Available online at www.sciencedirect.com
SCIENCE DIRECT®
Spectrochimica Acta Part A 61 (2005) 3097–3101
SPECTROCHIMICA ACTA PART A
www.elsevier.com/locate/saa

Organotin(IV) complexes of thiohydrazones: synthesis, characterization and antifungal study

A.K. Mishra, N. Manav, N.K. Kaushik*

Department of Chemistry, University of Delhi, Delhi-110007, India

Received 7 September 2004; accepted 2 November 2004

Abstract

Some new organotin(IV) complexes with salicylaldehyde aniline-*N*-thiohydrazone (L^1) and cinamaldehyde aniline-*N*-thiohydrazone (L^2) of the type $(p\text{-}ClC_6H_4)_3Sn[L]\ Cl$ and $(p\text{-}ClC_6H_4)_2Sn[L]Cl_2$ have been synthesized (where $L = L^1$ and L^2). The complexes and ligands were characterized by elemental analysis and spectral (UV–vis, IR and ^1H NMR) studies. In all the complexes, ligands act as bidentate, coordination through sulphur and azomethane nitrogen. Complexes are 1:1 metal ligands complexes. Antifungal studies of some complexes against Rhizoctonia bataticola fungal strain have been carried out.

Keywords: Synthesis; Antifungal; Spectral; Organotin; Thiohydrazone

1. Introduction

The organotin(IV) complexes possess significant biological activities [1–4]. These complexes have been found as antitumour [1], antibacterial [2], antifungal [3–5], antiviral [6,7] and PVC-stabilizer [8]. They have been widely used as agrochemicals and antifouling paints due to their low phototoxicity and favourable environmental degradation [9] to non-toxic inorganic tin residues. The work has been carried out by many workers [3–5,10–17] by synthesizing and characterizing the thiohydrazone complexes using different metals. In the present study, the authors have synthesized and characterized some new organotin(IV) complexes using salicylaldehyde aniline-*N*-thiohydrazone (complex 1 and 2) and cinnamaldehyde aniline-*N*-thiohydrazone (complex 3 and 4) ligands.

2. Experimental

2.1. Physical measurements

All reagents used were AR grades and the solvents were purified by standard method. IR and far IR spectra were recorded on KBr and polyethylene discs, respectively, using a Perkin-Elmer Spectrum 2000 FTIR spectrometer, electronic (UV–vis) spectra were recorded on a Varian cary 100 UV–vis spectrophotometer and ^1H NMR spectra were recorded on a Brucker spectrospin advance 300, Hitachi R-600 FT NMR spectrometer 60. Elemental analysis was carried out on Perkin Elmer 2400 series II CHN S/O Analyser.

2.2. Preparation of organotin and ligands

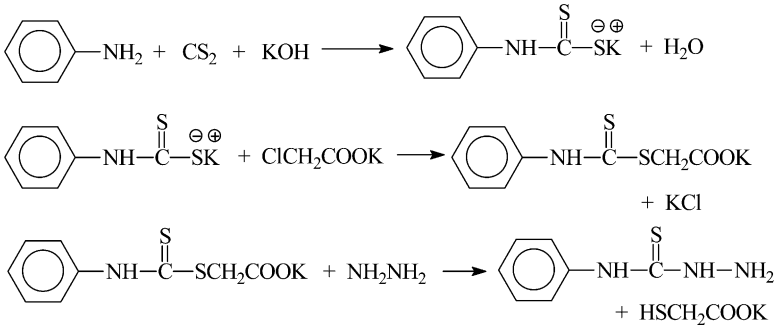
p-Chlorotribenzyl tin chloride $\{(p\text{-}ClC_6H_4CH_2)_3SnCl\}$ and *p*-Chlorodibenzyl tin dichloride $\{p\text{-}ClC_6H_4CH_2)_2SnCl_2\}$ were synthesized by the method given by Sisido et al. [18] All the ligands were synthesized in lab by Gilman and Blatt [19] method with some modifications.

* Corresponding author. Tel.: +91 11 27667725x1391.
E-mail addresses: ajaykmishra1@yahoo.com (A.K. Mishra), navneet92@rediffmail.com (N. Manav), narenderkumar_kaushik@yahoo.co.in (N.K. Kaushik).

1386-1425/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2004.11.035

2.2.1. Preparation of thiohydrazide

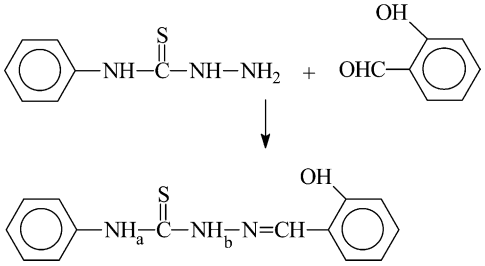
Aniline 18.2 ml (0.2 mol) (density 1.022) was dissolved in methanol and potassium hydroxide 11.2 gm (0.2 mol) in aqueous methanol was added with constant stirring in methanolic ice cold solution of carbon disulphide 12.06 ml (0.2 mol) (density 1.26) maintaining temperature below 10 °C. A white crystalline precipitate of aniline dithiocarbamate separated. Its aqueous solution was treated with freshly prepared potassiumchloroacetate (0.05 mol). The reaction temperature was maintained at 40 °C for an hour and the content was left overnight at room temperature. After 24 h methanolic solution of 2.43 ml (0.05 mol) hydrazine hydrate (density 1.03) was added to the reaction mixture. The content was heated on water bath till the desired product separated out. It was cooled in ice for 24 h and filtered. Aniline-*N*-thiohydrazide so obtained was recrystallised from hot water. The reactions are given below.



Analysis; found (calc.)% C, 50.07(50.29); H, 5.42(5.38); N, 25.18(25.38)

2.2.2. Preparation of salicylaldehyde aniline-N-thiohydrazone (L^1)

Aniline-*N*-thiohydrazide 4.2 g (0.025 mol) and salicylaldehyde 2.7 ml (0.025 mol) (1.146 density) were refluxed in methanol for 3 h. On cooling, a yellow precipitate obtained was filtered and washed with cold methanol.

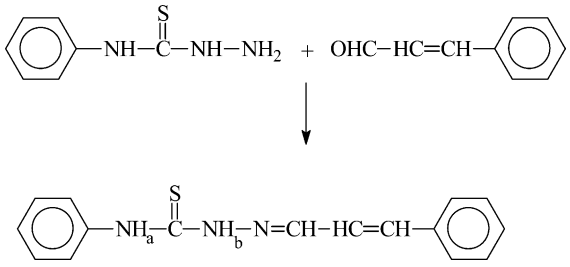


Analysis; found (calc.)% C, 61.34(61.99); H, 4.80(4.38); N, 15.50(14.36)

It was recrystallised from hot methanol. The reactions in the process are given above.

2.2.3. Preparation of cinnamaldehyde aniline-N-thiohydrazone (L^2)

Aniline-*N*-thiohydrazide 4.2 g (0.025 mol) and cinnamaldehyde 3.2 ml (0.025 mol) (1.048 density) were refluxed in methanol for 3 h. On cooling, a yellow precipitate obtained was filtered and washed with cold methanol. It was recrystallised from hot methanol. The reactions in the process are given below.



Analysis; found (calc.)% C, 68.42(68.33); H, 5.73(5.34); N, 15.07(14.95)

2.3. Preparation of thiohydrazone complexes

A solution of corresponding thiohydrozones, salicylaldehyde aniline-*N*-thiohydrazone [L^1, 0.54 g (0.002 mol)] and a solution of cinnamaldehyde aniline-*N*-thiohydrazone [L^2, 0.56 g (0.002 mol)] in 25 ml of acetone solution [1:7 (distilled water:acetone mixture was added)] slowly added to corresponding organotin chloride R_3SnCl or R_2SnCl_2 (0.002 mol) in 25 ml of [1:7 (distilled water:acetone)] mixture. The mixture so obtained was refluxed for half an hour, stirred continuously for additional 4 h and then evaporated to one-fourth of its original volume under vacuum. The complex so obtained was recrystallised in acetone, washed with petroleum ether and dried in a desiccator over $CaCl_2$ (where $R = p\text{-}ClC_6H_4CH_2$).

3. Results and discussion

Elemental analysis reveals that complexes are of good purity. All the synthesized complexes are soluble in acetone and DMSO solvents (Table 1). These are amorphous and grey in colour.

Table 1
Elemental analysis of thiohydrazone complexes

Complexes	Melting point (°C) and solubility	Empirical formula	Found (calc.) (%)				
			Sn	Cl	C	H	N
$(p\text{-}ClC_6H_4CH_2)_3Sn(L^1)Cl$	124 Acetone and DMSO	$C_{33}H_{31}SnN_3OSCl_4$	14.16 (14.84)	17.65 (17.71)	52.32 (52.37)	4.38 (3.87)	5.57 (5.24)
$(p\text{-}ClC_6H_4CH_2)_2Sn(L^1)Cl_2$	118 Acetone and DMSO	$C_{28}H_{25}SnN_3OSCl_4$	15.74 (16.71)	20.14 (19.94)	46.36 (47.19)	3.59 (3.51)	5.86 (5.90)
$(p\text{-}ClC_6H_4CH_2)_3Sn(L^2)Cl$	127 Acetone and DMSO	$C_{37}H_{33}SnN_3SCl_4$	14.86 (14.66)	17.32 (17.49)	54.93 (54.68)	4.12 (4.06)	5.23 (5.17)
$(p\text{-}ClC_6H_4CH_2)_2Sn(L^2)Cl_2$	113 Acetone and DMSO	$C_{30}H_{27}SnN_3SCl_4$	16.93 (16.49)	19.45 (19.67)	50.02 (49.86)	3.82 (3.74)	6.04 (5.82)

Table 2
UV–vis spectra of thiohydrazone complexes

Complexes	λ_{max}	Absorbance
L^1	270.32	2.36
	315.26	1.16
Complex 1	261.67	2.42
	293.33	1.23
L^1	270.32	2.36
	315.26	1.16
Complex 2	261.60	2.58
	300.00	1.98
L^2	267.43	2.18
	323.46	1.46
Complex 3	266.00	2.38
	309.16	1.87
L^2	267.43	2.18
	323.46	1.46
Complex 4	267.33	2.36
	305.83	1.56

3.1. Electronic spectra

In the electronic spectra [4,25] due to chromophore region, absorption bands at ∼300 nm are assigned as π–π^* intraligand electronic transition (N=C=S). In UV spectra of ligand (L^1) two absorption bands at 270 nm (log $\varepsilon = 3.37$) and 315 nm (log $\varepsilon = 3.06$). Ligand (L^2) absorbs at 267 nm (log $\varepsilon = 3.34$) and 323 nm (log $\varepsilon = 3.16$). On complexation these bonds are shifted lower revealing involvement of C=S group coordination in all the complexes (Table 2).

Table 4
^{1}H NMR Spectra analysis of thiohydrazone complexes

Complexes	Ar–H	–CH_2	–NH_a and –NH_b
L^1	6.8–7.7 (m-9H)	–	8.2 and 7.2 (s-1H)
Complex 1	7.1–7.3 (d-21H)	3.4 (s-6H)	8.5–8.7 and 7.5–7.7 (s-1H)
L^1	6.8–7.7 (m-9H)	–	8.2 and 7.2 (s-1H)
Complex 2	7.0–7.2 (d-17H)	3.3 (s-4H)	8.6 and 7.5 (s-1H)
L^2	6.5–7.8 (m-10H)	–	8.16 and 6.9 (s-1H)
Complex 3	6.9–7.1 (d-22H)	3.6 (s-6H)	8.5 and 7.4 (s-1H)
L^2	6.5–7.8 (m-10H)	–	8.16 and 6.9 (s-1H)
Complex 4	6.8–7.0 (d-18H)	3.4 (s-4H)	8.3 and 7.2 (s-1H)

3.2. I R spectra

In IR spectra, ν(C=N) and ν(N–N) shift to higher frequency on complexation showing the involvement of azomethine nitrogen [20] in coordination and ν(C=S) frequency from ∼800 cm^{-1} shifts to ∼825 cm^{-1} indicates coordination of ligands through thione sulphur. The metal complexes also show ν(Sn–S) [21] at ∼350 cm^{-1}, ν(Sn–N) [22] at ∼480 cm^{-1} and νSn–Cl [21] at ∼315 cm^{-1}. These indicate that ligands are coordinated to the metal through thione sulphur and azomethine nitrogen (Table 3). On comparing with the other synthesized compounds [4,5,25], the ν(C=S) and ν(C=N) frequency shift indicates more stable coordination on complexation.

3.3. ^{1}H NMR spectra

In ^{1}H NMR spectra [23–25] of complexes were recorded in d_6-DMSO taking TMS as internal standard (Table 4). The shift observed in the region δ (ppm) 6.5–7.8 (Ar–H), 8.7–6.9 (NH_a and NH_b) and 3.4–3.6 (–CH_2) on complexation. The shift in the position of resonance signal of the complexes to

Table 3
IR Spectra of thiohydrazone complexes

Complexes	ν(C=N)	ν(C–O)	ν(N–H)	ν(N–N)	ν(C=S)	ν(M–S)	ν(M–Cl)	ν(M–N)	ν(C–H)
L^1	1591	1240	3216	1008	809	–	–	–	2926
Complex 1	1595	1242	3207	1027	827	354	315	480	2929
L^1	1591	1240	3216	1008	809	–	–	–	2926
Complex 2	1596	1241	3208	1015	824	358	325	481	2936
L^2	1593	–	3201	1003	932	–	–	–	2926
Complex 3	1605	–	3180	1017	945	343	310	502	2928
L^2	1593	–	3201	1003	932	–	–	–	2926
Complex 4	1607	–	3186	1023	956	350	317	509	2930

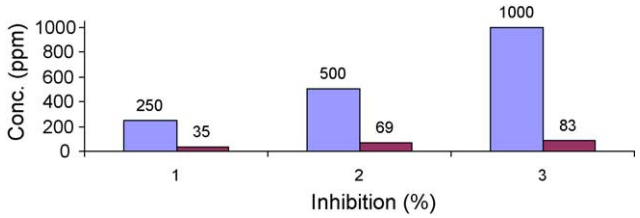


Fig. 1. Antifungal study against Rhizoctonia bataticola of complex 1.

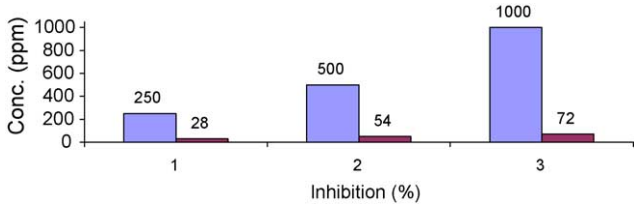


Fig. 2. Antifungal study against Rhizoctonia bataticola of complex 2.

ligand due to change in the electronic environment as a result of coordination of the ligands to the metal.

On comparing with the other synthesized compounds [4,25], significant change in the δ (ppm) value has been observed.

3.4. Antifungal screening

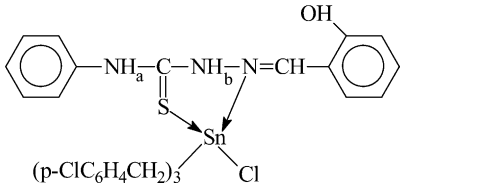
The organotin(IV) complexes show very high antimicrobial and fungicidal activities [4,26] against pathogenic strains of Rhizoctonia bataticoala. The compounds were directly mixed with the medium in different three concentrations (250, 500, 1000 $\mu g\,mL^{-1}$) in ethanol. The growth of fungus was measured by the recording the diameter of fungal colony. The relation for calculation of fungal growth inhibition: fungal growth inhibition $\% = (A - B) \times 100/A$, where A is the diameter of fungal colony in control plate and B is the diameter of the fungal colony in taste plate. The results show that organotin(IV) complexes (Figs. 1 and 2) are found to be active against pathogen Rhizoctonia bataticoala and show a higher percentage of inhibition at higher concentration (Table 5). A significant enhancement in the antifungal activity has been observed in the present investigations when compared with other biologically active compounds [26].

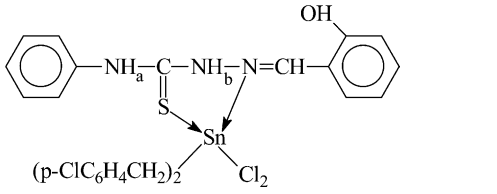
Table 5
Antifungal study against Rhizoctonia bataticola of thiohydrazone complexes

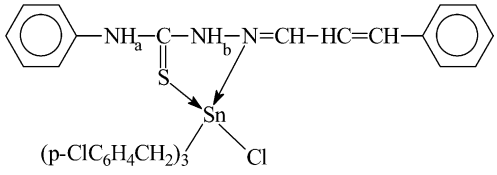
Complexes	Conc. (ppm)	Inhibition (%)	Fungal growth diameter (cm)
Complex 1	250	35	7.4
	500	69	6.3
	1000	83	4.1
Complex 2	250	28	7.1
	500	54	5.6
	1000	72	4.0

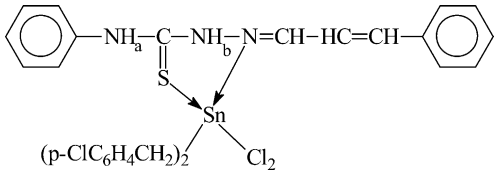
4. Conclusion

On the basis of elemental analysis, spectral (UV, IR, ^{1}H NMR) data; the following structures representing donation, have been proposed for the complexes synthesized.









Complex 1: Tri [(*p*-chlorobenzyl) tin (salicylaldehyde aniline-*N*-thiohydrazone)] chloride;
Complex 2: Di [(*p*-chlorobenzyl) tin (salicylaldehyde aniline-*N*-thiohydrazone)] dichloride;
Complex 3: Tri [(*p*-chlorobenzyl) tin (cinnamaldehyde aniline-*N*-thiohydrazone)] chloride;
Complex 4: Di [(*p*-chlorobenzyl) tin (cinnamaldehyde aniline-*N*-thiohydrazone)] dichloride.

Acknowledgement

The authors are thankful to Dr. R.L. Gupta, Division of Agricultural Chemicals, IARI, New Delhi, for the antifungal studies of the complexes.

References

[1] M. Mohan, A. Agarwal, N. Jha, J. Inorg. Biochem. 34 (1981) 41.
[2] A. Maiti, A.K. Guha, A. Gosh, J. Inorg. Biochem. 41 (1988) 13.
[3] H. Singh, L.D.S. Yadav, S.B.S. Mishra, J. Inorg. Nucl. Chem. 43 (1981) 1701.
[4] N.K. Kaushik, A.K. Mishra, Ind. J. Chem. 42A (2003) 2762.
[5] N. Manav, N. Gandhi, N.K. Kaushik, J. Therm. Anal. Calorom. 61 (2000).

[6] N.K. Singh, A. Srivastava, A. Sodhi, P. Ranjan, Transit. Metal Chem. 25 (2000) 133.
[7] T.D. Thangadurai, K. Natarajan, Transit. Metal Chem. 26 (2001) 717.
[8] D. Lanigan, Proceeding of International Conference on PVC Processing, Plastic and Rubber Institute, London, 1978, p. 41.
[9] A.G. Davies, P.J. Smith, Adv. Inorg. Chem. Rad. 23 (1980) 1.
[10] F. Basuli, S.M. Peng, S. Bhattacharya, Inorg. Chem. 36 (1997) 5645.
[11] F. Basuli, S.M. Peng, S. Bhattacharya, Inorg. Chem. 39 (2000) 1120.
[12] K. Dey, K. Chakrabarty, Ind. J. Chem. 38A (1999) 381.
[13] J.S. Casas, A. Cartineiras, M.C. Rodriguez-Arguelles, A. Sanchez, J. Sorodo, A.V. Lopez, A.M.V. Lopez, J. Chem. Soc. Dalton (2000) 4056.
[14] E.M. Joud, A. Riou, M. Allain, M. Khan, M.A. Khan, G.M. Bouet, Polyhedron 20 (2001) 67.
[15] R. Charles, J.M. Ostman, W.H. Ojala, Carbohydr. Res. 337 (2002) 21;
R. Charles, J.M. Ostman, W.H. Ojala, Chem. Abstr. 136 (16) (2001) 844.
[16] H. Beraldo, R. Lima, L.R. Teixeira, A.A. Moura, D.X. West, J. Mol. Struct. 559 (2001) 99.
[17] K. Ram, H. Agarwal, Bull. Chem. Soc. Ethiopia 15 (2001) 15;
K. Ram, H. Agarwal, Chem. Abstr. 136 (16) (2002) 1630.
[18] K. Sisido, Z. Takeda, Kinugawa, J. Am. Chem. Soc. 83 (1961) 538.
[19] H. Gilman, A.H. Blatt, Organic Synthesis Collective, vol. 1, John Wiley, New York, 1958, pp. 448.
[20] T.N. Srivastava, P.C. Srivastava, N. Bhakra, Ind. J. Chem. 55 (1978) 434.
[21] K. Nakamoto, Infrared and Raman Spectra of Inorganic Coordination Compounds, John Wiley, New York, 1978.
[22] D.J. Batyr, M.P. Starysh, V.N. Shafranskii, Y.Y. Kharitonov, Russ. J. Inorg. Chem. 19 (1974) 1517.
[23] P. Souza, M.A. Mendiola, A. Arquero, V. Fernandej, P.E. Gutierrez, C.R. Ruiz-Valero, Naturforch Teil B 49 (1994) 263.
[24] S. Mahmood, S. Ali, H.M. Bhatti, M. Mazhar, R. Iqbal, M.K. Khan, M.G. Maharvi, Turk. J. Chem. 27 (2003) 657.
[25] N. Agasti, N.K. Kaushik, Main Group Met. Chem. 27 (2004) 81.
[26] S. Chandra, L.K. Gupta, Spectrochim. Acta A 60 (2004) 3079.