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Preparation and characterization of some metal ion complexes

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ABSTRACT

Some complexes of isocyanato benzoic acid hydrazide [ICBAH] with Metal ion sulphates salts of Co(II), Ni(II), Cu(II), Pb(II) and Cr(III) have been synthesized in a water – ethanol medium. The formations of the complexes are endothermic processes. Complex metric titration was used to determined the stoichiometry of the formed complexes. The ligand was characterized by IR and melting point studies, while the complexes were characterized by melting point, elemental analysis, conductance, IR and electronic spectral studies. The molar conductance values reveal a non-electrolytic nature. The complexes were proposed to have the formulae $[ML2]SO^{2-4}$.nH₂O (where M = Ni(II), Co(II), Cr(III), Cu(II), Pb(II) and L = isocyanato benzoic acid hydrazide and n = 2-6). The complexes are non-hygroscopic, air and photo stable crystalline powder with different melting point ranging from 202 – 280°C. The solubility of the metal-complexes in various solvents confirmed the diversity of the complexes as the ligands. From analytical and spectroscopic data obtained, the complexes were proposed to be of octahedral. The coordination process takes place through the carbonyl oxygen and the amino nitrogen atom, the anionic ion is in the outer sphere of the complexes.

Keywords : Complexes, Isocyanato benzoic acid hydrazide, electronic spectra, complexation.

INTRODUCTION

As a result of their anticonvulsant , metal extracting agent , antimicrobial , coordination capacity , analgesic , anti-inflammatory , antiplatelets , antitubercular , and antitumoral

activities ;[1] acid hydrazides are of great biological importance . Their biological activity is known to be positively enhanced on complexation to certain metal ion . 4 hydroxybenzoic acid [(5-nitro-2-furyl)methylene]hydrazide (nifuroxazide)^[1,2] is an intestinal antiseptic ; 4-fluorobenzoic acid [(5-nitro-2-furyl)methylene]hydrazide and 2,3,4pentanetrione-3-[4-[[5-nitro-2-furyl]) methylene] hydrazino]carbonyl] phenyl] hydrazone [2], which were synthesized have antibacterial activity against both Staphylococcus aureus ATCC 29213 and Mycobacterium tuberculosis H37Rv at a concentration of 3.13 µg/mL. N^{1} -[(4-Methoxybenzamido) benzoyl] - N^{2} -[(5-nitro-2-furyl)methylene]hydrazine, which was also synthesized [3] demonstrated antibacterial activity. In addition, some of the new hydrazide - hydrazones that have recently synthesized were active against the same strain of M. tuberculosis H37Rv between the concentration of 0.78 - 6.25 µg/mL [4]. Isonicotinic acid hydrazide (isoniazid, INH) has very high in vivo inhibitory activity towards M. tuberculosis H37Rv . Sah and peoples synthesized INH hydrazide - hydrazones by reacting INH with various aldehydes and ketones . These compounds were reported to have Inhibitory activity in mice infected with various strains of M. tuberculosis. They also showed less toxicity in these mice than INH [4,5], Buu – Hoi et al. A number of studies have investigated the in-vitro and in -vivo metabolism of hydrazide - hydrazones. In in-vitro metabolism studies, it has been found that hydrazide-hydrazones undergoes hydrolytic reactions and aromatic rings undergo hydroxylation reactions [4,5]. GÜlerman et al. investigated the in vivo metabolism of 4-fluorobenzoic acid ((5-nitro-2furyl)-methylene-hydrazide, a hydrazide that is effective against S. aureus ATCC 29213. They confirmed the presence of the substrate and 4-fluorobenzoic acid metabolite in blood and blood cells [5] KÜcÜgÜzel et al. studied the invitro hepatic microsomal metabolism of N- (4-chlorobenzyl)-N'-benzoylhydrazine (CBBAH). The corresponding hydrazone, benzoic acid (4-chlorophenyl)-methylenehydrazide was detected as the major in vitro metabolic product [5]. The coordinating mode of hydrazones is also of interest. Hydrazones derived from 6 - amino -5-formyl -1,3-dimethyluracil and nicotinic and isonicotinic acid hydrazide formed four coordinate complexes within Ni^{2+} , Cu^{2+} , Zn^{2+} , and Cd²⁺ which are monomeric with three binding sites occupied by the dinegative tridentate ligand and the fourth position water [5,6]. The donor atoms are the deprotonated N of the 6-amino group, the azomethine N and the carbonyl O of the hydrazone moiety. Neither the carbonyl O atoms of the uracil ring nor the endocyclic N atom of pyridine are involved in the coordination to the metal [6]

MATERIALS AND METHODS

Reagents and solvents

Ethyl -2 – isocyanato benzoate , hydrazine hydrate and metal salts were obtained from commercial sources . Sigma – Aldrich Chemical Ltd , and used without further purification All solvents were of laboratory grade and were further purified according to standard methods (Vogel. 1974).

Preparation of the ligand

The isocyanato benzoic acid hydrazides were prepared by refluxing the appropriate esters with an excess of hydrazine hydrate for about six hours (6hrs). The crude Brown solids crystals

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obtained were recrystallised from ethanol and dried over anhydrous $CaCl_2$ in a vacuum desiccators . Yield =68\% .

Preparation of the complexes

Cobalt (II) sulphate - isocyanato benzoic acid hydrazide complex :

This was obtained by mixing cobalt(II) sulphate heptahydrate 1.50 g (0.005 mol) in 50ml of distilled water with isocyanato benzoic acid hydrazide (1.50g; 0.009mol) in 50ml of ethanol. The metal salt solution was added with stirring to the solution of the ligand. The light red crystals precipitated instantly. The precipitate was filtered, washed with water, then ethanol and dried over calcium chloride in a vacuum desiccators. Yield = 46%.

Nickel(II) sulphate - isocyanato benzoic acid hydrazide complex :

Nickel(II) sulphate hexahydrate (2.70g; 0.0174 mol) was dissolved in 50ml of distilled water with isocyanatobenzoic acid hydrazide (1.50 g; 0.009 mol) in 40ml of ethanol. The metal salt solution was added with string to the solution of the ligand. The deep green crystals precipitated instantly. The precipitate was filtered, washed with water, then ethanol and dried over calcium chloride in a vacuum desiccators. Yield = 53%.

Copper(II) - isocyanato benzoic acid hydrazide complex :

(4.89g) 0.0174mol of Copper(II) sulphate and the equimolar quantities of the ligand was dissolved in about 50ml of distilled water and the ligand in about 40ml of ethanol. The two solutions was added to one another slowly by string for a while . The Brownish black crystals precipitated instantly . The precipitate was filtered , washed and dried in a vacuum desiccators . Yield = 64%

Chromium (III) sulphate - isocyanato benzoic acid hydrazide complex :

Chromium(III) sulphate hydrate of about 1.44 g (0.0034 mol) was dissolved in 40ml of distilled water with while the ligand , isocyanato benzoic acid hydrazide (1.50 g; 0.009) was dissolved in 40ml of ethanol . The salt solution was added with string to the solution of the ligand. The light yellow crystals precipitated instantly . The precipitate was filtered , washed with water , then ethanol and dried over calcium chloride in a vacuum desiccators . Yield = 52%

Lead(II) sulphate – isocyanato benzoic acid hydrazide complex :

In the preparation of Pb – ICBAH complex , 1.50g (0.009mol) of isocyanato benzoic acid hydrazide was dissolved in 50ml of ethanol . The solution was added drop wise with stirring into a solution of 1.35g (0.0045mol) of Lead(II) sulphate in 50ml of water . Stirring was continued for about 15 minutes and left standing for about 1 hour . The resulting straw color crystals were filtered and dried over CaCl₂ in a vacuum desiccators . Yield = 73% .

Instrumental Measurements

The melting points /decomposition temperatures of the ligands and complexes were taken using Gallenkamp melting point apparatus . The infrared spectra of the ligands and complexes in Nujol were taken using Unicam Scla 969 IR spectrophotometer while the electronic spectra of the complexes were recorded using 21D Milton – Roy UV-VIS. Spectrophotometer . The elemental analysis of the complexes were carried out using Complex metric titration. Conductivity measurement in EtOH was made using a WTW LF340 conductivity meter .

RESULTS AND DICUSSION

The structures of the ligand are shown below :



The preparation of the ligand can be represented by the general equation :

ArCO₂C₂H₅ + N₂H₄.H₂O $\xrightarrow{\text{reflux}}$ ArCONHNH₂ + C₂H₅OH + H₂O (where Ar = P-OCN-C₆H₄).

While the reactions of equimolar amounts of the metal salts and hydrazides yielded complexes having 1:1, or 1:2 metal :ligand stoichiometry according to general equation.

The melting point/decomposition temperatures of the complexes are above $270^{\circ}c$; this, together with their insolubility in distilled water and common organic solvents like, acetone, and benzene, but soluble in ethanol and CHCl₃ and sparingly soluble in methanol suggests a polymeric nature for the complexes .[7,8]. The complexes are non electrolytes in CHCl₃. Some physical constants for the ligand and complexes are shown in table 1.

Infrared data

The relevant infrared spectral bands for the ligands and their complexes are shown Table 2. Assignments of bands in 3,500 – 3,000 cm⁻¹ range are only tentative because bands due to v(OH) and v(NH) vibrations appear in this region as unresolved bands [9,10]. Bands around 3400 cm⁻¹ may however be assigned to $v_s(OH)$ of water of crystallization or in the case of Co, Cu, Ni ,and Cr complexes . The amide (i.e. v(C=O)) band which is located in the spectrum of isocyanato benzoic acid hydrazide at 1601 cm⁻¹ and 1640 cm⁻¹ respectively undergoes a lower shift by between 6 - 50 cm⁻¹ in the spectra of their complexes due to coordination via the carbonyl oxygen [9]. The characteristic IR absorption bands assigned to the stretching vibration of NH₂ were found at 3443 – 3428 cm⁻¹ . while the band of the hydrazinic amino group was observed at 3180.5 cm⁻¹ . As expected , vNH was found at 3325 – 3347 cm⁻¹ . Although the ligand are potentially multidentate . The infrared band assignments of the complexes of Cr (III) and Pb (II) ions (Table 2) exhibit a broad band in the range of 3163-3398 cm⁻¹ corresponding to the presence of water molecules. The stretching vibrations of the sulphate ion are usually

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observed as a sharp singlet around 1100 cm⁻¹ and a medium band around 680 cm⁻¹[10]. The v (SO₄) band in all the complexes is found around 1100 cm⁻¹ as a singlet , this is consistent with an outer sphere sulphate group. Low frequency bands below 500 cm⁻¹ have been tentatively assigned to vibrations of M - O, and M - N bands . The v_1 mode of the sulphate group around 1100 cm⁻¹ is split for the complexes of [Cr[ICBAH]]SO₄.2H₂O and [Pb[ICBAH]]SO₄.2H₂O , this splitting is usually associated with a decrease in the symmetry of the anion resulting from its coordination to the metals [11].

Molar conductivity

The conductance measurements of the prepared complexes were carried out in CHCl3 solvent and the obtained values (Table 3) were taken as a good evidence for the existence of a non-electrolyte nature [12].

Electronic Spectra

The electronic spectrum of [Ni[ICBAH]₂]SO₄. 2H₂O shows three bands , two of which have been assigned to the spin – allowed transitions , ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}$ (P) and ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}$ (F) usually observed for octahedral nickel(II) complexes [11,12]. The slight splitting of the v₃ band indicates distortion from regular geometry . The third band located around 12,500 cm⁻¹ and appearing as shoulder of the v₂ band has been assigned to a spin – forbidden transition to the spin singlet ¹Eg level ^[12]. The v₁ band usually expected in the near infrared region (below 10,000 cm⁻¹) could not be observed as the region is outside the spectral range of the instrument[11,12]. For [Cu[ICBAH]₂]SO₄. 2H₂O , the electronic spectra of the complex show a single broad band which is d→d bands located at 14,184 cm⁻¹ and is a characteristic of a distorted octahedron.

The electronic spectrum of $[Co[ICBAH]_2]SO_4.H_2O$ shows a band at 20,000 cm⁻¹ and a shoulder at 19.048 cm⁻¹ which have been assigned to transitions from the ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ level and ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ levels respectively. The v_1 band expected around 8,000 cm⁻¹ could not be located due to the spectral limitations of the instrument. The Cr (III) complex spectrum shows several bands (Table 3) due to ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ and ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ transitions. An octahedral structure was suggested.

The electronic spectral data of the [Cr[ICBAH]]SO₄ $.2H_2O$ complex show three bands at 33222 cm-1, 29761cm-1 and 26809 cm-1 attributed to charge transfer transition and an octahedral geometry was proposed for this complex. The electronic spectrum of [Pb[ICBAH]]SO₄ $.2H_2O$ complex reveals two absorption bands at 33057cm-1 and 24844 cm-1 due to the presence of a charge transfer transition and an octahedral geometry was suggested for this complex .[10,11]

CONCLUSION

Based on their physiochemical properties, the following skeletal structures (**a** and **b**) were proposed for some of the complexes :



Table 1 : some physical constant of the ligands and complexes

Compounds	Formula	Formula Weight	Colour	MPT/DEC TEMP	Yield	l% %M	%SO4
ICBAH	$C_7H_7N_2O_2CN$	161.18	Brown	202 ⁰ c	68%	-	-
[Co[ICBAH]2]SO4.H	H ₂ O C ₁₄ H ₁₆ N ₄ O ₉ C	NSCo 493.36	Pink	264°c	46%	11.96	19.45
[Cu[ICBAH]2]SO4. 2H2O	C ₁₄ H ₁₈ N ₄ O ₁₀ C	NSCu 517.86	Blue	280°c	64%	(11.95) 12.26 (12.24)	(19.42) 18.54 (18.50)
[Ni[ICBAH]2]SO4. 2H2O	C ₁₄ H ₁₈ N ₄ O ₁₀ CN	NSNi 513.36	Light Green	275°c	53%	11.49	18.70
[Cr[ICBAH]]SO4 .2H ₂ O	$C_7 H_{11} N_2 O_6 CNSCr$	345.18	Light Yellow	278°c	52%	15.06	27.81
[Pb[ICBAH]]SO4.2H2O	$C_7 H_{11} N_2 O_{\delta} CNSPb$	500.18	Straw	265°c	73%	41.39 (41.29)	19.19 (18.22)

Note : Figures in bracket are calculated values

S/N	Compounds	v [OH]	v[NH]	v[C=O]	$\Delta v[C=O]$	v[C=N]	$\Delta v[C=N]$	$v[SO^{-2}_4]$	v[M-N]	v[M-O]
Ι	ICBAH	-	3320m	1640s	-	1620	-	-	-	-
II	[Co[ICBAH]2]SO4.H2O	-	3234m	1620s	-20	1568	-52	1115	431w	470w
III	$[Cu[ICBAH]_2]SO_4.$ 2H ₂ O	-	3191m	1601s	-39	1551	-69	1089	461w	485m
IV	[Ni[ICBAH] ₂]SO ₄ . 2H ₂ O	3427br	3159m	1646s	-6	1578	-42	1076	485w	554m
v	[Cr[ICBAH]]SO ₄ .2H ₂ O	-	3350m	1630s	-10	1608	-12	1100 632m	447w	536m
VI	[Pb[ICBAH]]SO ₄ .2H ₂ O	3300br	3300br	1590s	-50	1565	-55	1114 617m	400w	520w

Abbreviation : br = broad, S = strong, sp = Split, m = medium, w = weak

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S/N	Compounds	λ_{\max} (cm ⁻¹)	□ m*	suggested stereo – chemistry	
Ι	[Co[ICBAH]2]SO4.H2O	20,000	0.00	Octahedral	
Ii	[Cu[ICBAH] ₂]SO ₄ . 2H ₂ O	19,048 (sh)	0.00	distorted octabedral	
		14,184	0.00	distorted octanedral	
iii		21,053		distorted octahedral	
	[NI[ICBAII]2]504. 21120	13,793	0.00		
		12,500 (sh)			
iv		33,2222		octahedral	
	[CI[ICDAH]]504.2H20	29,761	0.00		
		26,809			
V	[Pb[ICBAH]]SO ₄ .2H ₂ O	33,057	0.00	ootobodrol	
		24,844	0.00	octaneurai	
		411	1 11		

Table 3 : Electronic Data for the Complexes

Abbreviation: sh = shoulder

Table 4. Solubility of the ligands and metal complexes in some selected solvents

Ligands/complexes	Ethanol	Distilled water	Benzene	CHCl ₃	Acetone	Methanol
ICBAH	S	NS	NS	S	SS	SS
[Co[ICBAH]2]SO4.H2O	S	NS	NS	S	NS	SS
[Ni[ICBAH] ₂]SO ₄ . 2H ₂ O	S	NS	NS	S	NS	SS
[Cr[ICBAH]]SO _{4.} .2H ₂ O	S	NS	NS	S	NS	SS
[Pb[ICBAH]]SO ₄ .2H ₂ O	S	NS	NS	S	NS	SS
[Cu[ICBAH] ₂]SO ₄ . 2H ₂ O	S	NS	NS	S	NS	SS

Note : S-Soluble, SS-Slightly Soluble, NS-Not Soluble

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