

Metal Chelates of Heterocyclic Thioamides Having Metal- Metal Bond

R.N. PANDEY* and PRAMILA SHARMA^a

*P.G. Centre of Chemistry (M.U.),
College of Commerce, Patna- 800020 (INDIA)
email : rameshwarnath.pandey@yahoo.com

^aDepartment of Chemistry,
Ganga Devi Mahila Mahavidyalaya, Patna- 800020 (INDIA)
E-mail : reachpramilaji@gmail.com

(Acceptance Date 11th October, 2013)

Abstract

A number of metal chelates containing Hg-Hg bond with methyl derivatives of 1-phenyl tetrazoline-5-thione have been prepared and characterized using elemental analysis, conductometric, magnetic, IR, UV-vis and ¹H NMR Spectral data. All thioamide ligands act as bidentate (N, S) and no disproportionation of Hg(I) occurs during complex formation.

Key words: Hg-Hg bond, Heterocyclic thioamides, Spectra.

Introduction

The literature survey reveals that complexes containing metal- metal bond have been reviewed by several workers¹⁻³. However, metal chelates having Hg-Hg bond are very interesting which may display disproportionation during complex formation to give metallic mercury⁴. It is failed to occur in the present case and almost quantitative yield of Hg(I) complexes was obtained. In continuation of our study on metal complexes having metal-metal bond⁵. We report here, IR, PMR and other physico-chemical investigation of

mercury (I) complexes ligated by heterocyclic thioamides.

Experimental

All the chemicals used were of AR-grade or CP-grade. The ligands⁶ and complexes⁷ were prepared by the methods reported in literature. The elemental analysis, IR, ¹H NMR, Conductometric and magnetic susceptibilities data were obtained as reported in our previous paper⁵. The analytical and spectral data are given in table 1 and table 2 respectively.

Results and Discussion

The analytical data results the stoichiometry $\text{HgL}(\text{LH}=\text{ligands})$. The diamagnetic nature of Hg(I) complexes indicated the presence of Hg_2^{++} moiety and formation of $\overset{+}{\text{Hg}}-\overset{+}{\text{Hg}}$ bond by 6s-6s overlapping⁸. The Hg(I) ion either chelates with both N and S of the same ligand with a formation of four membered ring or it coordinates with N and S of different ligand molecules giving rise to polymeric species. However, many thioamide complexes are known to form stable four membered ring chelates including metal ion⁹. Cartwright *et al.*¹⁰ have reported considerable stability of four membered ring chelates of thioamide ligands using X-Rays crystallographic studies. The four membered ring of HgL containing both Hg-S and Hg-N bond is assigned in most probable structure (I). The stability of these chelates is attributed due to back bonding to the vacant d-orbitals of sulphur atom. The electronic spectra of complexes exhibit a very strong absorption between $31255-30310 \text{ cm}^{-1}$ due to charge transfer band of coordinated ligands.

IR Spectra :

The IR spectra of ligands and complexes are given in table 2 which indicates simultaneous formation of Hg-N and Hg-S bond considering our previous observations¹¹⁻¹². The red shift of thioamide band I, blue shift of thioamide band II, and red shift of thioamide band III and band IV of ligands, confirms bonding through nitrogen and sulphur of thioamide group¹³⁻¹⁵. This is also supported by the presence of new bands of medium to weak

intensities in the region $335-460 \text{ cm}^{-1}$. These new bands occur either a broad or split bands which may be inter and / or intramolecular interaction of Hg-N and Hg-S bonds in the solid structure¹⁶.

¹H NMR Spectra :

To substantiate further nature of bonding in the complexes ¹H NMR spectra of free ligands and their complexes were compared. The chemical shift values and the integrated intensities of the signals agree well with the assigned structure of complexes. All complexes display broad multiplet in the region $\delta 7.42$ to $\delta 7.72$ PPM due to phenyl protons of the ligands are slightly low field shifted and the integrated intensities of these signals agree well with the formulation of the complexes(I). The broad nature of peak may be due to large quadrupole resonance broadening effect of tetrazoline nitrogen atoms¹⁷. The signal due to imino proton is always difficult to identify because of the quadrupole moment of nitrogen and exchange of this proton in solution¹⁸. However, a peak observed at $\delta 1.25$ PPM of the ligand is absent in the spectra of complexes indicating the formation Hg-N bond and deprotonation of N-H group during complex formation.

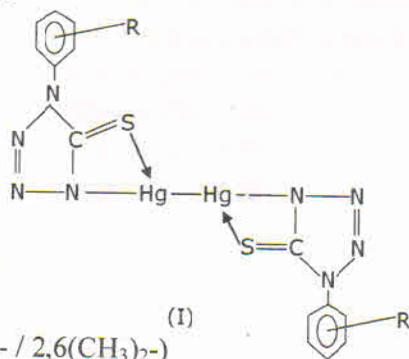


Table 1. Analytical data of complexes

Complexes	Analysis (%) : Calculated/ (found)			Molar cond. ($\pi^{-1} \text{ cm}^2 \text{ mol}^{-1}$)
	Hg	N	S	
[Hg(O-CH ₃ -L)]	51.22 (50.56)	14.30 (14.20)	8.17 (8.25)	6.20
[Hg(m-CH ₃ -L)]	51.22 (51.11)	14.30 (14.32)	8.17 (8.26)	8.20
[Hg(P-CH ₃ -L)]	51.22 (51.66)	14.32 (14.42)	8.17 (8.28)	6.82
[Hg(2,6-(CH ₃) ₂ -L)]	49.45 (49.82)	13.80 (13.68)	7.88 (7.68)	5.32

LH = 1-phenyl tetrazoline-5-thione(C₇H₆N₄S)

Table 2.

Compounds	Thioamide Bands ^a (cm ⁻¹)				ν N-H
	Band I	Band II	Band III	Band IV	
O-CH ₃ -L (ligand)	1500 (m)	1300 (m)	1055 (m)	810 (m)	3090 (sb)
Hg(O-CH ₃ -L)	1485 (m)	1320 (m)	1030 (m)	780 (m)	-
m-CH ₃ -L (ligand)	1500 (s)	1285 (m)	1052 (m)	790 (ms)	3050 (mb)
[Hg(m-CH ₃ -L)]	1485 (m)	1300 (ms)	1020 (m)	765 (m)	-
P-CH ₃ -L (ligand)	1500 (m)	1280 s	1044 m	810 m	.3060 (sb)
Hg(P-CH ₃ -L)	1480 (m)	1295 s	1030 m	760 m	-
2,6(CH ₃) ₂ -L (ligand)	1504 (ms)	1286 (m)	1055 (m)	790 (m)	3070 (sb)
[Hg(2,6(CH ₃) ₂ -L)]	1485 (m)	1310 (ms)	990 (m)	760 (m)	-

a. Band I = δ NH + δ CH + ν C = N; Band II = ν C-N + δ NH + δ CH + ν C-S;Band III = ν C^{...}N + ν C^{...}S; Band IV = ν C^{...}S

References

1. B. J. Bulkin and C. A. Rundell, *Coord. Chem. Rev.* 2, 371 (1967).
2. K.L. Watters and W.M. Risen Jr., *Inorgchim. Acta Rev.* 3, 129 (1969).
3. E. Maslowsky Jr., *Chem. Rev.* 71, 507 (1971).
4. T. Yamane and N. Davidson, *J. Am. Chem. Soc.* 82, 2123 (1960).
5. R. N. Pandey, Gunjan Kumari and R. K. Singh, *Oriental J. Chem.* Vol. 25 (3), 625 (2009).
6. E. Lieber and J. Ramchandran, *Can. J. Chem.* 37, 101 (1959).
7. R.N. Pandey and Pramila Sharma, *Asian J. Pure & appl. Chem.* 1(3), 185 (1995).
8. N.N. Greenwood and A. Earnshaw, "Chemistry of elements" Pergamon Press, Inc., N.Y., P. 1410 (1989).
9. M. Hass and GBBM Sutherland, *Proc. R. Soc. A* 236, 427 (1956).
10. B.A. Cartwright, P.O. Langguth, Jr. and A.C. Skapski, *Acta crystallogr. (B)*, 36, 63 (1979).
11. R.N. Pandey, A.K. Nag and D.K. Sharma, *Oriental J. Chem.* Vol. 28(4), 1809 (2012).
12. R.N. Pandey, A. anand, R.K. Singh, A. Kumar, *Asian J. Chem.* Vol. 22(7), 5601 (2010).
13. B. Singh, R. Singh, R.V. Choudhary and K.P. Thakur, *Indian J. Chem.* 11, 174 (1973).
14. R.N. Pandey, S.S. Kumar, Pramila Sharma and Renu Kumari, *Int. J. Chem. Sci.* 11(1), 665 (2013).
15. R.N. Pandey and Pramila Sharma, *Ultra Scientist*, Vol. 25(2)B, 221 (2013).
16. R.N. Pandey, A.K. Sinha, R.N. Sharma, R.K. Ranjan *Asian J. Chem.* Vol. 6, 246 (1994).
17. E.O. Greaves, C.J.L. Lock and Mactlis, *Can J. Chem.* 46, 3879 (1968).
18. L.D. Dave, C. Mathew and V. Oommen, *J. Indian Chem. Soc.* 65, 377 (1988).