



COMPLEXES OF Zn(II) AND Cd(II) WITH 1-(FURAN-2-YLMETHYLENE)UREA AND N-(PROPAN-2-YLIDENE)BENZOHYDRAZIDE

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Received: January 31, 2013; Accepted: March 11, 2013

Abstract- Complexes of Zn(II) and Cd(II) with 1-(furan-2-ylmethylene)urea (A) and N-(propan-2-ylidene)benzohydrazide (B) have been synthesized and characterized by IR, UV/Vis spectroscopy, powdered X-ray diffractometry, scanning electron microscopy, conductivity, elemental study and solubility study. The ligands were also characterized by HNMR spectroscopy. The result showed that the ligands acted as bidentate donors coordinating through the azomethine nitrogen and the carbonyl oxygen. The elemental analysis indicates that the complexes of Zn and Cd with A precipitated as ML₁ types complex while complexes of B with Zn precipitated as an ML₂ type complex. The complex of Cd with B however the not precipitate from solution. The conductivity study also indicates that the complexes A are electrolytes while B complex is a non-electrolyte.

Keywords- Zinc, Cadmium, 1-(furan-2-ylmethylene)urea, N-(propan-2-ylidene)benzohydrazide, complex, coordination, ligand

Citation: Emmanuel S.A., et al. (2013) Complexes of Zn(II) and Cd(II) with 1-(furan-2-ylmethylene)urea and N-(propan-2-ylidene)benzohydrazide. International Journal of Chemical Research, ISSN: 0975-3699 & E-ISSN: 0975-9131, Volume 5, Issue 1, pp.-140-143.

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Introduction

Investigation on group 12(IIB) elements containing complexes is of interest due to their properties and broad applications in the field of magnetic functional materials, catalysis and luminescent probes in biological system [1]. Complexes of these elements with various ligands have been reported [2-7]. They form complexes with O and N as well as S donor ligands. Majority of their complexes exists as four coordinated tetrahedral complexes [9]. Zinc and cadmium belong to this group of elements. Zn is known for its essential role in biological system and is found in many enzymes exhibiting catalytic and structural role [10]. In this work, we report the synthesis and physicochemical properties of Zn(II) and Cd(II) complexes of 1-(furan-2-ylmethylene)urea (A) and N-(propan-2-ylidene)benzohydrazide (B). These compounds present four and three possible coordination sites respectively. These are the two nitrogen atoms in the amine and azomethine groups and the two oxygen group in the furan ring and carbonyl group of (A) while (B) has two nitrogen atoms in the amine and azomethine group and one oxygen in the carbonyl group. It is expected that the ligands will react with the metal ions to produce metal complexes like ligands of other moiety. The physicochemical properties of the complexes will be studied in comparison with the ligands.

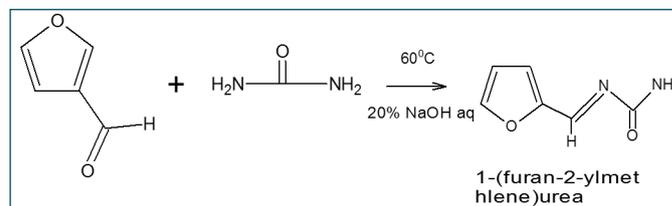
Materials and Methods

Reagents

All the reagents used for this study are of analytical grade and were obtained from Sigma Aldrich Company and BDH. They were used without further purification.

Preparation of Ligand 1-(furan-2-ylmethylene)Urea

About 40cm³ of analar grade furfuraldehyde was measured and poured into a 250cm³ flat bottom flask, 40g of urea added, followed by 9cm³ of distilled water. The mixture was heated on a water bath until a temperature of 60°C was reached, 1cm³ of 20% NaOH solution was then added and heating continued for another 20 minutes. The mixture was cooled on an ice bath and the precipitate filtered and washed with cold water (10°C) and then it was dried at a temperature between 50°C. The dried powder obtained was washed with n-hexane and recrystallized twice from methanol- water solution (30/70%) and dried. [Scheme-1] shows reaction of furfuraldehyde with urea to form (A) [11].

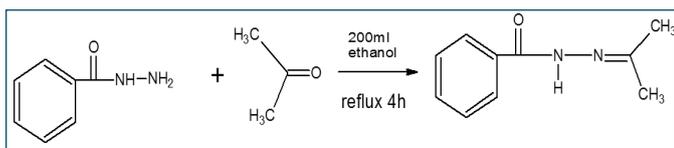


Scheme 1- Reaction of furfuraldehyde with urea

Preparation of Ligand N-(propan-2-ylidene)benzohydrazide B

Approximately 7.8g of benzoic acid hydrazide was dissolved in 100cm³ ethanol and 4.14cm³ (3.3g) of acetone was added. The mixture was heated under reflux for four hours. It was poured into a beaker for crystallization. The resulting crystals were filtered and recrystallized in 20cm³ of methanol and were latter dried in vacuum dessicator [12]. [Scheme-2] shows the reaction of benzoic acid

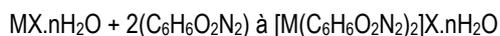
hydrazide with acetone.



Scheme 2- Reaction of benzoic acid with acetone

Synthesis of Metal Complexes

1(furan-2-yl-methylene)urea (4.83, 4.35g) was dissolved in 100cm⁻³ of boiling distilled water in a 250ml beaker and then zinc sulphate and cadmium acetate (5.13, 5.00g) were dissolved in 50ml of distilled water and added to the ligand solution respectively. The mixture was heated for 10 minutes and then filtered while hot. The filtrate was concentrated and allowed to cool. The resulting precipitates were filtered and dried.



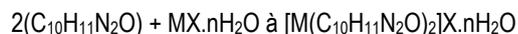
(Where M is Zn and Cd, X is SO₄, (CH₃COO)₂ and n is 1, 2, 3)

Scheme 3-

 Reaction of preparation of 1(furan-2-yl-methylene)urea metal complexes

Preparation of the Complex of N-(propan-2-ylidene)Benzohydrazide

The complex of N-(propan-2-ylidene)benzohydrazide was synthesized by dissolving 0.82g, 0.85g of ligand in 70cm⁻³ ethanol in a 250cm⁻³ beaker. Then 0.65g, 0.67g zinc sulphate and cadmium acetate salts were dissolved in 50cm⁻³ water and added to the ligand solutions respectively with. The resulting crystals were filtered and dried.



Scheme 4-

 Reaction of preparation of acetone benzoic acid metal complexes

Physical Measurements

The metal ions were determined gravimetrically after removing the

Table 1- The analytical data and some physical properties of the ligands and their metal complexes

Parameters	A	B	[Zn(A)]SO ₄	[Zn(B)]SO ₄	[Cd(A)](CH ₃)(COO) ₂
Formula			[Zn(C ₆ H ₆ O ₂ N ₂) ₂]SO ₄	[Zn(C ₁₀ H ₁₁ N ₂ O) ₂]SO ₄	[Cd((C ₆ H ₆ O ₂ N ₂))(CH ₃)(COO) ₂ .H ₂ O
Formula weight (g)	139	175.21	299.52	601.89	524.76
%metal composition	-	-	22.77(21.23)	10.18(10.86)	21.14(21.42)
% C			24.06(25.00)	39.91(38.10)	27.46(27.55)
% H			1.52	5.31	2.3
% N			7.05(7.45)	9.30(9.50)	10.67(10.88)
Mp °C	186-187 ^D	95-100 ^M	215.0-221.3 ^D	116.0-120.5 ^M	156.4-158.4 ^D
Conductivity (mS/cm)	0.36	0.277	1.32	0.29	5.23

Key: Mp denotes melting point, D denotes decomposition and M denotes melt

The ¹HNMR analysis of the ligand 1-(furan-2-ylmethylene)urea in DMSO showed multiplet peaks in the range(δ) 6.65-6.99 (6.00-7.50) corresponds to the furan ring: the peak at 7.55 (7.50) is due to the H around the carbonyl group while peaks in the range 5.4-5.75 (6.50) is assigned to the amine (NH₂). While the N-(propan-2-ylidene)benzohydrazide ligand showed multiple peaks in the range 7.5-7.99 (7.75-8.0) corresponding to the benzene ring, NH₂ was observed at and the peak at 1.90 (1.93) is assigned to CH₃. The values in bracket are the value assigned by the chemdraw Ultra 10.0 software. These when compared with the NMR data of the ligand generated by chemdraw Ultra 10.0 confirmed the structures of the ligands.

organic residue by digesting with a few drops of concentrated nitric acid. The infra red spectra data of ligand and complex were recorded on Genesis II FTIR spectrometer as KBr discs over a range of 4000-500cm⁻¹. The conductivity was determined on Jenway 4330 conductivity and pH meter in DMSO. Melting point analysis was done on Electrothermal melting point apparatus and UV analysis was carried out on Cecil 9000 series UV/Visible spectrophotometer. The HNMR of the ligand was carried out on ¹H and ¹³C Mercury-200BB in DMSO.

The SEM Images of the complexes and ligands were captured on a scanning electron microscope (SEM) EVO/MAIO Carl Zeiss mounted with EDX Oxford instruments INCA.X. The samples were mounted on a carbon type placed on an aluminium stub. The percentage carbon and nitrogen was determined using the energy disperse X-ray. It was also used to confirm the percentage metal ion present in the complex.

The x-ray diffraction patterns of the powdered samples were measured on X'pert PRO MPD using a Monochromator Cuka at 30mA, 40KV. Measurements were taken using a glancing angle of incidence detector at an angle of 10° for 2θ value over 10-70° in steps of 30mins.

Results

The ligand (A) precipitated as a brown powdered solid insoluble in most organic solvent and has a melting point > 200°C while ligand (B) precipitated as a white crystalline solid soluble in most organic solvents. The physicochemical properties of the compounds are shown on [Table-1]. The result indicates that the complexes of Zn and Cd with ligand (A) precipitated as 1:1 molar ratio metal-ligand complex while the complex of Zn with ligand (B) precipitated as a 1:2 molar ratio metal-ligand. The complex of Cd with (B) did not precipitate from solution. This may be due to the bulky nature of the ligand as well as the large nature of Cd ion. The compounds are insoluble in most organic solvents. The conductivity study showed that the complexes of ligand A with the metal are electrolytes while the complex of ligand B is a non electrolyte.

The infrared spectra of the ligand and the metal complex showed vibration bands due to carbonyl O, azomethine N and the primary amine N [Table-2]. These bands were observed in the ligand A at 1672.03cm⁻¹, 1532.87cm⁻¹ and 3323.01cm⁻¹ and B at 3218.34cm⁻¹, 1632.80 and 1546.96cm⁻¹. These shifted by ca 3.25-21.21cm⁻¹ on complexation with the metal ions. The observations made are similar to reported results in the literature [4,5,9-11]. The involvement of the SO₄²⁻ ion in coordination is observed in the Zn complex with A as shown by the splitting of the vibration frequency at 1200cm⁻¹.

The solubility study is shown in [Table-3]. The result showed that the ligand (A) is insoluble in most solvents while its complexes

showed partial solubility in the most of the test solvents. The ligand (B) showed solubility in some polar solvents and insoluble in non polar solvents while its metal complex is insoluble in all the test solvents except water.

Table 2- Infrared spectra data showing relevant absorption bands of ligands and their metal complexes

Compounds	$\nu(\text{NH})(\text{OH})$,	νCO	νCN	$\Delta\nu\text{CO}$	$\Delta\nu\text{CN}$
A	3323	1672.03	1532.87	-	-
B	3218.34	1632.8	1546.96	-	-
[Zn(B)]SO ₄	3214.48	1654.01	1540.1	21.21	-6.86
[Cd(A)](CH ₃) ₂ (COO) ₂	3446.71	1625.26	-	-	-
[Zn(A)]SO ₄	3418	1675.28	-	3.25	-

Table 3- Result of solubility test of the ligands and their metal complexes in some solvents

Compounds	MeOH	EtOH	Hex	ACN	DMSO	H ₂ O
A	INS	INS	INS	INS	S	INS
B	S	S	INS	INS	S	INS
[Zn(B)]SO ₄	INS	INS	INS	INS	INS	S
[Cd(A)](CH ₃) ₂ (COO) ₂	S	PS	INS	INS	INS	S
[Zn(A)]SO ₄	PS	PS	INS	PS	PS	PS

Key: Abbreviations used for solvents are: water (H₂O), ethanol (EtOH), methanol (MeOH), hexane (HEX), dimethylsulphoxide (DMSO), acetonitrile (ACN), partially soluble (PS), insoluble (INS) and soluble (S)

The electronic (UV/Visible) spectral data for the ligands and their metal complexes recorded in DMSO are summarized in [Table-4] The electronic spectra study showed bands at 31,085cm⁻¹, 28,678cm⁻¹, 28,409cm⁻¹ in ligand A and at 32,573cm⁻¹ in B. These are assigned to transition due to $\pi-\pi^*$ and $n-\pi^*$. On complexation these bands shifted in the complexes and were observed at 40,453cm⁻¹ in [Zn(A)]SO₄, 30,769 cm⁻¹ in [Zn(B)]SO₄ and at 37,037 cm⁻¹ in [Cd(A)](CH₃)₂(COO)₂. This suggests the involvement of the ligand in coordination with the metal ions. Similar results have been reported by earlier researchers [10,11].

Table 4- Electronic spectra data of the ligands and their metal complexes

Compounds	λ_{max} cm ⁻¹	Assignment	Possible geometry
A	31,085,	$\pi-\pi^*$,	-
	28,678, 28409	$n-\pi^*$	-
B	32,573	$\pi-\pi^*$	-
[Zn(A)]SO ₄	40,453	LMCT	Tetrahedral
[Zn(B)]SO ₄	33,898	LMCT	Tetrahedral
[Cd(A)](CH ₃) ₂ (COO) ₂	34,496	LMCT	Tetrahedral

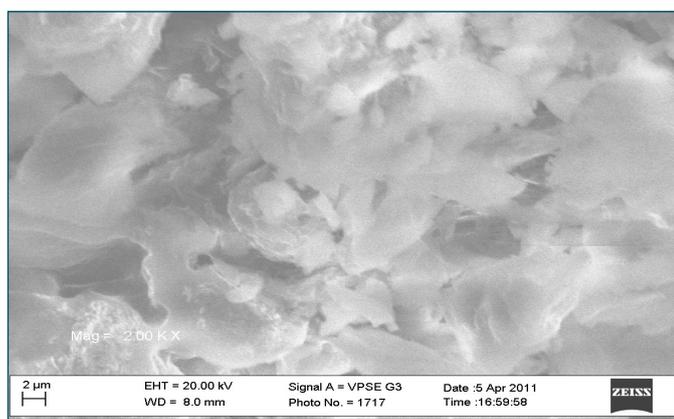


Fig. 1a- Ligand A

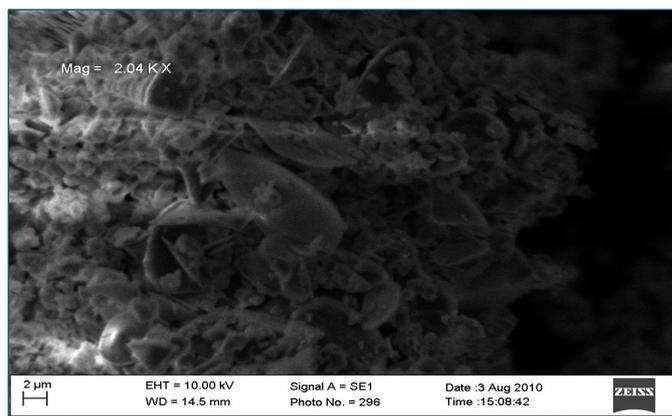


Fig. 1b- [Zn(A)]SO₄

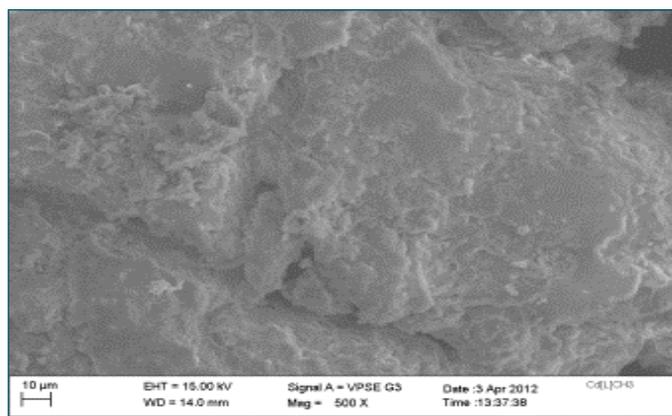


Fig. 1c- [Cd(A)](CH₃)₂(COO)₂

Fig. 1- SEM images of ligand A and its metal complexes at 2µm showing the change in surface morphology of the compounds

The SEM images [Fig-1a], [Fig-1b], [Fig-1c], [Fig-2a] and [Fig-2b] of the ligands and complexes revealed changes in the surface morphology of the compounds. The change in surface morphology indicates that a reaction had taken place between the ligands and the metal ions. A flake-like particle was observed in ligand A. This changed upon complexation to the metal ion to oval like particles in Zn complex and a solid surface in the Cd complex. Ligand B gave a spongy surface while its metal complex with Zn showed plate shaped complex. The result of a morphological change observed on the surface of a polymer matrix (aryl halide) after complexing with the palladium metal ion was reported [12].

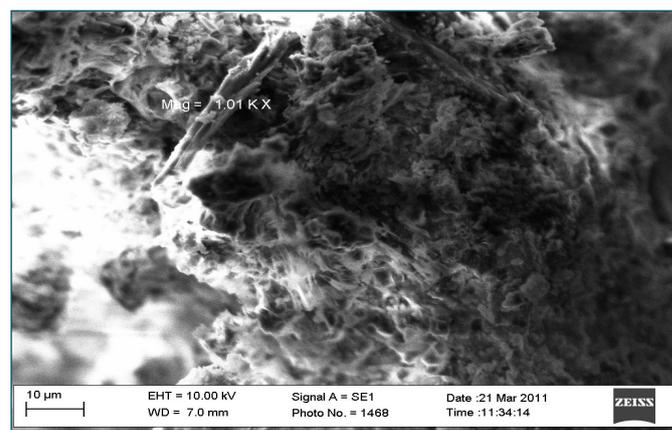


Fig. 2a- Ligand B

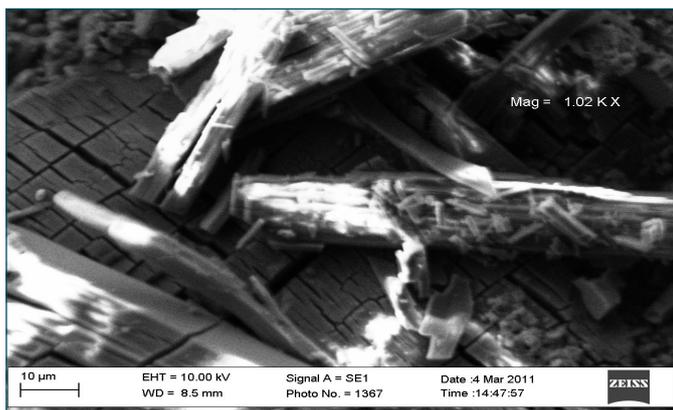

Fig. 2b- [Zn(B)]SO₄

Fig. 2- SEM images of ligand B and its metal complex at 10µm showing the change in surface morphology of the compounds

The XRD patterns of the powdered complexes and ligands revealed a crystalline nature for the complexes as indicated by the peaks given on the diffractogram. The samples showed peaks between 10° and 65°. The clarity of most of the peaks suggests that the compounds were pure [13]. The diffraction patterns of the metal complexes in comparison to the ligand showed variation in the position, height, full width at half maximum (FWHM) and d-spacing of the maximum peak (100%). This variation [Table-5] is an indication that the compounds are not the same. Which also suggests that the reaction between the li.

Table 5- X-ray diffractogram data of powdered ligand (A), (B) and their metal complexes showing the relative intensity of their peaks at 100%

Sample	Pos.[°2Th.]	Height [cts]	FWHM[°2Th.]	d-spacing
A	22.2043	5582.25	0.1536	4.00033
[Cd(A)]	11.5488	877.19	0.063	7.6625
[Zn(B)]	16.1111	1463.61	0.0787	5.46774
B	6.3402	10486.3	0.0787	13.9409
[Zn(B) ₂]	11.9018	3615.33	0.0394	7.43602

Discussion

The analysis carried out in the present study revealed that the ligands A and B reacted with Zn and A only reacted with Cd. Both coordinated to the metal ions as bidentate donor ligands. This is revealed by the IR spectra analysis of the compounds. The observed shift in the absorption bands of the carbonyl oxygen and the azomethine nitrogen of the complexes is attributed to the coordination of these sites to the metal ions. The shift in the electronic spectra also indicates coordination of the ligands to the metal ions. The high decomposition temperature of Zn with ligand (A) indicates a possible polymeric nature for the complex. The present X-ray analysis carried could not be used to determine the bond length and the geometry of the complexes, however the result of the diffractogram showed that the ligands as well as the metal complexes are pure and crystalline in nature. This indicates a possibility of carrying out a single crystal x-ray analysis of the compounds where a single crystal of the compounds can be generated. Ligand A did not proceed according to the stoichiometry of reaction of the compounds. This may be due to steric hindrance. The inability of ligand B to react with Cd is attributed to the bulky nature of the ligand as well as the large nature of Cd metal ion.

From available data the skeletal structure shown in [Fig-3] and [Fig-

4] below indicating the coordination sites to the metal ion is proposed for the metal complexes.

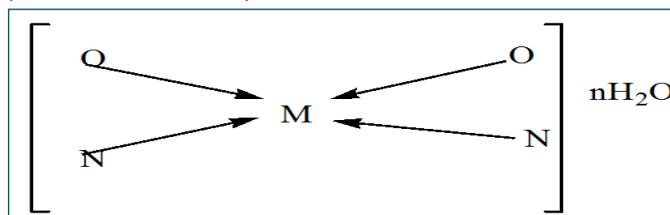


Fig. 3- Proposed structure for the ML₂ type complex (where M is Zn).

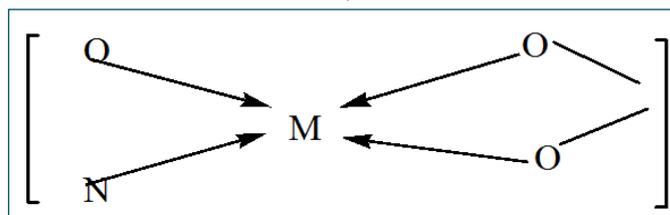


Fig. 4- Proposed structure for the ML₁ type complex (where M is Zn or Cd)

Conclusion

We have synthesized new complexes of Zn and Cd with nitrogen and oxygen donor ligands. The present study showed that the complexes of Zn(II) with A precipitated as ML₁ and B as ML₂ type complexes while Cd(II) precipitated as ML₁ with ligand A. However in ligand B there was no precipitation of any solid from solution. This is thought to be a result of the bulky nature of the ligand and the larger size of Cd(II) ion.

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