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Synthesis and Characterization of Some Nicotinic Acid Complexes

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Abstract: The research deals with the preparation of some complexes of transition and non transition elements of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and uranium (VI) with nicotinic acid. The synthesized complexes were characterized by infrared, ultraviolet spectra, magnetic susceptibilities, atomic absorption and conductivity measurements. The results indicate that all complexes were non electrolyte in chloroform solvent. The results also showed that the complexes of Cu (II), Ni (II) and Co (II) have square planar configuration, while zinc and cadmium complexes have an octahedral geometry. The uranium nitrate complexes showed a good indication that the nitro group were coordinated in a bidentate manner.

Key words: nicotinic acid, uranium complexes, bidentate ligand.

I. INTRODUCTION

Heterocyclic complexes with transition and non transition metals have elicited much interest [1-7]. Pyridine-2,6-dicarboxylic acid (or dipicolinic acid) forms stable chelates with simple metal ions and oxometal cations and can display widely varying coordination behavior, functioning as a multidentate ligand. A very important characteristic of these ligands is their diverse biological activity.

Pyridine-2,3-dicarboxylic acid is an intermediate in the tryptophan degradation pathway and is a precursor for NAD[8]. The reaction of Me₂Sn(IV) with pyridoxine [3-hydroxy-4,5-bis(hydroxymethyl)-2-methylpyridine, PN, vitamin B₆], yields three complexes, one with the composition [SnMe₂(PN-H)]NO₃ · 2H₂O. This complex is polymeric. The anhydrous compound displays higher in vitro antitumor activity than that of cis platin or carboplatin[8,9]. The diorgano tin(IV) pyridine-2,6-dicarboxylates exhibit in vitro antitumor activities[10]. Atassi assumed that water-soluble organotin(IV) compounds are probably more active than complexes soluble only in organic solvents[11]. Therefore,[12,13] prepared tetra ethyl ammonium diorgano halogeno pyridine-2,6-dicarboxylatostannates (halogeno Cl,F) whose water solubility's under physiological conditions are higher than those of the parent compounds [14].

The present work aim to the isolation of some complexes of nicotinic acid as ligand with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and UO₂(VI) salts metals.

II. EXPERIMENTAL

Starting materials: Nicotinic acid from SDI Company(99.99%), uranium nitrate hexahydrate (BDH) grade. All other chemicals were used without further purification.

Infrared spectra (400-4000 cm⁻¹) were recorded as KBr disc on Thermo Nicolet, Fourier-Transform Infrared(FTIR) spectrophotometer, electronic spectral measurements were made in chloroform solvent by using Citra 5 GBC Scientific equipment, Uv-Visible spectrophotometer at 25°C Magnetic susceptibilities were measured by using Bruker BM6 at 25°C by a Faraday method. Conductivity was obtained an approximately 1x10⁻³ concentration in chloroform solvent by conductivity meter models PCM3 Jenway. Nickel and copper elements were determined by using Pyeunicam SP Atomic Absorption spectrophotometer. Determination of cobalt, zinc and cadmium elements were determinate by using the pyridine method[15]. The uranium content of the complexes was determined by using a previously published method[16]. Elemental analysis was carried in the Mosul University.

III. PREPARATION OF THE COMPLEXES

The complexes were synthesized by the following general method:

To an ethanolic solution 25 ml of metal salt [CoCl₂.6H₂O, NiCl₂.6H₂O, CuCl₂. 2H₂O, ZnCl₂, CdCl₂. 2H₂O and UO₂(NO₃)₂.6H₂O] (10mM) was added to a solution of ligand (20mM) in ethanol solvent. The pH of the solution was raised to 7-7.5 by adding 2% of sodium bicarbonate solution with continuous stirring. The precipitated of the complex was filtered off, washed with a small amount of ethanol, dry ether, and then dried in a vacuum. The colors, melting point, elemental analysis of the prepared complexes is tabulated in (Table1).

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IV. RESULTS AND DISCUSSION

The conductivity values for all complexes were lying between (2.33-11.11 $\Lambda_{\text{M}}\text{ohm}^{-1}\text{cm}^{-1}$) in chloroform solvent (Table1) these values have clearly shown that these complexes were non-electrolyte nature of this solvent.

Study of the ultraviolet –visible spectra of the complexes in chloroform solvent showed bands at 31746-38461 nm which due to π to π^* transition. A new band appears in the region (495-510 cm^{-1}) which is due to the charge transfer from ligand to metal[16]. Cobalt (II) complex showed bands at (18475 cm^{-1} and 10250 cm^{-1}) which is due to dxy-dyz allowed transition and this is a good indication that the complex has square planar geometry. The magnetic measurement of this complex gives a value of 2.70 BM; this value confirms a low spin cobalt (II) complex. The nickel (II) complex was a diamagnetic and this is due to a square planar geometry, the UV spectra showed two bands at 21978 cm^{-1} and 27155 cm^{-1} region, which attributed to ${}^1\text{A}_1\text{g}$ ${}^1\text{A}_2\text{g}$ and ${}^1\text{A}_1\text{g}$ ${}^1\text{B}_1\text{g}$ electronic transitions respectively and this results confirm a square planar configuration.

The electronic spectra of the copper (II) complex show a single broadband around 17500 cm^{-1} . This result was consistent with a square planar structure [17]. The magnetic measurement of this complex show a value of 1.81 BM at room temperature, this value is due to the presence of one electron in a square-planar configuration.

The analysis of Zn and Cd elements of the complexes showed that these complexes have two molecules of water is bounded to the metal, these results was confirmed by infrared spectra measurements which give broad bands at 3430-3450 cm^{-1} which is due to the νOH strength group. These data were suggested that these complexes have an octahedral geometry as figure 1.

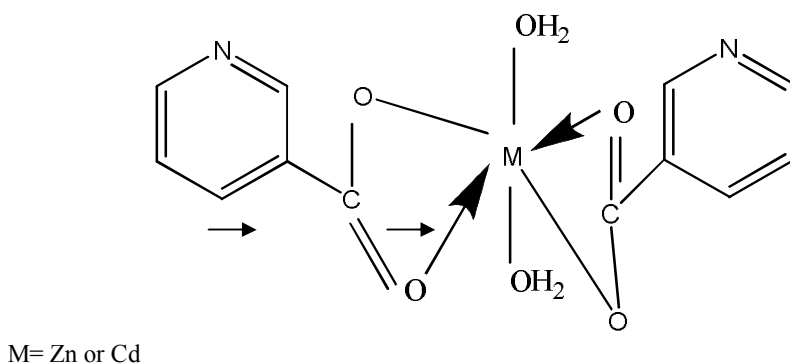


Figure 1: The suggested structure of zinc and cadmium $[\text{ML}_2]$ complexes

It can be seen from (Figure 1) for zinc and cadmium complexes that ionic coordination is formed between metals and oxygen of the carboxylic group of each molecule of ligand. Two further co-ordinate bonds are formed by donation of pairs of electron from the oxygen of the carboxyl group to metal.

The uranium nitrate complex showed weak frequency near 750 cm^{-1} due to ν_5 while a strong and sharp band at 770 cm^{-1} due to ν_3 , and 850 due to ν_6 these three bands characterized to symmetrical bending for the two bonds N-O that near the metal atom and a symmetrical bending for the same bond and for out of the plane rocking mode respectively. The symmetrical stretching for the two bands near the metal ν_2 showed band at 1040 cm^{-1} . The frequency at 1525 cm^{-1} due to ν_1 , symmetrical stretching for the third oxygen atom and the band near 1250 cm^{-1} , ν_4 , is assigned to the asymmetric stretching of two N-O bands closet to the metal atom. The ν_1 and ν_4 were both strong and found to be separated by 275 cm^{-1} for these complexes hence the nitrate group appeared to be bidentate in these complexes, however, the size of this splitter was not a good criterion for distinguishing unidentate and bidentate nitrate groups[18]. The study of the overtones and combination bands for the nitrate complex showed that the separation of $\nu_2+\nu_1$ and $\nu_2+\nu_4$, and also the separation of $\nu_2+\nu_3$ and $\nu_2+\nu_5$ were 275 cm^{-1} , and 20 respectively, since these differences were of high value, this was a good indication that the nitro group were coordinated in bidentate manner[18,19]. The infrared spectra for the uranyl group vibration UO_2^{+2} (which have three vibration ν_1 , ν_2 and ν_3 , symmetric and asymmetric stretch) (Table 2) show strong band in the region 920 cm^{-1} attributed to ν_3 of uranyl group vibration. A weak and frequency appears between 880-830 cm^{-1} which could not be attributed definitely or excluded from being ν_1 .

The analysis of the ir spectra of all complexes, there are good approximations with which to investigate the absorption bands of the -COO- group. The ν (C=C) vibrations of the pyridine ring are found in the range 3070-3020 cm^{-1} . The skeleton vibrations of the pyridine ring appear at band 1615 cm^{-1} .

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The ir spectrum of the complexes (Table2) confirms the absence of the free carboxylic acid group[20,2]. The other bands are in the 1800-1600 cm^{-1} region (Table2) is assigned bands to $\nu(\text{C}=\text{C})$ or $\nu(\text{C}=\text{N})$ of the pyridine.

The limitation to obtain a good single crystals of the complexes make us to suggest these structure and we plan in the next work to react this ligand with a large different metal ions and using ^1H NMR and C^{13} and also try to obtain a single crystals in order to more confirm the suggest structure.

Table 1: color, melting point, conductivity measurements, elemental analysis and for the complexes

Complex	Structure formula	Color	m.p. °c	$A_M(\text{ohm}^{-1}\text{cm}^{-1})$	Elemental analysis%
Co(nicotinate) ₂	Co(C ₁₀ H ₈ N ₂ O ₄)	Blue	>360	8.06	21.11(21.03)
Ni(nicotinate) ₂	Ni(C ₁₀ H ₈ N ₂ O ₄)	Pink	290d	7.16	21.04(21.61)
Cu(nicotinate) ₂	Cu(C ₁₀ H ₈ N ₂ O ₄)	Green	>360	10.11	22.39(22.35)
Zn(nicotinate) ₂	Zn(C ₁₀ H ₁₂ N ₂ O ₆)	White	>360	10.1	20.33(19.89)
Cd(nicotinate) ₂	Cd(C ₁₀ H ₁₂ N ₂ O ₆)	White	230	11.11	30.49(30.55)
UO ₂ (nicotinate) ₂	UO ₂ NO ₃ (C ₁₀ H ₈ N ₂ O ₄)	Pale yellow	>360	2.33	38.78(39.02)

Table 2: The infrared and ultraviolet spectra of the complexes

Complex	$\nu_a\text{C}$	$\nu_s\text{COO}$	$\nu_{as}\text{C}=\text{C}$	$\nu\text{C}=\text{N}$	μ_{eff}	ν_1	ν_2	ν_3	νCOH	νUO_2
Co(nicotinate) ₂	1610 _{vs}	1410 _m	1590 _s	1430 _{vs}	2.70	10250	18475	----	-----	-----
Ni(nicotinate) ₂	1630 _s	1415 _m	1610 _m	1400 _s	3.12	----	21987	27155	-----	-----
Cu(nicotinate) ₂	1600 _s	1420 _s	1590 _{sh}	1430 _m	1.81	17500	-----	-----	-----	-----
Zn(nicotinate) ₂	1600 _s	1430 _s	1570 _s	1425 _m	----	----	-----	-----	3430m	-----
Cd(nicotinate) ₂	1600 _{sh}	1430 _m	1580 _{vs}	1430 _s	-----	-----	-----	-----	3450b	-----
UO ₂ (nicotinate) ₂	1630 _s	1425 _m	1600 _s	1410 _{vs}	----	-----	-----	----	-----	920vs

Abbreviations: a:symmetrical, as: asymmetrical, b:broad, m:medium, s:strong, vs:very strong, sh: shoulder.

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