(OKH and SS) express their sincere thanks to CSIR, New Delhi and U.G.C. for the award of Post-doctoral and Teacher Fellowship respectively.

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MONOMETHYL AMMONIUM SUBSTITUTED CHLORO COMPLEXES OF COBALT(II), NICKEL(II) AND ZINC(II)

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ABSTRACT

When tetrachloro cobalt(II), nickel(II) and zinc(II) complexes were treated with a variety of ligands containing nitrogen donor atoms, the following mixed ligand anionic complexes were isolated.

$[L]_2[MCl_4B]$, $[L]_2[MCl_4B'_2]$ and $[L][MCl_3B''_2]$

where, L = monomethyl ammonium ion, M = Co(II), Ni(II) or Zn(II); B = ortho-phenanthroline, 2,2′-bipyridyl or ethylene diamine; B′ = Morpholine or pyridine; and B″ = *v*-picoline, pyridine or aniline. ΛM values of the complexes in acetone are quite high indicating the 2:1 and 1:1 electrolytic nature of the above complexes. Magnetic moment values show the presence of three and two unpaired electrons in the case of cobalt(II) and nickel(II) complexes. The IR spectra of the complexes indicate strong absorption bands of both the monomethyl ammonium ion and the nitrogen donor ligands. The ligand absorption bands are modified as a result of bonding to the metal. Direct evidence of bonding was obtained by the occurrence of ν (M–N) ~ 350 cm^{-1} in the fat IR of the complexes. Studies of bands in the visible electronic spectra provide evidence for an octahedral geometry for Co(II) and Ni(II) complexes. The Zn(II) complexes are probably octahedral on the basis of analysis, conductance and IR spectral data.

INTRODUCTION

ALTHOUGH a large number of tetrahalo complexes of the composition $[L]_2[MX_4]$ where LX = tetraalkylammonium halide or pseudo halide and M = Co(II), Ni(II), Cu(II) and Zn(II) have been prepared[1–6] but little work has been done to change the stereochemistry of these complexes by reacting with other nitrogen, oxygen or sulfur donor ligands. We have earlier reported[7,8] anionic mixed ligand complexes starting from these type of tetrahalo compounds. This communication describes the preparation and

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TABLE I

Conductance, magnetic susceptibility and IR spectral data of the compounds

Compounds	Molar conductance Λ M mhos cm^2	μ_{eff} B.M.	ν(M–N)	ν(M–Cl)
$[L]_2[CoCl_4(o\text{-Phen})]$ (260°)*	212	4·90	350	220
$[L]_2[CoCl_4(2,2'\text{-bipy})]$ (260°)	220	5·10	345	210
$[L]_2[CoCl_4(en)]$ (260°)	224	4·84	350	220
$[L][CoCl_3(Py)_2]$ (130°)	152	4·96	340	225
$[L][CoCl_3(\nu\text{-Pic})_2]$ (116°)	128	5·00	355	215
$[L][CoCl_3(An)_2]$ (141°)	144	4·92	345	220
$[L]_2[NiCl_4(o\text{-Phen})]$ (260°)	232	3·12	345	220
$[L]_2[NiCl_4(2,2'\text{-bipy})]$ (260°)	224	3·04	360	215
$[L]_2[NiCl_4(en)]$ (260°)	216	2·96	340	225
$[L][NiCl_3(Py)_2]$ (167°)	130	2·90	350	210
$[L]_2[NiCl_4(Morph)_2]$ (191°)	228	3·00	340	225
$[L]_2[ZnCl_4(o\text{-Phen})]$ (260°)	208	..	360	210
$[L]_2[ZnCl_4(2,2'\text{-bipy})]$ (260°)	206	..	355	220
$[L]_2[ZnCl_4(Py)_2]$ (132°)	216	..	345	225
$[L]_2[ZnCl_4(en)]$ (260°)	202	..	360	220
$[L][ZnCl_3(\nu\text{-pic})_2]$ (124°)	140	..	350	210
$[L][ZnCl_3(An)_2]$ (154°)	154	..	360	215

* The values in the parenthesis indicate the melting points of the complexes.

characterisation of Co(II), Ni(II) and Zn(II) complexes using monomethyl ammonium cation and various mono- and bi-dentate nitrogen donor ligands.

EXPERIMENTAL

All the chemicals used were of Analar grade. To an ethanolic solution of metal chlorides, an ethanolic solution of monomethyl ammonium chloride was added in 1:2 ratio when crystalline compounds separated out. This was then filtered, washed with ether and dried *in vacuo*. The mixed ligand complexes were prepared by adding calculated amounts of ligands (1:2 proportion) separately to ethanolic suspension of simple anionic complex of the type $[L]_2[MX_4]$ and refluxing for about 1 hour. On cooling, crystalline compounds separated out which were then filtered, washed with ethanol followed by ether and dried *in vacuo*.

Metal and chloride in the complexes were determined by complexometric titration and Mohr's method and nitrogen by micro analysis. Conductance was measured in M/1000 acetone solution using Toshniwal conductivity bridge. Magnetic susceptibility measurements were made over solid specimen by Gouy method. IR spectra were recorded on KBr phase using Perkin-Elmer-221 spectrophotometer. Electronic spectra were recorded using M/100 (Chloroform base) solution by Hilger-Watt Uvispeck spectrophotometer. The conductance data, magnetic moment values and some IR bands are recorded in Table I. The analytical results for the metal, nitrogen and chlorine in the complexes closely agreed with the calculated values within the limits of experimental errors.

RESULTS AND DISCUSSION

When the tetrachloro cobalt(II), nickel(II) and zinc(II) complexes were reacted with ligands containing nitrogen donor atoms, any of the following possibilities can take place:

(i) No reaction may occur leaving the existing complex unchanged.
(ii) The ligand may simply add on to the existing complex, or
(iii) The ligand may replace either equal or unequal number of other ligands.

The first and second possibilities are ruled out since reaction did take place resulting in the formation of well defined beautiful, shining crystalline compounds differing in appearance and properties of the starting material.

Study of IR spectra is quite illustrative. Absorption bands are noticed at 920 (vs), 1000 (s), 1250 (vs), 1405 (s), 1490 (s) and 3050 (s) cm^{-1} due to monomethyl ammonium ion modified due to protonation. Most of the absorption bands due to free nitrogen donor ligands have been modified in the mixed anionic complexes indicating their coordination to metal ions. Since the ligand is not free but bonded to the metal most of the ligand absorption bands are split and/or shifted to shorter wavelength or a higher frequency region. This is expected in the case of complexes due to charge in bond order consequent to the metal ligand bonding. The sharp bands obtained at 782, 835, 1015, 1235 and 1610 cm^{-1} in case of *v*-picoline changed to around 800, 860, 1030, 1245 and 1620 cm^{-1} respectively in the complexes. In case of aniline, the weak symmetrical and asymmetrical N–H stretching modes at 3370 and 3265 cm^{-1} respectively changed to ~ 3330 and 3250 cm^{-1} in the complexes. Also the ν(C–N) vibration in case of aniline at 1240 cm^{-1} changed to ~ 1215 cm^{-1} in the complexes. Evidence for the coordination of the bases have been further substantiated by the appearance of bands ~ 350 cm^{-1} in the low frequency region assignable[9] to ν(M–N). In addition absorption band ~220 cm^{-1} can be attributable to ν(M–Cl) vibration.

The electrical conductance values in acetone solutions adequately confirmed the anionic nature of the complexes. Magnetic moment values show the presence of three and two unpaired electrons in case of cobalt(II) and nickel(II) complexes.

From the analytical, spectral and conductance data evidenc, the compounds now reported fall under two categories.

1. Hexa coordinated :

   $[L]_2[MCl_4B]$ where B = ortho-phenanthroline, 2,2′-bipyridyl or ethylene diamine,
   M = Co(II), Ni(II) or Zn(II) and

   $[L]_2[MCl_4B'_2]$ where B′ = morpholine or pyridine,
   M = Ni(II), Zn(II).

These compounds are 2:1 electrolytes as indicated by their molar conductance values and these are expected to have octahedral structure.

2. Penta coordinated :

   $[L][MCl_2B''_2]$ where M = Co(II), Ni(II) or Zn(II). B* = *v*-picoline, pyridine or aniline.

The molar conductance values indicate 1 : 1 electrolytic nature of the complexes.

In octahedral nickel(II) complexes three bands due to the transitions $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3), $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2) and $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ (ν_1) are possible[10]. In our complexes the bands due to ν_3, ν_2 and ν_1 are observed in the regions ~ 25000, 15500 and 9000 cm^{-1} respectively. In octahedral cobalt(II) complexes, three transitions namely $^4T_{1g}(F) \rightarrow {}^4T_{2g}(\nu_1)$. $^4T_{1g}(F) \rightarrow {}^4A_{2g}(\nu_2)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) are possible, out of which absorption bands due to ν_1 and ν_3 are generally observed. The ν_1 is generally broad and ν_3 is a set of multiple bands and may be mixed with spin forbidden transition. In the present case bands due to ν_1 and ν_3 are observed in the region ~ 9500 and ~ 20000 cm^{-1} respectively. The ν_2 band is very weak and is observed in the region of ~ 18000 cm^{-1}.

From the analytical, conductance and IR spectral studies, zinc(II) complexes are found to be six coordinated having an octahedral environment around the metal ion.

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