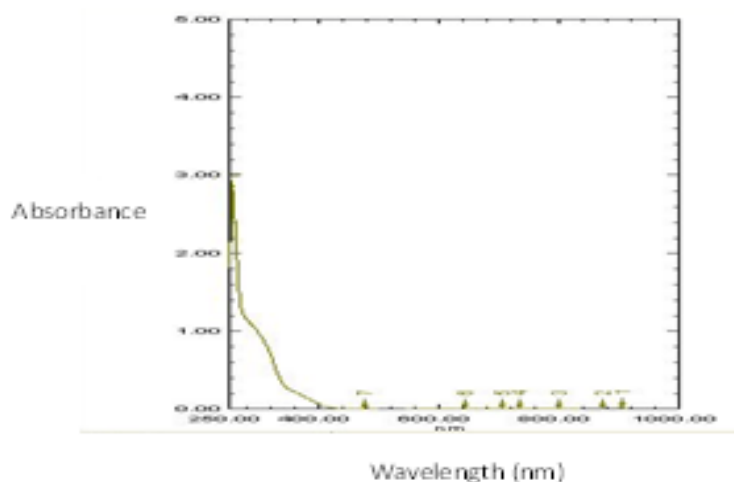
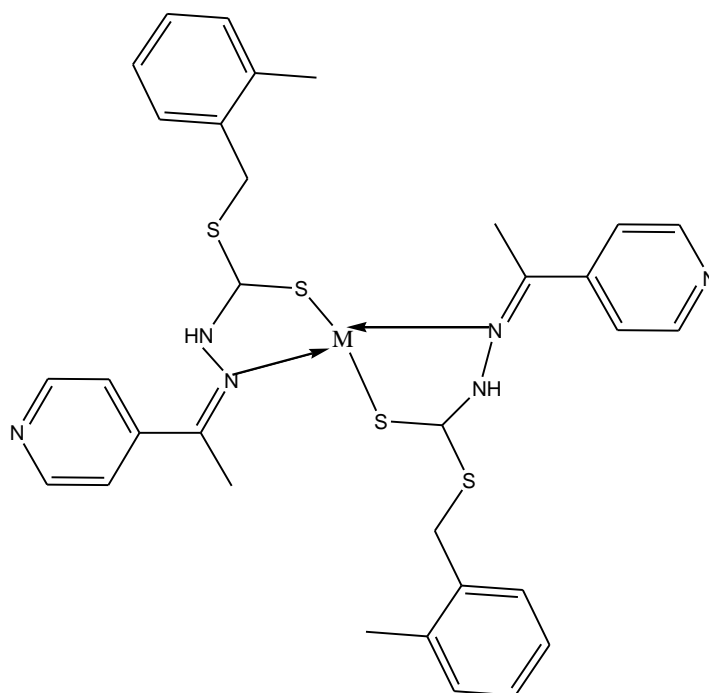


Fig. (6) UV/Vis Spectrum of Cd (PE3MBC)₂(10⁻⁴ M).

The expected structures of the metal complexes can be seen in Scheme (2).



Scheme (2) Expected structure of the complexed Where M = Cd(II), Zn(II).

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الخلاصة

تم تحضير قاعدة شف جديدة تحوي النتروجين والكبريت من تكثيف ١-(بيريدين-٤-يل) ايثانون مع ٣-مثيل بنزائل هايدرازين كاربوداي ثايويت والذي أدى الة تكوين ليكاند جديد ٣-مثيل بنزائل (٢ زد) -٢- (١-بيريدين-٤-يل)أثيليدين) هيدرازين كاربوداي ثايويتز (PE3MBC) تم مفاعلة الليكند مع املاح الزنك والكادميوم الثنائيه التكافؤ لتكوين معقدات تناسقية وتم تشخيص الليكند الجديد ومعقداته باستخدام مختلف التقنيات الفيزيو- كيميائية والتقنيات الطيفية وبناءا على تحليل النتائج المستخلصة من المتوقع ان يكون شكل المعقدات التناسقية رباعي السطوح.