

The Complexes of Ni(II) and Cu (II) with N- Phenyl - Glycineamide-p- Arsenic Acid

Abstract

A survey of Literature 1-12 has revealed a large number of alkyl and aryl arsenic acids, which form complexes with the divalent and quadric valent metal ions. But there is no mention of the complexes of N-Phenyl glycineamide-p-arsenic acid (RH₃). So the present investigation describes its M(RH). 2H₂O types of complexes with the nickel and copper ions.

Keywords: Ligand, Spectrum, complexes, Band Frequencies, Assignable, Transition, Tentative, Tautomeric, Imidolic.

Introduction

The ligand, RH₃ of Sarabhai grade was used Nickel sulphate hexahydrate, and copper sulphate pentahydrate and other chemicals used were of B.D.H Analar grade.

M(RH₂).2H₂O- Complexes

The aqueous solution of each of the metal ions was mixed with ethanolic solution of the ligand in 1:1 molar ratio and refluxed for 30 min. On cooling, the crystals were separated. The crystals were filtered, washed 30% Warm ethanol and dried in air.

M(RH₂)₂- Complexes

The cold aqueous solutions of nickel and copper ions were treated separately with ethanolic solution of the ligand in 1:2 molar ratio. Their pH values were raised by adding 2(N) NH₄ OH and NaOH solutions respectively. The complexes formed, were filtered, washed with hot distilled water and dried over fused Ca Cl₂ in a desiccator.

Physical Measurements

The IR spectra of the ligand and complexes in nujol mulls, in the range of 4000-200 cm⁻¹ were recorded on Perkin Elmer Spectrophotometer.

No. 621 The electronic spectra of the complexes in acetone solutions were recorded on Hilger Unisec, Spectroni 20. The magnetic studies were done on Guoy's balance.

Aim of the Study

The aim of investigation describes to its M (RH).2H₂O and M(RH₂)₂ types of with the complexes with the Nickel and Copper ions.

Results Discussion

The M(RH).2H₂O- and M(RH₂)₂ complexes are slightly soluble in methanol, acetone and carbon tetrachloride. The pH Values of the formation of the complexes, their colours, analytical data, absorption maxima in their electronic spectra and magnetic moment values were incorporated in table 1



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Table-1

Complexes	Colours	ph of Formation	Analytical date			%N. Found (Caled)	Electronic spectra max, cm ⁻¹	μ eff BM
			%M Found (Caled)	%C Found (Caled)	%H Found (Caled)			
Ni(RH) 2H ₂ O	Blue	6.0	(16.00) (16.01)	26.10 (26.18)	3.51 3.54	7.60 7.63	8100 15240	3.4
Cu(RH) 2H ₂ O	Blue	6.5	17.00 (17.10)	25.82 (25.84)	3.45 (3.49)	7.50 (7.53)	16430 (35100)	2.1
Ni(RH ₂) ₂	Greenish yellow	8.5	8.18 (8.19)	31.05 (31.90)	3.30 (3.33)	8.50 (8.15)	22500 29250	0.0
Cu(RH ₂) ₂	Green	8.0	10.40 (10.42)	3.46 (31.50)	3.16 (3.28)	9.16 (9.18)	14200 17200	1.91

Magnetic Moment

$\mu_{\text{eff}}=3.4$ BM for Ni(RH). 2H₂O shows two unpaired electrons in it. Besides this, It also suggests it to have tetrahedral structure, formed by the use of sp₃ hybrid orbital's. For Cu(RH). 2H₂O, the Value has been found to be 2.1 BM, which does not fully account for its exact geometry. Each complex has magnetic moment greater than the spin only value, probably due to large orbital contribution. Ni(RH₂)₂ ($\mu_{\text{eff}}=0$) is diamagnetic but Cu(RH₂)₂ ($\mu_{\text{eff}}=1.91$ BM) is paramagnetic. Both are square planer through dsp² hybridisation.

Electronic Spectra

The absorption band at 8100 15,240 cm⁻¹ in the electronic spectrum of the Ni(RH).2H₂O Suggest the tetrahedral structure. 12 The bands may be assigned to 3T₁(F) → 3 A₂(F) and 3T₁(F) = 3T₁(P) transitions respectively. In the spectrum of

Cu(RH).2H₂O, an Intense band, which appears at 16430 cm⁻¹ may be assigned to 2 T₂ → 2E transfer. Another Band at 35100cm⁻¹ may be attributed due to charge transfer. There band positions suggest it to have tetrahedral geometry.

Intense bands at 22500 and 29500 cm⁻¹ in the spectrum of Ni (RH₂)₂, assignable to I A_{1g} → I B_{1g} and I A_{1g} → I E

Transition respectively suggest it to have the square planer structure. 14 The bands at 14200 and 17200 cm⁻¹ in the spectrum of Cu(RH₂)₂ may be assigned to


2B_{1g} → 2A_{1g} and 2B → E_g transitions respectively in favor of the square planer geometry.¹³

Infrared Spectra

A few relevant IR band are inserted in Table

2.

TABLE -2

RH ₃ cm ⁻¹	Ni(RH).2H ₂ O cm ⁻¹	Cu(RH).2H ₂ O cm ⁻¹	Ni(RH ₂) ₂ cm ⁻¹	Cu(RH ₂) ₂ cm ⁻¹	Assignments.
...	3390 bs	3395 bs.	Coordinated H ₂ O
3360 m	3360 m	3360 m	v (NH ₂)
3205 m	3205 m	3205 m	3160 m	3170 m	v(NH)
2890 s	2890 m	2890 m	2890 m	2890 w	v(ch ₂)
2790 s	2790 s	2790 s	v(OH) of arsenic acid.
2790 s	2770 s	2770 s	"
2770 s	1680 m	1680 m	v (c=o)
1680 m	1630 s	1630 s	NH ₂ deform
1630 s	1570 m	1580 m	v (c=n)
1480 s	1480 s	785 m	v (as o)
800 m	780 m	765 m	v (as o) A 
775 m	760 m	...	525 m	535 m	v (M-O)
...	...	525 vs	v (M-O)
...	520 vs	...	505 m	510 m	v (M-n)
...	v (M-n)

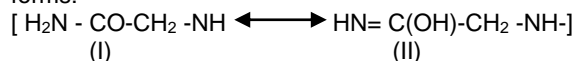
M(RH).2H₂O –Complexes

The bands at 2790 and 2770 cm⁻¹, assigned to v(oh) of - AsO₃H disappear in the complexes showing thus deprotonation and formation of M-o bonds 12. The Bands at 3360,3205,1680,1630 and 1480 cm⁻¹ assigned to v(NH₂), v (NH), v(C=o), NH₂ deformation and v(c-n) respectively remain unchanged in the complexes. The broad sharp bands at 3395-90 cm⁻¹ in the complexes may be assigned to lattice of coordinated water molecules very sharp bands 14 at 525-20 cm⁻¹ in the

complexes may be assigned to v(M-O) or superimposition of two M-O bonds.

M(RH₂)₂- Complexes

Glycineamide group of the ligand may coordinate to metal atoms either through amino nitrogen or carbonyl oxygen. But this is not alone the fact. This group may be depicted in the following two forms:

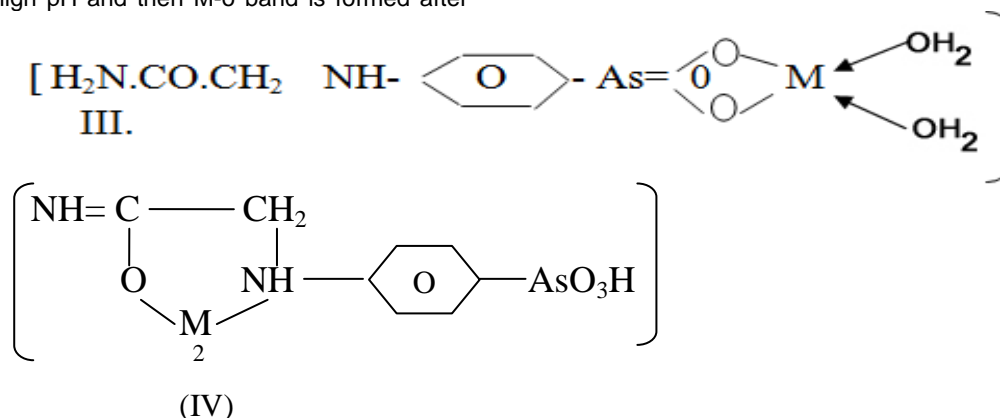


(I)

(II)

NH₂ and c=O frequencies are not observed in the complexes. CH₂ frequency also remains unchanged. So H of CH₂ does not change c=O to C(OH). If the form II be supposed to be involved in the complexation, then appearance of ν(C=N) and ν(C-O) at 15802-70 and 1270-60 cm⁻¹ respectively in the complexes explained. Since free ligand does not show ν(C=N), ν(C-O) or imidolic OH, it may be concluded that form I is formed due to tautomeric change or resonance 15 of I only at high pH and then M-O band is formed after

loss of one H⁺ (Proton). Besides this, M-N bonds are formed by coordination through imino nitrogen 16 (NH) of α= position. The fact is supported by the negative 16 (NH) from 3250 cm⁻¹ (in the legend.) To 3170-60 cm⁻¹ (in the complexes) The newly developed band 14 at 535 and 510-05 cm⁻¹ in the complexes may be assigned to ν(M-O) and ν(M-N) in further support of the facts. So the tentative structures of M(RH).2H₂O and M(RH₂) are proposed as follows.



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