

Synthesis, spectroscopic characterization and *invitro* antimicrobial investigation of some Hg(II) complex of carbohydrazone

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ABSTRACT

The synthesis of novel mercury (II) complex with new ligands derived from Carbohydrazides has been reported. The complexes have general composition $[HgL_2X_2]$, Where L= Carbohydrazone and X = Cl⁻, NO₃⁻. The ligand carbohydrazone behave as neutral bidentate Ligand through the carbonyl oxygen and azomethine nitrogen. On the basis of elemental analysis, Electrochemical and spectroscopic studies, the new complex have been characterized with octahedral geometry. The antifungal studies of the present complex show that they are moderate antifungal agent.

Key words: Antimicrobial activity, Hg(II) complex. Carbohydrazone.

INTRODUCTION

The synthesis of transition metal complex with schiff bases of nitrogen and oxygen donor has stimulated interest due to their vast variety of biological activities ranging from pharmacological, antitumour, fungicide, bactericide, anti-inflammatory and antiviral activities^{1,2}. The chemistry of bidentate organic ligands containing O, N donor atoms like, semicarbazide, urea, semicarbazone, carbohydrazine³⁻⁶ and the chemistry of thiocarbohydrazides⁷ has been investigated extensively. However, the chemistry of organic ligand 1, 5 – bis (carbohydrazone) has been recently studied⁸⁻¹¹, but to a limited extent only.

In this paper the chemistry of 1,5-bis (Carbohydrazone) of various ketones and aldehydes is being reported with HgCl₂ and Hg(NO₃)₂, so as to get new molecular adducts and to assign their structure and geometry both.

EXPERIMENTAL

A mixture of carbohydrazide (2 mmol) and the aromatic aldehyde (1 mmol) in methanol

was refluxed for 3 hrs. The examination suggested complete conversion of the starting materials to the respective schiff bases. The HgX₂ (1 mmol) was then added and the mixture was refluxed for 3 hrs. The resulting solid was washed with methanol and air – dried.

Conductance was measured in DMF at room temperature using a digisun conductivity bridge. Infrared spectra (Nujol/KBr) were recorded on a Perkin-Elmer 457 spectrophotometer. The X-ray photo-

Electron spectra was recorded on a VG Scientific ESCA-3MK II electron spectrometer. The Alk_K X-ray line (1486.8 eV) was used for photoexcitation. The Cu2p_{3/2} (BE = 932.8 ± 0.2 eV) lines were used to calibrate the instrument and Ag3d_{5/2} (BE = 368.2 eV) was used for crosschecking. All the spectra were recorded using the same spectrometric parameters of 50 eV pass-energy and 4mm slit-width. The reduced full-width at half maximum (FWHM) at Au4f (BE = 83.3eV) level under these conditions was 1.2 eV. The powered sample was mixed with high purity silver powder to reduce charging effect. A thin layer of this sample

was pressed on gold gauze which was welded to nickel sample holder. The Ag3d_{5/2} level (BE = 368.2 eV) obtained from this sample was sharp and did not show any observable shift. Thus the charging of the sample if at all present was negligible⁹. The spectra were recorded in triplicate in the region of interest. In most of the cases the binding energy was reproducible within ± 0.1 eV. the usual least-square fitting procedure for determining peak position, line-width and area was used.

RESULTS AND DISCUSSION

All these molecular adducts of Hg(II), HgX₂L, HgX₂L₂ and HgX₄L were stable with high melting points. They were all insoluble in organic solvents except DMF and DMSO. The elemental analysis (within error $\pm 0.5\%$ for C, H and N) and molar conductance data (less than 60 ohm⁻¹ cm²mol⁻¹) in DMF suggest that all these complexes were non-electrolytes¹² within composition of HgX₂-SB.

The IR spectra of 1,5-bis (carbohydrazone) of salicylaldehyde, acetophenone, benzaldehyde and cinnamaldehyde give a band in the region 1640-1650 cm⁻¹ due to C=N vibration and a band in the region 3300-3200 cm⁻¹ due to N-H vibrations. These bands were observed split in to two components in the spectra of HgX₂XL and HgX₂L complexes. The γ C=N of one component appears at frequency (~ 1640 - 1650 cm⁻¹) and the other at a lower frequency (1620 - 1610 cm⁻¹), while γ N-H of one component also appears at frequency (~ 3360 - 3260 cm⁻¹) and at the lower frequency side (~ 3240 - 3160 cm⁻¹). But in the IR spectra of Hg₂X₄L: γ C=N and $\bar{\alpha}$ N-H bands have shifted to lower frequency side (~ 1620 - 1610 cm⁻¹) and (~ 3240 - 3160 cm⁻¹) respectively without splitting. This indicated that in HgX₂L₂ and HgX₂L complexes one of the C=N¹³⁻¹⁴ groups and one of the N-H¹⁵ groups are only coordinated to mercury metal ion and other to be uncoordinated but in Hg₂X₄L both $\bar{\alpha}$ C=N and both γ N=H groups are coordinated to mercury metal ion. The bands at ~ 470 cm⁻¹ and both ~ 285 cm⁻¹ in all these complexes are assigned to γ M-N¹⁴ and γ M-Cl¹⁶ respectively.

The binding energy data of Hg4p, O1s and N1s photoelectron peaks for the HgX₂ and HgX₂-SB showed that Hg4p binding energy is the highest in HgX₂ than in HgX₂.L or Hg₂X₄L₂. HgX₂L₂ These

XPS data suggest that 1, 5 -bis (carbohydrazone) ligands are coordinated to mercury metal ion¹⁸.

Further O1s photoelectron peaks of 1,5-bis (carbohydrazone) and their metal complexes have shown a single symmetrical photoelectron peak with same binding energy. These observations suggest non-coordination of the oxygen atom of carbonyl group in all these complexes of 1,5-bis (Carbohydrazone)¹⁸. The binding energy of C12p photoelectron peak was observed at ~ 199.3 eV in all HgCl₂.L or Hg₂Cl₄L or HgCl₂L₂ complexes, which suggested that in each molecular adduct the chloride ion is coordinated in the inner coordination sphere of metal ion¹⁸. It was observed that in Hg3s photoelectron peak multiple splitting was absent, which suggested that all these molecular adducts are diamagnetic¹⁸.

Antifungal activity

The invitro biological screening effects of the investigated compounds were tested against the keastolytic fungus by the well diffusion method using potato dextrose agarics as the medium. The screening effects of the corresponding ligands against the same fungus were also tested and results were compared with those obtained with complexes. The test solutions were prepared by dissolving the ligands and complexes in DMSO. In a typical procedure¹⁹, a well was made on the agar medium inoculated with microorganism.

The well was filled with the test solution using micropipette and the plate was incubated at 30°C for 48hr. During this period, the test solution was diffused and the growth of the inoculated microorganism was affected. The inhibition zone developed on the plate was measured. Here DMSO was used as the control. The zone of inhibition values of the compounds against the growth of microorganisms are given in table 1. A comparative study of the ligands and complexes exhibit higher activity than the free ligand.

The overall experiment evidences thus show that the studied mercury (II) Complexes [HgX₂L], display a coordination number six and have an octahedral environment around the metallon. The complexes appear to be moderate antifungal agents.

Table 1: Antifungal activity of the ligands and their complexes

S.No.	Compound	Zone of inhibition (mm)
1.	DMSO	16.5
2.	HgX ₂ .SB ₁	8.0
3.	HgX ₂ .SB ₂	12.0
4.	HgX ₂ .SB ₃	11.0
5.	HgX ₂ .SB ₄	24.0

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REFERENCES

1. A.chaudhary, A. phor, and R.V. singh, "Potentially biodynamic tetra aza macro cycles and their manganese complex; antiandrogen, antimicrobial and PDI studies." *Bioinorganic chemistry and applications*, **3**(3-4), 161-177, (2005).
2. S.Prasad and R.K. Agarwal, "Cobalt (II) complexes of various thiosemicarbazones of 4-aminoantipyrine: Synthesis, spectral, thermal and antimicrobial studies," *Transition metal chemistry*, **32**(2), 143-149, (2007).
3. R.C.Paul, P.Sharma, L.Subbiah, H.Singh and S.L. Chaddha, *J.Inorg. Nucl.chem*, **38**, 169 (1976).
4. R.N. Ray and B.K. Mohapatra: *Ind.J.Chem*, **19A**, 590 (1980).
5. A.V. Ablov, N.I.Delichuk and L.F. Chapurina, *Russ. J. Inorg. Chem.*, **15**, 571, (1970)
6. M.F.A. Dove and D.B. Sowerby, *Coord. Chem. Rev.*, **34**, 350 (1981).
7. F.Kurzner and M.Wilkinson, *Chem. Rev.*, **70**, 145 (1970).
8. Shekhar Shrivastava and vanita Shrivastava, *Asian J. Chem.*, **4**, 950 (1992).
9. Shekhar Shrivastava, *Asian J. Chem.*, **5**, 568 (1993).
10. R. Rastogi, G.K. Parashar and R.N. Kapoor, *Synth. React. Inorg. Met-Org. Chem.*, **15**, 1061 (1985).
11. E.B. Mohr, J.J.Brezinski and L.F. Audrieth, *Inorg. Chem.*, **4**, 32, (1965).
12. W.L. Greary. *Coord. Chem. Rev.* **13**, 47 (1971).
13. S. Satpathy and B.Sahoo. *J. Inorg. Nucl. Chem.* **32**, 2223 (1970).
14. E.P. Dudek and G. Dudek, *Inorg. Nucl. Chem. Lett.*, **3**, 241 (1969).
15. B. A. Gingras, R.L. Samorajai and C.H. Baley, *Can. J. Chem.*, **39**, 973 (1961).
16. H. R. Singh and B.V. Agarwal, *J. Ind. Chem. Soc.*, 591 (1988).
17. D.P. Singh and V.B. Rana, *J. Ind. Chem. Soc.*, 266 (1989).
18. Shekhar Shrivastva, *Appl. Spectrosc. Rev.*, **22**, 401 (1988).
19. Pelczar MJ, Chan ECS & Krieg NR, *Microbiology*, 5th Edn (McGraw Hill Inc. New York) 1998.