APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2001; **15**: 762–768
DOI: 10.1002/aoc.234

Synthesis and characterization of coordination compounds of organotin(IV) with nitrogen and sulfur donor ligands

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The reactions of dimethyltin dichloride with nitrogen and sulfur donor ligands derived by condensation of *S*-benzyldithiocarbazate with indol-3-carboxylaldehyde, thiophene-2-aldehyde and furfuraldehyde have been investigated in 1:1 and 1:2 molar ratios in anhydrous alcohol. These ligands act as mononegatively charged bidentate species and coordinate to the central tin(IV) atom through the thiosulfur by proton exchange with the azomethine nitrogen. The newly synthesized complexes have been characterized by elemental analysis, conductance measurements and molecular weight determinations. The mode of bonding and the geometry of the complexes have been suggested on the basis of infrared, electronic and ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopy, and probable structures have been assigned to these complexes. A few representative ligands and their tin(IV) complexes have also been screened for their antifungal and antibacterial activities and found to be quite active in this respect.

Keywords: dimethyltin dichloride; S-benzyldithiocarbazate; heterocyclic aldehyde; tin(IV) complexes; spectral studies; microorganisms

Received 28 August 2000; accepted 22 May 2001

INTRODUCTION

During the past few years a number of metal complexes of Schiff bases containing NS or ONS donor atoms have been studied.[1–12] Increased interest in this field may be attributed to their structural features and the reported antimicrobial, carcinostatic and antiviral activity of NS and ONS donor ligands and their metal complexes.[5,8] It has also been observed that a small structural change, such as the change of a substituent in the ligand, may lead to enhanced anticancer and antiviral activity of the transition-metal complexes.[5] To date no work has been carried out on the reactions of dimethyltin dichloride with Schiff bases derived from *S*-benzyldithiocarbazate. With this in view, it was considered worthwhile to study the reactions of dimethyltin dichloride with Schiff bases derived by condensation of *S*-benzyldithiocarbazate and indol-3-carboxylaldehyde, thiophene-2-aldehyde and furfuraldehyde. The structures of the ligands are shown in Fig. 1.

EXPERIMENTAL

Chemicals and solvents used were dried and purified by standard methods and moisture was excluded from glass apparatus using $CaCl_2$ drying tubes.

Preparation of *S*-benzyldithiocarbazate

This compound was prepared by the method of Bähr and Schleitzer.[13] Since the literature details were brief and conditions for a good yield are important, the method is given here in detail.

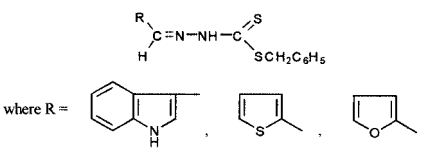

Figure 1 Schiff bases used as ligands in this work.

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Contract/grant sponsor: Council of Scientific Industrial Research, New Delhi.

Potassium hydroxide (28.5 g) was completely dissolved in a 9:1 alcohol–water mixture (150 ml) and the mixture was cooled in ice. To the solution, hydrazine hydrate (25 g) was added slowly with stirring. A solution of carbon disulfide (36.5 g) in alcohol (30 ml) was then added dropwise from a burette, with constant stirring, over a period of 1 h. The temperature of the mixture was kept below 10 °C during the addition. The resulting yellow oil was separated by means of a separatory funnel and dissolved in 2:3 alcohol–water mixture (120 ml) and this solution was cooled in ice. Benzyl chloride (62.16 g) was added slowly with vigorous mechanical stirring; after the addition the mixture was stirred for a further 10 min during which a white product separated. Ice-cooled water (100 ml) was then added and the stirring was continued for another 10 min.

The product was separated by filtration, washed with water and dried in air. The crude product was recrystallized from benzene (150 ml); yield, 45.63 g (45.4%); m.p. 139 °C. Anal. Found: C, 48.52; H, 5.00; N, 14.02. Calc. for $C_8H_{10}N_2S_2$: C, 48.48; H, 5.05; N, 14.14%.

Preparation of the Schiff bases

A solution of *S*-benzyldithiocarbazate (9.9 g; 0.043 mol) and the appropriate heterocylic aldehyde (0.043 mol) in alcohol (80 ml) containing 10 M hydrochloric acid (five drops) was heated at reflux for 2 h. On cooling, solid product separated out, which was dried in vacuum and further purified by recystallization from the same solvent (Table 1).

Preparation of organotin(IV) complexes

To a weighed amount of dimethyltin dichloride was added the calculated amount of ligand and triethylamine in 1:1:1 and 1:2:2 molar ratios, using dry tetrahydrafuran (THF) as reaction medium. The colour of the contents changed immediately, with precipitation of triethylamine hydrochloride. The solution was stirred using a magnetic stirrer for about 3–4 h. The precipitate of triethylamine hydrochloride was filtered off and discarded. Excess solvent was removed from the filtrate and the compound was finally dried in vacuum at a bath temperature of 40 ± 5 °C after being repeatedly washed with dry cyclohexane. The purity of the compound was checked by thin-layer chromatography using silica gel-G as adsorbent. Their physical properties and analytical data are recorded in Table 2.

Analytical methods

Tin was estimated gravimetrically as SnO_2 and chlorine was estimated volumetrically using Volhard's method.[14] Nitrogen and sulfur were estimated by the Kjeldahl and Messenger methods respectively.[15] Molar conductance measurements were made in anhydrous dimethylformamide (DMF) at 36 ± 1 °C using a Systronics conductivity bridge model-305. Molecular weight determinations were carried out by the Rast camphor method.

Spectral measurements

Electronic spectra were recorded in methanol on a Toshniwal spectrophotometer. Infrared spectra were obtained on a Perkin–Elmer 577 grating spectrophotometer as Nujol mulls on KBr optics. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution and ^{119}Sn NMR spectra were recorded $CHCl_3$ solution on a Jeol Fx-90 Q spectrometer. Tetramethylsilane was used as an internal reference for ^1H and ^{13}C NMR. For ^{119}Sn NMR, tetramethyltin (TMT) was used as an external reference.

Antimicrobial testing

The *in vitro* antimicrobial activities of the ligands and their corresponding tin complexes were tested by a paper disc diffusion method[16,17] at 100 ppm concentration in broth agar medium. *Escherichia coli, Staphyllococcus aureus, Bacillus thurengiensis, Klebsiella pneumoniae, Aspergillus flavus, Aspergillus niger, Rhizoctonia phaseoli* and *Penicillium crysogenes* were used as the test organisms. The liquid medium containing the bacterial subcultures was autoclaved for 20 min at 15 lb pressure before inoculation. The bacteria were cultured for 24 h at 36 °C in an incubator. Mueller Hinton broth was used for preparing basal media for the bioassay of the organisms. Nutrient agar was poured onto a plate and allowed to solidify. The test compounds in methanol solution were added dropwise on a 5 mm diameter filter paper disk placed in the centre of the agar plates. The plates were then kept at 5 °C for 1 h and transferred to an incubator maintained at 36 °C and 27 °C respectively for bacteria and fungi. The width of the growth inhibition zone around the disk was measured after 24 h and 60 h incubation

Table 1 Analytical data for Schiff bases

Compound	Colour and state	M.p. (°C)	Analysis Found (Calc.) (%)			
			C	H	N	S
S-Benzyl-*β*-*N*(indlymethylidene)-dithiocarbazate	Brownish yellow solid	132	61.80 (61.98)	4.55 (4.59)	12.50 (12.75)	19.35 (19.46)
S-Benzyl-*β*-*N*(thienylmethylidene)-dithiocarbazate	Greenish solid	120	53.22 (53.39)	4.11 (4.14)	9.42 (9.58)	32.73 (32.89)
S-Benzyl-*β*-*N*(furylmethylidene)-dithiocarbazate	Black shining solid	167	56.33 (56.50)	4.30 (4.38)	10.06 (10.14)	21.98 (23.20)

Table 2 Synthesis and characterization of organotin(IV) complexes and conductance values

Compound	Ligand	Molar ratio	Product, colour and state	Analysis Found (Calc.) (%)						Mol. wt, Found (Calc.)	Molar conductance (Ω^{-1} cm^2 mol^{-1})
				Sn	C	H	N	S	Cl		
Me_2SnCl_2	L^1H	1:1	$Me_2Sn(Cl)L^1$ Brown, oily liquid	23.31 (23.50)	45.87 (45.95)	3.88 (3.93)	8.11 (8.25)	10.22 (12.57)	6.85 (6.97)	496.8 (509.3)	12
Me_2SnCl_2	L^1H	1:2	$Me_2Sn(L^1)_2$ Light brown, oily liquid	14.88 (15.01)	54.75 (54.91)	4.21 (4.26)	10.38 (10.53)	15.30 (16.05)	—	789.8 (797.7)	16
Me_2SnCl_2	L^2H	1:1	$Me_2Sn(Cl)L^2$ Dark brown, oily liquid	25.07 (25.13)	39.00 (39.04)	3.32 (3.36)	5.70 (5.88)	19.50 (20.19)	7.32 (7.45)	467.1 (476.4)	13
Me_2SnCl_2	L^2H	1:2	$Me_2Sn(L^2)_2$ Dark yellow, semi-solid	16.28 (16.35)	46.59 (46.72)	3.78 (3.83)	7.56 (7.65)	26.00 (26.28)	—	728.0 (732.1)	18
Me_2SnCl_2	L^3H	1:1	$Me_2Sn(Cl)L^3$ Reddish brown, semi-solid	25.74 (25.99)	40.32 (40.40)	3.57 (3.69)	6.90 (6.08)	13.72 (13.93)	7.65 (7.71)	448.5 (460.4)	15
Me_2SnCl_2	L^3H	1:2	$Me_2Sn(L^3)_2$ Yellowish brown, semi-solid	17.02 (17.11)	48.70 (48.88)	3.92 (4.00)	7.00 (8.00)	18.21 (18.33)	—	682.4 (699.7)	17

for bacteria and fungi respectively. Four replicates were taken for each treatment.

RESULTS AND DISCUSSION

There is a tautometric equilibrium between the thione (solid state) and thiolo (solution state) forms of these ligands. These monofunctional bidentate species undergo 1:1 and 1:2 (metal:ligand) molar reactions with dimethyltin dichloride (Eqns [1] and [2]):

$$Me_2SnCl_2 + LH + (C_2H_5)_3N \longrightarrow Me_2SnCl(L) + (C_2H_5)_3N \cdot HCl \quad [1]$$

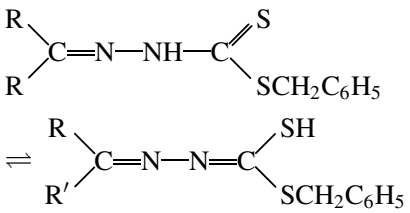
$$Me_2SnCl_2 + 2LH + 2(C_2H_5)_3N \longrightarrow Me_2Sn(L)_2 + 2(C_2H_5)_3N \cdot HCl \quad [2]$$

where LH represents of the Schiff bases of *S*-benzyldithiocarbazates.

Reactions [1] and [2] are quite facile and could be completed in 8–10 h of refluxing. The resulting new derivatives are obtained in the form of monomeric, coloured oily liquids and are mostly soluble in common organic solvents. The molar conductivity measurements (12–18 $\Omega^{-1}\,cm^2\,mol^{-1}$) in anhydrous DMF at room temperature show that the present complexes behave as non-electrolytes. The physical characteristics of these complexes are given in Table 2.

Infrared spectra

The infrared spectra of the ligands[2,18] show strong bands appearing in the region 3450–3180 cm^{-1} attributable to ν(NH) vibrations, but no band is observed at ~2500 cm^{-1}, showing the absence of ν(SH). However, it does appear in the solution spectra with the disappearance of ν(NH) and ν(C=S) bands. This demonstrates the existence of a tautomeric equilibrium[19] between the two forms of ligand, as shown in [3]:



[3]

In the IR spectra of the complexes, the ν(SH) band is absent, showing the bonding of sulfur to tin by loss of the thiolic proton of the ligands. A band of medium to strong intensity at ~1590 cm^{-1} in the complexes may be assigned to the ν(C=N) vibration,[20] and which originally appeared in the region at 1597–1610 cm^{-1} in both the solution and solid states. The shift of this band to the lower side indicates coordination of the azomethine nitrogen to the tin atom.[21,22] Besides this, several new bands in the complexes observed at ~612 cm^{-1}, ~435 cm^{-1}, ~320 cm^{-1} and ~302 cm^{-1} may be assigned to ν(Sn—C),[8] ν(Sn—S),[23] ν(Sn⟶N)[20] and ν(Sn—Cl)[24] respectively, thus lending support to the proposed coordination in the complexes.

Electronic spectra

In the electronic spectra of the ligands,[25] a band at 216 nm is observed which may be assigned to the 1B band of the phenyl ring. This shifts to higher wavelength on complexation and is observed at 222 nm in the complexes. Also, the ligand chro-

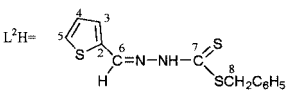
Table 3 ^1H and ^{119}Sn NMR data (δ ppm) of ligands and complexes

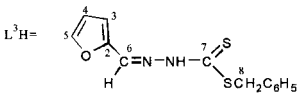
Ligands and complexes	HC=N	NH	—CH_2—	Aromatic protons[a]	—CH_3	^{119}Sn
L^1H	8.50	10.75	4.20	7.10	–	–
$Me_2SnL^1(Cl)$	8.76	–	4.18	7.08	1.18	−125.4
$Me_2Sn(L^1)_2$	8.82	–	4.15	7.06	1.20	−356.8
L^2H	8.55	10.82	4.22	7.15	–	–
$Me_2SnL^2(Cl)$	8.80	–	4.20	7.10	1.18	−130.7
$Me_2Sn(L^2)_2$	8.86	–	4.17	7.09	1.21	−377.3
L^3H	8.54	10.80	4.25	7.12	–	–
$Me_2SnL^3(Cl)$	8.78	–	4.23	7.07	1.20	−126.6
$Me_2Sn(L^3)_2$	8.83	–	4.18	7.04	1.22	−360.1

[a] Centre of multiplet.

Table 4 ^{13}C NMR spectral data for ligands and their corresponding organotin(IV) complexes

Compound	Chemical shift δ (ppm)								
	C-2	C-3	C-4	C-5	C-6	C-7	C-8	Aromatic carbon	Sn—Me
L^2H	143.3	124.8	122.1	134.4	149.0	195.7	39.4	137.2, 127.1, 128.2, 127.6	–
$Me_2Sn(Cl)L^2$	143.1	122.9	121.6	135.4	162.3	178.6	39.1	137.3, 128.2, 128.1, 127.9	7.9
$Me_2Sn(L^2)_2$	144.1	124.2	122.2	135.7	160.8	177.8	37.9	137.1, 127.4, 127.7, 127.6	10.1
L^3H	141.8	125.4	124.7	127.6	144.3	198.5	38.7	137.4, 127.5, 128.6, 127.1	–
$Me_2Sn(Cl)L^3$	140.1	127.1	124.9	126.3	161.4	174.7	39.5	137.3, 129.3, 130.5, 125.4	7.6
$Me_2Sn(L^3)_2$	140.2	127.3	126.5	127.8	156.8	180.3	41.2	135.7, 127.9, 127.3, 126.5	9.2





mophone >C═N, which absorbs at ~290 nm, shifts to a higher wavelength and is observed at ~298 nm in the complexes. Further, a few sharp bands were observed in the region 240–280 nm in the spectra of complexes, which could be assigned as charge transfer bands, suggesting the formation of σ bonds[26] and $d\pi \longrightarrow p\pi$ bonds[27] between the *p*-orbitals of nitrogen and sulfur and vacant 5*d* orbitals of tin.

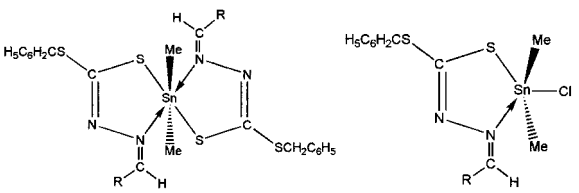


Figure 2 Geometry of the organotin(IV) complexes.

^{1}H NMR spectra

The proton magnetic resonance spectra of the ligands and their corresponding 1:1 and 1:2 tin complexes are shown in Table 3. In the ^{1}H NMR spectra, a broad signal at δ 7.60–6.60 ppm is observed in all the complexes, and this is due to the phenyl protons. A further sharp signal observed at ~δ 4.20 ppm is attributable to the —CH_2— protons of the benzyl group. In the complexes, the disappearance of the signal at δ 10.82 ppm, assigned to NH protons, in the spectra of the ligands indicates their deprotonation. The signal at δ 8.50 ppm observed in the ligand is assigned to the azomethine proton (—CH═N—). This is shifted downfield compared with the original positions in the ligands owing to the coordination of the C═N group with the tin atom. The complexes show additional signals at ~δ 1.20 ppm owing to the protons of the methyl group.

Table 5 Anti-microbial activity of Schiff bases and their corresponding organotin(IV) complexes

Microorganism	Inhibition zone for compound[a] (mm)								
	L^1H	$Me_2Sn(Cl)L^1$	$Me_2Sn(L^1)_2$	L^2H	$Me_2Sn(Cl)L^2$	$Me_2Sn(L^2)_2$	L^3H	$Me_2Sn(Cl)L^3$	$Me_2Sn(L^3)_2$
B. thurengiensis	10	18	21	10	16	20	9	12	15
S. aureus	8	15	16	7	10	14	8	12	13
K. pneumoniae	8	12	16	9	11	16	8	10	14
E. coli	6	10	12	10	14	16	7	11	15
A. niger	6	11	13	5	8	12	4	8	11
A. flavus	5	10	15	6	10	14	4	8	10
R. phaseoli	6	9	11	6	11	15	6	9	12
P. crysogenes	8	10	14	6	12	15	6	10	13

[a] See Table 1 for identities of ligands L^1H–L^3H and their corresponding organotin(IV) complexes.

^{13}C NMR spectra

^{13}C NMR data have been recorded for all the ligands and their corresponding tin complexes (Table 4). The signals due to the carbon atoms attached to the thiolic and the azomethine groups in the ligands appear at $\sim\delta$ 196.5 ppm and 145 ppm respectively. However, in the spectra of the corresponding tin complexes, these appear at $\sim\delta$ 175.3 ppm (thiolic group) and at $\sim\delta$ 160 ppm (azomethine group) respectively. The considerable shifts in the resonances of the carbon atoms attached to sulfur and nitrogen indicate the involvement of sulfur and nitrogen atoms in coordination. The α (C) shifts and $^{1}J(^{119}Sn—^{13}C)$ values of ~568 Hz and ~976 Hz indicate five and six coordination around the tin atom in these complexes respectively. Singh *et al.*[28] have reported values of 570 Hz and 977 Hz for Bu_2Sn/Bu_3Sn complexes of benzilmonothiosemicarbazone.

^{119}Sn NMR spectra

The Me_2Sn(IV) complexes give sharp signals at $\sim\delta$ −125.4 ppm and $\sim\delta$ −356.8 ppm in ^{119}Sn NMR spectra, which strongly supports the suggestion of five and six coordination around tin in trigonal-bipyramidal and distorted octahedral geometries respectively. Values[29,30] for similar five- and six-coordinated Bu_2Sn(IV) complexes have been reported in the range of δ −128 to −138 ppm and $\sim\delta$ −355 to −503 ppm respectively.

On the basis of the spectral evidence, the structures presented in Fig. 2 with (probably distorted) trigonal-bipyramidal and octahedral geometries can be proposed.

Antimicrobial results

In general, when the compounds were tested against *E. coli, S. aureus, B. thurengiensis, K. pneumoniae, A. niger, A. flavus, R. phaseoli* and *P. crysogenes* strains the metal complexes were found to posses higher activity than the ligands. The results show that all compounds exhibit antibacterial and antifungal activities.

The results reported in Table 5 reveal that the tin complexes of the dithiocarbazates are more active for all the test organisms than the corresponding Schiff base complexes reported in our earlier publications,[31,32] and this also indicates that sulfur is more effective than oxygen, as suggested by Tweedy.[33] Compounds containing a halogen atom attached directly to the tin atom also showed moderate activity. The mode of action of these compounds may involve the formation of a hydrogen bond through the —N═C—S group with the active centre of the cell constituents, resulting in interference with normal cell processes. The results achieved here suggest that these types of compound should be studied further for their applications in these areas.

Acknowledgements The authors thank Professor J. P. Tandon, former Head, Department of Chemistry, University of Rajasthan, Jaipur, for his helpful suggestions. One of the authors (H. L. Singh) wishes to thank the Council of Scientific Industrial Research, New Delhi, for financial assistance.

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