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Inorganic Coordination Complexes—Part I : Synthesis and Structural Studies on Some Copper(II) Complexes of 2- and 4-Amyl Pyridines

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Complexes of 2- and 4-amyl pyridines with bivalent copper have been synthesised and their structures have been resolved on the basis of elemental analysis, conductance measurement, infrared spectra, electronic spectra and magneto-chemical investigations. Some of these complexes have been found to possess polymeric structures.

EXCELLENT coordination ability and ready availability have made pyridine and its derivatives one of the most studied classes of ligands. Complexes of various substituted pyridines with several dipositive transition metal ions have been investigated thoroughly[1-5]. The present communication entails the synthesis, characterization and stereochemistry of some newer copper(II) complexes with 2- and 4-amyl pyridines.

Materials and Methods

All the chemicals used were of B.D.H. A.R. Grade or equivalent quality. Solvents were purified and made anhydrous employing the standard literature procedures.

(i) *Preparation and Analysis of the Compounds :*

Complexes were prepared by refluxing a mixture of amine and corresponding copper(II) salt in 1 : 1, 1 : 2, 1 : 3 and 1 : 4 molar quantities in ethanol for 8-10 hours on steam bath. However, the compounds No. 7 and 8 of Table 1 are the exceptions and were obtained by heating the 1 : 1 mixture of 2-amyl pyridine with $CuCl_2$ and $Cu(NCO)_2$ respectively for 30 minutes on steam bath. The contents were allowed to stand overnight. The resulting complexes were filtered, washed with ethanol and ether, and dried in vacuum. Only 1 : 1 and 1 : 2 complexes were resulted.

In all the complexes metal copper was determined complexometrically by standard procedure[6] after destroying the organic part at first with a mixture of nitric and hydrochloric acids and then with concentrated sulphuric acid. Carbon, Hydrogen, Nitrogen, were estimated micro-analytically. Halide was determined gravimetrically as the silver salt. The results of analysis with pertinent data have been depicted in Table 1.

TABLE 1—ANALYTICAL RESULTS

Sl. No.	Compound	Colour	%Metal	%C	%H	%N	%X
1.	$Cu(4\text{-ampy})_2Cl_2$	Blue	14.58 (14.69)	55.50 (55.49)	7.02 (6.93)	6.52 (6.47)	16.35 (16.42)
2.	$Cu(4\text{-ampy})_2Br_2$	Bluish green	12.14 (12.19)	46.15 (46.02)	5.80 (5.75)	5.30 (5.37)	30.56 (30.67)
3.	$Cu(4\text{-ampy})_2(N_3)_2$	Yellowish green	14.30 (14.27)	53.85 (53.87)	6.70 (6.73)	25.00 (25.13)	–
4.	$Cu(4\text{-ampy})_2(NCO)_2$	Yellowish green	14.25 (14.27)	59.26 (59.26)	6.70 (6.73)	12.48 (12.56)	–
5.	$Cu(4\text{-ampy})_2(NCS)_2$	Bluish green	13.35 (13.30)	55.25 (55.29)	6.30 (6.28)	11.80 (11.73)	–
6.	$Cu(2\text{-ampy})_2Cl_2$	Blue	14.50 (14.69)	55.48 (55.49)	6.96 (6.93)	6.39 (6.47)	16.30 (16.42)
7.	$Cu(2\text{-ampy})Cl_2$	Pale yellow	22.46 (22.42)	42.28 (42.33)	5.25 (5.29)	4.86 (4.93)	24.95 (25.03)
8.	$Cu(2\text{-ampy})(NCO)_2$	Bluish green	21.28 (21.43)	48.49 (48.56)	5.16 (5.05)	14.20 (14.17)	–

Calculated values are given in parenthesis.
am=amyl ; py=pyridine ; X=Cl or Br.

(ii) *Physical Measurements :*

Magnetic measurements of the metal complexes were carried out on a Cahn Faraday Electrobalance using Hg[Co(CNS)$_4$] as calibrant, and diamagnetic corrections were estimated by procedure of Figgis and Lewis[7]. Electronic spectra were obtained on a Cary-14 recording spectrophotometer in nujol mull using the technique described by Lee[8]. Infrared spectrograms were recorded on a Perkin-Elmer spectrophotometer model 521 in nujol in the 2000-200 cm^{-1} region. Conductometric measurements were made in methanol.

Results and Discussion

The results of analysis have been recorded in Table 1 whereas the spectroscopic and conductance data are listed in Table 2. The magnetic measurements at various temperatures have been summarized in Table 3.

Infrared Spectral Studies :

During the early stages of investigation Cu-(2-ampy)Cl$_2$ was considered to be a monomer but at latter stages, the slight change in i.r. spectral bands as compared to ligand, poor solubility and electronic spectrum confirmed its polymeric nature.

Two absorption bands observed in the spectra of Cu(4-ampy)$_2$Cl$_2$ and Cu(4-ampy)$_2$Br$_2$ in 340-270 cm^{-1} region have been assigned as halogen sensitive vibrations[9-11]. The i.r. spectrum of Cu(2-ampy)$_2$Cl$_2$ exhibits only one obvious but broad absorption band at 326 cm^{-1}, which has been attributed to Cu–Cl mode. On the basis of similar electronic spectrum, method of preparation and poor solubility this complex resembles with Cu(2-methyl pyridine)$_2$Cl$_2$ which is a pentacoordinate dimer[12]. In Cu(2-ampy)$_2$Cl$_2$ the 2-amyl groups apparently prevent the approach of a chlorine atom of another molecule at one axial site to produce the common tetragonal polymeric structure[13,14].

TABLE 2—RESULTS OF PHYSICAL MEASUREMENTS (INFRARED SPECTRA, ELECTRONIC SPECTRA AND CONDUCTANCE)

Sl. No.	Compounds	Pseudohalogen vibrations (cm^{-1}) asym.	Pseudohalogen vibrations (cm^{-1}) sym.	(M–X)	Cu–N (hetero)	Electronic spectra cm^{-1}	Molar conductance in mhos.
1.	Cu(4-ampy)$_2$Cl$_2$	–	–	340 s 276 m	264 s 260 sh	15000	0.30
2.	Cu(4-ampy)$_2$Br$_2$	–	–	350 m 272 m	245 m 230 s	15000	0.20
3.	Cu(4-ampy)$_2$(N$_3$)$_2$	2076 s	1320 m 1302 m	–	260 s	15000	0.20
4.	Cu(4-ampy)$_2$(NCO)$_2$	2224 s	1326 m 1320 m	–	240 m 230 sh	16300	0.24
5.	Cu(4-ampy)$_2$(NCS)$_2$	2136 s	826 m	–	255 s 230 m	15000	0.18
6.	Cu(2-ampy)$_2$Cl$_2$	–	–	326 s	256 s 235 m	15500	0.20
7.	Cu(2-ampy)Cl$_2$	–	–	316 s 256 m	246 w 230 m	13000	0.25
8.	Cu(2-ampy)(NCO)$_2$	2225 s 2200 s	1300 m	–	260 s 245 m	13500	0.15

TABLE 3—MAGNETIC DATA

Sl. No.	Compound	μ B.M. at temp. 297°K	273°K	247°K	185°K	167°K
1.	Cu(4-ampy)$_2$Cl$_2$	1.83	1.81	1.80	1.78	1.76
2.	Cu(4-ampy)$_2$Br	1.82	1.81	1.80	1.79	1.75
3.	Cu(4-ampy)$_2$(N$_3$)$_2$	1.87	1.86	1.83	1.82	1.78
4.	Cu(4-ampy)$_2$(NCO)$_2$	1.95	1.92	1.91	1.87	1.83
5.	Cu(4-ampy)$_2$(NCS)$_2$	1.83	1.83	1.82	1.80	1.77
6.	Cu(2-ampy)$_2$Cl$_2$	1.82	1.80	1.79	1.76	1.75
7.	Cu(2-ampy)Cl$_2$	1.90	1.87	1.85	1.82	1.79
8.	Cu(2-ampy)(NCO)$_2$	2.10	2.16	2.23	2.27	2.30

On the basis of elemental analysis the general molecular formula comes out to be Cu(am)$_n$(X)$_2$, where am = 2- or 4-amyl pyridine X = Cl, Br, NCO, SCN, N$_3$ and n = 1 or 2. The molecular structure and geometry of the complexes have been elucidated on the basis of i.r. and electronic spectral studies, magnetic and conductance measurements.

Pseudohalogen vibrations for the complexes studied have been listed in Table 2. A sharp band in 2220-2070 cm^{-1} region and another medium absorption band in 1325-820 cm^{-1} region are assigned to asymmetrical and symmetrical pseudohalogen vibrations. Both the pseudohalogen frequencies evidently indicate the Metal-Nitrogen bonding[15].

In far infrared spectra of the complexes the absorption bands occurring in the 264-230 cm^{-1} region are attributed to $Cu-N$(hetero) stretching modes. This clearly indicates the co-ordination of amyl pyridines to $Copper^{2+}$ ion through the nitrogen of pyridine ring. The conclusion of author is in good agreement with the observation of Noji et al[16].

Magneto-Chemical Studies :

For Cu^{2+}, a d^9 system having only one unpaired electron in 3d orbitals, a magnetic moment of 1.73 B.M. is expected. The values of the magnetic moments for square planar and tetrahedral Cu(II) complexes lie in the ranges 1.83-1.86 and 1.89-1.92 B.M. respectively[17]. The magnetic susceptibility of copper(II) complexes has been studied over the temperature range 167°-297° K. The fresh samples were taken every time for all the determinations. The magnetic data are recorded in Table 3.

The azido-copper(II) complex shows weak antiferromagnetism which is probably due to the linear bridged structure similar to $Cu(pyridine)_2(N_3)_2$[18]. The azide ion may bridge either through a chain of nitrogen atoms or through only one nitrogen atom. Antiferromagnetism is expected only when the paramagnetic centres are in close proximity. All the complexes of this series except Cu(2-ampy) $(NCO)_2$ have been found to exhibit weak antiferromagnetism.

The complex Cu(2-ampy)$(NCO)_2$, unlike other copper(II) complexes of this series has been found to show weak ferromagnetic behaviour. Further, it has been observed that this complex has a greater magnetic moment than expected for the spin only value (1.73 B.M.). This unexpected behaviour may be due to the large separation of bridged planar units.

Electronic Spectral Studies :

Only one absorption band due to $^2Eg \rightarrow {}^2T_2g$ transition is expected for octahedral Cu(II) complexes[19,20]. Since ^2Eg state is highly susceptible to Jahn-Teller distortion, the Cu(II) complexes of this series possessed distorted octahedral geometry.

One broad absorption band in 13000-16500 cm^{-1} region in electronic spectra of all bis (4-ampy) copper(II) complexes have suggested tetragonally distorted octahedral structures to these complexes with halogen or pseudohalogen bridging[21-23].

The complex $Cu(2\text{-ampy})_2Cl_2$ shows an absorption band at still higher frequencies than in $Cu(4\text{-ampy})_2Cl_2$ complex, which is an indication of greater distortion. This complex is most probably a pentacoordinate dimer, which has also been supported by i.r. spectral results. Other complexes of this series give similar spectral informations and are believed to have tetragonally distorted octahedral structures.

Conductometric Studies :

A very dilute solution (conc. 10^{-3} *M*) of these complexes in formamide was subjected to conductometric studies. The measurements of molar conductance gave values ranging between 0.15-0.30 mhos. The low molar conductance values suggested the non-electrolytic nature of these complexes[24]. Thus complexes can be represented by the formula given as under :

$$[Cu(am)_n(X)_2]^\circ$$

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