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Physicochemical Studies of Cobalt(II) and Copper(II) Complexes of Butyrylacetic Acid Hydrazides

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ABSTRACT

Butrylacetic acid hydrazide (BUTAH) and its Cobalt(II) and Copper(II) complexes were synthesized and characterized by elemental analysis, infrared and ultraviolet spectroscopy. The results showed that the hydrazides reacted with the cobalt (II) metal salts in 1:3 (metal-ligand) molar ratio and 1:2 molar ratio for copper(II) .The infrared spectra of the BUTAH showed that ν(C=O), the carbonyl stretching mode called "amide1" band, the coupling between the in-plane bending δ(N-H) and ν(C-N) called the "amide II" band and the stretching frequency for the amino group ν(NH_2). All experienced bathochromic shifts in the complexes suggesting the coordination of the moieties to the metal ions. The absorption spectra of Co(BUTAH) $)_3X_2$ (where X = NO_3, Cl, OAc and 1/2 SO_4 showed $^4T_{1g} \rightarrow {}^4T_{2g}$ transitions at 15,337-16,077cm^{-1} with a shoulder each at 14,706 cm^{-1} and 16,103 cm^{-1} and 16051 respectively. The $^4T_{1g} \rightarrow {}^4T_{1g}$ (P) were observed at 18,382 18,484 cm^{-1} , 18,939 cm^{-1} and 19,230 cm^{-1} for $Co(BUTAH)_3Cl_2$, $Co(BUTAH)_3NO_3$, $Co(BUTAH)_3(OAc)_2$ and $Co(BUTAH)_3SO_4$ respectively consistent with a six-coordinate octahedral geometry. All the copper(II) complexes experienced a single broad band between 13,870-14,993 cm^{-1}assigned to a $^2T_2 \rightarrow {}^2E$ transition for a tetrahedral geometry.

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INTRODUCTION

Hydrazides, its analogues and metal complexes have continued to attract interest in the literature because of their ability to readily coordinate to a variety of elements particularly transition metals using carbonyl oxygen and amino nitrogen as donor atoms [1-3]. The study of the chemistry of the metals in such systems and the biological studies of the various complexes formed have continued to receive the attention of coordination Chemists [4-6].

Apart from the interesting structural chemistry of hydrazides and its metal complexes, they have found applications in the industry as metal extractants, in wastewaters, polymer stabilization and ion exchange problems [7-12]. There are strong and documented evidences that a great number of hydrazides and their complexes exhibit biological activity [13-21].

In this report we present the results of our investigations on the synthesis, spectral and biological studies of Co(II) and Cu(II) complexes of butyrylacetic acid hydrazides. The complexes are new and represent the first systematic study of butyrlacetic acid hydrazides.

MATERIALS AND METHODS

Reagents grade

$Co(CH_3COO)_2\cdot 4H_2O$, $CoCl_2\cdot 6H_20$, $CoSO_4\cdot 7H_2O$, $Co(NO_3)_2\cdot 6H_2O$ $Cu(CH_3COO)_2\cdot H_2O$, $CuCl_2\cdot 2H_2O$, $CuSO_4\cdot 5H_2O$, $Cu(NO_3)_2\cdot 2.5H_2O$, $Zn(CH_3COO)_2\cdot 2H_2O$, $ZnSO_4\cdot 7H_2O$ were of reagent grade or purer.

Preparation of the ligands

Ethyl butyrylacetate (30 ml, 0.019 mol) was added dropwisely to hydrazine hydrate (9 ml 0.019 mol) in a quick fit conical flask fitted with a reflux condenser. On the addition of about 20ml of the ester, an off-white coloured paste was observed. The remaining 10 ml was added and the mixture heated under reflux for the next 15 minutes after which 140 ml ethanol was added which dissolved the paste to give a resulting faint yellow solution. The reflux process was continued for the next 4 hours after which the ethanol was distilled off. The remaining peach coloured suspension was transferred to a 250 ml beaker which on cooling gave a crystalline cream precipitate that was later filtered by suction, washed with deionised water and dried in a dessicator over calcium chloride (Yield 16.6 g; 62 %).

Synthesis of the Complexes

Preparation of $[Co(BUTAH)_3NO_3]$

$Co(NO_3)_2\cdot 6H_2O$ (2.02 g, 0.0069 mol) dissolved in 40 % methanol (15 ml) was added dropwisely to butyrylacetic acid hydrazide (2 g, 0.0139 mol) dissolved in 10 ml methanol with stirring on a magnetic stirrer. The resulting mixture was left to stir for an hour after which it was filtered washed with 40% methanol, deionised water and dried over calcium chloride (Yield 2.33 g, 72 %). The other complexes were similarly prepared.

Physical measurements

Elemental analysis for C, H, and N were determined using a Perkin-Elmer 240C elemental analyzer. The percentage metal was determined using complexometric titration using EDTA [22]. Infrared spectra were recorded on a Nicolet Avatar 330 FT-IR spectrophotometer using KBr discs. Electronic reflectance spectra of the ligands and complexes were recorded using Genesys 10 scanning spectrophotometer (Thermo Electron Corporation).

RESULTS AND DISCUSSION

The formation of butyrylacetic acid hydrazides proceeded generally in appreciable yields as shown in the following equations:

$C_3H_7COCH_2COOR' + H_2NNH_2 \rightarrow C_3H_7COCH_2CONHNH_2 + R'OH$

The reaction of the metal salts and the respective ligands to form complexes can be represented as:

$MX_2\cdot xH_2O + yC_3H_7COCH_2CONHNH_2 \rightarrow M[C_3H_7COCH_2CONHNH_2]_n + xH_2O$

M = Co (y = 3, n = 3) or Cu (y = 2, n = 2)

The analytical data are presented in Table 1. The complexes were obtained in different shades of colours ranging from purple to green. The complexes showed varying degree of solubility in protic solvents like methanol and ethanol but are insoluble in water.

Table 1: Analytical data of ligand and complexes

Compound	FW	Colour	% Yield	Mpt (^{0}C)	% Metal Calculated (Observed)			
					Metal	C	H	N
BUTAH	144.18	White	62	218-220	—	49.99 (49.66)	8.39 (8.32)	19.43 (19.31)
$Co(BUTAH)_3(OAc)_2$	609.55	Purple	56	256	9.67 (9.60)	43.35 (43.25)	6.95 (6.63)	13.79 (13.72)
$Co(BUTAH)_3Cl_2$	562.46	Purple	79	196	10.48 (10.03)	38.44 (38.53)	6.45 (6.68)	14.94 (15.02)
$Co(BUTAH)_3SO_4$	587.53	Purple	72	286	10.03 (10.23)	38.80 (38.70)	6.18 (6.25)	14.30 (14.40)
$Co(BUTAH)_3NO_3$	615.47	Purple	72	270	9.57 (9.62)	35.13 (35.01)	5.90 (6.04)	18.21 (18.36)
$Cu(BUTAH)_2(OAc)_2$	469.98	Dirty green	36	206	13.52 (13.69)	40.89 (41.20)	6.43 (6.30)	11.92 (11.63)
$Cu(BUTAH)_2Cl_2$	422.89	Reddish brown	39	210	15.03 (14.92)	34.08 (34.22)	5.72 (5.47)	13.25 (13.20)
$Cu(BUTAH)_2SO_4$	447.96	Dirty green	56	174	14.18 (14.21)	32.18 (43.70)	5.40 (6.67)	12.51 (16.46)
$Cu(BUTAH)_2(NO_3)_2$	475.91	Dirty green	34	188	13.35 (13.45)	30.29 (30.32)	5.08 (5.31)	17.66 (17.41)

Infrared Spectra

The principal infrared bands for the ligands and its complexes are presented in Table 2. There are three major vibrations that have been used successfully to infer coordination of ligands to the metal in the spectra of complexes of hydrazides [2]. These are the ν(C=O), the carbonyl stretching mode called "amide1" band, the coupling between the in-plane bending δ(N-H) and ν(C-N) called the "amide II" band and the stretching frequency for the amino group $\nu(NH_2)$. In the butyrylacetic acid ligand, the amino band $\nu(NH_2)$ was observed as a medium strong band centred at 3460 cm^{-1}. This band was shifted to 3200-3180 cm^{-1} in the cobalt (II) complexes and 3404-3237 cm^{-1} in the copper(II) complexes. This indicates coordination of the metal to the amino group. Similarly, the "amide I" band observed at 1618 cm^{-1} in the ligand was shifted to 1570-1500 cm^{-1} in the cobalt(II) complexes and 1580-1561 cm^{-1} in the copper(II) complexes. The "amide II" band observed at 1592 cm^{-1} in the ligand, also shifted to between 1486- 1456 cm^{-1} in the cobalt(II) complexes and 1487-1573 cm^{-1} in the copper(II) complexes. The spectral features observed are consistent with the structural patterns of the compound and those of the hydrazides already reported in the literature [1, 2, 5, 6].

Electronic Spectra

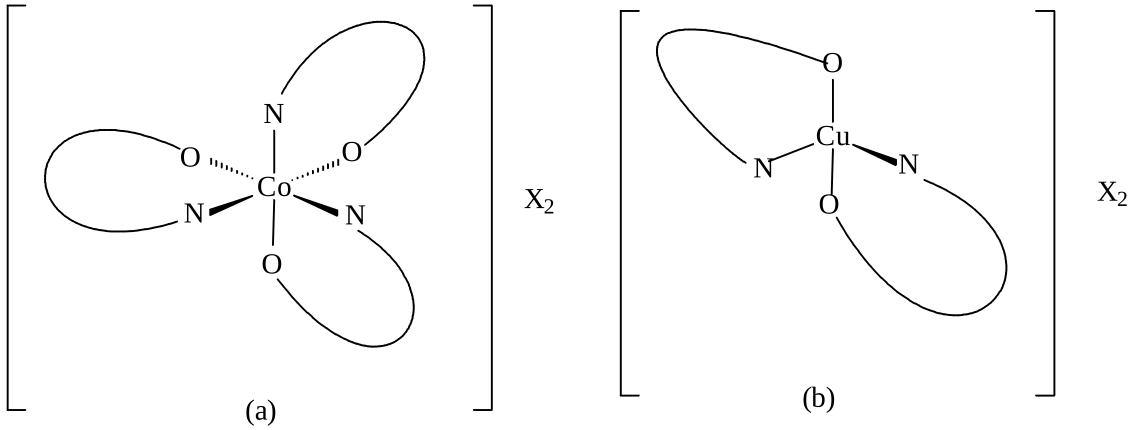
The solid electronic reflectance spectra of the ligands and complexes studied are presented in Table 3. The spectra of the compounds have been assigned by comparing the observed values with previous work done on similar systems [24-26]. The absorption spectra of BUTAH in the uv region exhibited a band at 45,045 cm^{-1} assigned to $\pi \rightarrow \pi^*$ transitions of the carbonyl group within the ligand. In the complexes, this band was observed between 41,494 - 48,077 cm^{-1}. A second band present in the complexes in the range 35,335 - 36101 cm^{-1} correlated with the $\pi \rightarrow n$ transition of the carbonyl. The $n \rightarrow \pi^*$ transitions in the complexes were observed at 31,949 – 33,223 cm^{-1}. The uv absorption spectra of the metal complexes were similar. The presence of different cations leads to a weak shift towards higher energies in some of the complexes. These might be correlated with the involvement of nitrogen and oxygen atoms from the ligand in coordination which causes a strengthening of C=O and NH_2 bonds involved in the charge transfer process [24-26].

In the visible region, the experimentally observed transitions for cobalt(II) have been reported as $^{4}T_{1}g \rightarrow {}^{4}T_{2}g$, $^{4}T_{1}g \rightarrow {}^{4}A_{2}g$, and $^{4}T_{1}g \rightarrow {}^{4}T_{1}g(P)$ denoted as ν_1, ν_2 and ν_3 transitions respectively [7-12] . $Co(BUTAH)_3(NO_3)_2$, $Co(BUTAH)_3Cl_2$, $Co(BUTAH)_3SO_4$ and $Co(BUTAH)_3(OAc)_2$ showed the $^{4}T_{1}g \rightarrow {}^{4}A_{2}g$ transitions at 15,337 – 16,077 cm^{-1} with $Co(BUTAH)_3Cl_2$, $Co(BUTAH)_3(OAc)_2$ and $Co(BUTAH)_3SO_4$ having a shoulder each at 14,706 cm^{-1} , 16,103 cm^{-1} and 16,051 cm^{-1} respectively. $^{4}T_{1}g \rightarrow {}^{4}T_{1}g(P)$ transition was observed at 18,382 cm^{-1}, 18,484 cm^{-1}, 18939 cm^{-1} and 19,230 cm^{-1} for $Co(BUTAH)_3Cl_2$, $Co(BUTAH)_3(NO_3)_2$, $Co(BUTAH)_3(OAc)_2$ and $Co(BUTAH)_3SO_4$ respectively. This is consistent with observations expected for a high spin octahedral geometry.

The electronic absorption spectra of $Cu(BUTAH)_2Cl_2$, $Cu(BUTAH)_2(OAc)_2$, $Cu(BUTAH)_2(NO_3)_2$ and $Cu(BUTAH)_2SO_4$ showed one broad absorption band at 13,870 cm^{-1}, 14,993 cm^{-1} , 14,925 cm^{-1} and 14,556 cm^{-1} respectively and is assigned to a $^{2}T_{2} \rightarrow {}^{2}E$ transition. These bands are assigned to the d-d transitions in the complexes. The observed spectra of the Cu(II) complexes are in conformation with tetrahedral geometry as there were no splitting of bands as a result of Jahn-Teller distortion found in octahedral geometry arising from unequal occupation of the e_g pair of orbitals (d_{z^2}, $d_{x^2-y^2}$).

CONCLUSION

The cobalt(II) and copper(II) ions coordinates to three and two units of the hydrazides moiety respectively using the amide carbonyl C=O and the amino moiety of the hydrazides. This is supported by the elemental analysis and the infrared spectral studies. The electronic spectral bands observed are consistent with an octahedral geometry Fig 1(a) for the cobalt(II) complexes while the copper(II) complexes adopt a plausible four coordinate tetrahedral geometry Fig.1(b).



(a) (b)

R = $CH_3CH_2CH_2COCH_2$; X = Cl, NO_3, CH_3COO, or 1/2SO_4 ;  = $RCONHNH_2$

Fig. 1: Suggested Structures for the Complexes

Table 2: Infrared and Electronic Spectra of the Compounds

Compound	Infrared Bands (cm^{-1})				Electronic Transitions (cm^{-1})	
	Amide I	AmideII	v(NH_2)	v(C=O)	d-d bands	Intra ligand bands
BUTAH	1618(m)	1592(w)	3460(m)	1727(w)		45,045
Co(BUTAH)$_3$(OAc)$_2$	1508(w)	1456(w)	3183(w)	—	18,939, 16,103sh, 15,385	
Co(BUTAH)$_3$Cl$_2$	1500(w)	1486(w)	3200(w)	1568(s)	18,382, 16,077sh, 14,706	47,373, 35,336
Co(BUTAH)$_3$SO$_4$	1570(s)	1485(s)	3196(m)	—	19,230, 16,051sh, 15,385	
Co(BUTAH)$_3$NO$_3$	1500(w)	1485(w)	3195(w)	1568(s)	18,484, 15,924sh, 15,337	41,494, 35,336
Cu(BUTAH)$_2$(OAc)$_2$	1566(s)	1487(m)	3237(w)	1711(m)	14,993	48,083, 32,258
Cu(BUTAH)$_2$Cl$_2$	1561(s)	1491(m)	3275(w)	1701(m)	13,870	46,083, 36,101
Cu(BUTAH)$_2$SO$_4$	1583(s)	1570(s)	3405(w)	1727(m)	14,556	
Cu(BUTAH)$_2$(NO$_3$)$_2$	1580(s)	1573(w)	3308(w)	1709(m)	14,925	31,949

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