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NOTES

Reactions of 1,5-bis (salicylaldehyde) Carbohydrazone with Mn (II), Co (II) & Ni (II) Chlorides

SHEKHAR SRIVASTAVA* AND VANITA SRIVASTAVA

School of Studies in Chemistry
Jiwaji Univ ersity, Gwalior-474 011, India

Nine complexes of $MnCl_2$. $CoCl_2$ and $NiCl_2$ of the type $MLCl_2$, M_2LCl_4 and ML_2Cl_2 (where L = 1, 5-bis (salicylaldehyde) carbohydrazone and M = Ni, Mn and Co) have been synthesised and characterised by elemental analysis, conductivity, IR and XPS data.

The chemistry of bidentate organic ligands containing O, N donor atoms like semicarbazide, urea, semicarbozone, carbohydrazine[1-4] and the chemistry of thiocarbohyrazide[5] have been investigated extensively. But the chemistry of organic ligand 1, 5-bis (carbohydrazone) is very little studied[6]. So it was considered to carry out the reaction of $NiCl_2$, $MnCl_2$ and $CoCl_2$ with 1, 5-bis (salicylaldehyde) carbohydrazone.

Carbohydrazide was prepared by the reported method[7]. The 1,5-bis (salicylaldehyde) carbohydrazone was prepared by reacting carbohydrazide with salicylaldehyde in 1 : 2 molar ratio.

The $MLCl_2$ complexes were prepared when 1,5-bis(salicylaldehyde) (1 mmol) was dissolved in dry methanol, to it was added MCl_2 (M = Ni, Mn and Co) (1 mmol). The mixture was then refluxed for 8 hrs. The resulting solid product was filtered, washed with methanol and air-dried.

The ML_2Cl_2 and M_2LCl_4 complexes were prepared by similar procedure, by mixing and refluxing 1, 5-bis (salicylaldehyde) carbohydrazone and MCl_2 (M = Co, Ni and Mn) in 2 mmol : 1 mmol and 1 mmol : 2 mmol ratio respectively.

The X-ray photoelectron spectra were recorded on a VG Scientific ESCA—MK II electron spectrometer. The MgKα X-ray line (1253.6 eV) was used for photoexcitation. The $Cu2P_{3/2}$ (BE = 932.8 ± 0.2) and $Au4f_{7/2}$ (BE = 83.8 ± 0.1 eV) lines were used to a calibrate the instrument and $Ag3d_{5/2}$ (BE 368.2 eV) was used for cross-checking.[8]

All these complexes $MLCl_2$, ML_2Cl_2 and M_2LCl_4 are stable with high melting points. They all are insoluble in organic solvents except DMF and DMSO. Elemental analysis were within ± 0.5% for C, H, N and Cl. The molar conductance data below than 60 ohm^{-1} cm^2 mol^{-1} in DMF suggest that all these complexes are non-electrolyte[9] with composition of $MLCl_2$, ML_2Cl_2 and M_2LCl_4

The IR spectra of 1,5-bis (salicylaldehyde) carbohydrazone give a band in the region 1620–1600 cm^{-1} due to $\nu_{C=N}$ vibrations and a band

in the region 3300–3200 cm^{-1} due to ν_{N-H} vibrations. These bands were observed to split into two components in the spectra of ML_2Cl_2 and $MLCl_2$ complexes. The $\nu_{C=N}$ one component band appears at higher frequency *ca.* 1640–1610 cm^{-1} and the other at lower frequency 1600–1585 cm^{-1}, while ν_{N-H} one component band also appears at higher frequency *ca.* 3360–3220 cm^{-1} and other at lower frequency side *ca.* 3240–3160 cm^{-1}. But in the IR spectra of M_2LCl_4, $\nu_{C=N}$ and ν_{N-H} bands have shifted higher frequency side *ca.* 1645–1615 cm^{-1} and *ca.* 3365–3230 cm^{-1} respectively without splitting. This indicates that in ML_2Cl_2 and $MLCl_2$ complexes one of the $\nu_{C=N}$[10–11] groups and one of the ν_{N-H}[12] groups are only coordinated to metal ion and the other to be uncoordinated, but in M_2LCl_4 both $\nu_{C=N}$ and both ν_{N-H} groups are coordinated to metal ion. The bands at *ca.* 470 cm^{-1} and *ca.* 285 cm^{-1} in all these complexes are assigned to ν_{M-N}[13] and ν_{M-Cl}[14] respectively.

The binding energy data of Ols and $M2p_{3/2,\ 1/2}$ photoelectron peaks for 1,5-bis (salicylaldehyde) carbohydrazone, MCl_2, ML_2Cl_2, $MLCl_2$ and M_2LCl_4 have shown that $M2p_{3/2,\ 1/2}$ binding energy value is highest in MCl_2 and lowest in ML_2Cl_2 complexes and decreases in the order: $MCl_2 > MLCl_2 = M_2LCl_4 > ML_2Cl_2$ (when L and M is same). From these XPS data one can conclude that 1,5-bis (salicylaldehyde) carbohydrazone is coordinated to metal ion. Further, Ols photoelectron peaks of 1,5-bis-(salicylaldehyde) carbohydrazone and their all metal complexes have shown a single symmetrical photoelectron peak with same binding energy. These observations suggest noncoordination of the oxygen atoms of carbonyl group in all these complexes of 1,5-bis(salicylaldehyde) carbohydrazone[15].

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