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Studies on Cu (II) and Ni (II) Sulphate Chelates of Benzyl, Salicylic and Acetyl Salicylo-Hydrazones

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Abstract: Six complexes of Cu(II) and Ni(II) sulphate of acetaldehyde, benzaldehyde and salicylic acid with salicylic hydrazide were synthesized and characterized. The hydrazone acts as neutral bidentate clones coordinating *via* the carbonyl oxygen and its azomethine nitrogen, while the sulphate ions are in the outer coordination sphere. The bioactivities of ligands were enhanced on complexation.

Keywords: sulphate chelates, salicylic hydrazides, acetyl salicylo-hydrazones, hydrazones

Introduction

The chemistry of hydrazones has been of interest due to their biological and physiological activities (Nwabueze, 1992; Iskander *et al*., 1974). Hydrazones have known biological activity that can be positively altered on complexation to some metals (Ni, Co and Cu) (Gallego *et al*., 1979). Solvent medium and the method of preparation often determine the chemical nature of the complexes formed by the ligands (Alcock *et al*., 1972). Divalent metal ions are required in many biological processes, which can either help to define and maintain proper or active conformation of biopolymers or mediate an interaction between two or more molecules (Aliyu *et al*., 2006). Their coordinating capacity and their use as metal extracting activities are also of interest. Hydrazones can coordinate with metal ions through three possible coordinating sites: carbonyl oxygen, nitrogen of the primary amino group and azomethene nitrogen (Bassete *et al.,* 1979). Hydrazones derived from the condensation of salicylohydrazides with acetaldehyde, benzaldehyde and salicylaldehyde with their Fe(II) and Co(II) complexes, have already been reported (Karau *et al.,* 2006).

This study investigates the acetaldehyde salicylo-hydrazone (A_aSH), benzylaldehyde salicylo-hydrazone (A_bSH) and salicylaldehyde salicylo-hydrazone (SSH) ligands and their Ni(II) and Cu(II) complexes, their geometry and biological activity.

Materials and Methods

All the solvents used were of molar grade. The reagents were the product of Aldrich Chemical Co. and BDH and used without further purification.

Preparation of ligands. The ligands were prepared *via* their hydrazides as described in the literature (Aliyu, 2006) and recrystalized from absolute dry ethanol.

Preparation of complexes: For preparation of $[Ni(A_aSH)_2]SO_4.H_2O$, one gram (0.060 M) of A_aSH in 80 ml of absolute ethanol was added to 2.4 g (0.009 M) $NiSO_4.H_2O$ in 50 ml of deionised water while stirring in a 250 ml beaker. Yellowish green crystals pecipitated immediately. Stirring was continued for further 10 min then allowed to stand for one hour. The precipitate was washed with water, then ethanol and dried in a desicator over $CaCl_2$.

$[Cu(A_aSH)_2]SO_4.H_2O$ was prepared in similar manner.

For preparation of $[Cu(A_bSH)_2]SO_4.H_2O$, 1.08 g (0.0075 M) A_bSH in 75 ml of absolute ethanol was mixed with 1.2 g (0.0075 M) $CuSO_4$ in 50 ml deionised water in 250 ml beaker and stirred. There was an instant precipitation of grey crystals. Stirring was continued for 10 min and then left to stand for one hour. The crystals were filtered, washed with water followed by ethanol and finally dried over $CaCl_2$ in desicator overnight.

$[Ni(A_bSH)_2]SO_4.H_2O$ was prepared similarly.

$[Cu(ASSH)SO_4.H_2O$ and $[Ni(SSH)SO_4.H_2O$ were also prepared in similar manner as given above.

Instruments. The infrared spectra of the ligand and complexes were recorded in nujol on a Perkin-Elmer 1750 FT spectrophotometer, while the electronic spectra of complexes in ethanol were recorded on a Pe-unicam ps-750 UV-visible spectrophotometer. The magnetic susceptibility of the complexes to room temperature was taken on a MBS automagnetic susceptibility balance, whereas the melting points of the ligands and the complexes were taken on Gallenkamp melting point apparatus.

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Microanalysis. The metal and SO_4 ions were determined, titrimetrically, according to the standard methods (Bassete *et al.,* 1979).

Antibacterial assays. Agar-well diffusion method as described by Karau *et al.* (2006) was used for assay. Microorganism growth from nutrient agar incubated at 37 °C for 18 h was suspended in saline solution (0.88% NaCl) and adjusted to a turbidity of 0.5 McFarland standards. The suspension was used to inoculate 90 mm diameter petri plates with sterile non-toxic cotton swab on a wooden applicator. Six milimeter diameter wells were made in the agar and filled with 50 µl of 2000 µg/ml compounds. Dissolution of the compounds was aided by 20 % v/v ethanol, which did not affect growth of microorganism; the control plates were incubated in air at 37 °C for 24 h. Antibacterial activities were evaluated by measuring diameter of inhibition zone; experiments were conducted in duplicate.

Results and Discussion

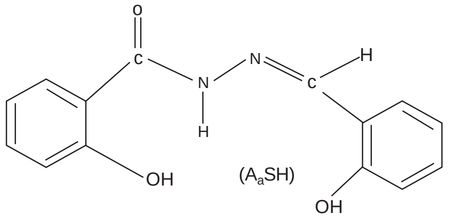
Preparation of the ligands can be represented as follows:

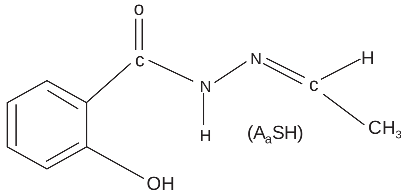
$$ArCOOC_2H_5 + N_2H_4H_2O \xrightarrow[4h]{reflux} ArCONHNH_2 + C_2H_5OH + H_2O$$

$$ArCONHNH_2 + RCHO \xrightarrow[4h]{reflux} ArCONHNCHR + H_2O$$

($Ar = C_6H_5$, $R = CH_3CHO$, C_5H_5CHO and C_6H_4OHCHO)

The complexes are insoluble in water and have high melting point/decomposition temperature above 250 °C. Both these observations are suggestive of the polymeric nature of the complexes. The physicochemical properties of the compounds are given in Table 1. The mass spectra of A_aSH, A_bSH and ASSH recorded at 70 eV electron energy show well defined peaks at *m/z*=177, 239 and 255 (M^+) with relative intensities of 84%, 82% and 78%, respectively. This data is consistent with the structures of the ligands as shown below:


(A_aSH)


(A_aSH)

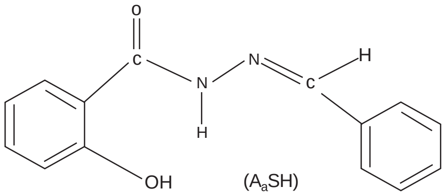

(A_aSH)

Table 1. Physicochemical properties of the compounds

Compound	Empirical formula	Formula weight	Colour	MP °C	Yield	Composition (%)				
						C	H	N	M	S
A_aSH	$C_9H_{10}N_2O_2$	178	White	300	62.30	65.58 (65.63)	4.58 (4.69)	10.98 (10.94)		
$Ni(A_aSH)_2SO_4.H_2O$	$NiC_{18}H_{22}N_4O_9S$	529	Yellow green	321	19.20	40.88 (40.83)	4.18 (4.16)	10.56 (10.58)	11.12 (11.15)	6.13 (6.05)
$Cu(A_aSH)_2SO_4.H_2O$	$CuC_{18}H_{22}N_4O_9S$	534	Dark green	214	64.70	40.40 (40.45)	4.10 (4.12)	10.46 (10.49)	11.96 (11.98)	5.98 (5.99)
A_bSH	$C_{14}H_{12}N_2O_2$	240	White	280	63.30	60.68 (60.67)	5.58 (5.67)	15.78 (15.75)		
$Ni(A_bSH)_2SO_4.H_2O$	$NiC_{14}H_{14}N_2O_7S$	413	Milky	312	67.90	40.59 (40.68)	3.28 (3.39)	6.64 (6.78)	14.16 (14.28)	7.69 (7.74)
$Cu(A_bSH)_2SO_4.H_2O$	$CuC_{14}H_{14}N_2O_7S$	418	Grey	320	69.70	40.12 (40.19)	3.26 (3.35)	6.54 (6.69)	15.24 (15.31)	7.62 (7.66)
ASSH	$C_{14}H_{12}N_2O_3$	256	Yellow	260	89.50	70.10 (70.0)	5.12 (5.0)	11.68 (11.67)		
$Ni(ASSH)SO_4.H_2O$	$NiC_{14}H_{14}N_2C_8S$	429	Light green	>360	69.70	39.12 (39.16)	3.08 (3.26)	6.48 (6.53)	13.82 (13.75)	7.38 (7.46)
$Cu(ASSH)SO_4.H_2O$	$CuC_{14}H_{14}N_2O_8S$	434	Green	>360	66.90	38.64 (38.71)	3.12 (3.23)	6.32 (6.45)	14. 64 (14.75)	7.22 (7.37)

Magnetic and electronic properties. ***Ni (II) complexes.*** The electronic spectrum of Ni $(A_aSH)_2SO_4.2H_2O$ shows two bands (Table 2), which have been assigned to the spin-allowed transitions, ^3A ® $^3T_{1g}$(P) and $^3A_{2g}$ ® $^3T_{1g}$ (F), usually observed for octahedral Ni (II) complexes. The third band could not be observed as the region is outside the expected range (below 10,000 cm^{-1}) of the instrument. The electronic spectrum of $Ni(A_bSH)_2SO_4.2H_2O$ shows two bands which have been assigned $^3A_{2g}$® $^3T_{1g}$(P) and $^3A_{2g}$® $^3T_{1g}$(F); while the electronic spectrum of Ni $(SSH)_2$ $SO_4.H_2O$ shows two bands, which have been assigned to the spin-allowed transitions, $^3A_{2g}$ ® $^3T_{1g}$ (P) and $^3A_2$® $^3T_{1g}$(F), usually observed for octahedral Ni(II) complexes (Nwabueze, 1992). The metal complexes, $Ni(A_aSH)_2$ $SO_4.2H_2O$, Ni $(A_bSH)_2$ $SO_4.2H_2O$ and $Ni(ASSH)_2$ $SO_4.2H_2O$ have magnetic moments of 2.33B.M, 2.78B.M, respectively, and are very close to the range expected for octahedral Ni(II) complexes at 2.8-2.4 B.M (Nwabueze, 1992).

Copper (II) complexes. Magnetic moments of $Cu(A_aSH)_2$ $SO_4.H_2O$, Cu $(A_bSH)_2$ $SO_4.H_2O$ and $Cu(ASSH)_2SO_4.H_2O$ are lower than the moments 1.73 – 2.2 B.M, usually expected for Cu(II) complexes. The lower values may be due to strong interaction between the Cu(II) and hydrates. The electronic spectra of the complexes show d-d bands at 3226 and 2528 cm^{-1} for A_aSH, 3205 cm^{-1} for A_bSH, 2857 cm^{-1} for ASSH and 2500 cm^{-1} as a charge transfer transition.

Infrared spectral. The diagnostic bands of the ligands and complexes (Table 3) indicate the presence of water molecules as given by the bands around 3400 cm^{-1}, while the OH bands of both the ligands and metal complexes are sited around 3200 and 3300 cm^{-1} of the spectral. The shift in the C=O and C=N frequency bands is an indication of linkage *via* the oxygen of the carbonyl and the nitrogen of the azomethine group. However, there is no evidence to suggest coordination *via* imino nitrogen and the hydroxyl group. The stretching vibrational

Table 2. Electronic and magnetic data

Compound	1_{max} (cm^{-1})	Assignment	µeff (B.M)	Deflet spectrochemistry
$Ni(A_aSH)_2SO_4.H_2O$	32981, 25008	$^3A_{2g}$(F) —® $^3T_{1g}$(P) $^3A_{2g}$ —® $^3T_{1g}$ (F)	2.33	Distorted Octahedral
$Cu(A_aSH)_2SO_4.H_2O$	32269	d —® d	1.42	Octahedral
$Ni(A_bSH)_2SO_4.H_2O$	33332, 24397	$^3A_{2g}$(F) —® $^3T_{1g}$(P) $^3A_{2g}$ —® $^3T_{1g}$ (F)	2.78	Octahedral
$Cu(A_bSH)_2SO_4.H_2O$	32057	d —® d	1.66	Square
$Ni(SSH)_2SO_4.H_2O$	32265, 28576	^3T(F) —® $^3T_1$(P) $^3A_{2g}$ —® $^3T_{1g}$(F)	2.42	Octahedral
$Cu(SSH)_2SO_4.H_2O$	25004, 28575	C —® T, d —® d	1.88	Square planar

Table 3. Diagnostic infrared data for the complexes (cm^{-1})

Compound	Du(OH)	u (C=O)	Du (C=O)	Y (C=N)	Du (C=N)	uSO_4^{2-}	u (M-O)	u (M-N)
A_aSH	3272	1643		1545	–	–	–	–
$Ni(A_aSH)_2SO_4.H_2O$	3471, 3304	1608	33	1569	24	1097 1035	532	468
$Cu(A_aSH)_2SO_4.H_2O$	3383, 3310	1618	25	1569	14	1005	567	467
A_bSH	3240	1628		1564	–	–	–	–
$Ni(A_bSH)_2SO_4.H_2O$	3443, 3236	1620	8	1566	4	1098 1031	534	468
$Cu(A_bSH)_2SO_4.H_2O$	3445, 3237	1617	11	1563	1	1097 1039	533	448
SSH	3202	1617		1560	–	–	–	–
$Ni(SSH)_2SO_4.H_2O$	3429, 3195	1608	09	1562	2	1086	533	469
$Cu(SSH)_2SO_4.H_2O$	3401, 3200	1599	18	1590	30	1076	536	469

Table 4. Bioassay of the compounds

Compound	*E.coli*	*Staphylococcus* sp.
A_aSH	+	+
$Ni(A_aSH)_2SO_4.H_2O$	++	++
$Cu(A_aSH)_2SO_4.H_2O$	++	++
A_bSH	+	+
$Ni(A_bSH)_2SO_4.H_2O$	++	++
$Cu(A_bSH)_2SO_4.H_2O$	+	+++
SSH	+	+
$Ni(SSH)_2SO_4.H_2O$	+	+
$Cu(SSH)_2SO_4.H_2O$	--	+

+++ = very active; ++ = moderately active; + = fairly active; - = non-active.

frequency of SO_4^{-2} is sited as sharp band around 1100 cm^{-1} in the spectrals of the complexes, which is an indication of non-coordination to the metal ions (Nwabueze, 1992). The M-O and M-N bonds have been tentatively assigned to frequency bands below 500 cm^{-1}.

Bioassay. The ligands, A_aSH, A_bSH and ASSH, are partially positive against *E. coli* and *Staphylococcus* sp. (Table 4). On complexation, the activity against the microbes was enhanced except for SSH complexes, which do not alter the activity against both the microbes.

Conclusion

The biological activities of ligands and their metal ion complexes follow the similar trends for hydrazones and their complexes (Nwabueze, 1992). Generally, the activity of these complexes shows promising activity against microorganisms. The ligands bind to the metal ions *via* C=O and C=N, while the SO_4^{-2} ions exist as counter ions in the complexes.

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