

IR and PMR spectral studies on complex derivatives of heterocyclic thioamides with metal-metal bond

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ABSTRACT

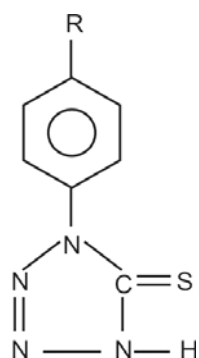
A number of complexes containing Hg-Hg bond with derivatives of 1-para substituted phenyl tetrazoline-5-thione have been prepared and investigated using elemental analysis, conductometric, magnetic, IR, UV-vis and ¹H NMR spectra data. All thioamide ligands acts as bidentate (N,S) and no disproportionation of Hg(I) occurs during complex formation.

Key words: Metal- Metal bond, thioamide ligands, spectral studies.

INTRODUCTION

A large number of complexes containing metal – metal bonds are known and their vibrational spectra have been reviewed extensively.¹⁻⁴ Of special interest is the mercurous ion complex which display disproportionation during complex formation to give metallic mercury and the complexed mercuric ion⁵⁻⁶. It is failed to occur in the present case and almost quantitative yield of the mercurous complex is obtained with several para-substituted derivatives of 1-substituted phenyltetrazoline-5-thione(I).

(R = CH₃ - O -,
CH₃CH₂ - O -,
Cl⁻, CH₃ - , -OH)



(I)

EXPERIMENTAL

All the chemicals used were of AR-grade or CP-grade. The paramethoxy (m.p= 160°C), Paraethoxy (MP = 205°C) parachloro (m.p= 157°C), Paramethyl (MP = 149°C) and p-hydroxyl (MP = 160°C) derivatives of 1-substituted phenyl tetrazoline-5-thione were prepared by the method reported in literature⁷. All the complexes were prepared using a general method. Hot aqueous solution of mercurous nitrate (50 mL, 0.1M) was mixed with methanolic solution of ligand (75 mL, 0.1M) to give white precipitate which was filtered, washed successively with hot water, methanol and dried under vacuum.

Magnetic susceptibilities of complexes were measured on gouy balance and the diamagnetic corrections for the ligand molecules were applied. The IR spectra of the ligands and complexes were recorded on a Perkin – Elmer model – 577 spectrophotometer in the range 4000-200cm⁻¹ as KBr pellets. The UV and visible spectra of the ligands and complexes were recorded on a Beckmann and Carl Zeiss (Jenna) spectrophotometer. The ¹H NMR spectra

Table 1 : Analytical, IR and PMR Spectral data of ligands and complexes.

Compd ^a .	Analysis % Found/(Calcd)			Thioamide Bands ^b				¹ H NMR Signals (δPPM)	
	Hg	N	S	I	II	III	IV	NHProtons	Phenyl Protons
HA	-	26.90 (26.92)	15.37 (15.38)	1505(s)	1290 (m)	1050(s)	800(s)	1.31	7.46 & 8.12
HgA	49.10 (49.21)	13.68 (13.73)	7.96 (7.85)	1485 (m)	1310	1020(m)	780 (m)	-	7.47 & 8.13
HB	-	25.08 (25.22)	14.51 (14.41)	1515(s)	1285 (m)	1060 (m)	805 (s)	1.32	7.47 & 8.10
HgB	47.32 (47.58)	13.10 (13.28)	7.60 (7.59)	1495 (m)	1305 (m)	1040 (m)	790 (m)	-	7.46 & 8.12
HC	-	26.31 (26.35)	15.10 (15.05)	1498(s)	1280 (s)	1055 (m)	780 (m)	1.31	7.4 & 8.3
HgC	48.80 (48.67)	13.52 (13.58)	8.01 (7.76)	1500 (m)	1275 (w)	1020 (w)	745 (m)	-	7.4 & 8.31
HD	-	29.31 (29.16)	16.68 (16.66)	1500 (m)	1280 (s)	1044 (m)	810 (m)	1.25	7.30 & 7.95
HgD	50.50 (51.22)	14.20 (14.30)	8.20 (8.17)	1480 (m)	1295 (m)	1030 (m)	760 (m)	-	7.40 & 8.10
HE	-	29.01 (28.86)	16.50 (16.49)	1510 S	1285 (s)	1050 (m)	810 (m)	1.26	7.41 & 8.10
HgE	51.10 (50.96)	14.32 (14.22)	8.10 (8.13)	1495 (m)	1310 (m)	1020 (m)	780 (m)	-	7.42 & 7.79

a. HA = p - CH₃O - C₇H₉N₄S, HB = p - CH₃CH₂O - C₇H₉N₄S; HC = p - Cl - C₇H₉N₄S HD = p - CH₃ - C₇H₉N₄S, HE = p - OH - C₇H₉N₄S

b. Band I = δNH + δCH + ν_{C=N}ⁱ
 Band II = ν_{C-N} + δNH + δCH + ν_{C=S}
 Band III = ν_{C=N} + ν_{C=S}
 Band IV =

were recorded on a high resolution varian HR-100 (cross coli type) NMR spectrometer in CDCl_3 solution using TMS as the internal indicator in the range of 0 to 10 PPM. The analytical, IR, and ^1H NMR spectral data are given in table 1.

RESULTS AND DISCUSSION

The analytical results indicate the stoichiometry HgL (LH = ligand). All ligands contain one replaceable imino hydrogen in thione – tautomeric form or thiolhydrogen in thiol-form. At room temperature the thione – form of the ligands is preferred⁸. Hence, deprotonation of iminio hydrogen atom was assumed on complexation. All products were stable solid and diamagnetic. The diamagnetic nature of Hg(I) complexes indicated the presence of Hg_2^{++} moiety. The two electrons each from Hg^+ ($5d^{10}6s^1$) in s-bonding molecular orbital are paired forming Hg_2^{++} and formation of metal – metal bond ($^+\text{Hg} - \text{Hg}^+$) by 6s – 6s overlapping.⁹ The Hg(I) ion either chelates with both N and S of the same ligand with a formation of four membered ring or it coordinate with nitrogen and sulphur of different ligand molecules giving rise to polymeric species. However, many thioamide complexes are known to form stable four membered ring including metal ion¹⁰. Cartwright *et al*¹¹ have

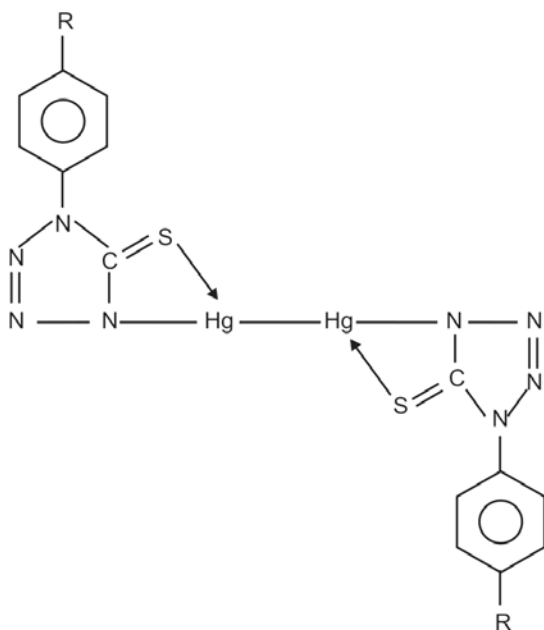
reported considerable stability of four membered ring chelates of thioamide ligands using X-rays crystallographic studies. The four membered ring of HgL stoichiometry may contains both Hg-S and Hg-N bond in assigned structure (Str. II)

The stability of chelates are attributed due to back bonding to the vacant d-orbitals of sulphur atom.

The electronic spectra display a very strong absorption between $31250 - 30300 \text{ cm}^{-1}$ assigned to charge transfer band of coordinated ligand.

IR Spectra

All the derivatives of 1-substituted phenyl tetrazoline – 5- thione contain thioamide group and give rise to four characteristic thioamide bands¹²⁻¹⁴ in the region of 1500, 1300, 1000 and 800 cm^{-1} respectively. The normal coordinates analysis (NCA) of various thioamides have been performed by Agarwala *et al*¹⁵ and Suzuki¹⁶ and observed that these are mixed bands having contributions from $\nu_{\text{C}=\text{S}}$, $\nu_{\text{C}-\text{N}}$, $\delta_{\text{C}-\text{H}}$ and $\delta_{\text{N}-\text{H}}$ modes. All the four thioamide bands disappear in the spectra of complexes but two new bands around $1130-1165 \text{ cm}^{-1}$ and $1050-1070 \text{ cm}^{-1}$ appear which may be assigned to the $\nu_{\text{C}-\text{N}}$ and $\nu_{\text{C}=\text{S}}$ modes of vibration respectively. These two new bands may not be due to $\nu_{\text{C}-\text{N}}$ and $\nu_{\text{C}=\text{S}}$ but mixed ones. This indicates that mixing $\nu_{\text{C}=\text{S}}$, $\nu_{\text{C}-\text{N}}$, $\delta_{\text{C}-\text{H}}$ and $\delta_{\text{N}-\text{H}}$ is disturbed when the hydrogen of N – H group is replaced by Hg^+ ion. However, simultaneous formation of Hg – N and Hg – S bond results splitting and red shift of thioamide band I, blue shift of thioamide band II, red shift of band III and band IV (Table 1) of ligand¹⁷⁻¹⁹. This is also supported by the presence of new bands of medium to weak intensities in the region $330 - 450 \text{ cm}^{-1}$ which are not present in the spectra of the ligands. These new bands occur either a broad or split bands which may be inter-and/or intramolecular interaction of Hg – N and Hg – S bands in the solid structure.²⁰ The deprotonation of imino group hydrogen of ligands are also supported by the absent of $\nu_{\text{N}-\text{H}}$ band observed at 3145 cm^{-1} . Thus, formation of Hg – N and Hg – S bond in all complexes was assumed.



(Str. II)

¹H NMR spectra

To substantiate further nature of bonding in the complexes ¹H NMR spectra of free ligands and their corresponding complexes were compared. The chemical shift values of the main groups associated with derivatives of 1 – substituted phenyl tetrazoline – 5- thione reveal that there is bonding of metal ion through thione sulphur after deprotonation of imino hydrogen of the ligands. All complexes display broad multiplet in the region δ 7.41 to 7.72 PPM due to phenyl protons of the ligands in complexes. The broad nature of peak may be due to large quadrupole resonance broadening effect of tetrazoline nitrogen atoms.²¹ The signal due

to imino proton is always difficult to identify because of the quadrupole moment of nitrogen and exchange of this proton in solution²². However, a peak observed at δ 1.25 PPM in the ligand is absent in the spectra of complexes suggesting the formation of Hg – N bond and deprotonation of N – H group on complexation. The methoxy protons observed as a sharp singlet at δ 3.76 PPM in complexes coincides with that of methoxy group proton in literature²³. The signal at δ 2.4 PPM assigned to methyl protons of coordinated ligand. These observations are consistent with the conclusions drawn from IR spectra.

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