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Mixed Ligand Chelates of Ni(II) and Cu(II) with Tridentate and Bidentate Schiff Bases

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Mixed ligand chelates of the type $(NH_4)_2MGNX$ where M = Cu(II) and Ni(II), G = deprotonated tridentate dibasic Schiff's bases, N = deprotonated bidentate monobasic Schiff's bases, X = Cl^- ion. All the complexes are octahedral in geometry. The complexes have been characterised on the basis of elemental analysis, magnetic conductance and spectral data.

INTRODUCTION

Schiff bases derived from semicarbazide and amidoguanidene are reported for the formation of metal complexes. In the present study a series of Schiff's bases derived from 1-aminoguanidinium hydrogen carbonate and semicarbazide hydrochloride were synthesised. Schiff bases are acetophenone amidoguanidine (AAGH), acetophenone semicarbazone (ASCH), *o*-hydroxy acetophenone amidoguanidine ($OHAAGH_2$), salicylidine semicarbazone ($SSCH_2$), *o*-hydroxy acetophenone semicarbazone ($OHASCH_2$) and salicylidine amidoguanidine ($SAGH_2$).

EXPERIMENTAL

The chemicals used were of BDH, AR of E. Merck extra pure grade.

Preparation of Ligands

1-Aminoguanidinium hydrogen carbonate derivatives (AAGH, $OHAAGH_2$*,* $SAGH_2$*)*: The guanidine derivatives were prepared by heating methanolic solution of aldehydes and ketones (0.01 M) with dilute hydrochloric acid solution of 1-amidoguanidinium hydrogen carbonate (0.015 M).

Semicarbazide derivatives (ASCH, $SSCH_2$*,* $OHASCH_2$*)*: The semicarbazide, derivatives were prepared by heating methanolic solution of aldehydes and ketones (0.01 M) with aqueous solution of semicarbazide hydrochloride (0.015 M).

$(NH_4)_2MGNX$ *complexes:* Aqueous metal chloride (0.01 M) was treated with NH_4OH solution till blue colouration. Methanolic solution of tridentate dibasic Schiff's bases ($OHAAGH_2$, $OHASCH_2$, $SAGH_2$ and $SSCH_2$) and bidentate monobasic Schiff's bases (AAGH and ASCH) were mixed with the metal solution simultaneously in the ratio M : tridentate : bidentate : : 1 : 1 : 1. The mixture was digested on water bath for about 30–45 min. The solid coloured compounds were filtered, washed with water and methanol and dried over fused calcium chloride.

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The metal complexes were decomposed with fuming nitric acid and metal content was determined with the method reported in literature[1, 2]. C, H and N were determined and CDRI Lucknow. The analytical data are reported in Table-1. Magnetic moment measurements were carried out at room temperature by Gouy method. The magnetic moment data were made available to us at Patna Science

TABLE-1
ANALYTICAL DATA AND CONDUCTIVITY MEASUREMENT OF THE $(NH_4)_2(MGN)X$ COMPLEXES

Name of the complex (Colour)	Formula	% Analysis, found (calcd.)				Conductivity ohm cm mol
		C	H	N	M	
$(NH_4)_2Ni(AAG)(OHAAG)Cl$ (Yellowish red)	$NiC_{18}H_{29}N_{10}OCl$	43.49 (43.61)	6.01 (5.01)	28.12 (28.27)	11.61 (11.85)	195
$(NH_4)Ni(AAG)(OHASC)Cl$ (Light green)	$NiC_{18}H_{28}N_9O_2Cl$	43.41 (43.54)	5.84 (5.64)	25.14 (25.39)	11.58 (11.82)	181
$(NH_4)_2Ni(AAG)(SAG)Cl$ (Yellowish red)	$NiC_{17}H_{27}N_{10}OCl$	42.30 (42.39)	5.81 (5.61)	28.93 (29.09)	11.95 (12.19)	201
$(NH_4)_2Ni(AAG)(SSC)Cl$ (Yellowish green)	$NiC_{17}H_{26}N_9O_2Cl$	43.18 (42.27)	5.59 (5.39)	25.98 (26.13)	11.93 (12.17)	165
$(NH_4)_2Ni(ASC)(OHAAG)Cl$ (Green)	$NiC_{18}H_{28}N_9O_2Cl$	43.41 (43.53)	5.74 (5.64)	25.26 (25.39)	11.59 (11.82)	197
$(NH_4)_2Ni(ASC)(OHASC)Cl$ (Light green)	$NiC_{18}H_{27}N_8O_3Cl$	43.32 (43.44)	5.63 (5.43)	22.39 (22.52)	11.56 (11.80)	183
$(NH_4)_2Ni(ASC)(SAG)Cl$ (Brick red)	$NiC_{17}H_{26}N_9O_2Cl$	42.18 (42.30)	5.63 (5.43)	26.01 (26.13)	11.92 (12.17)	173
$(NH_4)_2Ni(ASC)(SSC)Cl$ (Yellowish green)	$NiC_{17}H_{25}N_8O_3Cl$	42.18 (42..30)	5.17 (5.07)	23.09 (23.22)	11.92 (12.17)	205
$(NH_4)_2Cu(AAG)(OHAAG)Cl$ (Grey)	$CuC_{18}H_{29}N_{10}OCl$	43.10 (43.20)	6.01 (5.80)	27.85 (28.00)	12.45 (12.00)	203
$(NH_4)_2Cu(AAG)(OHASC)Cl$ (Grey)	$CuC_{18}H_{28}N_9O_2Cl$	43.01 (43.11)	5.78 (5.58)	24.98 (25.14)	12.43 (12.67)	172
$(NH_4)_2Cu(AAG)(SAG)Cl$ (Grey)	$CuC_{17}H_{27}N_{10}OCl$	41.50 (41.97)	5.75 (5.55)	28.65 (28.80)	12.82 (13.05)	195
$(NH_4)_2Cu(AAG)(SSC)Cl$ (Deep green)	$CuC_{17}H_{26}N_9O_2Cl$	41.76 (41.88)	5.55 (5.33)	25.73 (25.87)	12.81 (13.03)	162
$(NH_4)_2Cu(ASC)(OHAAG)Cl$ (Light green)	$CuC_{18}H_{28}N_9O_2Cl$	43.00 (43.11)	5.80 (5.58)	25.00 (25.14)	12.48 (12.67)	185
$(NH_4)_2Cu(ASC)(OHASC)Cl$ (Chocolate)	$CuC_{18}H_{27}N_8O_3Cl$	42.90 (43.02)	5.50 (5.37)	22.16 (22.31)	12.40 (12.64)	175
$(NH_4)_2Cu(ASC)(SAG)Cl$ (Chocolate)	$CuC_{17}H_{26}N_9O_2Cl$	41.76 (41.88)	5.55 (5.33)	25.73 (25.87)	12.79 (13.03)	195
$(NH_4)_2Cu(ASC)(SSC)Cl$ (Deep green)	$CuC_{17}H_{25}N_8O_3Cl$	41.76 (41.88)	5.11 (4.92)	22.89 (22.99)	12.79 (13.03)	187

College laboratory, Patna. The conductivities of the complexes were determined with the help of systronics conductivity meter bridge in 10^{-3} M DMF solution. Electronic spectra of the complexes were recorded in department of chemistry, IIT, New Delhi and CDRI, Lucknow. Infrared spectra of the ligand and the metal complexes were recorded in KBr pellets on a Perkin-Elmer model 221 spectrophotometer, in the range 4000–400 cm^{-1} in the Department of Chemistry, IIT, New Delhi and CDRI, Lucknow.

RESULTS AND DISCUSSION

Elemental analysis, metal-ligand ratio and conductivity measurements data indicate these complexes to be of 2 : 1 electrolyte established in formula of compound. Magnetic moments of Ni(II) complexes lie in the range of 3 to 3.07 B.M. (Table-2). These observations indicate some orbital contribution, as the spin only value of 2 unpaired electrons system should be 2.83 B.M. The ground state electronic configuration of Ni(II) octahedral complexes is $^3A_{2g}$ and next excited state is $^3T_{2g}$. Thus due to second order Zeeman effect, magnetic moment can be calculated by the expression $\mu_{eff} = \mu_s (1 - \alpha\lambda/10Dq)$. Thus small orbiral contribution is characteristic of octahedral stereochemistry[3]. Magnetic moments of Cu(II) complexes lie in the range of 1.89–1.96 B.M. The magnetic moment value corresponds to one unpaired electron (tetrahedral, square planar, tetragonal). Ray and Sen[4] have categorised magnetic moments between 1.73–1.84 B.M. to be

TABLE-2
ELECTRONIC SPECTRA (IN SOLID STATE) AND MAGNETIC SUSCEPTIBILITY OF TYPE $[(NH_4)_2(MGNX)]$ COMPLEXES BAND ASSIGNMENT (kk)

Complexes	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	μ_{eff}
$(NH_4)_2Ni(AAG)(OHAAG)Cl$	10.4	17.2	27.5	3.05
$(NH_4)_2Ni(AAG)(OHASC)Cl$	10.5	17.7	26.0	3.03
$(NH_4)_2Ni(AAG)(SAG)Cl$	10.0	16.3	26.3	3.04
$(NH_4)_2Ni(AAG)(SSC)Cl$	10.6	16.7	26.9	3.05
$(NH_4)_2Ni(ASC)(OHAAG)Cl$	10.5	17.9	26.5	3.06
$(NH_4)_2Ni(ASC)(OHASC)Cl$	10.4	17.2	27.5	3.07
$(NH_4)_2Ni(ASC)(SAG)Cl$	10.4	16.3	26.3	3.06
$(NH_4)_2Ni(ASC)(SSC)Cl$	10.5	17.7	26.3	3.05
	$^2T_{2g} \rightarrow {}^2E_g$			
$(NH_4)_2Cu(AAG)(OHAAG)Cl$	12.8 15.5			1.94
$(NH_4)_2Cu(AAG)(OHASC)Cl$	14.5			1.96
$(NH_4)_2Cu(AAG)(SAG)Cl$	12.5 14.8			1.93
$(NH_4)_2Cu(AAG)(SSC)Cl$	12.0			1.95
$(NH_4)_2Cu(ASC)(OHAAG)Cl$	15.2			1.92
$(NH_4)_2Cu(ASC)(OHASC)Cl$	12.6 15.0			1.89
$(NH_4)_2Cu(ASC)(SAG)Cl$	12.7 15.4			1.94
$(NH_4)_2Cu(ASC)(SSC)Cl$	15.2			1.95

associated with square planar geometry and those of 1.90–2.2 B.M. belonging to tetrahedral (sp^3) or octahedral (sp^3d^2). Sacconi *et al.*[5] and Kettle[6] suggested that the values of magnetic moment for square planar complexes lie in the range 1.83–1.86 B.M. whereas for tetrahedral configuration the magnetic moment will be larger than 2.0 B.M. due to orbital contribution for the ground state configuration $^2T_2$. Thus the magnetic moment values of all the Cu(II) complexes indicate them to be Cu(II) octahedral (tetragonal geometry).

TABLE-3

INFRARED SPECTRAL DATA (cm^{-1}) AND TENTATIVE BANDS ASSIGNEMNTS OF $[(NH_4)_2(MGNX)]$ COMPLEX

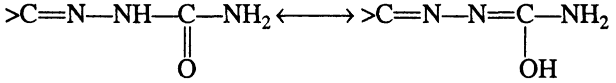
Complex	ν(C═N)	Phenolic ν(C—O)	ν(Ni—N)	ν(Ni—O)
$(NH_4)_2$Ni(AAG)(OHAAG)Cl	1625 1590	1360	500	425
$(NH_4)_2$Ni(AAG)(OHASC)Cl	1625 1595	1365	490	430
$(NH_4)_2$Ni(AAG)(SAG)Cl	1630 1610	1365	490	435
$(NH_4)_2$Ni(AAG)(SSC)Cl	1635 1585	1360	495	435
$(NH_4)_2$Ni(ASC)(OHAAG)Cl	1625 1595	1370	495	430
$(NH_4)_2$Ni(ASC)(OHASC)Cl	1630 1610	1370	490	430
$(NH_4)_2$Ni(ASC)(SAG)Cl	1635 1615	1360	490	430
$(NH_4)_2$Ni(ASC)(SSC)Cl	1625 1590	1375	480	435
$(NH_4)_2$Cu(AAG)(OHAAG)Cl	1630 1600	1365	470	450
$(NH_4)_2$Cu(AAG)(OHASC)Cl	1635 1600	1370	460	450
$(NH_4)_2$Cu(AAG)(SAG)Cl	1635 1615	1365	470	460
$(NH_4)_2$Cu(AAG)(SSC)Cl	1635 1590	1390	470	460
$(NH_4)_2$Cu(ASC)(OHAAG)Cl	1630 1600	1370	460	450
$(NH_4)_2$Cu(ASC)(OHASC)Cl	1625 1595	1380	470	450
$(NH_4)_2$Cu(ASC)(SAG)Cl	1630 1610	1360	460	460
$(NH_4)_2$Cu(ASC)(SSC)Cl	1625 1590	1385	460	460

Electronic spectra of Ni(II) complexes show three bands in the range of

10.02–10.5 kk, 16.02–1.7 kk and 26.02–27.5 kk (Table-2) and these bands are quite similar to those observed in the spectrum of $Ni(en)_3^{2+}$ species which is octahedral in nature[7]. The electronic spectral values are quite in agreement with the observed spectra[8] of the octahedral Ni(II) complexes. The band ratio ν_2/ν_1 lies in the range of 1.58–1.68 indicating octahedral stereochemistry. Electronic spectra of Cu(II) complexes shows a band maximum in the range of 14.5–15.5 kk (Table-2) which is similar to that of octahedral cupric amine complexes[9]. Some complexes show a broad shoulder 12.5 kk which may be due to Jahn-Teller distortion. Distorted octahedral structure[10] are proposed for these complexes as the spectra do not show any resemblance with those of tetrahedral[5, 11 12], or penta coordinated[13] Cu(II) complexes.

Infrared spectra

Semicarbazones (=N—NH—CO—NH_2) exhibit tautomerism due to the presence of (C=O) group in the neighbourhood of —NH, H being enolizable. This semicarbazone may coordinate with metals in both keto (I) or enolic (II) form.



$$>\mathrm{C{=}N{-}NH{-}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}NH_2} \longleftrightarrow >\mathrm{C{=}N{-}N{=}}\underset{\underset{\mathrm{OH}}{|}}{\mathrm{C}}\mathrm{{-}NH_2}$$

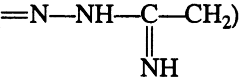
(I) (II)

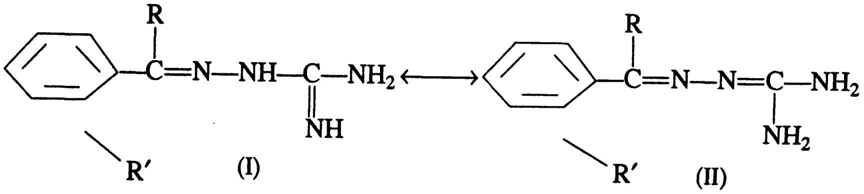
Schiff's base ligands ($SSCH_2$), $OHASCH_2$ and ASCH showed the ν(C=N) stretching frequency at around 1650–1600 cm^{-1}. This band is shifted to a lower value by about 10–25 cm^{-1} in all the complexes indicating the coordination of the nitrogen atom of the Schiff residue to the metal ion. The band at 1670–1660 cm^{-1} due to ν(C=O) in ligand disappears in complexes indicating the coordination through oxygen atom of enol from (II) by deprotonation. (Table-3)

A broad band observed around 3200 cm^{-1} in the free ligand is assigned to ν(OH) (H-bonded). This band disappears upon complexation indicating coordination through phenolic oxygen by deprotonation. This fact is further strengthened by observing a positive shift in the frequency of (C—O phenolic) vibration by 10–15 cm^{-1}.

The coordination through oxygen and nitrogen is further confirmed by the occurrence of new bands at around 460–425 cm^{-1} and 500–460 cm^{-1} in the spectra of all these complexes which may be assigned to ν(M—O) and ν(M—N) stretching frequencies respectively[14]

Thus it may be concluded that the ligands $SSCH_2$ and $OHASCH_2$ function as biprotonic tridentate ligand coordinating through deprotonation of phenolic OH and azomethine group (Schiff residue) and the ligand ASCH functions as monoprotonic bidentate coordination through deprotonation of enolic —OH and azomethine nitrogen (Schiff residue).

The amidoguanidines  $(\mathrm{{=}N{-}NH{-}}\underset{\underset{\mathrm{NH}}{\|}}{\mathrm{C}}\mathrm{{-}CH_2})$ can occur either in form (I) or form (II)



where R = CH_3, H; R′ = OH, H.

By the comparative study of IR spectra of the free ligand and their complex it is inferred that in free ligand form (I) persists but (II) is responsible for coordination mainly in alkaline medium (pH = 9–10).

An interesting feature observed in the IR spectra of their complexes is found in the region of 1700 cm^{-1}. A doublet band[15, 16] is observed at about 1700 cm^{-1}. The doublet band observed at 1700 cm^{-1} in the free ligand changes its position upon complexation, the higher one goes up to 1725–1715 cm^{-1} which is probably due to the bending mode of the $\nu(NH_2)$ group which remains practically unaffected in the complexes and shows that the NH_2 moiety does not take part in the coordination. The other component which is due to the other —NH_2 group or double band NH group disappears in the complex. This indicates involvement of one of the CN groups in coordination by deprotonation.

A strong and sharp band in the range of 500–490 $cm^{-1}$for Ni(II) complex and 470–460 cm^{-1} for Cu(II) complex were observed. No band was observed in the free ligand in this range. This band is assigned to the (M—N) streching frequency[17]. The coordination through nitrogen is further confirmed by the occurrence of these new bands.

Thus it may be concluded that the ligands $SAGH_2$ and $OHAAGH_2$ function as biprotonic tridentate ligand coordinating through deprotonation of NH_2, phenolic OH and azomethine group (Schiff residue). The ligand AAGH functions as monoprotonic bidentate coordinating through deprotonation of NH_2 and azomethine nitrogen (Schiff residue).

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