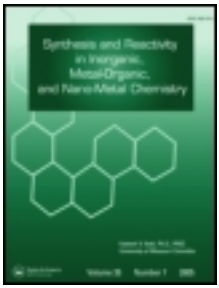

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Synthesis and Spectral Studies of Copper(II) Sulfate Complexes with Some Acetophenone Acylhydrazones

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SYNTHESIS AND SPECTRAL STUDIES OF COPPER(II) SULFATE COMPLEXES WITH SOME ACETOPHENONE ACYLHYDRAZONES

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ABSTRACT

The copper(II) complexes of the type $[CuSO_4(L)(H_2O)_2].nH_2O$ and $[CuSO_4(L^1)].nH_2O$ where L = acetophenone-benzoylhydrazone (ABH), -isonicotinoylhydrazone (AINH), -salicyloylhydrazone (ASH), -*p*-aminobenzoyl (APABH) and L^1 = acetophenone oxaloyldihydrazone (AODH), -malonoyl-dihydrazone (AMDH) and -succinoyldihydrazone (ASDH) and n = 0, 1 or 2, were prepared and characterized by elemental analyses, dehydration studies, molar conductance, magnetic moments, electronic, ESR and infrared spectra. The electronic and ESR spectra indicate a six-coordinate distorted octahedral

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geometry for all of the complexes in the solid state. ESR spectral data reveal an axial symmetry for the ABH, AINH and APABH complexes whereas the AODH, AMDH and ASDH complexes are isotropic. Most of the ligands are bidentate, coordinating through the >C=O and >C=N groups to the metal ion except AMDH and ASDH which act as quadridentate ligands bonding through two >C=O and two >C=N groups.

INTRODUCTION

Acylhydrazones, RCONHN=CR'R, exist as amide-imidol tautomers in alkaline solution and coordinate or chelate to metal ions via their carbonyl/imidolate oxygen and imido group depending on the pH of the medium, as shown in Fig. 1.

The copper(II) complexes of 2-pyridinecarboxylaldehyde-2-pyridylhydrazone[1] and salicylaldehydebenzoylhydrazone[2] show antitumor activity. The transition metal complexes of isonicotinoylhydrazide have been found to be useful in polymer coating inks and pigments[3]. Monoacyl hydrazones and acyl dihydrazones have been found to be flexidentate ligands and form complexes of structural and biochemical interest[4].

Recently, 5-halouracil complexes with Fe(III), Cr(III) and Al(III) have been reported from this laboratory[5-7] and represent potential systems for further investigation for anticancer activity. The functional group similarity between acyl hydrazones and uracil derivatives (Fig. 2), has prompted us to further investigate the bonding potentialities of acyl hydrazones.

The bis(acetophenone) oxaloyl, -malonoyl and -succinoyl dihydrazones have a multiplicity of donor groups and also have two -CONH groups like the 5-halo uracil.

We have, therefore, synthesized a number of Cu(II) sulfate complexes with the title ligands and studied their structure and bonding employing elemental analyses and physico-chemical studies such as electrical conductance in solution, magnetic succeptibility and electronic, IR and ESR spectroscopy. The results are presented in this paper.

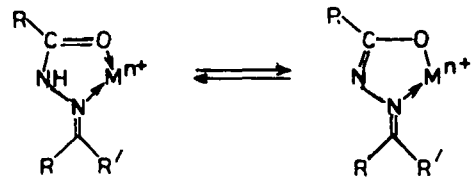


FIG. 1 Modes of Bonding of Acylhydrazones.

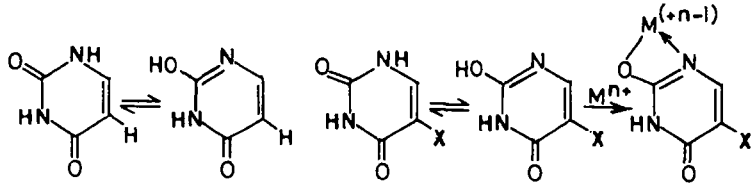


FIG. 2 Structures of Uracils and their Complexes.

EXPERIMENTAL

Materials and Synthesis of Ligands

All chemicals used were of analytical reagent or equivalent grade. The ligands acetophenone benzoylhydrazone (ABH), -isonicotinoylhydrazone, -*p*-aminobenzoylhydrazone (APABH), -salicyloylhydrazone were prepared by refluxing the corresponding hydrazides with acetophenone in dry ethanol in 1:1 molar ratio for 7-8 h[8]. Similarly, acetophenone oxaloyldihydrazone, -malonoyldihydrazone and -succinoyldihydrazone were prepared by refluxing the corresponding hydrazides with actophenone in 1:2 molar ratio. The precursor hydrazides benzoic acid hydrazide (BH) m.p. 110^0 C (lit. 112^0 C) salicylic acid hydrazide (SH) m.p. 221^0 C (lit. 220^0 C), *p*-aminobenzoic acid hydrazide (PABH) m.p. 225^0 C (lit. 226^0 C), oxalic acid dihydrazide (ODH) m.p. 234^0 C (lit. 232^0 C), malonic acid dihyrazide (MDH) m.p. 151^0 C (lit. 152^0 C) and succinic acid dihydrazide (SDH) m.p. 167^0 C (lit. 167^0 C) were prepared by literature

procedures[9]. Isonicotinic acid hydrazide (INH) was obtained from CDH Chemicals, New Delhi and used after recrystallization in ethanol.

The ligands were characterized by elemental analyses, (C,H,N) melting points, NMR and infrared spectra (Table 1).

Synthesis of Complexes

The copper(II) sulfate complexes were synthesized by reacting 50 mL of an aqueous ethanol solution (50%, v/v) containing 10 mmol (2.50 g) of $CuSO_4.5H_2O$ with the ligand solutions (10 mmol each) of ABH (2.38 g), AINH (2.39 g) ASH (2.54 g), APABH (2.38 g), AODH (3.22 g), AMDH (3.36 g) and ASDH (3.50 g) in 50 mL aqueous ethanol (50%, v/v) at room temperature (25^0 C). The precipitated compelexes were first heated on a water bath at ~90^0 C for half an hour and then filtered, washed with aqueous ethanol (50%, v/v) and finally with ether and dried in a desiccator over anhydrous calcium chloride.

Analysis and Instrumentation

The complexes were analysed gravimetrically as copper salicylaldoximate for their copper contents by literature procedures[10] after decomposition of the organic matter with aqua regia and evaporation of the residue with concentrated H_2SO_4. Sulfate was determined gravimetrically as $BaSO_4$. The C, H, N contents were determined microanalytically on a Perkin-Elmer 240C model at the Regional Sophisticated Instrumentation Centre (RSIC) and Central Drug Research Institute (CDRI), Lucknow.

Molar conductances in DMSO and DMF (10^{-3} M solutions) were measured at room temperature on a WTW conductivity meter. Room temperature magnetic susceptibilities were determined on a Faraday balance using $[CoHg(SCN)_4]$ as standard and were corrected for diamagnetism[11]. IR spectra were recorded in Nujol mulls on a Fourier-Transform infrared spectrophotometer. X-band ESR spectra were recorded on a Varian X-band spectrophotometer model E-4 at room temperature (300K) in the solid powder state using TCNE as g marker (g = 2.00277) at RSIC, Bose Institute, Calcutta. Electronic spectra were recorded on a Cary 14 spectrophotometer in Nujol mulls.

TABLE I. Analytical and Physico-Chemical Data of the Ligands.

Compound/ Empirical Formula	Colour (Formula Wt.)	Melting Point (°C)	Found (Calcd.) %			Yield (%)
			C	H	N	
ABH $C_{15}H_{14}N_2O$	White (238)	145	75.72 (75.63)	5.80 (5.88)	11.86 (11.76)	65
AINH $C_{14}H_{13}N_3O$	White (239)	162	70.43 (70.29)	5.41 (5.44)	17.50 (17.57)	65
ASH $C_{15}H_{14}N_2O_2$	White (254)	205	70.35 (70.86)	5.31 (5.51)	11.18 (11.02)	70
APABH $C_{15}H_{15}N_3O$	White (253)	170	71.54 (71.15)	5.82 (5.93)	16.49 (16.60)	60
AODH $C_{18}H_{18}N_4O_2$	White (322)	275	67.21 (67.08)	5.51 (5.59)	17.17 (17.39)	80
AMDH $C_{19}H_{20}N_4O_2$	White (336)	215	67.91 (67.86)	6.00 (5.95)	16.57 (16.67)	75
ASDH $C_{20}H_{22}N_4O_2$	White (350)	245	68.80 (68.57)	6.31 (6.28)	16.14 (16.00)	70

RESULTS AND DISCUSSION

The reactions between copper(II) sulfate pentahydrate and the ligands (L = ABH, ASH, AINH, APABH, AODH, AMDH and ASDH) were initially carried out in 1:2 (M : L) molar ratio but in all the cases only 1:1 (M : L) complexes were formed (Table II). The reactions are shown below:

$$CuSO_4.5H_2O + L \rightarrow [CuSO_4(L)(H_2O)_2].nH_2O + n'H_2O$$

n = 1 and n' = 2 for ABH and n = 0, n' = 3 for AINH, ASH, APABH and AODH

$$CuSO_4.5H_2O + L \rightarrow [CuSO_4(L)].nH_2O + n'H_2O$$

n = 1 for AMDH and 2 for ASDH, n' = 4 for AMDH and 3 for ASDH

The complexes are insoluble in common organic solvents such as ethanol, methanol, benzene, chloroform and acetone but soluble in DMF and DMSO. They were light green to light blue in colour and melted with decomposition in the 180-240^0 C temperature range. The low molar conductances (16.6-27.5 $\Omega^{-1}cm^2\,mol^{-1}$) of 10^{-3} M solutions of the complexes in DMSO or DMF suggested that they are non-electrolytes[12].

Dehyration studies in the 80-150^0 C temperature range showed a weight loss up to 110^0 C in the ABH, AMDH and ASDH complexes suggesting the presence of lattice water in the complexes. However, the ABH, ASH, AINH, APABH and AODH complexes also showed a weight loss in the range 130-150^0 C corresponding to two water molecules indicating the presence of two coordinated water molecules.

Magnetic Moments and Electronic Spectra

The copper(II) complexes in this study showed magnetic moment values between 1.76-1.95 B.M. corresponding to one unpaired electron. These values suggest the absence of spin-spin interactions between copper(II) ions. The complexes showed an intense broad absorption band in the region

TABLE II. Analytical and Physico-Chemical Data of the Metal Complexes

Compound/Empirical Formula	Colour (Formula Wt.)	M.P. / Decomp. Temp. (^{0}C)	Found (calcd.) %					Molar conductance (Ω_M) Ω^{-1} cm^2 mol^{-1}	Yield (%)
			Cu	SO_4	C	H	N		
$[CuSO_4(ABH)(H_2O)_2].H_2O$	Light Blue	210 [a]	13.93	21.17	39.66	4.41	6.16	21.4[b]	60
$C_{15}H_{20}N_2O_8S.Cu$	(451.5)		(14.06)	(21.26)	(39.87)	(4.43)	(6.20)		
$[CuSO_4(AINH)(H_2O)_2]$	Light Green	220 [a]	14.42	22.20	38.58	3.93	9.61	16.3[b]	60
$C_{14}H_{17}N_3O_7S.Cu$	(434.5)		(14.61)	(22.09)	(38.66)	(3.91)	(9.67)		
$[CuSO_4(ASH)(H_2O)_2]$	Light Blue	190[a]	14.08	21.27	40.16	3.96	6.20	16.6	70
$C_{15}H_{18}N_2O_8S.Cu$	(439.5)		(14.13)	(21.36)	(40.04)	(4.00)	(6.23)		
$[CuSO_4(APABH)(H_2O)_2]$	Light Brown	240[a]	14.21	21.33	40.28	4.20	9.31	22.6[b]	65
$C_{15}H_{19}N_3O_7S.Cu$	(448.5)		(14.16)	(21.40)	(40.13)	(4.24)	(9.36)		
$[CuSO_4(AODH)(H_2O)_2]$	Light Green	180[a]	12.20	18.45	41.56	4.22	10.80	27.5	75
$C_{18}H_{22}N_4O_8S.Cu$	(517.5)		(12.27)	(18.55)	(41.74)	(4.25)	(10.82)		
$[CuSO_4(AMDH)].H_2O$	Light Blue	215[a]	12.28	18.60	44.23	4.25	10.78	21.4	70
$C_{19}H_{22}N_4O_7S.Cu$	(513.5)		(12.37)	(18.69)	(44.40)	(4.28)	(10.90)		
$[CuSO_4(ASDH)].2H_2O$	Yellowish	185[a]	11.60	17.50	43.86	4.68	10.22	24.6	65
$C_{20}H_{26}N_4O_8S.Cu$	Green		(11.64)	(17.60)	(44.00)	(4.77)	(10.26)		
	(545.5)								

a = melts with decomposition

b = molar conductance in DMF

12,760-16,110 cm^{-1} which may be assigned to superimposed transitions $^2B_1g \rightarrow {}^2B_2g$ and ^2Eg and suggest a distorted octahedral configuration[13] (Table III).

ESR Spectra

ESR spectra of powdered samples of the ABH, AINH and APABH complexes exhibited an axial signal with two g-values at 300K (Fig. 3). The $g_{\|}$ and $g_{\perp}$ values are >2.04 (Table IV) and are consistent with copper(II) in axial symmetry with all the principal axes aligned parallel. This observation would be consistent with an elongated tetragonally distorted octahedral stereochemistry. The G factor defined as $G = g_{\|}-2/g_{\perp} -2$ which was found in the range 3.7 to 4.7 suggested that exchange between copper(II) centres is negligible[14]. The AODH, AMDH and ASDH complexes exhibited isotropic spectra with no hyperfine structure (Fig. 4). This may be due to dipolar exchange and unresolved hyperfine interactions[15]. The g_{iso} values are 2.122, 2.057 and 2.103, respectively, suggesting a geometry involving grossly misaligned tetragonal axes. The ASH complex showed rhombic spectra with $g_{zz} = 2.020$, $g_{xx} = 2.205$ and $g_{yy} = 2.274$. Such a spectral pattern may be observed for a copper(II) complex in an elongated rhombic symmetry with all the axes aligned parallel and would be consistent with distorted octahedral stereo chemistry. The R factor calculated as $R = (g_{\perp}-g_{\|})/(g_{av}-g_{\perp})$ is less than unity suggesting an essentially $d_{x^2-y^2}$ ground state[16].

Infrared Spectra

In all the ligands the ν(N-H) bands were generally broad and were observed in the 3300-3200 cm^{-1} region. In the complexes these bands either occur nearly at the same position as in the ligands or are slightly shifted to higher wave numbers suggesting no participation of the -NH group in bonding.

TABLE III. Magnetic Moment and Electronic Spectral Data of the Complexes.

Complexes	μ_{eff} (B.M.)	λ_{max} (cm^{-1})
$[CuSO_4(ABH)(H_2O)_2].H_2O$	1.95	14815
$[CuSO_4(AINH)(H_2O)_2]$	1.88	14770
$[CuSO_4(ASH)(H_2O)_2]$	1.90	15430
$[CuSO_4(APABH)(H_2O)_2]$	1.77	12760
$[CuSO_4(AODH)(H_2O)_2]$	1.85	14815
$[CuSO_4(AMDH)]H_2O$	1.76	16110
$[CuSO_4(ASDH)].2H_2O$	1.78	14770

TABLE IV. ESR Spectral Parameters of the Complexes

Complexes	$g_{\parallel}/g_{zz}$	g_{yy}	$g_{\perp}$	g_{xx}	g_{av}	G
$[CuSO_4(ABH)(H_2O)_2].H_2O$	2.193	-	2.020	-	2.079	4.7
$[CuSO_4(AINH)(H_2O)_2]$	2.293	-	2.070	-	2.176	4.1
$[CuSO_4(APABH)(H_2O)_2]$	2.289	-	2.076	-	2.177	3.7
$[CuSO_4(ASH)(H_2O)_2]$	g_{zz} =2.020	2.273	-	2.205	2.214	-

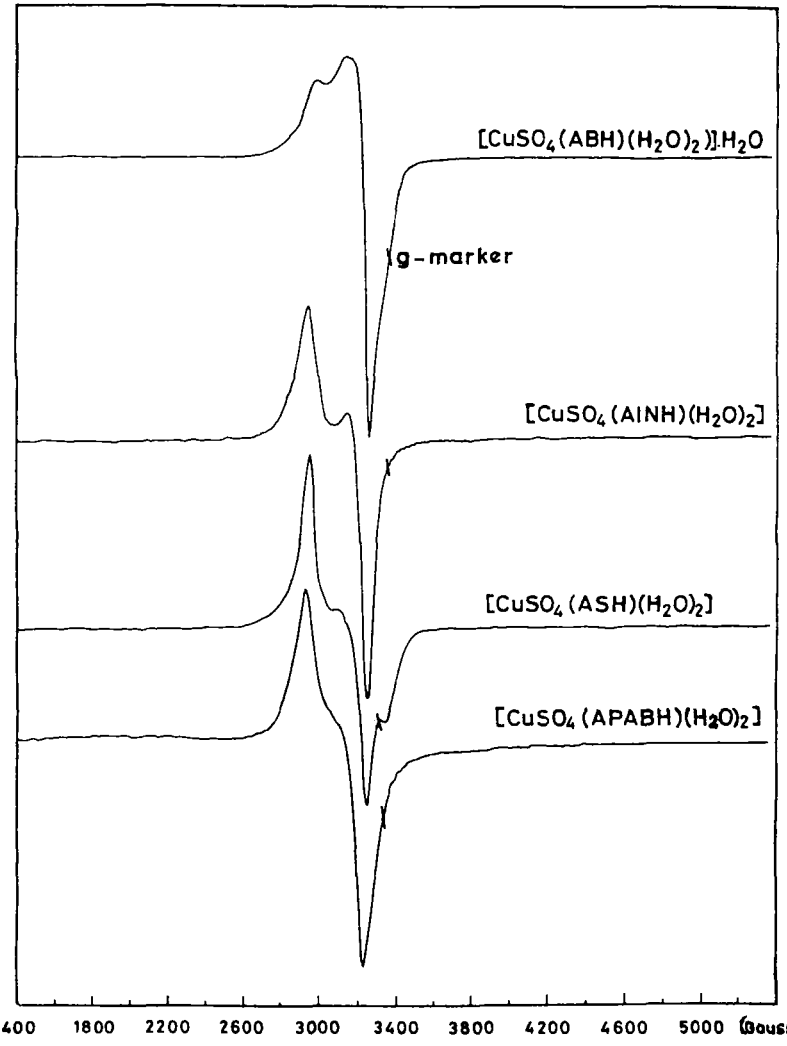


FIG. 3 ESR Spectra of Cu(II) Complexes in the Solid State at Room Temperature (300K)

In most of the complexes ν(C=O) shifted to lower frequencies by -10-30 cm^{-1} compared to ν(C=O) in the parent ligands (Table V) indicating coordination of the >C=O group to the metal ion[17].

The amide II bands in the complexes appeared to have shifted

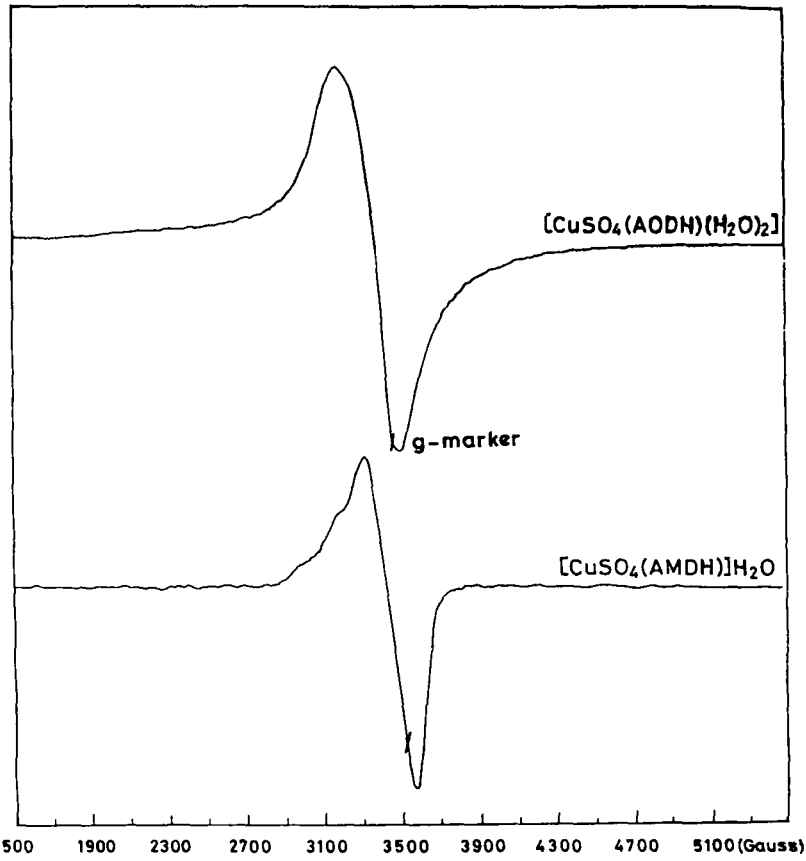


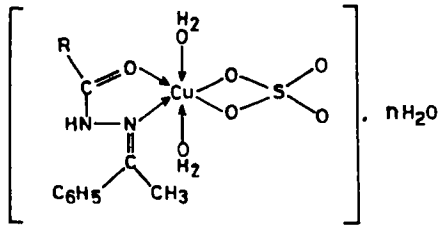
FIG. 4 ESR Spectra of Cu(II) Complexes in the Solid State at Room Temperature (300K).

considerably to lower frequency (5-15 cm^{-1}) and overlapped with aromatic ring vibrations in the same region compared to the ligand bands. A shift to higher frequency (5-20 cm^{-1}) was observed in the amide III bands in all metal complexes, further supporting coordination through the >C=O group. In the copper(II) AODH complex, ν(C=O) occurred at the same position as in the AODH ligand indicating non-involvement of the >C=O group in bonding.

The ν(C=N) frequency observed in the 1650-1620 cm^{-1} region in the spectrum of the ligands shifted to lower frequencies by 15-25 cm^{-1} in the metal

TABLE V. Important IR Spectral Bands (cm^{-1}) and their Assignments

Compounds	ν(OH) / ν(NH)	Amide I ν(C = O)	ν(C = N)	Amide II	Amide III	ν(N-N)	ν(MO)	ν(M-N)
ABH	3280 b	1650 s	1620 s	1520-1530 m	1365 s	998 w	-	-
AINH	3260 b	1665 s	1630 s	1560 m	1375 s	980 w	-	-
ASH	3410, 3250 m	1655 s	1625 s	1550 w	1380 m	972 w	-	-
APABH	3260 m	1660 s	1640 s	1550 m	1380 w	970 w	-	-
AODH	3310 m	1690 s	1650 m	1578 m	1340 w	990 w	-	-
AMDH	3290 b	1685 s	1645 m	1570 w	1350 w	998 w	-	-
ASDH	3260 m	1680 s	1640 s	1565 w	1355 m	960 w	-	-
$[CuSO_4(ABH)(H_2O)_2].H_2O$	3410 b, 3290 s	1640 s	1606 s	1545 m	1375 m	1018 s	560 w	454 w
$[CuSO_4(AINH)(H_2O)_2]$.	3390 b, 3260 s	1645 s	1610 s	1550 m	1380 m	1005 w	550 w	440 w
$[CuSO_4(ASH)(H_2O)_2]$.	3360 b, 3260 m	1640 s	1600 m	1545 m	1388 m	1010 w	560 w	450 w
$[CuSO_4(APABH)(H_2O)_2]$.	3380 b, 3260 m	1648 s	1615 m	1540 m	1390 m	1005 w	555 w	430 w
$[CuSO_4(AODH)(H_2O)_2]$.	3420 b, 3300 m	1690 m	1630 s	1575 m	1345 m	1040 w	570 w	430 w
$[CuSO_4(AMDH)].H_2O$.	3410 b, 3290 b	1660 s	1625 s	1560 m	1360 m	1010 w	565 w	425 w
$[CuSO_4(ASDH)].2H_2O$	3420 b, 3280 b	1650 s	1620 s	1550 m	1360 m	1010 w	565 w	460 w

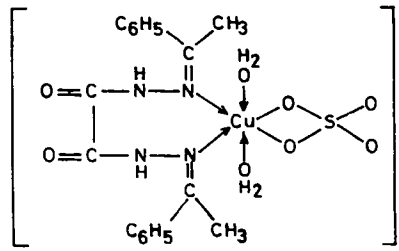


$[CuSO_4(L)(H_2O)_2].nH_2O$

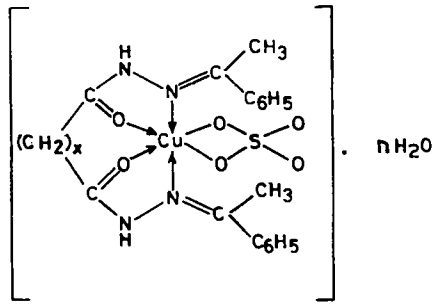
R = C_6H_5, C_5H_4N, $C_6H_4(OH)$ or $C_6H_4(NH_2)$

n = 0 for ASH, AINH and APABH

n = 1 for ABH



$[CuSO_4(AODH)(H_2O)_2]$



$[CuSO_4(L)].nH_2O$

n and x = 1 for AMDH and 2 for ASDH Complexes

FIG. 5 Representative Structures of the Complexes.

complexes suggesting coordination through the imido nitrogen[18]. A broad band in the region 3420-3380 cm^{-1} due to antisymmetric and asymmetric O-H stretching modes was observed in all the metal complexes indicating the presence of water molecules[19]. Most of the complexes also showed bands in the 900-950, 750-770

and 650-660 cm^{-1} regions due to wagging, twisting and rocking modes of the coordinated water. The pyridine ring vibrations remained either unaltered or shifted to slightly higher frequencies in the IR spectrum of the AINH complex indicating that the pyridine nitrogen is not coordinated with the metal ion.

The weak bands due to ν(N-N) appearing in the 998-960 cm^{-1} region in the ligands shifted to higher frequencies by 20-40 cm^{-1} in the complexes. This suggests involvement of the nitrogen atom of the N-N group in bonding[20]. The non-ligand bands occurring in the 570-550 cm^{-1} and 460-425 cm^{-1} regions were assigned ν(M-O)[21] and ν(M-N)[22], respectively. The bands observed in the 1050-1210 cm^{-1} region in all the complexes suggested the presence of a chelating sulfate group[23]. Based on the above observations and discussion several general structures for the metal complexes have been proposed (Fig. 5).

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